Book of Abstracts

International Symposium on Enhanced Electrochemical Capacitors
7th Annual edition

11st-15th July 2022

Bologna, Italy| DamsLab

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PROGRAM OF

THE ORAL PRESENTATIONS

MONDAY 11st JULY

8:15 – 18:00 **Registration**

Tutorial session

Chair: M. Giorgetti, K. Fic, C. Arbizzani

08:30 – 09:00 Welcome coffee

09:00 – 09:10 Introduction

09:10 – 10:00 **T1**. **John Miller** (JME Inc., USA) *"EC fabrication, measurement and testing"*

10:00 – 10:50 **T2. Masashi Ishikawa** (Kansai University, Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and Bioengineering, Suita, Japan) *"Redox-based electrolytes, hybrid systems"*

10:50 – 11:10 Coffee break

11:10 – 11:50 **T3**. **Catia Arbizzani** (University of Bologna, Italy) *"Capacitive and redox-based metrics"*

11:50 – 12:30 **T4**. **Marco Giorgetti** (University of Bologna, Italy) *"Operando vs. ex situ techniques"*

Opening – Plenary session

Chair: F. Soavi, C. Arbizzani

14:00 – 14:20 Introduction

14:20 – 15:00 **Opening Lecture.** **Marina Mastragostino** (Accademia delle Scienze dell'Istituto di Bologna, Bologna, Italy) *"Supercapacitors since the early nineties of the last century"*

15:00 – 15:40 **Plenary Lecture.** **Patrice Simon** (Université Toulouse III Paul Sabatier, Toulouse, France) *"Electrochemistry under confinement in 3- and 2-Dimensional electrodes for capacitive energy storage"*

15:40 – 16:05 **Keynote.** **Andrea Balducci** (Institute for Technical and Environmental Chemistry ITUC and Center for Energy and Environmental Chemistry CEEC Jena, Friedrich Schiller University Jena, Germany) "*Novel strategies for the development and characterization of sustainable electrolytes for electrochemical capacitors*"

16:05 – 16:25 **Invited Lecture.** **Volodymyr Khomenko** (Kyiv National University of Technologies and Design, Department for Electrochemical Power Engineering & Chemistry, Kyiv, Ukraine), D. Putlun "*High Voltage Hybrid Supercapacitor with Ionic Liquid Electrolytes*" (remote lecture).

16:25-17:00 Coffee break

Chair: P. Simon, A. Balducci

17:00 – 17:25 **Keynote.** **Mathieu Salanne** (Sorbonne Université, CNRS, Laboratoire PHENIX, Paris, France; Institut Universitaire de France, Paris, France), R. Berthin, C. Bacon, A. Serva *"Simulating supercapacitors with complex electrolytes using polarizable molecular dynamics"*

17:25 – 17:45 **Invited Lecture. Simon Fleischmann** (Helmholtz Institute Ulm HIU, Ulm, Germany; Karlsruhe Institute of Technology KIT, Karlsruhe, Germany) *"Charge storage mechanisms in confined electrolytes"*

17:45 – 18:05 **Invited Lecture. Krzysztof Fic** (Poznan University of Technology, Poznan, Poland; Kansai University, Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and Bioengineering, Japan), A. Maćkowiak, P. Jeżowski, Y. Matsui, K. Soeda, M. Ishikawa, *"Hybrid electrochemical capacitor with redox active electrolyte"*

18:05-19:30 *Welcome reception*

TUESDAY 12nd JULY

Plenary Session

Chair: F. Beguin, M. Ishikawa

09:00 – 09:40 **Plenary Lecture.** **Thierry Brousse** (Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, IMN, Nantes, France; Réseau sur le Stockage Electrochimique de l'Energie (RS2E), CNRS, Amiens Cedex, France) *"From supercapacitors to high power batteries: over 50 shades of gray"*

09:40 – 10:05 **Keynote.** **Wataru Sugimoto** (Research Initiative for Supra-Materials, Faculty of Textile Science and Technology, Shinshu University, Japan) *"Impact of Macro/microstructure of Nanosheet Architectures on Pseudocapacitive Charge Storage"*

10:05 – 10:25 **Invited Lecture.** **George Z. Chen** (Department of Chemical and Environmental Engineering, and Advanced Materials Research Group, Faculty of Engineering, University of Nottingham, Nottingham, UK) *"Box-like versus peak-shaped cyclic voltammograms for "pseudocapacitance"*

10:25 – 11:00 Coffee break

Chair: W. Sugimoto, J. Ajuria

11:00 – 11:20 **Invited Lecture.** **François Béguin**, A. Chojnacka (Poznan University of Technology, ICTE, Poznan, Poland) *"A smart way to enhance the energy output of electrochemical capacitors by internal hybridization of electrodes"*

11:20 – 11:40 **Invited Lecture.** **Masashi Ishikawa**, T. Nishino (Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and Bioengineering, Kansai University, Suita, Japan) *"Impact of negative electrode utilization on cycle performance for LIC"*

11:40 – 12:00 **Invited Lecture.** **Karl-Heinz Pettinger** (Technology Center Energy – University of Applied Sciences Landshut - Ruhstorf an der Rott, Germany), Christina Schubert, *"Enabling redox flow batteries for grid stabilization by hybridization with supercapacitors*

12:00 – 12:15 **Olivier Crosnier** (Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, Nantes, France; RS2E, French Network on Electrochemical Energy Storage CNRS, Amiens, France), J.C. Espinosa-Angeles, E. Quarez, C. Douard and T. Brousse *"Tungsten bronzes A_xWO_3 (A = Li, Na, and K) as electrode materials for high energy aqueous storage devices"*

12:15 – 14:20 Lunch

Chair: T. Brousse, G. Z. Chen

14:20 – 14:45 **Keynote.** **Sebastian Pohlmann** (Skeleton Technologies, Tallinn, Estonia) *"Creating Innovation from Research: How to improve performance characteristics in industrial Supercapacitor energy storage"*

14:45 – 15:05 **Invited Lecture.** **John R. Miller** (JME, Inc., Ohio, USA), Sue Butler *"Electrochemical Capacitor System Design Using Spec-Sheet Data"*

15:05 – 15:25 **Invited Lecture.** **Jon Ajuria** (Alava Technology Park, Vitoria-Gasteiz, Basque Country, Spain*)*, Maria Arnaiz, Maria Canal, Daniel Carriazo, Aitor Villaverde *"From 1F lab-scale LIC to a roll-to-roll fabricated 100F prototype: the story of an adventurous journey"*

15:25 – 15:40 **Massimo Melchiorre** (Dipartimento di Scienze Chimiche, Università degli Studi di Napoli Federico II, Napoli, Italy; CapTop S.r.l., Caivano, Italy)**,** Khai Shin Teoh, Andrea Balducci, Martino Di Serio, Giancarlo Abbate, Francesco Ruffo *"alfa-hydroxy acids ketals as bio-based solvents for Electrical Double Layer Capacitors: a structure-performance case study"*

15:40 – 15:55 **Martina Mernini** (MARPOSS S.p.A, Bologna, Italy), J. Belcari, F. Stanghellini, C. Arbizzani *"Powerful dilatometric investigation of Li-ion capacitor materials"*

15:55 – 16:10 **Mofredj Kenza**, Negre Léo, Zimmermann Marc, Boisset Aurélien (NAWATechnologies, Rousset, France) *"Industrial manufacturing of VACNT electrodes until high power Supercapacitors: VACNTs as material with numerous possibilities"*

16:10 – 16:40 Coffee break

Young Scientists Session

Chair: J. Miller, O. Crosnier

16:40 – 16:50 **Maria Arnaiz** (Centre for Cooperative Research on Alternative Energies CIC energiGUNE, Basque Research and Technology Alliance BRTA, Alava Technology Park, Vitoria-Gasteiz, Spain)**,** Jon Ajuria *"Pre-lithiated TiSb$_2$ alloy-based lithium-ion capacitor exceeding 20000 cycles and standing for more than 1000 hours of float time"*

16:50 – 17:00 **Mara Serrapede** (Istituto Italiano di Tecnologia, CSFT@PoliTO, Torino, Italy), J. Zenga, M. Fontana, P. Rivolo, C.F. Pirria, A. Lamberti *"Mixed 1T-2H MoS$_2$ nanoflakes electrodes for Li-ion supercapacitors and electrocatalyst for HER"*

17:00 – 17:10 **Marie-Eve Yvenat** (CEA, Grenoble, France)**,** Benoit Chavillon, Eric Mayousse, Fabien Perdu, Philippe Azaïs *"A non-aqueous potassium-ion hybrid supercapacitor for high power applications"*

17:10 – 17:20 **Anita Cymann-Sachajdak** (Department of Energy Conversion and Storage, Faculty of Chemistry, Gdańsk University of Technology, Narutowicza, Gdańsk, Poland), Monika Wilamowska-Zawłocka, *"Novel synthesis method of carbon decorated Na$_3$V$_2$(PO$_4$)$_3$ flower-structured hybrids to boost the electrochemical performance of sodium-ion cathodes"*

17:20 – 17:30 **Rui S. Sampaio** (CQE, Institute of Molecular Sciences, Instituto Superior Técnico, Universidade de Lisboa, Lisboa, Portugal), T. M. Silva, M. F. Montemor *"Double pulse potentiostatic synthesis of MnO$_2$ for electrochemical capacitors"*

17:30 – 17:40 **Etienne Le Calvez** (Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, IMN, Nantes, France; Réseau sur le Stockage Electrochimique de l'Energie (RS2E), CNRS , Amiens, France), Jeronimo Miranda, Yucheng Zhou, Eric Gautron, Nicolas Dupré, Laurent Pilon , Bruce Dunn, Olivier Crosnier, Thierry Brousse *"Revisiting old structure for developing high-power battery: The case of KTiNbO$_5$ family."*

17:40 – 17:50 **Jamie W. Gittins** (Department of Chemistry, University of Cambridge, Cambridge, U.K), Chloe J. Balhatchet, Alexander C. Forse, Yusuf Hamied *"Enhancing the Performance of Layered Metal-Organic Framework Supercapacitors by Coordination Modulation"*

17:50 – 18:00 Kamil Walczak, **Adam Moyseowicz** (Department of Process Engineering and Technology of Polymer and Carbon Materials, Faculty of Chemistry, Wrocław University of Science and Technology, Wrocław, Poland), Katarzyna Gajewska, Grażyna Gryglewicz, *"Iron and* *manganese-based composites as pseudocapacitive electrodes for aqueous asymmetric capacitors"*

18:00 – 19:30 ***Poster Session & refreshments***

20:30 ***International Advisory Board Dinner*** *(on invitation at Trattoria Osteria Buca Manzoni, Via Manzoni, 6g, Bologna)*

WEDNESDAY 13rd JULY

Plenary Session

Chair: D. Rochefort, O. Fontaine

09:00 – 09:40 **Plenary Lecture.** **Elzbieta Frackowiak** (Poznan University of Technology, Institute of Chemistry and Technical Electrochemistry - Poznan, Poland), *"Why EC electrolytes should not be ignored?"*

09:40 – 10:05 **Keynote.** **Volker Presser** (INM - Leibniz Institute for New Materials, Saarland University, Saarene - Saarland Center for Energy Materials and Sustainability - Saarbrücken, Germany), Y. Zhang, G. Feng, *"Permselectivity of Sub-Nanometer Carbon Pores: From Prediction to Experimental Verification"*

10:05 – 10:25 **Invited Lecture.** **Scott W. Donne** (Discipline of Chemistry, University of Newcastle - Callaghan NSW, Australia), Sofia B. Davey, Amanda P. Cameron, Kenneth G. Latham, Caitlin Callahan, Nicholas S. Wilson, *"Evaluation of the Electrified Interface in Electrochemical Capacitors"*

10:25 – 11:00 Coffee break

Chair: E. Frackowiak, S. Donne

11:00 – 11:25 **Keynote.** **Clara Santato** (Dept of Engineering Physics, Polytechnique Montreal - Montreal, QC Canada), Abdelaziz Gouda, Molood Hoseinizadeh, Francesca Soavi, *"Greener electrochemical energy storage based on biosourced materials"*

11:25 – 11:45 **Invited Lecture.** **Céline Merlet** (CIRIMAT, Université de Toulouse, CNRS, Université Toulouse - France), Anouar Belhboub, El Hassane Lahrar, Anagha Sasikumar, Patrice Simon, *"Multi-scale models for a better understanding and performance prediction of the carbon electrode / electrolyte interface in supercapacitors"*

11:45 – 12:05 **Invited Lecture.** **Olivier Fontaine** (Molecular Electrochemistry for Energy laboratory, VISTEC - Rayong, Thailand), Yachao Zhu, Siraprapha, Thierry Brousse, Frederic Favier, *"An inclusive mathematical model for Faradaic Electrode Materials in electrochemical energy storage"*

12:05 – 12:20 **Minghao Yu** (Faculty of Chemistry and Food Chemistry & Center for Advancing Electronics Dresden (cfaed), Technische Universität Dresden - Dresden, Germany), Xinliang Feng, *"Controlling charge carrier ions for high-kinetics battery chemistries"*

12:20 – 14:20 Lunch

Chair: V. Presser, C. Merlet

14:20 – 14:40 **Invited Lecture.** **Dominic Rochefort** (Département de chimie, Université de Montréal - Montreal, Canada), Hassina Nadour, Jensheer Shamsudeen Seenath, Yanyu Wang, David Pech, *"Ionic liquids in Electrochemical Capacitors: From Macro to Micro"*

14:40 – 15:00 **Invited Lecture.** **Ouassim Ghodbane** (National Institute of Research and Physico-chemical Analysis (INRAP), Biotechpole Sidi Thabet - Tunisia), Moomen MARZOUKI, Ramzi ZARROUGUI, *"Application of cobalt oxide electrodes in the presence of aprotic ionic liquids for symmetric supercapacitors"*

15:00 – 15:20 **Invited Lecture.** **Frédéric Favier** (ICGM UMR5253 CNRS-Univ. Montpellier, Réseau sur le Stockage Electrochimique de l'énergie (RS2E), FR CNRS - France), Yachao Zhu, Mathieu Deschanels, Olivier Fontaine, Patrice Simon, Steven Le Vot, *“Redox-active organic molecules on carbon”*

15:20 – 15:35 **Timo Stettner** (Institute for Technical and Environmental Chemistry (ITUC) and Center for Energy and Environmental Chemistry (CEEC), Friedrich Schiller University Jena - Jena, Germany), Leonard Dick, Barbara Kirchner, Andrea Balducci, *“Hygroscopic protic ionic liquids as electrolyte for electrical double layer capacitors”*

15:35 – 15:50 **Roman Mysyk** (Centre for Cooperative Research on Alternative Energies (CIC energiGUNE, Basque Research and Technology Alliance (BRTA), Alava Technology Park - Vitoria-Gasteiz, Spain), Gelines Moreno-Fernández, Noel Díez, Daniel Carriazo, Juan Miguel, López del Amo, *“Ion transport from water-in-salt electrolyte through porosity of hierarchical porous carbons”*

15:50 – 16:05 **Jean Le Bideau** (Nantes Université, CNRS, Institut des Matériaux Jean Rouxel - Nantes, France), *“Ionogels: past, present and future”*

16:05 – 16:30 Coffee break

Young Scientists Session

Chair: C. Santato, O. Ghodbane

16:30 – 16:40 **Siqi Liu** (Friedrich-Schiller-University Jena, Institute of Technical Chemistry and Environmental Chemistry and Center for Energy and Environmental Chemistry Jena (CEEC Jena) - Jena, Germany), Ronald Klukas, Thomas Porada, Kristina Furda, Alba Martín Fernández, Andrea Balducci, *“Potassium formate-based electrolytes for high performance aqueous electrochemical capacitors”*

16:40 – 16:50 **Lukas Köps** (Institute for Technical Chemistry and Environmental Chemistry and Center for Energy and Environmental Chemistry Jena (CEEC Jena) - Jena, Germany), Fabian Kreth, Annika Bothe, Andrea Balducci, *“Novel pyrrolidinium based salts and sulfone-based solvents for high voltage electrical double layer capacitors”*

16:50 – 17:00 **Zallouz Sirine** (Université Haute Alsace, CNRS, Institut de Sciences des Matériaux de Mulhouse (IS2M) - Mulhouse, France, Université de Strasbourg - Strasbourg, France), Jean-Marc Le Meins, Camélia Matei Ghimbeu, *“Enhanced energy density and safety of carbon-carbon supercapacitor by development of a green hydrogel electrolyte”*

17:00 – 17:10 **Pietro Zaccagnini** (Dipartimento di scienze applicate e tecnologia – Politecnico di Torino - Torino,Italy, Centre for Sustainable and Future Technologies – Istituto Italiano di Tecnologia - Torino, Italy), Mara Serrapede, Marco Fontana, Paola Rivolo, Stefano Bianco, Stefano Carminati, Massimo Zampato, Candido Fabrizio Pirri, Andrea Lamberti, *“Electric Double Layer and Pseudocapacitive Ionic Liquid-based Supercapacitors for Harsh Environment applications”*

17:10 – 17:20 **Siraprapha Deebansok** (Molecular Electrochemistry for Energy laboratory, VISTEC - Rayong, Thailand), Konthee Boonmeeprakob, Khwanrudee Chitbankluai, Olivier Fontaine, *“Artificial intelligence for pseudocapacitive tendency prediction of faradaic electrode material electrochemical behavior”*

17:20 – 17:30 **Andrés Parejo-Tovar** (Institute of Chemistry and Technical Electrochemistry - Poznan, Poland), François Béguin, Paula Ratajczak, *“Comprehensive Analysis of Electrodes Performance in Carbon-based Hybrid Capacitors by Cyclic Voltammetry”*

17:30 – 17:40 **Delvina Tarimo** (Department of Physics, Institute of Applied Materials, SARChI Chair in Carbon Technology and Materials, University of Pretoria, South Africa), Kabir O. Oyedotun, Ndeye Fatou Sylla, Abdulmajid A. Mirghni, Ndeye Maty Ndiaye, Ncholu Manyala, *“High specific energy* *obtained after long floating time from high surface area activated carbon for supercapacitor application”*

17:40 – 17:50 **Elisabetta Petri** (Department of Chemistry “Giacomo Ciamician”, Alma Mater Studiorum – Università di Bologna, Bologna, Italy), Federico Poli, Alessandro Brilloni, Andrea Fasolini, Francesco Basile, Francesca Soavi, *“Challenge for upscaling activated carbon production for supercapacitor applications from real lignin waste”*

18:00 ISEECap group picture 📷

18:00 – 19:30 ***Poster Session & refreshments***

THURSDAY 14th JULY

Plenary Session

Chair: A. Lamberti, K. Naoi

09:00 – 09:40 **Plenary Lecture.** **Yury Gogotsi** (A.J. Drexel Nanomaterials Institute and Department of Materials Science and Engineering, Drexel University - Philadelphia, USA), Armin VahidMohammadi, *“MXenes in Next Generation Energy Storage Devices”*

09:40 – 10:05 **Keynote.** **Valeria Nicolosi** (Trinity College Dublin, School of Chemistry, CRANN Institute, AMBER and I-Form Centres - Dublin, Ireland), *“Processing and applications of MXenes inks”*

10:05 – 10:20 **Julien Dangbegnon** (Center for Sustainable Future Technologies @POLITO, Istituto Italiano di Tecnologia - Turin, Italy), Nadia Gardino, Mara Serrapede, Pietro Zaccarini, Francesco Seller, Matteo Cocuzza, Matteo Angelozzi, Thierry Ouisse, Jesus Gonzalez-Julian, Andrea Lamberti, Candido Pirri, *“High performance novel asymmetric MXene@CNT//N-doped CNT flexible hybrid device with large working voltage for energy storage”*

10:20 – 11:00 Coffee break

Chair: V. Nicolosi, B. Ballarin

11:00 – 11:20 **Invited Lecture.** **Ncholu Manyala** (Department of Physics, Institute of Applied Materials, SARChI Chair in Carbon Technology and Materials, University of Pretoria - Pretoria, South Africa), N. F. Sylla, S. Sarr, N. M. Ndiaye, B. D. Ngom, *“Enhanced electrochemical performance of activated carbons derived from peanut shell waste”*

11:20 – 11:40 **Invited Lecture.** **Andrea Lamberti** (Department of Applied Science and Technology, Polytechnic of Turin, Italian Institute of Technology, Center for sustainable future technologies - Turin, Italy), Pietro Zaccagnini, Marco Fontana, Mara Serrapede, Sergio Ferrero, Candido F. Pirri, *“Laser-induced graphene: a disruptive material for micro-supercapacitors”*

11:40 – 11:55 **Filipe Braga** (Stephenson Institute for Renewable Energy, University of Liverpool - Liverpool, UK), Gabriel Casano, Marco Caffio, Laurence J. Hardwick, *“Electrodeposition of FeOOH and MnO_2 on flexible carbon substrates for asymmetric aqueous capacitor applications”*

11:55 – 12:10 **Botayna Bounor** (LAAS, Université de Toulouse, CNRS - Toulouse, France), Jensheer Shamsudeen Seenath, David Bourrier, David Pech, *“3D microdevice from high-capacitance microsupercapacitor electrodes”*

12:10 – 12:25 **Carola Esposito Corcione** (Università del Salento - Lecce, Italy, CNR-NANOTEC-Istituto di Nanotecnologia, Polo di Nanotecnologia, c/o Campus Ecotekne - Lecce, Italy), Eleonora Ferraris, Giuseppe Greco, Miriam Seiti, Antonella Giuri, Olivier Degryse, Aurora Rizzo, Sonia Bagheri , Claudio Mele, *“Fabrication and characterization of GO-PEDOT:PSS nanocomposites for supercapacitors”*

12:25 – 14:20 Lunch

Chair: Y. Gogotsi, N. Manyala

14:20 – 14:45 **Keynote. Katsuhiko Naoi** (Department of Applied Chemistry, Tokyo University of Agriculture & Technology,Naka-cho, Tokyo, Japan), Wako Naoi, *"Microcurrents for Macroefficiency Effective Harvesting of Solar Energy by TNG Supercapacitors"*

14:45– 15:00 **Daniel Carriazo** (Centre for Cooperative Research on Alternative Energies CIC energiGUNE, Basque Research and Technology Alliance BRTA, Alava Technology Park, Vitoria-Gasteiz; IKERBASQUE, Basque Foundation for Science, Bilbao, Spain), Miguel Granados-Moreno, Gelines Moreno-Fernández, Rosalía Cid, Juan Luis Gómez-Urbano *"Microstructured nitrogen-doped graphene-Sn composites as a negative electrode for high performance lithium-ion hybrid supercapacitors"*

15:00 – 15:15 **Joana S. Teixeira** (REQUIMTE/LAQV, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto (FCUP), IFIMUP, Institute of Physics for Advanced Materials, Nanotechnology and Photonics, Department of Physics and Astronomy, FCUP - Porto, Portugal), André M. Pereira, Clara Pereira, *"Hybrid Glow-in-the-Dark Energy Storage Textile Device: Phosphorescent ZnS:Cu-based Redox-active Electrolyte for Fashion/Safety Applications"*

15:15 – 15:30 **Angelina Sarapulova** (Institute for Applied Materials (IAM), Karlsruhe Institute of Technology (KIT) - Eggenstein-Leopoldshafen, Germany), Mona M. Ismail, Ahmed G. El-Deen, Sonia Dsoke, *"A Hybrid supercapacitor based on Mn-MOF and Activated Carbon in water- and organic-based electrolytes"*

15:30 – 15:45 **Alexander Forse** (University of Cambridge - Cambridge, U.K.), Grace Mapstone, Trevor Binford, Israel Temprano, Michael de Volder, *"Understanding Electrochemical CO$_2$ Capture by Supercapacitors"*

15:45 – 16:30 Coffee break

Young Scientists Session

Chair: S. Pohlmann, S. Fleischmann

16:30 – 16:40 **Przemysław Galek** (Institute of Chemistry and Technical Electrochemistry, Poznan University of Technology), Paulina Bujewska, Krzysztof Fic, *"Impact of OH$^-$ and H$^+$ ions concentration on electrical double-layer formation and electrode expansion in porous carbon materials"*

16:40 – 16:50 **Mariam Maisuradze** (Department of Industrial Chemistry "Toso Montanari", University of Bologna - Bologna Italy), Min Li, Mattia Gaboardi, Jasper Rikkert Plaisier, Marco Giorgetti, *"Operando PXRD Study of Ni-doped Manganese Hexacyanoferrate Cathode Material in Aqueous Zn-ion Battery System"*

16:50 – 17:00 **Paulina Bujewska** (Institute of Chemistry and Technical Electrochemistry, Poznan University of Technology - Poznan, Poland), Krzysztof Fic, *"Intriguing Role of the Cation in the Electrical Double-Layer Formation at Nanoporous Carbons Monitored by Electrochemical Dilatometry"*

17:00 – 17:10 **Jakub Menzel** (Poznan University of Technology, Institute of Chemistry and Technical Electrochemistry - Poznan, Poland), Adam Slesinski, Przemyslaw Galek, Paulina Bujewska, Elżbieta Frąckowiak, Krzysztof Fic, *"Analysis of carbon electrode dilatometric strain determined by Scanning Electrochemical Microscopy and internal pressure measurements"*

17:10 – 17:20 **Adam Slesinski** (Poznan University of Technology, Institute of Chemistry and Technical Electrochemistry - Poznan, Poland), Sylwia Sroka, Jakub Menzel, Elzbieta Frackowiak, Krzysztof Fic, *"Operando monitoring of local pH value changes at carbon electrode surface in aqueous electrochemical capacitors"*

17:20 – 17:30 **Nicolas Demarthe** (Nantes university, CNRS, Institut des Matériaux Jean Rouxel, IMN - Nantes, France), Thibaud Guillemin, Maxime Bayle, Bernard Humbert, Dario Arrua, Drew Evans, Thierry Brousse, Jean Le Bideau, *"Divalent metal solid-state electrolyte for hybrid capacitors: study of the coordination anion-to-*Mg^{2+} *via Raman spectroscopy"*

17:30 – 17:40 **Annika Bothe** (Institute for Technical and Environmental Chemistry (ITUC) and Center for Energy and Environmental Chemistry (CEEC), Friedrich Schiller University Jena - Jena, Germany), Lars Henning Hess, Andrea Balducci, *"Development and Use of an in-situ simultaneous thermal analysis (STA) cell"*

20:30 ***Gala Dinner*** *(open to all registered participants at Cantina Bentivoglio, Via Mascarella, 4b, Bologna)*

FRIDAY 15th JULY

09:30 – 10:00 Welcome coffee

Plenary Session

Chair: F. Favier, K. Fic

10:00 – 10:15 **Andres M.R. Ramírez** (Grupo de electroquímica de nanomateriales (GENM), Centro de Nanotecnología Aplicada, Facultad de Ciencias, Universidad Mayor - Santiago, Chile), Lorca-Ponce J., Vergara A., *“Electrosynthesis of nanostructured polyindole adorned with* MnO_2 *nanorod and its evaluation in properties as a supercapacitor”*

10:15 – 10:30 **Michael R.C. Hunt** (Centre for Materials Physics, Durham University - Durham, United Kingdom), R.E. Williams, S. Sukumaran, Q. Abbas, *“Few-layer graphene as an electrode, electrode additive and an interfacial layer in aqueous supercapacitors”.*

10:30– 10:45 **Nicolo' Pianta** (Department of Materials Science, University of Milano Bicocca - Milano, Italy), Federico Scarpioni, Fabio La Mantia, Riccardo Ruffo, *“Dynamic Electrochemical Impedance Spectroscopy as a valid tool to monitor EDLCs operando”*

10:45 – 11:00 **Francesco Lufrano** (CNR-ITAE, Istituto di Tecnologie Avanzate per L’Energia “Nicola Giordano” - Messina, Italy), Minju Thomas, Svetlana Veleva, Boriana Karmanova, Antonino Brigandì, Ana Arenillas, Antonia Stoyanova, *“Hybrid Supercapacitors based on Manganese oxide and Activated carbon Electrodes Using Sodium Exchange Aquivion Electrolyte Membrane”*

11:00 – 11:15 **Lyubomir Soserov** (Institute of Electrochemistry and Energy Systems – Bulgarian Academy of Sciences - Sofia, Bulgaria), B. Karamanova, S. Veleva, A. Arenillas, F. Lufrano, A. Stoyanova, *“Optimizing the pair carbon xerogels-electrolyte for high performance supercapacitors”*

11:15 – 11:30 **Federico Poli** (Department of Chemistry “Giacomo Ciamician”, Alma Mater Studiorum Università di Bologna - Bologna, Italy, Center for the Environment, Energy, and Sea - Interdepartmental Centre for Industrial Research in Renewable Resources, Environment, Sea and Energy (CIRI-FRAME) - Marina di Ravenna, Italy), Carlo Santoro, Francesca Soavi, *“Green supercapacitive systems”*

*11:30 **Closing remarks***

PROGRAM OF THE POSTER PRESENTATIONS

POSTER PRESENTATIONS

Electrolytes and membranes

P01	**Adam Mackowiak** (University of Technology, Poznan, Poland), Paweł Jeżowski , Yukiko Matsui , Kazunari Soeda , Masashi Ishikawa , Krzysztof Fic, *“Redox-active electrolytes for pre-lithiation of graphite electrode in lithium-ion capacitors”*
P02	**Amelia Klimek** (Poznan University of Technology, Institute of Chemistry and Technical Electrochemistry, Poznan, Poland)**,** Justyna Piwek, Elzbieta Frackowiak **“***Improving the performance of electrochemical capacitors by addition of iodide”*
P03	**Minju Thomas** (CNR-ITAE, Istituto di Tecnologie Avanzate per l’Energia “Nicola Giordano” S. Lucia, Messina, Italy; Department of Chemistry and Chemical Technology, University of Calabria, Rende, Italy), , Catia Cannilla, Antonino Brigandì, Francesco Lufrano, Isabella Nicotera, ***“****Mesoporous Carbon Electrodes for Supercapacitor with Sodium ion Exchange Aquivion as Electrolyte membrane”*
P04	**Svetlana Veleva** (Institute of Electrochemistry and Energy Systems, Bulgarian Academy of Sciences, Sofia, Bulgaria), B.Karamanova, A. Stoyanova, A. Arenillas, Natalia Rey, *“Effect of polymer-based electrolyte on electrochemical properties of supercapacitor systems“*
P05	**Ilona Acznik** (Łukasiewicz Research Network - Institute of Non-Ferrous Metals Division in Poznan, Poznan Poland), Paulina Bujewska, Krzysztof Fic, Katarzyna Lota, “*Influence of the phenomenon of self-organization of liquid crystals on the performance of an electrochemical capacitor”*
P06	**Paulina Bujewska** (Łukasiewicz Research Network - Institute of Non-Ferrous Metals Division in Poznan, Poznan Poland), Krzysztof Fic, Katarzyna Lota, Ilona Acznik, *”Effect of Pluronic triblock copolymer as the electrolyte additive on the electrochemical capacitors performance”*
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P11 **Rebecka Gläßner** (Institute for Technical and Environmental Chemistry (ITUC) and Center for Energy and Environmental Chemistry (CEEC), Friedrich Schiller University Jena, Philosophenweg 7a, 07743 Jena, Germany), Patrick Gerlach, Gauthier Studer, Birgit Esser, Andrea Balducci, *"High Power Hybrid System based on poly(3-vinyl-N-methylphenothiazine) "*

P12 **Luisa Baudino** (DISAT Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Italy), Pietro Zaccagnini, Nadia Garino, Mara Serrapede, Marco Laurenti, Alessandro Pedico, Andrea Lamberti, C. Fabrizio Pirri, *"TiO_2 nanotubes-based electrodes for hybrid lithium-ion capacitor and for desalination purposes"*

P13 **Mitra Bagheri** (Department of Physics, Vali-e-Asr University of Rafsanjan, Rafsanjan, Iran), P. Zaccagnini, M. Serrapede, A. Lamberti, M. Molaei, M. Rohani, Moghadam, M. Karimipour, *"Highly-efficient hybrid nanostructure of rGO-TiO_2 as cathode electrode in sodium based aqueous electrolyte"*

P14 **Sirine Zallouz** (Université Haute Alsace, CNRS, Institut de Sciences des Matériaux de Mulhouse IS2M), Mulhouse, Université de Strasbourg, Strasbourg, France), Bénédicte Réty, Loic Vidal, Jean-Marc Le Meins, Camélia Matei Ghimbeu, *"Mesoporous carbon with high load of Co_3O_4 nanoparticles and their performance in supercapacitors"*

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P16 **Daria Roda** (Department of Chemistry and Technology of Functional Materials, Faculty of Chemistry, Gdańsk University of Technology, Gdańsk, Poland) Z. Zarach, , M. Łapiński, K. Trzciński, M. Szkoda, *"Electrochemical properties of TiO_2NT/MoS_2/PANI composite electrode for supercapacitors"*

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P18 **Camille Douard** (Université de Nantes, CNRS, Institut des Matériaux Jean Rouxel, IMN, Nantes, Réseau sur le Stockage Electrochimique de l'Energie RS2E, CNRS Amiens, France), Laurence Athouël, David Brown, Olivier Crosnier, Guillaume Rebmann, Oliver Schilling, Thierry Brousse, *"Electrode Design for MnO_2-Based Aqueous Electrochemical Capacitors: Influence of Porosity and Mass Loading"*

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P21 **Jakub Menzel** (Poznan University of Technology, Institute of Chemistry and Technical Electrochemistry, Poznan, Poland), Sylwia Sroka, *"Ageing of carbon electrodes in Li-ion hybrid capacitors"*

P22 **Jon Rodriguez-Romero** (Departamento de Química Orgánica e Inorgánica, Facultad de Ciencia y Tecnología, Universidad del País Vasco UPV/EHU, Leioa, Spain), Nekane Nieto, Veronica Palomares, Idoia Ruiz de Larramendi, Eider Goikolea, *"Exploring an alternative cell configuration for Sodium-ion capacitors using $Na_3(VO)_2(PO_4)_2F$ and biomass derived carbon"*

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P25 ***Yuta Harada*** (Department of Applied Chemistry, Institute of Global Innovation Research Organization, Tokyo Univ. of Agri. & Tech., Tokyo, Japan), Masahiro Fukuyama, Naohisa Okita, Etsuro Iwama, Wako Naoi, Katsuhiko Naoi *"Ultralong-Lifespan* $Li_4Ti_5O_{12}$*//Ti doped* $Li_3V_2(PO_4)_3$ *Full Cell by Significant Suppression of Vanadium Dissolution from LVP electrode"*

P26 Kang Ho Shin, **Min Jun Hwang**, Puritut Nakhanivej, Ho Seok Park, (School of Chemical Engineering, Sungkyunkwan University, Suwon, South Korea), *"Structural/Chemical Modification of Sodium Vanadium Phosphate for Ultrahigh Rate Sodium Ion Storage"*

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P28 **Dong Hyun Min**, Min Kyu Jung, Ho Seok Park (School of Chemical Engineering, Sungkyunkwan University, Suwon, South Korea) *"Liquid-phase exfoliated hexagonal boron nitride/reduced oxide graphene hybrid electrodes for pseudocapacitive energy storage"*

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P29 **Norman Baltes (**Fraunhofer Institute for chemical technology ICT, Pfinztal, Germany), Johannes Heumann, Jens Tübke, *"Vinyl Acetate/Ethylene as a prospective way out for fluorine free binders in supercapacitors"*

P30 **Johannes Heumann** (Fraunhofer Institute for chemical technology ICT,Pfinztal, Germany), Norman Baltes, Jens Tübke, *"Investigation of commercial supercapacitor materials for industrial application"*

P31 **Sandesh Magar** (Institute for Technical Chemistry and Environmental Chemistry and Center for Energy and Environmental Chemistry, Jena, Germany), Andrea Balducci, *"Brewers' Spent Grains derived activated carbons for high performance electrochemical capacitor"*

P32 **Michael Hunt** (Centre for Materials Physics, Durham University, United Kingdom), K.E. Ninham, *"Steam-activated oat hulls: a sustainable material for supercapacitor electrodes"*

P33 **Alessandro Pedico** (Dipartimento di Scienza Applicata e Tecnologia DISAT, Politecnico di Torino, Italy), Nadia Garino, Sergio Bocchini, Andrea Lamberti, *"Performance study on the addition of novel functionalized graphene oxide in activated carbon-based electrodes for capacitive deionization"*

P34 **Davide Molino** (Politecnico di Torino, Dipartimento di Scienza Applicata e Tecnologia DISAT, Italy), Alessandro Pedico, Andrea Lamberti, Sergio Bocchini, *"Novel infiltration method of membranes over activated carbons electrodes"*

P35 **Omar Hassan, Yassine Ben Cherifi** (Univ. Grenoble Alpes, CEA, CNRS, IRIG, SyMMES, Grenoble, France), Giovanna Franklin, Yves Chenavier, Patrice Simon, Pierre-Louis Taberna, Lionel Dubois, Stéphanie Pouget, Hakima Mendil-Jakani, Florence Duclairoir, *"Graphene based materials:*

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P36 **Min Li** (Department of Industrial Chemistry "Toso Montanari", University of Bologna, Italy), Mariam Maisuradze, Mattia Gaboardi, Giuliana Aquilanti, Jasper Rikkert Plaisier, Marco Giorgetti, *"Operando synchrotron XAS/XRD Investigation of Zn Insertion into Manganese Hexacyanoferrate Cathode Material"*

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P39 **Andrés Camilo Parejo Tovar** (Institute of Chemistry and Technical Electrochemistry, Poznan, Poland), François Béguin, Paula Ratajczak, *"Assessment of Electrodes Operation in Carbon-based Na-ion Capacitors by Potentiostatic Electrochemical Impedance Spectroscopy"*

P40 **Federico Raffone** (Center for Sustainable Future Technologies CSFT@Polito, Istituto Italiano di Tecnologia, Turin, Italy), Giancarlo Cicero, Andrea Lamberti, "*Origin of charge distribution asymmetry at the ionic liquid/electrode interface"*

P41 **Laurence Athouël** (Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, IMN, Nantes, France), Camille Douard, Olivier Crosnier, Thierry Brousse, *"Effect of the intercalated cation size in birnessite on charge storage in neutral aqueous electrolyte"*

P42 **Sylwia Sroka** (Institute of Chemistry and Technical Electrochemistry, Poznan University of Technology, Poland), Przemyslaw Galek, Anetta Platek-Mielczarek, Jakub Menzel, Krzysztof Fic, *"New insights into Point of Zero Charge determination with Electrochemical Quartz Crystal Microbalance"*

Micro and flexible supercapacitors

P43 **Davide Arcoraci** (Department of Applied Science and Technology, Polytechnic of Turin, Italian Institute of Technology, Centre for Sustainable Future Technologies, Turin, Italy), M. Reina, P. Zaccagnini, A. Pedico, A. Lamberti, F. Pirri, *"Enhancing the Performance and Mechanically Stability of Planar Hybrid Micro-Supercapacitors Using Dendritic-Gold as Current Collector"*

P44 **Marco Reina** (Department of Applied Science and Technology, Polytechnic of Turin, Italian Institute of Technology, Centre for Sustainable Future Technologies, Turin, Italy*),* Davide Arcoraci,, Pietro Zaccagnini, Andrea Lamberti , Matteo Angelozzi, Matteo Cocuzza,, Thierry Ouisse,, Jesus Gonzalez-Julian, *"Electrodeposition of MXene and Manganese Oxide onto laser induced graphene for fabrication of a green hybrid supercapacitor"*

P45 **Roberto Speranza** (Department of Applied Science and Technology, Polytechnic of Turin, Italian Institute of Technology, Centre for Sustainable Future Technologies, Turin, Italy), Pietro Zaccagnini, Andrea Lamberti, *"High voltage indoor photo-capacitor: flexible and rigid energy source for IoT devices under ambient light"*

P46 **Francesco Seller** (Department of Applied Science and Technology, Polytechnic of Turin, Italian Institute of Technology, Center for sustainable and future technology, Turin, Italy), Mara Serrapede, Alessandro Pedico, Francesco Perrucci, Luciano Scaltrito, Jennifer Tata, Andrea Lamberti, *“Carbon based electrodes for Wire-Shaped Supercapacitor”*

P47 **Yannik Bräuniger** (Dresden University of Technology, Department of Inorganic Chemistry I, Dresden, Germany), Dr. S. Lochmann, C. Gellrich, Dr. L. Galle, Dr. J. Grothe, Prof. S. Kaskel, *“Monolithic in-plane integration of gate-modulated switchable supercapacitors (ipG-Cap)”*

P48 **Federico Poli** (Department of Chemistry “Giacomo Ciamician” Alma Mater Studiorum Universita’ di Bologna, Italy), Giacomo Selleri, Riccardo Neri, Leonardo Gasperini, Chiara Gualandi, Francesca Soavi, Davide Fabiani, *“Ionic liquid-based-Electrospun piezo-supercapacitors: a strategy to design autonomous devices”*

P49 **Agata Moyseowicz** (Department of Process Engineering and Technology of Polymer and Carbon Materials, Faculty of Chemistry, Wrocław University of Science and Technology, Wrocław, Poland), Karolina Kordek-Khalil, Adam Moyseowicz, *“Carbon cloth decorated with nanostructured manganese oxide as a flexible electrode for supercapacitor applications”*

P50 **Daniele Pontiroli** (Department of Mathematical, Physical and Computer Sciences, University of Parma, Italy), Fornasini, G. Magnani, S. Scaravonati, A. Morenghi, M. Sidoli, D. Bersani, G. Bertoni, L. Aversa, R. Verucchi, M. Riccò, *“In-situ decoration of laser-scribed graphene with TiO2 nanoparticles for scalable micro-supercapacitor applications”*

OPENING LECTURE

Supercapacitors since the early nineties of the last century

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Electric double-layer capacitors (EDLC) featuring porous carbon electrodes have a long history with the first patent by General Electric in 1957. The Standard oil Ohio Company (SOHIO) patented in 1966 a device that stored energy at the double-layer interface and in 1970 a disk-shaped capacitor that featured electrolyte-soaked carbon paste. SOHIO licensed in 1971 the technology to Nippon Electric Corporation (NEC) that produced under the name "supercapacitors" the first commercially successful EDLCs, designed for memory backup applications. In early 1990, the US Department of Energy (DoE), in the frame of the hybrid electric vehicles programs, strongly supported battery and supercapacitor development, creating awareness of the importance of supercapacitors. Since then, great research efforts have been focused on such systems that no longer were a niche topic in the field of the energy storage and many Companies, like Panasonic (Japan), Maxwell (California), ECOND (Russia) and Elna (Japan) began manufacturing EDLCs.

To increase energy density more advanced systems, the so called pseudocapacitors, were, then, developed. By exploiting faradic charge/discharge processes, pseudocapacitors achieve greater specific capacitance and energy density compared to EDLCs. Two classes of electrode materials were used in pseudocapacitors, the metal oxides, e.g. NiO, RuO_2 and MnO_2, and the electronically conducting polymers (ECP), e.g. polyaniline, polythiophene and its derivatives. ECPs were widely investigated and the polymers of the polytiophene family were tested in different configurations with the n/p type with one electrode negatively charged (n-doped) and one positively (p-doped) having the highest energy density because of the high operating voltage. Further designs of such devices were developed, the so-called hybrid supercapacitors in which the charge storage was both electrostatic and Faradic. The research was focused on different types of such devices: i) hybrid devices with composite electrodes that combine in a single electrode carbon materials with either metal oxides or ECPs; ii) asymmetric hybrid devices that combine Faradic and non-Faradic processes by coupling a carbon electrode with a pseudocapacitive one, a metal oxide or an ECP; iii) battery-like hybrid devices that combine a pseudocapacitive or EDLC electrode with a battery electrode.

Some results of our work carried out more than 10 years ago in the frame of European Projects on polymer based pseudocapacitors and asymmetric hybrid pseudocapacitors, even operating with ionic liquid electrolytes, will be briefly reviewed. Starting from these achievements, the exponential growth of publications on supercapacitors, in the last years, mainly driven by the development of novel electrode materials both for EDLC and hybrid cells, will be highlighted.

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PLENARY LECTURES

Electrochemistry under confinement in 3- and 2-Dimmensional electrodes for capacitive energy storage

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This presentation will give an overview of the research work achieved on capacitive 3-Dimmensional (porous carbon) and high-rate 2-D redox (pseudocapacitive) materials, and will show the challenges/limitations associated with the development of these materials. Starting with porous carbons [1,2], we will present the state-of-the art of the fundamental of ion adsorption mechanism in porous carbons and its practical applications. Moving from double layer to high rate redox materials, we will show how the control of the electrodes structure can help in preparing high capacitance electrodes using 2-Dimensional MXene materials [3-5]. In a last part, we will show how the electrolyte ion partial desolvation observed when confined in nanopores (porous carbons) or in interlayer spacing (2D materials) can result in a continuous transition from EDL formation to typical intercalation-type battery process [5].

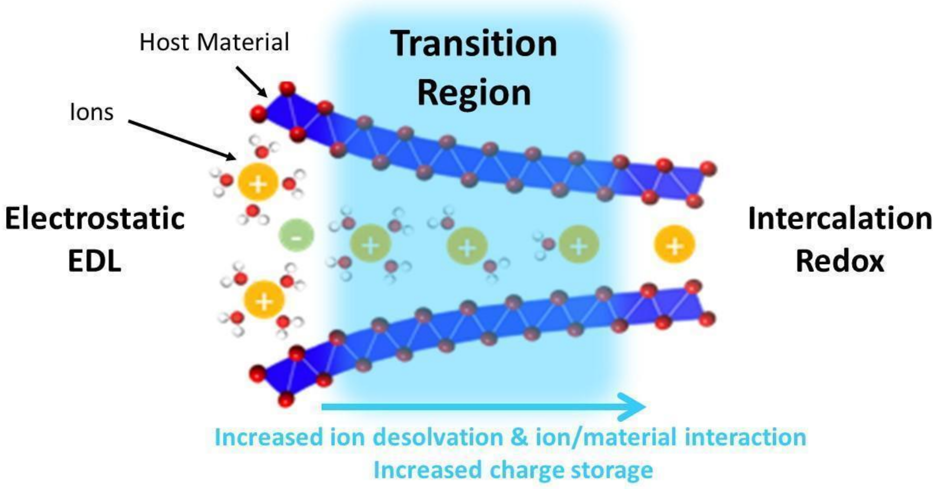

Figure 1: *Sketch of the transition between double layer adsorption of fully solvated ions (left) and intercalation of desolvated ions (right) when increasing the electrolyte confinement [5].*

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From supercapacitors to high power batteries: over 50 shades of gray

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Upon the last decade, the frontiers between electrochemical double layer capacitors (EDLCs) and high power batteries have become increasingly blurred due to the discovery of fast electrode materials depicting various kind of electrochemical behaviors. Moreover, these charge storage mechanisms are depicted either separately, depending on the kinetic at which the electrode is operated, or altogether whatever the charge/discharge regime.1 Pseudocapacitance can be coupled with cations intercalation, and intercalation can take different meanings depending if intercalated species are solvated or not. One example is the capacitive charge storage in birnessite which is governed by interlayer cation intercalation. Thus, the intercalation appears capacitive due to the presence of nanoconfined interlayer structural water, which mediates the interaction between the intercalated cation and the birnessite host and leads to minimal structural changes.2 Similar behavior can be observed in hexagonal tungsten bronzes as depicted in Fig. 1, where lithium cations are intercalated with few water molecules giving rise to such peculiar CV shape.3

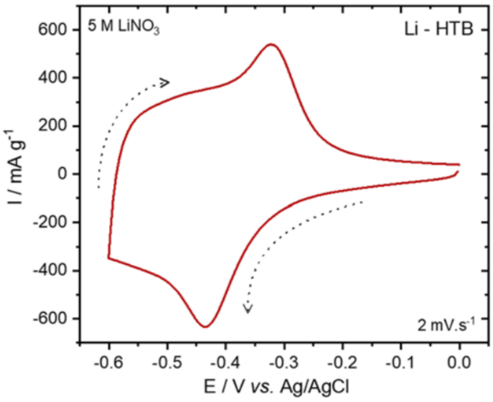

Figure 1: *Cyclic voltammogram of Li-Hexagonal Tungsten Bronze at 2 mV.s-1 in 5M LiNO3.*

However, electrodes exhibiting such intercalation behavior (capacitive, pseudocapacitive or purely Faradaic) have not shown up to now as high power capability as that demonstrated by carbon electrodes in EDLC, for which only ion adsorption mechanism is involved in charge storage without charge transfer between the adsorbed species and the electrode surface. It seems there is a continuum in the observed charge storage mechanisms,4 from capacitive, as in EDLC, to purely Faradaic as in lithium-ion host electrodes, which offers to device designers a wide range of possibilities for targeting various needs. Thus, the traditional black and white image is gradually being repainted with an increasingly expending palette of grays.

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Why EC electrolytes should not be ignored?

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Electrochemical capacitors (ECs) are high power density devices characterized by a long-term cyclability. The electrostatic attraction of ions at the electrode/electrolyte interface is mainly responsible for the quick charging/discharging process. The main components of ECs consist of two electrodes with developed specific surface area which are soaked in an electrolytic medium and separated by a membrane. The electrolyte plays a pivotal role for EC performance [1-8]. It is the source of charged ionic species affecting the conductivity, electrical permittivity and electrochemical window of the device. Obviously the size of ions must be adapted to the electrode porosity for efficient EC performance, however, during operation, the solvated ions can partially lose their solvation shell to be adjusted to the size of ultramicropores. The hydration/solvation energy of ions and their kosmotropic and chaotropic character are another important characteristics of electrolytes. It is noteworthy that presence of the redox active species (e.g. I-1 , Br-1, SCN-1) in the electrolyte can boost the EC energy through reversible redox reactions [1-3]. Neutral aq. electrolytes are the most attractive for EC voltage extension, however, one should take into account that pH can vary in the vicinity of electrodes [5]. H bonding is especially important affecting EC performance in supersaturated solutions and deep eutectic solvents [8]. The problem of electrolyte versus corrosion of current collectors must not be neglected as well. During the lecture, a special attention will be devoted to the following issues:

- Organic versus aqueous electrolytic solutions, the role of electrolyte conductivity
- Why neutral electrolytes are concurrent to acidic, basic, organic and ILs?
- Physical state of electrolyte versus leakage problems
- Deep eutectic solvents as potential electrolytes
- Redox active species for boosting EC energy
- Supersaturated electrolytes: pros & cons
- Effect of electrolyte on the current collector corrosion

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MXenes in Next Generation Energy Storage Devices

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The market and policy shift from use of fossil fuels to electricity for powering cars and future cities, has created an enormous demand for development of next generation energy storage devices that can meet such criteria as low manufacturing cost, scalability, long operating life, and high power and energy delivery. Discovery of new materials, design of electrode structures, cell components, and manufacturing processes are a key in meeting these targets by 2030. Nanomaterials, particularly, two-dimensional (2D) materials, are among promising candidates that can be used to address some of the ongoing challenges in manufacturing batteries and supercapacitors and enable devices with superior performance metrics and lower cost.[1,2] Two-dimensional metal carbides and nitrides (MXenes) are a very large and yet quickly growing family of 2D materials with formula of $M_{n+1}X_nT_x$ where M is an early transition metal, X is carbon or nitrogen, and T_x refers to the surface terminations. The unique electronic, optical, and most importantly, electrochemical properties of MXenes have distinguished them from other widely studied 2D materials. The high conductivity (~20,000 S cm^{-1}), redox active surfaces, cation intercalation in 2D slits, and rich chemistry of these materials with more than 50 different compositions reported, has enabled their use as charge storage hosts and building blocks of passive cell components in various types of energy storage devices.[3] Freestanding, binder free films of $Ti_3C_2T_x$ are capable of ultra-high-rate pseudocapacitive charge storage in protic electrolytes delivering ~400 F g^{-1} (1500 F/cm^{-3}) at rates of up to 100 V s^{-1} and volumetric energy and power densities several times higher than conventional carbon based capacitive electrodes. MXenes can intercalate a variety of monovalent and multivalent cations from aqueous or non-aqueous electrolytes and, therefore, can be used as electrodes for emerging new battery chemistries. Their mechanical robustness and high conductivity expand their use as conductive additives in electrodes and as building blocks for conformal coatings to avoid dendrite growth in metal batteries. Yet, unlike most other 2D materials, synthesis and processing of MXenes is scalable and cost effective, and they can be processed in large batches from aqueous solution into various forms of powders, dispersions, and films. The combination of these properties and scalable synthesis, not only renders MXenes as interesting materials for academic research and development studies, but also as practical materials of choice for future charge storage applications. This talk will discuss the properties and use of MXenes in next generation energy storage devices.

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KEYNOTE LECTURES

Novel strategies for the development and characterization of sustainable electrolytes for electrochemical capacitors

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Electrochemical double layer capacitors (EDLCs) are nowadays considered one of the most important energy storage devices in our life [1]. Several studies showed that to further extend the use of these devices, and thus their market, their energy density need to be increased. Furthermore, also their sustainability needs to be overall improved. To reach these goals, and to realize advanced EDLCs, the development of innovative electrolytes is essential [1].

To develop innovative electrolytes several aspects need to be considered and carefully addressed and, among them, the sustainability and the stability (chemical, electrochemical and thermal) of the electrolytic solutions are of great importance. These points will be addressed in this work.

Initially, the development of an innovative concept for the realization of a sustainable "in-situ electrolyte" will be considered. In this novel approach the by-product salts that are formed during the synthesis of electrode material from bio-sources are utilized for the realization of organic electrolyte for EDLC [2]. Furthermore, the possibility to utilize sustainable solvents that can be produced from largely available bio-sources will be considered [3]. Afterwards, the interfacial processes taking place between these novel electrolytes and electrode materials will be addressed. In this case the development and use of innovative *in-situ* STA cell [4] and *in-operando* GC-MS cells, suitable for the investigation of the aging processes taking place in EDLCs, will be considered in detail.

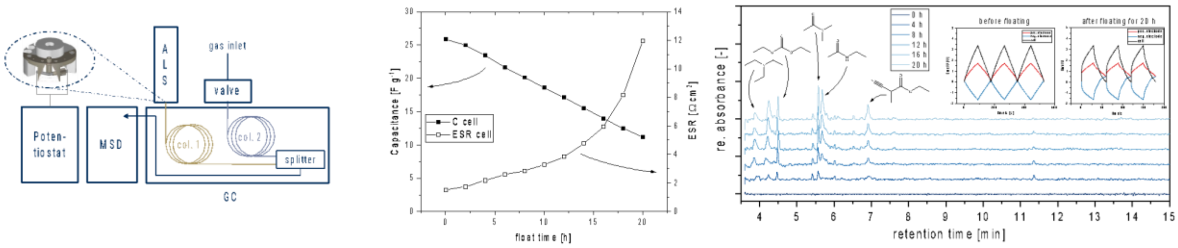

Figure 1: *In-operando GC-MC cell suitable for the investigation of aging processes taking place in EDLCs*

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Simulating supercapacitors with complex electrolytes using polarizable molecular dynamics

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Over the past decade we have developed a classical molecular dynamics code that allows to simulate electrochemical cells, with a special focus on carbon/carbon supercapacitors [1]. The main improvement with respect to conventional molecular dynamics code was the use of realistic models for electrified nanoporous carbon electrodes [2]. However, the electrolytes were modeled using a coarse-grained representation, in which the chemical description of the ionic species was oversimplified. Recently, we have introduced new models for the electrolytes, in which all the atoms are represented explicitly and polarization effects are included. These simulations allow us to simulate nanoporous carbons-based supercapacitors with a much better accuracy. They were first validated on a well-known electrolyte, namely the EMIM-TFSI either pure or dissolved in acetonitrile.

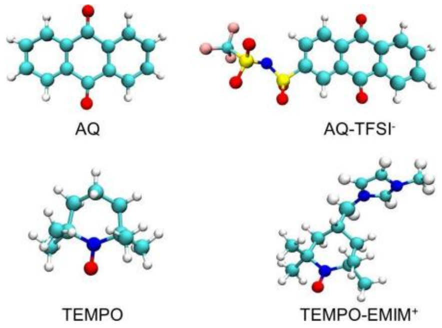

Figure 1- *Biredox ionic liquids*

We have then focused on biredox ionic liquids, which are made redox-active by grafting redox moieties to both the cation and the anion of the IL. As shown on Figure 1, the studied system is composed of the anion $TFSI^-$ grafted with an anthraquinone (AQ) group, while the cation $EMIM^+$ is functionalized by TEMPO. These systems were recently studied experimentally, showing very promising capacitances [3]. Yet their charging mechanisms is not completely elucidated, in particular the interplay between redox reactions and confinement effects remains to be understood. By studying the structure of the liquid, both in the bulk and confined in pores with various widths, we show that the redox moieties tend to form some structural arrangements which are reminiscent of nanoporous carbon materials. This result provides an interesting lead for explaining the charging mechanisms of these systems.

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Impact of Macro/microstructure of Nanosheet Architectures on Pseudocapacitive Charge Storage

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Conducting two dimensional nanosheets with thickness of a sub- to single-nanometer scale has drawn considerable attention for supercapacitor electrodes owing to their potentially high surface area. The capacitive properties of nanosheet electrodes are governed by the nanostructure of the individual nanosheets and the three-dimensional architecture of the re-stacked nanosheets.

Electrical double layer capacitors based on CVD grown vertically aligned graphene thin films provides power performance comparable with Al electrolytic capacitors.[1] We have succeeded in the fabrication of thick electrodes composed of vertically aligned graphene by electrophoretic deposition and freeze-drying.[2] The macroporosity of the electrode can be controlled by altering the concentration of the colloid and the speed of freeze drying. The vertically aligned graphene electrodes have enhanced power performance compared to horizontally aligned nanosheets.

Vertically aligned nanosheets can be fabricated from TiO2 nanosheets (ns) and converted to TiO_2(B)-ns for high-rate Li-insertion electrodes (Fig. 1). The size and porosity of TiO_2(B) are important factors for high power performance. For TiO_2(B)-ns with equivalent diameter (D_e)=300 nm, the orientation does not affect the lithiation property and the amount of lithiation (SOC) was almost the same (20% SOC at 0.2C). By downsizing to D_e=30 nm, the rate performance is improved two times for vertically aligned electrodes.[3]

Although the orientation of small-sized TiO_2(B)-ns had a large influence on Li^+ transfer kinetics, 100% SOC could not be achieved, suggesting the lack of electronic conductivity. The lack of electronic conductivity could be circumvented by adopting a vertically aligned reduced graphene oxide (V-rGO) electrode as a porous current collector. 100% SOC was obtained for TiO_2(B)-ns/V-rGO with D_e=70 and 150 nm at 0.5 mV/s. On the other hand, only 55% SOC was achieved for nanosheets with D_e= 300 nm.

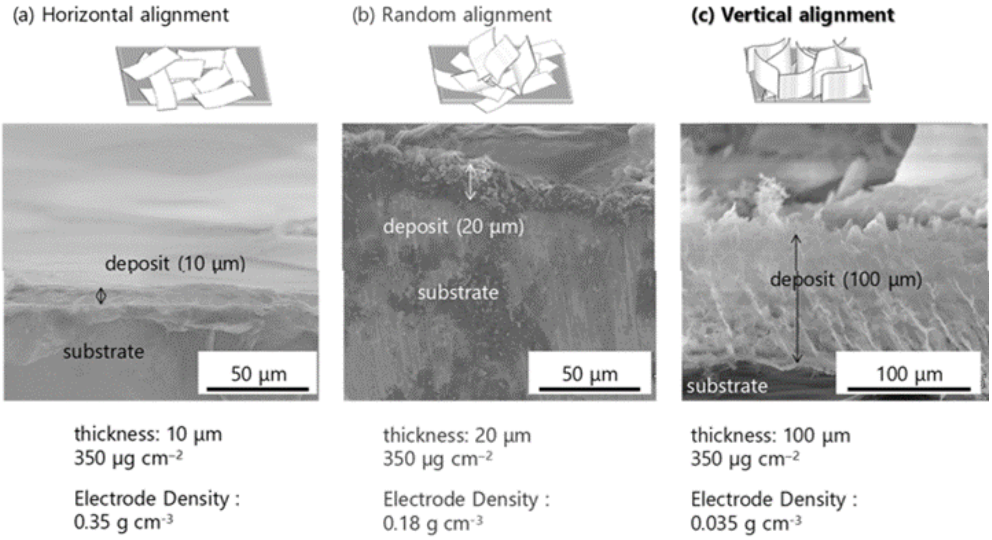

Figure 1. FE-SEM images of TiO2(B) electrodes with different alignment. (a) horizontal., (b) random, and (c) vertical.

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Creating Innovation from Research: How to improve performance characteristics in industrial Supercapacitor energy storage

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Although all innovation is based on research, not all research leads to innovation. This oral presentation is based on a recently published manuscript [1] and aims to give the listener an overview on the recent advances in increasing energy density in industrial Supercapacitor devices, including the research behind the innovations which resulted in increased energy density.

The presentation also aims to give food for thought on the importance of metrics in turning research into innovation, focusing on the evolution of supercapacitor devices as a case study.

It is important to understand that all innovation begins with research, but not all research is innovative. Indeed, innovation is an idea that has a practical impact on our daily reality. That, in turn, means that an idea (and the research activities associated with it) is not entirely innovative until a practical and beneficial effect on human lives, societies or the environment is demonstrated. It also means that research does not necessarily result in immediate innovation. For example, research projects operating at low technology readiness levels usually generate scientifically accurate and methodically correct discoveries. However, in most cases, these research works cannot immediately impact the day-to-day reality, although, in the long-term, they could become relevant for future innovations that are not yet foreseeable during the initial research period.
Using supercapacitor technology as an example, the presenter aims to answer the question: Which ground rules can be followed to spark innovation from research? To answer, three aspects should be considered: (i) the topic of research activities, (ii) the methods applied and, (iii) the approach to publishing.

The presentation will also cover aspects of industrial Supercapacitor design and its impact on energy and power density.

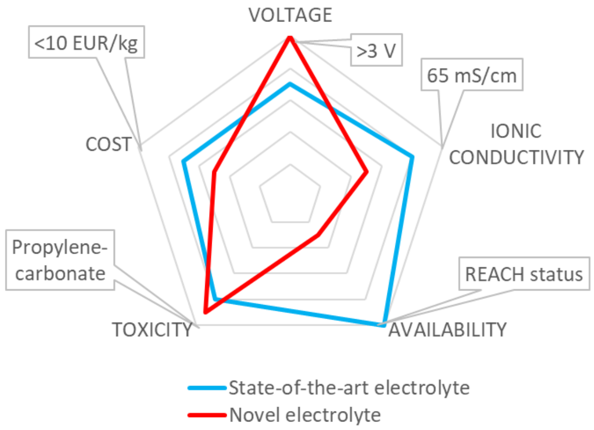

Figure 1: Comparison of electrolytes as a mean to increase energy density in Supercapacitors. The comparison concerns "secondary" properties such as cost, toxicity and availability and serves the purpose to alert the reader to different performance indicators next to energy and power density.

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Permselectivity of Sub-Nanometer Carbon Pores: From Prediction to Experimental Verification

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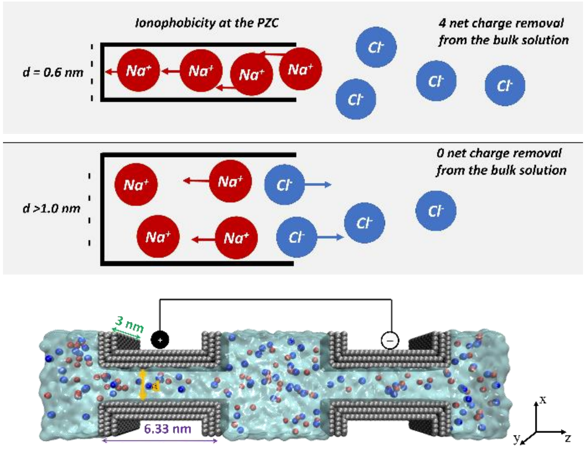
Supercapacitors are not the only application of electrical double-layer technologies. Capacitive deionization (CDI) uses ion electrosorption to remove salt ions from saline media. This process favors large surface areas and high pore volumes in electrically conductive electrode materials. Accordingly, materials such as activated carbon is particularly attractive. However, the in-pore volume "interacts" with the bulk electrolyte. In meso- and micropores, commonly, there are already anions and cations present within the pore in the uncharged state. This results in an energetically unfavorable situation: the applied surface charge of the electrode is not exclusively used to attract more ions into the pore (counter-ions) but also to eject ions with the same charge as the electrode from the pore. In the worst case, at a very high initial salt concentration, this will "just" store charge (like a supercapacitor) but fail to deliver any desalination performance. Accordingly, CDI has remained limited to low-concentration regimes (such as those provided by brackish water) or mandated the addition of permselective components, such as ion-exchange membranes (MCDI).[1, 2]

Recently, molecular dynamic (MD) simulation carried out for high molar saline media (600-800 mM) predicted the ability of sub-nanometer-sized pores to remain free of ions in the uncharged state. This feature is enabled by the need of ions to (partially) shed (parts of) their solvation shell to enter the pore. However, the required activation energy for this process is overcome only when an electric charge is applied. Therefore, such ultramicropores should overcome the permselectivity dilemma, which formerly had prohibited direct seawater desalination via CDI.

Based on our MD simulations, we carried out desalination experiments with novolac-derived activated carbon with controlled ultramicroporosity. Our data show the strong dependency of the desalination performance at high molar strength on the pore size and confirm the predicted, unique ability to directly desalinate seawater efficiently without the need for any ion-exchange membrane or other system-related modification.[3, 4]



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Greener electrochemical energy storage based on biosourced materials

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Electrode materials based on redox-active organic molecules deposited on carbon and capable to operate in aqueous electrolytes offer the opportunity to avoid toxic, critical, and expensive chemical elements and materials for electrochemical energy storage.

In principle, when deposited on carbon current collectors, redox-active organic materials add a faradaic contribution to the typical electrostatic capacitance of carbon.

In the last few years, our groups explored biosourced (i.e. extracted from natural sources) organic molecular materials featuring quinone groups in their molecular structures as redox-active materials for low-cost and biodegradable electrochemical energy storage devices (supercapacitors) featuring enhanced sustainability.

In this contribution, we will discuss results obtained with Sepia Melanin, the brown-black member of the Melanin family of biopigments, as well as Catechin and Tannic Acid, members of the Tannin family, employed as biosourced redox-active materials deposited by solution-based processing on carbon [1-4].

A great deal of attention during the contribution will be devoted to share our efforts in interface engineering. The interface between the redox-active quinone-based organic molecular materials and the carbon is the key to achieve efficient electronic coupling and long cycling stability. SEM, XPS, Raman, FTIR analyses helped us to shed light on the chemical and morphological features of carbon, that we treated by hydrothermal methods to increase its surface area and wettability as well as to introduce heteroatoms imparting faradic activity, prior the deposition of the quinone-based molecular materials. Fundamental aspects of the electrochemical behavior of the electrode materials as well as and device performance will be discussed and critically compared with current literature to figure out the priority challenges that will have to be tackled in short and medium terms.

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Processing and applications of MXenes inks

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Liquid phase exfoliation has been proved to be a cheap, scalable method for the mass production of 2D sheets. This talk will first discuss the galaxy of existent layered materials, with emphasis on synthesis, liquid-phase exfoliation, and characterization, focussing on some key applications recently developed in our laboratories, ranging from energy storage to printed electronics. We will for example discuss how two-dimensional Ti3C2 (MXene) can be formulated in aqueous and organic viscous inks for extrusion printing and inkjet printing, respectively, and demonstrate direct MXene printing on various substrates. The additive- and binary solvent-free MXene inks do not show coffee ring effect, enabling high-resolution printing without substrate pre-treatment. The resulting all-MXene printed micro-supercapacitors showcase excellent charge storage performance, including areal capacitance up to 43 mF/cm2 and volumetric capacitance up to 562 F/cm3 in protic gel electrolyte, coupled with long lifetime and good flexibility. We also show examples of all-inkjet-printed MXene arrays for ohmic resistors. The versatile direct-ink-printing technique highlights the promise of MXene functional inks for scalable fabrication of easy-to-integrate components of printable electronics. We will also discuss how MXenes can be used as a conductive binder for the fabrication of printable porous hydrogels. A universal 4D printing technology for manufacturing MXene hydrogels with customizable geometries will be discussed. The obtained MXene hydrogels present 3D porous architectures, large specific surface areas, high electrical conductivity, and satisfying mechanical strengths. Consequently, ultrahigh capacitances (232.9 F g^{-1} (10 V s^{-1}), 3.32 F cm^{-2} (10 mV s^{-1})) and unprecedented mass loading/thickness-independent rate capabilities are achieved. The further 4D-printed Ti3C2Tx hydrogels micro-supercapacitors (MSCs) showcase low-temperature tolerance (down to –20 °C) and deliver ultrahigh energy and power densities up to 92.88 μWh cm−2 and 6.96 mW cm^{-2}, respectively, surpassing most state-of-the-art MSCs.

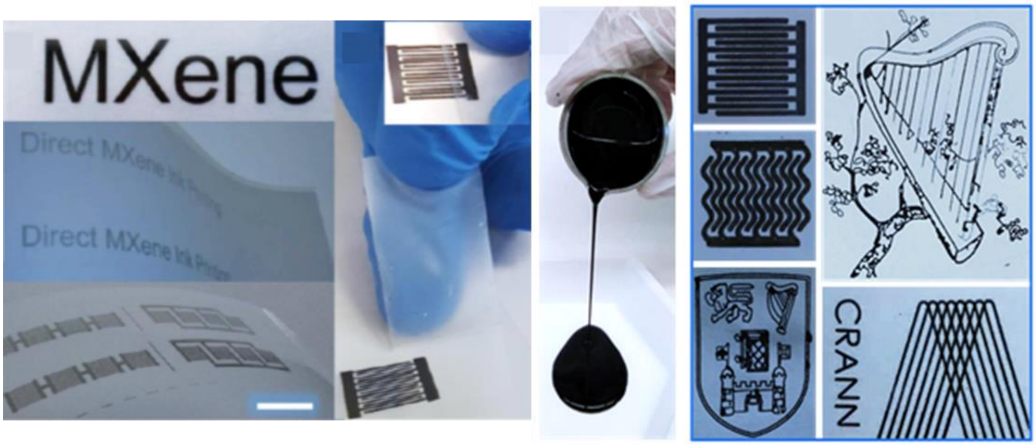

Figure 1: *Printed devices based on MXenes inks*

Microcurrents for Macroefficiency
Effective Harvesting of Solar Energy by TNG Supercapacitors

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Under low-sunlight conditions—dawn, dusk, and occlusion by clouds—the electric current produced by a photovoltaic (PV) cell drops to a microscopic trickle, which conventional solar-power systems simply discard. Here we show that these tiny currents may in fact be effectively captured and used for substantial energy harvesting, significantly improving overall system efficiency. Our system involves an innovative mechanism, enabled by sensors and an AI-powered microcontroller, for automatically routing PVC currents through conventional (standard-current) or modified (microscopic-current) circuits. A decisive role in the design of our system is played by the rapid pace of global climate change; as we show, changes in the magnitude of sunlight-intensity variations over just the past ten years are an essential driver of the surprisingly large efficiency gains enabled by our innovation. In the talk we introduce the basic ideas of our technique, present results of a prototype study achieving significant improvement in power-system efficiency.

2nd-GEN NanoHybrid Capacitor: Material innovation has led to the development of revolutionary 2nd-GEN NanoHybrid Capacitors for stationary application. A new family of magneli (Ti_4O_7)-edged $Li_4Ti_5O_{12}$(LTO) nanosheets have been utilized for the anode that is combined with activated carbon (AC) cathode. Dedicated PCS has also been developed for higher efficiency by implementing NHC supercapacitors. With AI-fostered PCS (Power Conditioner system), 10-kW field trial on our university campus has shown a significant net system output by 33.5% on bad weather conditions.

3rd-GEN SuperRedox Capacitor: A newly developed "SuperRedox" capacitor (Li_3VO_4(LVO)//$Li_3V_2(PO_4)_3$ (LVP)) will be presented by featuring their ultrafast nanocrystalline electrodes. The SRC is specifically designed for stationary application just to fit our solar system. The SRC further enhances the efficiency, cost effectiveness, and space utilization. The volumetric energy density of the device amounts to more than 6-fold of EDLC which even exceeds the NHC.

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INVITED LECTURES

High Voltage Hybrid Supercapacitor with Ionic Liquid Electrolytes

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Lithium-ion batteries (LIBs) and electrochemical capacitors (supercapacitors) dominate the energy supply for portable electronics. To meet the power and energy demands of various electronic devices, high-performance electrodes and systems have to be designed. Asymmetric hybrid supercapacitors have opened up a new opportunity for the fabrication of such power sources. In this work, we demonstrate the fabrication of advanced asymmetric hybrid supercapacitors using ionic liquids (IL) as electrolytes. ILs have been attracting interest for power sources, as they show high thermal stability and, in general, they are not environmentally hazardous. In this research, we present an approach to assembling system based on anode with graphite and cathode with activated carbon. Aqueous-based technique for the preparation of LIB and LIC electrodes was developed. Electrodes with the flexible and mechanically strong film of active materials were prepared by a tape-casting process. The electrodes were prepared by coating slurry on Al foil as a current collector. The slurry was prepared by mixing 85.0 wt% active materials, 10.0 wt% Carbon Black as a conductive agent, and 5.0 wt% of mixture carboxymethyl cellulose sodium (NaCMC) salt and styrene-butadiene rubber (SBR) as a binder. For optimization, different types of thickness for electrodes were prepared. Electrolyte formulation remains a fundamental element of these state-of-the-art systems. 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (electronic grade) so-called $Pyr_{14}TFSI$ has chosen them for asymmetric hybrid supercapacitors.

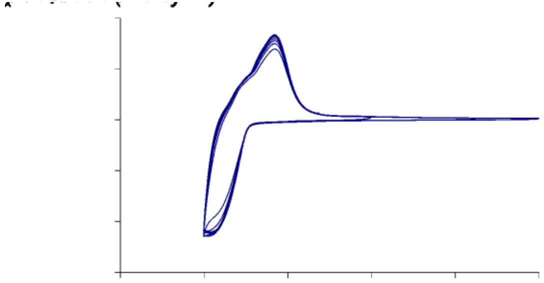

Figure 1: *Cyclic voltammograms of graphite in $Pyr_{14}TFSI$. Sweep rate was 2.0 mV/s.*

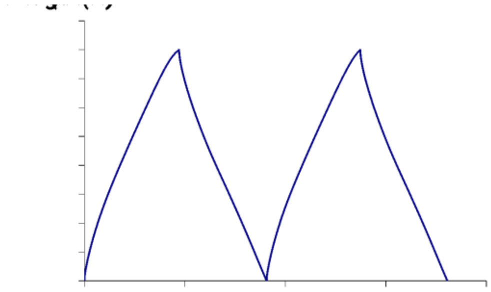

Figure 2: *Cell voltage vs. time profile during the constant current charge/discharge cycling process.*

Fig. 1 shows the CV of electrodes based on graphite. In the CVs, reduction current and oxidation current were observed below 1.5V vs. Al quasi-reference electrode. Peaks on the CV would be attributed to the intercalation/deintercalation of Pyr_{14}^+ into/from the graphite electrode. From Raman spectra and XRD patterns of graphite materials held at 2.0V potential, intercalation of IL cation into graphite electrode and formation of graphite intercalation compound (GIC) were revealed. A specific discharge capacity of about 109 mAh/g was found for the cations (Pyr_{14}^+) uptake into graphite, which corresponds to a stage-1 GIC with a stoichiometry ranging between $C_{19}Pyr$ and $C_{20}Pyr$. The energy storage mechanism of this system is based on the simultaneous cation intercalation/deintercalation into/from the graphite electrode and adsorption/desorption of TFSI- anion through the electric double layer on the porous carbon during charge/discharge. During discharge, both ions are released back into the electrolyte. The intercalation of Pyr_{14}^+ cations into the graphite anode was limited by a stage -1 GIC in order to prevent irreversible exfoliation of graphite. As shown in Fig.2 supercapacitors with 4.0 V maximum working voltage were successfully fabricated. Our prototype cells already reach high specific energies of ~80 Wh/kg, while maintaining a specific power of up to 1 kW/kg and cycling stability of over 1000 cycles. Owing to high energy density, asymmetric hybrid supercapacitors based on GIC exhibit great potential as high-performance energy sources for advanced technologies where high power and energy density are required.

Acknowledgement

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Charge storage mechanisms in confined electrolytes

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For decades, electrochemical charge storage mechanisms have been separated into electric double-layer formation and Faradaic redox reactions. However, this strict binary classification does not sufficiently consider the spatial constraints of electrolytes at nanoconfined electrochemical interfaces, nor is it helpful to explain the emergence of so-called "pseudocapacitance" in several two-dimensional or layered materials. Pseudocapacitive charge storage shows electrical similarity to capacitors, where charge is proportional to the applied potential, but it originates mostly from Faradaic reactions. There are vigorous discussions in the scientific community about the origin of pseudocapacitive phenomena, with some rejecting the concept entirely.

In this presentation, it is demonstrated how the nanoconfinement environment within layered or porous host materials influences charge storage phenomena. We show how interlayer properties, such as interlayer distance and interlayer chemistry, can affect electrochemical ion intercalation processes in layered host materials. The presence of interlayer structural molecules can increase the accessibility of intercalating ions to the interlayer space and influence transport properties. Increased interlayer spacing and reduced deformation during ion intercalation can lead to a change from diffusion-limited to non-diffusion limited (or pseudocapacitive) charge storage behavior, enabling favorable charge storage kinetics.[1]

The talk will give an overview of my research group's efforts to synthesize interlayer-functionalized layered and two-dimensional materials with tailored interlayer properties. It is hypothesized that there can be a **smooth transition between EDL and Faradaic charge storage phenomena based on the degree of ion solvation**, which in turn impacts the interaction of inserted ion and host electrode.[2] In this transition region, pseudocapacitive charge storage behavior could be observed.

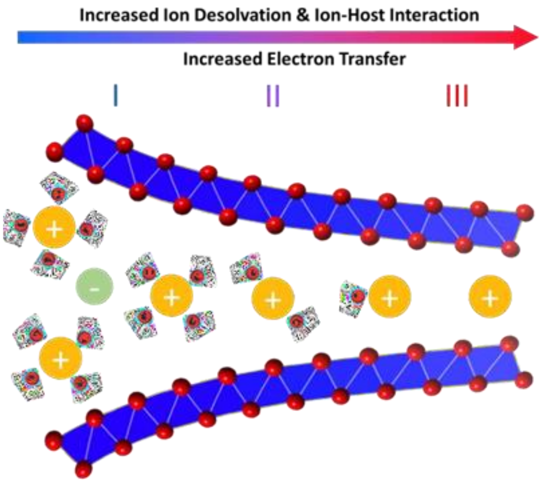

Figure 1: *A unified model for charge storage in the nanoconfined interlayer environment of a layered or 2D host material: Interlayer spacing determines the degree of desolvation of inserted ions, which in turn leads to increased ion- host interaction and electron transfer. Reproduced from Ref.* [2].

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Hybrid electrochemical capacitor with redox active electrolyte

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Constantly, the world is looking for the perfect energy storage and conversion system. Two energy storage technologies are currently the most popular - electric double-layer capacitors (EDLCs) and lithium-ion batteries (LIBs). On the one hand, EDLCs cannot (and is not obliged to) compete with Li-based technology in terms of energy density; this feature is quite often sought as the reason for the limited commercialization of EDLCs. On the other hand, LIBs have shorter lifespan and lower power values comparing to EDLCs. Therefore, it seems reasonable to merge both technologies into one compact device, called a hybrid lithium-ion capacitor (LIC). The hybridization of energy storage mechanisms allows for acquiring higher energy density values than EDLCs while maintaining high specific power and a great number of charge/discharge cycles. The major problem occurring during LICs assembling is the pre-lithiation stage. Auxiliary metallic lithium electrode is one of the solutions – in fact, this approach was encouraging; however, after the pre-lithiation process, the metallic lithium electrode should be entirely utilized or removed and become replaced by a carbon electrode. This raises technical and safety issues because the exchange requires an inert environment. Another approach uses composite materials as positive electrodes, allowing full intercalation of lithium into graphite structure.
Nonetheless, after the pre-lithiation process, the dead mass of the composite stays in the system and deteriorates the efficiency [1]. A different method of pre-lithiation using lithium from electrolyte was presented by Béguin et al. [2]. In this approach, the main problem identified was the consumption of lithium ions from the electrolyte and the diminished electrolytic conductivity of the solution.

In our work, we propose another concept that allows for full intercalation of the negative electrode without an auxiliary electrode or less-conductive composite on the positive side. In principle, the redox-active lithium salt dissolved in 1 mol·L^{-1} $LiPF_6$ in EC:DMC electrolyte served as a charge-balancer. Thus, additional Li^+ in the redox agent structure made the Li^+ concentration in the electrolyte non-affected. Full electrochemical tests, including cyclic voltammetry, galvanostatic charge/discharge and impedance spectroscopy, constant power discharge were carried out. In further studies, optimal LIC operating conditions, i.e., voltage (2.2 – 4.2 V) and current density (0.2 A·g^{-1}), were determined. The system has also been compared with commercial products.

Both, redox and non-redox processes occurring on both electrodes were identified. The capacitor's cycle life and the effect of the addition of inorganic salt on the conductivity were also investigated. Furthermore, detailed analysis has been conducted using operando mass spectrometry coupled with gas chromatography, SEM/EDS, Raman and FTIR spectroscopy.

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Box-like versus peak-shaped cyclic voltammograms for “pseudocapacitance”

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Electrical charge storage in electrodes can be achieved via one or the combination of three mechanisms, namely, Nernstian or electron transfer reactions, electric double layer (EDL) capacitance, and pseudocapacitance. The Nernstian storage has been widely recognized to happen in rechargeable batteries, whilst EDL capacitance in supercapacitors. Pseudocapacitance is a promoted mechanism in relation with supercapacitor, but the term first appeared in literature in early 1960s for description of reversible electro- adsorption. The connection of pseudocapacitance with the apparent capacitive features of some redox active materials, such as transition metal oxides and conducting polymers, has hugely promoted academic and industrial interests in supercapacitor, but it has never been unanimously explained or accepted. The confusion actually reflects very well the contrast differences in electrochemical performances as shown in Figure 1 between the pseudocapacitance from electro-adsorption, and hydrous ruthenium dioxide which is a typical electrode material for supercapacitor. Obviously, the former is Nernstian but the latter is capacitive, although both have been claimed to result from pseudocapacitance. This confusing situation has led to efforts to restrict pseudocapacitance to materials exhibiting box-like or rectangular cyclic voltammograms [3], but also a claim that pseudocapacitance is a “basically incorrect notion” [4]. This presentation aims to offer some analyses and clarifications of the development.

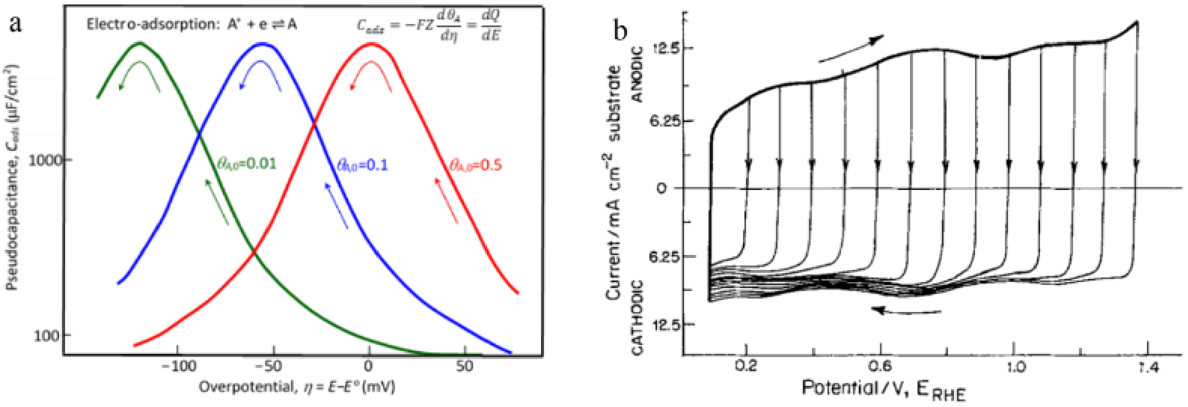

Figure 1. Electrochemical features of “pseudocapacitance” resulting from (a) the Bockris-Kita model on reversible electro-adsorption [1] and (b) hydrous RuO2 in 1 M H2SO4 [2].

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A smart way to enhance the energy output of electrochemical capacitors by internal hybridization of electrodes

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The relatively low amount of energy stored is the main technical disadvantage of electrical double-layer capacitors (EDLCs). Lately, the concept of hybrid capacitors, combining capacitive and battery-type electrodes, and behaving as classical EDLCs, appears as a promising alternative to enhance the energy output. Since the battery-type electrode operates in a narrow potential range, the potential excursion of the EDL electrode is ca. twice broader than in a symmetric EDLC, leading to the doubling of the discharge capacitance. Consequently, for the same voltage range, the specific energy output of the HC hybrid capacitor is twice higher than for an EDLC [1]. In the last decade, hybrid metal-ion capacitors (MICs) [2] have emerged as a very promising technology, essentially owing to the highly conductive properties and low cost of carbon electrodes.

MICs implement a metalated anode operating slightly above the metal deposition potential and an EDL positive electrode made from activated carbon (AC), allowing the maximum cell voltage to reach 4 V [3]. Hence, the specific energy output of an MIC at a given power is around four times higher than for an EDLC using the same AC. However, the necessary pre-intercalation/insertion of the metal in the anodic host before creating a MIC complicates the cell construction and increases the expenditure. Therefore, we have recently implemented a new strategy based on adding a sacrificial metalated material (for example sodium squarate – $Na_2C_4O_4$ [4]) in the positive AC electrode. During the preliminary oxidation of this electrode, the anions of the salt are oxidized, leading the metal ions to be irreversibly extracted and intercalated/inserted in the anodic host. However, to be regarded as a beneficial pre-metalation agent, a sacrificial material must gather essential criteria as a sufficiently high irreversible capacity, a relatively low oxidation potential, be oxidized without gas production, and its decomposition products should not alter the technical characteristics of the device. During our research on sodium-ion capacitors (NICs), we have identified few materials leading to improve the properties to the device after the sodium transfer. For example, when using $Na_2C_4O_4$, the squarate anions are oxidized with the production of CO, which is partly disproportionated to form carbon (blended in the AC electrode and enhancing its conductivity) and CO_2 reacting with sodium to form a Na_2CO_3 enriched S.E.I. on the anode, leading to improve the life span of the NIC. Nonetheless, to build an MIC with enhance simultaneously theed cycle life and energy output of an MIC, it is crucial to optimize the capacity ratio Q_-/Q_+ between the anode and the AC electrode and to consider the effects of the EDL electrode mass and metal insertion depth in the anode host [5].

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Impact of negative electrode utilization on cycle performance for LIC

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Lithium ion capacitors (LICs) are unique energy storage devices that combine the high power technology of conventional EDLCs with the high energy density characteristics of lithium ion batteries. An important technology in LICs is lithium pre-dope to a carbon negative electrode (NE), but how the depth of charge by pre-dope affects the charging and discharging performance of LICs is not well understood so far. In this study, pitch-coated graphite (PCG), which suppresses self-discharge, was used as NE. Noting that PCG has several stage structures, the objective of this study is to investigate the effects of NE utilization conditions (utilization stages and cycle utilization capacity) on the cycling behavior of LICs. In other words, we will report the effect of different utilizing stages with controlled depth of charge by pre-doping on the cycle behavior.

A four-terminal aluminum laminate cell was used with activated carbon as the positive electrode material, PCG as NE, Li metal foil as the counter electrode and reference electrode for pre-doping, and 1.2 M $LiPF_6$ /EC : PC : DEC (3 : 1 : 4 v/v/v) as the electrolyte. The NE utilization conditions are shown in Fig. 1 indicating the relationship between stage structure and pre-doping potential, and the horizontal arrows indicate NE utilization conditions. Pre-doping and cycling tests were performed according to the negative electrode utilization conditions. Pre-doping was performed up to a certain utilizing stage in a high-temperature environment, and the cycle test was conducted at room temperature for 500 cycles under constant current conditions at 5C.

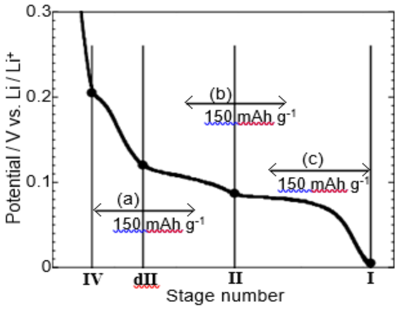
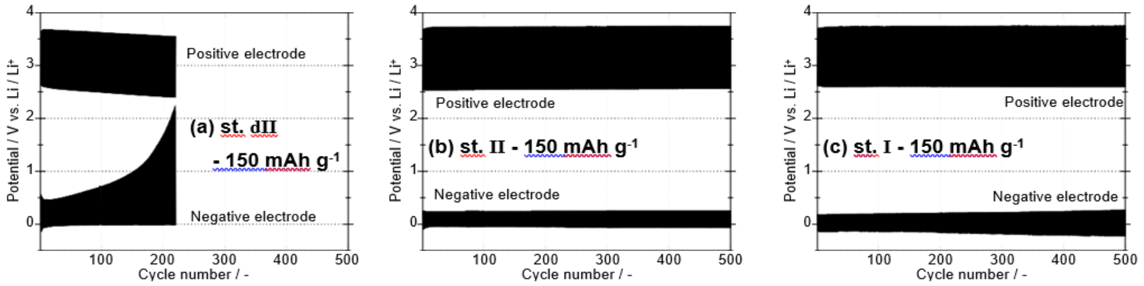


Fig. 1 Potential-stage diagram for negative electrode on pre-doping; indicated widths are cycling utilization ranges of negative electrode.

First, we found that the smaller the cycle capacity, the more stable the cycle behavior is, and that there is obvious Li loss in the early cycles, which does not affect the cycle stability regardless of the neutilization conditions. Fig. 2 shows the change in electrode potential (potential swing) for three cycle test conditions with a cycle capacity range of 150 mAh g^{-1} at different utilizing stages. In (a), the cycling is centered on “dilute stage II”. The utilization stage shifts to a shallower direction with cycling, and the NE potential increases and degrades. It is considered that Li is continuously lost from the NE during cycling. (b) shows the results with “stage II” as the utilizing stage. Compared to (a), the NE potential does not change with cycling and shows stable cycling behavior. (c) shows the utilization of “stage I” when the cell is charged. Although there is a concern about an increase in the resistance of the NE because the electrode potential falls below 0 V vs. Li / Li$^+$ during charging, the cycle behavior looks stable. From the present results, it is considered that the utilizing stage has a significant impact on the cycle characteristics. Based on the above, we will extensively discuss the influence of the utilizing stage on the cycle behavior

Fig. 2 Cycle behavior of a LIC showing the positive and negative electrode potential swing during cycle test; in condition (a) st. dII - 150 mAh g^{-1}, (b) st. II - 150 mAh g^{-1}, and (c) st. I - 150 mAh g^{-1}.



Enabling redox flow batteries for grid stabilization by hybridization with supercapacitors

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Based on the Paris Agreement and the Sustainable Development Goals [1], among others, efficiency improvements and a higher contribution of renewable energies in the grid are essential to achieve an affordable and clean energy system with a high degree of awareness of ecological sustainability. With increasing amounts of renewable energies in the European energy market, new challenges for private and public grids arise. Batteries in stationary applications are essential to ensure a high share of renewables, while meeting efficiency goals, secure supply, affordable prices, and low environmental impact. The project HyFlow addresses all these challenges by developing a hybrid energy storage system (HESS) that is capable to deliver high-energy and high-power needs on laboratory (5 kW) and industry scale (300 kW).

To this end, a high-power vanadium redox flow battery (HP-VRFB), a supercapacitor (SC), operating as two distinct systems are electrically hybridized to optimize power and energy requirements. The hybridization of battery systems for stationary energy storage will play an outstanding role beyond already known battery technologies to simultaneously serve high-energy and high-power needs in industrial, private, and weak distribution grids. New developed HESS should be able to balance out power and energy requirements in critical local grid conditions, e.g. with high load or generation peaks. In these demanding applications, hybridization leads to more efficient storage systems, with longer lifetimes. In addition, the ability to create a storage solution operating on all timescale from seconds to days can be beneficial for applications like virtual inertia or a specialized, large-scale uninterruptible power supply. The strategy to tailor storage systems to special load or generation requirements is an important part to reduce the dependency on fossil fuels and emissions as well as to provide future energy storage solutions for diverse applications.

The innovative HESS is developed and validated on demonstrator-scale (5 kW scale) including sustainability analysis. Application scenarios of the HEES will be investigated based on real load profiles, subdivided into four application categories: (1) Peak shaving of short duration peaks, (2) Weak distribution grids, (3) Uninterruptible power supply, and (4) Grid services (virtual inertia). Based on two demonstrators (lab-scale and industrial application-scale), experimental data and simulation models will be used to develop and optimize the HESS components, topologies, and control strategies. Therefore, the new Energy Management System should be able to predict all power demand precisely and dedicate the most efficient power flow between the HP-VRFB and the SC.

Acknowledgments

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Electrochemical Capacitor System Design Using Spec-Shee Data

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Electrochemical capacitor specification sheets typically list electrical properties such as rated voltage, capacitance, and series resistance plus the physical dimensions and mass. Specification sheet information from eight electrochemical capacitor products [1] was used to estimate their performance ranking in meeting storage system needs in four applications. Rankings were based on storage system volume, mass, cost, and efficiency. Minimum-size storage systems for each of these applications had previously been designed for the same eight capacitors using experimental data with equivalent circuit models and SPICE (Simulation Program with Integrated Circuit Emphasis) circuit simulation software [2]. Thus, a direct comparison could be made between the rankings based on spec-sheet data and the rankings of rigorously designed systems.

Conclusions are unambiguous--spec-sheet information is inadequate for ranking the suitability of the different electrochemical capacitors for specific applications. In other words, product information from the manufacturers was insufficient to allow consistent selection of the “best” capacitor for each application. Selection mistakes occurred most frequently for applications having power profiles with short-duration (<10 s) charge or discharge features. Distributed charge storage was the primary source of this difficulty, i.e. porous-electrode behavior.

Performance of the eight capacitor products could be clearly differentiated using impedance spectroscopy, which directly measures effects due to distributed charge storage. Information gained from this single measurement was far superior to specification sheet data and it allowed for the more optimal selection of which capacitor was best suited for each application. This presentation discusses the difficulty of selecting the optimal commercial electrochemical capacitor product by only using spec-sheet data and then the value of adding impedance spectroscopy measurement data to help resolve this difficulty.

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From 1F lab-scale LIC to a roll-to-roll fabricated 100F prototype: the story of an adventurous journey

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Lithium ion capacitor (LIC) is an emerging technology that holds promise to bridge the energy-to-power gap between already market stablished lithium ion battery and electrochemical double-layer capacitor technologies. Academic research is mainly focused on increasing energy, power and cycle life metrics, but next, pre-lithiation strategy is the key that will open the final door, or not, towards industrialization and commercialization of the technology. Its relevance has only recently been thoroughly considered, but several strategies, all with their own particular set of assets, are already available within the state-of-the-art. From the initial auxiliary lithium metal electrode used only for laboratory research, to more sophisticated and industrially compatible strategies based on sacrificial salts. This transition attends to the logic evolution of a variety of strategies that started to consider market needs such as processability, safety and cost. However, none of these novel strategies have been demonstrated in a relevant environment, all remaining at the proof-of-concept level and still being metallic lithium the choice of industry for pre-lithiation. Thus, we faced the challenge of a scale-up effort to demonstrate technology viability (or not) of the sacrificial salt concept for pre-lithiation of a LIC. In this work, we will address and discuss the needs and challenges found along this journey; such as ink formulation and scale-up, electrode R2R fabrication, pouch cell assembly, pre-lithiation and finally, obtained electrochemical results including ageing tests.

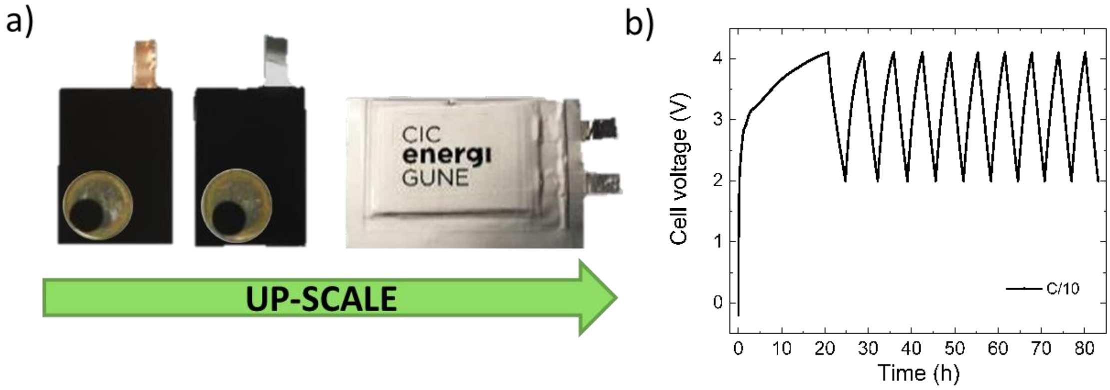

Figure 1: ***a)*** *Scale-up effort for a LIC device consisting on hard carbon as active material in the negative electrode and activated carbon combined with a sacrificial salt in the positive electrode. The sacrificial salt is used a source of lithium ions in order to compensate for the first cycle irreversibility. Lab-scale Swagelok-sized electrodes of 1 cm2 were upscaled to 20cm2 and assembled in pouch cell configuration.* ***b)*** *Pre-lithiation step of a 100F LIC prototype*

Evaluation of the Electrified Interface in Electrochemical Capacitors

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Abstract

Central to the behavior and performance of carbon-based electrochemical capacitors is the electrified interface that exists between the electrode and electrolyte. The structure of this interface has been the subject of considerable research, with sequential models gradually improving the understanding of the electrochemical nature of this interface. Many of the models that were proposed were based on the use of an aqueous electrolyte combined with a mercury electrode. The aqueous electrolyte was used because of the commonality, while mercury was used because of its high overpotential for hydrogen evolution and atomic smoothness. Improvements in these models were based generally on greater understanding of solvent and ion behavior, and interactions. Of course many other electrodes and electrolytes have been used and so it is appropriate to re-visit this understanding of the electrified interface with a view to considering electrode-electrolyte systems relevant to electrochemical capacitors with the application of advanced electrochemical methods.

Given that carbon materials form the basis of many electrochemical capacitor electrode systems, we have chosen glassy carbon as the starting point for study because of its non-porous nature and near atomic smoothness. This electrode has then been subjected to a number of electrochemical techniques including cyclic voltammetry (CV), step potential electrochemical spectroscopy (SPECS) and electrochemical impedance spectroscopy (EIS) in a number of common aqueous and non-aqueous electrolytes. A variety of experimental conditions have been used, including two- and three-electrode systems, different temperatures, rotating disk electrode studies, as well as combinations of the aforementioned electrochemical techniques.

This presentation will focus on the advanced in electrochemical techniques and understanding we have developed related to the glassy carbon electrode system, together with its associated properties. Outcomes include:

- (i) Combining the SPECS and EIS methods to probe the nature of the electrified interface, essentially providing a cross-sectional view of the interface at different frequencies;
- (ii) Characterization of the kinetics and thermodynamics of charge storage at the interface using entropimetry to quantify the entropy, enthalpy and Gibbs energy of charge storage at the interface; and,
- (iii) Provide indication that the thickness of the interface in the electrolyte is much thicker than that predicted by previous models, with implications for porous electrode behavior.

Multi-scale models for a better understanding and performance prediction of the carbon electrode / electrolyte interface in supercapacitors

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Progress in the development of novel energy storage systems is hampered by our lack of understanding of the microscopic mechanisms that determine their performance. The key issue is that phenomena on the atomistic scale have consequences on macroscopic length and timescales. In particular, the effects of ionic confinement and diffusion are crucial for device performance, yet experiments that probe properties related to local structure and diffusion are challenging and difficult to interpret without a parallel modelling approach. In this talk, I will focus on carbon-carbon supercapacitors in which the energy is stored by ion adsorption at the electrode surface. In order to understand fundamentally the macroscopic properties of such systems, it is essential to characterise finely the porous materials used and the structural and dynamic properties of the fluid adsorbed. But, in order to screen materials for energy storage applications, it is necessary to develop computationally efficient methods. Here, I will present insights from different approaches. I will first describe molecular dynamics simulations which provide a microscopic understanding of the charging mechanisms in supercapacitors. I will then show the promising results we obtain with a mesoscopic model we develop, 10,000 times faster than molecular dynamics simulations, for the prediction of electrochemical performance in these systems.

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An inclusive mathematical model for Faradaic Electrode Materials in electrochemical energy storage

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Electrochemical energy storage devices are built on the foundation of batteries and supercapacitors. Despite the fact that both depend on electrochemical processes, their charge-storage systems are distinct, resulting in varying energy and power densities. Pseudocapacitive materials store charge by Faradaic redox processes, but their electrochemical signature is similar to that of electrochemical double-layer capacitors. As a result, these materials provide a mean to simultaneously obtain both high energy and power densities. This peculiar electrochemical signal, which looks like an electrochemical double layer but is caused by redox processes, is still a mystery and a topic of considerable controversy. Surprisingly, there is no all-inclusive analytical model for analysing a battery material's voltammogram. But, the basic electrochemical features of batteries and pseudocapacitive materials are discussed in this presentation, with a focus on electron -ion transfer mechanisms. Our discovery establishes a basic mathematical relationship between all Faradaic electrode materials: battery and pseudocapacitor.

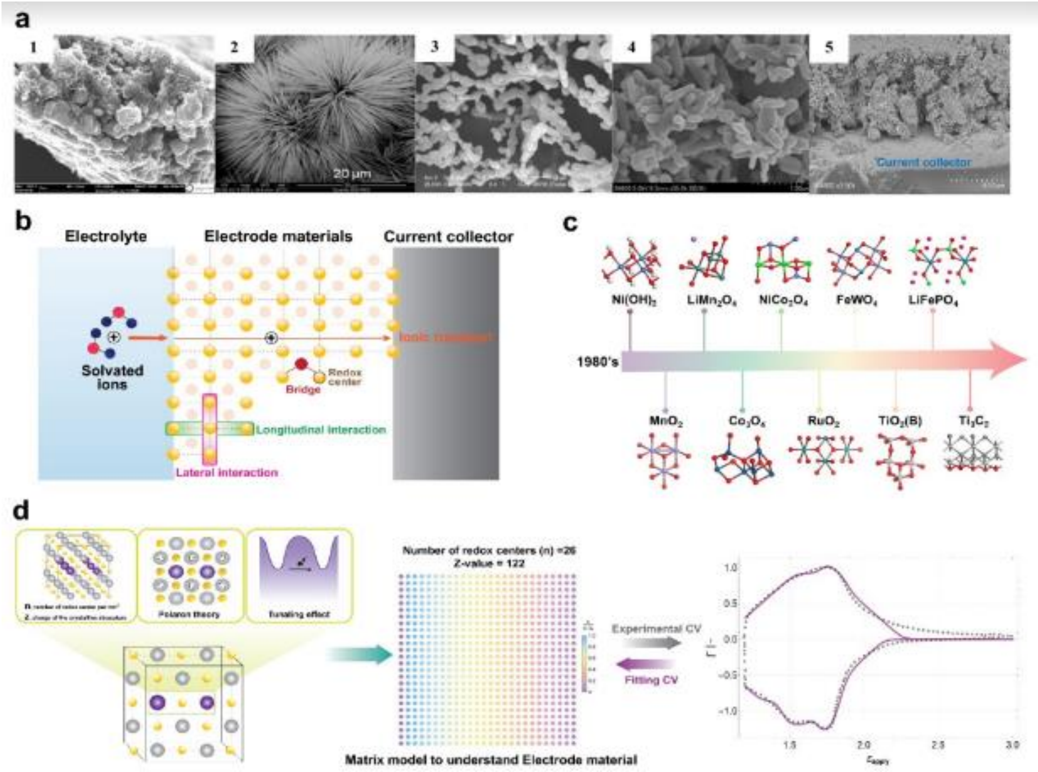

Figure 1: *model proposed in the present study including correlation between material structure and theoretical cyclic voltammogramm.*

Ionic liquids in Electrochemical Capacitors: From Macro to Micro

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Ionic liquids are very appealing electrolytes for electrochemical capacitors. Being organic molecules in nature (at least for the vast majority), they offer immense possibilities for structural modifications to adjust their properties (viscosity, electrochemical stability window, melting point, etc.) or to add a functionality to do chemical reactions. With a careful design, such modifications can be made while keeping the original properties of the ionic liquid which make them attractive. A nice example is the modification of an ionic liquid structure with a redox group to obtain a non-volatile, thermally stable liquid phase which is intrinsically electroactive.[1]
The first part of the presentation will cover the study of such electroactive ionic liquids as redox-active electrolytes electrochemical capacitors.Refs The redox ionic liquid EMIm-FcNTf (Fig. 1) obtained by substituting a trifluoromethyl group of the NTf_2 anion with a methaneferrocenyl group was studied in particular do to the 3.2 M concentration in redox centers that can be obtained. In comparison, ferrocene is only soluble to a few mM in EMIm-NTf_2. Capacitors using activated carbon electrodes with such electrolyte provide significantly high energy densities compared to unmodified ionic liquid electrolytes because of such high concentration in redox centers. In addition to the increase in energy density, the EMIm-FcNTf ionic liquid is also interesting to gain insight in the processes leading to charge storage in these systems. Using solid-state NMR, changes in the population of the FcNTf anions inside the pores of the activated carbon as a function of the potential applied was monitored with the ^{19}F NMR signal from the triflimide moiety on the ferrocene.[2] Du to the large size of the redox anion, only 33% of the FcNTf population was found within the YP-50F pores, suggesting that a significant fraction of the electron transfer between the ferrocene and the carbon was taking place on the surface of the carbon particles. This knowledge motivated further studies using carbon with different pore sizes and distributions, the results of which will be discussed during the presentation.
The second part of the presentation will focus on protic ionic liquids (PIL), obtained by the reaction between Bronsted acids and bases, that are able to transfer protons with metal oxide electrodes for pseudocapacitance.[3] The focus of this section will be on the use of the protic ionic liquid triethylammonium bis(trifluoromethanesulfonyl)imide (TEAH-TFSI, Fig. 1) to improve the energy density of RuO_2 microsupercapacitors.[4] These electrochemical capacitors are fabricated by photolithography and are expected to find application in microelectronic devices to power sensors and data transmission for Internet-of-Things. This first demonstration of the use of PILs for metal oxides microsupercapacitors showed an extended cell voltage up to 2 V with 4 times more energy density compared with conventional H_2SO_4 electrolyte.

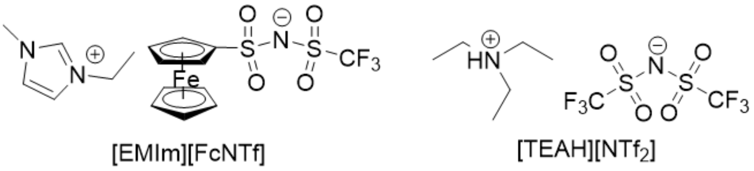

***Figure 1:** Redox-active and protic ionic liquids featured in this*

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Application of cobalt oxide electrodes in the presence of aprotic ionic liquids for symmetric supercapacitors

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Co_3O_4 nanowires were uniformly deposited onto Ni foam (Co_3O_4@Ni) [1] and applied as electrodes for symmetric supercapacitors [2]. The electrochemical performances of Co_3O_4@Ni were investigated in the presence of aprotic ionic liquids (ILs) and compared to the commonly used KOH electrolyte. The selected ILs are composed by the same bis(trifluoromethylsulfonyl)imide ($TFSI^-$) anion, paired with 1-Allyl-3-methylimidazolium ($AMIM^+$) or 1-Ethyl-3-methylimidazolium ($EMIM^+$) cations. Independently on the electrolyte nature, the profiles of cyclic voltammograms and galvanostatic charge/discharge curves are indicative of an electrochemical double-layer charge storage mechanism. Combining our Co_3O_4@Ni electrodes with selected ILs electrolytes showed good electrochemical stabilities with 85% and 97% retentions of the initial capacitances after 10 000 cycles in [AMIM-TFSI] and [EMIM-TFSI], respectively. At a current rate of 0.2 A g^{-1}, the lowest values of specific energy (2.8 Wh kg^{-1}) and specific power (201.9 W kg^{-1}) were exhibited in the presence of KOH electrolyte. This poor electrochemical performance was considerably improved by using aprotic ILs. For [AMIM-TFSI] and [EMIM-TFSI] based polymer gel electrolytes, high specific powers up to 811 and 680 W kg-1 were delivered at 0.2 A g^{-1} with enhanced specific energies of 29.4 and 23.3 Wh kg^{-1}, respectively. Hence, the specific energies of the devices assembled by PVDF-HFP/AMIM-TFSI or PVDF-HFP/EMIM-TFSI electrolytes were 8 to 10 times higher than that of the device assembled by PVA/KOH electrolyte.

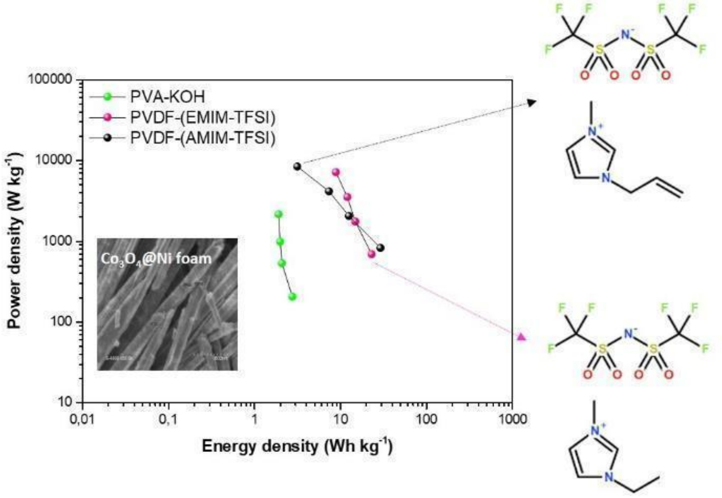

Figure 1: *Ragone plot of Co_3O_4@Ni//Co_3O_4@Ni symmetric supercapacitors exhibited in the presence of various electrolytes.*

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Redox-active organic molecules on carbon

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Grafting redox active moieties, including anthraquinone, on large surface area carbons has been for long considered has a good opportunity to increase the energy density of electrochemical capacitors.[1,2] From the CVs, usually looking like the merging of redox and capacitive signals, the storage capability obviously takes benefit from both contributions. Unfortunately, performances are not fully met: when increasing the anthraquinone loading above 10-15 w%, the double layer contribution decreases because of pore clogging. Cyclability is also poor: during the first few hundreds of cycles (often less), the capacity is progressively fading down because of either physisorb anthraquinone molecules being washed away from the carbon surface and molecule degradation.

Various approaches have been considered to address these limits. This paper is an introduction to two of those that we have explored. The first one consists in the covalent grafting of an anthraquinone propargyl molecule by a Diels Alders reaction using carbon surfaces as dienophyl. [3] For the second, various redox-active organic molecules are first simply adsorbed at the carbon surface. In a second step, flakes from exfoliated Ti_3C_2 MXene are deposited by dip-coating on top of the organic film. This carbide shell provides the resulting composite some extra electronic conductivity while allowing the electrolytic species to reach both organic layer and carbon surface thanks to its open structure.

Attractive electrochemical characteristics have been obtained from electrodes based on these different materials. These are discussed based on the compositions and morphologies of the prepared composite materials.

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Enhanced electrochemical performance of activated carbons derived from peanut shell waste

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In this work, peanut shell waste activated carbons and its composites were explored as potential electrode materials for supercapacitor applications. This study reports the enhancement of electrochemical performance of the peanut shell waste activated carbons (PAC) through (i) a pre-carbonization followed by an chemical activation (PAC), (ii) heteroatom-doping with nitrogen (NPAC) and (iii) an incorporation of pseudocapacitive materials (molybdenum-based components) into PAC by making a composite (PAC/MoO_2/Mo_2C). Their physicochemical, surface and electrochemical properties have been successfully achieved using various techniques. All activated carbon materials were synthesized using chemical vapour deposition (CVD) and characterized by N_2 adsorption-desorption, X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), high-resolution transmission electron microscopy (HR-TEM) and X-ray photoelectron spectroscopy (XPS). The textural properties obtained were depicted with relatively high specific surface area values of 2547 m^2 g^{-1}, 1442 m^2 g^{-1} and 711 m^2 g^{-1} for the PAC, NPAC and PAC/MoO_2/Mo_2C samples, respectively.

The electrochemical performance of the as-synthesized PAC and its composites electrodes materials have been tested in symmetric devices in 2.5 M KNO_3 aqueous electrolyte. The activated carbon-based electrodes exhibited a good electrochemical energy storage capability with a wide cell potential in the range of 1.8 - 2V. The as-fabricated symmetric supercapacitors exhibit remarkable specific energy ranging from 25 W h kg^{-1} to 52 W h kg^{-1} as a function of specific power from 900 W kg^{-1} to 1000 W kg^{-1} at a specific current of 1 A g^{-1}. Moreover, long term device stability was exhibited with an a 99.8% coulombic efficiency, 83% capacity retention over a 25 000 charge/ discharge cycles and also a good rate capability after 180 h of floating at 5 A g^{-1}.

Laser-induced graphene: a disruptive material for micro-supercapacitors

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Due to its unique features, laser-induced graphene (LIG) can be considered as disruptive technology for creating a few-layer graphene-based film that received much attention in the field of flexible electronics. Among all, energy storage, catalysis, sensing, and separation are the main applications that have been investigated in recent years with large improvements in the respective device performance. In particular, miniaturized supercapacitor—usually called a micro-supercapacitor (µSC)—is the most investigated field in which LIG can strongly provide outstanding results concerning the state-of-the-art simplification of the fabrication procedure and intrinsically allowing the flexibility of the device. However, many open points still limit the possible full exploitation of this technology in the energy storage sector. In this talk, a concise overview of the LIG application in µSCs will be provided suggesting where the community should direct efforts to enhance the results together with associated challenges. In particular some of the main issues are related to i) the charge balancing, i.e. an optimization procedure to let anodes and cathodes operate in their full potential window (allowing the device to exploit the maximum voltage window maximizing the energy density); ii) the electrical conductivity of LIG path, with impact of internal resistance and charge accumulation; and iii) the surface properties that strongly affect both the wettability (hence the electrolyte/electrode interface) and the electrochemical behavior of the LIG electrodes. Based on the research developments achieved and foreseen, we expect that also LIG will be exploited as electrode material for efficient, high fabrication yield µSCs for portable microelectronics.

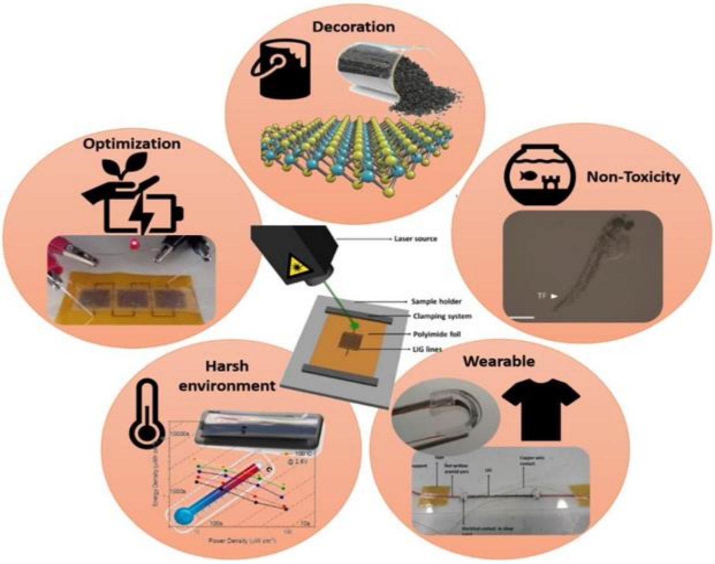

Figure 1: *Optimization strategies and application fields of LIG* [1]

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REGULAR ORAL PRESENTATIONS

Tungsten bronzes A_xWO_3 (A = Li, Na, and K) as electrode materials for high energy aqueous storage devices

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Tungsten oxide WO_3 is a well-studied material due to its electrochromic, photochromic, and catalytic properties and presents a wide diversity of polymorphs. Among them, is the metastable phase of hexagonal bronze (h-WO_3) which cannot be obtained by purely structural transformation upon temperature [1]. This structure possesses a rigid tungsten-oxygen framework built up of layers containing corner-shared WO6 octahedra that are arranged in six-membered rings. The layers are stacked along the [00l] axis, giving rise to one-dimensional tunnels being able to host different alkali cations such as Li^+, Na^+, and K^+ [2]. This arrangement can result in interesting electrochemical properties when the hexagonal bronze is used as an electrode material for energy storage devices [3].

Hexagonal tungsten oxides were successfully synthesized by hydrothermal synthesis. The materials were characterized by X-ray Diffraction, Scanning and Transmission Electron Microscopy, Energy dispersive X-ray spectroscopy, and BET specific surface area. As an example, Li_xWO_3 shows a nanorod-like morphology (Figure 1a) where the growth of the stacked hexagonal rings along the c direction is observed, (structure view from c direction is shown in Figure 1 b)). In this work, we report the synthesis of different hexagonal bronzes of tungsten oxide with the general formula A_xWO_3 (A= Li, Na, or K and $0 < x < 0.33$). We studied the electrochemical behavior in different aqueous electrolytes such as $LiNO_3$ (5M and 1M), Li_2SO_4, Na_2SO_4, and K_2SO_4. (0.5 M) obtaining specific capacities of ~70 C g^{-1}, ~49 C g^{-1}, ~41 C g^{-1}, ~24 C g^{-1} and ~13 C g^{-1}, respectively at 2 mV s-1 for Li_xWO_3. The cyclic voltammograms for all electrolytes are displayed in Figure 1 c). In this communication we will unveil the charge storage mechanisms of these tungsten bronze using advanced characterization techniques such as operando X-ray Absorption Spectroscopy (Rock beamline in Soleil synchrotron, France).

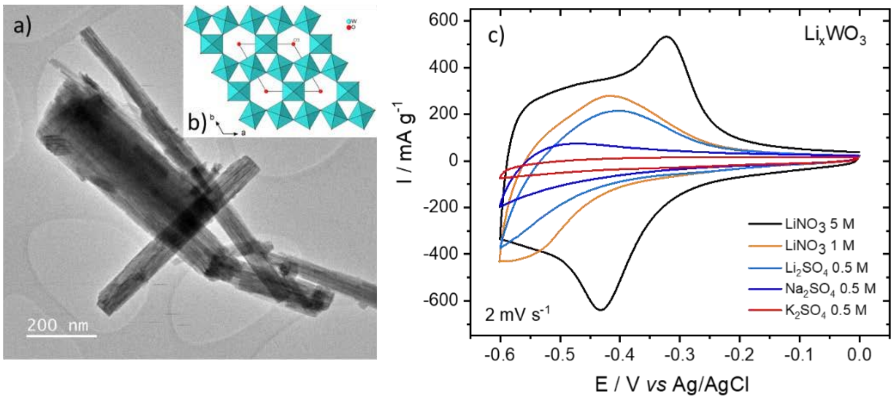

Figure 1: *a) TEM image of Li_xWO_3 nanorods, b) Crystal structure showing the hexagonal rings and c) Li_xWO_3 cyclic voltammogram in different aqueous electrolytes at 2 mV s^{-1}*

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α-hydroxy acids ketals as bio-based solvents for Electrical Double Layer Capacitors: a structure-performance case study

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The energy transition towards renewable sources is a collective challenge that fully involves scientific research, and in this context the development of new materials for energy storage is a crucial task. Among the storage devices, the electrical double layer capacitors (EDLCs) are attracting increasing interest thanks to their high-power densities, which are difficult to achieve with other devices. From the point of view of the environmental impact, EDLCs are highly *green* devices, in fact they have a long-life cycle (> 100,000 cycles) and can be produced for the most part by bio-based substances, such as activated carbon (AC) and carboxymethylcellulose (CMC) or completely recyclable, such as aluminum. In this aspect, the electrolyte is often considered a weak point, as it is generally prepared using fossil-based solvents (mostly acetonitrile, ACN; and propylene carbonate, PC) with high hazard and eco-toxicological profiles. [1]

The replacement of common dipolar organic solvent is a wide-ranging issue, and the direct replacement of fossil-based solvents with bio-based ones is still limited by a narrow choice of solvents (e.g.: Cyrene™, γ-valerolactone, dimethyl isosorbide). [2]

Here we report a preliminary study related to the use of an innovative class of solvents, obtainable through the ketalization of α-hydroxy acids (AHAs). AHAs, like lactic acid, are industrially produced through carbohydrate fermentation processes. We show how the molecular structure of the solvent strongly influences the electrolyte properties, and the most suitable in the applied conditions, namely 5-methyl-1,3-dioxolan-4- one, can be successfully utilized in EDLCs displaying high specific power as well as specific energy (22.5kWkg^{-1} and 13.4 Whkg^{-1}, respectively). [3]

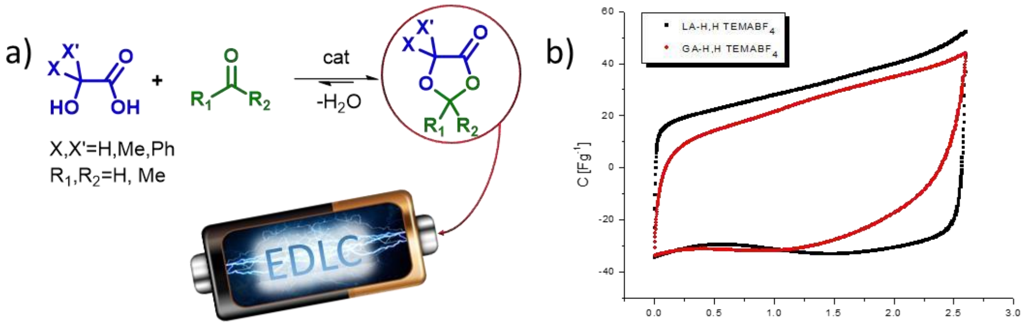

Figure 1: *a) α-hydroxy acid ketals synthesis scheme; b) Cyclic voltammetries of electrolytes based on 1,3-dioxolan-4-one (GA-H,H) and 5-methyl-1,3-dioxolan-4-one (LA-H,H) as solvents for electrolyte.*

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Powerful dilatometric investigation of Li-ion capacitor materials

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One of the strategies to improve energy storage is to enlarge the working voltage range with the use of asymmetric combination of a battery-like electrode (providing high energy density) and EDLC electrode (providing high power capability), the so-called "asymmetric hybrid capacitors". A simple example is given by a system composed of activated carbon electrode and a graphite-based electrode, the latter working through insertion/de-insertion of lithium ions into graphite layers during charge/discharge cycles, respectively. The underlined mechanisms will cause electrode materials (graphite, in this case) to be subjected to volume variation during operation. The volume changes of the electrode materials during capacitor charging and discharging can limit the performance of the capacitor itself [1-4].

A study of the volumetric stability of the material during charge-discharge cycles is crucial for the design of hybrid capacitors able to maintain their efficiency characteristics as long as possible. In-situ electrochemical dilatometry is a powerful tool that recreate the conditions in which the electrode material works inside the hybrid capacitor. This allows to evaluate and quantify the macroscopic expansion and contraction of materials caused by the insertion/deinsertion of guest ions, which eventually lead to the deformation of crystal lattice. In addition, through this analysis it is possible to quantify the irreversible deformation of the electrode material and any secondary phenomena that may occur during operation [5, 6] .

The present study takes advantage of a novel equipment for testing different typologies of materials under diverse operating conditions. The dynamic behaviour of the electrode thickness change was monitored over several consecutive cycles.

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Industrial manufacturing of VACNT electrodes until high power Supercapacitors: VACNTs as material with numerous possibilities

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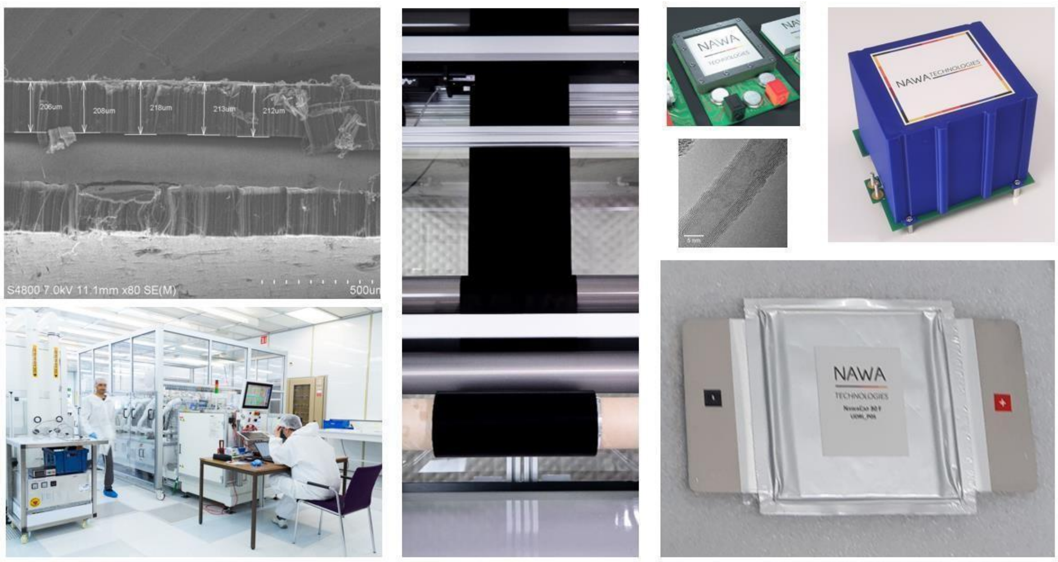

Figure 1: *VACNT electrode, NAWACap Power (big cell) and its applications*.

Vertically Aligned Carbon NanoTubes (VACNT) [1] have demonstrated outstanding potentialities as novel material to prepare structural composite or elaborate multifunctional materials for a wide range of application [2]. NAWA breakthrough in electricity storage is the industrialization of a new electrode based on VACNT. This high conductive electrode material (both for electrons, ions and phonons) and a physical anchoring on current collector let to obtain electrodes and cells with lower equivalent serie resistance.

This technology offers new ways for high power needed applications or hybrid solutions to avoid the oversizing of usual electrical storage solution for power peak management. Our last results and some specific savoir-faires will be presented.

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Controlling charge carrier ions for high-kinetics battery chemistries

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Electrochemical energy storage technologies have been brought into the spotlight as they provide elegant and efficient approaches to store, transport, and deliver energy harvested from sustainable energy resources.[1-2] Typically, supercapacitors and batteries differ in electrochemical mechanisms, hence featuring almost opposite energy and power characteristics. However, the demand for power and energy supply is equally imperative in actual use and is keen to expand in the future. Thus it is highly desirable to design new electrode chemistries for energy storage devices to mitigate the power-energy tradeoff.

Here, I will present our recent studies in controlling the charge carrier ions of 2D layered electrode materials for high-power energy storage applications.[3-5] Specially, we have demonstrated several interlayer space engineering strategies for inorganic 2D layered materials to regulate the ion transport phenomena, such as solid-state diffusion kinetics,[6] selective-ion transport properties[7], and additional ion-storage sites[8]. Moreover, we will also introduce our latest efforts in manipulating interfacial ion behaviours (*e.g.*, ion desolvation, anion-cation dissociation), by the manner of constructing crystal polymer-based artificial interface and precisely electrolyte engineering.[9-10]

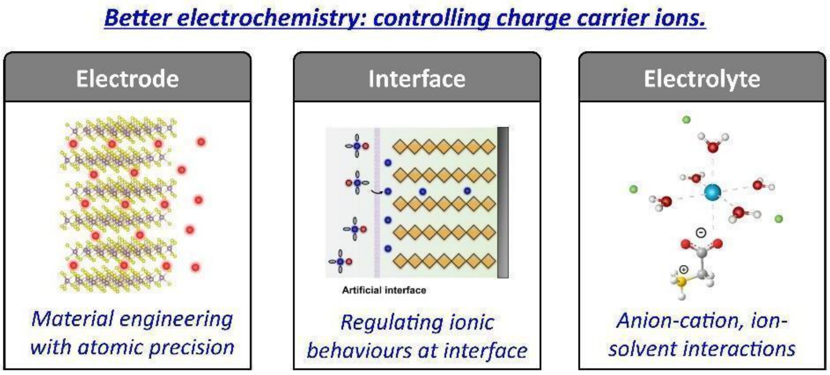

Figure 1: *Our strategies to control charge carrier ions*.

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Hygroscopic protic ionic liquids as electrolyte for electrical double layer capacitors

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The influence of water on protic ionic liquids (PILs) has been investigated in the past due to a variety of reasons. On the one hand, PILs are an interesting model electrolyte to study the behavior of water molecules and especially the movement of protons. It can be similar to the behavior in pure water and even result in fast non-vehicular ion transport mechanisms, i.e., the Grotthuss-mechanism.[1] On the other hand, PILs are often hygroscopic, making the exclusion of water in applications like supercapacitors difficult. Thus, the impact of very low water concentrations, residual after drying, on the performance of energy storage devices has been studied and found to be detrimental. Especially for electrical double layer capacitors (EDLCs), in which the energy is drastically lowered by the resulting smaller operative voltage (OPV).[2]

In a previous work, we showed that using the hydrophobic PIL 1-butylpyrrolidinium bis(trifluoromethyl sulfonyl)imide ([$\mathrm{Pyr_{H4}}$][TFSI], it is possible to design water-in-PIL electrolytes, which can be utilized for the realization of EDLCs able to display high power at room temperature.[3]

In this work, we consider for the first time the use of a very hygroscopic PIL, 1-methylpyrrolidinium tetrafluroborate ([$\mathrm{Pyr_{H1}}$][$\mathrm{BF_4}$]), with the aim to decrease the amount of water necessary to impact the PILs' properties, keeping the electrolytes electrochemical stability as high as possible. Additionally, as in our previous work, the interactions between anions, cations as well as water molecules is investigated using classical molecular dynamic simulations.

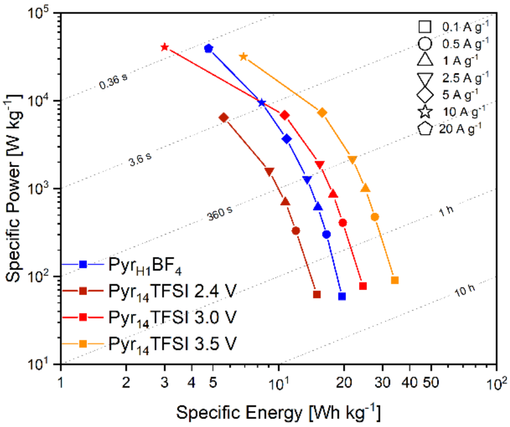

Figure 1: *Ragone plot comparing the performance of EDLCs employing the aprotic IL [Pyr14][TFSI] at different OPVs as well as our water-in-PIL electrolyte based on [$\mathrm{Pyr_{H1}}$][$\mathrm{BF_4}$].*

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Ion transport from water-in-salt electrolyte through porosity of hierarchical porous carbons

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Water-in-salt electrolytes (WiSE) have recently emerged as an avenue for potentially more affordable and certainly easier-to-build energy storage cells, but the high viscosity and limited conductivity of WiSE are poorly compatible with high-power devices such as electrochemical capacitors. To understand the real value of WiSE in carbon/carbon double-layer capacitors, we carried out a solid-state NMR spectroscopy for in-pore ion and solvent propagation from a WiSE, 5M LiTFSI, when it wets two carbons with completely different porosities. The first (MTK) has almost exclusive suprananometer micropores (above 95% of the micropore volume) and a significant mesopore volume distributed between 4 and 13 nm while the second (MTKN) features at least 50% of pores in the subnanometer range (Fig. 1A). The results show that a high share of the subnanometer pore volume is not accessible to the WiSE (MTKN) while the presence of an abundant mesopore volume gives rise to a two-step process where the WiSE first fills the mesopores up, and later propagates to the micropores, yet in deeper pore positions due to the prevailing suprananometer micropores in MTK, as distinct from the major subnanometer micropores in MTKN. In agreement with the NMR results on carbon wetting with the WiSE, efficient capacitive features can be observed for both slow and rapid charging in suprananometer micropores and mesopores (MTK, Fig.1B) whereas the substantial capacitive response is only clear at a low rate if subnanometer pores dominate the porosity (MTKN, Fig.1c). High-rate conditions prevent a sizeable charge build-up due to the steric hindrance to the ion transport from the WiSE deep down such narrow pores (MTKN, Fig.1C). Thus, the NMR approach enables direct ionic-level observation of the drastic impact that the relative pore/ion size exerts on electrolyte propagation deep down the pore volume, which can otherwise be only presumed considering bulk textural properties and estimates of ionic dimensions. The NMR results also provide a rationale for the radical changes in low-and high-rate electrochemical responses when using differently nanosized pores (Fig. 1 B and C). The electrochemical results show that WiSE can be successfully used in electrochemical capacitors provided the carbon texture is properly adapted.

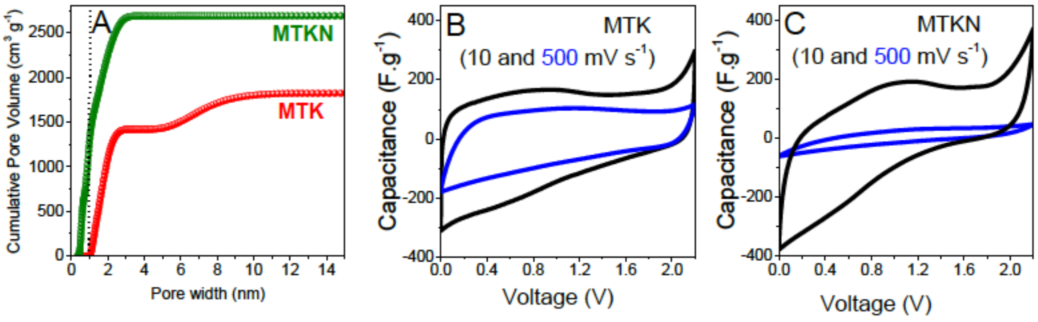

Figure 1: *Cumulative pore volume (A), CV at 10 mV.s^{-1} (black curves) and 500 mV.s^{-1} (blue curves) for MTK (B) and MTKN (C) in 5M LiTFSI. The dotted line (A) is provided as a visual guideline to separate the subnanometer pores.*

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Ionogels: past, present and futur

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After almost 20 years since their first developments, ionogels continue to be the subject of research. Their performances, the increased safety they bring, their industrializable formulations motivate this attraction. The current work sometimes shows an increasing complexity of the confining network, as well as confirming the versatility of ionogels for most ionic liquids.

Within an ionogel, a solid network confines a major part of the ionic liquid, with the formation of two continuous interconnected networks. These are biphasic electrolytes, with a real liquid state demonstrated at the micron scale. They allow not only to have all-solid devices very often with performances very close to those of liquid electrolytes, but sometimes even with higher performances.

The effect of the interface is one of the determining elements: it locally modifies the physics of ionic liquids, through short-range anion-cation interactions, but also limits the size of the aggregates to an immediately larger scale. In other words, the interface moderates some of the detrimental characteristics of ionic liquids. Examples of a wide range of studies, both with rigid inorganic confining arrays and with polymeric and dynamic confining arrays at the nanometer scale will be presented. Preferential segregation effects of certain species at the interfaces can also be exploited, in order to modify the cation-anion interaction and thus favor the diffusion at the interface of certain ions of interest: it is here the balance of the chemistry of the confining network and that of the confined species that must be found.

The degree of confinement itself, i.e. the quantity of ionic liquid confined and the dimensions of the confinement space, influences the macroscopic performances: on the one hand the ionic conductivity is proportional by definition to the quantity of ionic species, but on the other hand the ratio between the interface surface area and the quantity confined must be optimized. Some physical effects such as changes in phase transition temperatures are often reported, while others such as the equivalence of the pressure increase in situ are less so.

The diversity of applications is increasing: supercapacitors, batteries, photovoltaics, low temperature fuel cells, sensors, actuators, electronics, vacuum or high temperature environment ... Their processing is currently undergoing spectacular developments, motivated by the diversity of applications, but also by the versatility of the chemistry, from liquid to solid phase, used for the synthesis of ionogels.

High performance novel asymmetric MXene@CNT//N-doped CNT flexible hybrid device with large working voltage for energy storage

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Electrophoresis deposited Mxene on carbon nanotube yarn and microwave-assisted nitrogen-doped carbon nanotube yarns are electrochemically characterized as negative and positive electrodes, respectively. Interestingly, the nitrogen doping shows excellent repeatability with sole pyridine nitrogen observed. The assembled cell based on these electrodes exhibited a large operating voltage window of 2.0 V in a PVDF membrane saturated with 0.5 M of H_2SO_4 solid gel electrolyte. The device displayed excellent stability over 5000 cycles with a Coulombic efficiency of 90%. The cell withstood an aging test for 70 hours with a 100% capacity retention. Areal energy density as high as 298.5 µWh.cm^{-2} was recorded for a power density value of 855.5 µW.cm^{-2} at an areal current value of 0.5 mA.cm^{-2}. At a high current density of 10 mA.cm^{-2}, the energy density remained high at 99.0 µWh.cm^{-2} for a corresponding power density of 8113.4 µW.cm^{-2}. These reported values remained among the highest obtained for carbon nanotubes-based supercapacitors.

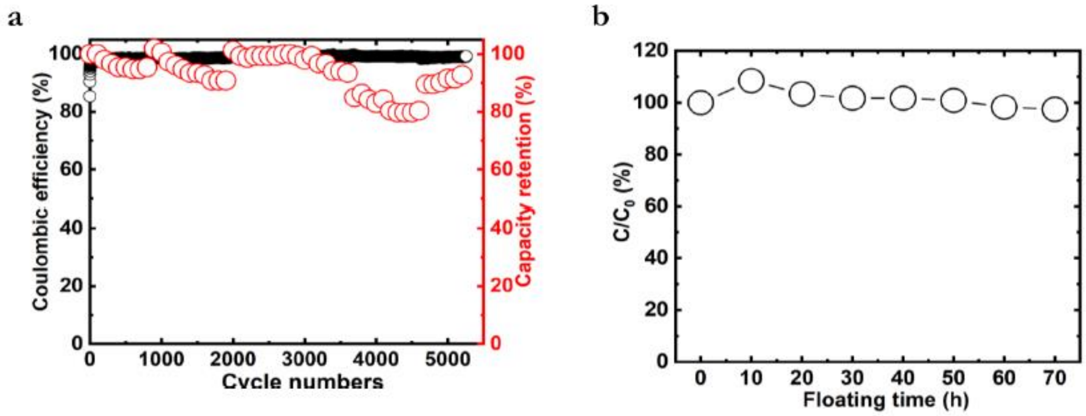

Figure 1: *a) Coulombic efficiency and capacity retention after 5000 GDC at 5 mA.cm^{-2} of the full cell, b) floating test results for 70 hours at 5 mA.cm^{-2}.*

Electrodeposition of FeOOH and MnO_2 on flexible carbon substrates for asymmetric aqueous capacitor applications.

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There is a growing interest in the miniaturisation of energy storage devices due to market demands for various wireless network applications, such as autonomous integrated circuits, wearable flexible sensors and robotics[1,2]. On chip electrochemical capacitors can be integrated to microelectronics due to their fast charge/discharge and long-term cycling. To make microsupercapacitors attractive for these applications, it is necessary to boost the energy that can be stored in these systems. One approach is to combine materials that exhibit pseudo capacitance, such as transition metal oxides, to a conductive porous substrate. Herein, an on-chip micro-supercapacitor using a 3D graphene foam (GF) network (Integrated Graphene Ltd), was investigated as a flexible substrate to deposit iron oxyhydroxide (FeOOH) and manganese dioxide (MnO_2). The areal capacitance of three current and potential based electrodeposition procedures were compared as well as the effect of pre-oxidation of the carbon before electrodeposition (**Figure 1**). Furthermore, the charge storage mechanism was investigated via *in situ* Raman microscopy.

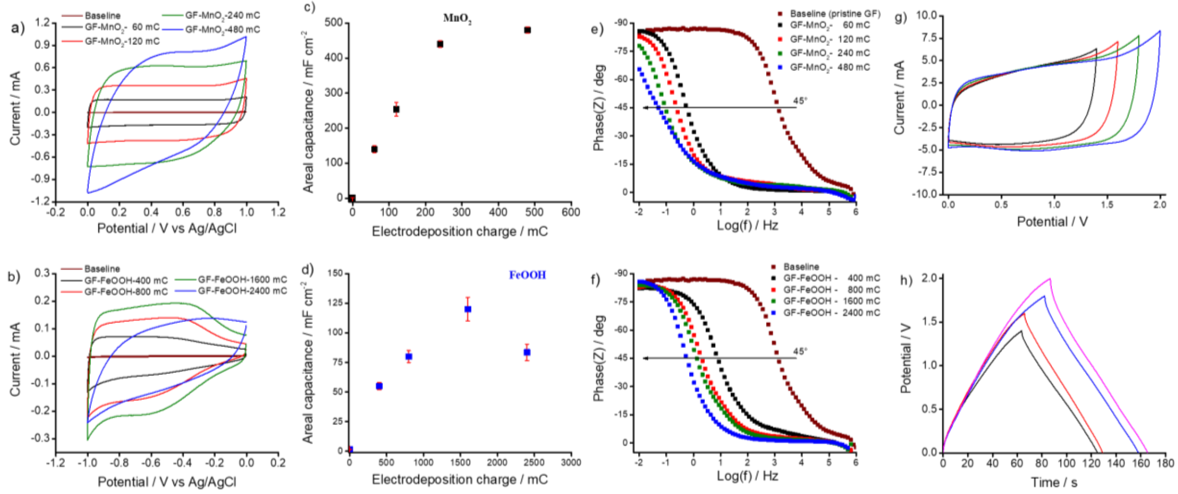

Figure 1: Cyclic voltammograms of a) MnO_2 and b) FeOOH electrodeposited at different charge cut-offs at 25 mV/s in an aqueous electrolyte. Dependence of areal capacitance plots and electrodeposition charge for c) MnO_2 and d) FeOOH. EIS bode plots for different e) MnO_2 and f) FeOOH electrodes. (g) Cyclic voltammograms at 25 mV/s and (h) galvanostatic charge-discharge curves at 0.5 mA/cm^2 of an asymmetric FeOOH vs MnO_2 cell in an aqueous electrolyte.

The performance of both the electrodes indicate an ideal capacitor behaviour on the CV curves with symmetrical profiles up to a critical film thickness. The areal capacitance increases linearly with the charge deposition cut-off cycles reaching a maximum of 120 mF/cm^2 for the FeOOH and 440 mF/cm^2 for the MnO_2 electrode showing optimum thickness. Upon further electrodeposition, both systems start to deviate becoming more resistive due to conductivity limitations and to blockage of the carbon porous structure. EIS bode phase angle plots for both metal oxide electrodes show a profile equivalent to a resistor and a capacitor connected in series, while further increase in the oxide film thickness resulting in a shift of the capacitive behaviour to lower frequency. **Figure 1g and h** show CV and GCD curves of a FeOOH vs MnO_2 full cell up to 2.0 V with relatively minor distortions. A full cell areal capacitance of 20 mF/cm^2 is obtained for the upper voltage window. This can improve upon careful charge balancing of the system to achieve long cycle-life devices.

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3D microdevice from high-capacitance microsupercapacitor electrodes

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Microsupercapacitors [1,2] (MSCs) are considered as promising on-chip energy storage units owing to their high-power density and long-life span. Unfortunately, the low energy density and low technological readiness level of MSCs still remain challenging for their practical application. To develop high-performance MSC, it's imperative to have a rational choice of the electrode materials and proper designing of the device components. One promising approach to achieve MSCs with high areal energy density is by enhancing the surface area of the electrode material using high aspect ratio micro/nanostructured scaffolds. In this study, we developed highly porous metallic current collector substrates using dynamic hydrogen bubble templating (DHBT)-assisted electrodeposition process[3]. The developed 3D metal current collectors of Au, Pt or Cu exhibited highly porous interconnected morphology with dendritic nanowalls for the active material (hydrous ruthenium dioxide) loading [4,5]. To realize practical on chip integration-based application of MSCs, interdigitated and stacked configurations were developed with areal energy densities exceeding 330 mJ cm^{-2} and 250 mJ cm^{-2} in aqueous (0.5 M H_2SO_4) and solid-state electrolytes (PVA- H_2SO_4-SiWA), respectively.

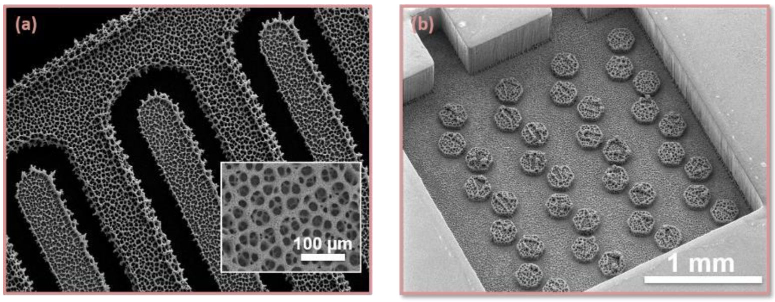

Figure 1: *Top view SEM images of interdigitated MSC* ***(a)*** *and 3D electrode for stack-interdigitated MSC* ***(b)****.*

Though interdigitated electrode pattern is very appealing for practical on-chip applications owing to reduced electrode interspace, it comes at the expense of low active material loading (***Figure 1-a***). On the other hand, stacked configuration can offer higher mass loading and higher areal energy performance, the power delivery is limited due to longer ion diffusion path. To address this challenge, we present novel designing of 3D MSCs combining the advantages of stacked and interdigitated configuration (***Figure 1-b***). This enabled a large 3D active surface area while ensuring low spacing between the electrodes.

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FABRICATION AND CHARACTERISATION OF GO-PEDOT:PSS NANOCOMPOSITES FOR SUPERCAPACITORS

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Among conductive polymers, Poly(3,4 ethylenedioxythiophene)polystyrene sulfonate (PEDOT:PSS) has been widely used as an electrode material for supercapacitors [1], solar cells [2], etc.. However, the processes of forming PEDOT:PSS-based thin films with good capacitive, electrical and biocompatibility properties are still a challenge. This work is aimed at fabricating and characterising ternary nanocomposites based on PEDOT:PSS+GO (graphene oxide), blended with a green additive (i.e. ascorbic acid), with low environmental impact, low cost and easy to use.
Via drop casting technique, thin films of the ternary nanocomposites were produced and their main properties were evaluated such as: capacitive and biocompatible properties. Particularly, Cyclic Voltammetry, as reported in Figure 1, indirect biocompatibility tests and Live/Dead assays were performed. In addition, the GO reduction process by means of the green additives was monitored through different tests, which confirmed that it took place in air within both ternary nanocomposites.
The inks were finally printed by Aerosol Jet® Printing (AJ®P), an innovative direct writing technique belonging to the Additive Manufacturing for printed electronics applications. The rheological and surface tension properties of the inks were indeed studied and showed that the viscosity and surface tension were in the optimal range of AJ®P. The inks were then printed in the form of thin films (10 layers, 8x8mm) and were chemically analysed by FT-IR to investigate whether all components of the formulation were successfully aerosolised and printed.

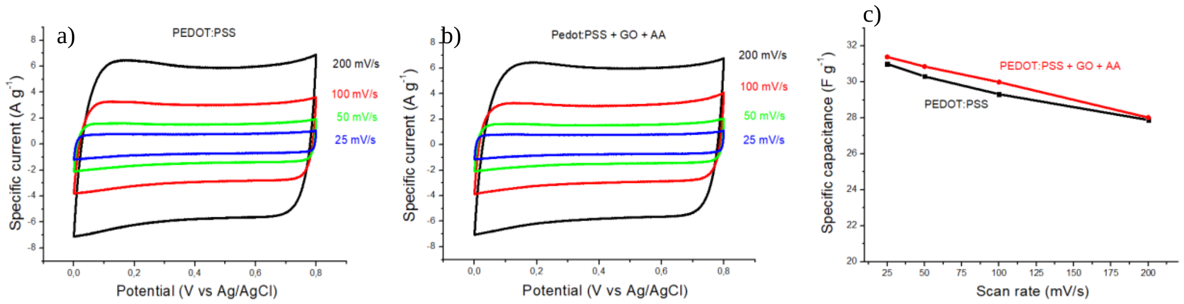

Figure 1: *a) and b) Cyclic Voltammograms of PEDOT:PSS and PEDOT:PSS+GO+Ascorbic acid at different scan rates (25,50,100 and 200mV/s) deposited on Pt substrate and tested on PBS solution; c) Comparison of Specific Capacitance of PEDOT:PSS and PEDOT:PSS+GO+Ascorbic acid.*

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Microstructured nitrogen-doped graphene-Sn composites as a negative electrode for high performance lithium-ion hybrid supercapacitors

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In this work we report a simplistic approach for the synthesis of nitrogen-doped graphene decorated with tin particles suitable as a negative (battery-type) electrode for lithium-ion hybrid capacitors.[1] An activated carbon derived from a graphene–carbon composite is used as a positive (capacitor-type) electrode. [2] The excellent features of the nitrogen-doped graphene matrix combined with the homogeneous distribution and high theoretical capacity (994 mA h g-1) of the submicrometer-sized tin particles lead to an improved performance of the negative electrode, especially at high current densities. An optimized dual-carbon lithium-ion capacitor with 2 : 1 positive to negative mass ratio delivers high energy and power densities (133 W h kg^{-1} at 142 W kg^{-1} and 51 W h kg^{-1} at 25 600 W kg^{-1}). Furthermore, within a discharge time of 1 min, the device reaches 19 000 cycles with full capacity retention, delivering ca. 100 W h kg^{-1} at 5600 W kg^{-1}.

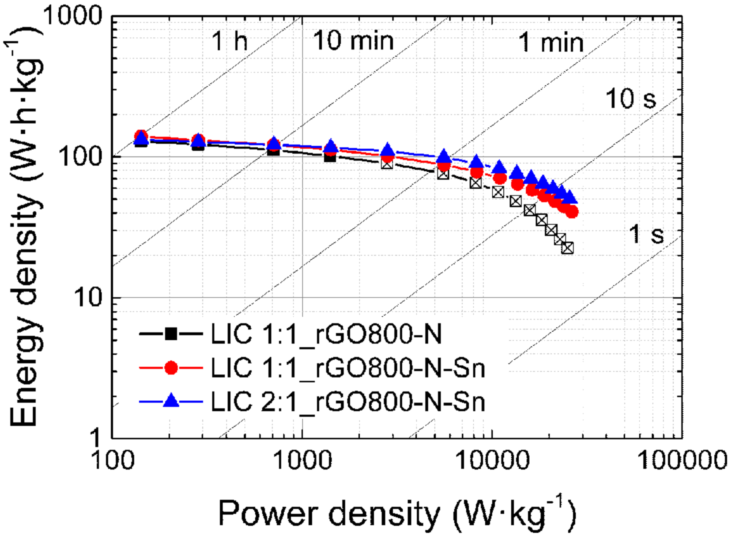

Figure 1. *Ragone plot of some of the assembled graphene-based lithium-ion hybrid capacitors with indicated electrode mass balances.*

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Hybrid Glow-in-the-Dark Energy Storage Textile Device: Phosphorescent ZnS:Cu-based Redox-active Electrolyte for Fashion/Safety Applications

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The design of innovative energy storage technologies for wearable applications has been a significant request for high-tech consumers. Additionally, functionalized fabrics endowing additional properties have been used for many applications (*e.g.*, healthcare, safety, military), creating higher value-added products [1]. Carbon (CN)-based textile supercapacitors (SCs) have gained widespread attention as energy storage solutions due to their higher lifetime, fast charging, power density, and robustness [1]. To improve the energy density of SCs, CNs have been hybridized with transition metal oxides. Magnetic spinel-type ferrites (MF) are of paramount importance for the hybridization of CNs due to their different oxidation states and magnetic properties, enhancing the energy storage performance of devices. Despite substantial advancements in energy storage systems, multi-functionality represents a step towards the advent of new devices. Bright phosphorescent pigments (P) induce the change of optical properties being very used in textile applications, such as for safety of nighttime users (*e.g.*, traffic police, sanitation workers, night sport) [2]. In this work, a hybrid glow-in-the-dark textile SC simultaneously exhibits phosphorescent and energy storage properties. The high energy storage capability was produced based on CN@MF-coated textile electrodes and a novel redox-active phosphorescent solid gel electrolyte. Textile electrodes were prepared using cotton fabrics impregnated with an aqueous dispersions of nearly spherical MF nanoparticles (cubic spinel structure; crystalline size = 5.5 nm) immobilized on CN. *In situ* coprecipitation was the method used for preparation of MF. The asymmetric SC_CN//CNN@MF_P device was fabricated using two textile electrodes sandwiched with a novel phosphorescent redox-active solid gel electrolyte based on polyvinyl alcohol/orthophosphoric acid doped with a ZnS:Cu redox-active pigment. For comparison, an asymmetric device prepared with undoped electrolyte (SC_CN//CN@MF) was used. The SC_CN//CN@MF_P presented an energy density of 10.59 59 μW h cm^{-2} at a power density of 1000.26 μW cm^{-2}. The addition of P into the electrolyte improved 23% in specific capacitance (38.64 *vs*. 31.50 mF cm^{-2}), highlighting the enhancements of 30% and 20% in energy and power density for SC_CN//CN@MF than for SC_CN/CN@MF. Additionally, SC_CN//CN@MF_P device exhibited an intense green phosphorescence under a dark environment (Figure 1), overcoming the limitation of the dark color of carbon-based SCs. Finally, SC_CN//CN@MF_P highlights the usefulness of this type of dual-functional textile SCs for dark environment applications, namely in reflective/safety electronic clothing for nighttime users.

***Figure 1:** Optical properties of SC_CN//CN@MF_P device in visible light conditions and under nighttime.*

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Acknowledgments: JST thanks FCT for PhD grant (SFRH/BD/145513/2019).

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A Hybrid supercapacitor based on Mn-MOF and Activated Carbon in water- and organic-based electrolytes

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Because of their ultrahigh porosity, large specific surface area, and ease of functionalization, Metal-Organic Frameworks (MOFs) exhibit exceptional electrochemical performance. According to these unique characteristics, MOFs have emerged as promising and efficient electrode materials with excellent electrochemical performance in lithium-based batteries or Li-ion capacitors [1, 2]. In this work, we prepared MnMOF//AC based-hybrid supercapacitor device, described by surface or pure adsorption controlled process. The Mn-MOF material can quickly intercalate lithium in an aqueous, environment-friendly electrolyte and an organic electrolyte.

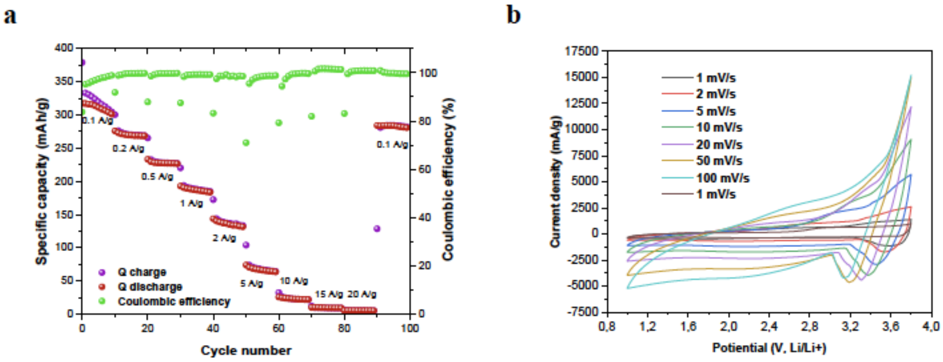

Figure 1: *Electrochemical Activity of MnMOF// AC hybrid capacitor with Li metal reference (three electrode Swagelok cell configuration). Rate capability (a) and Cyclic voltammetry at the different scan rates(b). Specific capacity and current were normalized to the MnMOF active mass.*

The manganese-1, 4 benzene dicarboxylic acid-based MOF (MnMOF) was successfully synthesized with a monoclinic crystal structure using a solvothermal method with DMF (dimethylformamide).

The electrochemical performance of MnMOF as an active material for the hybrid supercapacitors was compared in the water-electrolyte and the organic electrolyte.

In the water-based MnMOF//AC hybrid supercapacitors with 1M Li_2SO_4 in H_2O and DMSO (dimethylsulfoxide) mixture, the highest energy density of 8.06 Wh/kg (normalized to the sum of negative and positive electrode masses) was reached for the MnMOF with PTFE binder as a positive electrode.

The preliminary electrochemical test of a full Li-ion capacitor device with organic LP30 electrolyte, AC positive electrode, pre-lithiated MnMOF negative electrode, and Li metal reference shows a stable specific capacity of 300 mAh/g (normalized to the negative electrode mass) at 0.1 A/g (Fig.1).

Operando investigation of the electrochemical mechanism by X-ray Absorption Spectroscopy shows that Mn is not electrochemically active at the high current density. Instead, redox processes with Mn ions are diffusion-controlled and can occur only at low current density.

Acknowledgement

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Understanding Electrochemical CO_2 Capture by Supercapacitors

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Electrochemical CO_2 capture is rapidly emerging as a next generation technology for mitigating greenhouse gas emissions. In this approach, the charging of an electrochemical cell brings about the selective capture of carbon dioxide. Here I will review recent progress from our research group on understanding and improving electrochemical CO_2 capture by carbon-based supercapacitors. Carbon-based supercapacitors benefit from their simplicity and the use of sustainable materials, but a major challenge is to increase electrochemical CO_2 capture capacities, which currently lag far behind those of alternative systems based on quinone redox. I will show that by varying the supercapacitor charging protocol, CO_2 capacity increases can be obtained.[1] At the same time, our measurements provide new insights into the molecular mechanisms of electrochemical capture which may aid the design of improved systems.[1] Finally, for the case of quinone-based hybrid systems which employ fast redox reactions, a major practical limitation is oxygen sensitivity. It has been proposed that this issue can be overcome by tuning the quinone chemistry, but we show that there exists a trade off between quinone redox potential and CO_2 capture strength.[2] I will outline potential strategies to overcome performance trade-offs in electrochemical CO_2 capture.

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Electrosynthesis of nanostructured polyindole adorned with MnO_2 nanorod and its evaluation in properties as a supercapacitor

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The manganese oxide (MnO_2) has recently attracted attention due to its interesting pseudo-capacitive properties have been studied, reaching a high specific capacitance for three-electrode systems [1]. However, this would not guarantee optimal conductivity since the electrodes consisting of MnO_2 have a low conductivity, 10^{-5} to 10^{-6} Scm^{-1}, which is a problem that translates into low efficiency. However, the conductivity problem is still far from being worked out. Therefore, the possibility that MnO_2 nanostructures are being supported in conductive polymers (CP) as a substrate can be a promising solution for the conductivity of the MnO_2 electrode. The CPs present high conductivity in a doped state and achieve a higher specific capacitance using a nanostructured morphology. In this way, the nanostructured polyindoles have been reported without using some type of template by cyclic voltammetry and with disposition perpendicularity, essential for free diffusion of the doping ions [2-3]. Consequently, it is interesting to study the synergistic effect generated by obtaining PIn nanostructures adorned with MnO_2 nanostructures, evaluating their capacitive properties.

Fig. 1A shows the TEM micrograph of the MnO_2 nanorods obtained through hydrothermal reaction, which are later incorporated during the electropolymerization of 6-indole carboxy acid (6-ICA) on conductive glass (ITO). Fig. 1B shows the modified electrode ITO|6-PICA|MnO_2, observing a good homogeneity on the surface. Subsequently, the modified electrodes were characterized electrochemically by cyclic voltammetry, using a solution of 0.5 mol L^{-1} of H_2SO_4. From this, it is initially observed that the scanning speed used during the electropolymerization directly relates to incorporating the MnO_2 nanorods, achieving a 97.1% increase in capacitance under optimal conditions compared with a modified electrode without MnO_2. On the other hand, the study of the concentration of MnO2 nanorods suspended in solution varies between 0.05% and 1%, obtaining in optimal conditions a 110% increase in capacitance compared to the modified electrode in the absence of MnO_2.

Finally, these results show an important tendency to improve the capacitive properties of both compounds, being a possible candidate for energy storage devices.

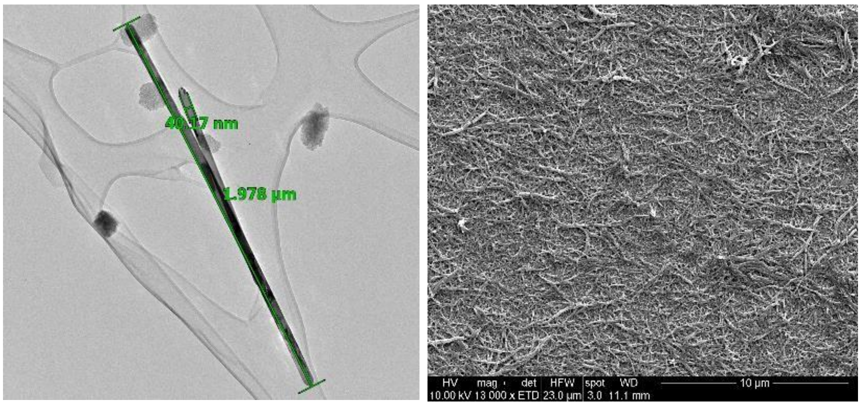

Figure 1: *(a) TEM micrographs of MnO_2 nanorod and (b) modified electrodes ITO |6-PICA*

Acknowledgment

The authors acknowledge the financial support of ANID-Chile through Fondecyt, grant number Project N° 11190995.

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Few-layer graphene as an electrode, electrode additive and an interfacial layer in aqueous supercapacitors

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The intermittent nature of many renewable energy sources such as wind and solar, coupled with fluctuations in energy demand, creates a pressing need for efficient, low-cost energy storage technologies. Supercapacitors are promising candidates to play a role in next-generation energy storage systems. They have a higher power density and better cycle life (although lower energy density) than batteries making them ideal for rapid energy storage and deployment [1]. Activated carbon is a favoured electrode material due to high surface area, although low conductivity requires use of a conductive additive (often carbon black), reducing available surface area for charge storage. In contrast, the high conductivity and specific surface area of graphene has made it a promising material for electrochemical double layer supercapacitors (EDLCs) [2], however, performance is limited by restacking of the graphene sheets, reducing available surface area.

In this work, high-shear exfoliated few layer graphene (FLG) [3] is investigated both as an electrode material and as a conductive additive/interfacial layer for EDLCs. FLG suspensions were produced under a variety of exfoliation conditions, with platelet thickness and linear dimension determined from Raman spectroscopy based on metrics developed by Backes *et al.* [4] and through scanning electron microscopy (SEM).

The FLG suspensions were used in three ways: i) to create thin ‘graphene paper’ electrodes; ii) as a conductive additive, mixed into the activated carbon electrode material; iii) deposited onto the back of (and diffused within) activated carbon electrodes. These electrodes were investigated by Raman spectroscopy and Scanning Electron Microscopy, before being assembled into symmetric two-terminal aqueous cells then evaluated by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS), and their electrochemical performance related to structure and composition.

As expected, pure FLG electrodes often showed excellent low series resistance values, however specific capacitance was low, due to restacking. Directly mixing 5% FLG into activated carbon as a conventional conductive additive led to a specific capacitance of 63 F/g (from CV at 10 mV/s), and a series resistance of 19 Ω (from GCD at 1 A/g) - markedly inferior to those with 5% carbon black as a conductive additive (95 F/g and 2 Ω) and inferior even to electrodes with no conductive additive (87 F/g and 10 Ω).

However, post fabrication deposition/infusion of FLG offers comparable performance to carbon black (90 F/g and 1 Ω) at 7% FLG by weight. As the quantity of FLG is increased the specific capacitance decreases sharply. This behaviour is attributed to FLG restacking on the rear of the electrode, so adding mass whilst providing limited additional capacitance, and compression of the electrode.

Adding high-shear exfoliated FLG to activated carbon electrodes shows promise for obtaining the benefits of both materials. At present, FLG/activated carbon electrodes can match the performance of those produced from activated carbon with a carbon black conductive additive and, with further optimization, we expect will be able to exceed them.

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Dynamic Electrochemical Impedance Spectroscopy as a valid tool to monitor EDLCs *operando*

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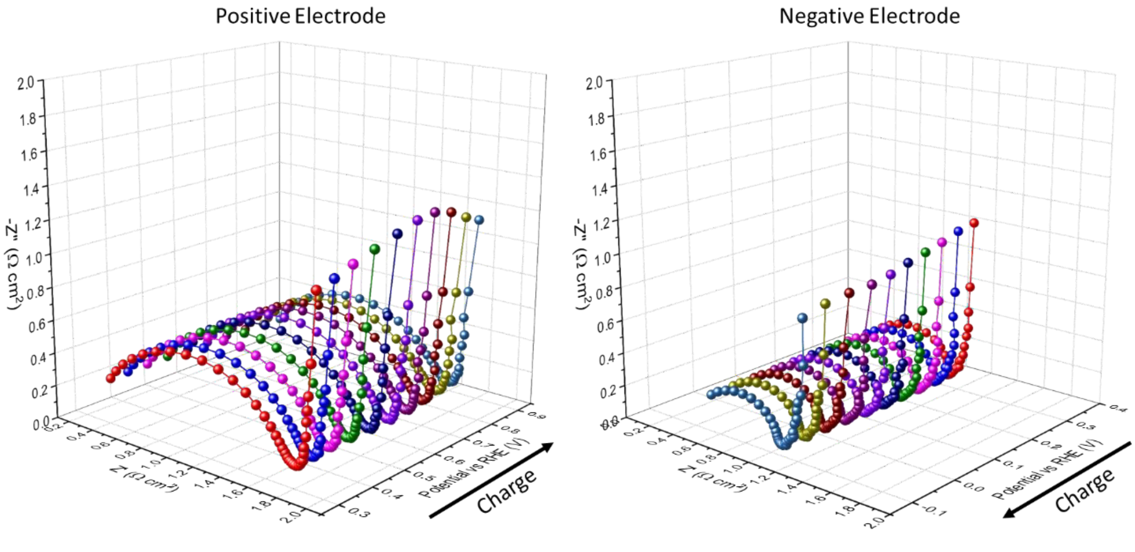
Electrochemical double-layer capacitors are a class of electrochemical devices known for their ability to deliver high power densities (up to 10^4 W kg^{-1}) while being able to store decent amount of energy (around 10 – 10^2 Wh kg^{-1}) [1]. While in such devices charges are stored thanks to the formation of two double-layers, side reactions or processes (e.g. adsorption of ions on the surface of the electrodes) may still occur and their dependance on the state of charge of the device can be interesting for both first principle studies and device's monitoring. Electrochemical impedance spectroscopy is a valuable device for such purposes, as it can be used to evaluate the kinetic parameters (i.e. capacitances, resistances etc.) that define the occurring electrochemical processes. The use of EIS on evolving systems is, however, strongly limited by the intrinsic slowness of the technique itself, which is inversely proportional to the value and the number of frequencies under exam. This is particularly incompatible with EDLCs because of their generally high self-discharge[2], making it hard to maintain such devices static for a time long enough to allow EIS to be performed. This issue, however, can be worked around by using dynamic multi-frequency analysis (DMFA), a version of EIS where all the periodic stimuli are superimposed together (multisine) so to extract time-dependent impedance spectra at a rate only limited by the frequency of the slower stimulus used[3]. Moreover, DMFA can be applied while charging and discharging a device, providing an efficient tool to extract dynamic electrochemical impedance spectra (dEIS). DMFA was successfully used to analyze a symmetric aqueous EDLC (8m solution of KF in H_2O) with activated carbon as active material for both electrodes. The potential and impedance of the two carbon electrodes were monitored adding a PbF_2/Pb reference electrode. Both pouch and Swagelok-type® cells were used, in both cases obtaining good and reliable spectra. It was also possible to fit the spectra so to obtain state-of-charge-dependent kinetic parameters.


Positive Electrode

Negative Electrode

***Figure 1**: impedance spectra obtained using DMFA during the charge process of an EDLC*

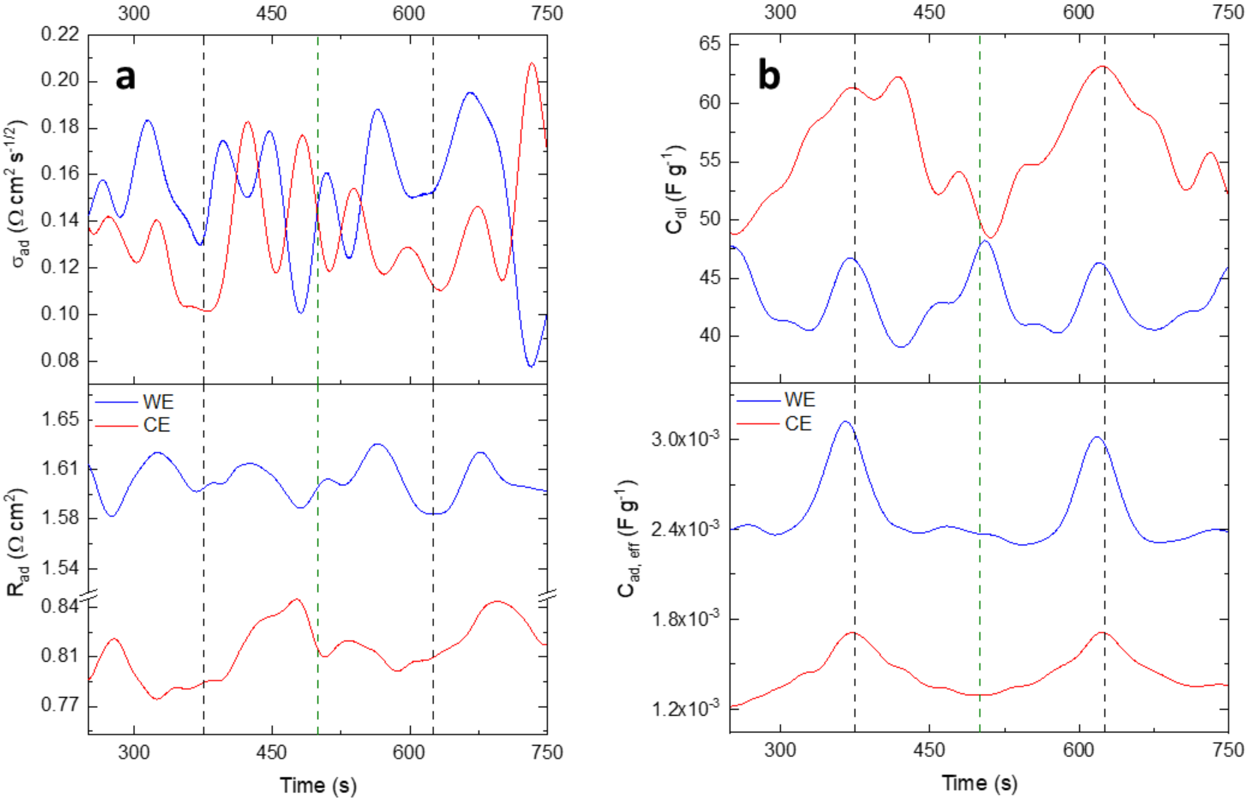


***Figure 2**: Parameters extracted from the fitting of the dynamic impedance spectra. (a) Warburg constant and adsorption resistance, (b) double-layer and effective adsorption capacitances. Dotted lines represent the times at which the EDLC is charged (black) and discharged (green)*

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Hybrid Supercapacitors based on Manganese oxide and Activated carbon Electrodes Using Sodium Exchange Aquivion Electrolyte Membrane

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The current scenario of energy storage and generation is demanding higher energy density supercapacitors. We need economic and green systems to adapt to the recent climate policies as well. Supercapacitors are eco-friendly energy storage devices with high power density and long-life cycle.[1] There are mainly three different configuration of supercapacitor, symmetric, asymmetric, and hybrid based on the electrode material. Symmetric cells are constructed using identical materials in both electrodes. The performance of symmetric capacitor is limited by their small voltage window and lower energy density. Hybrid supercapacitors with asymmetric configuration are new alternatives with relatively high energy density compared to their symmetric counter parts. Generally, different materials are used in each electrode to design both the asymmetric cells or hybrid cells.[2,3]

Manganese oxide (MnO_2) is a well-known electrode material for supercapacitor, due to its high theoretical capacitance (1370 F/g), stability in aqueous electrolyte, low toxicity and very low cost. Charging and discharging occurs mainly by fast surface redox reactions occurring in manganese oxide materials electrode with the help of cations (e.g. K^+, H^+, Na^+). Apart from its good electrochemical behavior, MnO_2 suffers from a low electronic conductivity and in a limited potential range. The performance of MnO_2 electrodes might be enhanced by combining the oxide with electrically conductive carbon materials.[4,5] Herein, we report the synthesis of MnO_2 by a simple co-precipitation technique and its use as the positive electrode of the supercapacitor. Hybrid supercapacitors with asymmetric configuration has been constructed with a commercial activated carbon as negative electrode, MnO_2 as positive electrode and Na^+ exchange Aquivion membrane that has the dual function of separator and electrolyte. The hybrid cell exhibited well rectangular voltammograms at different scan rates and exhibiting high specific capacitance of 124 F/g at 0.2 A/g and energy density of 11 Wh kg^{-1}. In addition, the type of hybrid supercapacitor was able to withstand harsh cycling by combining galvanostatic charging and discharging and floating conditions (i.e. 140 hours at 1.6 V) for up to 10,000 cycles without affecting the capacitance stability. Self-discharge studies on the cell were carried out, after 10000 charge discharge cycles. The cell was charged at 1.6 V for 3 h, then during the self-discharge, it retained more than 1 V up to 400 min. Further, the well EDLC behavior of the cell was improved by using a combination of MnO_2 - carbon as positive electrode and activated carbon as negative electrode. Well rectangular cyclic voltammograms was exhibited for the fast charge discharge rates. The modified cell showed a high specific capacitance of about 100 F/g at 0.2 A/g. The synergistic effect of MnO_2 and carbon resulted in a perfectly reversible charge storage redox processes, which occurs at the positive electrode. A detailed electrochemical study of these cells was carried out and compared with the symmetric carbon/carbon supercapacitor. A comprehensive analysis will be given during presentation.

Acknowledgment

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Optimizing the pair carbon xerogels-electrolyte for high performance supercapacitors

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Supercapacitors have received a lot of research attention and are promising energy storage devices due to their high power and long cycle life. In order to developed an advanced device with significant capacity for storing charge and cheap carbon materials, efforts must focus not only on improving synthesis by controlling the morphology and pore size, but also on improving electrode-electrolyte compatibility of the resulting systems.

The present study examines the relationship between the surface chemistry of different kind activated carbon xerogels, the electrolyte type and the electrochemical properties of supercapacitors.

Activated carbon xerogels were prepared by varying the initial pH of the resorcinol-formaldehyde aqueous solution (AX6.5, AX5.97, pH=6.5 and 5.97, respectively). An activated carbon xerogel doped with graphene (AX6.5-G) was also evaluated. This latter material has a very good combination of high porosity and a superior electrical conductivity. The materials produced are physicochemical characterized by DTA/TGA, porous characterization and SEM analysis.

The carbon xerogel based electrodes were prepared by spreading over glass plate a slurry containing the carbon gel, graphite and poly vinylidene difluoride (PVDF) binder. The layer formed was thermally treated to improve its mechanical stability.

The developed electrode materials and the sodium form (for soaking in 1M Na_2SO_4) of Aquivion® membrane (code membrane E87-05S, Solvay Specialty Polymers), were used to assembly symmetric solid- state supercapacitor. The supercapacitor cells composed by same electrodes and 1 M KOH electrolytes are also assembled and tested for comparison.

The supercapacitor performances are verified by different electrochemical methods - cyclic voltammetry, galvanostatic charge/discharge measurements and long-term durability tests in neutral and alkaline environments.

Specific capacitance, energy and power density, energy efficiency and lifetime were compared in the studied supercapacitors. The results are discussed on the basis of electrode-electrolyte interactions and a correlation is found that could be important to design sustainable solid-state supercapacitors with high power density and faster charge and discharge rates.

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Green supercapacitive systems

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The valorization of wastes by their transformation into functional materials to be implemented in technologies that enable efficient energy management and water treatment is a valuable strategy to address the Water-Energy-Waste Nexus challenges.

In this context, the exploitation of carbonaceous material obtained from waste pyrolysis as the main electrode component for supercapacitors and Microbial Fuel Cells (MFCs) is extremely attractive. MFCs use microorganisms as biocatalysts to convert chemical energy stored in wastewater's organic matter into electricity and can degrade a plethora of simple organics and complex civil and industrial wastewaters.

Despite this, the low power produced by MFCs makes difficult their direct use in practical applications.

Usually, MFCs are coupled with an external energy storage system that accumulates the energy produced, delivering it at higher power pulses when needed [1]. For this application, Electrical Double-Layer Capacitors (EDLCs) store electric energy through fast and highly reversible electrostatic processes and are a system of choice [2,3]. Indeed, sustainability is intrinsic in this system in which no critical raw materials such as transition metal oxides or lithium are exploited. The use of water-processable, biodegradable electrodes and separators is a viable approach to developing green and easy-to-dispose devices. Natural polymers processed by aqueous solutions are a very promising alternative to fluorinated polymers like polyvinylidene difluoride which also requires the use of the toxic N-Methyl-2-pyrrolidone solvent to realize green supercapacitors.

Here we report about the direct introduction of supercapacitive features and coupling with external green supercapcitors as strategies to improve the power output of MFCs. To further push the system's sustainability, electrodes based on Lignin-derived Activated Carbon (LAC), generated by a one-step carbonization route of lignin solid waste, exploiting the mild activating agent $KHCO_3$, have been realized and tested for EDLCs and MFC's electrodes. The electrochemical responses of the systems are here investigated and discussed to address the challenging task of improving MFC's power output while improving the system sustainability.

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YOUNG SCIENTIST PRESENTATIONS

Pre-lithiated TiSb2 alloy-based lithium-ion capacitor exceeding 20000 cycles and standing for more than 1000 hours of float time

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The dream of using beyond-carbon metalloids or transition metals as anode materials in electrochemical energy storage systems has been long pursued for the sake of greater capacity. However, two major challenges remain unresolved: the high volumetric expansion suffered by those materials, causing severe mechanical stress ending up in device failure, and the large first cycle irreversibility. In this work, both issues are tackled in a single approach, by using titanium to buffer mechanical stress of antimony ($TiSb_2$) and by adopting the recently proven dilithium squarate sacrificial salt ($Li_2C_4O_4$) strategy to pre-lithiate the system (**Figure 1**). Overall, herein developed alloy-based lithium-ion capacitor (LIC) demonstrates the possibility to successfully pre- lithiate materials of different nature, moving from typical graphite or hard carbon to an intermetallic compound such as $TiSb_2$, by modifying and optimizing positive electrode formulation and protocol. Its higher capacity owing to the alloying charge storage mechanism, allows to achieve between double and triple volumetric performance respect to a dual carbon LIC. Moreover, the system is shown to be stable over 20000 cycles and 1000 h of floating at 3.8 V and room temperature. Post-mortem analysis correlates the origin of failure to the electrolyte oxidation and not to the degradation of the alloying material itself. Re-assembled $TiSb_2$, activated carbon (AC), and full device with fresh electrolyte show to almost perform as good as the original.[1, 2]

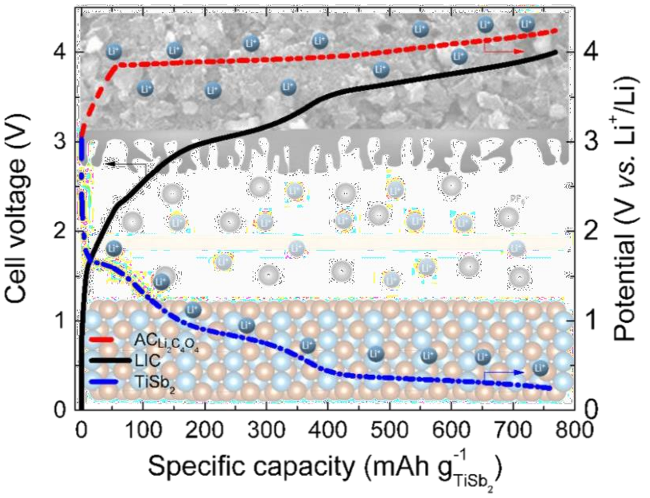

Figure 1: *Pre-lithiation step for LIC (black straight line) together with potential profiles for the AC positive electrode (red dash line) and the $TiSb_2$ negative electrode (blue dash-dot line).*

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Mixed 1T-2H MoS2 nanoflakes electrodes for Li-ion supercapacitors and electrocatalyst for HER.

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Molybdenum disulfide (MoS_2) is a layered transition-metal dichalcogenide which has attracted great interest as material for energy conversion and storage. MoS_2 exists in three different polymorphs that are the stable 2H, the meta-stable 1T and 3R with the possibility of obtaining 2D nanostructures. Herein, we report the synthesis and characterization of a few-layer hybrid material containing both metallic 1T and semiconducting 2H phases (1T-2H MoS_2 nanoflakes) obtained with phosphomolybdic acid and L-cysteine as precursors in one-pot hydrothermal synthesis. Morphological and structural characterization's results are presented and compared to commercially available 2H-MoS_2 powder. The thermal conversion of the 1T-2H MoS_2 into fully 2H MoS_2 is studied by means of X-ray Photoelectron Spectroscopy to quantify the relative amount of 1T and 2H phase and maintaining the same morphology. This conversion allows to appreciate the superior properties of the 1T-2H mixed phases as catalyst for hydrogen evolution reaction (HER) and as electrode material in both aqueous and Li-ion supercapacitors. In order to enhance the capacitive proprieties of the mixed phases, the 1T- 2H nanoflakes were finely alternated to reduced graphene oxide (rGO) sheets by obtaining a tridimensional matrix of rGO-MoS_2 (aerogel). This co-synthesis allowed to increase the cycling life and stability of aqueous supercapacitors.

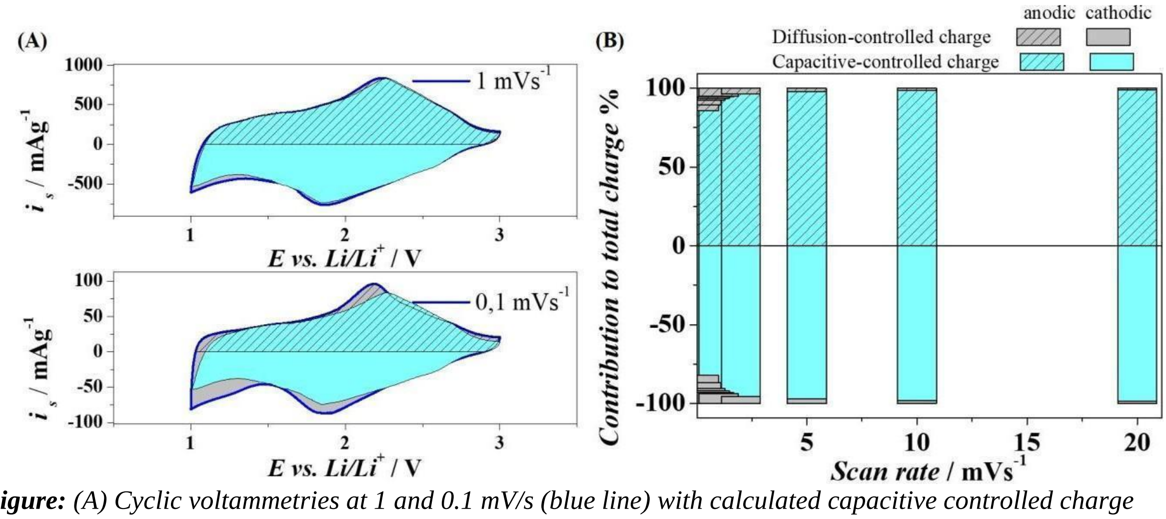

Figure: *(A) Cyclic voltammetries at 1 and 0.1 mV/s (blue line) with calculated capacitive controlled charge (light blue area) and diffusion-controlled charge (grey area); (B) Percentage of capacitive-controlled and diffusion-controlled on the overall charge at different scan rates*

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A non-aqueous potassium-ion hybrid supercapacitor for high power applications

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Combine fast charging and high energy density is possible with M-ion hybrid supercapacitor (MICs) by associating the electrostatic phenomena at a positive capacitor-type electrode and the faradic process at a negative battery-type electrode. Higher energy density than conventional EDLCs is ensured thanks to the higher voltage in hybrid configuration. Issues of dependency on critical and strategic materials as well as security are pushing research to turn to other alkali materials than lithium. Our study is focused on potassium, which benefits from abundant resources, low standard electrode potential as well as low costs. The potassium-ion supercapacitor (KIC) presented here consists of an activated carbon positive electrode and an oversized graphite negative one immersed in an acetonitrile based-non-aqueous electrolyte and a potassium salt [1]. The hybrid configuration avoids specific problems inherent in the use of potassium. Indeed, the system is designed so that a high stage of graphite intercalation compound (GIC) is obtained in order to avoid critical volume expansion. Furthermore, with the spontaneous reaction between acetonitrile and metallic alkali elements, dendrites formation is not possible. The non-reproducibility of the results was a major obstacle to the development of this KIC technology. It was lifted thanks to the development of an adequate formation protocol [2]. Cells that undergo this protocol show an excellent stability in cycling over more than 500,000 cycles at 100C/100D ($t_{\text{charge/discharge}}$ = 30 seconds) with C the cell capacity. These results at pouch cell level are highly remarkable and hardly observed in the case of other MICs.

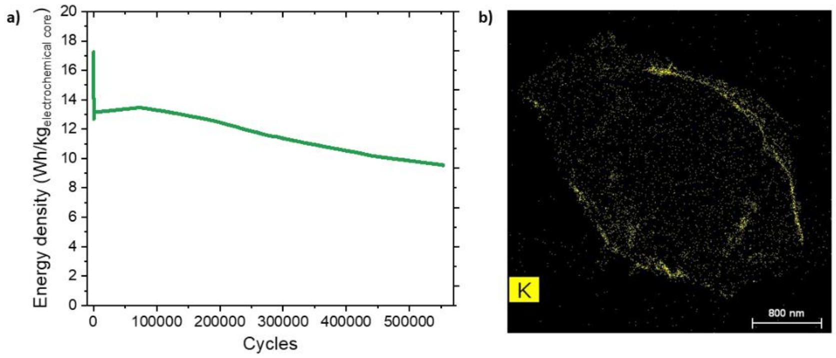

Figure 1: *a) Long term cycling of a KIC pouch cell at 100C/100D, b) Element mapping of K on a graphite particle that undergoes the formation protocol developed*

The influence of different formation parameters (current, temperature, floating) on the system, and more precisely on the negative electrode, is being studied using several characterization techniques (SEM, TEM, XPS) in order to understand how the formation protocol developed makes it possible to obtain stable and reproducible results. Following the good performance at pouch cell level, a scale-up of the technology at stack format (20 times the capacity of the pouch cell) was attempted. However, the capacities obtained were far from those expected and a heating problem within the cells was highlighted. The study of this phenomenon by calorimetry is in progress. To conclude, the potassium-ion capacitor presented offers a good energy density of more than 10 Wh/kg$_{\text{electrochemical core}}$ at pouch cell level with an excellent stability at fast charging rate. Structural and surface analysis combined with calorimetry tests are in progress to refine the understanding of the system and pave the way towards the scale-up for real applications.

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Novel synthesis method of carbon decorated $Na_3V_2(PO_4)_3$ flower-structured hybrids to boost the electrochemical performance of sodium-ion cathodes

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Abstract

Sodium (Na) Superionic Conductors (NASICON) with a three-dimensional framework are promising candidates as cathode materials for sodium-ion batteries (SIB) due to their high structural stability and fast Na^+ conductivity. Among these structures the most representative material is $Na_3V_2(PO_4)_3$ (NVP) with a theoretical capacity of 117 mAh g^{-1} [1]. However, its low intrinsic electronic conductivity is the main drawback for its use as cathode in SIB. This issue can be overcome by coating NVP particles with conducting carbon films [2]. Introducing porous structure can further boost the charge-discharge performance and prolong cycling stability. The study is focused on developing novel synthesis methods to achieve materials of improved electrochemical properties. This work shows importance of tailoring the composition and structure of novel hybrid materials to boost the capacity values and the rate capability performance. The morphology (**Fig. 1a)**, structure, physicochemical and electrochemical properties (**Fig. 1b)** of flower-shaped carbon-decorated NVP hybrids (NVP/C-fs) are presented.

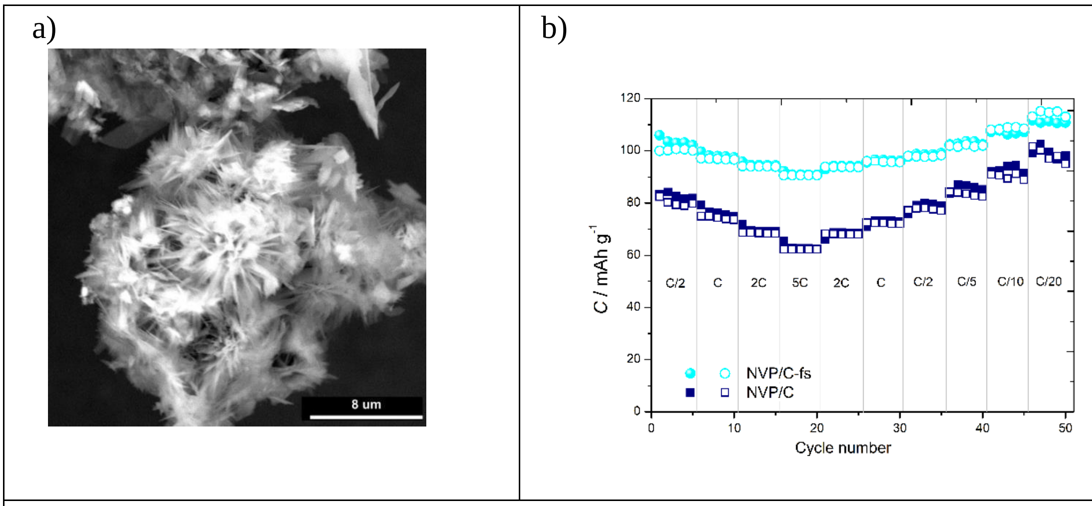

Figure 1: a) SEM image of carbon-decorated flower-like structure of sodium vanadium phosphate (NVP/C-fs) and b) comparison of rate capability for NVP/C and NVP/C-fs, electrolyte: 1 M $NaPF_6$ in EC:DEC (30:70wt%) + 5wt% FEC; (1C = 117 mA g^{-1}).

Such hybrid materials appear to be promising candidates as cathodes for fast charging sodium-ion batteries. NVP/C-fs showed 45% higher capacity at 5C rate in comparison to hydrothermally synthesized carbon- coated NVP (NVP/C).

Acknowledgements

Financial support from BEETHOVEN CLASSIC 3 program of National Science Centre is gratefully acknowledged (Project "Beyond Li-ion batteries: on novel and Efficient electrode materials for Sodium Storage", Grant No. UMO- 2018/31/G/ST5/02056).

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Double pulse potentiostatic synthesis of MnO_2 for electrochemical capacitors

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Supercapacitors play an important role in the energy transition to renewable sources due to their high specific power and immediate response. The main materials that have been studied for supercapacitor electrodes can be divided into carbon-based materials, transition-metal oxides and conducting polymers. Among several metal oxides, MnO_2 emerges as the most promising material due to its high specific capacity, low cost and environmentally friendly synthesis. The performance of MnO_2 films is significantly affected by the method of film growth and electrode architecture [1]. The synthesis can be carried out through electrodeposition and thermal or chemical reactions. In the case of electrochemically grown films, the main advantages are the simpler and faster synthesis, lower contact resistance with the substrate and greater control of film properties, such as thickness and porosity. However, the increase in the deposited mass leads to a decrease in the electrical conductivity and specific capacity of the modified electrodes. In addition, the stability of these films may reduce with charge/discharge cycling. Therefore, is essential to understand the film growth mechanism in order to design an electrode with a good electrochemical performance.

The present work aims at studying the effect of the experimental parameters of the potentiostatic synthesis of MnO_2 films on their pseudocapacitive response and, consequently, to optimize the synthesis strategy. The physico-chemical analysis of the electrodes was carried out through monochromatic *in situ* ellipsometry during the growth, and electrochemical impedance, Raman spectroscopy and scanning electron microscopy after their synthesis. The electrochemical characterization was performed in a three-electrode configuration through galvanostatic charge-discharge and cyclic voltammetry and a 2 electrodes cell was assembled to determine relevant metrics. Finally, the electrodes stability was determined by a long-term charge-discharge cycling.

Acknowledgments: authors acknowledge FCT funding for the projects: CQE - UIDB/00100/2020, UIDP/00100/2020, LA/P/0056/2020 and PTDC/QUI-ELT/2075/2020

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Revisiting old structure for developing high-power battery: The case of $KTiNbO_5$ family.

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Today, one of the main challenges of electrochemical devices is to meet the gap between electrochemical capacitors and li-ion batteries. In order word, it is to have the ability to charge faster and to provide high power during longer periods, thus allowing a larger development of intermittent electric power sources [1]. The actual negative electrode materials of li-ion battery (graphite and silicon) cannot sustain such high rate capabilities.

In this work, we are therefore revisited the plentiful family of niobium-based oxides. A presentation of old and interesting structure will be briefly review. As well, the case of $KTiNbO_5$ will be exposed and proposed as efficient negative electrode materials for next generation of high power devices. The layered $KTiNbO_5$ with a two-dimensional framework represents a playground to produce a large range of closely related phases (Figure1.A).[2] The protonated $HTiNbO_5$ analogue is obtained by ion exchange in acidic solution and it preserves a layered structure with a smaller interlayer distance. After dehydration of $HTiNbO_5$ at 400°C, the so-obtained $Ti_2Nb_2O_9$ phase displays a 2D arrangement with empty channels unlike tunnels of $H(K)TiNbO_5$. In this work, all the synthesized phases were studied as negative electrode materials between 1.0V and 3.0V vs Li^+/Li and tested in 1M $LiPF_6$ in EC/DMC. Interestingly, these phases have shown different electrochemical behaviors. When $HTiNbO_5$ exhibits a typical plateau during the charge/discharge experiment corresponding to a biphasic phenomenon, lithiation of $Ti_2Nb_2O_9$ is governed by a solid—solution mechanism. For a better understanding of the charge storage mechanism, we have combined electrochemical experiments with *in situ* XRD measurements (Figure 1.D). We have shown that multielectron redox and corner/edge sharing system of Ti/Nb octaedra are at the origin of an interesting capacity of more than 100 $mAh.g^{-1}$ at a rate of 0.2 $A.g^{-1}$. Another synthesis method, using *Chimie Douce* techniques, leads to nanoparticules for both $HTiNbO_5$ and $Ti_2Nb_2O_9$ and allows an increase of the electrochemical performance of these materials (Figure 1.B-C). *Operando* isothermal calorimetry revealed smaller instantaneous and time-averaged irreversible heat generation rates at $Ti_2Nb_2O_9$ electrodes made by the sol-gel synthesis method, highlight their smaller resistive losses and larger electrical conductivity.

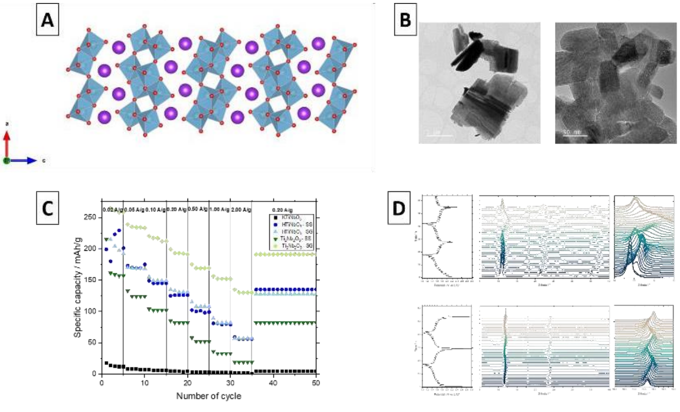

Figure 1: (A) Structure of KTiNbO5. (B) TEM images of solid state and sol-gel KTiNbO5 particles. (C) Electrochemical performances of all the materials (D) In situ XRD of HTiNbO5 and Ti2Nb2O9 solid state materials.

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Enhancing the Performance of Layered Metal-Organic Framework Supercapacitors by Coordination Modulation

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Layered electrically conductive metal-organic frameworks (MOFs) are emerging as new electrode materials for supercapacitor devices. This class of materials is formed from the square planar coordination of transition metal nodes by planar conjugated organic linker molecules. The resulting π-d conjugated 2D sheets then stack to form an extended 3D structure, with porous channels running through the material (Fig. 1). Their intrinsic high porosities and electrical conductivities make them attractive for energy storage applications, and several recent publications have highlighted their promise in supercapacitors.[1-3] Interestingly, layered conductive MOFs can be synthesised with a variety of different particle morphologies and degrees of agglomeration; however, it is currently unclear how the electrode microstructure impacts the energy storage performances of these materials. To address this, here we used coordination modulation to synthesise three samples of the layered conductive MOF $Cu_3(HHTP)_2$ (HHTP = 2,3,6,7,10,11-hexahydroxytriphenylene) with distinct microstructures. To the best of our knowledge, this is the first work to systematically vary the microstructure of MOF electrodes in supercapacitors using this technique**.** With this approach, we present a detailed study into the influence of microstructure on the capacitive performance of $Cu_3(HHTP)_2$ in symmetric supercapacitors. From these studies, we demonstrate the superior capacitive performance of weakly agglomerated 'flake-like' MOF particles compared to samples with 'rod-like' particles and samples with strong agglomeration. Samples with a 'flake- like' electrode microstructure, with a three-dimensional pore network comprised of many short pores, displayed faster charging rates with organic electrolytes and significantly higher capacitances with ionic liquid electrolytes, confirming their enhanced performance with a range of commercially applicable electrolytes. This is a significant advance in the understanding of layered MOFs for energy storage and provides a target microstructure for layered MOFs for supercapacitors in the future.

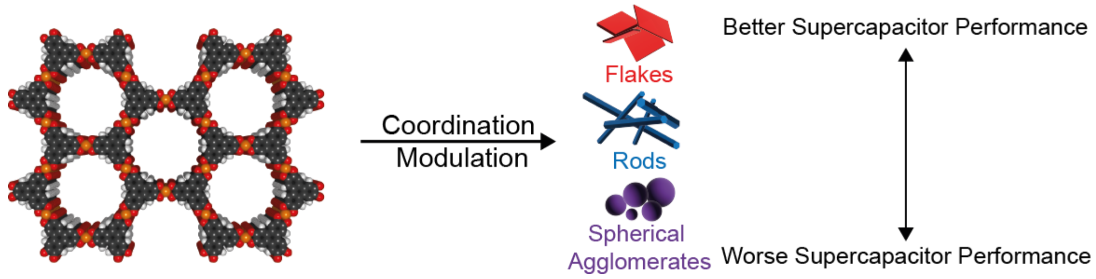

Figure 1*: Coordination modulation was used to synthesise three samples of a layered conductive metal-organic framework (MOF) (left) for use in supercapacitors, enabling a far-reaching study to investigate the impact of electrode microstructure on the supercapacitive performance of these frameworks. The results provide a target microstructure for MOF electrodes in future energy storage devices.*

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Iron and manganese-based composites as pseudocapacitive electrodes for aqueous asymmetric capacitors

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The ever-growing demand for portable electronics, smart textiles, and electrical vehicles warrants the development of new-generation efficient and durable energy storage devices that will meet our expectations. Supercapacitors are effective for this purpose, as they are characterized by high power, good energy densities, excellent long-term performance, and a wide range of possible applications in different conditions. Furthermore, asymmetric capacitors are intensively investigated due to their wider operating voltage window and the higher energy density values delivered [1]. Among the different pseudocapacitive materials used for the asymmetric configuration, transition metal oxides including iron and manganese oxides are considered a viable choice due to their high theoretical capacitance, low cost, natural abundance and the possibility of structure modification [2].

In this work, we investigated the electrochemical performance of a full pseudocapacitive asymmetric capacitor based on an iron oxide/reduced graphene oxide (FG) negative electrode and a manganese oxide/reduced graphene oxide (MG) positive electrode. The FG and MG composites were synthesized using hydrothermal conditions, and their morphology, crystalline and porous structure were investigated. Two FG composites with different mass ratios of iron oxide to reduced graphene oxide (FG/1:4 and FG/1:1) were investigated. Electrochemical measurements were performed in an aqueous neutral electrolyte of 1 M Na_2SO_4 with an operating voltage window of 2 V.

Preliminary results from a three-electrode configuration have shown that the MG composite exhibits 1.4 and 2.1 times higher specific capacitance compared with the FG/1:4 and FG/1:1 composite, respectively. Therefore, the mass ratio of the positive and negative electrodes was adjusted for equal capacitances at each of the capacitor electrodes. The assembled all pseudocapacitive asymmetric devices exhibited specific capacitance values of 127 and 152 F g^{-1} for configuration with FG/1:4 and FG/1:1 as negative electrodes, respectively at a current density of 0.5 A g^{-1}.

The results mentioned above suggest that the combination of iron and manganese oxides with reduced graphene oxide shows promising potential for aqueous asymmetric capacitors with wide operating voltage of 2 V.

Acknowledgement

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Potassium formate-based electrolytes for high performance aqueous electrochemical capacitors

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Aqueous electrolytes are attractive for their low cost and high sustainability, but their narrow electrochemical stability window (1.23 V) is limiting their application in several energy storage devices, including electrical double layer capacitors (EDLCs).[1]

In the last years, the use of highly concentrated electrolytes, often indicated as water-in-salt electrolytes (WiSE), proved to be a convenient strategy to increase the operative voltage of aqueous EDLCs. As aqueous electrolytes, they do not suffer from high toxicity, cost and flammability as that of organic electrolyte. [2]

In this work, we report about the use of the saturated 14 M HCOOK in H_2O solution as electrolyte for EDLCs. This electrolyte is not only cost effective, environmentally friendly, but also has low toxicity and displays promising transport properties as well as large electrochemical stability. It has been demonstrated using this electrolyte is possible to realize EDLCs operating at 1.7V, display high energy (10.6 Wh kg^{-1}), and power densities (471 W kg^{-1}) and extraordinary cycling stability (90% of capacitance retention after 1700 hours of float at 1.7V). Taking these results into account, 14 M HCOOK in H_2O can be certainly considered as a very promising for the realization of a novel generation of cheap and high performance aqueous EDLCs. [3]

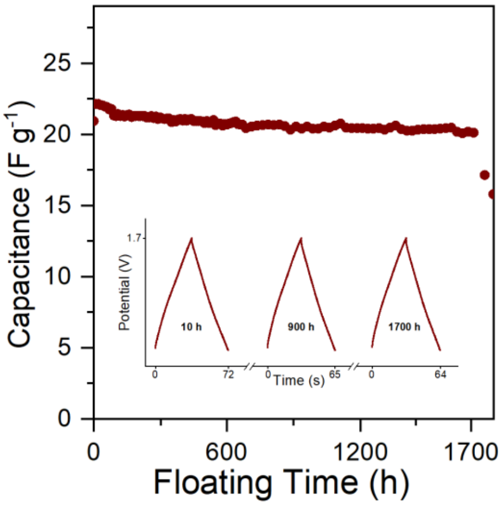

Figure 1: *float test and voltage profiles after 10 h, 900 h and 1700 h floating at 1.7 V (inset).*

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Novel pyrrolidinium based salts and sulfone-based solvents for high voltage electrical double layer capacitors

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The implementation of electrical double-layer capacitors (EDLCs) as energy storage for applications with high power demand is becoming more and more popular in the last years. However, the low energy density of these devices is still limiting the number of possible applications and therefore the market for these devices. One approach to increase the energy density of EDLCs is to increase their operative voltage. Since the maximum voltage of an EDLC is mainly limited by the decomposition of the used electrolyte, great efforts were made in the last years to identify possible alternatives to the state-of-the-art electrolyte components. In order to improve the stability of the electrolyte significantly, both, the conducting salt and solvent, need to be replaced by more stable compounds. Especially at elevated temperatures, the development of enhanced electrolytes is extremely challenging due to several effects such as accelerated reaction kinetics of parasitic reactions.

Recently, the use of *N*,*N*-dimethylpyrrolidinium tetrafluoroborate (Pyr11BF4) as conducting salt for EDLC electrolytes was proposed [1-2]. Figure 1a displays the stability of a Pyr11BF4 based EDLC compared to an EDLC containing the state-of-the-art electrolyte 1 M TEABF4 in ACN at 60 °C. While both systems show fast loss of capacitance at 3.4 V, the alternative electrolyte displays significantly higher stability at 3.0 V with a capacitance retention of 91 %. Still, the high temperature capability of ACN is limited due to its low boiling point. Thus, ethylisopropyl sulfone (EiPS) was proposed as alternative for high energy EDLCs [3-4]. EiPS features high electrochemical stability but inferior ability to dissolve salts and relatively high viscosity compared to other solvents. However, especially at elevated temperatures these drawbacks become less relevant due to the increasing ionic conductivity of the electrolyte with increasing temperature. In this work, we show that at 60 °C, EDLCs containing the electrolyte 0.5 M TEABF4 in EiPS feature an extraordinary stability with 79 % capacitance retention after 500 h of floating at 3.2 V.

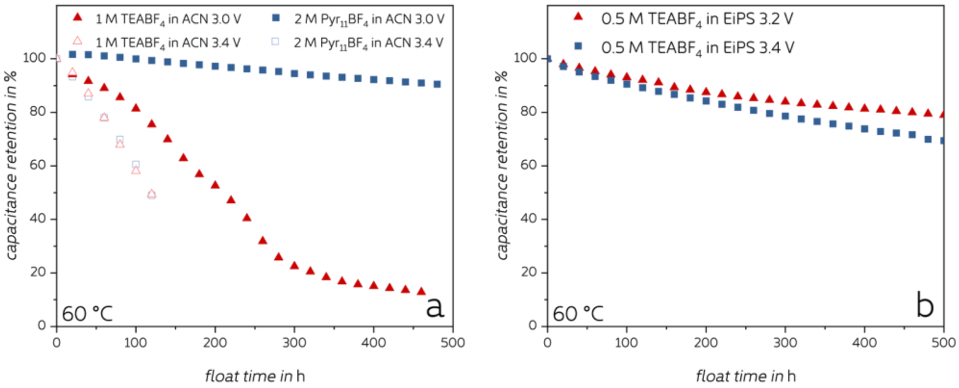

Figure 1: *Comparison of the stability of a) 1 M TEABF4 in ACN, 2 M Pyr11BF4 in ACN and b) 0.5 M TEABF$_4$ in EiPS at 60 °C during float tests at different voltages.*

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Enhanced energy density and safety of carbon-carbon supercapacitor by development of a green hydrogel electrolyte

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Electrochemical supercapacitors (ES) are fast energy storage devices with highly reversible charge storage processes. Yet, they suffer from limited energy density and significant research is conducted to improve it. ES employ two carbon electrodes, a separator and an electrolyte, generally in liquid state, that ensures the transport and diffusion of ions. Lately, safety issues related to liquid electrolyte such as the occurrence of hazardous gases or corrosive solvent leakage has been observed. Therefore, new attempts to overcome these limitations have been explored and led to the generation of a new form of solid-like electrolyte, i.e. polymer electrolytes (PEs). Nevertheless, the most used polymers are of synthetic base matrix that rise environmental problems and biodegradability issues, and in addition the fabrication process requires multiple steps. In this concern, the idea of using a green biodegradable polymer to form an ecofriendly gel electrolyte is of great importance. In this work, chitosan is proposed as a low cost natural polymer to host KOH electrolyte via a simple synthesis method involving the cross-linking with glyoxylic acid. Then by a drop cast technique the gel is formed at room temperature and the chitosan-KOH gel electrolyte is cut in a circular shape (Figure, inset).[1] The gel electrolytes formation at different reticulation time periods (4 to 21 days) was studied in detail. Through time, reticulation occurs between amine and hydroxyl groups of chitosan and the groups of the cross-linker. This process is slow and it was found that starting from 4 days of aging the gel has a good mechanical strength and adhesion. In two electrode system based on porous carbon, the capacitance and rate capability delivered by the device in the presence of different chitosan-KOH gel electrolytes after 4 days is higher than in the device with liquid 2M KOH (Figure, left). A test in 3-electrode system vs. Hg/HgO as reference electrode permitted to extend the operational voltage window until 1.3 V with the alkaline chitosan-KOH gel electrolyte. The Ragone plot is calculated for the devices using the gel electrolyte and liquid 2M KOH at 0.8 and 1.3V and a considerable gain in the energy density can be seen while using the chitosan-KOH gel electrolyte. Moreover, after 10000 cycles of the carbon supercapacitor using chitosan-KOH gel electrolyte at 1 Ag^{-1} at 1.3 V, the device keeps 92% of its initial capacitance. All these results prove that the carbon supercapacitor employed with the chitosan-KOH gel electrolyte allows an improvement by 3 times in the energy density, an increase in the voltage window, good retention and suppression of corrosion attesting the safety of the carbon/carbon supercapacitor.

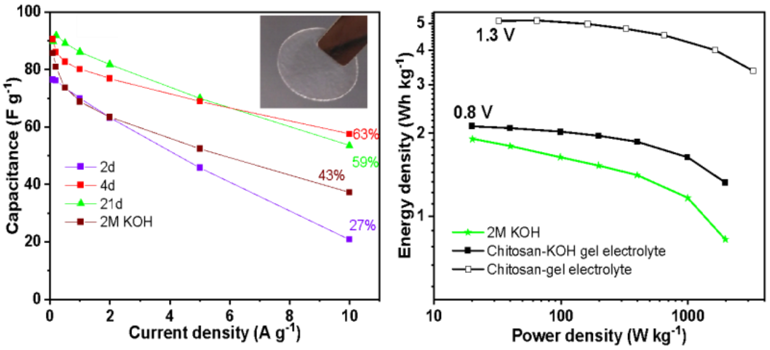

Figure: *(Left) Capacitance and rate capability from 0.1 to 10 Ag^{-1} of two-electrode symmetric devices using different electrolytes, (inset) Photo of gel electrolyte cut and ready to insert in a two-electrode device, (right) Ragone plot of capacitors with chitosan-gel electrolyte and liquid 2M KOH electrolyte*

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Electric Double Layer and Pseudocapacitive Ionic Liquid-based Supercapacitors for Harsh Environment applications

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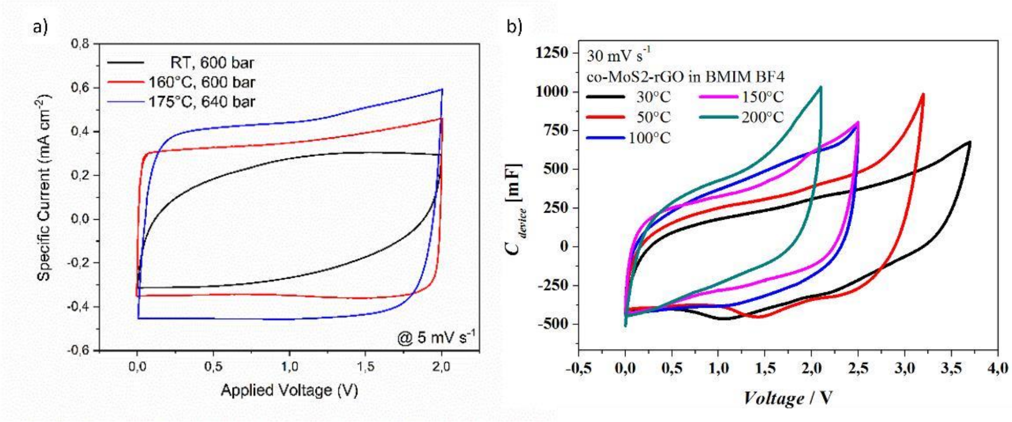
The study of energy storage devices able to work in harsh environments is becoming of paramount importance. [1–3] Numerous applications require devices to be able to sustain extreme temperatures (in some case up to 200°C). Herein, we propose the study of both EDLC and pseudocapacitive (PCs) systems in ionic liquid electrolyte based on activated carbons (AC) and MoS2 decorated reduced graphene oxide (rGO), respectively. Ionic liquids (ILs) represent a suitable class of electrolytes for the present application because of the high temperature stability. In this work, [PYR14][TFSI] and [BMIM][BF4] were used for the EDLC and PCs systems, respectively.

The PC device was tested in temperature in coin cell configuration up to 200°C. The coin cell was slightly modified with Teflon o-ring to guarantee temperature stability of the packaging. The EDLC device was tested in pouch cell configuration also under high pressure condition, at 175°C and 640 bar. The results show an overall increase in the device capacitance and a reduction of the voltage window. The PC device showed a starting capacitance of 100 mF cm^{-2} while the EDLC one started at 35 mF cm^{-2}. An overall increase in the devices performances was observed in terms of either areal capacitance and energies. Both devices ended up at maximum voltage of 2V at temperatures above 150°C according to the graphs shown in Figure 1.

Figure 1: *Cyclic voltammetries of the EDLC device, on the left, and PC one, on the right, carried out at constant scan rate, and different temperature and pressure.*



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Artificial intelligence for pseudocapacitive tendency prediction of faradaic electrode material electrochemical behavior

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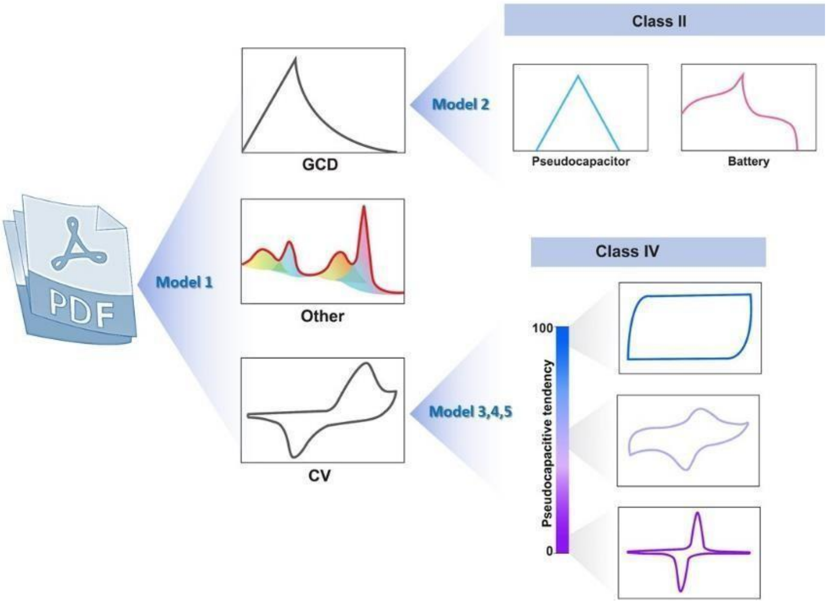

Figure 1: *The cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) classification models using pseudocapacitance tendency as indicator.*

It has been a huge number of publications on electrode materials in energy storage research including battery and pseudocapacitor demonstrating the electrochemical behaviors as observed from cyclic voltammetry or galvanostatic charge-discharge measurements. In general, the behaviors are often classified as so-called pseudocapacitor or battery materials based on different perspectives associated with, for example, the performance or the characteristic of the materials. It was clearly defined that pseudocapacitor signal is originated from faradaic processes that sometimes appear similarly to that of an Electrochemical Double Layer Capacitor (EDLC). Anyway, in many cases EDLC signals are much more different from pseudocapacitor.

It became to our research objective to overcome this confusion and to classify the signal types using artificial intelligence. The classification model is based on a supervised deep learning using dataset without ambiguity. Surprisingly, the correlation between the title of publication and its signals (CV and GCD) emphasized the non-correlation between the types of electrode material defined in the title and the experimental observations.

By a simple binary classification, the difference between battery and pseudocapacitor material is not completely separated as they are all resulted from the same origin: a faradaic electrode material. For that, the descriptor, the pseudocapacitance tendency, determined by artificial intelligence classification can orient researchers in the field to be able to define their electrode materials. Moreover, we provide the interactive channel for users to classify CV and GCD online following our website (*http://supercapacitor-battery- artificialintelligence.vistec.ac.th*).

Comprehensive Analysis of Electrodes Performance in Carbon-based Hybrid Capacitors by Cyclic Voltammetry

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Metal-ion capacitors (MICs) are hybrid electrochemical energy storage systems displaying up to ca. 4 times higher specific energy than electrical double-layer capacitors (EDLCs) at comparable power [1], by associating a battery-type negative electrode (into which alkali cations are reversibly inserted/intercalated) with an EDL positive electrode (generally, from activated carbon (AC)) in which the anions from the electrolyte are electrosorbed [2]. Said MICs exhibit as well lower self-discharge than EDLCs, as well as longer lifespan than metal-ion batteries (MIBs) [3]. Nonetheless, little is known on the synergy of electrodes in these types of hybrid capacitors (HCs). Therefore, information on the performance of individual electrodes during the operation of MICs is a cornerstone for their improvement.

Herein, the electrochemical characteristics of the individual electrodes in Li-ion and Na-ion capacitors (LIC and NIC, respectively) as well as symmetric EDLCs have been analyzed by cyclic voltammetry (CV) on cells equipped with a reference electrode. By adapting the calculation methodology initially presented by Ślesiński and Frackowiak [4] for the determination of accurate electrode contribution during potentiodynamic analysis of electrochemical capacitors, it has been possible to confirm that in the case of MICs, the scan rate attributable for the single electrodes (dE^+/dt and dE^-/dt) is not constant in time. Interestingly, when the potential of each electrode is varied at a constant sweep rate (***Figure 1a***), the voltammogram of the battery-type negative electrode does not provide the same current response as in the real hybrid capacitor where only the cell potential scan rate, dU/dt, is controlled (***Figure 1b***). In fact, in a MIC, the EDL electrode dictates the rate at which the two electrodes are charged at each point of the test. Hence, the proposed analysis of potentiodynamic behavior of individual electrodes brings crucial information for improving hybrid energy storage systems.

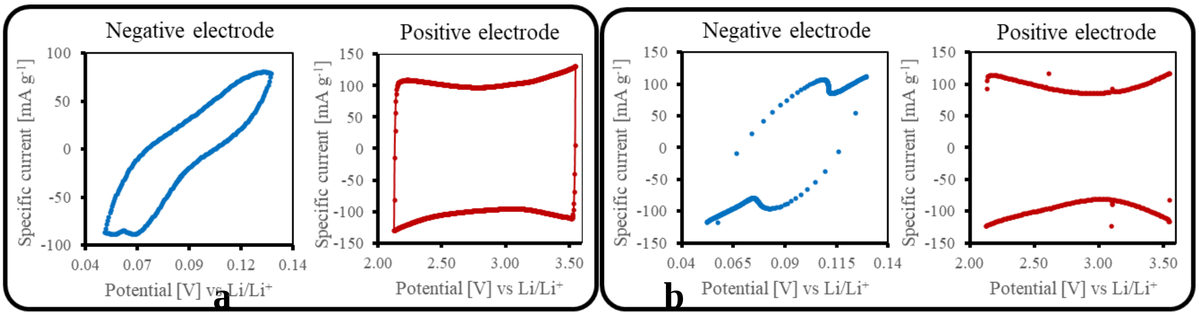

Figure 1: Cyclic voltammograms of individual electrodes for an (+)AC//Li_xC_6 (-) cell in 1 mol L^{-1} $LiPF_6$;EC:DMC operating from 2 to 3.5 V at (a) constant electrode potential scan rates, dE^+/dt and dE^-/dt, of 0.001 and 0.999 mV s^{-1}, respectively; and (b) constant cell potential scan rate, dU/dt, of 1 mV s^{-1}.

This work was supported by the Foundation for Polish Science (FNP) in the frame of the CARBionCAP project [POIR.04.04.00-00-5EF5/18-00] and by the Ministry of Education and Science, Poland [0911/SBAD/2201].

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High specific energy obtained after long floating time from high surface area activated carbon for supercapacitor application

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Abstract

In this study, we have successfully synthesized high surface area activated carbon through economical and simple activation process for supercapacitor applications. The electrochemical investigation was done in aqueous basic (3 M KOH) electrolyte and different neutral (1 M Li_2SO_4, 1 M $NaNO_3$, 1 M Na_2SO_4 and 2.5 M KNO_3) electrolytes to study the influence of cation and anion sizes in supercapacitor performance. The optimal performance was noted for 1 M $NaNO_3$ electrolyte in a positive and negative potential window of 0.0 – 0.7 V vs Ag/AgCl and -0.9 – 0.0 V vs Ag/AgCl, respectively. The fabricated symmetric device presented a maximum specific energy and power of 33.1 Wh kg^{-1} and 4,250 W kg^{-1} after 300 h floating time. The device revealed an outstanding columbic efficiency of 99.8% and capacitance retention of 90.1% after 20,000 cycling at 5 A g^{-1}. The results propose that the produced activated carbon will add value in different applications and the fabricated supercapacitor device can be employed in energy-storage and various portable electronic devices.

Challenge for upscaling activated carbon production for supercapacitor applications from real lignin waste

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Electrical double-layer capacitors (EDLCs) store electric energy by fast and highly reversible electrostatic processes. Activated carbon-based EDLCs arise as preferential choices when it comes to store electric energy for short times releasing it with high power pulses. Nowadays, activated-carbon-based materials are among the most exploited, as main components for EDLCs electrodes, given their unique combination of chemical inertia, electrochemical stability, conductivity, and specific surface area together with the possibility to highly engineer the textural properties of these materials in term of surface moieties and pores size distributions [1]. To improve the sustainability of the supply chain of these materials, the pyrolysis of bio-derived-waste enables both their valorization as well as the exploitation of a ubiquitous and scalable raw material that is not related to the fossil economy. For practical purposes, to enable an effective scale-up, biomass sources must be abundant and cheap [2]. Lignin stands out, because it is the third most abundant natural polymer and one of the major wastes of anaerobic digestion processes and pulp and paper making industries [3]. Here we report about a systematic study to scale up the production of Lignin Activated Carbon (LAC) generated by a one-step carbonization route starting from a real lignin waste, using $KHCO_3$ as mild activating agent [3]. Different process routes have been explored and the effect of the process parameter on the textural and chemical physical properties of the activated carbon are analyzed and discussed as well as the electrochemical characterization of the different tested batch as main components of EDLCs electrodes both on lab scale and preindustrial ones.

Acknowledgments

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Impact of OH^- and H^+ ions concentration on electrical double-layer formation and electrode expansion in porous carbon materials

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Scientists work on novel materials (e.g., electrodes and electrolytes) that can be useful for energy storage systems. However, such progress requires extensive fundamental knowledge and insightful study. It is not only about promising materials development but the key is to fit properties of the electrode material to the electrolytic solution. Pore/ion size ratio and ions number are crucial for the device performance improvement. Hence, the description of ionic fluxes at the electrode/electrolyte interface during polarization is of great importance. The behavior of ionic fluxes (under various OH^- and H^+ ions concentrations – different pH) in pores of carbon materials is the main research subject for authors.

In this work, operando electrochemical dilatometry (ECD) experiments, incorporating various electrochemical techniques like cyclic voltammetry (CV), large amplitude sinusoidal voltammetry (LASV) and Step Potential Electrochemical Dilatometry (SPECS), were utilized in order to understand and describe the fundamentals concerning the behavior and solvation effect of cations and anions at various electrolyte's pH.

The experiments were performed for systems operating in 1 mol L^{-1} Li_2SO_4 of different pH (6, 9 and 12) and 1 mol L^{-1} LiOH (for comparative purposes); a microporous carbon (Kuraray YP-80F) was used as an electrode material. It was shown that the trend is comparable for electrolytes of pH 6 and 9; however, the cell with the solution of pH 12 exhibits similar behavior to LiOH solution, suggesting that during positive polarization, the primary role is played by OH^- – despite the same salt concentration. SPECS allowed the current to be divided into components; it appeared that the separated electric double-layer (EDL) capacitances (in pores and on easily accessible for electrolyte electrode surface) correlate with the electrode height changes. This result raises an essential concern of the actual ion population at the electrode/electrolyte interface, affecting the water decomposition potentials and triggers various parasitic reactions impacting the long-term electrochemical capacitors performance.

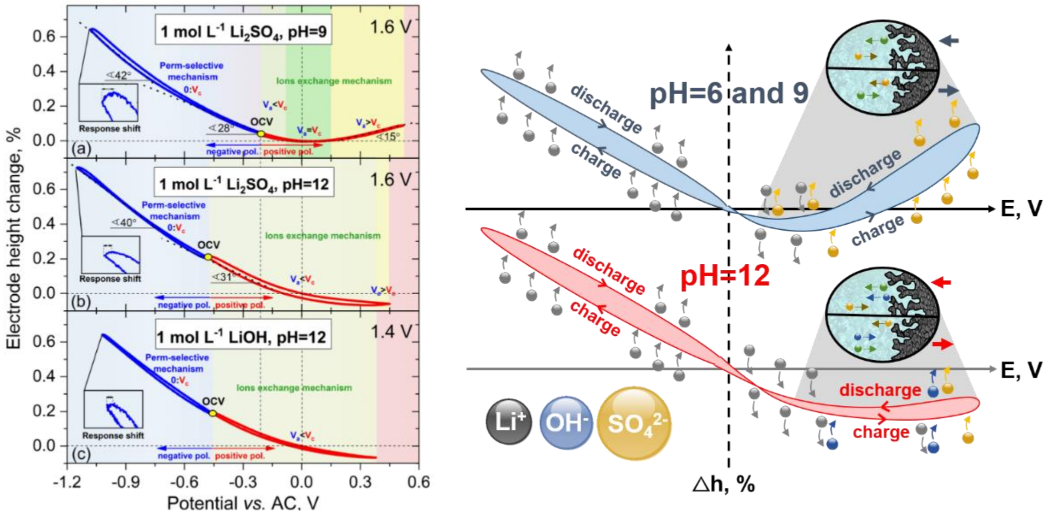

***Figure 1**: The electrode height changes in the function of potential applied for the electrodes polarized negatively (blue curves) and positively (red curves) in 1 mol L^{-1} Li_2SO_4 of pH (a) 9 and (b) 12, as well as in (c) 1 mol L^{-1} LiOH.*

Acknowledgment: This work was financially supported by **European Research Council** within the Starting Grant project (GA 759603) under European Unions' Horizon 2020 research and innovation programme.

Operando PXRD Study of Ni-doped Manganese Hexacyanoferrate Cathode Material in Aqueous Zn-ion Battery System

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Operando experiments provide the data which are expected to be a realistic representation of the sample behavior found under the normal operating conditions [1]. In our group, we work on battery materials, and in operando modality, the typical drawbacks of ex situ experiments can be avoided, such as sample transfer or relaxation reactions that may occur when the electric circuit is opened. Also, studies can be performed on a single test cell, which unlike ex-situ experiments, makes it possible to avoid uncontrolled differences between cells [1]. For operando PXRD studies in MCX beamline in Elettra synchrotron facility EL-CELL was used in reflection mode with CCD detector.

Our study material is manganese hexacyanoferrate (MnHCF), which is one of the Prussian Blue analogues (PBAs). To improve the performance of MnHCF as a cathode material, metal doping technique is widely applied, one of them being nickel, which generally is used to relax the Jahn-Teller distortion and therefore improve the long-time stability throughout the cycling [2]. Our material has been tested in several systems, among them aqueous zinc-ion batteries (AZIBs). Here the experimental results of 10% Ni doped MnHCF will be highlighted in AZIB system with 3M ZnSO4 electrolyte and Zn metal anode.

Generally, inside the cathode material during the cycling some changes might occur including the structural changes or the new phase formation. The confirmation of the structural exchange of Mn with Zn in AZIB system based on XAS analysis has been reported before in pure MnHCF material [3]. According to our operando PXRD measurements the same phenomena were observed for Ni-doped material. By having the pure powder and pristine ex-situ samples tested, the information about the cubic (F m -3 m) structure of the material has been already known [4]. In operando mode the lattice parameter has changed alongside with addition of the new peaks even during the resting mode, just by electrode being exposed to the electrolyte. Changes continued to occur during the consecutive charge and discharge process. Additional peaks prove new phase formation inside the material. The PXRD patterns show only partial reversibility of the structure during the discharge process. Also, by having the first cycle charged and discharged ex-situ samples, the comparison in-between them and operando sample were made [4].

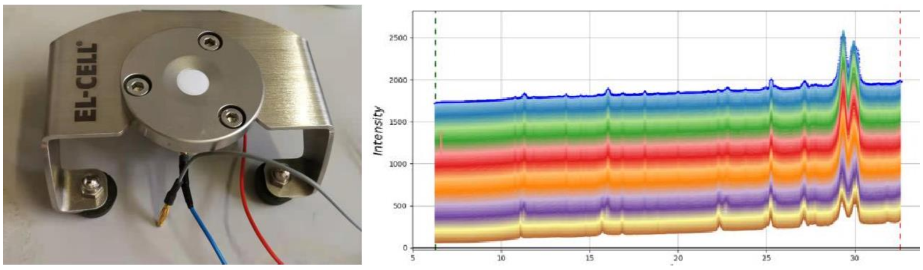

Figure 1: *El-cell (left) and operando PXRD pattern of Ni-doped MnHCF (right).*

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Intriguing Role of the Cation in the Electrical Double-Layer Formation at Nanoporous Carbons Monitored by Electrochemical Dilatometry

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Development of energy storage devices requires deep understanding of the fundamental phenomena ongoing in the system during its operation. In electrochemical capacitors (ECs) the description of the processes at the electrode/electrolyte interface are of the greatest importance. The aim of this study is to investigate the ionic fluxes in ECs operating with environmentally friendly aqueous electrolytes and activated carbon-based electrodes. As already shown, cation type strongly affects the electrochemical behavior of both electrodes and, in consequence, the performance of the cell. It is caused by differences in solvated ion diameters and diffusion coefficients. However, the detailed explanation of the charge storage mechanism depending on the cation type is still ambiguous.

In this work, the electrochemical dilatometry technique was used, giving the information of the electrode height change during its polarization in *operando* mode. Aqueous solutions of alkali metal sulfate salts (0.5 mol L^{-1} Li_2SO_4, Na_2SO_4, K_2SO4, Cs_2SO4) were used as electrolytes. Ions interactions with microporous carbon electrodes (Kuraray YP-80F) were investigated. Different electrochemical techniques (cyclic voltammetry and large amplitude sinusoidal voltammetry) at various conditions (scan rates and frequencies) for two-electrode and three-electrode configurations were applied.

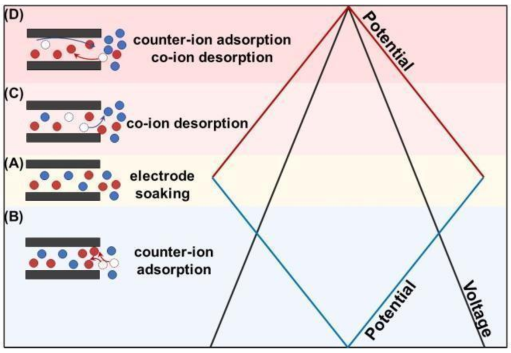

Figure 1: *Schematic picture of the ions movement at the surface and within the porosity of the electrode material immersed in the electrolyte **(a)** and during the EC charging – for the electrode polarized negatively **(b)** and positively **(c, d)***

The cation type can strongly impact the volumetric changes of both electrodes in ECs, due to the proposed EDL formation mechanism (Figure 1). It is seen that in the electrode polarized negatively, the charge is balanced by cations adsorption – therefore depending on the cation size different electrode expansion is expected. In the case of the positively polarized electrode charge is balanced first by the cation desorption (so electrode shrinkage is expected). When the potential is high enough, the anions adsorption is responsible for charge balancing.

The data presented and compared for four electrolytes of different cations and the same anion allows the mechanism of charge accumulation in ECs to be understood and the impact of cation type to be explained. The outcome of the study, discussed in the context of double-layer charging/discharging is of essential importance for power retention in electrochemical capacitors and designing new materials for high power applications.

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Analysis of carbon electrode dilatometric strain determined by Scanning Electrochemical Microscopy and internal pressure measurements

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Rational energy management is currently one of the most important challenges expected from developed countries. Among many solutions proposed for energy storage, such as batteries, redox flow systems, hydroelectric storage, or electrochemical capacitors, the latter seems to have the upper hand owing to their high power density and long cycle life features.

Despite the broad spectrum of the energy storage systems proposed, recent capabilities seem to be insufficient for societal demands. In addition to manipulation at the nanoscale, aiming to improve the performance of energy storage materials, today, the most attractive approach for examining device components exploits so-called in situ and operando methods. In the field of carbon-based electrochemical capacitors, operando techniques have provided novel insights into ionic fluxes and ion behaviour at the electrode/electrolyte interface.

In this work, we are majorly focused on the macroscale changes occurring in the activated carbon structure, monitored by scanning electrochemical microscopy (SECM). In this method, the micrometer-sized tip of the so-called ultramicroelectrode is moved above the targeted surface to be investigated, and the electron transfer reaction at the tip or the substrate surface under the tip is monitored. Briefly, the changes in the current recorded are used to characterize the processes and structural features of the substrate as the tip is moved above the surface.

The results from SECM and dilatometric measurements are complemented by *operando* contact angle observations, where interesting changes in electrolyte behavior were observed. To complete the picture, *operando* measurements of internal pressure changes during capacitor operation were also recorded. Thus, we believe that the correlation of these techniques provides an insightful overview of the influence of polarization on electrode dilatometric changes and gas generation in carbon-based capacitors operating with an aqueous electrolytic medium.

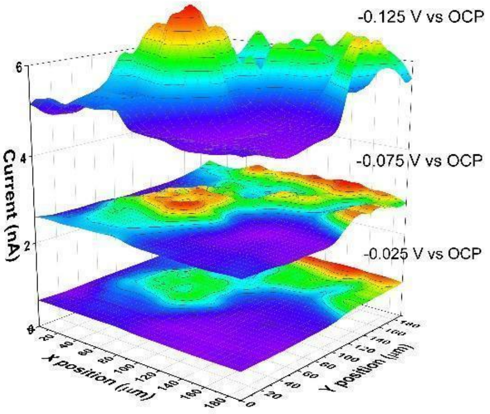

Figure 1: *The surface of the carbon electrode operated with 1 mol L-1 Li2SO4 solution and scanned with a scanning electrochemical microscope in feedback mode, changes of the tip current recorded for mild polarized electrode surface.*

This work was financially supported by European Research Council within the Starting Grant project (GA 759603) under European Unions' Horizon 2020 research and innovation programme, Polish National Science Centre within the SONATA scheme (Project No.2019/35/D/ST4/02582)

Operando monitoring of local pH value changes at carbon electrode surface in aqueous electrochemical capacitors

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The operation of electrochemical capacitor (EC) is related to the attraction and repulsion of charged ions originating from electrolyte dissociation. In ECs operating with aqueous-based electrolyte, the migration of water autoprotolysis products such as H_3O^+ and OH^- must be additionally taken into account. The concentrations of these ions are responsible for pH changes in a capacitor cell. It is imperative as the pH impose the potential values of water decomposition reactions (water oxidation and reduction) which can eventually lead to oxygen and hydrogen evolution reactions (OER and HER) as indicated in Pourbaix diagram. The electrochemical capacitor comprises of carbon electrodes which are reactive by nature, hence, multiple electrochemical reactions take place contributing to the increase of pH gradient within the system. Often, the estimation of pH was done using pH indicator papers, which show acidic environment in a positive electrode vicinity and alkaline in a negative one. Consequently, the capacitor voltage could be increased over 1.23 V. Herein, we present the results of operando measurements of pH during capacitor operation. These measurements allow a true identification of the instantaneous pH at the electrodes, and therefore enable the correct assignment of theoretical equilibrium potentials of OER and HER. These measurements are done in typical Swagelok cell of increased inner electrode-to-electrode distance. Additionally, the cell has open upper body, where pH and reference electrodes could be introduced. The obtained results are supported by EQCM and GCMS experiments. Figure 1 shows the results of pH monitoring during potentiodynamic cell voltage increase (5 mV s^{-1}):

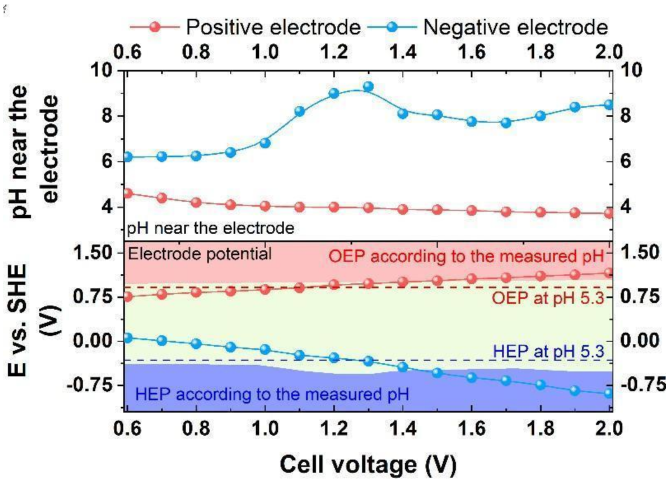

Figure 1: *Upper graph: Electrolyte pH at the electrode surfaces of the capacitor charged to different voltages in 1 mol* L^{-1} Li_2SO_4*. Lower graph: measured terminal electrode potential values and corresponding HEP and OEP at these pH values. The dashed lines indicate the theoretical OEP and HEP at constant pH.*

This approach improves the understanding of the behaviour at the electrode/electrolyte interface which can contribute to more accurate and controlled voltage window extension for further energy density enhancement.

Acknowledgements
This work was financially supported by European Research Council within the Starting Grant project (GA 759603) under European Unions' Horizon 2020 research and innovation programme (AS, KF), Polish National Science Centre within the SONATA scheme (Project No.2019/35/D/ST4/02582) (SS, JM) and by the Ministry of Education and Science within the project 0911/SBAD/2201 (EF).

Divalent metal solid-state electrolyte for hybrid capacitors: study of the coordination anion-to-Mg^{2+} via Raman spectroscopy

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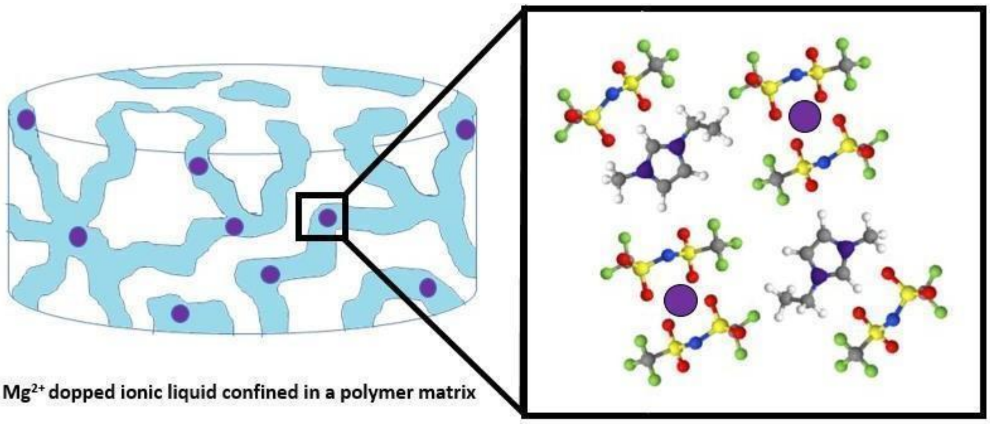

Figure 1: *Magnesium conductive ionogel as a solid electrolyte for hybrid capacitors*

The emergence of all-solid-state energy storage devices implies new solid materials as electrolytes. They have to be as competitive as the current liquid electrolytes in terms of ionic conductivity and electrochemical stability. Ionics liquids (ILs) are well known for their properties such as very low vapour pressure, low melting points, non-flammability and wide electrochemical window. Nevertheless, they are still liquid and difficult to package in a battery. Ionogels are a new kind of biphasic material composed of an IL confined in a solid matrix based on silica or polymer (Figure 1).

We have been studying the effect of the confinement of ILs in polymer-based ionogels. The addition of Li or Mg salts to the IL enables ionogels to be tuned to specific applications such as supercapacitors, batteries and hybrid devices such as metal-ion capacitors. Switching from monovalent to divalent cations insure more energy in the storage system.

The present work focuses on anion-to-cation interaction in solid electrolytes. We studied the competition of the interaction between the TFSI anion, either with the counter cation of the IL: 1-ethyl-3-methylimidazolium or with the cation of interest (Li^+/Mg^{2+}). This competition is disrupted by the confinement because of the addition of another interaction with the confining solid matrix that results in improved mobility for these cations. Furthermore, the chemistry and physical properties of the polymer play a key role in diffusion mechanisms at the solid-liquid interface. A collaboration with UniSA is planned to design new kind of polymers in this perspective.

Investigation of the coordination number for Li^+ and Mg^{2+} is a route to understanding the interactions at this solid-liquid interface[1]. The aim is to disaggregate the ionic pairs, enhancing the ionicity and thus the ionic conductivity of the solid electrolyte. The mobility of alkalis and alkaline earths cations in electrolytes is strongly correlated to their coordination. Trying to understand fundamental ionic interactions is necessary to include ionogels as electrolytes for electrochemical applications.

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Development and Use of an *in-situ* simultaneous thermal analysis (STA) cell

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The transition from energy production based on fossil fuels to renewable energy sources is essential for a sustainable development of our society. A prerequisite for a successful implementation of renewable energy sources are fast, efficient and reliable energy storage devices, which can balance fluctuations and guarantee a stable grid.[1] In this context, electrical double layer capacitors (EDLCs) seem to be suitable energy storage devices, since they feature properties like long cycle life (>1,000,000 cycles) and high power density (~ 10 kW kg^{-1}) which allows the device to be charged and discharged within seconds.[2]

In many applications EDLCs experience a large temperature change, which might cause intense aging processes and a premature cell failure. Therefore, a deep understanding of the impact of the temperature of use and of temperature variation on the EDLCs performance are crucial for a successful implementation of these devices in various application.[3]

In this work we present the development and use of an innovative *in-situ* simultaneous thermal analysis (STA) cell, which allows a simultaneous investigation of the variation of heat flow, mass, resistance and capacitance occurring in EDLCs. The *in-situ* STA cell was utilized to investigate the impact of operating voltage and ambient temperature on the stability of EDLCs during float testing.

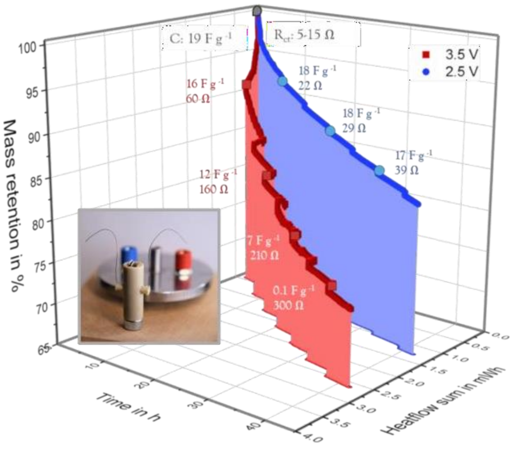

Figure 1: *3D diagram of the variation of mass, heat flow, resistance and capacitance occurring in EDLCs during floating up to 2.5 V (blue) and 3.5 V (red) at RT. [4]*

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POSTER PRESENTATIONS

Redox-active electrolytes for pre-lithiation of graphite electrode in lithium-ion capacitors

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The hybrid method of energy storage is a promising solution for life cycle and power extension relative to lithium ion-batteries (LIBs). However, the major problem during assembling lithium-ion capacitors (LICs) is the pre-lithiation stage. To date, several methods of pre-lithiation have been proposed in the literature. The primary one used an auxiliary metallic lithium electrode. Nonetheless, it raises safety issues concerning the exchange of the electrode in an inert atmosphere after first cycle and utilization of expensive metal. The second one uses composite materials - mostly lithium salts mixed with activated carbon and polymer binder. This method is very efficient but the dead mass left in the cell causes the deterioration of the system including capacity drop [1]. The last method proposed synchronic current pulses to put the lithium between graphite layers [2]. However, the loss of conductivity and negligible efficiency made this approach questionable. Modification of the last method by adding electroactive species in the proper amount may bring a new look on LICs pre-lithiation process.

In this work, the properties of novel approach in pre-lithiating the LICs using redox-active electrolytes were examined. A number of salts (lithium bromide, lithium sulfide, lithium acetate, lithium thiocyanate and lithium carbonate lithium nitrate) were dissolved in the classical electrolyte (1M LiPF6, EC:DMC, 1:1) based on the calculation of the charge amount used for the redox reaction to balance the Faradaic pre-lithiation process [3]. This work will discuss an example of successful lithium intercalation and a number of problems associated with the use of electroactive species in lithium-ion capacitors. In addition, the new approach will be compared with the currently used techniques. Since the intercalated lithium ions come from the additive, the conductivity of the electrolyte is not affected. Moreover, the dead mass is also eliminated due to the use of right amount of electroactive species in the electrolyte. Basic electrochemical tests were carried out, such as cyclic voltammetry, galvanostatic charge/discharge and impedance spectroscopy.

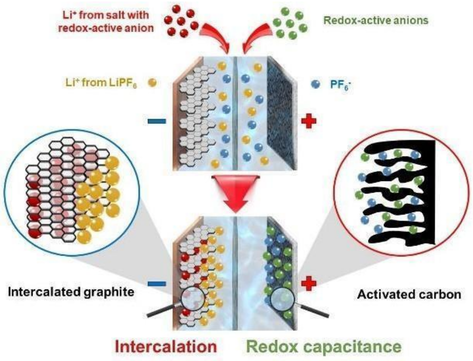

Figure 1: *Scheme of lithium intercalation into the graphite structure using redox-active electrolyte*

The European Research Council is acknowledged for the financial support within the Starting Grant project (GA 759603) under European Unions' Horizon 2020 Research and Innovation Programme.

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Improving the performance of electrochemical capacitors by addition of iodide

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Electrochemical capacitors (ECs) exhibit higher power density compared to batteries, long term cyclability and wide range of applications. ECs consist of three components: two porous carbon-based electrodes immersed in electrolyte and separated by membrane. An increase of the energy and achievement higher capacitance of ECs can be obtained by pseudocapacitive effects connected to quick faradic reactions. Therefore, electrochemically active electrolytes like aqueous iodide solutions, where $I2/I^-$ redox couple is present, are gaining attention owing to their environmental friendliness and safety.

In this study the main importance is focused on the improvement of electrochemical capacitors performance through the addition of iodide redox active species. Considering Pourbaix diagram, the crucial pH range for efficient work of iodide/iodine redox pair is acidic. In consequence, the use of acetate buffer which provides an acidic pH is justified. The sodium acetate buffer with addition of 0.2 mol L^{-1} sodium iodide was characterized physiochemically (pH, conductivity). It served as an electrolyte solution. Electrodes were prepared using activated carbon YP50F. Then, assembled ECs were electrochemically characterized using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) in two-electrode cell setup. Afterwards, the potentiostatic floating test has been applied in order to investigate long-term performance of the system. What is worth mentioning, EC based on sodium acetate buffer with addition of sodium iodide shows better long-term stability during constant voltage polarization at 1.5V (20% decrease of initial capacitance after 310 h) compared to sodium acetate buffer (20% decrease of initial capacitance after 100 h). Interestingly the use of sodium acetate buffer with addition of sodium iodide allowed to extend the operation voltage in aqueous medium (>1.5V), exceeding the limit of thermodynamic stability of water.

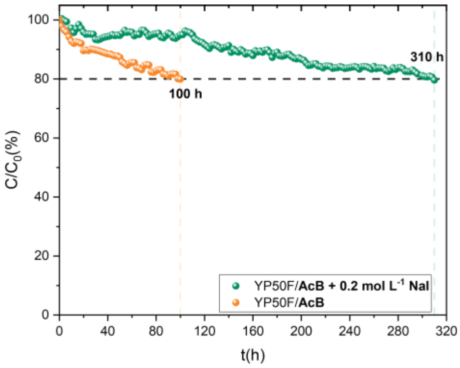

Figure 1 *Capacitance retention evaluated by GCD (1 A g^{-1}) during floating at 1.5V using YP50F in pure sodium acetate buffer and with additive of 0.2 mol L^{-1} NaI*

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Mesoporous Carbon Electrodes for Supercapacitor with Sodium ion Exchange Aquivion as Electrolyte membrane

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Mesoporous carbons are potential electrode material for energy storage systems owing to their interconnected pore characteristics, high surface area and conductivity. Among them, CMK-3 is a good candidate as materials electrode for supercapacitor and battery due to its ordered porosity, and chemical and mechanical stability.[1] Highly ordered mesoporous carbon can be normally achieved by templating with ordered porous silica. SBA-15, the well-known ordered mesoporous silica, is an appropriate template for obtaining high quality interconnected mesoporous carbon compared to other silica templates. The derived carbon (CMK-3) was found to be a true replica of SBA-15 with one dimensional carbon tubes connected by carbon channels. The synthesis process of CMK-3 involved multiple steps such as preparation of SBA-15, impregnation of carbon precursor, followed by pyrolysis and removal of the template.[2,3] Alternative strategies are needed to replace this complex and time-consuming standard procedure to make the process commercially feasible.

Here, we adopted two methods of synthesis for the silica template: i) standard method of synthesis and ii) ultrasonication assisted synthesis. Rapid condensation of silica precursors occurred during sonication and effectively reduced the time for the synthesis of silica template. Mesoporous carbons with high surface area were obtained through both methods. Symmetric supercapacitors were constructed with these carbons using sodium ion exchange Aquivion membrane as both separator and electrolyte. Both cells exhibited rectangular cyclic voltammograms with the electrical double layer behaviour. Specific capacitances of 55 F/g and 75 F/g were obtained for cells with ultrasonication method derived carbon (USC) and standard method derived carbon (SMC), respectively. Furthermore, hybrid supercapacitors with asymmetric configuration based on manganese oxide and CMK-3 at positive and negative electrodes, respectively were realized and investigated. The best cell exhibits better performance with a specific capacitance of 84 Fg^{-1}. The capacitor undergone 10,000 cycles under conditions of galvanostatic charging and discharge and floating at 1.6 V with a very long-term stability. Self-discharge measurements on the cell showed a very low voltage decay with time after charging the SC for 3 h at 1.6 V.

Acknowledgement

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Effect of polymer-based electrolyte on electrochemical properties of supercapacitor systems

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Keywords: porous carbons, hybrid supercapacitors, organic electrolyte, polymer additives, ionic liquids, physicochemical and electrochemical analysis

Supercapacitors are electrochemical energy storage devices that store and release energy by reversible adsorption and desorption of ions at the interfaces between electrode materials and electrolytes. In the last few years, the attention of scientists working in the field of supercapacitors has been focused mainly on the development of electrode structures based on carbon, metal oxide and conductive polymer. The right choice of electrolyte type is essential to achieve good electrochemical performance.

The most popular electrolytes for supercapacitors are aqueous and organic, with increasing use of ionic liquids (IL). They are served as solvents in a wide temperature range and possess high thermal, chemical and electrochemical stability, low volatility and non-flammability. Among the problems limiting their wider use is their poor compatibility with microporous carbon.

The development of polymer ionic liquids (PIL) is a modern approach with growing interest, as their significant advantage is the ability to create stable and highly efficient polymer electrolytes.

For the purposes of the present study, a polymeric ionic liquid based on pyrrolidine was produced. The anion exchange method was applied to a quaternized poly (diallyl methyl ammonium iodide) previously synthesized by the team. The obtained PIL was characterized by modern physicochemical methods and was used as an electrolyte in supercapacitor systems.

Two-electrode electrochemical cells based on activated carbon YP-50F a commercial product of the company "Kuraray Europe" or synthesized carbon xerogel, Ni-Mn phosphates as poly-composite electrodes and an electrolyte containing PIL, IL and $LiBF_4$ were assembled.

CV-curves, galvanostatic charging / discharging and long term tests were performed, with the help of which the capacitive characteristics and the stability of the developed supercapacitors were monitored. The correlation between polymer electrolyte composition and structure and morphology of studied electrode materials was discussed.

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Influence of the phenomenon of self-organization of liquid crystals on the performance of an electrochemical capacitor

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The main application of supercapacitors is fast energy storage - they are used wherever there is a need to use high power densities. However, their serious disadvantage is a relatively high self-discharge, if compared to e.g. lithium-ion batteries. So far, the main self-discharge processes have been identified as ohmic leakage, charge redistribution, and Faradaic reactions [1,2]. However, the solutions to limit the self-discharge of supercapacitors are limited.

It has been recently found that when EDLCs are charged, the electric field in the double-layer near the electrode surface might induce the alignment of the liquid crystal (LC) molecules, causing the fluid to become significantly viscous through the so-called electrorheological (ER) effect. As a result, the diffusion of ions and redox species in the electrolyte can be hampered and the rate of self-discharge can be reduced [3,4].

Herein, we present an approach to reduce self-discharge of a supercapacitor based on the electrorheological (ER) effect. For an optimized electrolyte composition with the addition of selected liquid crystals, the processes taking place at the electrode/electrolyte interface will be observed by measuring e.g., self-discharge, leakage current or system impedance. It is also planned to use spectroelectrochemical techniques such as scanning electrochemical microscopy (SECM) to measure the local electrochemical behavior of solid/liquid interfaces.

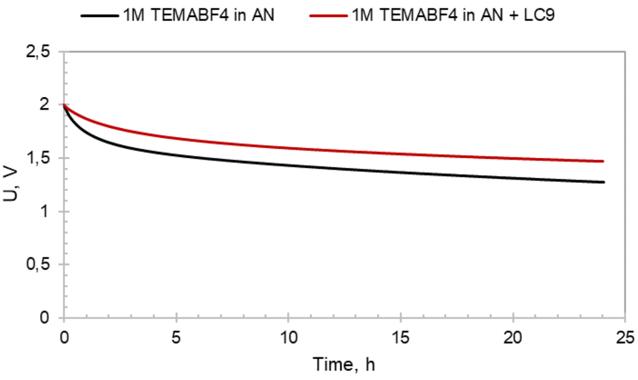

Figure 1: *Comparison of the self-discharge rate without and with the addition of liquid crystal.*

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Effect of Pluronic triblock copolymer as the electrolyte additive on the electrochemical capacitors performance

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Electrochemical capacitors (ECs) are promising electric energy storage devices. They are characterized by very high power rates and long cyclic lifetime. Nonetheless, their applications are limited because of significant self-discharge, causing voltage drop and loss of energy stored. In the case of ECs of purely capacitive behavior, charge redistribution, faradaic reactions and ohmic leakage are the main reasons for high self-discharge. Charge redistribution is related to the charged ions movement within the electrode and their desorption from its surface. Faradaic reactions occur because of the impurities in the electrolyte or electrode material or due to cell overcharging. Ohmic leakage is caused by internal ohmic leakage pathways between the electrodes [1]. Therefore, it is necessary to suppress self-discharge of ECs and, in consequence, expand the possible application of these devices. For this purpose, different approaches are adopted, i.e., modifications of ECs' components: electrode materials, by introducing functional groups, separators, by using ion-exchange membranes, and electrolytes, by introducing additives like surfactants or liquid crystals.
Herein, the use of Pluronic triblock copolymer as the electrolyte additive is proposed. They are self-assembly and low molar mass amphiphilic molecules. Their role is to reduce the surface tension of aqueous electrolyte and improve the electrode wettability. As already shown, such additives to the electrolytic solutions allow higher capacitance to be reached and self-discharge to be reduced [2]. Performance of the ECs operating in aqueous electrolytes – $LiNO_3$ and Li_2SO_4 solutions, with Pluronic addition of various concentrations will be tested. The concentration of surfactant should be carefully selected because when the critical micellar concentration is exceeded, the molecules aggregate and micelles are formed. Too large molecules can block the carbon electrode pores and also lower the surface activity of Pluronic. These undesired processes will adversely affect the cell performance, seen as capacitance decrease and worse charge propagation.

For the optimized electrolyte composition, the mechanism of charge storage and self-discharge processes will be determined by *operando* techniques, i.e., electrochemical dilatometry or electrochemical quartz crystal microbalance, where, respectively, the volumetric and mass changes of the electrode are recorded.

Acknowledgements

The authors acknowledge the financial support from the Łukasiewicz Center – agreement No 1/Ł-IMN/CŁ/2021

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Application of Water in Salt electrolytes for low environmental impact supercapacitors

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The market of electrochemical energy storage is growing exponentially and thus also the safety and environmental requirements. The devices require the substitution of flammable, volatile, and toxic electrolytes with less dangerous and sustainable ones. Aqueous electrolytes are a valuable alternative to solve most of the criticality of organic solvent-based electrolytes, but they come with the major drawback of a reduced potential stability window and thus a lower potential. Water in Salt Electrolyte (WiSE), given the high salt to water content, kinetically hinder the water splitting reaction spreading the maximum cell voltage over 2 V. For these reasons, these electrolytes are arising as a greener and safer alternative to organic ones, thanks to their higher safety, low cost, wide electrochemical stability, and high ionic conductivity [1]. Among the WiSE electrolytes, superconcentrated solutions of acetates have been extensively studied as novel aqueous electrolytes for lithium-ion batteries and supercapacitors [2,3].
Here, we report a comprehensive chemical-physical study of circumneutral WiSE based on acetate salts with focus on the effect of pH, density, viscosity, conductivity, and the ESW evaluated on different current collectors and high surface area carbons. WiSe are here investigated for application in electrochemical energy storage systems, such as electrical double layer supercapacitos.

Acknowledgments
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[4]

Glyoxylic acetals-based electrolytes for high power applications

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1,1,2,2-tetramethoxyethane and 1,1,2,2-tetraethoxyethaneglyoxal based solvents (TMG) and (TEG) have been recently proposed as alternative to conventional electrolytes due to their safety and high stability at higher temperatures with low toxicity, low flammability, high chemical, and electrochemical stability [1]. It has been shown that they can be successfully utilized as electrolytes in lithium-ion [2] and potassium-ion batteries [3] (LIB and PIB, respectively) and electrochemical double layer (EDCLs) [1] . So far, the use of glyoxal-based electrolytes in combination with pseudocapacitive materials such as metal oxide and MXenes, has not been considered. In this work, we therefore consider the use of glyoxal-based electrolytes, consisting of mixtures of TEG, TMG and various ether solvents, in combination with these interesting materials for high power devices. The chemical-physical properties of these electrolytes will be reported and their impact of the electrochemical performance of pseudocapacitive materials will be considered in detail.

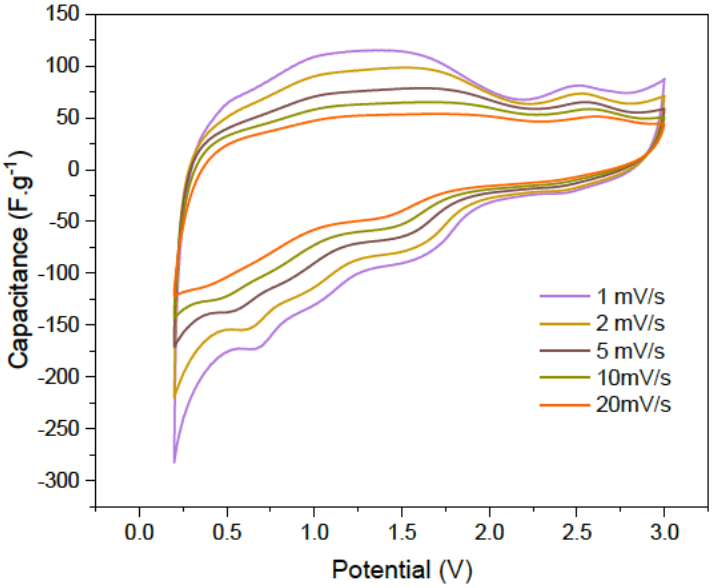

Figure 1: *CV with different scan rates of Molten Salt MXene with 1M LITFSI in Dioxolane: tetraethoxyethane (DOL: TEG, 1:1Vol%).*

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Sustainable solvents for electrical double layer capacitors

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The realization of high performance and sustainable EDLCs is nowadays considered of fundamental importance for this technology. Along with this goal, there have been exploration, investigations and utilization of electrode materials as well as binders for EDLCs that are originated from renewable feedstocks. Despite of that, significantly less work has been carried out towards the development of sustainable electrolytes in EDLCs [1].

The organic-based electrolytes in commercial EDLCs are commonly made up of tetraethylammonium tetrafluoroborate (Et_4NBF_4) dissolved in acetonitrile (ACN) or propylene carbonate (PC). However, they are obtained from non-renewable resources, which increases the reliance on fossil feedstocks [1]. From the economic point of view, despite the industrial processes for the synthesis of these dipolar solvents are well- established, the steps required to get them as dry grade lead to extra efforts and high costs. Besides, the non- sustainable solvents are less environmentally friendly. The issues related to flammability and toxicity are always concerning, and thus, extra precautions are required during the handling [2].

In this work, we report an investigation about the use of the bio-based solvent gamma-valerolactone (GVL) as electrolyte component for EDLCs. GVL is easily accessible, biodegradable and has a low eco-toxicological profile. It can be synthesized from biomasses, such as sugars, through simple chemical pathway, resulting in a high yield [3]. We showed that the use of an electrolyte containing 0.6 M Et_4NBF_4 in GVL makes possible the realization of EDLCs operating at 2.7 V, and displaying high capacitance, high capacitance retention and high stability during float test (**Figure 1**). Taking these results into account, bio-based GVL can be considered as a promising candidate for the realization of sustainable electrolytes for high performance EDLCs.

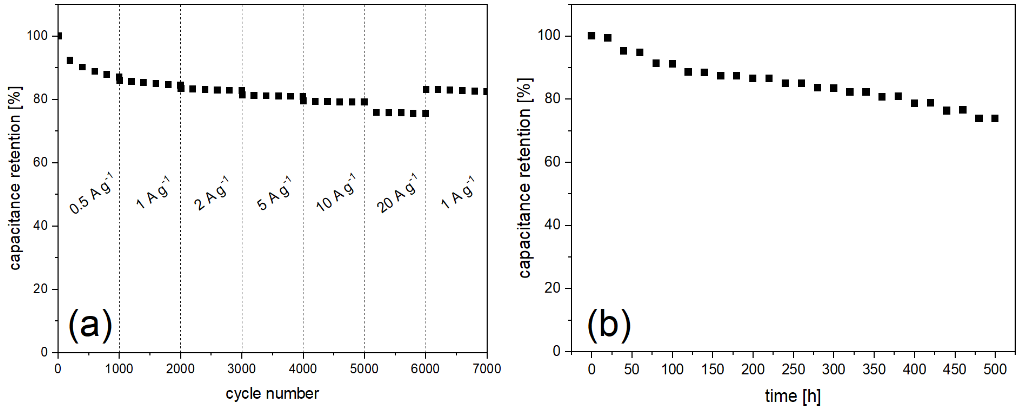

Figure 1: *Capacitance retention achieved by the asymmetrical EDLCs using 0.6 M Et_4NBF_4 in GVL investigated through (a) galvanostatic charge-discharge using cell voltage of 2.7 V over 0.5 to 20 A g^{-1} for 7000 cycles; (b) voltage hold of 20 h at 2.7 V for a total 500 h.*

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Physico-chemical investigation on the use of protic ionic liquids in supercapacitors: a joint experimental-theoretical study

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Research on advanced electrolytes that can be employed in large-scale energy storage units mainly focuses on safe and reliable materials to be proposed as viable alternatives to conventional organic solvents. Room Temperature Ionic liquids (RT-ILs) are low-melting salts that appear as suitable candidates thanks to high thermal stability, low flammability, and low volatility [1]. When the cation chemical structure displays one (or more) available proton(s), the resulting ILs are usually referred as Protic Ionic Liquids (PILs) [2]. Besides the claimed lower cost and the facile one-step synthetic path, PILs exhibit different electrochemical features compared to the aprotic since transport properties can benefit from the water-like hydrogen bonding network [3]. However, their employment as efficient electrolytes still relies on the understanding of the subtle structure- properties relationship. Our aim is to investigate to what extent the main cation-anion interactions can affect the physico-chemical as well as the electrochemical properties of interest for energy storage applications. The 1-butyl pyrrolidinium tetrafluoroborate (PyrH4BF4) has been synthesized and characterized in view of developing novel water-in-salt systems for supercapacitor applications. The impact of H2O amount on the overall electrolyte performances represents a key issue that should be assessed to develop less viscous PIL- based electrolytes with improved ion mobility. We also address the optimization of quasi-solid electrolyte formulations based on cross-linked polymeric matrixes and PILs, *e.g.*, the 1-butyl pyrrolidinium bis(trifluoromethanesulfonyl)imide (PyrH4TFSI), with potential promising applications in lithium and post- lithium batteries [5,6]. The foreseen integration of experimental outcomes with computational-assisted analysis can unveil the role of such complex interactions at the molecular level and lead to rational design strategies towards efficient electrolytes for high-performing energy storage devices.

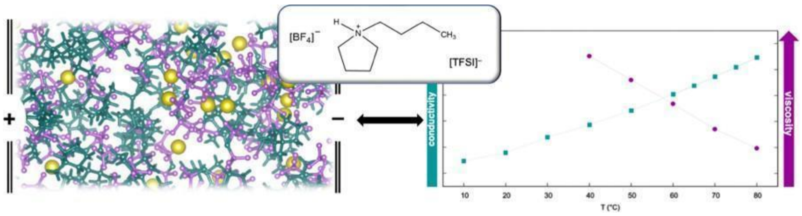

Figure 1: *Our theoretical-experimental approach to investigate transport properties in PIL-based electrolytes*

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High Power Hybrid System based on poly(3-vinyl-*N*-methylphenothiazine)

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The rising demand for environmentally friendly energy storage is calling for the development of green and sustainable devices, suited for different applications.[1] The organic redox polymer, poly(3-vinyl-*N*-methylphenothiazine) (PVMPT), and its crosslinked form X-PVMPT are considered a promising cathodic material for the development of a “green battery”.[2][3] Combining this sustainable cathode material with an activated carbon (AC) material, could give rise to a high power system, that cannot only be attained at a low cost, and good safety but also by being environmentally benign. In this work, we therefore investigated the use of PVMPT and X-PVMPT as high-power devices. First, the influence of the electrolytes capacity and capacity retention have been analyzed in a half-cell system, utilizing a mixture of tetraethoxy glyoxal (TEG) and dimethyl carbonate (DMC), both possess low toxicity and cost.[4] As a salt, the lithium bis(trifluoromethane)sulfonimide (LiTFSI) and lithium bis(fluorosulfonyl) imide (LiFSI) were chosen due to their good solubility in the solvents. The half-cell showed a redox potential at 3.5 V vs Li$^+$/Li in both PVMPT and X-PVMPT. As shown in Figure 1, when PVMPT and X-PVMPT are utilized in 1M LiTFSI in TEG/DMC, the electrodes are displaying good capacity retention at 0.5C. Furthermore, the systems demonstrated excellent rate capability and cycling stability with a specific capacity of 112 mAh g^{-1}.[2] After these tests, the X-PVMPT was combined with a negative electrode based on AC, and the electrochemical performance of this hybrid-ion capacitor has been investigated in detail. The results of these studies suggest that PVMPT is an interesting material not only for batteries, but also for innovative and safe high-power devices.

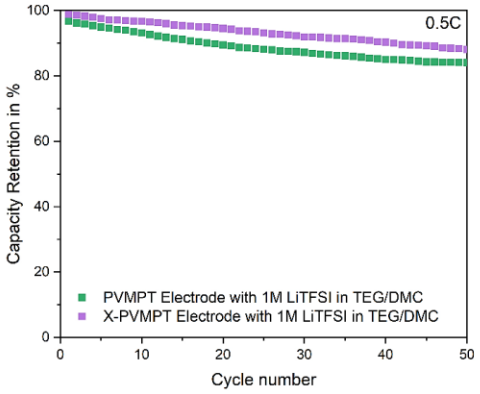

Figure 1: *Capacity Retention of PVMPT and X-PVMPT electrodes in 1M LiTFSI in TEG/DMC during test carried out at 0.5C.*

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TiO_2 nanotubes-based electrodes for hybrid lithium-ion capacitor and for desalination purposes

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Titanium dioxide (TiO_2) has been widely investigated in the field of material sciences in light of its several interesting properties that make him a suitable candidate for many different applications. Among the many possible nanostructures, self-organizing nanotubes grown by electrochemical anodic oxidation have been deeply studied for applications such as photovoltaics, batteries and supercapacitors. The tuneability of both morphology and properties while modifying anodization parameters make them indeed valuable electrodes for both the energy and environmental fields. [1, 2]

Titania-based electrodes, particularly TiO_2 and lithium titanate ($Li_4Ti_5O_{12}$), have been widely studied for batteries, supercapacitors and hybrid devices due to their good cyclability and stability. Lithium-ion capacitors are part of the hybrid ion capacitors (HIC) which try to bridge the gap between supercapacitors (displaying high cyclability and high specific powers) and batteries (displaying high energies). HIC generally exploit one battery-like and one capacitor-like electrodes, in the case of lithium ion capacitors the battery-like electrode will often be TiO_2-based. Furthermore, pre-lithiation has been widely recognized as a crucial step to build efficient devices to counterbalance the ion loss during the solid electrolyte interface formation. [3]

In this work we report a comparison between the behavior of two different TiO_2 nanotubes-based electrodes in hybrid lithium ion capacitor devices. The first electrode is composed of anodically grown anatase nanotubes, partially pre-lithiated by galvanostatic means. The anatase nanotubes were then assembled in a hybrid device with an active carbon-based cathode. The second electrode, instead, underwent a hydrothermal conversion into a mixed lithium titanium oxide after being anodically grown following the procedure reported elsewhere. [4] It was then also subjected to a further galvanostatic pre-lithiation and used in a hybrid device with the same kind of carbon-based cathode. These electrode show interesting characteristics and could be also considered as viable candidates for desalination purposes and raw material recovery from unconventional sources.

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Highly-efficient hybrid nanostructure of rGO-TiO_2 as cathode electrode in sodium based aqueous electrolyte

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Abstract

Hybrid graphene metal oxide nanostructures are used for energy storage applications [1][2]. The hybrid nanostructure of rGO-TiO2 is synthesized by growing nanosheets of rGO in the porous structure of TiO2 by a simple multi-step hydrothermal method fig.1. The structural characterization, including XRD, SEM, and Raman spectroscopy verified the hybrid nanostructure of rGO-TiO2. The electrochemical measurement of rGO-TiO2 was performed by a standard three-electrode cell using Ag/AgCl and Pt rod as the reference and counter electrode respectively. The novelty of this work is that in contrast to the other reports [3], the rGO- TiO2 hybrid nanostructure act as a cathode electrode in Na-based aqueous electrolyte, operating in a wide potential window that can be used in principle in an asymmetric supercapacitor configuration. To conduct the electrochemical measurement, the slurry solution of rGO-TiO2 was modified with the addition of binder material to form a high yield and smooth deposition on the glassy carbon. The electrochemical charge storage properties of rGO-TiO2 hybrid nanostructure were examined through cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and constant current charge/discharge (CCCD). The results showed high coulombic efficiency values of more than 94% within the cathodic potential window. The material rated 17.4 F g^{-1} and 27.0 mF cm^{-2} at 0.6 V cathodic polarization.

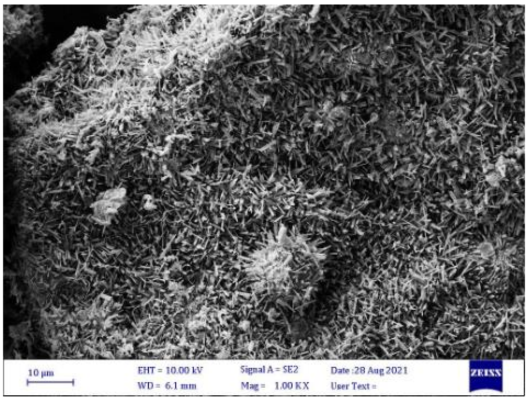

Figure 1: *SEM of hybrid nanostructure of rGO-TiO_2.*

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Mesoporous carbon with high load of Co_3O_4 nanoparticles and their performance in supercapacitors

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The great advantage for supercapacitors relies on their high-power density and fast charging-discharging performance. Nevertheless, their energy density still needs to be enhanced. The electrode-material is one of the key components in a supercapacitor playing a crucial role in storing the energy. Two categories are mostly reported, i.e., carbon materials operating via an electrochemical double layer (EDL), and pseudo-capacitive materials such as metal oxides operating by redox reactions. Among the different metal oxides, cobalt oxide (Co_3O_4) has been investigated in different forms, yet limited works have studied the effect of small particle size (< 10 nm). The combination of cobalt oxide and carbon is a promising approach to benefit from both materials advantages. In this context, the purpose of this work is to obtain nano-scaled Co_3O_4 by confinement in a mesoporous carbon matrix.[1] The preparation relies in the co-assembly of green and eco-friendly carbon precursors with a cobalt precursor by an evaporation induced self-assembly approach. Then the formed polymer/metal salt assembly is pyrolyzed under an inert atmosphere to attain C/Co composites, then oxidized under air to achieve the C/Co_3O_4 materials, with high Co_3O_4 content (43-59%, based on TGA studies). The impact of pyrolysis and oxidation temperature was investigated and several analyses were conducted to assess the modification of the material structure, surface chemistry and particle size. Carbon/Co_3O_4 composites were showed very small and well dispersed particles (2 to 7 nm) (Figure, inset). An increase in the particles size was noticed with the increase of the temperature (Figure, left) as well in the porosity and electronic conductivity. The pyrolysis and oxidation temperature had a crucial impact on the electrochemical performance. Galvanostatic cycling with potential limitation was used for capacitance and rate capability calculations (Figure, right). The materials treated at low temperatures showed a low performance with a quick drop of the capacitance due to poor conductivity. In contrast, the material treated at the highest temperature (800°C) showed a quick drop of capacitance as well due to particle aggregation. Whereas, the material treated at intermediate temperature, 750°C, showed the best behavior with a capacitance of 54 F g^{-1} at 0.1 A g^{-1} and a rate handling of 48.7% at 10 A g^{-1}. Therefore, the best results are obtained by combining simultaneously a series of properties.

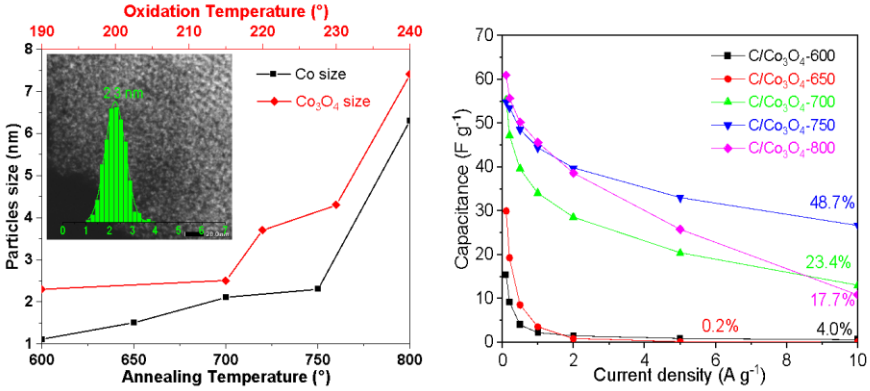

Figure: *(left) Evolution of particle size based on STEM analyses of C/Co composites as a function of pyrolysis temperature and of C/Co_3O_4 as a function of oxidation temperature, (inset) STEM picture with particle size distribution of C/Co_3O_4-1 treated at 600°C, (right) Capacitance vs current density for the different C/Co_3O_4 materials. The percent value shows the capacitance retention at 10 A g^{-1}.*

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Redox-enhanced Vertically Aligned Carbon Nanotubes as a Novel Electrode Material for Microcapacitors

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The rapid development of on-chip and miniaturized energy storage devices have attracted the considerable attention for further development of microcapacitor (MCs) technology. Nowadays, the research is mainly focused on the MCs energy density improvement via redox activity introduction which operates stable over many charging/discharging cycles. Carbon nanotubes (CNTs) are promising electrodes for MCs due to their tunable properties, higher conductivity than activated carbons and thus, faster charging/discharging rates for improved power densities of obtained devices [1].

In these studies, vertically aligned CNTs (VACNTs) were grown directly on current collectors, defined on Si wafers, using catalytic chemical vapor deposition (CVD) method at high temperatures [2]. The microfabrication enables us to control the length, diameter and density of CNT-based nanostructured electrodes. VACNTs were adapted as on-chip microcapacitors and electrochemically characterized in various electrolytes (organic and aqueous medium). The long-term performance of CNTs-based systems was compared using *galvanostatic cycling* and *floating* protocols according to the ageing criteria (IEC 62391-1). The CNTs surface was treated by oxygen-plasma in order to introduce oxygen functional groups to improve the wettability of electrode in aqueous electrolyte. The impact of oxygen content was studied taking into account the cycle-life and interaction with different redox active species in MCs device. An improved system was developed optimizing the tradeoff between specific capacitance and MCs lifetime.

In order to significantly improve the energy output, nanostructured MCs based on CNTs were enhanced with 2I$^-$/I2 species due to stable and reversible performance of redox reaction as well as an exceptional behavior of carbon/iodide interface. Therefore, iodide species were used in electrolyte but also confined in CNTs porosity. For this reason, VACNTs are ideal electrode materials to be combined with redox active layers due to their mesoporous structures. As shown in Figure 1C, the recorded current density for on-chip MC increased ca. 2.5-fold with 1M KI when compared to typically capacitive type electrolyte (1M Na2SO4). The effect of the redox activity placement (electrolyte and/or electrode) will be in-depth presented taking into account MCs long-term performance and physico-chemical characteristics defined via post-mortem approach. These studies demonstrate that the combination of the highly conductive and dense VACNT with redox active materials like iodides can provide a significant capacitance improvement and thus open a new chapter for redox-enhanced MC technologies.

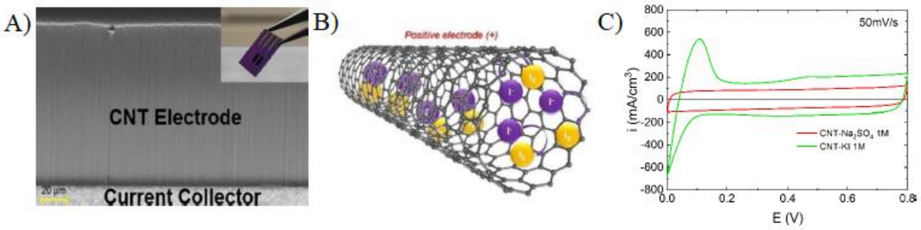

Figure 1: *A) SEM of VACNT inset: on-chip MC design; B) VACNT with $2I^-/I_2$ species; C) cyclic voltammograms (50 mV/s) of VACNT with 1M Na_2SO_4 and 1M KI electrolytes.*

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Electrochemical properties of $TiO_2NT/MoS_2/PANI$ composite electrode for supercapacitors

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Titanium dioxide nanotubes are one of the promising electrode materials, due to their high surface area, wide potential window, good stability and open-ended nanotubular structure provides direct charge transport pathways. The main drawbacks of TiO_2 nanotubes are poor electrochemical activity and therefore low capacitance [1]. A number of options have been considered to solve this problem i.a. deposition of active materials such as metal oxides, carbon based materials or conducting polymers [2].

In this work, titanium dioxide nanotubes were obtained using anodization. Molybdenum sulphide was deposited via electrodeposition using ammonium tetrathiomolybdate as a precursor. The $(NH_4)_2MoS_4$ was used in electrodeposition on TiO_2 nanotubes for the first time. The final stage was electropolymerization of polyaniline. Electrochemical measurements of the prepared composite were investigated by cyclic voltammetry (CV) and chronopotentiometry (CP). Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and Raman technique was also used to characterize topography and molecular structure of the pristine and modified TiO_2 nanotubes.

$TiO_2NT/MoS_2/PANI$ electrode exhibits good capacitive properties, which was confirmed by the results obtained with cyclic voltammetry (Figure 1). The composite electrode delivers an areal capacitance of 587.18 $mFcm^{-2}$, which is much higher than capacitance of 2,4 $mFcm^{-2}$ for pristine TiO_2 [3]. Specific capacitance of the obtained electrode reaches 436.19 Fg^{-1} at a discharge rate of 5 Ag^{-1} in 1M H_2SO4 electrolyte.

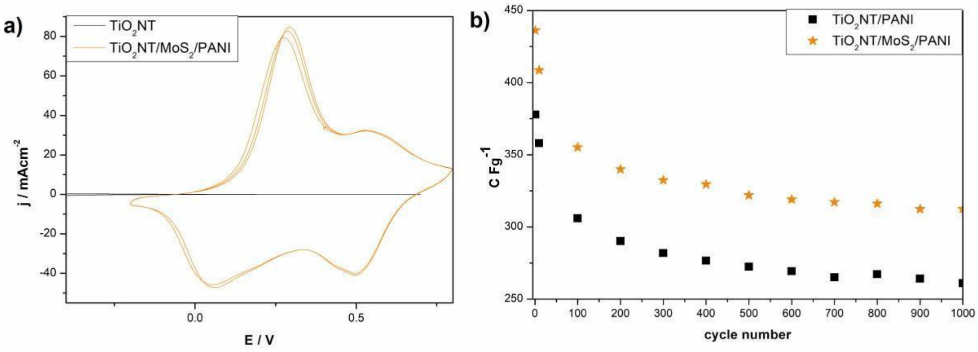

Figure 1 *a) Cyclic voltammetry curve of $TiO_2NT/MoS_2/PANI$ compared to TiO_2NT; b) capacity retention after 1000 cycles of $TiO_2NT/PANI$ and $TiO_2NT/MoS_2/PANI$ electrode materials*

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The phenomenon of the increasing capacitance induced by 1T/2H-MoS2 surface modification with Pt particles and its influence on composition and energy storage mechanism

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In this work, a complex analysis of the Pt-surface modification during multiple charging and discharging cycles of the electrode material prepared via anodization of molybdenum plate, followed by hydrothermal process in thiourea aqueous solution with the energy storage mechanism study, is presented. The influence of both platinum-surface modification and using platinum as a counter electrode on charge storage performance and charge storage mechanism is investigated, as well. It was shown that the prolonged process of modification of the electrode surface with platinum enhanced the phenomenon of the capacitance increase. After 60 000 cycles the specific capacitance of the electrode material modified with Pt particles (see Figure 1b) increased to over 1 F cm^{-2}, whereas symmetric two electrode system reached capacitance of 140 mF cm^{-2} and in each case the coulombic efficiency was above 97% during all the cycles. Furthermore, this study reveals the changes taking place in composition of 1T/2H-MoS_2 thin layer, presenting the transition to mixed molybdenum oxides. Together with the transition from sulfides to oxides and introducing oxygen vacancies, the contribution of pseudocapacitive energy storage mechanism is enhanced. It is also emphasized that when Pt counter electrode is used in the study of energy storage materials, careful consideration should be given to the investigation due to the dissolution-deposition phenomenon of platinum.

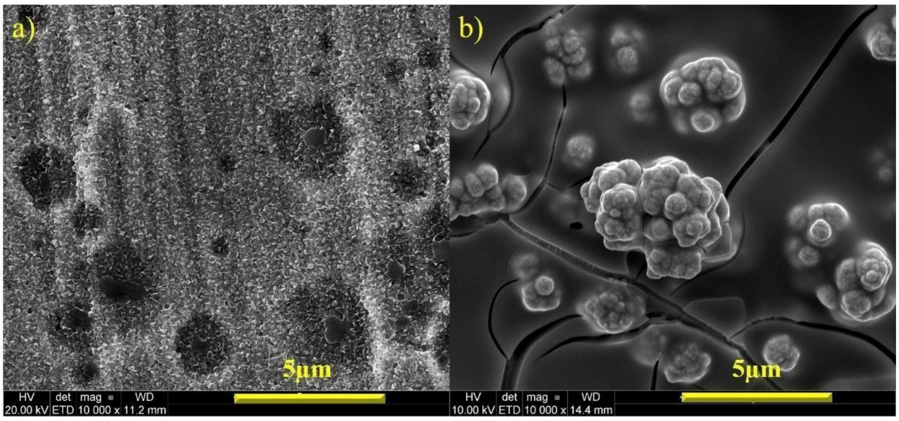

Figure 1: *SEM images of 1T/2H-MoS_2 electrode material a) before and b) after 15 000 galvanostatic charge-discharge cycles performed in 1M H_2SO_4 in three-electrode configuration with Pt as a counter electrode.*

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Electrode Design for MnO_2-Based Aqueous Electrochemical Capacitors:

Influence of Porosity and Mass Loading

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In the field of electrochemical capacitors, many studies are dedicated to new materials (eg. oxides, nitrides) but only few papers are focused on electrode fabrication. However, from the active material to the electrodes elaboration, many parameters can be optimized in order to improve performances. Moreover, most of the studies related to the fabrication of large scale devices are related to carbon-based electrodes.[1]

In this study, we propose to analyze two-electrode devices with symmetric MnO_2-based electrodes in an aqueous electrolyte. [2] More specifically, the influence of the mass loading combined with another important parameter which is the porosity have been investigated. Three different mass loadings have been studied and electrodes were calendered to reach different porosity ranging from ~40% to ~75%. Indeed, calendering enables to improve the compactness of the electrodes (and subsequently to decrease the porosity). The first main finding is that electrochemical capacitors require a certain level of porosity to optimize ionic conductivity and electronic conductivity. [3] The importance of a minimum mass loading is also highlighted while very few groups worldwide have understood that this is a main issue to provide meaningful gravimetric values in terms of performance [4]. Electrochemical tests were performed and demonstrated that the porosity is a key parameter that drastically influences the wettability, performances and response time, especially when high mass loading was used.

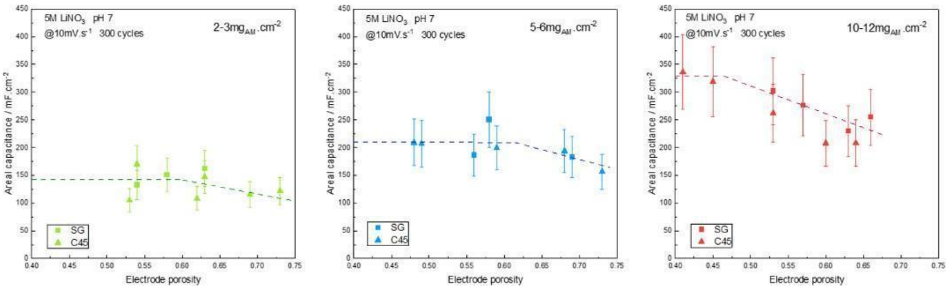

Figure 1: *Evolution of the areal capacitance in function of the electrode's porosity for three different mass loadings after 300 cycles @10mV/s, Electrochemical tests are performed with a cell potential of [0;1]V for MnO_2-MnO_2 devices with $LiNO_3$ 5M, pH 7 (adapted from ref [2])*

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Influence of Crystallinity on the Electrochemical Behavior of Sodium Birnessite Electrodes

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Sodium-birnessite, the layered hydrated Mn oxide, has received wide attention as a material for energy storage in aqueous electrolytes. Various synthesis routes differing by method and precursors, have been used to produce this material with different morphology, degree of crystallinity and amount of pre-intercalated Na and H2O. This structure/composition variability is reflected by variations in the response to potential cycling, leading ultimately to different electrochemical characteristics.[1] Literature studies focus on the role of crystal water to induce the transformation of manganese oxides into birnessite,[2,3] and emphasize its effect on charge storage [4]. On the other hand, there are no systematic electrochemical studies of the structural evolution of Na-birnessite in sodium based aqueous electrolytes.

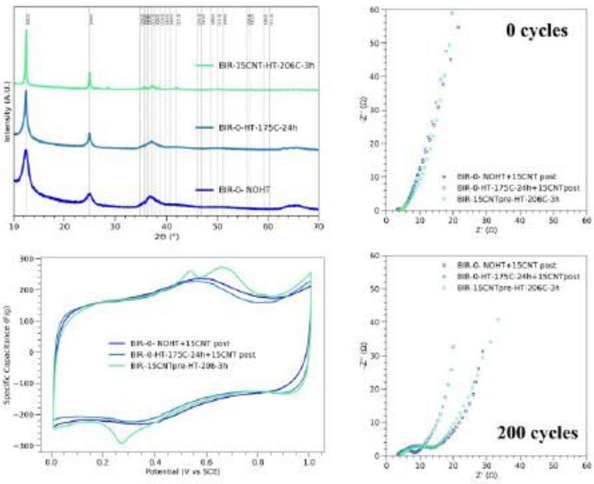

Figure 1: *a) XRD, b) 1 mV/s CVs, and EIS spectra at 0 cycles (c) and 200 cycles (d).*

Three different birnessite were produced. The first one is a poorly crystalline birnessite obtained through chemical precipitation in a NaOH and Mn(NO3)2 solution. The second one is obtained by hydrothermally treating the first sample into NaOH at 175 °C for 24 h. The third one is obtained by a hydrothermal synthesis reducing MnO2 in NaOH solution for 3h at 206 °C in presence of purified MWCNTs. XRD, EDS and TGA analysis show an increase of pre-intercalated water and sodium after the hydrothermal treatment. Electrode pastes with the addition of MWCNT (with final composition of 10 wt.% PTFE, 15 wt.% MWCNTs and 75 wt.% of birnessite) were used as WE in 1.0 M Na2SO4 electrolyte, with the active mass loading of 3.6 mg cm^{-2} and the thickness of about 50 µm. SPECS and EIS were performed over the potential window from 0 to 1 VSCE. A preliminary study shows that the three materials have slightly different electrochemical response and that cycling influences the equivalent circuit model parameters. The following work addresses the structural evolution of birnessite with cycling and its effects on electrode behavior, combining EIS, CV and step potential spectroscopy for a detailed study of the charge storage processes, in conjunction with structural analysis to evaluate changes in the crystal structure of the material. A specific objective of this work is to clarify whether the crystallinity induced by hydrothermal treatment could be beneficial to the charge storage performance of this material.

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Redox response at electrode/electrolyte interface in carbon/TMDs composites

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Electrochemical capacitors (ECs) are energy storage devices with superior power-rate response. Principal of ECs operation is based on reversible adsorption of ions at the electrode/electrolyte interface. Thus, the higher the specific surface area (SSA) the higher reachable capacitance of the system. Ideally, the ECs electrode material should possess well-developed SSA and uniform distribution of pores. Carbons suit well to this characteristics and are able to provide high values of capacitance ca. 100 F g^{-1} and high power rate response. Nonetheless, ECs based on carbons are not able to provide competitive values of specific energy density in comparison to metal-ion batteries. Therefore, the development of electrodes is directed toward synthesis of novel highly capacitive composite materials, e.g., transition metal dichalcogenides (TMDs). Due to their two-dimensional (2D) character, versatile physicochemical properties as well as large possible combinations, they have gained significant attention as an electrode materials for ECs. TMDs consist of one layer of metal atoms (e.g., Mo, Re, V, etc.) sandwiched between two layers of chalcogen atoms (i.e., S, Se, and Te). Typical representative of TMDs family, molybdenum disulphide (MoS_2), has been already proven to exhibit very high capacitance of 150 F g^{-1} when paired with carbon nanotubes. Although, the limiting factor of MoS_2 is a rapid hydrogen evolution during voltage extension which excludes this material for its further use due to narrow voltage window of around 0.8V [1]. Therefore, other TMDs materials, such as vanadium disulphide (VS_2) are being tested for its practical application as an ECs electrode materials in the form of carbon composite. Beside standard adsorption of ions during charging/discharging, VS_2 composite exhibits redox reaction related to the rich number of oxidation states of vanadium. Due to this fact, composites based on VS_2 are able to reach greater capacitance than other TMDs electrode based materials [2]. Additional aspect is the insertion/deinsertion of ions within the layered structure of VS_2 which could be accompanying during charging/discharging showing a battery-like behaviour. Despite designing the electrode material, it is also possible to add redox species to the electrolyte solution. Iodides are already known to significantly enhance performance of ECs due to exhibition of redox reactions [3]. In this study, several VS_2 composites were prepared with different carbon materials such as carbon nanotubes or graphene nanoplatelets by L-Cysteine assisted hydrothermal reaction. Additionally, pristine VS_2 sample was also prepared for the comparison. Various structural and textural properties were evaluated by CO_2 and N_2 sorption, X-Ray diffraction, Raman spectroscopy, and scanning electron microscopy. The electrochemical performance of the prepared EC cells was evaluated by cyclic voltammetry, galvanostatic charge/discharge, and impedance spectroscopy. Two- and three-electrode cells were employed for testing prepared composites. Cells were assembled with neutral (sulphates) and redox active (iodides) electrolytes.

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Ageing of carbon electrodes in li-ion hybrid capacitors

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The lifespan of the electrochemical capacitor is a crucial parameter discussed in the literature determining the usability of the proposed new electrode material or electrolyte composition. According to the international standard (IEC 62391-1) [1], a system failure is reported when the initial capacitance drops down below 80% of its initial value. However, in the scientific publications, only 10000 charge/discharge is required to evaluate the performance of the system, while the industry demands more than 1000000 cycles to accept the result. The experiments performed by other researchers show that the major cause of electrochemical capacitors failure either in the organic or aqueous medium can be related to the degradation of the positive electrode. In both cases, the measured BET surface area of the positive electrode after ageing was significantly affected and limited.

Lithium-ion Capacitors (LiC) are characterised by high energy and power aimed at filling the gap between Li-ion Battery (LiB) and electrochemical capacitors. As for the ageing of LiC, the considered patterns are similar to LiB with the main mechanism of passivation layer growth at the negative electrode. However, there is limited information about the ageing of the carbon electrodes in such systems, with pore-clogging being the only mechanism explored in that matter.

In our report, a detailed examination of the degradation path of carbon electrodes in the LiC is presented and discussed. In this work, carbon electrodes were aged at elevated voltages vs. metallic lithium, followed by post-mortem analysis. The research was performed with the application of the binderless Kynol® 507-20 activated carbon cloth as the working electrode and a typical PL30 electrolyte designed for Li-ion batteries. The combined information gathered from elemental analysis, Raman spectroscopy, XPS, and porosimetry aims to elucidate the degradation path and molecular changes of the electrodes which lead to energy fading and system failure.

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Exploring an alternative cell configuration for Sodium-ion capacitors using $Na_3(VO)_2(PO_4)_2F$ and biomass derived carbon

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In modern society, there is a high demand and concern regarding energy storage devices. Therefore, we all need to empower a further technology development while considering efficiency, cost, sustainability and safety as its main pillars. In this context, battery and supercapacitor hybrid systems are a very interesting research topic, since they are focused on enabling applications on need of both high power and high energy densities.[1]

Sodium-ion capacitors (NICs) are considered promising next generation devices, because of the vast and extensive progress made in the technologies they are based on; more specifically, electrical double layer capacitors (EDLCs) and sodium-ion batteries (NIBs). To circumvent the kinetic mismatch of the active materials from each of the electrodes, in this work we propose a *ca.* 2 V system using $Na_3(VO)_2(PO_4)_2F$ as a high rate battery-type material for the positive electrode, and an olive pit-derived activated carbon (AC) as the capacitor-type negative electrode material. In this not so typical cell configuration the charge/discharge process is associated with the transfer of sodium cations between the two electrodes, an analogue to the ‘‘rocking chair’’ mechanism of SIBs. Owing to the similar OCV of both electrode materials and the high cut-off voltage of the negative AC electrode (> 1.0 V *vs.* Na^+/Na), the operating voltage limits the widespread utilization of these cell configurations. Still, due to the difficulty to build a safe dual-carbon Na-ion capacitor, and the inconvenience of a presodiation step, this approach offers a tangible possibility to cover the gap between NIBs and supercapacitors.[2] For the sake of comparison, this full-cell concept has been carried out both in sodium- and lithium-ion chemistries by simply modifying the electrolyte composition. Thus, electrode materials have been tested using $LiPF_6$ and $NaPF_6$ salts in organic carbonates separately, and in each case, the optimal electrode mass balance has been established.

In summary, this communication aims at demonstrating the potential of a Na-ion capacitor with a $Na_3(VO)_2(PO_4)_2F$//AC cell configuration, as a safe alternative to the current state-of-the-art NICs by providing both high power and energy densities as well as a high cyclability.

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Effect of the synthesis method on the physical, chemical, and electrochemical properties of the flexible iron nitride-carbon cloth electrode

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The depletion of fossil fuels, energy crisis as well as global warming are current environmental issues which require solution in the nearest possible future. At the first line of development of clean energy technologies are high performance energy storage devices, which are needed for next generation consumer electronics, biomedical devices, and hybrid electric vehicles [1]. Among them, asymmetric electrochemical capacitors, hybrid capacitors and supercapatteries are strongly investigated to meet up with the current performance expectations. As each of these devices is characterized by a negative and positive electrode (negatrode and positrode, alternatively) and an adequate electrolyte. Among various materials used for negative electrodes, iron compounds, including oxides and nitrides, are considered a reasonable choice due to their electrochemical performance, wide operating potential window, low cost, and natural abundance [2,3].

In this work, we investigated the influence of the preparation method of flexible electrode composed of carbon cloth decorated with iron nitride on negatrode electrochemical performance in aqueous electrolyte. The precursor for iron nitride was iron oxide deposited on the hydrophilic carbon cloth, either from hydrothermal synthesis or from the direct electrodeposition performed in a standard 3-electrode system at a constant potential of -1.4 V vs. Ag/AgCl using 0.02 M $FeCl_3$ solution as an electrolyte. Crystalline structure, morphology, and electrochemical performance investigations of flexible iron-based electrodes in an aqueous 6 M KOH electrolyte were performed.

Results indicated that iron nitride-carbon cloth electrodes exhibit battery-like behavior, presenting both visible peaks at the specified potential, as well as show a distinct plateau during galvanostatic charge/discharge measurements. Flexible electrodes with deposited iron nitride displayed much higher capacity retention under increasing current load compared to their respective iron oxide counterparts, which is related to the improved electrical conductivity of the nitrides. Moreover, both iron oxide and iron nitride from the electrodeposition method exhibits superior electrochemical performance compared with the Fe-based electrode from hydrothermal synthesis. The results obtained demonstrate the potential of flexible iron-based electrodes for the applications of hybrid capacitors or supercapatteries.

Acknowledgement

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Spray dry synthesis of capsule-like γ-$Li_{3.2}V_{0.8}Si_{0.2}O_4$/C nanocomposite for pseudocapacitive anode material

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Introduction

γ-phase Li3.2V0.8Si0.2O4 (LVSiO) has been attracting attention as a promising pseudocapacitive anode material with regards to its high energy density, with a theoretical capacity of 323 mAh g^{-1} (based on V^{5+}/V^{3+}) at reaction potential of 0.4-1.3 V *vs.* Li/Li^{+}[1]. Owing to the sufficient potential margin against the risk of lithium dendrite formation during charge, LVSiO can ensure safe operation, while maintaining high cell voltage. Moreover, the Li^{+} conductivity in the original β- Li3VO4 phase can be drastically improved by Si^{4+} substitution, from 10^{-12}-10^{-10} S cm^{-1} (β- Li3VO4) to 10^{-7}-10^{-5} S cm^{-1} (γ-LVSiO)[2], enabling ultrafast charge/discharge behaviors. However, the development of LVSiO anodes is still hampered by its poor electronic conductivity ($<10^{-10}$ S m^{-1})[1]. Conductive additives can be added but kill the energy density; thus, the amount should be reduced to minimal. In this study, we report about the synthesis of unique capsule-like composites nanocrystalline LVSiO with minimal amount of carbon additive by a scalable spray-drying method. The structure and the electrochemical performance of the material were further investigated and analyzed.

Experimental

LVSiO was prepared by a simple powder calcination process. Dispersion of the obtained LVSiO powder in 10-50 wt% of sucrose aqueous solution was spray-dried and then annealed under N2 flow. The morphology was observed by scanning electron microscopy (SEM), and the weight of carbon was estimated from thermogravimetry (TG). Electrochemical performances were measured using 2032-type coin cells assembled of LVSiO and Li metal electrodes with a 1.0 M solution of LiPF6 dissolved in a mixture of ethylene carbonate and diethyl carbonate (50:50 in volume ratio).

Results and Discussion

SEM observation clarified that LVSiO/C formed a spherical capsule structure (2-5 µm diameter) with an outer shell (200 nm thick) and inner uniform-sized particles (50 nm diameter). Primary nanoparticles were evenly coated with graphitic carbon and interconnected with amorphous carbon (Fig. 1). The amount of the two different types of carbons was quantified by TG measurements. Regardless of the sucrose dosage, the weight ratio of graphitic carbon was found to be almost constant (2-4wt%), while that of amorphous carbon increased with the sucrose precursor content. To investigate the formation mechanism of graphitic carbon, Li3.2P0.8Si0.2O4/C (LPSiO/C) was synthesized by substituting V^{5+} with P^{5+}. As a result of TG measurement, LPSiO showed an only weight loss peak of amorphous carbon, indicating the presence of V^{5+}, as a transition metal, promoted the formation of graphitic carbon on the limited surface area. The V^{5+}-derived dual carbon matrix facilitated high reversible capacity of 290 mAh g^{-1} at 0.1 A g^{-1}, and excellent rate performance of 199 mAh g^{-1} at 10 A g^{-1}, which was 69 % of that at 0.1 A g^{-1} without any conductive additives.

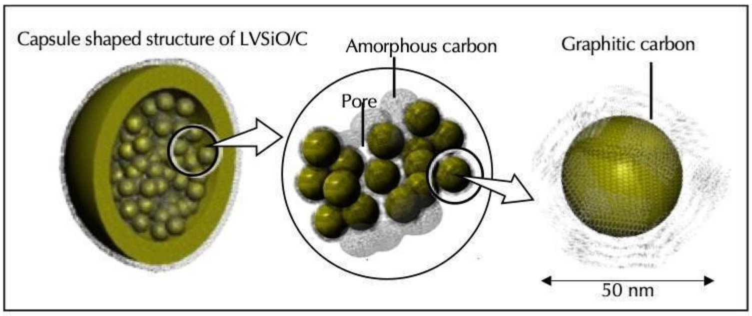

Fig. 1. Summarized illustrations of the morphology of LVSiO/C composite.

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Ultralong-Lifespan $Li_4Ti_5O_{12}$//Ti doped $Li_3V_2(PO_4)_3$ Full Cell by Significant Suppression of Vanadium Dissolution from LVP electrode

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1. Introduction

Lithium vanadium phosphate ($Li_3V_2(PO_4)_3$: LVP) is a promising candidate as a cathode material for next-generation energy storage device with high power and high energy density. However, full cells using LVP suffer significant capacity degradation with cycling caused by electrolyte decomposition on the anode due to vanadium dissolution from the LVP.1) This elution of vanadium from LVP is attributed to the high solubility of LVP in polar solvents. In this study, we report on the exceptional improvement of cycle characteristics of a full cell using LVP *via* Ti^{4+}-substitution in V^{3+} into LVP. We selected Ti^{4+} as a dopant because it has a higher electronegativity than V^{3+}(V^{3+}:1.545, Ti^{4+}:1.730)2). This approach transforms the ionic character of the V-O bond, caused by the inductive effect of the P-O unit, into a covalent character of the V-O bond, thus suppressing the dissolution of vanadium into polar solvents

2. Experimental

5%Ti^{4+}-doped LVP/multiwalled carbon nanotubes composite was prepared by the ultracentrifugation treatment[3]. The obtained precursor was first calcined at 300℃ for 3 h under air and then 800℃ for 30 min under N2 flow. Structure analysis was performed by XRD, SEM, TEM, and XAFS. Electrochemical measurements were performed with laminate-type LTO//LVP full cells. The electrolyte was a mixture of EC:DEC (1:1 vol.%) containing 1 M $LiPF_6$.

3. Results and Discussion

In 5% Ti^{4+}-doped LVP, ICP-MS showed a decrease in the amount of vanadium in the electrolyte, suggesting a decrease in the solubility of LVP in the electrolyte. TEM observation and XAFS measurement confirmed the formation of a few nanometer amorphous layer with high valence vanadium on the surface of Ti-doped LVP. In addition, increasing the electron density around the V-O bonds was confirmed by the calculation using the DV-Xa method (Figure 1). It is suggested that the increasing the covalent character of the V-O bond on the surface and inside of the crystal contributed to the suppression of vanadium dissolution.

The full cell using Ti^{4+}-doped LVP showed a significantly improved capacity retention rate of 90% after 10,000 cycles at a 10C rate (Figure 2). XPS measurement and SEM observation showed that the amount of deposition on the anode was reduced in the full cell after the cycle test. This suggests that the full-cell cycle performance was improved by suppressing the electrolyte decomposition on the anode due to the suppression of vanadium dissolution

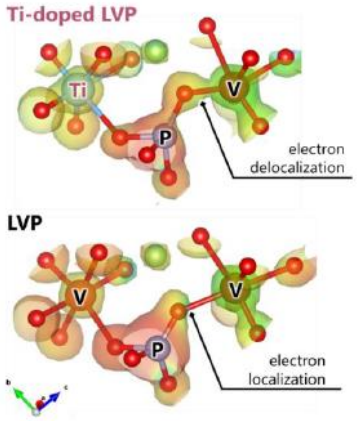

Figure 1: Computed electron density map of LVP and Ti-doped LVP.

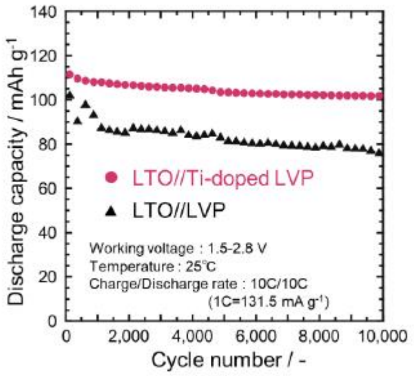

Figure 2: Cycle performance for LTO//LVP full cells

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Structural/Chemical Modification of Sodium Vanadium Phosphate for Ultrahigh Rate Sodium Ion Storage

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$Na_3V_2(PO_4)_3$ is one of the excellent cathode candidates of sodium ion system owing to its high theoretical specific capacity (117 mA h g^{-1}) and operating voltage (3.4 V vs. Na/Na^+)[1]. However, the inferior intrinsic electronic conductivity of NVP limits facile charge transfer, resulting in poor rate capability and long-term cycle stability[2]. In order to overcome these hurdles, studies are being conducted to improve electrical conductivity via forming a composite with a carbon material or doping/substitution of heteroatom. In this work, a composite with reduced graphene oxide (rGO) was fabricated to reduce particle size of NVP, organize a uniform 3D conductive network to minimize capacity loss, and greatly increase electrical conductivity. The composite, called 'BI-NVP', achieved excellent performance of a sodium ion storage and confirmed interfacial stability of NVP-rGO through various post-mortem analysis including HR-TEM and STEM-EELS.

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Dual Ion Hybrid Energy Storage based on Lanthanum Manganese Oxide Composites and MXenes

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The development and use of renewable energy is emerging due to indiscriminate development in industry and the use of non-renewable energy, and the dependence on energy storage devices due to the increase in the use of renewable energy is also increasing.

For the concept of an aqueous dual ion storage device, a cathode material for storing anions and an anode material for storing cations were introduced. LaMnO3 which is a perovskite oxide (ABO_3) structure for storing OH^- in the basic electrolyte, was introduced. It has the advantage of being rechargeable with a base storage material and having a fast reaction rate. The reaction activity is provided by increasing the oxygen voids in this material, which undergoes a reaction through the oxygen voids. However, the nanostructure $LaMnO_3$ also has a disadvantage of poor ionic conductivity. As a result, a complex of reduced $LaMnO_3$ (r-$LaMmO_3$) and Oxidized CNT (oCNT) was formed, and it was confirmed that the electrochemical performance was improved.

In this study, we design r-$LaMnO_3$/oCNT composite for anion storing materials, and reveal the reaction mechanism of $LaMnO_3$, which has not yet been accurately analyzed, through in situ analysis. In addition, the simultaneous storage system of OH^- and Na^+ was constructed for a large energy density of dual ion hybrid capacitor. Using these materials, a dual ion storage system was constructed using MXene as an anode for Na storage. Using 6M NaOH, MXene as a cathode has a range of -1.2V to -0.5V, r-$LaMnO_3$ / oCNT complex has a voltage range of -0.5V to 0,4V, so the energy storage device was designed with a total voltage range of 1.6V.

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Liquid-phase exfoliated hexagonal boron nitride/reduced oxide graphene hybrid electrodes for pseudocapacitive energy storage

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The two-dimensional (2D) hexagonal boron nitride (h-BN) has received tremendous interest due to its unique mechanical, thermal and electronic properties. However, the application of hexagonal boron nitride for energy storage devices has been restricted because of its low electrical conductivity. In this study, we synthesized 2D h-BN through liquid phase exfoliation and its hybrids with reduced oxide graphene (rGO). This h-BN/rGO hybrid showed a pair of distinct and reversible redox peaks in aqueous electrolyte along with high electrical conductivity. Moreover, the as-fabricated hybrid electrode delivered the specific capacity of 49.4 mAh/g.

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Vinyl Acetate/Ethylene as a prospective way out for fluorine free binders in supercapacitors

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Supercapacitors belong to an environmentally friendly energy storage technology and show a stable trend in an emerging market. However, binder material used in electrode materials often contains undesirable fluorine components. To meet growing ecological awareness and upcoming restrictions [1], we present the application of vinyl acetate/ethylene (VAE) modified carbon electrodes in aqueous supercapacitors.

First measurements were obtained by using standard carbon materials, commercial VAE-solutions and classical dispersion tools like a planetary mixer, an ultrasound sonifier and a three roll mill. The slurries have been applied into nickel foam or on top of different metal foils. Hereafter, the electrode material was assessed in a sandwich-type capacitor filled with KOH or Na_2SO_4. But in general, the applied materials can be used in other aqueous capacitors (and batteries), too.

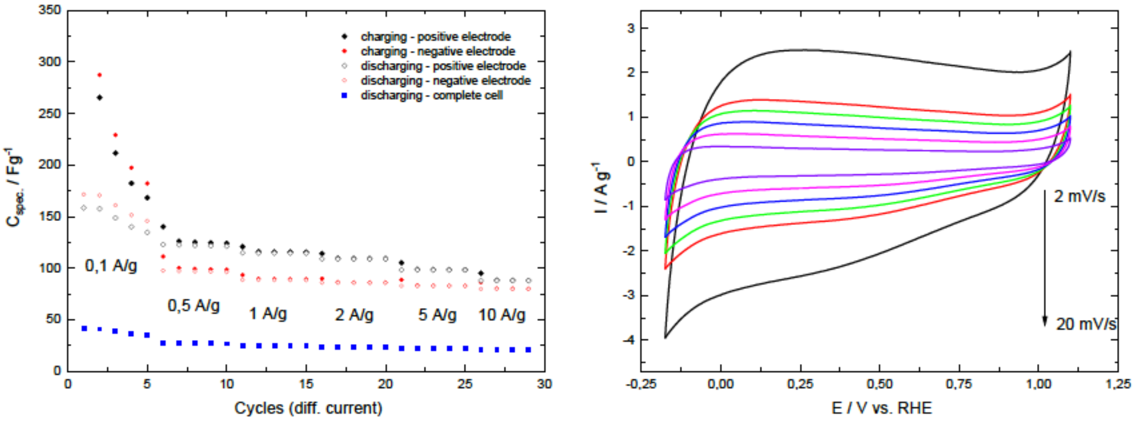

Figure 1: *Left) current dependent capacitance of a symmetric supercapacitor of Kuraray-YP80F/VAE-carbon primed Al-foil in 1 M Na_2SO_4. Right) Cyclic voltammograms of a Kuraray-YP80F/VAE-nickel foil electrode in aqueous 30 wt.% KOH – v: 20/10/8/6/4/2 mV/s.*

The obtained results showed a typical capacitance of 100 to 120 F/g tapped at the positive and negative electrode, respectively. However, the electrochemical performance (capacitance, energy and power density) depends obviously very much on the maximum cell potential, the charging current and cell/material properties. Overall, the first results seem to be promising and hinting into a future of fluorine free supercapacitor binders. Nevertheless, other influences need to be investigated thoroughly also, so that further research on this contribution would be of value and is in hand.

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Investigation of commercial supercapacitor materials for industrial application

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Our intention in supercapacitor research is to find materials and manufacturing methods being suitable for industrial and environmentally friendly applications. Therefore, we investigated commercially available carbon materials like graphenes and activated carbons (ACs) from different manufacturers. Electrochemical investigations showed different behavior for the two types of carbon materials investigated. The examined graphene material only showed an electrochemical stability window (ESW) of 0.6-0.8 V in KOH, whereas an ESW of 1.2 V was achieved with the AC material (Fig. 1). This behavior might be caused from different surface properties.

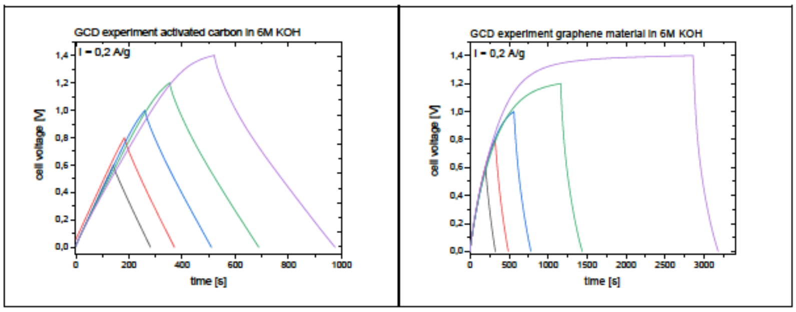

Figure 1: *Comparison of commercial activated carbon (left) material and commercial graphene (right) material*

BET measurements revealed that the graphene material and activated carbon material were completely different in their surface properties. The graphene material showed an unsatisfactory specific surface area of 762 m^2/g in contrast to the$_4$ activated carbon (1622 m^2/g). Moreover, both materials were different in their pore size distribution. The investigated activated carbon had a large proportion of micropores (< 2 nm), whereas the investigated graphene$_4$ showed$_3$barely m$_2$icropores$_3$ and pos$_4$sessed almost exclusively mesopores. These results confirmed the findings of electrochemical experiments. Thus, further commercial AC materials were investigated and it became apparent that there were also considerable differences in the specific surface area and electrochemical behavior of commercial ACs. In principle, a dependence on specific surface area and electrochemical behavior can be concluded, but the pore size distribution also plays an important role [1]. Besides the characterization of commercial ACs, our research also focuses on extending the ESW of aqueous electrolytes in order to generate higher specific energy densities. For these experiments, neutral electrolytes such as 1 M Na2SO [2] as well as "water-in-salt" (WIS) electrolytes were investigated. The desired WIS-electrolytes should be cheaper than the very expensive 21 m LiTFSI[3]. Therefore, the following electrolytes were used: 17 m NaClO [4]; 12 m NaNO [5], 8 m K CO [5] and 26 m KOAc[5]. Using 17 m NaClO , the best electrochemical results were obtained, so that an increase in energy density by a factor of four was achieved compared to the 6 M KOH electrolyte used initially. These results showed that the specific energy density could be increased with suitable and cheap commercially available materials, and would therefore be promising ideas for industrial applications.

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Brewers' Spent Grains derived activated carbons for high performance electrochemical capacitor

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The use of electrode materials realized from sustainable materials is of crucial importance for the development of advanced electrochemical capacitors. In this context, biomass can be certainly considered as a very appealing source. Among the various biomasses, brewers' spent grains (BSG) are of particular interest. BSG represent more than 80% of total waste generated in breweries[1] and with annual production of roughly 6.5 billion tons of wet BSG (2019 data[2]). When compared with other agro-industrial wastes, BSG represent a largely available, easy to process, as well as one of the cheapest lignocellulose precursors. The composition of BSG primarily composed of cellulose, hemicellulose, and lignin and additionally non-lignocellulose components such as starch, proteins, ash etc. are present, while the actual composition may change depending on factors such as harvesting time and processing. It is interesting to notice that despite this large availability, so far only one study has been dedicated to the use of brewers' spent grains as precursors of carbonaceous materials for energy storage device[3]. In this study we report about the realization of highly porous (~3600 $m^2 g^{-1}$) activated carbon (AC) synthesized by pyrolysis of BSG precursor in presence of KOH as activating agent. We showed that composite electrodes containing these AC display high capacitance (184 $F g^{-1}$) and high capacitance retention in organic electrolyte, and their use on EDLCs make possible the realization of high- performance devices. Furthermore, these AC can be successfully utilized for the realization of high energy lithium-ion capacitors.

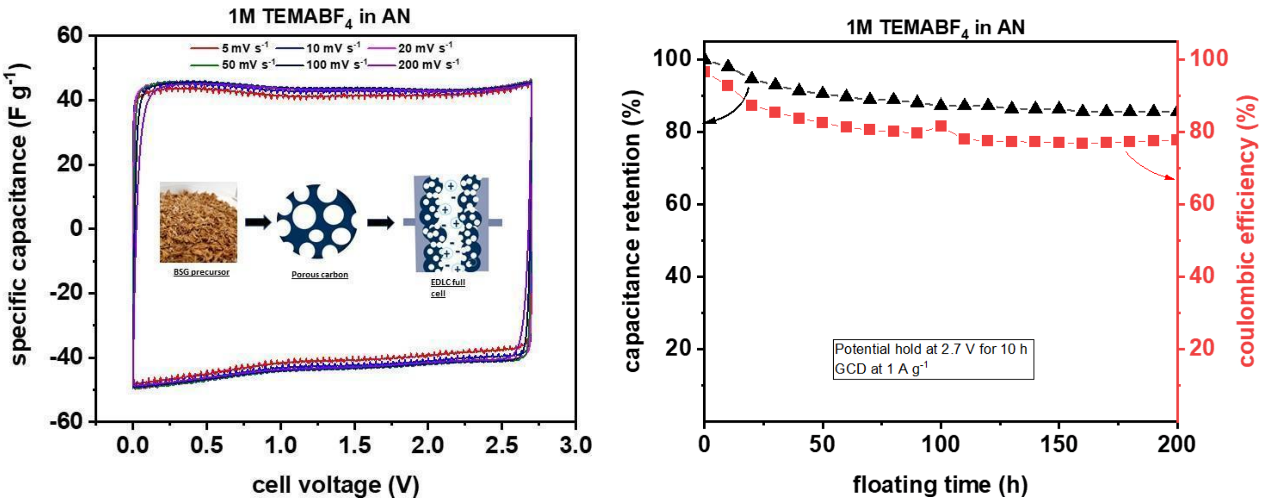

***Figure 1**: BSG derived porous carbon EDLC; cyclic voltammetry (left) and floating test (right)*

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Steam-activated oat hulls: a sustainable material for supercapacitor electrodes

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Although necessary for the ‘green energy revolution’, increasing use of electrochemical energy storage (EES) nonetheless presents a series of environmental challenges related to materials sourcing. Ideally, the component materials any EES device should be sustainably sourced and environmentally benign. Biomass offers an attractive source of the raw materials necessary to produce high surface area carbons [1], however, such biomass should not consist of edible components of food crops or compete with them. Hence, waste products from food grains are a plentiful source of biomass suitable for the production of high surface area carbon. While there have been a large number of studies on the use of rice husk for this purpose [2], little to no attention has been paid to oat hulls, despite their similarity to rice husks and oats being the fifth largest cereal crop produced globally [3].

In this work, activated carbon is produced from oat hulls via a two-step process of relatively low-temperature (500 °C) carbonization under a nitrogen gas flow to remove volatile materials, ball milling and steam activation with the latter chosen over other activation approaches due to its low environmental impact. Activation was undertaken at temperatures ranging from 700 to 1000 °C and the resulting carbons characterized by analytical Scanning Electron Microscopy (SEM) to determine morphology and local chemical composition, N_2 adsorption/desorption to determine surface area and Raman spectroscopy to estimate the level of ‘graphitisation’ before incorporation into electrodes using a PTFE binder and carbon black conductive additive. Electrodes were assembled into symmetric two-terminal aqueous (6M KOH electrolyte) supercapacitor cells and characterized by cyclic voltammetry (CV), galvanostatic charging/discharging (GCD) and electrochemical impedance spectroscopy (EIS). The electrochemical performance of the oat husk derived electrodes was compared directly with electrodes produced from commercially available activated carbon in the same manner.

The effects of activation at low temperatures is found to be extremely limited with electrodes derived from oat husks activated at 700 °C presenting high effective series resistance (ESR), low specific capacitance (C_{sp}) and poor Coulombic efficiency with an overall performance little better than carbonized material used without further activation. Analysis of the low temperature activated oat husks indicated little development of porosity and limited graphitization. In contrast, material activated at 850 °C shows a clear development of porosity and increased graphitisation, reflected in a considerably improved electrochemical performance across all performance metrics. ESR, C_{sp} and Coulombic efficiency are found to approach or exceed typical values obtained from electrodes produced from commercially-sourced activated carbon under identical test conditions. Increasing activation temperatures to 1000 °C led to excessive carbon loss, with a strongly reduced yield and decreased electrochemical performance as electrochemically inactive silica contributed an increasing fraction of the total mass.

Therefore, with an appropriate selection of activation conditions, porous carbon derived from oat hulls can perform competitively with commercially available material and offer a similar potential to rice husks as a suitable biomass for production of ‘green’ activated carbon for supercapacitor electrodes. Oat production has a geographic distribution complementary to that of rice, enabling the local sourcing of waste biomass for activated carbon production so reducing the impact of raw materials transportation.

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Performance study on the addition of novel functionalized graphene oxide in activated carbon-based electrodes for capacitive deionization

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Graphene oxide (GO) and its reduced and functionalized forms have been attracting the interest of the scientific community. Widely studied for its unique properties, GO finds applications in the vast and heterogenous scenario of various research fields. When focusing on porous electrodes for capacitive applications, GO is commonly proposed in its reduced form (rGO) for improved electrical conductivity. Specifically, designed functionalization procedures are also used to tune the charges spontaneously present on the surface of GO. In this context, this work reports on the investigation of few novel functionalized GO materials proposed for capacitive deionization application. The modification of the GO has been pursued following different strategies in order to achieve a controlled tuning of the surface charge of the GO. The functionalized materials have been widely characterized by means of morphological, physico-chemical and electrochemical characterization techniques. Finally, the materials have been mixed with activated carbons and coated onto metallic current collectors to assemble a device for capacitive deionization application. Performances of the different materials have been compared in terms of salt adsorption and charge efficiency, proving the beneficial effect of the presence of functionalized GO. Interestingly, the same approach and materials can also be applied for the case of aqueous supercapacitors, since they share many features and similar working mechanism with capacitive deionization.

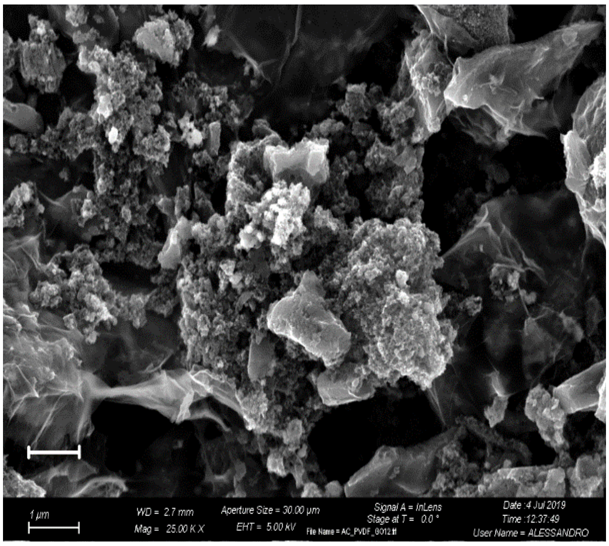

Figure 1: *Graphene oxide in activated carbon matrix.*

Novel infiltration method of membranes over activated carbons electrodes

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A novel method to modify activated carbons electrodes through addiction of selective ion exchange membrane (IEM) is presented. Nowadays the preferred method to modify an electrode in an electric double layer supercapacitor is to apply a stand-alone membrane in proximity of the electrode itself [1, 2]. This technique produces some drawbacks in terms of dimensions of the device, increase of the internal series resistance and reduction of the total capacitance. With the present method it is possible to use the membrane with a conformal contact with the electrode or directly in the production of the slurry. In particular the first approach studied consists into melting the membrane and casting and drying it under vacuum over activated carbons. This drying process, is performed in a glass oven B-585 from BÜCHI. In this way it is possible to reduce internal resistance of the device, providing good ion selectivity and maintaining a high capacitance.

The second approach consists in exploiting the IEM as polymeric functional binder inside the slurry. It is possible to exploit the long chains of ion exchange polymers to bind activated carbons together and onto the substrate. This strategy allows the substitution of common binders like PVDF, with several benefits in terms of reduced electrical resistance, tunable surface charge of the electrodes, reduced cost and increased sustainability.

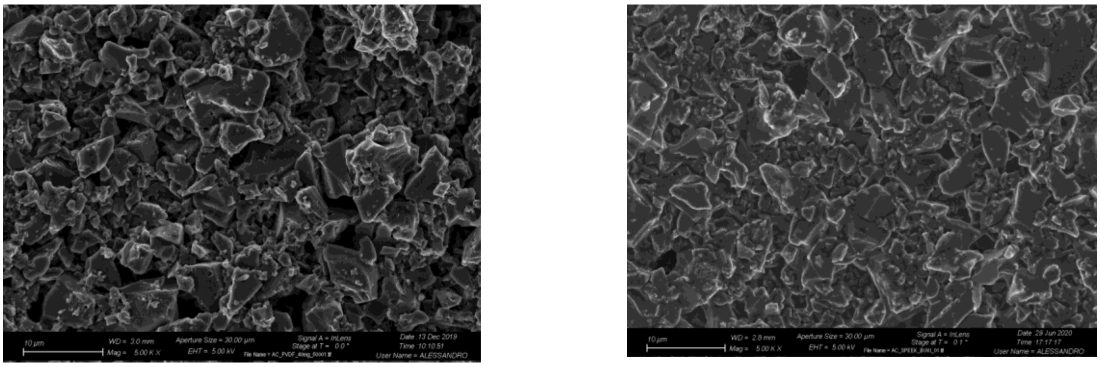

Figure 1: *Scanning electron microscope images. AC over Titanium current collector on the left and infiltrated IEM over AC on the right.*

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Graphene based materials: From Green Synthesis to Physico-Chemical Analysis and Electrochemical Performance as Supercapacitors

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Since the discovery of graphene in 2004 [1], it has been considered a "Wonder" material with lots of potential for many applications due to its attractive properties. Among such applications comes supercapacitors as graphene is expected, according to theoretical studies, to possess an electrochemical double layer specific capacitance of 500 F/g [2]. However, due to the high cost and difficulty of producing and handling single sheets of graphene, the presence of graphene in the market has been hindered. Luckily, many methods have been devised to synthesize graphene-like materials that would be easier and cheaper to produce. Among such methods, the chemical exfoliation of graphite, yielding reduced graphene oxide (rGO), is one of the commonly used synthesis methods nowadays. Unfortunately, such a method, although efficient and low cost, does not yield single rGO sheets but rather stacked rGO layers. Since stacking impedes the exploitation of the surface area of graphene, the notion of pillaring has been introduced to prevent the sheets from stacking by separating them using organic linkers [3]. This opens the door to a new tailor-able family of graphene based materials incorporating organic linkers of different lengths and functionalities and exhibiting multi-scale porosities. On the other hand, the chemical exfoliation of graphite is usually not a green method as it involves the use of hydrazine hydrate as a reducing agent. Since hydrazine is a very toxic chemical, research has been conducted to find alternatives to its use. Many reducing agents have been experimented, yet ascorbic acid (AA) proved itself to be an efficient reducing agent, offering a mild green reduction process [4]. While many diverse protocols involving AA have been used, a rationalization of the correlation between important reaction condition parameters and rGO properties is lacking. Herein, an introduction to the field of pillared graphene is presented, demonstrating different reaction routes and different pillars. In addition, the reduction of graphene oxide using AA is analysed by varying the reaction parameters such as the amount of AA, the reaction temperature and the reaction time. Various characterization techniques have been employed to analyse the structure and morphology of the synthesized samples, including XRD, TGA, XPS, SEM, Raman Spectroscopy, Elemental Analysis (EA) and conductivity measurements. To better understand the role of micro/meso-porosity, the use of advanced characterization techniques such as SAXS and SANS is emphasized. The relationship between experimental and the intrinsic properties of graphene based materials will hence be presented. Furthermore, being of high interest for supercapacitor applications, the electrochemical storage performances of the samples have been assessed. It will also be shown that the obtained results pave the road for the employment of (1) pillared graphene materials for supercapacitor applications, (2) Ascorbic Acid as a mild green reduction method for other rGO based materials and (3) SAXS and SANS to better correlate the performance of the materials to their structural properties.

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Operando synchrotron XAS/XRD Investigation of Zn Insertion into Manganese Hexacyanoferrate Cathode Material

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Manganese hexacyanoferrate (MnHCF), one of the Prussian blue analogues (PBAs), has attracted widely attention as promising cathode material for both Li-ion and post-Li ion batteries. The aqueous Zn/MnHCF cell, displaying high discharge potential (>1.6 V) and large specific capacity (>120 mAhg^{-1}), has gained wide attention as a rechargeable Zinc-ion battery (ZIB). However, the MnHCF cathode exhibits an unavoidable capacity fading and phase transformation during the cycling, and the underlying mechanisms have remained somewhat ambiguous [1]. Here, we present a study of MnHCF cathode by employing operando X-ray absorption spectroscopy (XAS) and synchrotron X-ray diffraction (XRD) techniques.

The operando XAS experiment was carried out using a pouched CR2032 cell with an X-ray transparent Kapton window on both sides. The cell consists of a Zn sheet (thickness 30um) anode, separator and cathode material, in 3 M $ZnSO_4$ electrolyte. XAS data were recorded at Mn K-edge in transition mode at the XAFS beamline (Elettra Synchrotron). The operando XRD data was collected using commercial EL-cell, with beryllium window, Aluminum foil, cathode material, separator and Zn-sheet from up-down setup, and the tests were in reflection mode on the MCX beamline of Sincrotrone Elettra. The XRD patterns were collected at λ=1.03318 Å on a MAR-CCD detector, with 15 seconds per acquisition separated by 5 min break [2]. From the XAS data we found the oxidation state of Mn-sites show a reversible change during the first cycle. However, the XRD patterns of MnHCF display obvious changes during the first cycle. The original monoclinic phase was totally disappeared, and several new peaks were appeared with the intercalation of Zn^{2+}. Combining the ex-situ XAS and XRD, we found the inserted Zn^{2+} partly replace the Mn-sites inside the framework and produce a new phase zinc hexacyanoferrate (ZnHCF) and some other Zn-related phases [3]. The detailed phase transformation process is still under studying. We expect that by combing the XAS and XRD data, the charge/discharge mechanism of MnHCF in aqueous Zn-ion battery can be more clearly illustrated.

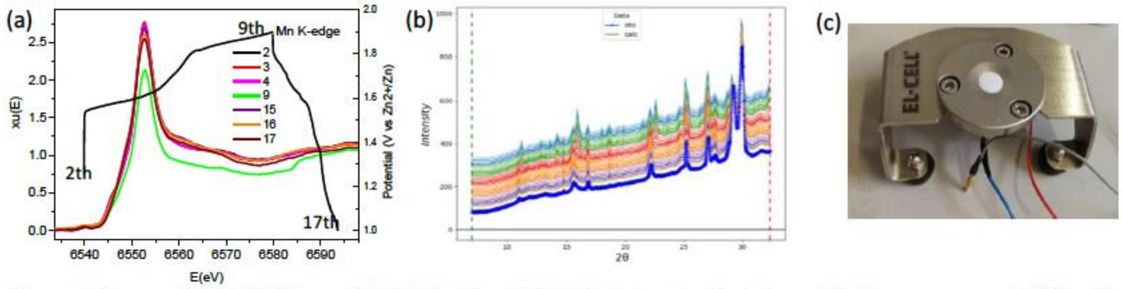

Figure 1 Operand (a) XAS data and (b) XRD data of MnHCF during the first charge/discharge process; (c)EL-cell setup.

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ORP-EIS and interfacial analysis of PEDOT:PSS – aluminium electrolytic capacitors

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Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) has been proven as a versatile and resistant conductive polymer with a wide range of applications [1]. Among others, its use as electrolyte in electrolytic capacitors is one of the most predominant. PEDOT:PSS – aluminium electrolytic capacitors show low internal equivalent series resistances (ESR) and can resist temperatures up to 280 ºC. The most common method of applying PEDOT:PSS is coating it from an aqueous dispersion. PEDOT:PSS dispersions admit additional components (secondary dopants) that enhance properties such as conductivity, rheology or electrochemical behavior of the final layer. There has been fundamental research about how the structure of PEDOT changes upon the interactions with the substrate it is coated on [2]. However, it has to the best of our knowledge never been studied experimentally how PEDOT:PSS behaves on top of the layer of aluminium oxide that works as the dielectric in polymer electrolytic capacitors.

This work aims to study the properties of model systems involving different PEDOT:PSS dispersions on top of aluminium substrates that work as anode in polymer electrolytic capacitors. In this study, two approaches will be used to analyze such systems: an electrochemical analysis and an analysis of the interface. Electrochemically, the systems will be studied using odd random phase electrochemical impedance spectroscopy (ORP-EIS). ORP-EIS is a technique that derives from impedance spectroscopy with the added value of exciting at once several odd frequencies with a multisine signal [3]. Thanks to the in-house developed data analysis the electrochemical behavior of the system is obtained as a function of the parameters of a constant phase element (CPE) and a resistor, that account for the capacitance, ideality and ESR of the system. Studying the latter will allow us to judge the properties of the polymer and the interaction between phases. Parallel to the electrochemical analysis, cross-sections will be obtained to access the interface between the polymer and the electrode thanks to an ion milling polisher. These complex systems (Al substrate, Al_2O_3 and PEDOT:PSS) are then studied via secondary electron spectroscopy (SEM), which provides morphological information, and energy-dispersive X-rays (EDX) and X-ray photoelectron spectroscopy (XPS) that provide elementary information of the systems and the interaction between layers.

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Microsupercapacitors: Scaling Down and Electrode Architecture Optimization

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Today, there is an increasing need for miniaturized energy storage devices for IoT sensing and portable electronics ap- plications. Miniaturized power systems can be compatible with semiconductor fabrication, which enables easy integration with electronic devices [1, 2]. However, a smaller area of current collectors will lead to higher resistance, which will in turn lead to a smaller capacitance. To overcome the drawback, we synthesized vertically aligned carbon nanotube (VACNT) on chip. The advantages of the use of VACNT and microfabrication techniques are the ability to control electrode morphology, enabling the possibility to use complex designs, shorten the ionic path between electrodes and remove the need of sepa- rators. To further investigating the influence of on-chip design, we are fabricating VACNT devices on-chip and comparing their capacitance to conventional assembly samples (Figure 1 (a)).

Our micro-supercapacitor devices are fabricated on silicon wafer by the following process: The current collectors are made of molybdenum (Mo) which is suitable for high density CNT growth. Subsequently the catalyst for the CNT growth (Fe) is deposited by sputtering. The CNT electrodes are grown directly on the current collector by a chemical vapor deposi- tion process and are presented in Figure 1 (b).This allows an easy processing and structuring of electrodes and a control of their height between few micrometers to 100 micrometers and their porosity and density. Due to their mesoporsity, CNTs were proven to be promising electrodes for ionic liquids electrolytes (EMIM-BF4), which have ion sizes around 0.8 nm. Through analysis electrochemistry measurement in EMIM-BF4, which has large voltage window (3.4 V) and is reusable, we are able to understand how the structuring of the electrodes impacts the capacitance of micro-supercapacitor. In Figure 1 (c), comparing on-chip supercapacitors with conventional stacked electrode cells, we observe a 4 fold increase in capaci- tance. We will present a comprehensive bench-marking study of VACNT based supercapacitors and discuss scaling down effects in depth: geometrical limits, processing limits, optimized designs, and the pathway to achieving 0.1 - 1 F/cm^2, required by commercial applications.

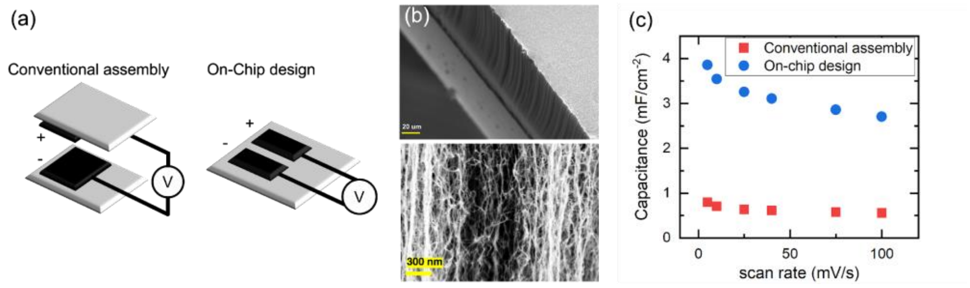

Figure 1: (a) Conventional assembly and On-Chip design (b) SEM images of microsupercapacitor electrode (up) and zoom in CNT SEM image (bottom) (c) The capacitance of different design.

Acknowledgements

This work is supported by OFEN Swistor: SWift energy charging SupercapaciTOR based on carbon nanotube arrays (591585), Center of MicroNano Technology (CMi) at EPFL, and Binnig and Rohrer Nanotechnology Center (BRNC).

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Assessment of Electrodes Operation in Carbon-based Na-ion Capacitors by Potentiostatic Electrochemical Impedance Spectroscopy

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Owing to their higher specific energy than electrical double-layer capacitors (EDLCs) and the high natural abundance of sodium, sodium ion capacitors (NICs) have recently attracted a lot of attention.

NICs are hybrid systems which associate a battery-type negative electrode (e.g., from pre-sodiated hard carbon), into which sodium is reversibly inserted, with an EDL positive electrode (generally from activated carbon (AC)), where the anions from the electrolyte are electrosorbed [2]. Recently, much attention has been paid to finding and modifying electrode materials in order to design devices exhibiting optimal performance. Hence, it is essential to study how the utilized components of the hybrid capacitor (each electrode, electrolyte) cooperate during its life time, and influence its energy density, power density and lifespan [3,4]. In this context, we herein present a detailed study of the electrochemical performance of an (+)AC(YP-80F(Kuraray))||Na_x(HC-J(Kureha))(-) pouch-type NIC in 1 mol L^{-1} $NaClO_4$/EC:PC by employing Staircase Potentiostatic Electrochemical Impedance Spectroscopy (SPEIS). To analyze the contribution of each electrode during the NIC operation, the EIS spectra were recorded on a cell equipped with a sodium reference electrode. As a result, the Nyquist plots at each applied voltage have been obtained (***Figure 1***), and the equivalent circuit of the cell and the individual battery- and EDL-type compartments (viz. negative and positive electrodes, respectively, in contact with the electrolyte solution) has been determined.Finally, each Randle element, attributed to a certain component property (bulk electrolyte conductivity) or phenomenon (charge transfer, SEI formation) occurring at a given electrode, has been plotted vs. voltage. Briefly, when the voltage is set at values between of 2.0 and 3.8 V, the charge transfer to the faradaic negative electrode contributes significantly to the resistive characteristics of the full cell ($R_{ct(-)}$ of ca. 10.5 Ohm and 13 Ohm, respectively), whereas the $R_{ct(+)}$ of the EDL positive electrode is only 2.5 Ohm. Furthermore, the diffusion coefficient for Na^+ insertion into the negative electrode increases from $0.8 \cdot 10^{-8}$ cm^2 s^{-1} to $1.3 \cdot 10^{-8}$ cm^2 s^{-1} when the voltage is increased from 2.0 V to 3.8 V, contributing to the progressive decrease of the Warburg coefficient for the negative electrode. It is expected that such analysis should provide detailed information on the phenomena occurring in the NIC, and consequently allow the degradation tendencies to be attributed to a given cell component. Such expertise is highly important from the point of view of designing hybrid capacitors with improved performance.

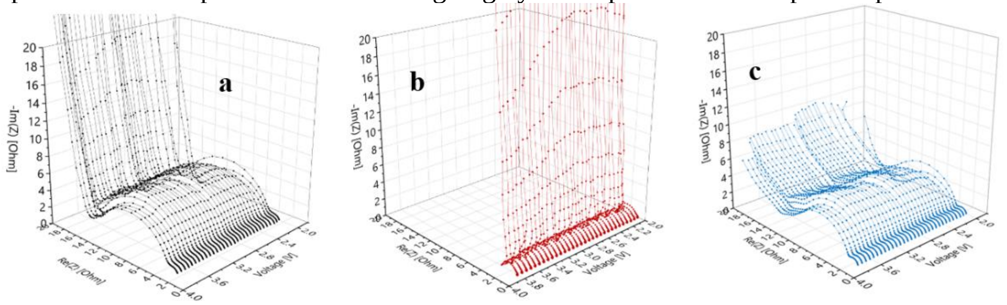

Figure 1: *Nyquist plots (in the frequency range from 100 kHz to 1 mHz) from SPEIS realized by steps of 60 mV (from 2.0 V to 3.8 V) on an (+)AC(YP-80F)||Na_x(HC-J)(-) NIC in 1 mol L^{-1} $NaClO_4$/EC:PC, for : (a) cell, and (b) positive and (c) negative electrodes.*

This work was supported by the Foundation for Polish Science (FNP) in the frame of the CARBionCAP project [POIR.04.04.00-00-5EF5/18-00] and by the Ministry of Education and Science, Poland [0911/SBAD/2201].

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Origin of charge distribution asymmetry at the ionic liquid/electrode interface

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Ionic liquids (IL) are largely employed in electrochemical capacitors thanks to their enhanced charge density, high stability, and large working window. The fact that ILs are far from conventionally used electrolytes poses a challenge in the understanding of how capacitance is affected. Current general models identify two main symmetric ways capacitance changes as function of the applied voltage: camel-like (the capacitance increases close to zero voltage while decreasing for larger values) or bell-like shape (monotonic decrease of capacitance as we move away from V=0). However, given the extreme sensitivity of the IL characteristics to the constituting ions, deviations of the general models are expected. Such deviations are still unknown and not characterized. The capacitance-voltage relationship must be studied on a case-by-case basis to determine additional factors which may playing an important role.

By means of classical molecular dynamics simulations, we report here an anomalous charge distribution at the ionic liquid/electrode interface that leads to an asymmetric behavior between positive and negative applied voltage found in $[DBUH^+][Im^-]$ at the interface with a carbon-based electrode. A positive peak in the charge density is seen next to the electrode surface (Figure 1). Such peak increases if the electrode gets negatively charged. However, the peak is found to persist even for positively charged electrodes, although its height is progressively reduced.

By inspecting the structural distribution at the interface, $[Im^-]$ is found to lie perpendicular to the electrode surface, mainly pointing the highly negative charged atoms away from the electrode, whereas $[DBUH^+]$ stays flat on the electrode. The reason is because $[DBUH^+]$ is characterized by a hexagonal and heptagonal ring mainly formed by carbon atoms which strongly interact with the carbon atoms of the electrode by Van der Waals forces. The flat position maximizes the interaction which wins over coulombic repulsion for moderate- to-low positive voltages. The positive charge distribution then represents an extension of the charge of the electrode for positive bias while it acts as countercharge for negative bias with effects on the capacitance variation.

The study sheds light on the fundamental importance of Van der Waals interactions at the electrode/IL interface. These cannot be ignored when modeling half-cells because they strongly influence the value of the overall measured capacitance.

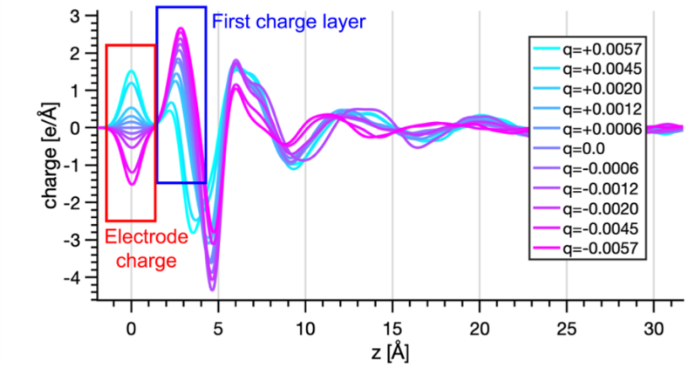

Figure 1: *Charge distribution at the ionic liquid/electrode interface as function of the distance from the electrode. The different line colors indicate the amount of charge per atom in the electrode in elementary charge units.*

Effect of the intercalated cation size in birnessite on charge storage in neutral aqueous electrolyte

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Manganese oxides have been substantially investigated as electrode materials for supercapacitors, potentially useful due to their low cost, and also their environmental friendliness in neutral aqueous electrolyte [1, 2]. The birnessite-type MnO_2 phyllomanganate, characterized by a two-dimensional layered nanostructure and containing probably confined structural water in their structure, allows high mobility of the intercalated cations in the interlayer space with a “breathing” of the structure during charge/discharge cycling [3]. Ex-situ and in- situ crystallographic investigations have evidenced the cations intercalation/deintercalation process in the birnessite interlayer, showing the reversible shifting of the (001) diffraction peak [3, 4]. Recently new experimental and simulation investigations have been performed to highlight the role of the confined interlayer structural water on capacitive charge storage in birnessite leading to a continuum between double-layer and faradaic behavior in the charge storage mechanism and then minimal structural changes in the material [5,6]. To further highlight the charge storage mechanism in birnessite and corroborate these new insights, some results about birnessite cycling in mild aqueous electrolytes are presented in this communication to introduce the effect of the cation size during the intercalation process.

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New insights into Point of Zero Charge determination with Electrochemical Quartz Crystal Microbalance

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The presented work elaborates on new methods for practical and accurate determination of the Point of Zero Charge (PZC) and demonstrates its essential role in the Electrochemical Quartz Crystal Microbalance (EQCM) measurements. EQCM experiments allowed for a better understanding and insightful description of the ion dynamics within the porous carbon electrode, which translates to charge storage in Electrochemical Capacitors (ECs). As already known, PZC determines the electrode potential value, at which the formation of the electric double-layer (EDL) does not require an additional charge. At this point, EDL forms spontaneously due to the natural potential difference between the electrodes and unequilibrated surface charge. In theory, anodic or cathodic polarization of the system from PZC should result in the attraction of cations or anions, respectively.

In our report, a detailed account of the comparison of PZC determination methods for EQCM application for aqueous electrolytes is given, where PZC obtained from different electrochemical techniques is compared and discussed. In this work, different electrolytes, namely: 0.1 mol L^{-1} $LiNO_3$, Li_2SO_4, and KI, and the application of three distinctive electrochemical techniques for PZC determination: cyclic voltammetry (CV), Staircase Potentio Electrochemical Impedance Spectroscopy (SPEIS), and Step Potential Electrochemical Spectroscopy (SPECS) were studied. Kuraray YP-50F activated carbon was applied as the electrode active material, in the ratio 80:20 with PVDF as a binder. All research was carried out in the EQCM cell. Since PZC corresponds to an electrostatic electrode-electrolyte interaction (electric double layer formation only), diffusion-limited processes such as redox reactions should be excluded. The use of the SPECS technique was found to be the most efficient in the determination of PZC mainly due to its' short implementation time and additional information regarding electrochemical processes it can provide. The knowledge extracted from these studies can be further used in future works where EQCM is concerned.

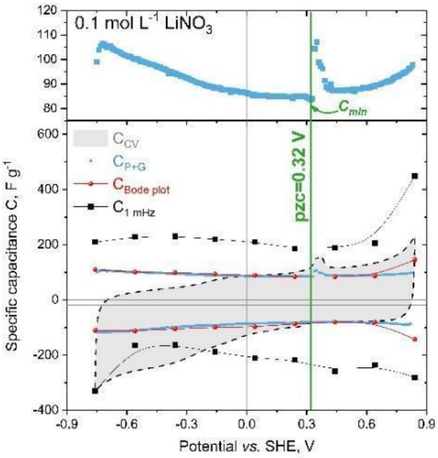

Figure 1: *Capacitances comparison obtained by three electrochemical techniques: CV, SPECS, and SPEIS in EQCM system (electrolyte 0.1 mol L^{-1} $LiNO_3$).*

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Enhancing the Performance and Mechanically Stability of Planar Hybrid Micro-Supercapacitors Using Dendritic-Gold as Current Collector

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Abstract

In the last years scaling down approach on supercapacitors led to the definition of micro-Supercapacitors (µSCs), the demand of those devices is increasing for many application in microelectronics, such as wearable electronics energy storage recovery and self-powered sensors. Recently, many efforts have been done to achieve good results in this field in terms of power and energy densities by using a sustainable chain production that become the driving force of research challenges. Moreover, particular attention was devoted to ecofriendly material, like water-based electrolytes, organic binders and low environmental impact active materials.

In this work the fabrication of the hybrid µSC required multiple steps and processes and we adopted two approaches: a top down for the patterning of the current collectors through photolithography technique, a bottom-up approach for the mass loading of the active material on the electrodes. For these a water-based solution was used. The material chosen as anode is MnO_2 deposited by electroplating and calcinated at 300 °C for 8 hour. The MnO_2 exhibits pseudocapacitive behavior. While the active material used for the cathode is the Activated Carbon (AC) deposited by drop-casting. AC works on Electric Double Layer (EDL) capacitance effect. The electrolyte was 1M Na_2SO_4 in water.

We investigated the effect of adding an interlayer micro-structured made of dendritic-gold. According to the result, the layer seems to have positive effects in terms of wettability and mechanical stability improving also the adhesion of the active material. The layer was grown using a commercial electroplating solution. The electron microscopy image reported in the Figure 1 shows the characteristic tree-like shape of the layer. A singular dendrite is about 3 µm high. Also in this case the solution is water-based in accordance to the sustainable adopted method. The cyclic voltammetry performed on the device reports a capacitance of about 3 mF cm^{-2} at large voltage window of 1.6 V.

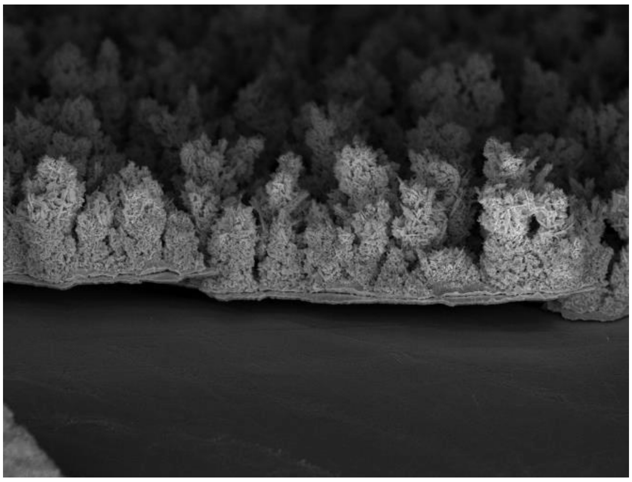

Figure 1: *Dendritic Gold layer growth on 100nm thin film gold*.

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Electrodeposition of MXene and Manganese Oxide onto laser induced graphene for fabrication of a green hybrid supercapacitor

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During the last years, Internet of Things has become a prominent topic of technical, social, and economic importance. One of the main consequences is the high demand for energy and power density from small energy storage devices.

In this field the laser induced graphene (LIG) has become a promising material to produce green, flexible and low-cost micro-supercapacitors.

The issue with this material is that the performances are strongly restrained by its limited surface area and the relatively low conductivity.

In this work we improve the performance of a LIG supercapacitor by decorating its surface through electrophoresis: one electrode will be decorated with metal nitrides and metal carbides (MXenes), the other with manganese oxide. These two materials have appreciable conductivity and are able to boost the capacitance of the device.[1][2]

Electrochemical measurements has been carried out on the device sealed in pouch cells, using different electrolytes.

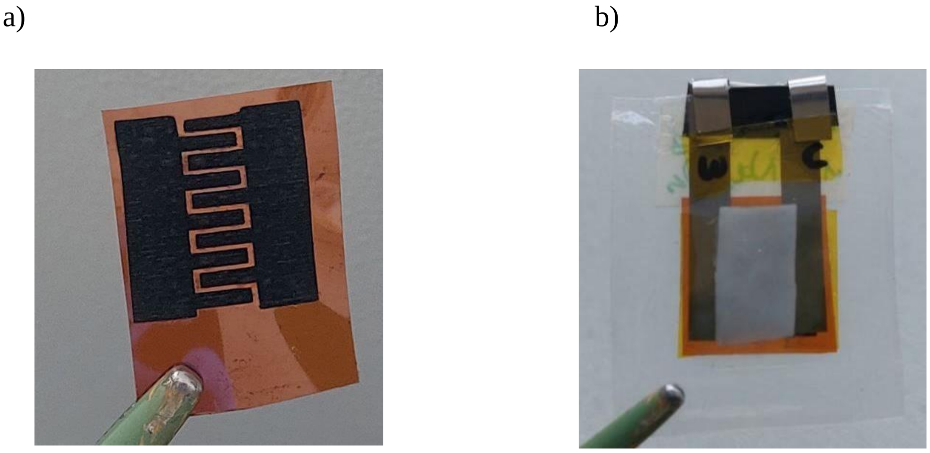

Figure 1: *a) a LIG interdigitated supercapacitor b) the decorated device, assembled and sealed in pouch cell*

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High voltage indoor photo-capacitor: flexible and rigid energy source for IoT devices under ambient light

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Lately, a growing interest have been directed toward the energy demand of low power Internet of Things (IoT) devices. [1]–[3] Usually, these are organized in large wireless sensor networks and are powered by disposable or rechargeable batteries which, despite being reliable power sources, have the need of be replaced/recharged periodically. When these sensors need to be placed in remote and inaccessible locations, the sole use of batteries as energy sources could lead to high maintenance costs. In many cases, a hybrid technology able to harvest and store energy from ambient energy sources would represent a viable alternative or complementary option to power low consuming IoT devices. [4] Different hybrid harvesting and storage technologies have been reported so far and, in many cases, solar cells were directly integrated with supercapacitors (SCs) [5]. Among photovoltaic technologies, dye-sensitized solar cells (DSSC) show a very high efficiency when employed under indoor illumination [6]. Supercapacitors, despite having lower energy density than batteries, are intrinsically more suitable to be integrated with solar cells thanks to their higher cycling stability and lower sensibility to charging current variation and working voltage. Nevertheless, a high output voltage is required to be suitable as an energy source for common portable electronics and sensors.

Herein we present the fabrication and characterization of high-voltage indoor photo-capacitor suitable for IoT application. We realized both rigid and flexible architectures where the series of five DSSC was integrated with an ionic liquid-based SC to harvest and directly store ambient light with a high output voltage (up to 3V). Rigid and flexible substrates as well as different encapsulation techniques were tested depending on the envisioned application. The fabricated devices were tested as energy sources to power ambient sensors and the charge-discharge mechanism was carefully investigated under real-life application. Further insight on the required properties of photo-capacitor to be suitable for application as IoT energy sources were acquired.

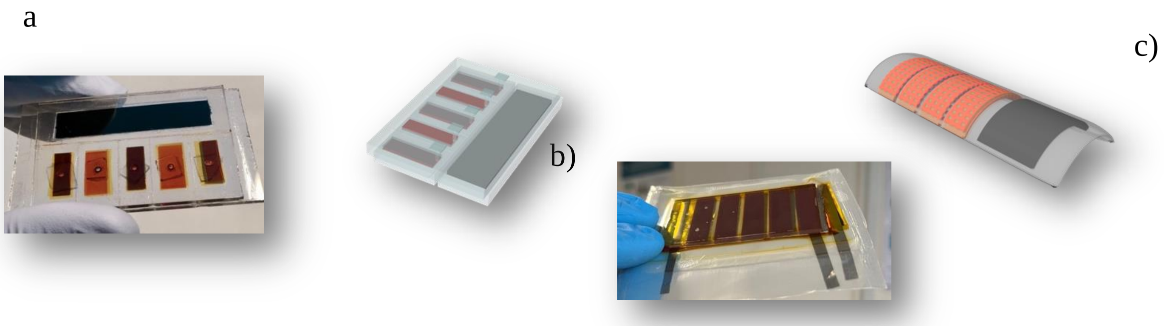

Figure 1: *a) Rigid high-voltage photo-capacitor on conductive glass, b) rigid high-voltage photo-capacitor on conductive glass and metallic current collector. c) flexible high-voltage photo-capacitor sealed in a transparent polymeric film.*

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Carbon based electrodes for Wire-Shaped Supercapacitor

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During the past decade, wearable devices have opened up many possibilities to improve our lifestyle with the ability of exchanging communications, health monitoring and general accessories. However, the existing energy storage products are often rigid and unwashable, generally unsuitable in the textile industry or for specific implementation in clothes. For these reasons, a general interest for fiber-shaped energy devices has increased [1] and researchers are working to achieve a flexible textile-integrable energy storage device with target requirements of light weight and mechanical roubustness.

Among all the choices proposed in literature[1-3], herein we show wire shaped supercapacitors fabricated with carbon nanotube yarns supplied by Dexmat (fig. 1), This material exhibits high specific capacitance, high electrical conductivity exceptional mechanical strength and low weight. Moreover, as another important advantage, CNT yarns act both as electrode and current collector, avoiding the typical hardening phenomena characteristic of metallic-based collectors in wire-based applications.

In this study, CNT yarns were deeply characterized as electrodes and they were functionalized to increase their capacitance. The electrochemical proprieties of this material were also investigated in solid electrolytes, gel and polymer-based in order to build a full wire-shaped cell.

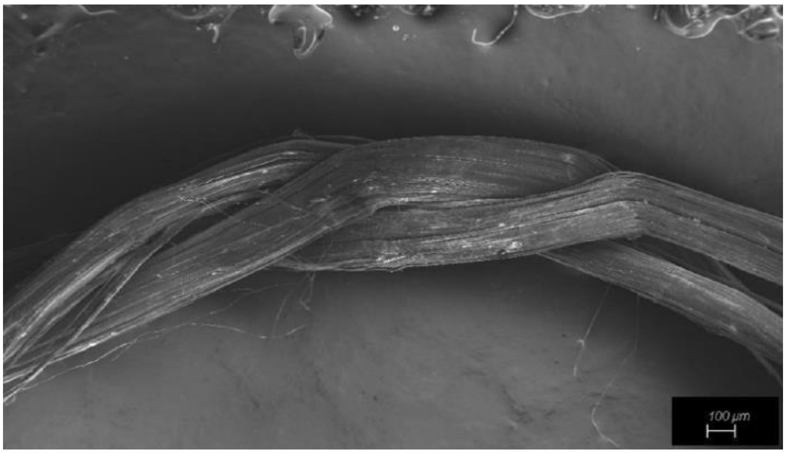

Figure 1: *A CNT yarn, 130µm diameter, exploited for the fabrication of a supercapacitor electrode.*

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Monolithic in-plane integration of gate-modulated switchable supercapacitors (*ip*G-Cap)

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Monolithic integration of iontronic devices is a key challenge for future miniaturization and system integration, in particular the interconnection of multiple functional elements as required for ion computing.[1] The G-Cap, a novel ionotronic concept, is a switchable supercapacitor with switching characteristics analogous to transistors in electronic circuits, but switching relies on ionic currents and ion electroadsorption.[2]

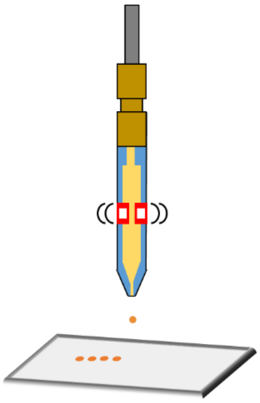

Figure 1: *3D-piezoelectric inkjet printing of supercapacitor architectures*.

Novel switchable supercapacitor architectures (*ip*G-Cap) were produced by 3D-piezoelectric inkjet printing as a planar device. Piezoelectric inkjet printing is an innovative method for the fabrication of carbon electrodes with high flexibilities in geometry.[3] The essential elements are three nanoporous high surface area carbon electrodes obtained from a non-toxic liquid carbon precursor with well-defined specific surface area (544 $m^2\ g^{-1}$). An in-plane nanoporous gate electrode (G-electrode) effectively controls the capacitance of a working capacitor (W-Cap) by regulating the ion concentration of a proton conducting PVA/H_2SO_4-hydrogel electrolyte. W-Cap capacitance (1.6 mF cm^{-2}) can be repeatedly switched on and off by applying a negative DC bias potential (−1.0 V) at the gate electrode, the AC electroadsorption in the coupled nanoporous carbon electrodes of the W−Cap is effectively suppressed leading to a stark capacitance drop.

Rapid prototyping of various G-electrode geometries gives insight into ion adsorption mechanisms, rate- determining transport and adsorption phenomena within the electrosorption device, allowing to optimize the capacitance switching characteristics by electrolyte depletion between on- and off-states, in particular rate and on/off-ratio.

This developed G-Cap concept offers new opportunities in fundamental research for the investigation of ion diffusion and electrosorption mechanisms through selective analysis of adsorption kinetics. Developing new functional iontronic devices and architectures is an essential step towards their implementation in ion transistor circuits, biointerfacing or neuromodulation in future.

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Ionic liquid-based-Electrospun piezo-supercapacitors: a strategy to design autonomous devices

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Remote sensors, soft robotics, wearable, and bio-medical devices require ultra-small, flexible, and compact energy-autonomous components.

Despite the different solutions employing renewable resources, such as light, the mechanical stress-based energy harvesting is an interesting technology, that is not affected by external conditions, Therefore, significant attention has been paid to piezoelectric (PE) materials, capable of transforming mechanical energy into electricity.

To fully exploit the generated electrical energy, it is necessary to couple an energy storage unit enabling energy accumulation. Supercapacitors (SCs) are ideal devices for this scope, but traditional bulky, rigid, and heavy SCs must be replaced with new lightweight and flexible SC.

Nonwovens made of nanofibers produced by electrospinning nanotechnology can combine flexibility with good electrical properties, thus can be excellent components to manufacture both PE and SC components.

Here we propose an integrated system PE ceramic disks and new flexible SCs are coupled for electricity generation and storage to be applied as a sustainable power source for low-energy loads. Specifically, an externally self-powered supercapacitor, developed by integrating a stuck of commercial ceramic piezoelectric disks and a flexible ionic-liquid-based micro supercapacitor is developed. In detail, a stack of 15 commercial lead zirconate titanate (PZT) disks has been used as the energy harvesting unit and mechanically stressed by a compressive force of 85 N at 2 Hz. The piezoelectric output successfully charged the 22-mF supercapacitor up to 3.1 V after 1.5 hours of the test, achieving a stored energy value equal to 110 mJ. The proposed integrated system outperforms the state-of-the-art SPSC assembled with micro-SC (both iSPSC and eSPSC). The flexibility of the supercapacitor and the piezoelectric transducing mechanism are promising features for the development of self-powering wearable applications.

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Carbon cloth decorated with nanostructured manganese oxide as a flexible electrode for supercapacitor applications

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The constant increase in the demand for high-energy and high-power density energy storage devices is favorable for the development of new-generation supercapacitors, especially in the asymmetric configuration, which allows wider operating voltage windows and higher energy density values delivered [1]. Among the different pseudocapacitive materials used for the asymmetric configuration, manganese oxide is considered a viable choice due to its high theoretical capacitance, low cost, and high electrochemical potential [2].

In this work, we have investigated the electrochemical performance of an asymmetric capacitor based on an activated carbon negative electrode and a flexible positive electrode from a carbon cloth decorated with nanostructured manganese oxide. MnOx films were deposited on preoxidized carbon cloth by potentiostatic electrodeposition of 20 mM Mn(NO3)2 aqueous solution at a potential of -1.4 V vs. Ag/AgCl. The loading of MnOx material was controlled by applying different deposition times (1h, 2h, 3h, and 5h). Electrochemical measurements were performed in an aqueous neutral electrolyte 0.5 M K2SO4 with an operating voltage window of 2 V.

The results have shown different variants of nanostructured manganese oxide with respect to the dependence of the electrodeposition time. Additionally, the amount of MnOx depositedis related to the duration of the deposition process. Figure 1 shows coated fibers of the carbon cloth with MnOx nanosheets. The best electrochemical performance was observed for a configuration with a flexible electrode from the 3 h electrodeposition process. The specific capacitance values for the asymmetric capacitors were in the range of 136 to 293 F g^{-1} at a current density of 0.2 A g^{-1}.

The aforementioned results confirm the potential of manganese oxide-carbon cloth flexible electrodes for high-energy and high-power asymmetric supercapacitors.

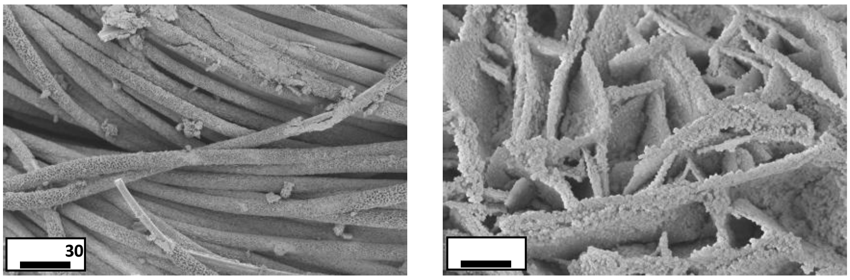

Figure 1: FESEM images of MnO_x deposited on the carbon cloth for 1 h.

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In-situ decoration of laser-scribed graphene with TiO2 nanoparticles for scalable micro-supercapacitor applications

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The increasing demand of micropower sources and small-scale energy storage devices has recently moved the attention to miniaturization. Micropower modules are required in devices such as sensors, portable and wearable electronics, or biomedical implants. Micro-supercapacitors (MSCs) can satisfy this requirement, thanks to their high specific power and their up to millions long life cycles. Graphene appears as the ideal material for MSCs, thanks to its low cost, low toxicity, good electrical conductivity, high polarizability, excellent mechanical strength and large specific surface area. Recently, noticeable results have been achieved in producing flexible interdigitated graphene-based MSCs using the laser photo-thermal conversion, from suitable precursors [1]. However, so far the energy stored in such devices is still limited by the inherently physical nature on the basis of the charge accumulation mechanism. Several strategies have been proposed to couple the physical charge adsorption on porous carbon with additional reversible faradic surface reactions (pseudocapacitance), arising from doping graphene with metal oxides nanoparticles, which could be able to boost the MSCs performances, thus reducing the gap of such devices with batteries. Nevertheless, these approaches pose some doubts both in terms of scalability and in terms of environment impact, raising the same recycling problems as batteries for such devices.

In this work we propose a novel approach to improve the performances of graphene based flexible interdigitated MSCs obtained with the LightScribe® technology [2]. We managed to synthetize one-pot porous graphene electrodes decorated with TiO2 nanoparticles by converting a precursor material through the absorption of the infrared laser light of a conventional DVD burner. TiO2 laser scribed graphene oxide (LSGO) MSCs showed improved specific capacitance, as compared with pristine LSGO devices and excellent retention after 3000 cycles, suggesting this material as a remarkable candidate in micro-supercapacitors for large-scale and low environment impact applications.

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Editors

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