ORGANIC
BATTERY DAYS

8-9 June 2017
Uppsala, Sweden

orgabattdays-17.sciencesconf.org

UPPSALA
UNIVERSITET

UNIVERSITÉ DE NANTES

UNIVERSITÉ de Picardie Jules Verne

cnrs
dépasser les frontières

IMN
INSTITUT DES MATÉRIAUX
JEAN ROUXEL

LG2A
Laboratoire de Glycochimie, des Antimicrobiens
et des Agroressources

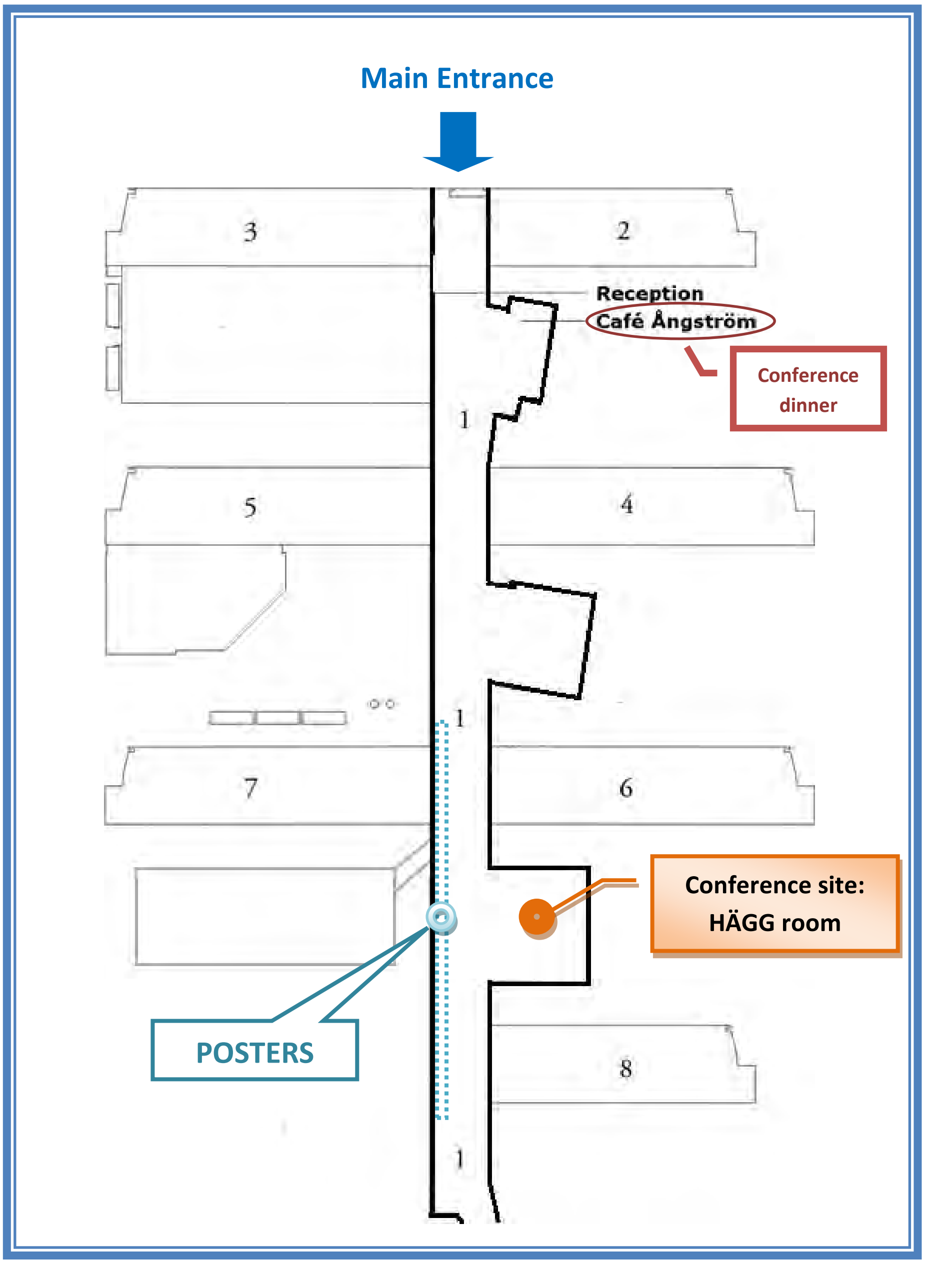
ORGANIC BATTERY DAYS

8-9 June 2017, Uppsala, Sweden

orgabattdays-17.sciencesconf.org

Conference location

Uppsala University - *Ångström Laboratory*



ORGANIC BATTERY DAYS

8-9 June 2017, Uppsala, Sweden

orgabattdays-17.sciencesconf.org

Institutional Partners

UPPSALA UNIVERSITET

UNIVERSITÉ DE NANTES

UNIVERSITÉ de Picardie Jules Verne

CNRS

IMN INSTITUT DES MATÉRIAUX JEAN ROUXEL

LG2A Laboratoire de Glycochimie, des Antimicrobiens et des Agroressources

Platinum Sponsor

ORGANIC BATTERY DAYS 2017

PLATINUM SPONSOR

EVONIK POWER TO CREATE

Sponsors

gammadata

Princeton Applied Research

solartron analytical

BioLogic Science Instruments

Represented by CROMOCOL

BlueSolutions Bolloré

CLARIANT

ARMOR INDUSTRY FOR PEOPLE

DE LA RECHERCHE À L'INDUSTRIE cea

INTERNATIONAL SOCIETY OF ELECTROCHEMISTRY ISE

WELCOME to the Organic Battery Days 2017

It is our great pleasure and honor to welcome you to the Organic Battery Days which is the first European workshop dedicated to electrochemical storage based on the use of redox-active organic species. This new event, jointly organized by Uppsala University (Sweden), the University of Nantes-IMN (France) and the University of Picardy-LG2A (France), aims at improving communication and cooperation among research institutions, academic organizations and manufacturing companies in this emerging field. It will also provide a new opportunity for scientists to share successful experiences and discuss future development. We have compiled a very appealing scientific program highlighting the crucial topics in terms of electrochemical storage systems based on the use of redox-active organic species. We would like to gratefully thank both our institutional and private sponsors, especially Evonik Creavis GmbH, our Platinum Sponsor.

We do thank you very much for attending the Organic Battery Days 2017 and we sincerely hope that you will have a most joyful conference with rewarding exchange of ideas with colleagues, enabling you to get new insights, setting up new collaborative projects or making contacts for job opportunities. And do not miss the opportunity to enjoy the beautiful city of Uppsala.

Philippe Poizot *Daniel Brandell* *Steven Renault* *Franck Dolhem*

Program of oral presentations

Wednesday 7

19:00 **Welcome Party & Registration Desk**

Location: 'The Orangery' (***Orangeriet***, Linnéträdgården Svartbäcksgatan 27, Uppsala)

Thursday 8

08:15 **Registration Desk**

09:15 **Welcome Address**

SESSION 1 **Chairman: Philippe POIZOT**

Keynote Lecture

09:30	**KEY1**	*Polymers for High-density and Fast Charging Batteries* **Kenichi OYAIZU**, Department of Applied Chemistry, Waseda University, Japan

Oral

10:00	**O1**	*Composite electrode materials based on organometallic polymers and polymers bearing free nitroxyl radicals* **Oleg LEVIN**, Saint Petersburg State University, Russia

10:20 COFFEE BREAK

SESSION 2 **Chairman: Franck DOLHEM**

10:40	**O2**	*Analytical tool for organic batteries: in-operando ATR-IR spectroscopy* **Tanja BANCIC**, National Institute of Chemistry, Slovenia
11:00	**O3**	*Organic redox-flow batteries* **Lionel DUBOIS**, Université Grenoble-Alpes, France
11:20	**O4**	*Ionic Modification of TEMPO and its Application in a Hybrid TEMPO/Zn Redox Flow Battery* **Ruiyong CHEN**, KIST Europe & Saarland University, Germany
11:40	**O5**	*Highly water-soluble organic dyes as potential bifunctional analytes for redox flow batteries* **Javier CARRETERO-GONZALEZ**, Institute of Polymer Science and Technology, Madrid, Spain

12:00 LUNCH

SESSION 3 Chairman: Daniel BRANDELL

Keynote Lecture

13:30 KEY2 *Organic materials for lithium battery*
Fannie ALLOIN, University Grenoble Alpes, CNRS-LEPMI, France

Oral

14:00 O6 *Redox polymers as electrode-active materials for organic batteries*
Birgit ESSER, University of Freiburg, Germany

14:20 O7 *Conducting Redox Polymer Based Batteries*
Martin SJODIN, Uppsala University, Sweden

14:40 O8 *Electroactive and electroresponsive polymer films*
Clemens LIEDEL, Max Planck Institute of Colloids and Interfaces, Germany

15:00 COFFEE BREAK

SESSION 4 Chairman: Steven RENAULT

Oral

15:30 O9 *Towards commercially viable organic electrodes?*
Thibaut GUTEL, CEA-LITEN Grenoble, France

15:50 O10 *2,5-Pyridinedicarboxylates as Organic Anode Materials for Li- and Na-Ion Batteries*
Abhinav TRIPATHI, National University of Singapore, Singapore

16:10 O11 *Toward the conception of higher performance conjugated lithium carboxylate as negative electrode for Li-ion battery*
Matthieu BECUWE, University of Picardy Jules Verne & RS2E Amiens, France

16:30 POSTER SESSION

19:00 CONFERENCE DINNER

Location: ‘Café Ångström’ (Uppsala University)

Friday 9

SESSION 5 Chairman: Daniel BRANDELL

Keynote Lecture

09:00 **KEY3** *Polymeric electrode materials for mobile and stationary energy-storage solutions*
Ulrich S. SCHUBERT, Friedrich Schiller University Jena, Germany

Platinum Sponsor

09:30 **PS** *A new Energy Storage Technology for the Internet-of-things*
Andreas WILD, Evonik Creavis GmbH, Germany

Oral

10:00 **O12** *High Capacity Organic Active Materials Carrying Naphthazarin Skeleton*
Masaru YAO, National Institute of Advanced Industrial Science and Technology (AIST), Japan

10:20 **O13** *Synthesis and charge storage characteristics of anthraquinone substituted poly(norbornene)*
Takuma KAWAI, Department of Applied Chemistry, Waseda University, Japan

10:40 COFFEE BREAK

SESSION 6 Chairman: Philippe POIZOT

Keynote Lecture

11:00 **KEY4** *Designing Redox-active Polymers for Safe and Low-cost Energy Storage*
Yan YAO, University of Houston, Texas, USA

11:30 **KEY5** *Stabilisation of redox active organic materials in batteries*
Robert DOMINKO, National Institute of Chemistry, Ljubljana, Slovenia

12:00 LUNCH

SESSION 7 Chairman: Franck DOLHEM

Keynote Lecture

13:30 **KEY6** *Novel -C=N- based Systems for large scale Organic Rechargeable Batteries*
Elizabeth CASTILLO MARTINEZ, University of Cambridge, United Kingdom

Oral

14:00 **O14** *Electrochemical Behavior of PEDOT/Lignin in Ionic Liquid Electrolytes: Suitable Cathode/Electrolyte System for Sodium Batteries*
Nerea CASADO, POLYMAT / University of the Basque Country, Donostia-San Sebastián, Spain

14:20 **O15** *Triptycene-based Multi-Quinone Molecules for High Capacity and High Energy Organic Cathode Materials in Lithium-Ion Battery*
Ji Eon KWON, Seoul National University, South Korea

14:40 **Closing Remarks**

15:00 COFFEE

15:30 **Board of Organic Battery Days – Discussions for the next event**

Abstracts of oral contributions

POLYMERS FOR HIGH-DENSITY AND FAST CHARGING BATTERIES

Kenichi Oyaizu
Department of Applied Chemistry, Waseda University, Tokyo, Japan

oyaizu@waseda.jp

High-density redox polymers bearing organic robust radicals, such as nitroxides, nitronyl nitroxides, verdazyls and galvinoxyls, and anthraquinone derivatives as a redox-active pendant group per repeating unit of non-conjugated main chains undergo reversible charging and discharging when they are applied as electrode-active materials. The charge-storage density of these polymers amounts to the theoretical density calculated for the formula weight-based redox equivalent weight of the repeating unit, which demonstrate that the charge propagation is established throughout the polymer layer by self-exchange reaction of the populated redox-active sites and electroneutralization with the counterion. These polymers have been employed to fabricate the organic batteries, which are characterized by excellent rate performance. Recent research trends in the development of the secondary battery are focused on how to accomplish fast charging and discharging properties while maintaining the energy density of the conventional Li-ion and LiS batteries. Here we report that composite electrodes of the high-density redox polymers and redox-active inorganic oxides such as $LiCoO_2$ and $LiFePO_4$ give rise to high power-rate performance and high density charge storage. Fast charging was accomplished by the potential tuning of the dissimilar materials in the composite electrode. Basic properties of this kind of polymers and potentials of the resulting batteries as well as the prospects for the fast charging devices will be discussed.

COMPOSITE ELECTRODE MATERIALS BASED ON ORGANOMETALLIC POLYMERS AND POLYMERS BEARING FREE NITROXYL RADICALS

P. Vlasov, S. Eliseeva, A. Vereschagin, A. Volkov, A. Konev, Oleg Levin
Department of Electrochemistry, Institute of Chemistry, Saint Petersburg State University
7/9 Universitetskaya nab., St. Petersburg, 199034, Russia

o.levin@spbu.ru

At present, several conceptions of devices for energy accumulation are known, ranging from supercapacitors enabling high power density to accumulators that have much larger energy density but maintain much lesser level of power. Design of novel kind of power sources that would combine the advantages of supercapacitors and accumulators represents an actual task. A possible solution might be creation of novel organic and metalorganic materials with designed functionality. Attractive candidates for application in batteries can be found among polymers bearing organic radical substituents as high-capacitance groups, in particular, radical polymers bearing stable nitroxide-radical groups. The attractiveness of these particular polymers is due to the high potential of charging/discharging and theoretical specific capacitance. An important advantage of such materials over traditional inorganic materials is availability and low cost of the starting materials for the synthesis of the target polymers combined with good mechanical properties of the latter such as flexibility, elasticity and ease of treatment. At the same time, low electron conductivity of materials based on nytroxyde radicals, as well as many other classes of organic cathode materials, hampers their broad application as cathode material. In this connection, creation of novel materials based on nitroxyl radicals that would possess high conductivity while retaining high power density, represents an actual task in the development of new kinds of organic batteries.

Here we present the recent progress in the search for composite materials or macromolecular compounds based on polymer complexes of transition metals possessing system of conjugated π-bonds and polymers with functional group bearing free nitroxyl radical. Creation of such materials solves simultaneously two tasks of the studied problem, namely it enables creation of organic materials with high electron conductivity due to the previously proved fact of high electron conductivity of the polymer complexes, and keeps the high redox capacitance of nitroxyl-radicals based materials by combining these two structural motifs in a single polymer molecule. We have developed composite electrode materials based on mixtures of TEMPO-containing polymers (TEMPO = 2,2,6,6-tetramethyl(piperidin-1-yloxyl)) with polymeric Ni- and Cu- complexes with specific tetradentate ligands (Schiff bases of salicylic aldehyde derivatives with diamines). The composite materials, prepared without addition of inert binders and conductive agents, were shown to possess high rate of charging/discharging both in thin-film systems and lithium ion batteries prototypes. The materials demonstrated excellent stability in different non-aqueous electrolytes as well as in water-based systems, allowing their application in various types of organic batteries.

The work was supported by the Russian Science Foundation (grant #16-13-00038). Scientific research was partially performed at the Research park of St. Petersburg State University: Interdisciplinary Center for Nanotechnology, Center for Chemical Analysis and Materials Research, Chemistry Educational Centre, Magnetic Resonance Research Centre, Centre for X-ray Diffraction Studies, Computing Centre.

ANALYTICAL TOOL FOR ORGANIC BATTERIES: IN-OPERANDO ATR-IR SPECTROSCOPY

Tanja Bancic[a], Jan Bitenc[a], Alen Vizintin[a], Klemen Pirnat[a], Robert Dominko[a]
[a] *National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia*

tanja.bancic@ki.si

Battery development has lately received considerable attention as batteries represent a bottleneck for shift from fossilized fuels to greener alternatives for variety of applications, such as electric vehicles and large grid energy storage. Promising candidates with minimum carbon footprint are organic batteries with many assets: cheaper and synthesis with low overall energy consumption, ease of their chemical modification and also suitability for multivalent-ion batteries as they are not limited by solid-state diffusion, which is the main culprit for a poor performance of inorganic materials in multivalent-ion batteries.

Chemical synthesis and analysis of the electrode material are usually followed by composite formation and its electrochemical evaluation. Batteries often act as a “black box”: we have known input to the system (e. g. current load) and we measure the output (e. g. voltage), but the exact mechanism of the process often remains not well understood. It is of importance to understand all mechanisms occuring during battery cycling and for that we need analytical tools that can monitor battery behaviour during cycling. In-operando attenuated total reflectance infrared (ATR-IR) spectroscopy is an uncommon technique in a battery world, although it can greatly benefit battery research, especially in the field of organic batteries. Without interrupting electrochemical process, we can track material’s changing infrared signal in a modified pouch cell and gain detailed data about the processes, which don’t give significant electrochemical signal, such as redox mechanism, state of health of a battery and potential side reactions. In the contrary of ex-situ IR spectroscopy, we avoid troublesome sample preparation, as they are often unstable in ambient atmosphere.

Polyimides have already shown their electrochemical activity in lithium system. [1–3] Their redox mechanism has been proposed, but this technique allowed us to directly track the changes in the chemical structure and helped us to confirm the proposed mechanism in lithium and magnesium battery.

[1] Z. Song, H. Zhan, Y. Zhou, Angew. Chem. Int. Ed. 49 (2010) 8444 –8448.
[2] P. Sharma, D. Damien, K. Nagarajan, M. M. Shaijumon, M. Hariharan, J. Phys. Chem. Lett. 4 (2013) 3192–3197.
[3] C. Chen, X. Zhao, H.-B. Li, F. Gan, J. Zhang, J. Dong, Q. Zhang, Electrochim. Acta, 229 (2017), 387–395.

ORGANIC REDOX-FLOW BATTERIES

T. Gutel[b], A. Morin[c], I. Mannai[c], J. Charoloy[a], L. Dubois[a]
[a] *Université Grenoble Alpes, INAC-SyMMES-CAMPE, UMR 5819 (CEA/CNRS/UGA)*
F-38054 Grenoble Cedex 9, France
[b]*CEA-LITEN, F-38054 Grenoble Cedex 9, France*
[c] *Commissariat à l'énergie atomique (CEA), 17 rue des martyrs, 38054, Grenoble, cedex 9, France*

lionel.dubois@cea.fr

Due to the strong penetration of intermittent renewable energies (ENR) in the energy production of European countries, it is necessary to increase our electricity storage capacity to a great extent. "Redox flow" batteries (RFB) are large-scale and long-term stationary storage systems for electrical energy. These devices suffer from two important limitations: the low energy density of the redox fluids (low solubility ≈ 1mol.L^{-1}) and the use of expensive and toxic metals such as vanadium. Unlike the US or Korea where several hundred kWh are already installed, RFBs are not very developed in Europe. Several CEA laboratories are working to improve this technique by using redox organic molecules. Some organic molecules are able to exchange several electrons per molecular unit with very fast electrochemical kinetics leading to high electrochemical performances. Moreover, it is possible to adjust their properties, in particular their solubility or their redox potentials, by modifying their molecular formula. New redox function/molecule need to be develop in order to satisfy to all the redox flow technology constrain.

We want to develop symmetric organic RFB in order to explore the real interest of this technological solution in terms of long term stability, power and energy efficiency. In this work solvent blue was chosen as test molecule for our devices.[1] New solvent blue derivatives are under synthesis to try to improve its solubility and the stability of the oxidized form. Focus will be made on the understanding of the redox behavior of the electrolyte component. Monitoring of the electrolyte by UV - Vis. and EPR spectroscopy will be undertaken.

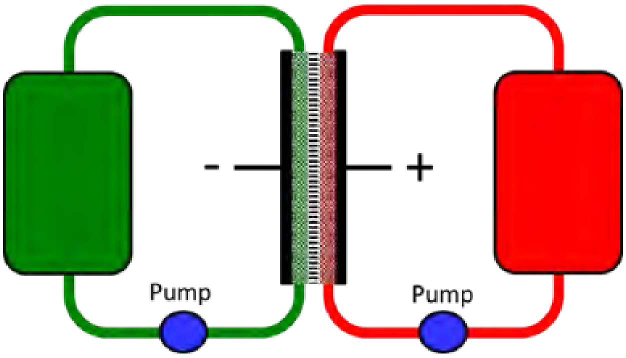


Figure 1: general scheme of a redox-flow battery

[1] Abruna and al. Cornell University, Journal of The Electrochemical Society, 163 (3) A338-A344 (2016)

O4

IONIC MODIFICATION OF TEMPO AND ITS APPLICATION IN A HYBRID TEMPO/Zn REDOX FLOW BATTERY

Ruiyong Chen[a,b], Zhenjun Chang[a,b,c]
[a]*KIST Europe, 66123 Saarbrücken, Germany;* [b]*Transfercenter Sustainable Electrochemistry, Saarland University, 66125 Saarbrücken, Germany;*
[c] *College of Materials Science and Engineering, Jiangsu University of Science and Technology, 212003 Zhenjiang, China.*

r.chen@kist-europe.de

Due to the high modularity, electrochemical energy storage techniques using batteries have received great success for transportable applications, and are promising for large-scale stationary energy storage in the future. In contrast to traditional lead acid and lithium-ion batteries, redox flow batteries can easily be designed to meet the needs of a broad range of applications with long life time and low up-scaling cost. Particularly, redox flow batteries have merits of decoupled energy storage and power generation capability. Electrolyte chemistry is a key consideration for the performance enhancement.[1,2] Compared to the limited number of metal ions suitable for flow batteries,[3,4] a wide range of organic molecules and polymers for flow batteries can be obtained by the diversity of synthetic organic chemistry.[5]

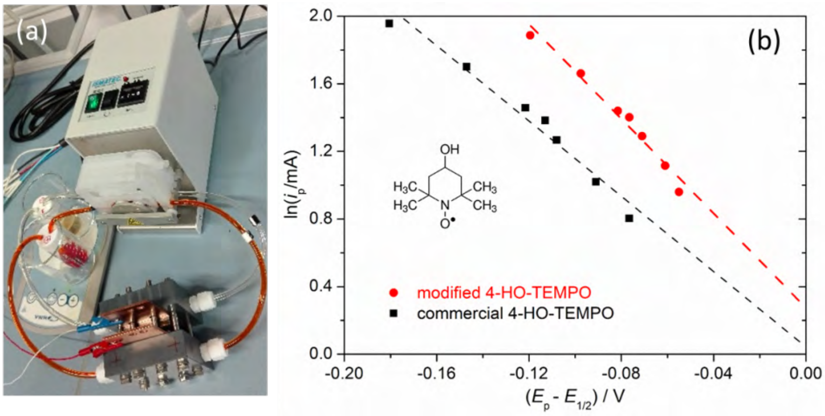


Fig. 1 (a) experimental setup, (b) comparison of reaction rates from the CV measurement.

Herein, we report new electrolytes for redox flow batteries with ionic modification of organic material (4-hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl, 4-HO-TEMPO) to improve the diffusion and kinetic properties of active species.[6] A custom built flow battery (Fig. 1a) with graphite felt as positive electrode, Zn plate as negative electrode and a cross-linked anion exchange membrane was used to evaluated the electrochemical cycling performance. The structure modification was analyzed by means of infrared spectroscopy. The kinetics and reaction rate were examined by cyclic voltammetry (CV, Fig. 1b) and galvanostatic charge/discharge experiments. Compared to commercial 4-HO-TEMPO, faster reaction rate has been achieved for the ionic modified one. Moreover, the feasibility to use organic solid suspension has also been tested.

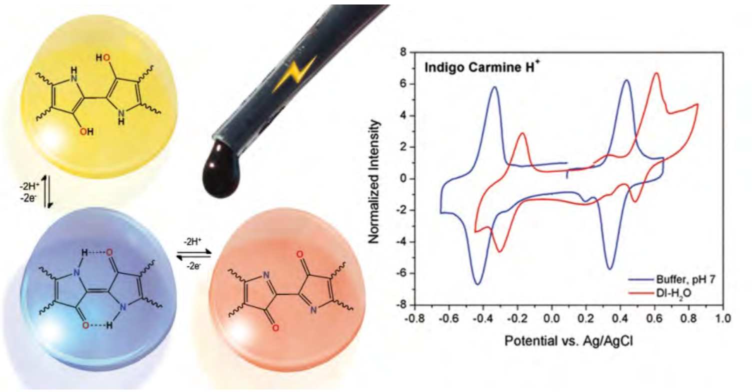
[1] R. Chen, R. Hempelmann, *Electrochem. Commun.* 70 (2016) 56.
[2] R. Chen, R. Hempelmann, The International Flow Battery Forum, Karlsruhe (2016) 22.
[3] M. Skyllas-Kazacos, M. Rychcik, R.G. Robins, et al., *J. Electrochem. Soc.* 133 (1986) 1057.
[4] G.L. Soloveichik, *Chem. Rev.* 115 (2015) 11533.
[5] S. Muench, A. Wild, C. Friebe, B. Häupler, T. Janoschka, U.S. Schubert, *Chem. Rev.* 116 (2016) 9438.
[6] Z. Chang, R. Chen, et al., *to be submitted*.

HIGHLY WATER-SOLUBLE ORGANIC DYES AS POTENTIAL BIFUNCTIONAL ANALYTES FOR REDOX FLOW BATTERIES

Javier Carretero-González[a], Elizabeth Castillo-Martínez[b] and Michel Armand[c]
[a]*Institute of Polymer Science and Technology, Juan de la Cierva 3, 28006, Madrid, Spain*
[b]*Department of Chemistry, University of Cambridge, Lensfield Rd, Cambridge, UK*
[c]*CIC energiGUNE, Alava Technology Park, Albert Einstein 48, Miñano, Álava, Spain*

jcarretero@ictp.csic.es

Dyes such as indigo and anthraquinone derivatives that find extensive use in industrial colorant applications contain electron density donor (–NH– or –OH) and acceptor (>C═O) groups linked by conjugated bonds in their molecular structure, which are responsible for their deep shades. Departing from this stabilized redox state (“push–pull”) requires substantial energy and we found that with a proper choice of aqueous electrolyte these dyes are able to both reversibly oxidize and reduce, developing two-sets of fast two proton–electron transfers separated by ~1 V. These large flat molecules are poorly soluble due to extensive “π” stacking, and the classical strategy of appending a sulphonate (–SO_3Na) group appeared insufficient to reach ≈1 M. Herein, we have further boosted the solubility of these dyes in water up to 1.6 M by replacing Na^+ with an organic cation such as tetrakis(hydroxyethyl)-ammonium $[N(CH_2CH_2OH)_4]^+$ or tetrakis(hydroxymethyl)-phosphonium $[P(CH_2OH)_4]^+$ that are non-chelatable and very hygroscopic while maintaining a reversible charge transfer and a large electrochemical potential window in dilute protic acids (0.1 M $HClO_4$), or in neutral pH buffered aqueous solutions (Britton–Robinson buffer). The corresponding pure salts melt even near ambient temperature. Our findings imply that the same electroactive material could be used as a catholyte and an analyte in a 1 V symmetrical redox flow cell at neutral or close to neutral pH, with all its advantages in terms of cell corrosion and membrane requirements.



[1] J. B. Goodenough, Energy Environ. Sci., 7, (2014) 14–18.
[2] G. L. Soloveichik, Annu. Rev. Chem. Biomol. Eng., 2, (2010), 503–527W.
[3] J. Carretero-González, E. Castillo-Martinez and M. Armand, Energy Environ. Sci, 9, (2016), 3521-3530.

ORGANIC MATERIALS FOR LITHIUM BATTERY

Fannie Alloin[1,2,3], Jean-claude.Leprêtre[1,2,3], Thibault Godet[1,2], Romain Guilmin[1,2], Clemence Iver[1,2]

[1] University Grenoble Alpes, LEPMI, 38000 Grenoble, France
[2] CNRS, LEPMI, 38000 Grenoble, France
3 Réseau sur le Stockage Electrochimique de l'Energie (RS2E), CNRS, FR3459, 33 Rue Saint Leu, 80039 Amiens Cedex, France

Fannie.alloin@lepmi.grenoble-inp.fr

The energy transition, at the heart of the challenges of the century, requires the growing development of electrochemical storage system. Lithium ion batteries have the best performances in terms of energy and power densities. An alternative of the use of inorganic compounds is to develop redox organic materials as positive electrode active material. Many organic materials have been developed for lithium rechargeable batteries as electronic conductive polymers[1-2], nitroxide radical based polymers[3], conjugated carbonyls or carboxylate[4], and quinone[5] based material. The organic materials are today a credible alternative to inorganic materials by their lower cost and toxicity, furthermore due to their versatility *versus* cation species, organic materials can be also used for sodium, magnesium batteries technologies. In this context, the *N*-methylphenothiazine (MPT) is a prime target with the aim of developing redox organic materials useful as positive electrode of lithium-ion battery[6]. The *N*-methylphenothiazine has two reversible systems but only the first one can be exploited in the electrolyte potential stability window. The chemical modification of the MPT, by the incorporation of donating electron groups, lowers the redox couple potential values and allows the use of two electrons. The effect of different moieties in regard to the MPT derivatives redox couples was investigated.

In order to obtain insoluble compounds, polymerizations of the phenothiazine derivatives have been performed and the electrochemical characterizations were done in LP30 (EC/DMC (1/1) $LiPF_6$ 1M).

The organic active materials can also exhibit some interesting spectroscopic properties (i.e. luminescence) which can be advantageously used to help the charge /discharge process of battery. Indeed, once the photon has been absorbed, the excited state of the material undergoes a huge modification of its redox properties. The photonic stimulus leads to both a decrease of the anodic and an increase cathodic potential in correlation with the emission wavelength. We recently demonstrated using boron dipyrromethene derivative polymer deposited onto a tin indium oxide electrode (ITO) that under light illumination, the charge process can be effectuated with a close to 1 Volt gain[7]. The first results obtained in this new strategy will be presented.

[1] J. Wang, C. O. Too, D. Zhou, and G. G. Wallace, *J. Power Sources*, **140**, 162–167 (2005).
[2] K. S. Ryu, K. M. Kim, Y. S. Hong, Y. J. Park, and S. H. Chang, *Bull. Korean Chem. Soc.*, **23**, 1144–1148 (2002).
[3] H. Nishide et al., *Electrochim. Acta*, **50**, 827–831 (2004).
[4] S. Renault, J. Geng, F. Dolhem, and P. Poizot, *Chem. Commun.*, **47**, 2414–2416 (2011)
[5] M. Lécuyer, J. Gaubicher, A.-L. Barrès, F. Dolhem, M. Deschamps, D. Guyomard, P. Poizot, Electrochemistry Communications 55 (2015) 22–25
[6] T. Godet-Bar, J.-C. Leprêtre, O. Le Bacq, J.-Y. Sanchez, A. Deronzier, A. Pasturel, *Phys. Chem. Chem. Phys.* 17 (2015) 25283–25296.
[7] T. Godet-Bar, J.-C. Leprêtre, P. Poizot, F. Massuyeau, E. Faulques, A. Christen, F. Minassian, J. -F. Poisson, F. Loiseau and F. Lafolet, to be published

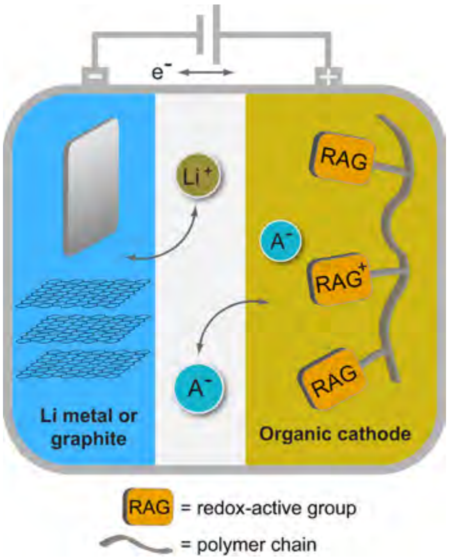
O6

REDOX POLYMERS AS ELECTRODE-ACTIVE MATERIALS FOR ORGANIC BATTERIES

Birgit Esser[a,]*, Martin E. Speer[a], Martin Kolek[b], Fabian Otteny[a], Pia Schmidt[a], Peter M. Bieker[b], Martin Winter[b]
[a] *Institute for Organic Chemistry, University of Freiburg, Albertstr. 21, 79104 Freiburg, Germany*
[b] *MEET Battery Research Center, Institute of Physical Chemistry, University of Münster, Corrensstraße 46, 48149 Münster, Germany*

besser@oc.uni-freiburg.de

In face of the climate change there is a strong and growing demand for the storage of renewable energies. Reliable electricity storage devices such as batteries and electrochemical capacitors are required.[1–3] Organic electrode materials have attracted great interest, as they can be prepared from renewable, sustainable or less-limited resources, they are easy to recycle as well as potentially safer and cheaper to produce, leading to a low carbon footprint.[4–6] A promising class of organic electrode materials are redox polymers – polymers containing groups that can be reversibly reduced or oxidized.[7] In this talk organic redox polymers will be presented containing (heteroaromatic) π-systems as redox-active functionalities.[8] The electrochemical properties of these polymers will be discussed as well as their application as cathode-active materials in batteries.



References:
[1] D. Lindley, *Nature* **2010**, *463*, 18–20.
[2] P. Poizot, F. Dolhem, *Energy Environ. Sci.* **2011**, *4*, 2003–2019.
[3] M. Armand, J.-M. Tarascon, *Nature* **2008**, *451*, 652–657.
[4] Y. Liang, Z. Tao, J. Chen, *Adv. Energy Mater.* **2012**, *2*, 742–769.
[5] Z. Song, H. Zhou, *Energy Environ. Sci.* **2013**, *6*, 2280–2301.
[6] T. B. Schon, B. T. McAllister, P.-F. Li, D. S. Seferos, *Chem. Soc. Rev.* **2016**, *45*, 6345–6404.
[7] S. Muench, A. Wild, C. Friebe, B. Häupler, T. Janoschka, U. S. Schubert, *Chem. Rev.* **2016**, *116*, 9438– 9484.
[8] M. E. Speer, M. Kolek, J. J. Jassoy, J. Heine, M. Winter, P. M. Bieker, B. Esser, *Chem. Commun.* **2015**,*51*, 15261–15264.

CONDUCTING REDOX POLYMER BASED BATTERIES

Martin Sjödin[a], Rikard Emanuelsson[a], Mia Sterby[a], Christian Strietzel[a], Li Yang[a], Hao Huang[a], Huan Wang[a], Xiao Huang[b], Adolf Gogoll[b], Maria Strømme[a]
[a] *Nanotechnology and Functional Materials, Department of Engineering Sciences, The Ångström Laboratory, Uppsala University, Box 534, SE-751 21 Uppsala, Sweden*
[b] *Department of Chemistry - BMC, Biomedical Centre, Uppsala University, Box 576, SE-751 23 Uppsala, Sweden*

martin.sjodin@angstrom.uu.se

Conducting redox polymers (CRPs) are composed of a conducting polymer (CP) backbone and a redox active functional group (RG) and they provide an attractive alternative as organic matter based electrical energy storage materials. The CP backbone renders the material conductive and, due to the large molecular size, prevents material dissolution thus mastering two of the most significant obstacles in achieving powerful and stable battery materials from organic compounds. The RG, on the other hand, can provide high charge storage capacities to the material. Combining CPs with high charge storage capacity RGs thus has the possibility to form powerful materials for battery applications provided that the individual properties of the CP- and the RG component can be preserved and operate in synergy in the CRP. One prerequisite for synergetic RG-CP combinations is redox matching [1]. As CPs are only conducting in their charged state successful RG-CP combinations rely on that the pendant group has a redox potential within the conducting region of the CP backbone, as exemplified by polyphenylthiophene in figure 1.

In this work we present data that explicitly show that redox matching in CRPs is indeed an absolute molecular-design requirement and we present a complete device based on proton cycling chemistries where redox matched CRPs are utilizing both as anode and cathode.

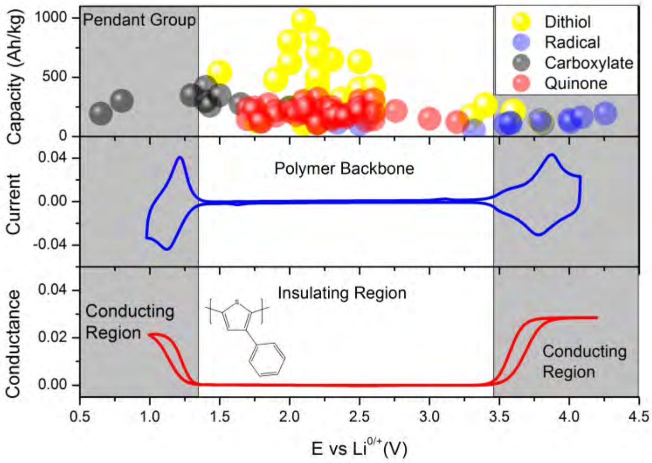


Figure 1: The cyclic voltammetry of polyphenylthiophene (central panel) together with the corresponding in-situ conductance data [2] (lower panel) and the redox potential of known possible RG [3] (upper panel). The conducting regions for this polymer are indicated as grey areas.

[1] R. Emanuelsson, M. Sterby, M. Strømme and M. Sjödin, J. Am. Chem. Soc. (2017) DOI: 10.1021/jacs.7b00159
[2] L. Yang, X. Huang, A. Gogoll, M. Strømme and M. Sjödin, J. Phys. Chem. C 119 (2015) 18956-18963.
[3] Y. Liang, Z. Tao and J. Chen, Adv. Energy Mater. 2 (2012) 742-769.

ELECTROACTIVE AND ELECTRORESPONSIVE POLYMER FILMS

Clemens Liedel
Department of Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Research Campus Golm, 14476 Potsdam, Germany

Clemens.Liedel@mpikg.mpg.de

It is well known in the organic battery community that polymers may carry electroactive groups and serve as redox active moiety in electrode materials. Also in electrolytes, polymers play an increasingly important role. Especially here, block copolymers have drawn many researchers’ attention. This presentation will focus on both and describe model systems for electrolytes and electrodes based on (block co-)polymers.

In block copolymer electrolyte systems, an often neglected question is whether the material is affected by repeated ion flow or by being exposed to an electric field (stationary or gradient). This problem will be discussed in the first part of the presentation. Block copolymers and composites were studied *in situ* while being exposed to constant or varying voltages. Influences of the composition and voltage on the electroresponsive behavior will be discussed.

The second part of the presentation will cover some insights about polymers and block copolymers as electroactive species in electrodes. Redox active species in a polymer based electrode are always mixed with conductive additive and binder, so an approach where multiple functional components are included in one polymer may be interesting for future battery systems. Influences of the composition on the structure and electrochemical behavior will be discussed.

TOWARDS COMMERCIALLY VIABLE ORGANIC ELECTRODES? THE CASE OF PTCLi$_4$

Adriana Iordache,[a] Dominic Bresser,[a,b,c] Sébastien Solan,[a] Vincent Maurel,[b,c]
Michel Bardet,[b,c] Lionel Picard,[1] Lionel Dubois[c,3] and Thibaut Gutel[a]
[a] *CEA, LITEN, F-38054 Grenoble, France*
[b] *CEA, INAC, F-38054 Grenoble, France*
[c] *University Grenoble Alpes, F-38000 Grenoble, France*

thibaut.gutel@cea.fr

Efficient, safe, and, in particular, low cost and sustainable energy storage is one of the major issues for the realization of next generation rechargeable batteries. For this reason, organic electrodes materials are recently attracting continuously increasing attention as it allows for energy-efficient synthesis methods employing widely available and cheap precursors as well as substantially facilitated recycling processes at the end of cycle life.

However, the practical use of this new generation of electrode materials is still hindered by electrolyte solubility problem and the commonly low electronic conductivity. To overcome this latter issue, large amounts of conductive carbon are added, accompanied by relatively low overall active material mass loadings, in sum, resulting in very low volumetric and gravimetric energy densities, being farm from practical viable values and commercial needs.

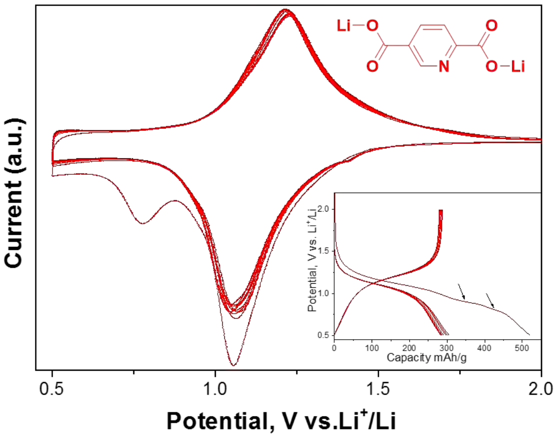
Within the presented study, the well-known salt derivative: PTCLi$_4$ (tetra-lithium perylene-3,4,9,10-tetracarboxylate) was investigated in order to optimize the electrode composition, i.e., the substantial decrease of the conductive additive ratio and the increase of the overall active material mass loading up to commercially relevant values. As a result, electrodes containing only 0.5 wt% of conductive carbon and an areal capacity of up to 1.5 mAh cm^{-2} were realized, revealing stable cycling performance for several hundreds of cycles with excellent energy storage efficiency. It may anticipate that these results present a great step forward towards the realization of commercially viable electrodes, thus paving the way for the implementation of fully sustainable organic active materials in next generation energy storage devices – not limited to solely lithium-ion batteries, but being applicable moreover to sodium- or potassium-ion rechargeable battery technologies

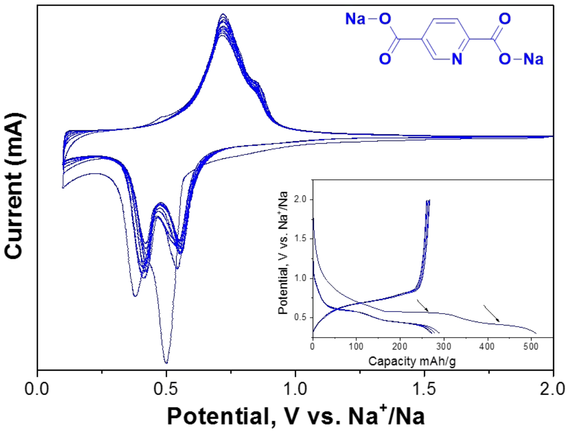
2,5-PYRIDINEDICARBOXYLATES AS ORGANIC ANODE MATERIALS FOR Li- AND Na-ION BATTERIES

Harihara Padhy,* Abhinav Tripathi,* Gajella Satyanarayana Reddy, Yingqian Chen, Johann Lueder, Sergei Manzhos, and Palani Balaya*
Department of Mechanical Engineering, National University of Singapore,
9 Engineering Drive, Singapore-117575

* mpehp@nus.edu.sg; e0010775@u.nus.edu; mpepb@nus.edu.sg

Owing to their structural diversity, molecular level controllability, eco-efficient processability and resource renewability, organic electrode materials have gained much interest for next generation energy storage applications.[1] The most critical issues related to the wide use of organic electrodes are their low electron conductivity and poor cycling performance due to high solubility in organic electrolyte. Focusing on one organic material, namely 2,5-pyridinedicarboxylic acid, we tackle the solubility problem via modifying its molecular structure by forming its lithium/sodium salt. These lithium/sodium salts of 2,5-pyridine carboxylic acid were investigated as anode materials for Li- and Na-ion batteries, respectively. These compounds were characterized by various spectroscopic methods, showing excellent thermal stability up to 500 °C. A combination of electrochemical, spectroscopic and computational studies revealed insertion of two Li^+/Na^+ ions per formula unit (i.e. equal to the theoretical capacity). A reversible capacity of 300 mAh g^{-1} and 270 mAh g^{-1} was achieved in Li- and Na-ion battery, respectively, at 0.05C rate with excellent cyclability. Good rate performance was also achieved with significant capacity retention up to 5C. Moreover, the material shows a better reversible capacity, cyclability and rate performance with respect to terephthalates.[2-3] Computations identified a different mechanism than in terephthalates, resulting in a voltage curve with two plateaus.





[1] T. B. Schon, B. T. McAllister, P.-F. Li, D. S. Seferos, Chem. Soc. Rev. 45 (2016) 6345.

[2] M. Armand, S. Grugeon, H. Vezin, S. Laruelle, P. Ribiere, P. Poizot, J. M. Tarascon, Nature Mater. 8, 2009, 120.

[3] L. Zhao, J. Zhao, Y.-S. Hu, H. Li, Z. Zhou, M. Armand and L. Chen, Adv. Energy Mater. 2 , 2012, 962.

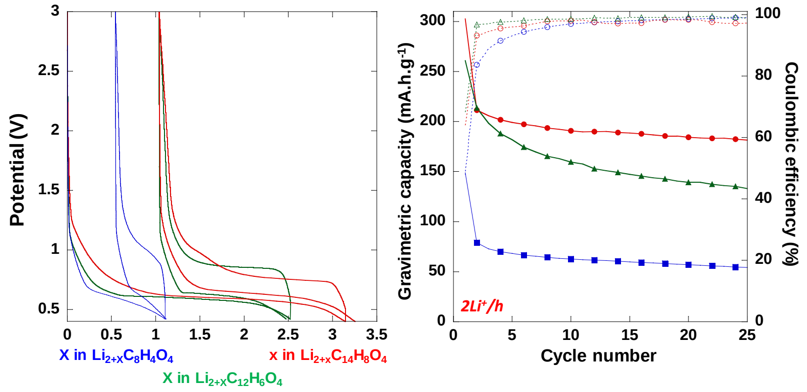
TOWARD THE CONCEPTION OF HIGHER PERFORMANCE CONJUGATED LITHIUM CARBOXYLATE AS NEGATIVE ELECTRODE FOR LI-ION BATTERY

Matthieu Becuwe[a-c], Lionel Fédèle[a-c], Frédéric Sauvage[a-c]
[a] *Laboratoire de Réactivité et Chimie des Solides, UMR CNRS 7314, Université de Picardie Jules Verne (UPJV), 33 rue Saint-leu, 80039 Amiens, France*
[b] *Institut de Chimie de Picardie (ICP), FR CNRS 3085, Amiens, France*
[c] *Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, France*

matthieu.becuwe@u-picardie.fr

Since the pioneer work of Armand *et al.* in 2009,[1] conjugated organic lithium carboxylate gained a particular attention from the scientific community. Indeed, owing to their low operating potential, ideally situated around 0.5-1.0 V vs. Li^+/Li, this family of compounds allows the substitution of the copper-based current collector by an aluminum-based one, inducing a reduction of cost and of the embodiment weight. Additionally, they present also several advantages like low volumetric expansion during cycling, slight toxicity, they can be obtained from an eco-friendly process through CO_2 sequestration and are easily recyclable. With all these properties, lithium carboxylates stand now as a good candidate to compete with classical LTO notably in terms of gravimetric energy density and sustainability but still remain behind in terms of rate capability and conductivity.

During the last five years we focused our attention on the improvement of the rate capability of lithium carboxylate. Starting from classical dilithium terephthalate and based on expected redox mechanism involving radical species, we proposed to replace the simple benzenic core by more delocalized ones to increase the stabilization of radical intermediate species. As a consequence, the rate capability was improved to 2 e^-/h with naphthalene core [2] and reached 10 e^-/h rate with a perylen unit. [3] Very recently, a crystallized 2D-layered organic lithium carboxylate including a 4,4'-biphenyl core as network spacer used as negative electrode material for lithium ion battery has attracted our attention.[4] Firstly, this material exhibits an improved rate capability displaying a gravimetric capacity of 190 mAh.g^{-1} after 25 cycles at 2Li^+ in one hour, and a reduction potential of 0.7V versus lithium. Secondly, a comparison with previous homologs (Li_2-BDC and Li_2-NDC) reveals that such rate capability improvement could also find its origin in the intrinsic properties of the material.



[1] M. Armand, S. Grugeon, H. Vezin, S. Laruelle, P. Ribière, P. Poizot and J.-M. Tarascon, *Nat. Mater.*, 2009, **8**, 120–125.
[2] L. Fédéle, F. Sauvage, J. Bois, J.-M. Tarascon and M. Bécuwe, *J. Electrochem. Soc.*, 2014, **161**, A46–A52.
[3] L. Fédèle, F. Sauvage and M. Bécuwe, *J. Mater. Chem. A*, 2014, **2**, 18225–18228.
[4] L. Fédèle, F. Sauvage, S. Gottis, C. Davoisne, E. Salager, J.-N. Chotard and M. Becuwe, *Chem. Mater.*, 2017, **29**, 546–554.

POLYMERIC ELECTRODE MATERIALS FOR MOBILE AND STATIONARY ENERGY-STORAGE SOLUTIONS

Ulrich S. Schubert
Laboratory of Organic and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Jena, Germany
Jena Center for Soft Matter (JCSM), Friedrich Schiller University Jena, Jena, Germany

ulrich.schubert@uni-jena.de

In times of an ever-growing energy demand, the development of sustainable energy-storage technologies requests more and more attention. Organic electrode materials have proven to be promising alternatives to traditional metals, which are problematic regarding their production and disposal as well as their operational safety and toxicity. Two groups of redox-active compounds are in the focus of our recent research: Stable organic radicals and quinone derivatives. The former impress with superior electrochemical kinetics, leading to short charging times and high discharging power capabilities, and enhanced long-term stability. Quinones, in particular anthraquinones, possess two-electron redox processes, which allow for increased capacities, and feature easily tunable properties through a broad range of possible chemical modifications.

Depending on the desired application, two different approaches of energy storage are utilized in our group: Thin-film devices and redox-flow batteries. Whereas the former are based on a layered arrangement of solid films of the different materials and are destined for high-power, mobile applications, redox-flow systems use large tanks of dissolved materials, mainly used for high-capacity, stationary energy storage. For both modes, redox-active moieties in form of polymers are advantageous. They offer, on the one hand, low solubility and roll-to-roll processability with regard to the cost-efficient fabrication of stable and mechanically flexible thin-film devices. On the other hand, polymers allow the utilization of cheap size-exclusion membranes for redox-flow batteries.

Hence, we developed various polymeric electrode materials, stable radicals as well as anthraquinone-based compounds, for the usage in fully organic thin-film and redox-flow batteries that are environmentally benign and, nevertheless, show superior charging/discharging characteristics.

A NEW ENERGY STORAGE TECHNOLOGY FOR THE INTERNET-OF-THINGS

Andreas Wild[a], Sébastien Cochet[a], Michael Korell[a]
[a] *Evonik Creavis GmbH, Gebäude 1420 / PB18, Paul-Baumann-Straße 1, 45772 Marl, Germany*

andreas.wild@evonik.com

The Internet of Things (IoT) is becoming reality now. Smart objects are entering our personal and professional lives and offer unprecedented opportunities. Low cost and non-toxic power sources with a flexible form factor are key elements for new IoT applications.
Conventional technologies mostly do not meet these requirements.

Creavis, the strategic innovation unit of the Evonik Industries AG, is developing materials for organic polymer batteries, enabling tailor-made solutions for powering the IoT. This new patent-pending technology is targeting IoT applications in markets like health and fitness, wireless sensor networks, and logistics.
Evonik's materials for flexible organic polymer batteries are metal-free, environmentally benign and can be processed via printing technologies. This allows for a seamless integration of the battery into the production process, creating new dimensions of design freedom.

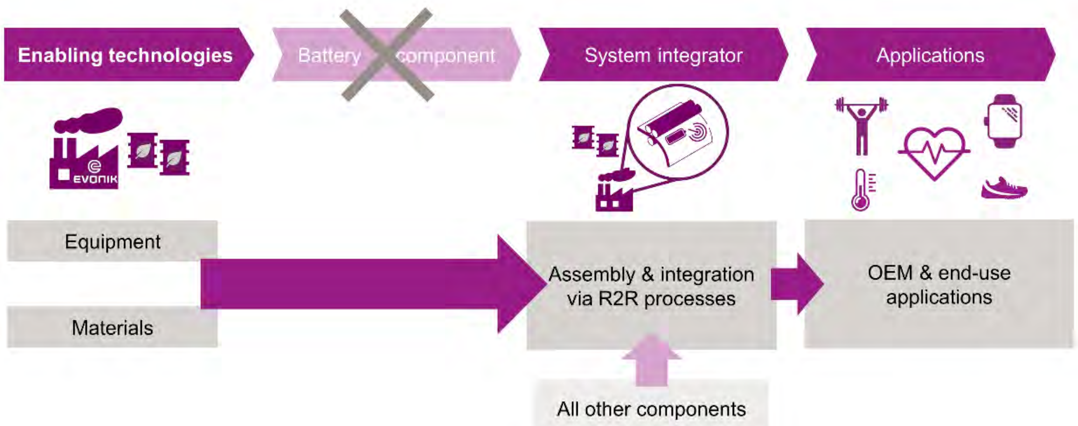


Figure 1. Printable, integrated batteries enable a disruptive change in the value chain of powered smart devices.

O12

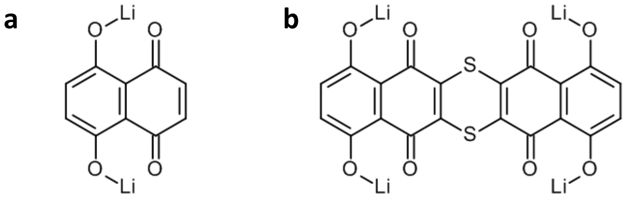
HIGH CAPACITY ORGANIC ACTIVE MATERIALS CARRYING NAPHTHAZARIN SKELETON

Masaru Yao*, Hisanori Ando, Tetsu Kiyobayashi, and Nobuhiko Takeichi
National Institute of Advanced Industrial Science and Technology (AIST),
1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan
m.yao@aist.go.jp

One of the recent requirements for the current rechargeable lithium battery system is to reduce the amount of minor metal-based materials. Our strategy for this issue is to replace the minor-metal oxides-based positive-electrode with redox active organic quinone derivatives [1-3]. In this study, we focused our attention on the naphthazarin (5,8-dihydroxy-1,4-naphthoquinone) skeleton as a redox unit capable of a four-electron transfer redox reaction, which should lead to large capacity up to about 500 mAh/g. The lithium salt of naphthazarin itself (**1**) and its dimer fused by dithiin ring (**2**) (Fig. 1) were prepared and their battery performance was examined.

The electrode using **1** showed a high capacity; however, its cycle stability was poor. On the other hand, the dimer **2** exhibited an improved performance as shown in Fig. 2. The initial capacity was 416 mAh/g which is close to the theoretical value based on assuming an eight-electron transfer reaction of **2**. Also, **2** showed a stable cycle-life performance: it maintained 380 mAh/g after 20 cycles. As we previous reported, small quinone derivatives easily dissolve in the electrolyte solutions during cycling, which results in a poor cycle-life. In the present study, the dimerization is considered to suppress the dissolution and effectively improve the cycle stability.

The use of such multi-electron transfer reaction and the extension of the molecular plane will be a guide for designing a new organic active material that can satisfy both the high energy density and long cycle-life requirements.



1 **2**

Fig. 1. Chemical structures of (a) naphthazarin dilithium salt: **1** and (b) its dimer: **2**.

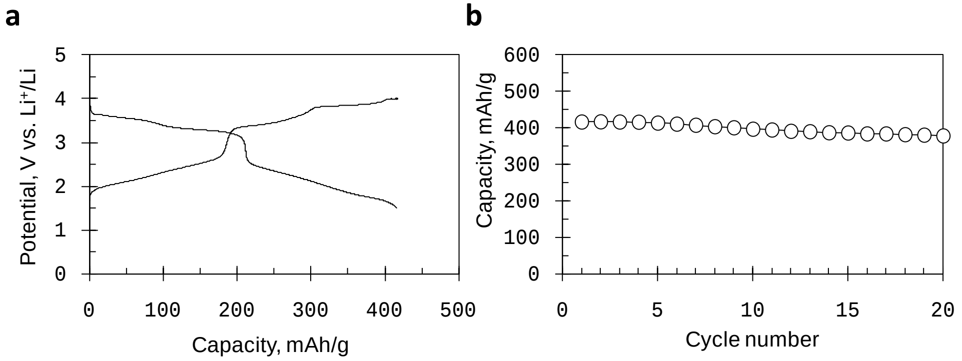


Fig. 2. Battery performance of the electrode using **2**. (a) Typical charge/discharge curves during early cycling. (b) Cycle-life performance. (Current density: 20 or 50 mA/g, Temperature: 30°C.)

References:

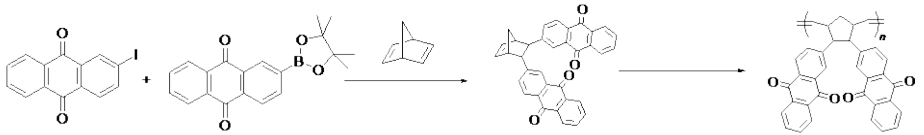
[1] M. Yao, H. Senoh, S. Yamazaki, Z. Siroma, T. Sakai, K. Yasuda, J. Power Sources, 195 (2010) 8336–8340.
[2] M. Yao, S. Yamazaki, H. Senoh, T. Sakai, T. Kiyobayashi, Mater. Sci. Eng. B, 177 (2012) 483–487.
[3] M. Yao, H. Ando, T. Kiyobayashi, Energy Procedia, 89 (2016) 222–230.

SYNTHESIS AND CHARGE STORAGE CHARACTERISTICS OF ANTHRAQUINONE SUBSTITUTED POLY(NORBORNENE)

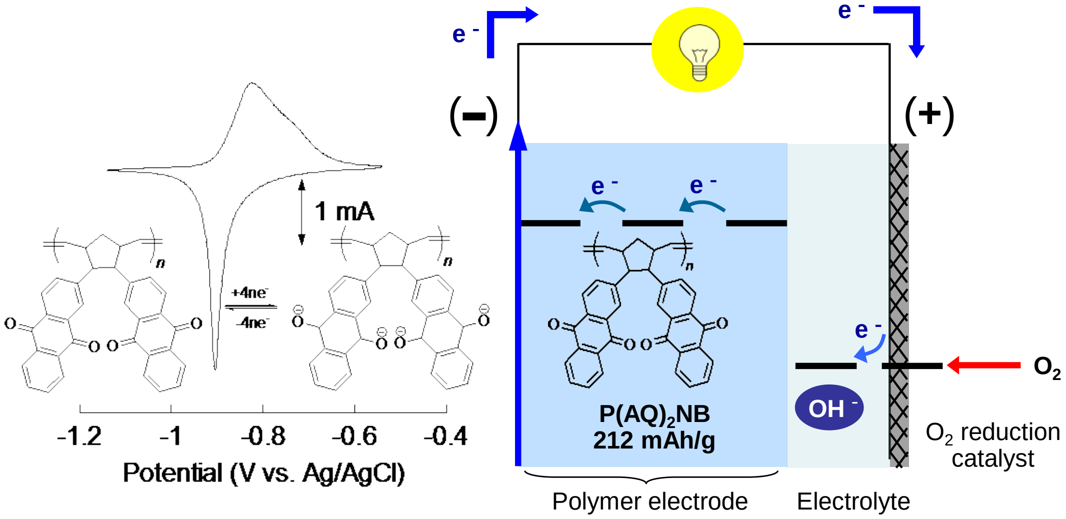
Takuma Kawai, Kenichi Oyaizu, Hiroyuki Nishide
Polymer Chemistry Lab. Department of Advanced Science and Engineering, Waseda University, Tokyo 169-8555, Japan

faith.is.4love@asagi.waseda.jp

We have previously reported that polymers densely substituted with anthraquinone (AQ) shows reversible two-electron redox behavior at a negative potential (< -0.8 V)[1]. Based on the high charge storage characteristic and stability of AQ in strong alkaline aqueous solutions, we have applied them to the anode of a polymer-air secondary battery[2]. In this report, to obtain a polymer with high capacity and stability, we synthesized poly(dianthraquinone substituted norbornene) PQNB and analyzed its electrochemical characteristics. Dianthraquinone substituted norbornene was synthesized from 2-Iodoanthraquinone, 2-Pinacolatoboron anthraquinone, and 2,5-Norbornadiene. PQNB was synthesized via ring-opening metathesis polymerization without unfavorable side-reactions ($M_w = 6.0\times10^5$). The polymer gave reversible redox behavior at $E_{1/2}$ = -0.86 V vs. Ag/AgCl in aqueous and at -1.1 and -1.4 V vs. Ag/AgCl in organic solutions. A layer of PQNB coated on GC substrate was fully charged and discharged in several seconds, and it maintained the initial capacity after 500 cycles of charge and discharge. PQNB was applied as the anode of a rechargeable air battery and showed no capacity decrease even after few hundred cycles.



Scheme



[1] W. Choi, D. Harada, K. Oyaizu, H. Nishide, J. Am. Chem. Soc., 133 (2011) 19839-19843
[2] T. Kawai, K. Oyaizu, H. Nishide, Macromolecules., 48 (2015) 2429-2434

DESIGNING REDOX-ACTIVE POLYMERS FOR SAFE AND LOW-COST ENERGY STORAGE

Yan Yao
Department of Electrical and Computer Engineering, University of Houston, Houston, Texas, 77204, USA.

yyao4@uh.edu

Safe, low-cost, and long-cycle-life rechargeable batteries are key enabling components for grid scale energy storage. Organic redox materials are promising due to the attractive features of high theoretical capacity, potentially low-cost, recyclable, and tunable properties that can be designed by modifying chemical structures. In this talk, I will first present a "π-conjugated redox polymer" (N2200) simultaneously featuring a π-conjugated backbone and integrated redox sites that can be stably and reversibly n-doped to a high doping level of 2.0. N2200 delivers 95% of its theoretical capacity at a high rate as well as 96% capacity retention after 3000 cycles of deep discharge−charge. I will then discuss a microscopic understanding of how ions, electrons, solvents interact with polymer chains during electrochemical process through a combined electrochemical, morphology, NMR, and charge transport study. Finally, I will demonstrate a class of polymeric electrode materials that enable long-cycle-life aqueous batteries that address the key limitations of current aqueous batteries.

STABILISATION OF REDOX ACTIVE ORGANIC MATERIALS IN BATTERIES

Robert Dominko
National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia

robert.dominko@ki.si

Rechargeable batteries based on the redox active organic compounds have several advantages compared to the classical inorganic insertion or conversion. They are considered as a cheap active material that can be obtained from different processes with low energy consumption. Organic redox active materials represent a big undiscovered field which enables sustainable approach and large scale applications. Their theoretical specific capacity can be more than 600 mAh/g and they are considered as safe active material. Operation voltage is typically between 2-3.5V versus metallic lithium or substantially lower if other alkali metals are used as a negative electrode. Nevertheless, organic redox active materials are not in the commercial products due to relative fast capacity fading caused by dissolution and potentially due to low volumetric energy density. Dissolution problem can be tuned either by grafting small moieties on non-soluble surface or by polymerisation. Both approaches are studied in our laboratory and it will be discussed. In this case a special attention should be paid to the accessibility of cations and electrons to obtain full capacity. Another possibility to stabilize capacity of organic based batteries is use of solvent with negligible or limited solubility of organic moieties.

NOVEL -C=N- BASED SYSTEMS FOR LARGE SCALE ORGANIC RECHARGEABLE BATTERIES

Elizabeth Castillo-Martinez
Prof. Grey Group, Department of Chemistry, The University of Cambridge
Lensfield Road, CB2 1EW, Cambridge

ec469@cam.ac.uk

Organic based batteries represent an affordable and abundant alternative to conventional batteries based in inorganic materials. Thus, they are key for the development of large scale electrochemical energy storage where energy density is not a constrain. In addition to their abundance, organic electrodes are very versatile since their redox voltage can be tuned by changing the conjugation length or by the presence of functional groups with different electron donating or withdrawing ability [1].
Among organic and metallorganic materials, those containing >C=N- units, although less explored than other organic functionalities, are showing promising performance for their application in EES systems. Indeed -C≡N- containing metallorganic compounds, such the Prussian Blue and its analogues [2] have shown excellent cathode performance in Na-ion based batteries and they have been broadly reported and patented by Alveo Energy or SHARP America [3]. Interestingly, >C=N- containing organic phases had remained unexplored for battery applications till recently. In the following presentation, I will show several examples of recent developments in which pi conjugated/>C=N- based electrode materials show good electrochemical performance for Na-ion batteries. They will cover from the polymeric Schiff-bases [4] to hybrid oligomeric Schiff bases with carboxylate end-groups [5], both systems able to store Na ions at voltages low enough to be used as anodes in Na-ion batteries. Current understanding of their mechanisms of Na insertion in organic media will be discussed against the Na insertion mechanisms into carbonyl units [6]. In a different vein, the application of organics in solution for redox flow batteries will be shown as well [7].

[1] V. Oltean *et al.* *"Sustainable Materials for Sustainable Energy storage: Organic Na Electrodes" Mat.* **9**, 142 (**2016**)

[2] Y. Lu et al. "*Prussian blue: a new framework of electrode materials for sodium batteries*" *Chem. Comm.* **48** 6544 (**2012**)

[3] US2012/0328936 A1;US2014/0050982 A1

[4] E. Castillo-Martínez, J. Carretero-González, M. Armand, "*Poly-Schiff bases as low voltage redox centres for sodium ion batteries*" *Angewandte Chemie Int. Ed.,* **53**, 5341-5345 (**2014**)

[5] M. Lopez-Herráiz*, et al*, "*Oligomeric-Schiff bases as negative electrodes for sodium ion batteries: unveiling the nature of their active redox centers*" *Energy and Environmental Science,* **8**, 3233-3241 (**2015**).

[6] X. Wu, S. Jin, Z. Zhang, L. Jiang, L. Mu, Y.-S. Hu, H. Li, X. Chen, M. Armand, L. Chen and X. Huang, *"Unraveling the storage mechanism in organic carbonyl electrodes for sodium-ion batteries" Sci. Adv.*, 2015, **1**, e1500330–e1500330.

[7] J. Carretero-González, E. Castillo-Martínez, M. Armand, "*Highly water-soluble three-redox state organic dyes as bifunctional analytes" Energy and Environmental Science* **,** **9**, 3521-3530 (**2016**).

ELECTROCHEMICAL BEHAVIOR OF PEDOT/LIGNIN IN IONIC LIQUID ELECTROLYTES: SUITABLE CATHODE/ELECTROLYTE SYSTEM FOR SODIUM BATTERIES

Nerea Casado[a], Matthias Hilder[b], Cristina Pozo-Gonzalo[b], Maria Forsyth[b],
David Mecerreyes[a,c]
[a] *POLYMAT, University of the Basque Country UPV/EHU, Joxe Mari Korta Center, Ave. Tolosa 72, 20018 Donostia-San Sebastián (Spain)*
[b] *ARC Centre of Excellence for Electromaterials Science, IFM-Institute for Frontier Materials, Deakin University, 75 Pigdons Road, Geelong 3216 (Australia)*
[c] *Ikerbasque, Basque Foundation for Science, E-48011, Bilbao (Spain)*

nerea_casado001@ehu.eus

Organic electrode materials, made of redox-active polymers are promising candidates for novel energy storage, as they are relatively inexpensive and diverse.[1] Organic materials exhibit higher rate capability than the current oxides and inorganic phosphates materials.[2] Moreover, they present low toxicity, processability, and recyclability, which make them good candidates to meet the challenging demand of green batteries.

Biomass-derived polymers, such as lignin, contain quinone/hydroquinone redox moieties that can be used to store charge. Composites based on the biopolymer lignin and several conjugated polymers have shown good charge-storage properties. However, their performance has been only studied in acidic aqueous media limiting their applications mainly to supercapacitors.

In this study, we show that PEDOT/lignin (PEDOT: poly(3,4-ethylenedioxythiophene)) biopolymers are electroactive in aprotic ionic liquids (ILs). The electrochemical activity and cycling of PEDOT/lignosulfonate electrodes are investigated in a series of four ILs composed of the combination of an imidazolium ($EMIm^+$) and pyrrolidinium ($BMPyr^+$) cation with bis(trifluoromethylsulfonyl) imide ($TFSI^-$) and bis(fluorosulfonyl)imide (FSI^-) anion. The effects of water and sodium salt addition to the ILs are investigated to obtain optimum electrolyte systems for sodium batteries. The final goal is to demonstrate the concept of a new battery cell using PEDOT/lignin as cathode material, the optimized IL as electrolyte, and a sodium anode.[3]

[1] N. Casado, G. Hernández, H. Sardon, D. Mecerreyes, Prog. Polym. Sci. 52 (2016), 107– 135.
[2] Z. Song, H. Zhou, Energy Environ. Sci. 6 (2013) 2280 – 2301.
[3] N. Casado, M. Hilder, C. Pozo-Gonzalo, M. Forsyth, D. Mecerreyes, ChemSusChem (2017), DOI: 10.1002/cssc.201700012.

TRIPTYCENE-BASED MULTI-QUINONE MOLECULES FOR HIGH CAPACITY AND HIGH ENERGY ORGANIC CATHODE MATERIALS IN LITHIUM-ION BATTERY

Ji Eon Kwon[a*],Chang Seok Hyun[b], Young Jun Ryu[b], Byeong-Kwan An[b*], Soo Young Park[a*]
[a] *Department of Materials Science and Engineering, Seoul National University*
[b] *Department of Chemistry, The Catholic University of Korea*

mracle2@snu.ac.kr

Organic electrode materials have attracted great attention in recent years due to their promising advantages in low-cost, natural abundance, environmental friendliness, and structural diversity. Particularly, organic molecules based on conjugated quinones are believed to be the most promising because of their high redox reversibility as well as high theoretical capacity. For example, *p*-benzoquinone (BQ) is the simplest π-conjugated quinone molecule possessing the lowest molecular weight (MW = 108.10 g/mol) that undergoes reversible reduction with two electrons. The theoretical specific capacity of BQ as electrode-active material is calculated to as high as 496 mAh/g. However, its high solubility in polar solvents and rather high vapor pressure at room temperature ($P_{\mathrm{BQ,\ 25°C}}$ = 0.1 mmHg) significantly limit its practical use as electrode material in lithium ion batteries.

To address this issues, several strategies have been proposed such as polymerization of BQ units and/or to synthesize bigger size molecules that contain multiple BQ units. But, these methods inevitably bring about significant loss of the specific capacity due to increase of redox-inactive weight and suffer from low utilization of redox-active sites as well.

Here, we propose a new molecular design strategy to achieve both high specific capacity and energy cathode materials for lithium ion battery using triptycene molecular scaffold. A series of triptycene derivatives containing multiple BQ units in a rigid tripod structure are synthesized and their multi-redox properties are thoroughly investigated by both theoretical DFT calculation methods and electrochemical analyses. It should be noted that three dimensional arrangements of BQ units of the triptycenes not only facilitate highly reversible access to a large number of redox states but also raise the redox potential. Finally, practical application potential of the triptycenes as cathode materials are evaluated in the 2032-type lithium-ion coin cells. Particularly, an electrode containing triptycene-tribenzoquinone (TT) molecules delivers a discharge capacity of 387 mAh/g and an energy density of 1032 Wh/kg, which are one of the highest values among the reported organic cathodes so far, at 0.1 C-rate. It clearly shows two charge/discharge plateaus at 2.6/2.5 V and 3.0/2.9 V, respectively.

List
of poster presentations

List of Posters

P0 *Exploring Exotic Organic Electrode Materials for Rechargeable Lithium Batteries*
Alia Jouhara, University of Nantes, France

P1 *Heteroaromatic redox polymers as electrode materials for batteries*
Fabian Otteny, University of Freiburg, Germany

P2 *π-Conjugated Redox Polymers as Electrode Materials for Organic Batteries*
Pascal Acker, University of Freiburg, Germany

P3 *Investigating the electrochemical behavior of kraft lignin for sustainable electrode materials*
Saowaluk Chaleawlert-Umpon, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany & National Nanotechnology Center, Pathumthani, Thailand

P4 *Electrochemical Properties of PEDOT-Based Conducting Redox Polymers*
Mia Sterby, Uppsala University, Sweden

P5 *Polyviologen–Graphene Nanocomposites for Flexible and High–Volumetric Density Organic Batteries*
S. Mohsen Beladi-Mousavi, University of Osnabrück, Germany

P6 *Porphyrin complex as self-conditioned electrode material for high performance energy storage*
Ping Gao, Helmholtz Institute Ulm (HIU), Germany

P7 *Modulites – Monolithically integrated electrochemical energy storage modules. Prototypes with passive balancing*
Mats Sandberg, RISE Acreo AB, Norrköping, Sweden

P8 *Tetrazine as a New Redox-active Group for Organic Electrode Materials in Li-ion Battery*
Dong Joo Min, Seoul National University, Korea

P9 *A Study on the Interfacial Chemistry of Organic Electrodes in Li- and Na-Batteries*
Viorica Alina Oltean, Uppsala University, Sweden

P10 *PFQ polymer – problematic low swelling*
Klemen Pirnat, National Institute of Chemistry, Ljubljana, Slovenia

P11 *Rechargeable lithium-ion batteries using benzoquinone derivatives as the cathode active materials*
Hiroshi Matsubara, Osaka Prefecture University, Japan

P12 *All-Organic Proton Batteries from Conducting Redox Polymers*
Rikard Emanuelsson, Uppsala University, Sweden

P13 *Effect of mass loading on pseudocapacitive behavior of polyaniline*
Elena Tomsik, Institute of Macromolecular Chemistry, Prague, Czech Republic

P14 *Boosting the Capacity of All-Organic Paper Supercapacitors Using Wood Derivatives*
Jesper Edberg, Linköping University, Sweden

P15 *Understanding doping strategies in the design of organic electrode materials for Li and Na ion batteries: an electronic structure perspective*
Johann Lüder, National University of Singapore, Singapore

P16 *Conducting Redox Polymer Batteries – Challenges and possibilities*
Christian Strietzel, Uppsala University, Sweden

P17 *Insights on the mechanism of organic electrodes superlithiation from first-principles theory*
C. Moyses Araujo, Uppsala University, Sweden

P18 *An electrolyte study on* Na_2BDA *anode for Na-based organic batteries*
Francesca Colò, Politecnico di Torino, Italy & Uppsala University, Sweden

P19 *Fundamental study of Terephthalate-Functionalized Poly(3,4-ethylenedioxythiophene) conducting redox polymer*
Huan Wang, Uppsala University, Sweden

P20 *Electrochemically polymerized Ni-complexes with salen type ligands as monocomponent electrode material for LIB*
Svetlana Eliseeva, Saint Petersburg State University, Russia

P21 Organic conductive polymers as modifier of the properties of cathode and anode materials of LIA
Svetlana Eliseeva, Saint Petersburg State University, Russia

P22 *Substituent Effect on Redox Potential of Small Organic Molecules: Toward high voltage all organic Li-ion battery*
A.-E. Lakraychi, University of Picardy Jules Verne, Amiens, France

P23 *Quinone-based cathode materials for high-voltage magnesium batteries*
Zhirong Zhao-Karger, Helmholtz Institute Ulm (HIU), Germany

P24 *Potential tuning in quinone-pyrrole dyad based conducting redox polymers*
Hao Huang, Uppsala University, Sweden

P25 *New Active Polymer for metal ion batteries based on Cyclooctatetraene*
Pierre Ranque, Delft University of Technology, The Netherlands & Alistore - European Research Institute, Amiens, France

P26 *Sulfonated quinones redox couples for application in aqueous redox flow batteries*
Petr Mazúr, University of West Bohemia Pilsen, Czech Republic

P27 *Use of copper phthalocyanine to enhance lithium/carbon monofluoride battery performance*
Joseph P. Fellner, Air Force Research Laboratory, Wright-Patterson AFB, Ohio, USA

P28 *Tuning critical characteristics of NFC-PEDOT supercapacitors*
Dagmawi Belaineh, Linköping University, Norrköping, Sweden

P29 *Dual anion-cation reversible insertion in bipyridinium-diimide negative electrode active materials for aqueous battery*
Sofia Perticarari, University of Nantes, France

P30 *Lithium-doped polyaniline as conducting, redox active component of positive electrodes*
Pablo Jiménez, University of Nantes, France & University of Picardy Jules Verne, Amiens, France

P31 *Reconsidering interactions in redox polymers*
Martin Kolek, University of Muenster, Muenster, Germany

Abstracts of poster presentations

EXPLORING EXOTIC ORGANIC ELECTRODE MATERIALS FOR RECHARGEABLE LITHIUM BATTERIES

Alia Jouhara[a], Nicolas Dupré[a], Dominique Guyomard[a], Franck Dolhem[b],
Philippe Poizot[a,c]
[a] *Institut des Matériaux Jean Rouxel (IMN), UMR CNRS 6502, Université de Nantes, 2 rue de la Houssinière, B.P. 32229, 44322 Nantes Cedex 3, France*
[b] *Laboratoire de Glycochimie, des Antimicrobiens et des Agroressources (LG2A), UMR CNRS 7378, Université de Picardie Jules Verne, 33 rue Saint-Leu, 80039 Amiens Cedex, France*
[c] *Institut Universitaire de France (IUF), 103 bd Saint-Michel, 75005 Paris Cedex 5, France*

Alia.Jouhara@cnrs-imn.fr

The Li-ion battery technology constitutes a reliable system for electricity storage displaying particularly high energy density and design flexibility. Widely used in “nomadic” electronic devices, such batteries also appear to be an important element to mitigate CO_2 releases i) as a promising power source for advanced electric vehicles and ii) as a potential buffer energy storage system to manage the intermittent renewable energy resources (both on- and off-the-grid). Thus the world production of Li-ion batteries is expected to keep on growing. However, whatever the considered technology, common electrode reactions involve redox-active inorganic materials especially metal-based electroactive compounds obtained from non-renewable resources (ores) whereas typically synthesized by ceramic route. At large-scale perspectives, the environmental impact of such Li-ion batteries could be significant. A possible alternative can be foreseen in the use of organic active materials. Indeed, switching from inorganic to organic matter-based electrode materials could enable a true possibility of preparation from renewable resources and eco-friendly processes coupled with a simplified recycling management. Moreover, the richness of organic chemistry provides great opportunities for designing novel and innovative electrode materials[1] . Today, a large number of organic compounds are being considered as electrode materials and display good electrochemical behavior such as quinones, amines or carboxylate-based molecules[1,2]. They also offer different electrochemical activities with both *n*- and *p*-type systems[3].

In this contribution, we report on the syntheses and characterizations of exotic organic electrode materials and in particular two compounds of the quinone family based on aromatic core structures such as triptycene and iptycene[4].

References:
[1] S. Renault, S. Gottis, A.-L. Barrès, M. Courty, O. Chauvet, F. Dolhem, P. Poizot, Energy Environ. Sci. 6 (2013) 2124.
[2] E. Deunf, P. Moreau, E. Quarez, D. Guyomard, F. Dolhem, P. Poizot, J. Mater. Chem. A. 4, (2016) 6131–6139.
[3] K. Deuchert, S. Hünig, Angew. Chem., Int. Ed. Engl. 17, (1978) 875–886.
[4] X.-Z. Zhu, C.-F. Chen, J. Org. Chem. 70, (2005) 917.

HETEROAROMATIC REDOX POLYMERS AS ELECTRODE MATERIALS FOR BATTERIES

Fabian Otteny[a], Martin Kolek[b], Pia Schmidt[a], Martin Winter[b], Peter M. Bieker*,[b]
and Birgit Esser*,[a]
[a] *Institute for Organic Chemistry, University of Freiburg,*
Albertstraße 21, 79104 Freiburg, Germany.
[b] *Institute for Physical Chemistry, MEET Battery Research Center,*
Corrensstraße 46, 48149 Münster, Germany.

fabian.otteny@mars.uni-freiburg.de

Due to the increasing demand for efficient electric energy storage the development of new redox-active materials for rechargeable (secondary) batteries is required.[1] In contrast to common inorganic materials employing heavy metals, organic compounds can be prepared from renewable or less limited resources, they are potentially safer and cheaper to produce.[2] Furthermore they are mechanically flexible and easier to recycle.[3]

A promising class of organic electrode materials are polymers, which contain redox-active groups (RAG). Herein, we present the syntheses as well as electrochemical properties of several redox polymers containing heteroaromatics as redox-active components, which undergo reversible redox processes. Depending on the redox potential of the redox-active groups, the corresponding polymers can be used as anode-active or cathode-active material in a composite cell, which could lead to an all-organic battery system (Fig. 1).

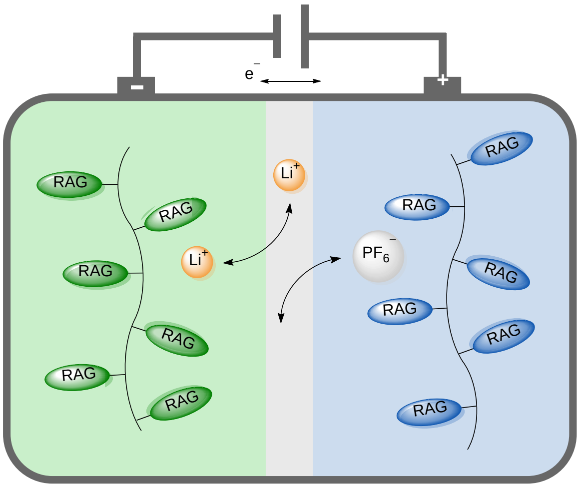


Fig. 1: Schematic drawing of an all-organic battery with redox-active polymers as electrode materials.

References:
[1] D. Lindley, Nature 463 (2010) 18–20.
[2] P. Poizot, F. Dolhem, Energy Environ. Sci. 4 (2011) 2003–2019.
[3] H. Nishide, K. Oyaizu, Science 319 (2008) 737–738.

P2

π -CONJUGATED REDOX POLYMERS AS ELECTRODE MATERIALS FOR ORGANIC BATTERIES

Pascal Acker, Birgit Esser*
Institute for Organic Chemistry, University of Freiburg, Albertstraße 21, 79104 Freiburg, Germany

pascal.acker@mars.uni-freiburg.de

The continuously increasing consumption of energy, especially electric power, and the unsteadiness of renewable energy sources like wind or solar power are responsible for the growing demand for suitable energy storage technologies. This development is not only important to secure a power supply network, but also to power everyday electric devices such as mobile phones, laptops and cars.[1,2] In this context organic batteries offer many advantages such as low production costs, ready availability and recyclable materials, tuneable properties (flexibility, thickness, weight) and lower toxicity, especially when compared with common state-of-the-art inorganic batteries.[3]

In order to build such batteries, redox-active organic materials are required. A relatively new and unexplored category of electrode materials is that of π -conjugated redox polymers, which consist of redox-active groups incorporated into a π -conjugated polymer backbone. Applying this concept, major drawbacks of π-conjugated polymers (sloping redox potential) or redox polymers (minor conductivity) can be eliminated.[4,5] Herein we present the syntheses and properties of such π -conjugated redox polymers and their study for usage in battery systems.

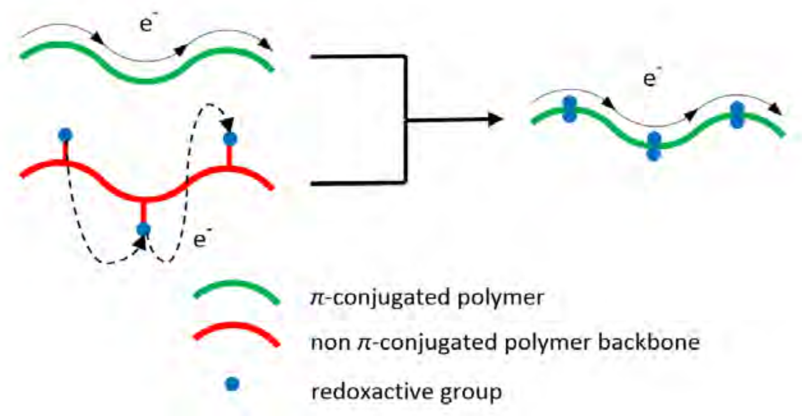


Figure 1: Schematic representations of a π -conjugated polymer (left, top), a redox polymer (left, bottom) and a π -conjugated redox polymer (right).

References:
[1] L. Caspeta, N. a. a. Buijs, J. Nielsen, Energy Environ. Sci. 6 (2013) 1077–1082.
[2] D. Larcher, J.-M. Tarascon, Nat. Chem. 7 (2015) 19–29.
[3] Z. Song, H. Zhou, Energy Environ. Sci. 6 (2013) 2280–2301.
[4] Y. Liang, Z. Chen, Y. Jing, Y. Rong, A. Facchetti, Y. Yao, J. Am. Chem. Soc. 137 (2015) 4956–4959.
[5] T. Janoschka, M. D. Hager, U. S. Schubert, Adv. Mater. 24 (2012) 6397–6409.

INVESTIGATING THE ELECTROCHEMICAL BEHAVIOR OF KRAFT LIGNIN FOR SUSTAINABLE ELECTRODE MATERIALS

Saowaluk Chaleawlert-umpon[a,b], Thomas Berthold[a], Xuewan Wang[a], Markus Antonietti[a], and Clemens Liedel[a]
[a] *Department of Colloid Chemistry, Max Planck Institute of Colloids and Interfaces, Research Campus Golm, 14476 Potsdam, Germany*
[b]*National Nanotechnology Center, 111 Thailand Science Park, Phahoyothin Rd., Klong 1, Klong Luang, Pathumthani 12120, Thailand*

saowaluk.chaleawlert-umpon@mpikg.mpg.de

Electrochemical energy storage using lignin as renewable electrode material is a cheap and sustainable approach for future batteries and supercapacitors [1-3]. Previous reports mainly focus on lignosulfonates (LS) or composites with conductive polymer additives [2, 4-5]. Disadvantages are declining LS supply or additional polymerization steps of often expensive monomers. More available Kraft lignin in combination with conductive carbon may be a promising alternative [6], and understanding the electrochemical behavior is crucial for future applications.

To better understand desired lignin properties for capacitive energy storage, we investigate lignin-carbon composites in a three-electrode system by cyclic voltammetry and analyze charge storage in terms of electrochemical double layer storage (EDL) and redox reactions. By modifying lignin content and surface area of the conductive carbon, accessibility of electroactive groups and insulating behavior of lignin can be evaluated. As expected, the total capacitance is significantly higher in samples employing carbon with a high surface area. However, this is also true for pseudocapacitive behavior, since redox capacitance amounts to approximately half of the total capacitance in different electrode compositions, independent on the carbon. Resulting electrodes are cheap, reliable, stable for at least 500 charge-discharge cycles, and represent a step towards more sustainable energy storage.

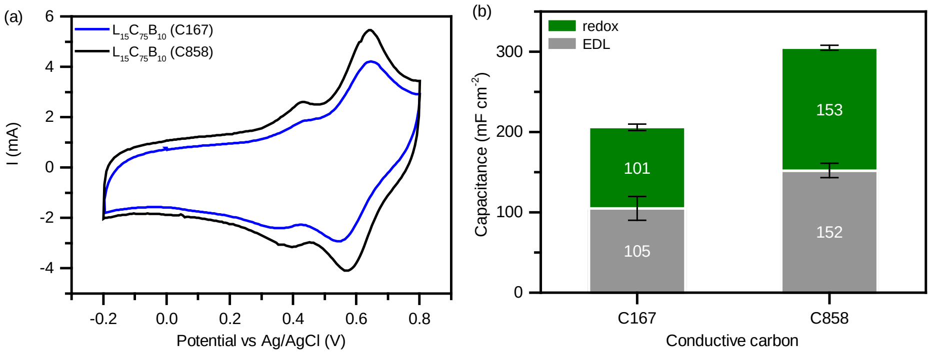


Figure 1: (a) CV profiles measured in 1 M $HClO_4$ electrolyte at 5 mV s^{-1} and (b) contributions to the total capacitance for electrodes with different conductive carbons.

References:
[1] S. Admassie, F.N. Ajjan, A. Elfwing, O. Inganäs,. Mater. Horiz. 3 (2016) 174–185.
[2] G. Milcazrek, O. Inganäs, Science, 335 (2012) 1468–1471.
[3] G. Milczarek, Langmuir 25 (2009) 10345–10353.
[4] H. Xu, H. Jiang, X. Li, G. Wang, RSC Adv. 5 (2015) 76116–76121.
[5] F.N. Ajjan, N. Casado, T. Rębiś, A. Elfwing, N. Solin, D. Mecerreyes, O. Inganäs, J. Mater. Chem. A 4 (2016) 1838–1847.
[6] R.J.A. Gosselink, E. de Jong, B. Guran, A. Abächerli, Ind. Crops Prod. 20 (2004) 121–129.

ELECTROCHEMICAL PROPERTIES OF PEDOT-BASED CONDUCTING REDOX POLYMERS

Mia Sterby, Rikard Emanuelsson, Maria Strømme, and Martin Sjödin
Nanotechnology and Functional Materials, Department of Engineering Sciences
The Ångström Laboratory, Uppsala University, Box 534, SE-751 21 Uppsala, Sweden

Mia.sterby@angstrom.uu.se

Organic molecules are generally insulating and to ensure electrical conductivity when organic matter is used as electrode materials, conducting additives are commonly used. Another approach is to use conducting polymers as a backbone to which the capacity carrying redox active pendant groups are attached. In this work we employed poly(3,4-ethylenedioxythiophene) (PEDOT) with different quinone moieties as pendant groups, forming conducting redox polymers (CRPs). By using quinones with different redox potentials, CRPs can be used as electrode materials in all-organic batteries where the difference in formal potential between the quinone redox reactions determines the cell-potential of the battery. To avoid the use of flammable and harmful organic electrolytes we used acidic water based electrolytes in the characterization of these polymers, including *in situ* conductance, electrochemical quartz crystal microbalance measurements, and cyclic voltammetry. The results from polymers carrying different quinones will be presented. For example: *in situ* conductance measurements of benzoquinone substituted CRPs show that redox matching is evident, i.e. the quinone pendant group has its redox reaction occurring in a potential window where the polymer is conducting (Figure 1). The polymers also show fast kinetics and during the quinone redox conversion only protons seem to be cycled in and out of the CRPs.

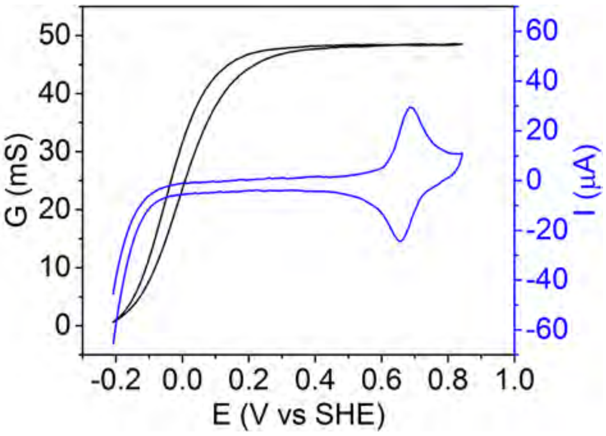


Figure 1. *In situ* conductance, showing redox matching between the polymer backbone and the redox active pendant group.

P5

POLYVIOLOGEN–GRAPHENE NANOCOMPOSITES FOR FLEXIBLE AND HIGH–VOLUMETRIC DENSITY ORGANIC BATTERIES

S. Mohsen Beladi-Mousavi, Lorenz Walder
Institute of Chemistry of New Materials, Center of Physics & Chemistry of New Materials,
University of Osnabrück, Barbarastr. 7, Osnabrück, D-49069 Germany

sbeladimousa@uos.de

Organic redox polymers have played only a niche role in battery technology so far. They have been blamed for their low volumetric and gravimetric capacity, their restriction to thin film applications and their volume change upon charging/discharging. As we have shown in the current [1-2] and previous studies,[3] most of these objections are not true. They rather reflect the current industrial focus on the optimization of the traditional inorganic Li-intercalation materials, leading to a neglect and an underestimate of alternative methods.

Herein, a viologen-based polymer (poly(ethylene diphenyl viologen) (PEdPV), with theoretical capacity 160 mAh g^{-1}) in tight molecular contact with reduced graphene oxide (rGO), i.e. PEdPV@rGO, was prepared and used as anodic battery materials. This composite shows exceptionally high areal, volumetric, and current density. Thus, PEdPV@rGO composite (with 15 wt% rGO, corresponding to 137 mAh g^{-1}) shows 13.3 mAh cm^{-2} at a thickness of 460 µm, and 288 mAh cm^{-3} with 98% coulumbic efficiency at current densities up to 1000 A g^{-1}, better than any reported organic materials. The rate performance of this composite was also significant i.e., discharge of 95% of a 3.6 µAh cm^{-2} film in only 0.15 second, significantly faster than the well-known “ultrafast” organic radical batteries.[4] The PEdPV@rGO composite on a thin graphite sheet electrode with an areal-capacity of 1.23 mAh cm^{-2} is stable over 200 bending cycles, making the material applicable for wearable electronics. These unprecedented performances are based on (i) the molecular self-assembling of PEdPV on individual GO sheets yielding colloidal PEdPV@GO (Zeta potential), (ii) the transfer of PEdPV@GO to a CC yielding (PEdPV@GO)@CC as a layered porous structure (AFM, STM, SEM), (iii) the efficient GO/rGO transformation electrocatalyzed by PEdPV (eQCM), (iv) the reversible thickness changes (ion breathing) during charging-discharging (ecAFM, eQCM), and (v) a supporting electrolyte optimization (Figure 1).

The main conclusion of the study is that high performances can only be achieved, if a molecular contact between the charge storing material, the electron conductor and the ion percolation system is guaranteed. A molecular self-assembly between negatively charged GO and positively charged polyviologen, followed by a smooth GO/rGO transformation fulfill these conditions.

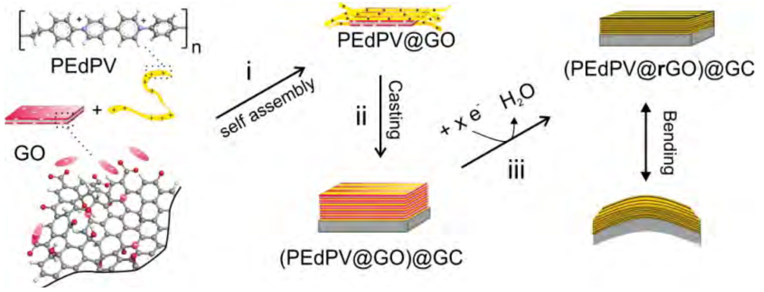


Figure 1

References:
[1] S. M. Beladi-Mousavi, L.Walder, Submitted (2017), *Patent application number: DE 10 2016 124 586.0.*
[2] S. M. Beladi-Mousavi, S. Sadaf, A. M. Mahmood, L. Walder, submitted (2017).
[3] S. M. Beladi-Mousavi, S. Sadaf, L. Walder, et al., Adv. Energy Mater. 6 (2016) 1600108.
[4] K. Koshika, N. Sano, K. Oyaizu, H. Nishide, Chem. Comm. (2009) 836–838.

P6

PORPHYRIN COMPLEX AS SELF-CONDITIONED ELECTRODE MATERIAL FOR HIGH PERFORMANCE ENERGY STORAGE

Ping Gao[a], Zhi Chen[b], Zhirong Zhao-Karger[a], Mario Ruben[b], Maximilian Fichtner[a]

[a] Helmholtz Institute Ulm (HIU), Helmholtzstr. 11, D-89081 Ulm, Germany.
[b]Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), D-76021 Karlsruhe, Germany.

ping.gao@kit.edu

Rechargeable lithium ion batteries have been successfully developed in the last two decades and widely used to power today's portable electronic devices. The aim at long term success in electric vehicles and grid-scale renewable energy storage raises grand challenges in the high energy density, long cycle lives, good safety and low-cost of the batteries. [1] Organic electrode materials have been considered as alternatives due to their tunable properties, environmental friendliness, flexibility, good safety and sustainability. [2]

Herein we present a porphyrin complex as a new electrode-active material for rechargeable batteries, which delivers good specific capacities up to 180 mAh g^{-1} at an average voltage of approx. 3.0 V.[3] By a simple modification of the material, the cell can be cycled more than 8000 times at high current density with good capacity retention. Fast charge and discharge capability of the electrode up to 50 C is demonstrated. The material can be used as a cathode, or as anode in different rechargeable batteries, such as Li-based, Na-based, and Mg-based systems. The outstanding properties of the porphyrin electrode highlight a promising approach for the design of new organic electrode materials.

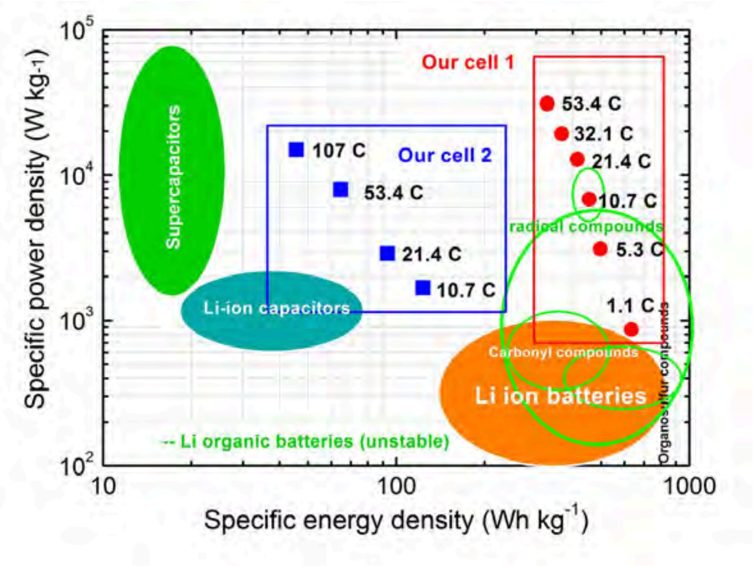


Figure 1. Ragone plots for various energy storage systems.

References:
[1] H.D. Yoo, E. Markevich, G. Salitra, D. Sharon, D. Aurbach. *Mater. Today,* 17 (2010) 110–121.
[2] Z. Song, H. Zhou. *Energy Environ. Sci.* 6 (2013), 2280–2301.
[3] M. Fichtner, P. Gao, Z.Chen, Z. Zhao-Karger, M. Ruben. *EP16000312.5*, paper submitted.

MODULITES – MONOLITHICALLY INTEGRATED ELECTROCHEMICAL ENERGY STORAGE MODULES. PROTOTYPES WITH PASSIVE BALANCING

Mats Sandberg[a], Negar Sani[a] , and Ulrika Linderhed[a]
[a] *RISE Acreo AB, Bredgatan 33, SE-60217 Norrköping, Sweden*

mats.sandberg@ri.se

Cost is the main hinder for increased used of electrochemical energy storage, and a large share of the cost originates form the costs of integrating the discrete storage cells with each other and with circuits for protection and balancing. Here, we introduce a new architecture for electrochemical storage modules; monolithic integration and using printing. Monolithic integration has been the main building scheme in microelectronics since it was introduced in the early 1960’s[1], while electrochemical storage devices are built by integrating discrete components. Printed electronics concepts are well suited for monolithically integrated energy storage devices of energy storage modules as both supercapacitor electrodes as well as circuits for balancing and protection can be printed. In previous publications, we have demonstrated protection and balancing schemes for a two-cell module using all printed circuit[2], and demonstrated balancing using a printed and silicon hybrid scheme[3]. In this work, we have manufactured a five-cell module of serially connected supercapacitor cells with a simple resistive balancing. Prototype manufacturing and properties are presented.

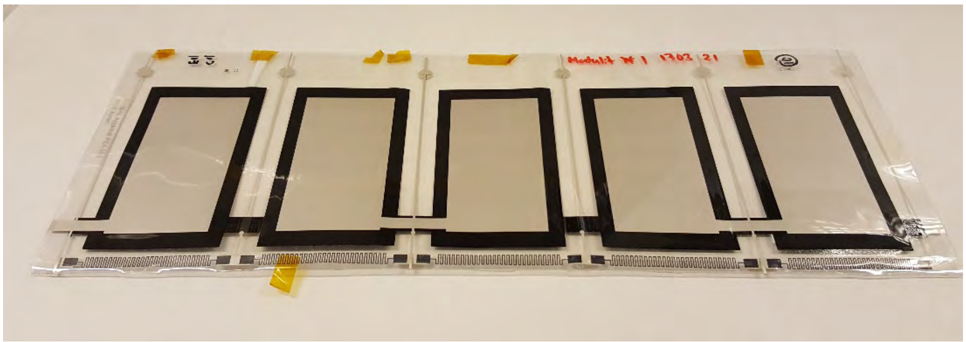


Figure 1. A prototype of a supercapacitor module manufactured be monolithic integration by printing to form a serial stack with resistances parallel to each cell.

Acknowledgement: This project is financed by the Swedish Energy Agency.

References:
[1] R. N., Noyce, US Pat. Appl. 2981877 A,” Semiconductor device and lead structure”.
[2] V. Keshmiri, R. Forchheimer, D. Tu, D.,Westerberg, and M. Sandberg,“The Applications of OECTs in Supercapacitor Balancing Circuits”, 7th International Conference on Computer Aided Design for Thin-Film Transistor Technologies (CAD-TFT), IEEE.
[3] V. Keshmiri, D. Westerberg, P. Andersson Ersman, M. Sandberg, R. Forchheimer, and D. Tu, “A Silicon-Organic Hybrid Voltage Equalizer for Supercapacitor Balancing”, IEEE Journal on Emerging and Selected Topics in Circuits and Systems, 7, (2017), 144.

TETRAZINE AS A NEW REDOX-ACTIVE GROUP FOR ORGANIC ELECTRODE MATERIALS IN LI-ION BATTERY

Dong Joo Min, Ji Eon Kwon,* and Soo Young Park*
Center for Supramolecular Optoelectronic Materials (CSOM),
Department of Materials Science and Engineering, Seoul National University, 1 Gwanak-ro,
Gwanak-gu, Seoul 151-744, Korea

*mracle2@snu.ac.kr (JEK) and parksy@snu.ac.kr (SYP)

Due to the inherent limitations of conventional inorganic electrode materials for Li-ion batteries, organic redox-active materials have emerged as a promising alternative. In the past few decades, a lot of efforts have been devoted to develop various organic electrode materials, but only a few redox-active groups have been successfully utilized including nitroxides, carbonyls, and organosulfurs. It is, therefore, imperative to develop a new redox-active group for high performance organic electrode materials.

Here, we report a series of tetrazine, which is one of the most electron deficient but stable aromatic ring, as a new redox-active group for organic electrode materials. It is well known that tetrazines undergo reversible one electron reduction to generate radical anion.

First, to evaluate potential applicability of tetrazines to electrode materials, three tetrazine derivatives including 3,6-dichloro-1,2,4,5-tetrazine (DCT), 3,6-dimethoxy-1,2,4,5-tetrazine (DMT), and 3,6-diphenyl-1,2,4,5-tetrazine (DPT) are tested in Li-ion coin cells. DCT and DPT show initial discharge capacities of 111 mAh/g and 130 mAh/g with discharge plateaus of 2.2 V and 2.5 V vs Li/Li+, respectively. But very fast capacity fading is observed along the repeated charge/discharge cycles from the tetrazine electrodes due to its high solubility in the carbonates electrolytes. It should be noted that using ether-based electrolytes (2 M LiTFSI in 1,3-dioxolane/dimethoxyethane) and fabricating nanocomposite with mesoporous carbon CMK-3 significantly enhance cycle performance of the tetrazine electrodes.

Next, to improve intrinsic cycling stability of the tetrazine-based organic electrodes, we synthesize a series of polyimide bearing tetrazines. Because the tetrazines are covalently linked to redox-active rylene-diimides by condensation polymerization, solubility of the tetrazines can be effectively suppressed without significant loss of specific capacity. Particularly, the polymer composed of tetrazine and naphthalene diimide (NDI) shows 202 mAh/g of discharge capacity at the second cycle but maintains 171 mAh/g of discharge capacity after 100 cycles.

A STUDY ON THE INTERFACIAL CHEMISTRY OF ORGANIC ELECTRODES IN LI- AND NA-BATTERIES

Viorica Alina Oltean[a], Bertrand Philippe[b], Stéven Renault[a], Roberto Felix Duarte[c], Håkan Rensmo[b], Daniel Brandell[a]
[a]*Dept. of Chemistry - Ångström Laboratory, Uppsala University, 751 21 Uppsala, Sweden*
[b]*Department of Physics and Astronomy, Uppsala University, 751 20, Uppsala, Sweden*
[c]*Helmholz-Zentrum Berlin für Materialien und Energie GmbH, 12489, Berlin, Germany*

alina.mihali@kemi.uu.se

Li-ion batteries are considered as promising energy-storage devices but still rely on inorganic non-renewable electrode materials. This will constitute a problem in the future due to the cost, finite nature of these materials and life cycle analysis of such materials (extraction, processing and recycling) which shows a negative impact on the environment.[1] Organic electrodes materials (OEMs) could replace them as more environmentally-friendly substitutes even if they also present different drawbacks one of them being aging. One of the severe problems connected to aging is the SEI layer formation considered also one of the major factors for the irreversible capacity observed in the first cycle for OEMs. However, the SEI layer formation and its influence on battery performance have still not been properly addressed in the literature.

We here present the first characterization of the organic electrode material SEI layer using hard X-ray photoelectron spectroscopy (HAXPES), for both Li- and Na-based electrodes. Dilithium and disodium benzenediacrylates[2,3] have been used as major components for battery construction followed by an electrochemical investigation and HAXPES measurements after contact with the electrolyte and after cycling. The Na-based electrodes react immediately with the electrolyte, and the SEI layer is dominated by inorganic species with continuous salt degradation during cycling. The Li-based electrodes display an SEI layer with primarily organic species from solvent degradation products appearing only after cycling and increasing in amount with the number of electrochemical cycles. It should be pointed out that the investigated systems contain different electrolytes, cycling condition and composite formulation so a direct comparison of the two systems is not possible.

References:
[1] P. Poizot, F. Dolhem, Energy Environ. Sci. 4 (2011) 2003-2019.
[2] S. Renault, D. Brandell, T. Gustafsson, K. Edström, Chem. Commun. 49 (2013) 1945-1947.
[3] V. A. Mihali, S. Renault, L. Nyholm, D. Brandell, RSC Adv. 4 (2014) 38004-38011.

PFQ POLYMER – PROBLEMATIC LOW SWELLING

Klemen Pirnat[a], Jan Bitenc[a], Miran Gaberscek[a,c], Robert Dominko[a,c]
[a] National Institute of Chemistry, Hajdrihova 19,1000 Ljubljana (Slovenia)
[c] Faculty for Chemistry and Chemical Technology, University of Ljubljana, Vecna pot 113, 1000 Ljubljana (Slovenia)

klemen.pirnat@ki.si

Li-organic batteries are promising substitute for current Li-battery systems in terms of cost, sustainability, safety and capacity. However main problem of organic materials is dissolution of electroactive compounds into the electrolyte which results in fast capacity fading during cycling. To avoid this phenomena several approaches were developed: use of ion selective separators, grafting [1] and synthesis of electroactive polymers which represents the most successful strategy [2]. Recently polymer poly(anthraquinone) or PAQ [3] was developed using direct coupling reaction. To increase electrochemical redox potential (and energy density) we prepared another polymer poly(9,10-phenanthrenequinone) or PFQ with ortho position of carbonyl groups. As expected PFQ shows higher redox potential of 2.5 V vs. Li/Li^+ compared to 2.15 V obtained with PAQ in Li battery while capacity retention is stable at 150 mAh/g (57 % of the theoretical capacity). We presume that swelling of electroactive polymers plays an important role for good utilization of material which can be achieved by at least partial solubility. On one hand zero solubility of PFQ polymer is a desired property, however this results in very limited swelling properties and as a consequence Li^+ ions in electrolyte cannot reach the bulk inside the polymer particles (low ionic conductivity). To improve ionic as also electronic conductivity high energy milling and incorporation of graphene during polymerization was implemented into the synthesis and improvement of capacity from 150 to 200 mAh/g (Figure 1) was obtained. For further improvements controlled polymer synthesis to obtain nanoparticles should be developed.

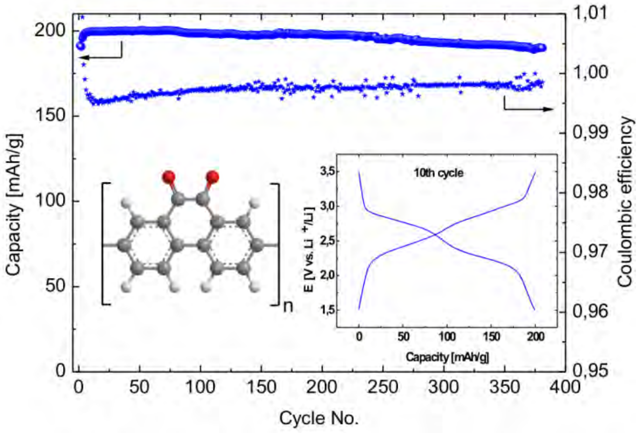


Figure 1: Cycling of PFQ after graphene addition, high energy milling.

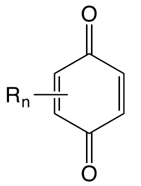
References:
[1] B. Genorio, K. Pirnat, R. Cerc-Korosec, R. Dominko, M. Gaberscek, Angew. Chemie - Int. Ed. 49 (2010) 7222–7224.
[2] K. Pirnat, G. Mali, M. Gaberscek, R. Dominko, J. Power Sources. 315 (2016) 169–178.
[3] Z. Song, Y. Qian, M.L. Gordin, D. Tang, T. Xu, M. Otani, et al., Angew. Chem. Int. Ed. Engl. 127 (2015) 14153–14157.

RECHARGEABLE LITHIUM-ION BATTERIES USING BENZOQUINONE DERIVATIVES AS THE CATHODE ACTIVE MATERIALS

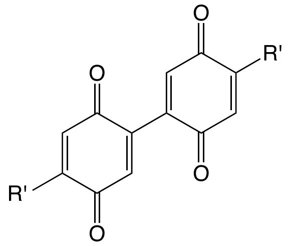
Hiroshi Matsubara, Takato Yokoji, Akihiro Seno
Department of Chemistry, Graduate School of Science, Osaka Prefecture University,
Sakai, Osaka 599-8531, Japan

matsu@c.s.osakafu-u.ac.jp

Recently, in addition to polymer cathode active materials, low-molecular-weight organic cathode active materials have attracted significant attention due to their expectations for the dramatic improvement of the mass energy density in lithium-ion batteries since the materials can undergo multiple electron redox reactions per molecule. However, the performance of the most advanced battery systems using low-molecular-weight organic cathode active materials has not reached a practical level, and further improvements of the batteries are required. We have focused on 1,4-benzoquinone (BQ) derivatives, which are expected to afford high capacities since they have simple, low-molecular-weight skeletons and can function as two-electron redox system. Thus, we prepared BQ derivatives to investigate the relationship between the molecular structure of the cathode active materials and the battery performance of cells based on those materials. In particular, we investigated the relationship between the electric/steric effects of the substituents on the BQ skeleton and battery performance [1][2]. In addition, polymeric BQ derivatives based on 2,2'-bis-p-benzoquinone (BBQ) framework were synthesized, and the charge-discharge behaviour of prepared cells using BBQs as the cathode active materials was investigated [3].



BQ derivatives



BBQ derivatives

References :
[1] T. Yokoji, H. Matsubara, M. Satoh, J. Mater. Chem. A 2 (2014) 19347–19354.
[2] T. Yokoji, Y. Kameyama, S. Sakaida, N. Maruyama, M. Satoh, H. Matsubara, Chem. Lett. 44 (2015) 1726–1728.
[3] T. Yokoji, Y. Kameyama, N. Maruyama, H. Matsubara, J. Mater. Chem. A 4 (2016) 5457–5466.

ALL-ORGANIC PROTON BATTERIES FROM CONDUCTING REDOX POLYMERS

Rikard Emanuelsson, Mia Sterby, Maria Strømme, and Martin Sjödin
Nanotechnology and Functional Materials, Department of Engineering Sciences
The Ångström Laboratory, Uppsala University, Box 534, SE-751 21 Uppsala, Sweden

Rikard.Emanuelsson@angstrom.uu.se

Utilizing conducting redox polymers based on poly(3,4-ethylenedioxythiophene) (PEDOT) functionalized with anthraquinone or benzoquinone moieties as the negative and positive electrode materials, respectively, we have recently assembled and characterized an all-organic proton battery [1]. Employing an electrolyte slurry of proton donors and acceptors allows the capacity carrying $2e^{-}/2H^{+}$ quinone/hydroquinone redox reactions and suppresses proton reduction in the battery cell. Additionally, the strength of the proton donor/acceptors can be tuned through chemical substitution, analogous to changing the pH of an aqueous solution [2]. This allows the formal potential of the quinone/hydroquinone redox reactions to be tuned into the potential region in which the PEDOT backbone is conductive, obviating the need for conducting additives. The design and characteristics of these batteries together with the opportunities and challenges ahead will be presented.

References:
[1] R. Emanuelsson, M. Sterby, M. Strømme, M. Sjödin, J. Am. Chem. Soc. (2017) DOI: 10.1021/jacs.7b00159
[2] R. Emanuelsson, H. Huang, A. Gogoll, M. Strømme, M. Sjödin, J. Phys. Chem. C 120 (2016) 21178–21183

P13

EFFECT OF MASS LOADING ON PSEUDOCAPACITIVE BEHAVIOR OF POLYANILINE

Elena Tomsik[a], Iryna Ivanko[a], Olena Kohut[a], Natalia Gospodinova[a]
[a] Institute of Macromolecular Chemistry, AS CR Heyrovsky Sq. 2, Prague, Czech Republic

tomsik@imc.cas.cz

Application of semiconducting polymers as pseudocapacitor's material has been intensively investigated over few decades. Polyaniline, among all semiconducting polymers, possesses the highest theoretical specific capacitance.[1] In real measurements, only part of the theoretical capacitance could be obtained. We have shown that obtained by us highly crystalline polyaniline film[2] deposited on flexible carbon cloth have the maximum specific capacitance at mass loading 0.5 mg/cm^2, and it is 1100 F/g. With increasing of the mass loading up to 2.7 mg/cm^2 the specific capacitance changes slightly with decreasing only up to 920 F/g (**Figure** 1.right), and with further increasing of the mass loading (3.8mg/cm^2) the specific capacitance dramatically dropped up to 600 F/g. On the other hand, the maximum areal capacitance has been obtained for the highest mass loading and it is 2800 mF/cm^2 (**Figure 1**. left). It has to be emphasized that such high values of the specific capacitance and the areal capacitance have been measured at the specific current of 60 A/g and the areal current density of 75 mA/cm^2 respectively.

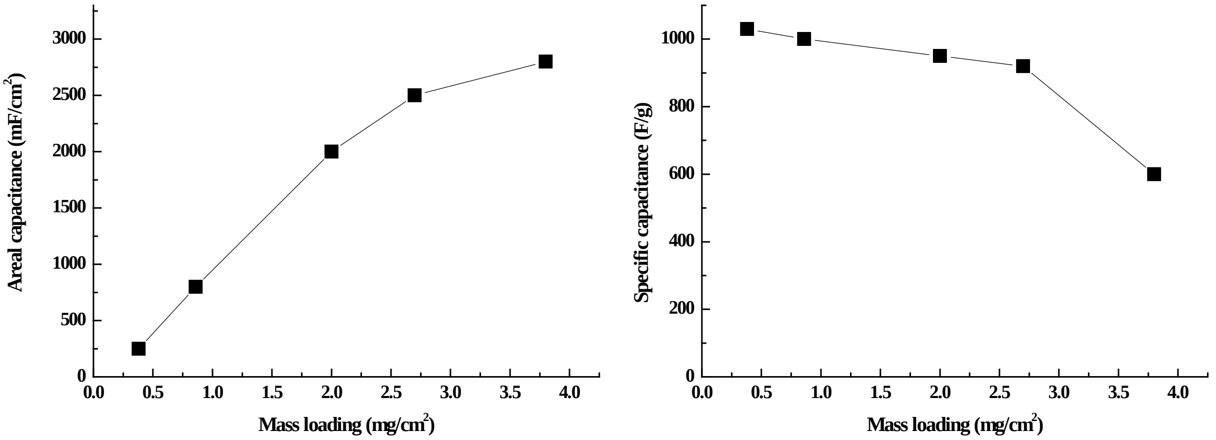


Figure 1. Dependence of areal (left) measured at 75 mA/cm^2 and specific (right) measured at 60 A/g capacitances on polyaniline mass loading. The results have been obtained in three-electrode cell.

References:
[1] B.E. Conway, Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications, Kluwer-Academic, Springer USA 1999.
[2] N. Gospodinova, D. Ivanov, D. Anokhin, I. Mihai, L. Vidal, S. Brun, J. Romanova, A. Tadjer, Macromol. Rapid Commun., 30 (2009) 29–33.

P14

BOOSTING THE CAPACITY OF ALL-ORGANIC PAPER SUPERCAPACITORS USING WOOD DERIVATIVES

Jesper Edberg[a], Olle Inganäs[b], Isak Engquist[a], and Magnus Berggren[a,c]
[a] *Laboratory of Organic Electronics, ITN, Linköping University, SE-601 74 Norrköping, Sweden*
[b] *Biomolecular and Organic Electronics, IFM, Linköping University, SE-581 83 Linköping, Sweden*
[c] *Stellenbosch Institute for Advanced Studies (STIAS), Wallenberg Research Center at Stellenbosch University, Stellenbosch 7600, South Africa*

jesper.edberg@liu.se

Printed and flexible organic electronics is a steadily expanding field of research and applications. One of the most attractive features of this technology is the possibility of large area and high throughput production to form low-cost electronics on different flexible substrates. With an increasing demand for sustainable energy production, low-cost and large volume technologies to store high-quality energy become equally important. These devices should be environmentally friendly with respect to their entire life cycle. Supercapacitors and batteries based on paper hold great promise for such applications due to the low cost and abundance of cellulose and other forest-derived components. We report a thick-film paper-supercapacitor system based on cellulose nanofibrils, the mixed ion-electron conducting polymer PEDOT:PSS and sulfonated lignin. We demonstrate that the introduction of sulfonated lignin into the cellulose-conducting polymer system increases the specific capacitance from 109 to 232 F/g and the areal capacitance from 160 mF/cm2 to 1 F/cm2. One of the great challenges when including additional redox molecules in supercapacitor electrodes relates to poor stability, which typically is due to chemical or physical degradation and/or that the redox polymer escapes the electrode system and enters the electrolyte. By introducing lignosulfonate also into the electrolyte solution, equilibrium, with respect to the concentration of the redox polymer, is established between the electrode and the electrolyte, thus allowing us to perform beyond 700 charge/discharge cycles with no observed decrease in performance.

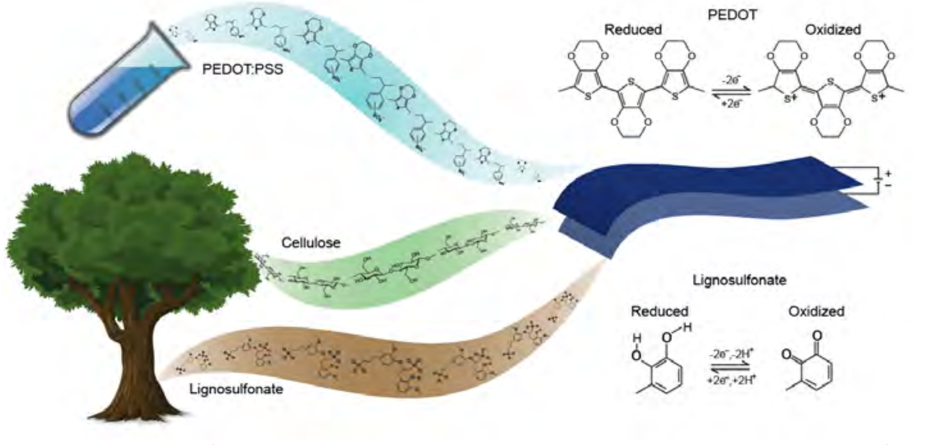


Figure 1. Schematic picture of the paper supercapacitor with the molecular structures of its constituent

UNDERSTANDING DOPING STRATEGIES IN THE DESIGN OF ORGANIC ELECTRODE MATERIALS FOR LI AND NA ION BATTERIES: AN ELECTRONIC STRUCTURE PERSPECTIVE

Johann Lüder, Mun Ho Cheow and Sergei Manzhos[a]
[a]*Department of Mechanical Engineering, National University of Singapore. 21 Lower Kent Ridge Rd, Singapore 119077, Singapore*

mpejoha@nus.edu.sg

We present a systematic theoretical study of the effects of p- and n-doping in small molecules on voltage and capacity in organic electrode materials for electrochemical batteries. Employing density functional theory, we show that p-doping can drastically increase the binding strength of Li and Na atoms to molecular building blocks of organic electrode materials. In particular, coronene, phenalene derivatives as well as disodium terephthalate and its fused ring derivatives are chosen as representative model systems for this purpose. On the other hand, n-doping generally has a much smaller effect on the voltage. The effects of n- and p- doping are rationalized based on the analysis of changes they induce in the band structure as well as in molecular structure. Our results show that p-doping is an effective strategy to design organic anode materials with higher voltages for both lithium and sodium ion batteries. It could also be used to increase the theoretical capacity.

CONDUCTING REDOX POLYMER BATTERIES – CHALLENGES AND POSSIBILITIES

Christian Strietzel, Rikard Emanuelsson, Maria Strømme, and Martin Sjödin
Nanotechnology and Functional Materials, Department of Engineering Sciences
The Ångström Laboratory, Uppsala University, Box 534, SE-751 21 Uppsala, Sweden

christian.strietzel@angstrom.uu.se

Apart from conventional metal based batteries, batteries consisting of naturally occurring organic materials can be envisioned, thus becoming fully sustainable and avoiding the negative environmental impact associated with the production and recycling of conventional metal based batteries. This way the negative environmental impact of the constantly increasing demand for secondary batteries is decreased. One class of fully organic batteries utilizes conducting redox polymers (CRPs) as electrode materials. CRPs combine the high charge storage capacity of a redox active pendant group (PG) with the conduction properties of a conducting polymer (CP) backbone, both to reduce the need for addition of conductive carbon black and increasing the stability of the PG redox conversion in a battery setup. In the current work, challenges and possibilities of this type of battery are discussed and a concept and initial results for a metal-free, fully organic battery based on CRP electrode materials is presented.

INSIGHTS ON THE MECHANISM OF ORAGNIC ELECTRODES SUPERLITHIATION FROM FIRST-PRINCIPLES THEORY

C. Moyses Araujo[a], Stéven Renault[b] and Daniel Brandell[b]
[a] *Condensed Matter Theory Group, Department of Physics and Astronomy, Uppsala University, Box 516, 751 21 Uppsala, Sweden*
[b] *Department of Chemistry - Ångström Laboratory, Uppsala University, Box 538, 751 21 Uppsala, Sweden*

moyses.araujo@physics.uu.se

The design of novel organic functional materials stands out as a promising strategy in the development of sustainable and environmentally friendly energy conversion and storage devices. In particular, the organic electrodes materials are emerging with the potential to establish the new generation of greener battery technologies. However, there are drawbacks that limit its faster implementation related to poor cycling stability and low energy densities. In a relatively recent work, Han et al. [1] reported that insertion of lithium ions in the 1,4,5,8naphthalenetetracarboxylic dianhydride compound goes beyond the expected enolization of the four carbonyls reaching the Li:C ratio of 1:1, which significantly increased its storage capacity. The proposed explanation is that the unsaturated C-C bonds start also to be reduced in the electrochemical process, forming the so-called super-lithiation state. In this work, we have investigated this phenomenon by means of first-principles calculations within density functional theory. We have combined evolutionary algorithm to predict crystal structure with molecular models to access the thermodynamics and electronic structure of different lithiation stages. We have developed a comparative study focused on the dilithium benzenedipropiolate compound (Li_2BDP) [2] and dilithium thiophenedicarboxylate (Li_2TDC) [3].

For the former, it was found that the propiolate arms undergo electrochemical reduction that is followed by the reduction of C-C bond in the benzene ring. In the case of Li_2TDC, the calculated cell voltage (using the predicted crystal structures) of 0.96 V vs. Li/Li^+ displays good agreement with the experimental value of 1.0 V vs. Li/Li^+. The predicted structure of the delithiated phase with space group P21/C is shown in figure 1. A detailed analysis of the correlation between structure, electronic structure and thermodynamics will be presented.

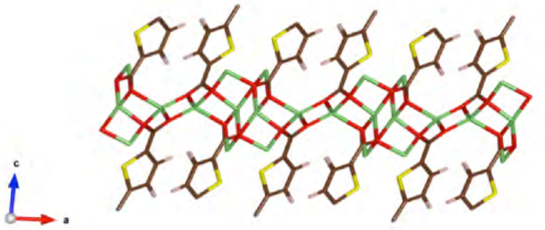


Figure 1. Crystal structure of dilithium thiophenedicarboxylate predicted from evolutionary algorithm. Space group P21/C. Color code: O (red), Li (green), C (brown) and S (yellow).

References:
[1] Han, X.; Qing, G.; Sun, J.; Sun, T. Angew. Chem., Int. Ed. 51 (2012), 5147−5151
[2] Renault, S.; Oltean, A.V.; Araujo, C.M.; Grigoriev, A.; Edström, K.; and Brandell, D. Chem. Mater. 28 (2016), 1920−1926.
[3] Lee, H. H.; Park, Y.; Shin, K.-H.; Lee, K. T.; Hong, S. Y. ACS Appl. Mater. Interfaces 6 (2014) 19118−19126

AN ELECTROLYTE STUDY ON Na_2BDA ANODE FOR Na-BASED ORGANIC BATTERIES

Francesca Colò[a,b], Stéven Renault[b], Federico Bella[a], Claudio Gerbaldi[a], Daniel Brandell[b]
[a] *GAME lab,CHENERGY group, Department of Applied Science and Technology – DISAT, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 – Torino, Italy*
[b] *Department of Chemistry-Ångström Laboratory, Uppsala University, Box 538, 751 21 Uppsala, Sweden*

Francesca.colo@polito.it, Francesca.colo@kemi.uu.se

Energy production and storage plays a key role in the development of portable devices, hybrid and electric vehicles and in the energy storage system for renewable energy, such as wind and solar resources. Lithium ion batteries (LIBs) dominate the global market on these, but the geographically constrained resources and the difficult extraction of metallic lithium lead to prices increment, removing the idea of low-cost technologies.

An alternative on lithium technology is sodium, very abundant, cheap and with suitable electrochemical properties, close to those of lithium. A lot of work on sodium technology has to be done in order to catch up with lithium[1].

Electrode materials research is the first step which must be done for meet the high energy storage demand. At the moment the most common chemistries used in batteries are based on inorganic compounds (e. g. $LiCoO_2$, $LiMn_2O_4$, $Li_4Ti_5O_{12}$, etc…), that are expensive and synthesized from high temperature reactions, and also the end-of-life treatment is difficult and energy greedy. One possible approach as alternative is switching to the organic based materials, in which a lot of synthesis routes can be chosen and a lots of compounds can be synthesized. Furthermore, the possibility to prepare materials from recyclable organic materials (e. g. biomass) is really appealing [2].

However, organic compounds are often associated with drawbacks such as poor conductivity, low energy density and high solubility in liquid electrolytes. Especially for the last point an accurate study on the electrolytes involved in the batteries is mandatory, because is well known how the ion-transport media affect the performances of the batteries system.

In this work we present an overview on our recent results on using disodium benzenediacrylate (Na_2BDA) as electrode material for Na-based organic batteries [3,4], in different electrolyte media. In particular, the galvanostatic cycling behaviors in Na|electrolyte|Na_2BDA pouch-cell configuration are shown.

References:

[1] B. E. Ellis, L. F. Nazar, Curr. Opin. Solid State Mater. Sci. 16 (2012) 168-177.

[2] P. Poizot, F. Dolhem, Energy Envim. Sci. 4 (2011) 2003.

[3] V. A. Mihali, S. Renault, L. Nyholm, D. Brandell, RSC Adv. 4 (2014) 38004-38011

[4] V. A. Oltean, B. Philippe, S. Renault, R. F. Duarte, H. Rensmo, D. Brandell, Chem. Mater. 28 (2016) 8742-8751

FUNDAMENTAL STUDY OF TEREPHTHALATE-FUNCTIONALIZED POLY(3,4-ETHYLENEDIOXYTHIOPHENE) CONDUCTING REDOX POLYMER

Huan Wang, Xiao Huang, Maria Strømme, and Martin Sjödin
Nanotechnology and Functional Materials, Department of Engineering Sciences
The Ångström Laboratory, Uppsala University, Box 534, SE-751 21 Uppsala, Sweden

huan.wang@angstrom.uu.se

Traditional inorganic energy storage materials burden the environment with a considerable amount of carbon dioxide and suffer from low renewability. As alternative battery materials organic conducting redox polymers (CRPs) have caught much attention due to the sustainable raw materials and low energy consumption in their production[1]. CRPs consist of a conducting polymer (CP) backbone, a redox active pendant group (PG) and a linker. The CP contributes to conductivity and hinders dissolution of the PGs, while the PGs provide capacity for the polymer through reversible redox reaction[2]. The present work involves the CP poly(3,4-ethylenedioxythiophene) (PEDOT) and a terephthalate PG. The electrochemical polymerized CRP is characterized by Electrochemical Quartz Crystal Microbalance and Electron Spin Resonance during the doping process. Temperature-dependent *in situ* conductance is measured to probe the thermodynamic behavior of the CRP. Cyclic voltammetry at different scan rates is employed to investigate the charge transfer process. The rate constant for electron transport in the polymer is calculated and the rate-limiting step is identified. Based on the results, the electron and ion transport during electrochemical redox conversion is discussed. Cycling stability, especially in the negative potential region, is investigated to improve the electrochemical performance so as to enhance the possibility of full organic battery fabrication.

References:
[1] Park, K. S.; Schougaard, S. B.; Goodenough, J. B. Adv. Mater. 2007, 19, 848−851.
[2] L. Yang, X. Huang, A. Gogoll, M. Strømme, M. Sjödin. C 119 (2015) 18956–18963.

ELECTROCHEMICALLY POLYMERIZED Ni-COMPLEXES WITH SALEN TYPE LIGANDS AS MONOCOMPONENT ELECTRODE MATERIAL FOR LIB

Svetlana Eliseeva, A. Vereschagin, A. Volkov, A. Konev, P. Vlasov, Oleg Levin
Department of Electrochemistry, Institute of Chemistry, Saint Petersburg State University
7/9 Universitetskaya nab., St. Petersburg, 199034, Russia

svetlana.eliseeva@spbu.ru

Design of novel kind of power sources that would combine the advantages of supercapacitors and accumulators represents an actual task. A possible solution might be creation of novel organic and metalorganic materials with designed functionality. Attractive candidates for application in lithium-ion batteries (LIB) can be found among polymers. The attractiveness of these particular polymers is due to the high potential of charging/discharging or high specific capacitance predicted theoretically.

Organometallic compounds have been extensively investigated in both fundamental research and practical applications due to their unique electrical and chemical properties. Conducting salen-type redox polymers are among them. Salen complexes of such metals as copper or nickel represent conductive polymers which are not inferior to classical conductive polymers in terms of stability and conductivity while surpassing them in terms of capacitance due to participation of metal atoms in redox processes. Based on these data, we suppose that application of polymer complexes of salen type as materials for LIB is new and perspective approach to the design of organic cathodes with high conductivity and specific capacitance. It is known that metal complexes with salen-type Schiff base ligands are used in supercapacitors [1]. Metal complexes are mostly used as thin films and carbon materials hybrids, e.g. carbon nanotubes. An important advantage of such materials over traditional inorganic materials is availability and low cost of the starting materials for the synthesis of the target polymers combined with good mechanical properties of the latter such as flexibility, elasticity and ease of treatment.

It was shown that substituted salen-type ligands allow to obtain materials with a higher rate of charge transfer, as well as 200 F g^{-1} capacitance value (for methoxy substituent). From this, a conjecture arises that such substances are suitable for use as monocomponent materials for current sources with higher mass than 0.5–1 mg, i.e. with “practically ponderable” load. Conventional cathode materials also contain large amounts (15–20 wt.%) of electron-conducting additives and inactive polymeric binders which do not contribute to the electrode capacity and thus reduce the energy and power density of the battery.

So, the goal of this work was set to load a thick (~1 mg/cm^2) film to create a lithium ion battery prototype in 1 M $LiPF_6$ + EC, DEC electrolyte, which has not been done prior to this. A comparative study of poly[Ni(salen)], poly[Ni(CH_3salen)] and poly[Ni(CH_3Osalen)] samples was performed in order to reveal the superior candidate in the series.

The work was supported by the Russian Science Foundation (grant #16-13-00038). The authors would like to thank the Interdisciplinary Center for Nanotechnology of Saint-Petersburg State University.

Reference:
[1] E.V. Alekseeva, I.A. Chepurnaya, V.V. Malev, A.M. Timonov, O.V. Levin, Electrochim. Acta 225 (2017) 378-391.

ORGANIC CONDUCTIVE POLYMERS AS MODIFIER OF THE PROPERTIES OF CATHODE AND ANODE MATERIALS OF LIA

S. Eliseeva, E. Shkreba, K. Vorobeva, R. Apraksin, E. Tolstopyatova, V. Kondratiev
Department of Electrochemistry, Institute of Chemistry, Saint Petersburg State University
7/9 Universitetskaya nab., St. Petersburg, 199034, Russia

svetlana.eliseeva@spbu.ru

Recently we have shown, that employment of conductive polymer, such as poly-3,4-ethylenedioxythiophene/polystyrene sulfonate (PEDOT:PSS) along with carboxymethylcellulose (CMC) as additive to $LiFePO_4$ [1] and $LiFe_{0.4}Mn_{0.6}PO_4$-based [2] cathode material greatly improved the specific capacitance and C-rate performance of electrodes. The electrochemical properties of the materials were studied in coin-cell CR2032 by cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy (EIS).

In this work we give a deeper insight on the positive role of PEDOT:PSS, CMC components and PEDOT:PSS/CMC-combined binder in electrochemical performance of $LiFePO_4$ [3], $LiFe_{0.4}Mn_{0.6}PO_4$, $LiMn_2O_4$ cathode materials and $Li_4Ti_5O_{12}$ – one of the most promising anode materials by evaluation and comparative analysis of the kinetic parameters of the system studied by EIS measurements. Impedance spectra of batteries with different compositions were measured and analyzed. Detailed analysis of electrochemical impedance spectra reveals that two main parameters suffer most drastic change at the transition from conventional (with PVDF) composition to electrodes composition with PEDOT:PSS/CMC modified by conducting polymer. The significant decrease of interfacial charge transfer resistance and the increase of Li^+ effective diffusion coefficient were found. These parameters are responsible for observed improvement of electrochemical performance of electrode materials with organic conductive polymers PEDOT:PSS. The replacement of PVDF binder and carbon black conducting additive by the new conducting composition leads to an increase of the specific capacitance, good capacitance retention and rate capability.

Acknowledgments: The financial support from the Russian Foundation for Basic Research (grant №16-03-00457) is gratefully acknowledged. The authors would like to thank the SPbSU Resource Centre of Nanothechnology, the Resource Centre of Physical methods of surface investigations and Chemical Analysis and Materials Research Centre for providing common STM, XPS, EDX and FTIR analysis.

References:

[1] S.N. Eliseeva, O.V. Levin, E.G. Tolstopjatova, E.V. Alekseeva, R.V. Apraksin, V.V. Kondratiev, Mater Lett 161 (2015) 117-119.
[2] R.V. Apraksin, S.N. Eliseeva, E.G. Tolstopjatova, A.M. Rumyantsev, V.V. Zhdanov, V.V. Kondratiev, Mater Lett 176 (2016) 248-252.
[3] S.N. Eliseeva, R.V. Apraksin, E.G. Tolstopjatova, V.V. Kondratiev, Electrochim Acta 227 (2017) 357-366.

SUBSTITUENT EFFECT ON REDOX POTENTIAL OF SMALL ORGANIC MOLECULES: TOWARD HIGH VOLTAGE ALL ORGANIC LI-ION BATTERY.

A.-E. Lakraychi[a,b], J.-P. Bonnet[b], P. Poizot[c], M. Becuwe[b], F. Dolhem[a]
[a] *Laboratoire LG2A, UMR CNRS 7378, 10 rue Baudelcoque, 80039 Amiens, FRANCE*
[b] *Laboratoire LRCS, UMR CNRS 7314, 33 rue Saint-Leu, 80039 Amiens, FRANCE*
[c] *IMN, UMR CNRS 6502, 2 rue de la Houssinière, 44322 Nantes, France*

alae.eddine.lakraychi@u-picardie.fr

Because of their low cost, potential sustainability, environmental friendliness, and most importantly their large structural diversity, which make it conceivably usable as both positive and negative electrodes, organic-based electrode materials become one of the most promising candidates to replace scarce inorganic materials coming from geological resources for the new generation of “greener lithium ion batteries”.[1,2,3] Conjugated carbonyls have thus been early recognized as interesting electroactive materials characterized by high energy/power density and high cycling stability, but their implementation is still limited to Li metal cells with the serious safety issue caused by Li dendrites.[2] To be successful the Li-ion organic battery technology needs first, the implementation of a lithiated positive electrode able of competing with $LiCoO_2$ or $LiFePO_4$ and second, a negative electrode material operating at the target potentials (0.5-1.0 V) providing high voltage as well as safety.

Seeking for such efficient organic materials, our research group has reported recently, for positive electrode application, two organic salts able to reversibly deintercalate Li ions with promising electrochemical performance.[4,5] However their operating redox potential remain still too low which makes them unstable in ambient environment (difficult to store) and reduce the final output voltage. Concerning the negative electrode application, we proposed π-extended carboxylate core unit thus improving the cycling rate capability.[6,7]

Herein we report on a substitution approach around the organic backbone allowing tuning of the lithium storage potential in order to increase the output voltage. Firstly we present an upshift of the working potential of a dilithiumoxyquinone-derivative as a lithiated organic positive electrode stable to air (>3.0 V vs. Li^+/Li^0). Secondly and following the same approach, we present a downshift of the working potential of a carboxylate-based structure as an organic negative electrode able to use aluminum-based current collector (<0.8 V vs. Li^+/Li^0). The matching of both materials will pave the way toward a novel n-type all-organic Li-ion cell with an attractive working voltage greater than 2 Volts.

References:
[1] Poizot, P.; Dolhem, F. Energy Environ. Sci. 4 (2011) 2003−2019.
[2] Song, Z.; Zhou, H. Energy Environ. Sci. 6 (2013) 2280−2301
[3] Liang, Y.; Tao, Z.; Chen, J. Adv. Energy Mater. 2 (2012) 742−769
[4] Renault, S.; Gottis, S.; Courty, M.; Chauvet, O.; Dolhem, F.;Poizot, P. Energy Environ. Sci. 6 (201”) 2124−2133.
[5] Gottis, S.; Barrès A-L.; Dolhem, F.;Poizot, P. ACS Appl. Mater. Interfaces. 6 (2014) 10870−10876.
[6] Fédèle, L.; Sauvage, F.; Bois, J.; Tarascon, J.-M.; Bécuwe, M. Electrochem. Soc. 161 (2014) A46−A52
[7] Fédèle, L.; Sauvage, F.; Bécuwe, M. J. Mater. Chem. 6 (2014) 18225−18228.

QUINONE-BASED CATHODE MATERIALS FOR HIGH-VOLTAGE MAGNESIUM BATTERIES

Zhirong Zhao-Karger,[a] Ping Gao [a] and Maximilian Fichtner [a,b]
[a]*Helmholtz Institute Ulm (HIU), Albert-Einstein-Allee 11, D-89081 Ulm, Germany*
[b]*Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), P.O. Box 3640, D-76021 Karlsruhe, Germany.*

zhirong.zhao-karger@kit.edu

Magnesium (Mg) metal is an attractive anode material for rechargeable batteries, which possesses a low reduction potential (–2.37 V vs. SHE), high volumetric capacity (3833 mAh cm^{-3} *vs* lithium 2062 mAh cm^{-3} or sodium 1136 mAh cm^{-3}), natural abundance, and nature of dendrite-free electrochemical deposition[1]. The main challenges for the realization of Mg batteries lie on the one hand in the development of electrolyte which is stable in contact with the electrode materials and one the other hand in the design of cathode material offering high voltage and high capacity. Recently great progress has been made in the development of efficient electrolytes with broader electrochemical windows and better compatibility with the electrode materials. In contrast, the discovery of high energy cathode material is far behind.[2,3] In fact, most of the conventional intercalation materials are not capable of storing Mg^{2+} ions reversibly due to the intrinsically sluggish Mg^{2+} ion diffusion kinetics in the cathode hosts.[2,3] Redox-active organic cathode material is a promising alternative for magnesium batteries. So far only a few organic materials have been reported for magnesium batteries.[4–7] More research effort should be devoted for the sustainable organic Mg batteries. Besides design of new organic cathodes, it is also necessary to determine the optimal combination of the cathode and the electrolyte to achieve the better battery performance.

Herein, we report the use of quinone-based cathode materials with a non-nucleophilic electrolyte[8] for high-voltage magnesium batteries. A initial discharge capacity of 200 mA h g^{-1} with a discharge voltage plateau above 2.2 V *(vs* Mg) was demonstrated with the cathodes based on 2,5-Dimethoxy-1,4-Benzoquinone (DMBQ). To the best of our knowledge, this is the highest cell voltage achieved in current Mg batteries. In addition, the 9,10-Anthraquinone (AQ) was also proved to be capable of offering high-voltage and stable cycling stability in Mg batteries. These results show that the non-nucleophilic electrolytes are well suited for quinone-based materials and are promising for be incorporated with other high-voltage organic materials for the further improvement of Mg batteries.

References:
[1] T. D. Gregory, R. J. Hoffman, R. C. Winterton, *J. Electrochem. Soc.,* 137 (1990) 775–780.
[2] Selected recent review: J. Song, E. Sahadeo, M.Noked, S. B. Lee, *J. Phys. Chem. Lett.*, 7 (2016) 1736−1749.
[3] Selected recent review: P. Canepa , G. S. Gautam,. D. C. Hannah, R.Malik, M. Liu, K.G. Gallagher, K,A. Persson, G. Ceder, *Chem. Rev.,* 117 (2017) 4287−4341.
[4] H. Sano, H. Senoh, M. Yao, H. Sakaebe, T. Kiyobayashi, *Chem. Lett.* 41(2012) 1594–1596.
[5] J. Bitenc, K. Pirnat, T. Bancic, M. Gaberscek, B. Genorio, A. R. Vitanova, R. Dominko, Anthraquinone-Based Polymer as Cathode in Rechargeable Magnesium Batteries, *ChemSusChem,* 8 (2015) 4128-4132.
[6] B. Pan, D. Zhou, J. Huang, L. Zhang, A. K. Burrell, J. T. Vaughey, Z. Zhang, C. Liao, *J. Electrochem. Soc.*, 163 (2016) A580-A583.
[7] B. Pan, J. Huang, Z. Feng, L. Zeng, M. He, L. Zhang, J. T. Vaughey, M. J. Bedzyk, P. Fenter, Z. Zhang, A, K. Burrell, C. Liao, *Adv. Energy Mater., 6 (2016) 1600140*
[8] Z. Zhao-Karger, X. Y. Zhao, O. Fuhr, aM. Fichtner, *RSC Adv.*, 3 (2013) 16330–16335.

POTENTIAL TUNING IN QUINONE-PYRROLE DYAD BASED CONDUCTING REDOX POLYMERS

Hao Huang[a], Maria Strømme[a], Adolf Gogoll[b] and Martin Sjödin[a]
[a] *Nanotechnology and Functional Materials, Department of Engineering Sciences, The Ångström Laboratory, Uppsala University, Box 534, SE-751 21 Uppsala, Sweden*
[b] *Department of Chemistry - BMC, Biomedical Centre, Uppsala University, Box 576, SE-751 23, Uppsala, Sweden*

hao.huang@angstrom.uu.se

As high demanding on sustainable energy resources, organic batteries have drawn widespread attention. In the research of organic matter based electrode material, conducting polymers (CPs) have been investigated for their pronounced properties of conductivity. However due to their limited doping level, they are usually found low in capacity. By introducing redox molecules onto the CPs as pendant groups (PGs) which is covalently attached to the CP, thus conducting redox polymers (CRPs) are constructed in which syngeneic properties from both CP and PG are expected, i.e. high capacity, high conductivity as well as high stability. In this study, polypyrrole and quinone are chosen to compose the CRP. Herein, a series of CRPs was synthesized with various substituents on the quinone. DFT calculation was employed to predict the redox potential of the monomer candidates and good agreement between the calculation and the experimental data of the redox potential was achieved. By the choice of substituents on the quinone, the redox potential of CRP could be tailored. Furthermore, in the electrochemical characterization of these CRPs it is shown that the redox potential of PG must be within the conducting region of the CP to ensure fast charge transfer from the electrode to PG. Finally, two battery cells were constructed by choosing two pairs of CRPs. Well performance of the cells demonstrated the promising applicability of the CRPs as electrode materials in organic batteries.

NEW ACTIVE POLYMER FOR METAL ION BATTERIES BASED ON CYCLOOCTATETRAENE

Pierre Ranque [a,c], Frans G. B. Ooms [a], Wolter F. Jager [a], Ernst J. R. Sudhölter [a], Rémi Dedryvère [b,c], Erik M. Kelder [a,c]
[a] *Delft University of Technology, Van der Maasweg 9, 2629 HZ Delft, The Netherlands*
[b] *University of Pau, Hélioparc, 2 av. Pierre Angot, Pau Cedex 9, France*
[c] *Alistore - European Research Institute, 33 rue Saint-Leu, Amiens, Cedex, France*

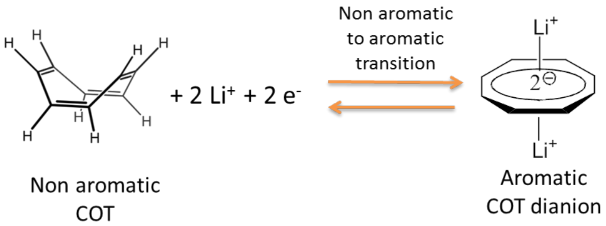
P.G.Ranque@TUDelft.nl

Electroactive organic material for ionic batteries are becoming seriously investigated during the past years [1]. Indeed, due to their composition of abundant elements (C, H, O, S …), these material are, at some extent, low cost, environmentally friendly and sustainable. Furthermore, these compounds display some interesting specific properties, such as conductivity [2], flexibility [1] and tuneable red/ox properties [3].

Until now, the most remarkable entity is the carbonyl group, which allows a reversible activity with lithium, sodium and potassium ions. Several compounds were recently explored such as quinones, polyimides and carbonyl derivatives [4].

The challenge of the research presented herein, is to investigate a new kind of active material utilizing a particular active group: the cyclooctatetraene, referred to as COT.

COT is an unsaturated hydrocarbon ring that can undergo a non aromatic to aromatic transition in presence of two electrons and two monovalent ions [5], as represented below. Intensely studied during the 70's, due to its complexion with uranium (cf. Uranocene) [6], this molecule is now mainly used for theoretical studies about its aromatic transition, or as a efficient π-type ligand for heavy metals [7].



Shape shifting properties of COT.

COT is a liquid at room temperature, and soluble in common electrolytes for batteries. This work will describe a way of obtaining a new useful electrode material for metal ion batteries, based on the affinity of electron acceptance in the π-system of COT. The compound synthesized has been elaborated to not be soluble in standard battery electrolytes anymore.

First we will present how to functionalize COT, to further polymerise it as an insoluble solid polymer. It is stressed that the basic π-system of COT will be preserved by this polymerization. Electrochemical tests using cyclic voltammetry and galvanostatic titration show that this new compound has a reversible capacity of 300 mAh/g.

References:
[1] Z. Song and H. Zhou, Energy Environ. Sci. 6 (2013) 2280-2301.
[2] P. Jiménez et al., Angew. Chem. Int. Ed. 56 (2017) 1553-1556.
[3] G. S. Vadehra et al., Chem. Mater. 26 (2014) 7151-7157.
[4] S. Muench et al., Chem. Rev. 116 (2016) 9438-9484.
[5] T. J. Katz, J. Am. Chem. Soc. 82 (1960) 3784-3785.
[6] A. Streitwieser Jr. and U. Mueller-Westerhoff, J. Am. Chem. Soc. 90 (1968) 7364-7364.
[7] F. T. Edelmann, Coordination Chemistry Reviews 338 (2017) 27–140.

SULFONATED QUINONES REDOX COUPLES FOR APPLICATION IN AQUEOUS REDOX FLOW BATTERIES

Petr Mazúr[a], Vojtěch Svoboda[b], Jiří Vrána[b], Jan Dundálek[b], Jaromír Pocedič[a], Juraj Kosek[a]
[a]University of West Bohemia Pilsen, New technologies – Research centre, 306 14 Pilsen, Czech Republic
[b]University of Chemistry and Technology, Prague, Dep. of Chemical Engineering, Technická 5, 166 28 Prague 6, Czech Republic

mazurp@vscht.cz

The increased share of renewable energy sources with intermittent production regime (such as photovoltaics and wind turbines) emphasized the need for reliable, safe and economic energy storage technology. Due to decoupled power from capacity, simplified heat regime and extended durability, redox flow batteries are promising candidate for stationary storage of large energy volumes. However, the negative economic and environmental aspects connected with typically used metal-based battery electrolytes (e.g., vanadium, chromium etc.) motivate the research for alternative electroactive compounds with suitable properties for the application. Organic molecules of quinone-type represent promising alternative as they are stable and react reversibly even on cheap carbon-based electrodes [1]. Moreover, the solubility in aqueous solutions and reduction potential can be tailored by suitable substituents [2].

In our contribution, the selected sulfonated and hydroxylated benzoquinones and anthraquinones are comprehensively characterized with the respect to the application. We study the effect of pH, temperature and cation type on the solubility in aqueous solutions and kinetics of electrode reactions on graphite felt. Fast electrode reaction kinetics was observed in acidic environment (pH of 0) for all the tested molecules, however, it deteriorated at higher pH, probably due to the change of reaction mechanism. The optimized electrolytes were finally tested in a flow battery single cell.

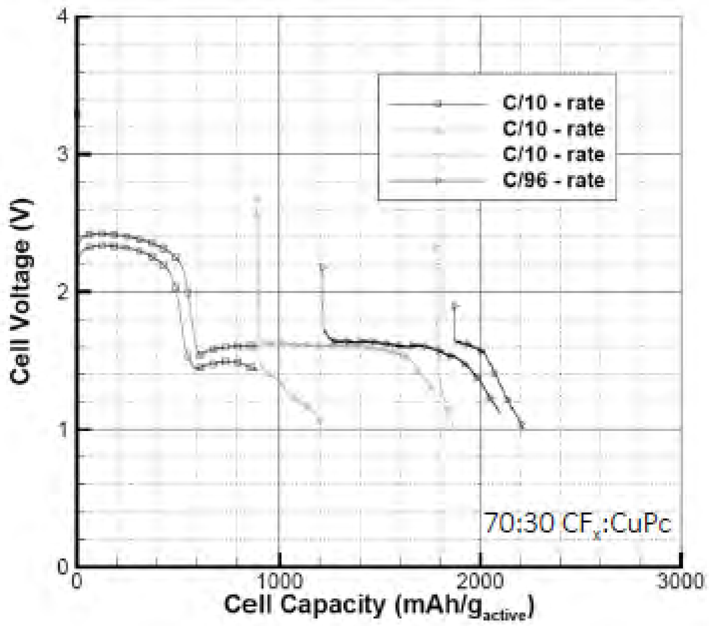
References:
[1] J. Winsberg, T. Hagemann, T. Janoschka, M. D. Hager, U. S. Schubert , Angew. Chem. Int. Ed. 56 (2017) 686 – 711
[2] S. Er, C. Suh, M.P. Marshak, A. Aspuru-Guzik, Chemical Science, 6 (2015) 885-893.

USE OF COPPER PHTHALOCYANINE TO ENHANCE LITHIUM/CARBON MONOFLUORIDE BATTERY PERFORMANCE

Joseph P. Fellner[a], Max Tsao[b]
[a] *Air Force Research Laboratory, 2130 8th Street, Wright-Patterson AFB, OH 45433-7103*
[b] *University of Dayton Research Institute, 300 College Park, Dayton, OH 45469-0074*

joseph.fellner@us.af.mil

The lithium carbon monofluoride primary battery has a very high energy density (>500 Wh/kg) due to the high theoretical and observable coulombic capacity (~865 mAh/g) and moderate discharge voltage (~2.5 volts). Several problems associated with this type of lithium primary battery are high heat generation at moderate to high discharge rates and a lack of state-of-charge indication due to a flat discharge voltage profile. We have demonstrated in coin cells that by using mixtures of various ratios of carbon monofluoride to copper phthalocyanine, the observable coulombic capacity based on the cathode active materials can be greatly enhanced from 865 mAh/g to over 2000 mAh/g. Also, two different voltage plateaus are observed during the discharge which can be used as a state-of-charge indication. Further work is needed to characterize the amount of heat reduction as a function of the amount of copper phthalocyanine used in the cathode mixture.



TUNING CRITICAL CHARACTERISTICS OF NFC-PEDOT SUPERCAPACITORS

Dagmawi Belaineh[a], Sapiens Malti[b], Andrea Grimoldi[a], Xavier Crispin[a], Magnus Berggren[a],
Isak Engquist[a]
[a] *Laboratory of Organic Electronics, Department of Science and Technology, Linköping University, Norrköping, Sweden*
[b] *Department of Fibre and Polymer Technology, KTH—Royal Institute of Technology, Stockholm, Sweden*

dagmawi.belaineh@liu.se

Recently a robust conducting paper composed of Poly(3,4-ethylene- dioxythiophene) : poly(styrene-sulfonate) (PEDOT:PSS) and nanofibrillated cellulose (NFC) has been demonstrated. NFC-PEDOT is flexible, scalable and exhibits excellent electrical and mechanical properties. [1] The superior mixed ion-electron conductivity of this paper promises a scalable bulk manufactory of supercapacitors which otherwise would not be possible using only PEDOT:PSS. In this report we do a systematic study of some key material parameters which determine the remarkable mechanical and electrical properties of this composite system. For this purpose, we use a range of PEDOT:PSS with varying conductivity, ionic purity and chemical stability. We also illustrate the direct effect of the chemical and morphological makeup of the cellulose material on device properties by using cellulose with varying charged groups and molecular weights to tune the power and energy characteristics of supercapacitors.

Reference:
[1] A. Malti , J. Edberg , H. Granberg , Z. U. Khan , J. W. Andreasen , X. Liu , D. Zhao , H. Zhang , Y. Yao , J. W. Brill , I. Engquist , M. Fahlman , L. Wågberg , X. Crispin, and M. Berggren, Adv. Sci. 3 (2016) 1500305.

DUAL ANION-CATION REVERSIBLE INSERTION IN BIPYRIDINIUM-DIIMIDE NEGATIVE ELECTRODE ACTIVE MATERIALS FOR AQUEOUS BATTERY

Sofia Perticarari[a], Chris Ewels[a], Dominique Guyomard[a], Michel Armand[c], Fabrice Odobel[b],
Philippe Poizot[a] and Joel Gaubicher[a]

[a] *Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, 2 rue de la Houssiniere, 44322 Nantes Cedex 3, France.*
[b]*CEISAM, Chimie et Interdisciplinarité, Synthèse, Analyse, Modélisation, Université de Nantes, 2, rue de la Houssinière, 44322 Nantes Cedex 3, France*
[c]*CIC energigune, Alava Technology Park, Albert Einstein 48,01510 Miñano Álava, Spain*

sofia.perticarari@cnrs-imn.fr

With increasing diffusion of renewable energy sources, such as solar and wind power, into the global energy markets, electric energy storage technologies are mandatory to suppress the impact of intermittent power and integrate renewable energy sources into the electric grid. Although different types of electrochemical systems, from conventional lead-acid to vanadium-flow batteries and advanced Li-ion batteries, have been proposed, none of them have been recognized as an enabling technology for grid-scale electric storage because of their cost and resource restrictions. Aqueous rechargeable Na-ion batteries seem to be a good choice as storage systems. However, today, the performances of these batteries are limited by low capacity negative electrodes and among the enormous range of active materials available from the field of non-aqueous batteries, only few of them offer the combination of appropriate potential as well as high chemical and electrochemical stability in aqueous media. Therefore the use of cheap, abundant, recyclable and non-toxic organic active materials appears as a logical step towards the improvement of environmental and economic aspects. This communication will present the electrochemical and physical behaviors of p-n type derivatives, obtained by means of low cost and highly scalable synthesis route, in neutral aqueous electrolytes. All results point to very optimistic prognostic for the use of this kind of materials, thanks to the advantageous coupling of the two subunits at the molecular level, i.e. high capacity and low solubility of the n-type Naphthalene diimide core and low potential hysteresis and high cyclability of the p-type Pyridinium one. Outstanding cyclability and coulombic efficiency were achieved opening up new directions for designing cheap rocking chair dual ions aqueous batteries for grid storage.

LITHIUM-DOPED POLYANILINE AS CONDUCTING, REDOX ACTIVE COMPONENT OF POSITIVE ELECTRODES

Pablo Jiménez [a,b], Michael Lejeune [c], Dominique Guyomard [a], Joël Gaubicher [a], Franck Dolhem [b], Philippe Poizot [a]

[a]Institut des Matériaux Jean Rouxel (IMN), UMR CNRS 6502, Université de Nantes, 2 rue de la Houssinière, B.P. 32229, 44322 Nantes Cedex 3, France

[b]Laboratoire de Glycochimie, des Antimicrobiens et des Agroressources (LG2A), UMR CNRS 7378, Université de Picardie Jules Verne, 33 rue Saint-Leu, 80039 Amiens, France

[c] Laboratoire de Physique de la Matière Condensée, Université de Picardie Jules Verne, 33 rue Saint-Leu, 80039 Amiens, France

pablo.jimenez-manero@cnrs-imn.fr

Within the great variety of organic redox-active materials available for electrochemical storage of energy, conducting polymers represent an interesting class due to their intrinsic properties. Firstly their polymeric nature makes them less prone to solubilize in liquid electrolytes than discrete, low molecular weight organic molecules. Secondly, their extended conjugated structure is able to effectively delocalize charge along the backbone giving them a better stability in the charged state. In addition conducting polymers usually present a good electrical conductivity in the so called “doped” oxidation states which would help to reduce the amount of conductive additive, usually high for organic active materials, in the electrode mixture.

Here we report the use of a recently developed[1] form of polyaniline (PANI) especially adapted for lithium-ion batteries. It is the product of the substitution of nitrogen-bonded hydrogens for lithium cations yielding a conducting, formally n-doped PANI which we named lithium emeraldinate (ELi). The electrochemical performance of ELi as positive active material is superior to other previously reported forms of PANI. The set of favorable properties of ELi includes, *inter alia*, a high specific capacity (230 $mAh.g^{-1}$), an excellent coulombic efficiency, good rate capability and long term cycling stability.

One of the strong points of this material is the versatility of its processing: in fact ELi state of PANI can be produced through a sequence of reactions under mild conditions starting either from the *in situ* polymerized emeraldine salt (ES) state or from solution-processed emeraldine base (EB) state. This enables the exploitation of the properties of ELi not only as a bulk active material but as a functional additive. For example thin coatings of ELi can act as an electrical and ionic conducting layer on a non-conducting inorganic active material for Li-ion batteries like $LiFePO_4$; or act as a pseudocapacitative material on a high surface area mesoporous carbon for Li-ion capacitor electrodes. In both cases the energy density and power performance of the electrodes is improved thanks to the presence of ELi. Regarding the last example the mesoporous carbon employed, produced from the pyrolysis of squaric acid[2], −a good candidate material for capacitative energy storage thanks to its good conductivity and high specific surface area− it presents some drawbacks (like a bad coulombic efficiency at low current rates and a relatively low specific capacity) which can be swiftly overcome with the presence of an uniform coating of ELi on the surface of the carbon.

References:
[1] P. Jiménez, E. Levillain, O. Alévêque, D. Guyomard, B. Lestriez, J. Gaubicher, *Angew. Chem.* 129 (2017) 1575.
[2] Leclère, M., Lejeune, M., Dupont, L., Barrès, A.L., Renault, S., Dolhem, F., Poizot, P. *Mater. Lett.*, 137 (2014) 233-236.

RECONSIDERING INTERACTIONS IN REDOX POLYMERS

Martin Kolek[a], Fabian Otteny[b], Pia Schmidt[b], Martin Winter[a,c], Birgit Esser[b],
Peter M. Bieker[a]

[a] *MEET Battery Research Center, Institute of Physical Chemistry, University of Muenster, Corrensstraße 46, 48149 Muenster, Germany*
[b] *Institute for Organic Chemistry, University of Freiburg, Albertstr. 21, 79104 Freiburg, Germany*
[c] *Helmholtz-Institute Muenster (HI MS), IEK-12, Forschungszentrum Juelich GmbH, Corrensstrasse 46, 48149 Muenster, Germany*

martin.kolek@uni-muenster.de

The next generation of energy storage devices based on batteries or supercapacitors will have to fulfill several requirements such as high specific energy and power, long cell life and cost efficiency. Additionally, factors regarding greener approaches are focused considering reliability and recyclability.[1] Some of the “new” approaches in energy storage are just reviving battery chemistries which were already studied in the past but become a niche research field with the rise of the lithium-ion battery technology.[2,3] One of these approaches are electrochemically active polymers. A very early investigated example is the conducting polymer poly(acetylene) which allows the doping and undoping of its structure due to unsaturated bonds with partially oxidized and/or reduced chains.[4] Polymers with redox activity along the chains are often sensitive to the harsh environment during electrochemical processes. The shifting of the redox activity to side chains was a promising way to stabilize the cycling behavior of the redox polymers. In 2004, Nishide and coworkers published a TEMPO functionalized polymer, PTMA, with high cycling stabilities and a redox potential around 3.5 V *vs*. Li/Li^+.[5] With increasing publications on this polymer the strength of side chain-functionalized polymers was proven.[6]

We focused on this kind of redox-active polymers and studied several approaches of alternatives to the TEMPO group.[7] Our investigations guided us to some general principles which seem to be a drawback on the first view but can lead to improved cycling behavior if they are understood in the correct context.[8]

In this contribution, we would like to present some of these ideas, which are based on inter- and intramolecular interactions, studied by classical spectroscopic techniques as UV/Vis and EPR spectroscopy as well as XPS. In the end we contribute this findings to electrochemical data and discuss the beneficial aspects of our approach.

References:
[1]Armand, M.; Tarascon, J. M., *Nature* 451 (2008) 652-657.
[2]Novák, P.; Müller, K.; Santhanam, K. S. V.; Haas, O., *Chem. Rev.* 97 (1997) 207-282.
[3]Schon, T. B.; McAllister, B. T.; Li, P.-F.; Seferos, D. S., *Chem. Soc. Rev.* 45 (2016) 6345-6404.
[4]Nigrey, P. J.; MacInnes, D.; Nairns, D. P.; MacDiarmid, A. G.; Heeger, A. J., *J. Electrochem. Soc.* 128 (1981) 1651-1654.
[5]Nishide, H.; Iwasa, S.; Pu, Y.-J.; Suga, T.; Nakahara, K.; Satoh, M., *Electrochim. Acta* 50 (2004) 827-831.
[6]Muench, S.; Wild, A.; Friebe, C.; Häupler, B.; Janoschka, T.; Schubert, U. S., *Chem. Rev.* 114 (2016) 9438-9484.
[7]Speer, M. E.; Kolek, M.; Jassoy, J. J.; Heine, J.; Winter, M.; Bieker, P. M.; Esser, B., *Chem. Commun.* 51 (2015) 15261-15264.
[8]Kolek, M.; Otteny, F.; Schmidt, P.; Mück-Lichtenfeld, C.; Becking, J.; Einholz, C.; Schleicher, E.; Winter, M.; Bieker, P. M.; Esser, B., *submitted* (2017).

List of Participants

NAME	First Name	Organization	City	Country	e-mail address	# abs.
Acker	Pascal	University of Freiburg	Freiburg	Germany	pascal.acker@mars.uni-freiburg.de	P2
Alloin	Fannie	University Grenoble Alpes, CNRS	Grenoble	France	fannie.alloin@lepmi.grenoble-inp.fr	K2
Araujo	C. Moyses	Uppsala University	Uppsala	Sweden	moyses.araujo@physics.uu.se	P17
Bančič	Tanja	National Institute of Chemistry	Ljubljana	Slovenia	tanja.bancic@ki.si	O2
Becuwe	Matthieu	University of Picardy Jules Verne	Amiens	France	matthieu.becuwe@u-picardie.fr	O11
Beladi-Mousavi	S. Mohsen	University of Osnabrück	Osnabrück	Germany	sbeladimousa@uos.de	P5
Belaineh Yilma	Dagmawi	Linköping University	Norrköping	Sweden	dagmawi.belaineh@liu.se	P28
Björklund	Erik	Uppsala University	Uppsala	Sweden	erik.bjorklund@kemi.uu.se	--
Bradburn	Chris	Gammadata Instrument AB	Uppsala	Sweden	chris.bradburn@gammadata.se	--
Brandell	Daniel	Uppsala University	Uppsala	Sweden	daniel.brandell@kemi.uu.se	--
Burak	Aktekin	Uppsala University	Uppsala	Sweden	Burak.aktekin@kemi.uu.se	--
Carboni	Marco	Uppsala University	Uppsala	Sweden	marco.carboni@kemi.uu.se	--
Carretero González	Javier	Institute of Polymer Science and Technology	Madrid	Spain	jcarretero@ictp.csic.es	O5

NAME	First Name	Organization	City	Country	e-mail address	# abs.
Casado	Nerea	POLYMAT, University of the Basque Country	Donostia	Spain	nerea_casado001@ehu.eus	O14
Castillo Martínez	Elizabeth	University of Cambridge	Cambridge	United Kingdom	ec469@cam.ac.uk	K6
Chaleawlert-umpon	Saowaluk	Max Planck Institute of Colloids and Interface	Potsdam	Germany	saowaluk.chaleawlert-umpon@mpikg.mpg.de	P3
Chen	Ruiyong	KIST Europe, Saarland University	Saarbrücken	Germany	r.chen@kist-europe.de	O4
Colò	Francesca	Uppsala University	Uppsala	Sweden	francesca.colo@polito.it, francesca.colo@kemi.uu.se	P18
Dagron	Thierry	Armor group	La Chevrolière	France	thierry.dagron@armor-group.com	--
Delaboissière	Arthur	SCE-France	Lacq	France		--
Dolhem	Franck	University of Picardy Jules Verne	Amiens	France	franck.dolhem@u-picardie.fr	--
Dominko	Robert	National Institute of Chemistry	Ljubljana	Slovenia	robert.dominko@ki.si	K5
Dubois	Lionel	Université Grenoble Alpes	Grenoble	France	lionel.dubois@cea.fr	O3
Ebadi	Mahsa	Uppsala University	Uppsala	Sweden	mahsa.ebadi@kemi.uu.se	--
Edberg	Jesper	Linköping University	Norrköping	Sweden	jesper.edberg@liu.se	P14
Edström	Kristina	Uppsala University	Uppsala	Sweden	Kristina.Edstrom@kemi.uu.se	--
Eliseeva	Svetlana	Saint Petersburg State University	St. Petersburg	Russia	svetlana.eliseeva@spbu.ru	P20&21

NAME	First Name	Organization	City	Country	e-mail address	# abs.
Emanuelsson	Rikard	Uppsala University	Uppsala	Sweden	rikard.emanuelsson@angstrom.uu.se	P12
Eriksson	Therese	Uppsala University	Uppsala	Sweden	therese.linnea.eriksson@kemi.uu.se	--
Esser	Birgit	University of Freiburg	Freiburg	Germany	besser@oc.uni-freiburg.de	O6
Fellner	Joseph P.	Air Force Research Laboratory	Dayton, OH	USA	joseph.fellner@us.af.mil	P27
Gao	Ping	Helmholtz Institute Ulm	Ulm	Germany	ping.gao@kit.edu	P6
Gaubicher	Joël	IMN-CNRS University of Nantes	Nantes	France	joel.gaubicher@cnrs-imn.fr	--
Guichard	Pierre	Armor group	La Chevrolière	France	pierre.guichard@armor-group.com	--
Gustafsson	Torbjörn	Uppsala University	Uppsala	Sweden	Torbjorn.Gustafsson@kemi.uu.se	--
Gutel	Thibaut	LITEN, CEA	Grenoble	France	thibaut.gutel@cea.fr	O9
Hausen	Florian	Institute of Energy and Climate Research, IEK-9	Jülich	Germany	f.hausen@fz-juelich.de	--
Huang	Hao	Uppsala University	Uppsala	Sweden	hao.huang@angstrom.uu.se	P24
Jiménez	Pablo	IMN-CNRS University of Nantes	Nantes	France	pablo.jimenez-manero@cnrs-imn.fr	P30
Jouhara	Alia	IMN-CNRS University of Nantes	Nantes	France	Alia.Jouhara@cnrs-imn.fr	P0
Kawai	Takuma	Waseda University	Tokyo	Japan	faith.is.4love@asagi.waseda.jp	O13

NAME	First Name	Organization	City	Country	e-mail address	# abs.
Kolek	Martin	University of Münster	Münster	Germany	martin.kolek@uni-muenster.de	P31
Korell	Michael	Evonik Creavis GmbH	Marl	Germany	michael.korell@evonik.com	--
Kotronia	Antonia	Uppsala University	Uppsala	Sweden	antonia.kotronia@kemi.uu.se	--
Kwon	Ji Eon	Seoul National University	Seoul	South Korea	mracle2@snu.ac.kr	O15
Lacey	Matthew	Uppsala University	Uppsala	Sweden	matthew.lacey@kemi.uu.se	--
Lakraychi	Alae Eddine	University of Picardy Jules Verne	Amiens	France	alae.eddine.lakraychi@u-picardie.fr	P22
Leprêtre	Jean-claude	University Grenoble Alpes, CNRS	Grenoble	France	jean-claude.lepretre@lepmi.grenoble-inp.fr	--
Levin	Oleg	Saint Petersburg State University	St. Petersburg	Russia	o.levin@spbu.ru	O1
Liedel	Clemens	Max Planck Institute of Colloids and Interfaces	Potsdam	Germany	Clemens.Liedel@mpikg.mpg.de	O8
Lüder	Johann	National University of Singapore	Singapore	Singapore	mpejoha@nus.edu.sg	P15
Ma	Le Anh	Uppsala University	Uppsala	Sweden	le.anh.ma@kemi.uu.se	--
Mallet	Charlotte	Esstalion Technology Inc.	Varennes	Canada	mallet.charlotte@esstalion.com	--
Marchiori	Cleber	Uppsala University	Uppsala	Sweden	c.marchiori@physics.uu.se	--
Matsubara	Hiroshi	Osaka Prefecture University	Osaka	Japan	matsu@c.s.osakafu-u.ac.jp	P11

NAME	First Name	Organization	City	Country	e-mail address	# abs.
Mazúr	Petr	University of West Bohemia Pilsen	Pilsen	Czech Republic	mazurp@vscht.cz	P26
Min	Dong Joo	Seoul National University	Seoul	South Korea	mracle2@snu.ac.kr (JEK) and parksy@snu.ac.kr (SYP)	P8
Mogensen	Ronnie	Uppsala University	Uppsala	Sweden	ronnie.mogensen@kemi.uu.se	--
Morizur	Vincent	SCE-France	Lacq	France		--
Nordh	Tim	Uppsala University	Uppsala	Sweden	Tim.nordh@kemi.uu.se	--
Oltean	Viorica Alina	Uppsala University	Uppsala	Sweden	alina.mihali@kemi.uu.se	P9
Otteny	Fabian	University of Freiburg	Freiburg	Germany	fabian.otteny@mars.uni-freiburg.de	P1
Oyaizu	Kenichi	Waseda University	Tokyo	Japan	oyaizu@waseda.jp	K1
Perticarari	Sofia	IMN-CNRS University of Nantes	Nantes	France	sofia.perticarari@cnrs-imn.fr	P29
Pirnat	Klemen	National Institute of Chemistry	Ljubljana	Slovenia	klemen.pirnat@ki.si	P10
Poizot	Philippe	IMN-CNRS University of Nantes	Nantes	France	philippe.poizot@cnrs-imn.fr	--
Ranque	Pierre	Delft University of Technology	Delft	The Netherlands	P.G.Ranque@TUDelft.nl	P25
Renault	Steven	Uppsala University	Uppsala	Sweden	steven.renault@kemi.uu.se	--
Reza	Younesi	Uppsala University	Uppsala	Sweden	reza.younesi@kemi.uu.se	--

NAME	First Name	Organization	City	Country	e-mail address	# abs.
Sandberg	Mats	RISE Acreo	Norrköping	Sweden	mats.sandberg@ri.se	P7
Sångeland	Christofer	Uppsala University	Uppsala	Sweden	christofer.sangeland@kemi.uu.se	--
Schubert	Ulrich S.	Friedrich Schiller University	Jena	Germany	ulrich.schubert@uni-jena.de	K3
Sjödin	Martin	Uppsala University	Uppsala	Sweden	martin.sjodin@angstrom.uu.se	O7
Sterby	Mia	Uppsala University	Uppsala	Sweden	Mia.sterby@angstrom.uu.se	P4
Strietzel	Christian	Uppsala University	Uppsala	Sweden	christian.strietzel@angstrom.uu.se	P16
Tomšík	Elena	Institute of Macromolecular Chemistry	Prague	Czech Republic	tomsik@imc.cas.cz	P13
Tripathi	Abhinav	National University of Singapore	Singapore	Singapore	e0010775@u.nus.edu	O10
Wang	Huan	Uppsala University	Uppsala	Sweden	huan.wang@angstrom.uu.se	P19
Wild	Andreas	Evonik Creavis GmbH	Marl	Germany	andreas.wild@evonik.com	PS
Yao	Yan	University of Houston	Houston, TX	USA	yyao4@uh.edu	K4
Yao	Masaru	National Institute of Advanced Industrial Science and Technology	Osaka	Japan	m.yao@aist.go.jp	O12
Zhao-Karger	Zhirong	Helmholtz Institute Ulm	Ulm	Germany	zhirong.zhao-karger@kit.edu	P23
Zielinski	Dennis	Cromocol Scandinavia AB/Bio-Logic SAS	Borås	Sweden	dennis@cromocol.se	--

WEDNESDAY 06/07	THURSDAY 06/08	FRIDAY 06/09
	08:15 Registration Desk	
		09:00 K3 **U.S. SCHUBERT**
	09:15 Welcome address	
	09:30 K1 **K. OYAIZU**	**09:30** PS **A. WILD**
	10:00 O1 **O. LEVIN**	**10:00** O12 **M. YAO**
	10:20 Coffee break	**10:20** O13 **T. KAWAI**
	10:40 O2 **T. BANCIC**	**10:40** Coffee break
	11:00 O3 **L. DUBOIS**	**11:00** K4 **Y. YAO**
	11:20 O4 **R. CHEN**	
		11:30 K5 **R. DOMINKO**
	11:40 O5 **J. CARRETERO-GONZALEZ**	
	12:00 Lunch	**12:00** Lunch
	13:30 K2 **F. ALLOIN**	**13:30** K6 **E. CASTILLO MARTINEZ**
	14:00 O6 **B. ESSER**	**14:00** O14 **N. CASADO**
	14:20 O7 **M. SJODIN**	**14:20** O15 **J. E. KWON**
	14:40 O8 **C. LIEDEL**	**14:40** Closing Remarks
	15:00 Coffee break	**15:00** Coffee break
	15:30 O9 **T. GUTEL**	**15:30** Board of Organic Battery Days Discussions for the next event
	15:50 O10 **A. TRIPATHI**	
	16:10 O11 **M. BECUWE**	**(K) => KEYNOTE (25' + 5')** **(O) => ORAL (15' + 5')**  ORGANIC BATTERY DAYS 8-9 June 2017, Uppsala, Sweden
	16:30 Poster Session	
19:00 Welcome Party & Registration Desk **"The Orangery"**	**19:00** Conference Dinner **"Café Ångström"**	