Short summary of the oral and poster presentations by students awarded in CESEP 2019 Conference

1. Award for the best oral presentation, provided by the Spanish Carbon Group TO Emmanuel Pameté Yambou. ***"Low temperature performance of carbon/carbon EDLCs down to -50°C in ionic liquid binary mixture".***

2. Award for the best oral presentation, provided by PID Eng & Tech. A Micromeritics Company TO Stefan Breitenbach. ***"Cellulose based activated carbon fibers for use as supercapacitor electrodes".***

3. Award for the best poster presentation, provided by the journal Energy & Environmental Science, Royal Society of Chemistry TO Borja Ferrández-Gómez. ***"Effect of electrode composition and electrolyte flow in electrochemical regeneration of activated carbon in a kilogram batch reactor".***

4. Award for the best poster presentation, provided by the journal Sustainable Energy & Fuels, Royal Society of Chemistry TO Hande Alptekin. ***"Structure Performance Correlations in Hard carbons for Na-ion Batteries".***

Low temperature performance of carbon/carbon EDLCs down to 50ºC in ionic liquid mixture

Emmanuel Pameté Yambou*, Bárbara Górska and François Béguin

Poznan University of Technology, ul. Berdychowo 4, 60-965, Poznan, Poland

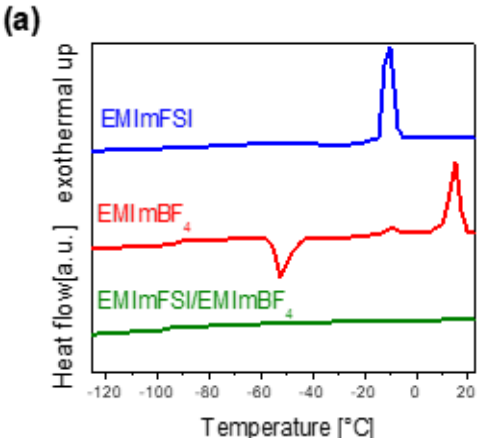
* *e-mail:* emmanuel.yambou@doctorate.put.poznan.pl

The 8th «**international conference on Carbon for Energy Storage and Environment Protection**, CESEP'19 », took place from October 20 to 24, 2019 in Alicante, Spain.

The scientific program proposed by the Spanish Carbon Group was very rich and included plenary and keynote lectures by recognized speakers, and a special emphasis was made in oral and poster communications. This scientific event brought together more than 200 internationally renowned speakers and exhibitors from around the world. More specifically, this conference aimed to bring together experts, researchers and Ph.D students to discuss high-level scientific issues on the fundamental and technological aspects of carbon applications related to energy storage and environment protection.

In our talk, we presented a strategy for the realization of ionic liquids (ILs) based electrical double-layer capacitors (EDLCs) capable of efficient operation down to -40 °C. We focussed on the use of imidazolium-based ILs, due to their relatively low viscosity and relatively high conductivity in contrast to their pyrrolidinium [1] or piperidinium [2] counterparts. Binary mixtures with various molar ratios were formulated using two ILs with 1-ethyl-3-methylimidazolium cation, $[EMIm]^+$, coupled with bis(trifluosulfonyl)imide $[FSI]^-$ or tetrafluoroborate $[BF_4]^-$ anions. Taking into account our differential scanning calorimetry (DSC) investigations as well as viscosity and conductivity measurements on various binary mixtures of imidazolium based ILs, we selected the EMImFSI/EMImBF$_4$ (1:1 molar ratio) mixture, as it exhibited only a glass transition at -97 °C (Fig 1a), relatively low viscosity of 33.0 mP s and relatively good conductivity of 12.1 mS cm^{-1} (at 20 °C).

To uphold the low-temperature performance of carbon-based EDLCs in 1:1 EMImFSI/EMIMBF$_4$ electrolyte, we applied electrodes made of mesoporous materials: SC2A carbon black (by Cabot, S_{DFT} = 1502 m^2 g^{-1}; V_{meso} = 1.05 cm^3 g^{-1}) and a home-made carbon [3] MP98B (S_{DFT} = 1556 m^2 g^{-1}; V_{meso} = 1.30 cm^3 g^{-1}) having well-defined mesoporous with average size of 3.5 nm. The EDLCs based on both electrode types demonstrate capacitive performance down to -40 °C, however at all temperatures the cell with MP98B exhibits better charge propagation (Fig 1b,c), greater specific capacitance and energy. Contrarily, the capacitor incorporating the denser SC2A material displays higher volumetric capacitance and slightly higher volumetric energy than the cell with MP98B. The advantages of the two materials were combined in a mixture of SC2A and MP98B (in 1:1 mass ratio), termed as SCMP, which revealed optimized volumetric capacitance and greater volumetric energy at low temperature. During the presentation, the electrochemical properties of EDLCs at low temperature were discussed in light of the porous texture of carbons and thermal properties of ionic liquid mixtures.



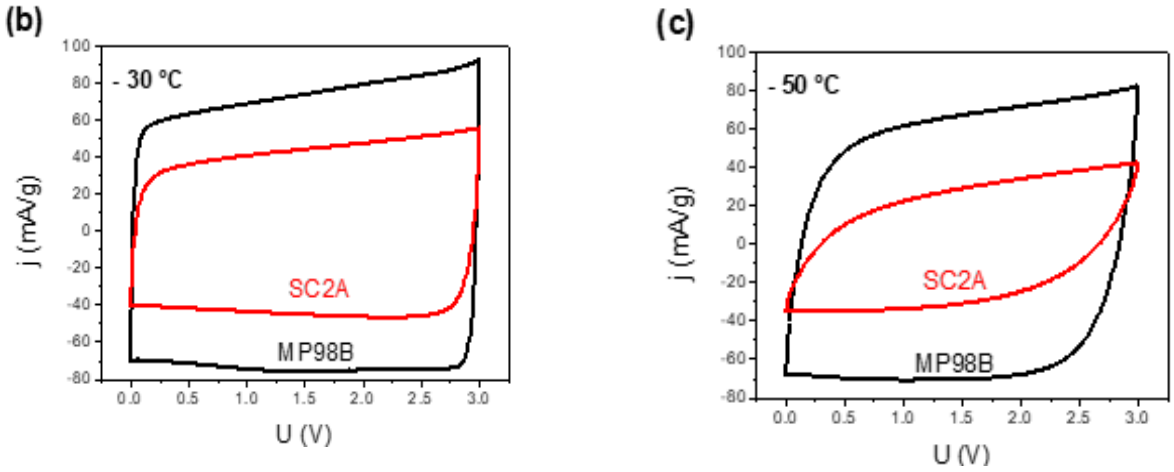


Figure 1: (a) DSC thermograms of neat ILs and EMImFSI/EMIMBF$_4$ upon heating at 10 K min^{-1}; Cyclic voltammograms (v = 1 mV s^{-1}) of EDLCs based on SC2A and MP98B electrodes in EMImFSI/EMIMBF$_4$ (1:1 molar ratio) mixture at (b) -30 °C and (c) -50 °C.

Acknowledgements

The Polish National Science Center (NCN) is acknowledged for supporting the MAESTRO project UMO-2016/22/A/ST4/00092. We express our deep gratitude to the Spanish Carbon Group for the excellent organization of CESEP'19, for the best Oral Presentation Award and for the warm hospitality we enjoyed during our stay in Alicante.

References

[1] *M. Kunze, S. Jeong, E. Paillard, M. Winter, S. Passerini*, *J. Phys. Chem. C, 269* (2018) 12364-12369.

[2] *W.-Y. Tsai, R. Lin, S. Murali, L.L. Zhang, J.K. McDonough, R.S. Ruoff, P.-L. Taberna, Y. Gogotsi, P. Simon*, *Nano Energy, 2* (2013) 989-997.

[3] *T. Morishita, T. Tsumura, M. Toyoda, J. Przepiórski, A.W. Morawski, H. Konno, M. Inagaki,* *Carbon, 48* (2010) 2690-2707.

Viscose-based activated carbon fibers for use as supercapacitor electrodes

Breitenbach Stefan[1,2*], Unterweger Christoph[1], Fürst Christian[1], Hassel Achim Walter[2]

[1]*Wood K plus Kompetenzzentrum Holz GmbH, Altenberger Strasse 69, 4040 Linz, Austria*

[2] *Johannes Kepler University Linz, Institute for Chemical Technology of Inorganic Materials,*

During my dissertation I am working on the carbonization and activation of viscose fibers and their use as electrode material for supercapacitors. The activation step is done by physical activation, carbon dioxide or water vapor are used. A statistical approach (design of experiments) is chosen to optimize the parameters of the individual production steps such as temperature and heating rate during carbonization or gas flow, activation time and activation temperature during the activation step (see Figure 1). In addition, different impregnation agents such as phosphoric acid, diammonium hydrogen phosphate or ammonium sulfate are used to further improve the yield and to observe effects on characteristic properties of the activated carbon fiber. By various analytical methods on the fiber after carbonization and after activation (SEM, EDX, XRD, Raman- & FTIR-spectroscopy, XPS, and physisorption) as well as electrochemical characterization on the produced electrode and supercapacitor (sheet resistance, CV, GDC, and EIS), cause-and-effect relationships can be established between the chemical composition (e.g. the influence of heteroatoms), the physical properties (such as pore size distribution) and the electrical properties of the material, such as specific capacitance, energy and power. This approach has already made it possible to produce activated carbon fibers with very high specific surface areas of up to 3200 m^2 g^{-1}. Due to a pore size distribution that is well suited for use as a supercapacitor electrode and a very low internal resistance due to the fibrous precursor, excellent electrical properties are obtained (see Figure 2).

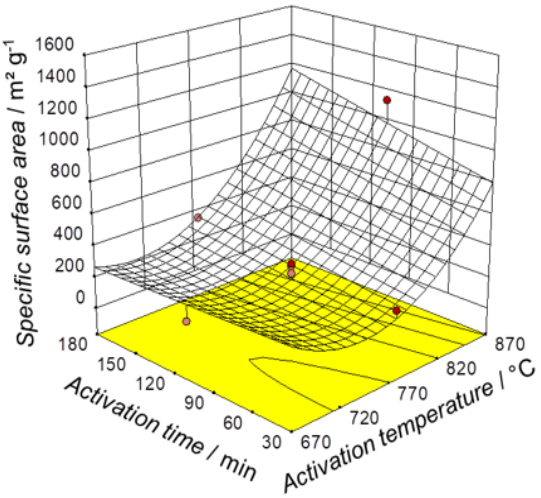


Figure 1: Response surface of the specific surface against activation time and activation temperature of an activated carbon fiber made from viscose.

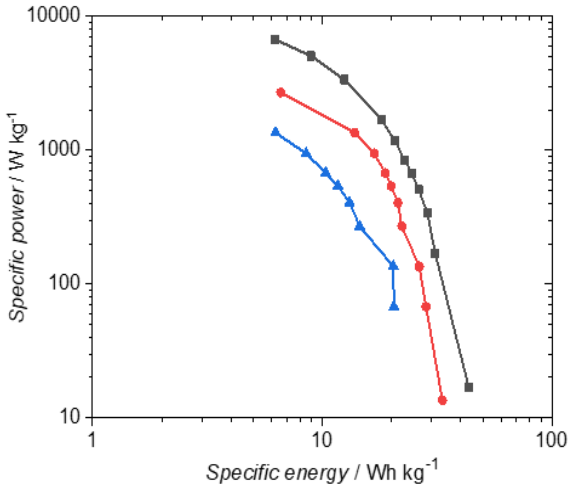


Figure 2: Ragone plot of three supercapacitors made using three different activated carbon fibers as electrode materials (derived by GDC using 1 mol l^{-1} TEMA BF_4 as electrolyte). The values are calculated by device.

Effect of electrode composition and electrolyte flow in electrochemical regeneration of activated carbon in a kilogram batch reactor

Borja Ferrández-Gómez[1*], Samuel Beaumont[1], Diego Cazorla-Amorós[2], Emilia Morallón[1]

[1]Materials Institute and Department of Physical Chemistry, University of Alicante, PO Box 99, 03080-Alicante, Spain.
[2]Materials Institute and Department of Inorganic Chemistry, University of Alicante, PO Box 99, 03080-Alicante, Spain

[*] *e-mail: borja.ferrandez@ua.es*

The 8th International Conference on Carbon for Energy Storage and Environment Protection (CESEP'19) was organized by the Spanish Group of Carbon (GEC) and was held in Alicante, Spain, in October 20-24th, 2019.

First of all, I would like to thank the executive committee, the organizing committee and the local committee for the development of CESEP'19 and to provide a forum for discussion on fundamental and technological scientific aspects of carbon applications related to energy storage and environment protection.

From the Institute of Materials of the University of Alicante, we presented in poster format a study carried out as part of my thesis, under the supervision of Diego Cazorla-Amorós and Emilia Morallón, with title: "Effect of electrode composition and electrolyte flow in electrochemical regeneration of activated carbon in a kilogram batch reactor". This work is being carried out within the H2020 PORTABLECRAC project, whose objective is to offer a flexible solution tackling different niches that will allow an *in-site* regeneration of spent activated carbon by compact/portable prototypes able to adapt to client's needs with economic and environmental positive impacts, determined through LCA and LCC analysis.

Electrochemical regeneration of activated carbon is a greener alternative to the thermal regeneration methods due to the reduction of CO_2 emissions and lower energy consumption. However, the main disadvantage is the difficulty for reproducing it at large scale. The aim of this work was to analyze the effect of anode composition and electrolyte flow on the regeneration efficiency of activated carbon by electrochemical methods in a kilogram scale batch reactor. For this, experiments were carried out with spent activated carbons from drinking water treatment plants and tests were carried out by varying the flow rate and testing different commercial anodes in order to reduce the potential windows of the process and the cost of the electrodes. The conclusions were that the three anodes produced a recovery of porosity of 100% and the higher the electrolyte flow, the higher the recovery of the porosity. For these reasons, the electrochemical regeneration is an efficient method for the regeneration of around 10-15kg of spent AC and could be a real alternative to thermal methods at an industrial level.

Finally, I would like to thank the prize awarded by the Royal Society of Chemistry for the best poster presentations by students at the CESEP 2019 conference, offered by the journal *Energy & Environmental Science.*

Structure-Performance Correlations in Hard Carbons for Sodium-ion Batteries

Hande Alptekin[1], Heather Au[1], Anders Jensen[2], Alan Drew[2], Madalena Titirici[1]

[1] *Department of Chemical Engineering, Imperial College London, London SW7 2AZ, UK*

[2] *School of Physics and Astronomy and Materials Science and Materials Research Institute, Queen Mary University of London, London E14 NS, UK*

[*] *e-mail:* h.alptekin19@imperial.ac.uk; m.titirici@imperial.ac.uk

Introduction

Inexpensive, efficient energy storage systems are essential for the wide-scale successful implementation of renewable energy technologies. Among the various available energy storage technologies, Li-ion batteries (LIB) have been have received considerable attention. However, in terms of largescale application they are not suitable because their price is very high, which is resulting from the uneven distribution of lithium reserve around the world and increasing consumption. Hence, it is crucial to research low-cost secondary batteries for energy storage technologies. Sodium is located below Li in the periodic table, so it possesses similar chemical and physical properties to Li in many aspects. First of all, regarding availability sodium is fourth most abundant element in the Earth's crust, making sodium relatively inexpensive [1-6]. Namely, sodium-based batteries could provide an alternative chemistry to lithium batteries, and might become competitive to lithium-ion batteries. However, there are still inevitable drawbacks related to discovery of suitable anode materials. Optimizing the porous and graphitic structure of the anode materials is important to achieve electrochemically elevated Na-ion battery technology.

Experimental

In this study, we will present the preparation of a series of hard carbon anode materials prepared via the Hydrothermal Carbonisation (HTC) followed by high temperature carbonisation. Applying various carbon precursors, carbonization temperatures, templating agents and dopants results in materials with different pore morphologies, functional groups and graphitisation degrees which were characterised by HRTEM, XPS, Raman and SAXS. The influence of material morphology, type of the dopant and change microstructure on electrochemical performance and Na-storage mechanism were investigated by Galvanostatic Intermittent Titration Technique (GITT) and Electrochemical Dilatometry.

Results and Conclusions

In conclusion, we studied the effect of the carbonisation temperature on the storage mechanism and electrochemical performance of hard carbons obtained via HTC of glucose with citric acid. The Na storage mechanism can be correlated with the pore structure and degree of graphitisation.

Acknowledgements

The authors would like to thank the EPSRC (EP/N509899/1) for funding.

References

[1] Ponrouch, A. *et al.* Non-aqueous electrolytes for sodium-ion batteries. *J. Mater. Chem. A* **3**, 22–42 (2015).

[2] Barpanda, P., Oyama, G., Nishimura, S., Chung, S.-C. & Yamada, A. A 3.8-V earth-abundant sodium battery electrode. *Nat. Commun.* **5**, 4358 (2014).

[3] Zhou, G. *et al.* Graphene-Wrapped Fe_3O_4 Anode Material with Improved Reversible Capacity and Cyclic Stability for Lithium Ion Batteries. *Chem. Mater.* **22**, 5306–5313 (2010).

[4] Lu, L., Han, X., Li, J., Hua, J. & Ouyang, M. A review on the key issues for lithium-ion battery management in electric vehicles. *J. Power Sources* **226**, 272–288 (2013).

[5] Li, L. *et al.* Recent progress on sodium ion batteries: potential high-performance anodes. *Energy Environ. Sci.* **11**, 2310–2340 (2018).

[6] Li, Y., Hu, Y. S., Titirici, M. M., Chen, L. & Huang, X. Hard Carbon Microtubes Made from Renewable Cotton as High-Performance Anode Material for Sodium□Ion Batteries. Advanced Energy Materials 6, 1600659 (2016).