RedoxFlow2020

November 09-10th 2020

Web-Conference

Organized by the French Network on Redox-Flow batteries (GDR RedoxFlow)

https://gdr-redoxflow.cnrs.fr/

Program

Monday, November 9th

10:00 Introduction

Chair: Florence Geneste

10:10 Invited talk: **Peter Fischer** (Fraunhofer Institute for Chemical Technology), Jens Tübke "What kind of flow battery chemistry has the potential to replace the all-vanadium flow battery in the future?"

10:55 "Anthraquinone and viologen derivatives for aqueous redox flow battery electrolytes", *Petr Mazur (University of Chemistry and Technology Prague), Jaroslav Kvíčala, Filip Bures, Milan Klikar, Zuzana Burešová, Kubáč Lubomír*

11:15 "Aqueous Organic Redox Flow Batteries: challenges and achievements", *Thibault Godet-Bar (Kemiwatt)*

11:35 "Organic redox active materials: on the importance of the structure and counterion design", *Eduardo Sanchez* (CIC Energigune), *Ana Catarina Lopes, Oihane Zugazua, Maddalen Agirre, Michel Armand, Raquel Ferret*

11:55 *Flash presentation* "Lignin-based electrolytes for organic RFBs", Evgeny Larionov *(CMBlu Energy AG), Olga Ekkert, Doris Neumann, Peter Geigle*

12:00 *Flash presentation "In situ study of ORFB using NMR/MRI and additive manufacturing"* Borja *Caja Munoz (CEA Saclay)*

12:05 *Lunch*

Chair: Steven Le Vot

14:00 "Synthesis, Characterization and DFT Calculation of New Bipyridine-type Electrolytes for Aqueous Redox Flow Batteries." *Juan Asenjo (Universidad Autonoma de Madrid), Ivan Salmeron-Sànchez, Eduardo Sánchez-Díez, Pablo Mauleón, Juan Ramón Aviles, Pilar Ocón*

14:20 "Use of the dye 3,4-dihydroxy-9,10-anthraquinone-2-sulfonic acid in alkaline AORFB: a case study", *Solene Guiheneuf (Université de Rennes), Florence Geneste, Didier Floner, Thibault Godet-Bar, Jean-Marie Fontmorin*

14:40 "Aqueous solubility of Organic compounds for flow Battery applications", *Denes Konya (Research center for natural Sciences), Sergio Navarro Garcia*

15:00 "Characterization of Ion-Exchange Membranes for Aqueous Redox Flow Battery Application" *Ivan Salmeron-Sànchez (Universidad Autonoma de Madrid), Juan Asenjo-Pascual, Pablo Mauleón, Juan Ramón Avilés-Moreno, Pilar Ocón*

15:20 *Flash presentation* "Correlation study of polymer structure, membrane properties and cell performance in an aqueous organic redox flow battery"

Misgina Tilahun Tsehaye (Université Grenoble Alpes), Xian Yang, Tobias Janoschka, Fannie Alloin, Cristina Iojoiu

15:25 *Break*

Chair: Hyacinthe Randriamahazaka

15:45 Invited talk: **Peljo Pekka** (University of Turku) "Pathways Towards Next Generation Energy Storage Technologies Based on Redox Flow Batteries: Aqueous Organics and Solid Boosters"

16:30 "Synergic effects between carbon nanofluids and redox couples dispersed in O2 reduction electrolytes", *Eulalia Pujades-Otero (Institut de Ciencia de Materials de Barcelona), Nieves Casañ-Pastor, Dino Tonti*

16:50 "Experimental aspects of the redox-targeting reaction of $LiFePO_4$ with ferri/ferrocyanide in aqueous posolyte", *Jose Francisco Vivo-Vilches (Université de Picardie Jules Verne), Arina Nadeina, Noura Rahbani, Vincent Seznec, Dominique Larcher, Emmanuel Baudrin*

17:10 *Open discussion about COST action, Mathieu Etienne*

Tuesday, November 10th

Chair: Cristina Iojoiu

10:00	“Composite Anion Exchange Membrane Proposed for RFBs.” *Martyna Charyton (Amer-sil), Mathieu Etienne, Mateusz Donten*
10:20	“Composite polymer-ceramic ion-conducting membranes based on LATP and LAGTP ceramics for novel all-organic redox-flow batteries”, *Nikolay Ovsyannikov (Skoltech), Elena Romadina, Nikita Akhmetov, Alexey Sanin, Irina Krasnikova, Mariam Pogosova, Pavel Troshin, Keith Stevenson*
10:40	“Effect of membrane properties on the performance of vanadium oxygen fuel cell”, *Jiří Charvát (University of Chemistry and Technology Prague), Petr Mazur, Martin Paidar, Jaromír Pocedič, Juraj Kosek*
11:00	“Highly Conductive and Selective Anion Exchange Membranes for High Performance TMA-TEMPO/MV-based Neutral Aqueous Organic Redox Flow Battery”, *Misgina Tilahun Tsehaye (Université Grenoble Alpes), Xian Yang, Tobias Janoschka, Fannie Alloin, Cristina Iojoiu*
11:20	“Chemical compatibility of commercial seals in next generation redox flow batteries”, *Detlef Jannes (University of Stuttgart), Lothar Hörl, Frank Bauer*
11:40	“Overcoming the limitations of membranes: high performant anionic exchange membranes for aqueous organic redox flow batteries”, *Caterina Sansone, Xian Yang (Université Grenoble Alpes), Tobias Janoschka, Martin Hager, Ulrich Schubert, Cristina Iojoiu*
12:00	*Flash presentation* “Effect of operation conditions on the performance of alkaline Zinc-air flow battery”, *Přemysl Richtr (University of Chemistry and Technology Prague), Jan Dundálek, Petr Mazur, Jiří Charvát, Jaromír Pocedič, Juraj Kosek*
12:05	*Flash presentation “Graphene-based materials as electrodes in vanadium redox flow batteries*”, *Antonio Jesús Molina-Serrano (Instituto de Carboquimica), C. Alegre , J. Vivo, D. Sebastián., F. Carrasco,M.J. Lázaro.*
12:10	*Lunch*

Chair: Mathieu Etienne

14:00	“Development of safe and performant bromine based electrolytes for hydrogen/bromine redox flow batteries”, *Michael Kuettinger (Fraunhofer Institute for Chemical Technology), Raphael Riasse, Theo Faverge, Ruben Brunetaud, Peter Fischer, Jens Tuebke*
14:20	“Redox Flow Battery - Application to Salt Cavern”, *Cyriane Fournier (Geostock), Florence Geneste, Didier Floner, Philippe Barboux*

14:40 “Understanding the vanadium redox-flow battery: an in-depth study using the distribution of relaxation times analysis”, *Jonathan Schneider (Freie Universitat Berlin), Tim Tichter, Christina Roth*

15:00 “Deactivation of negative felt electrode of vanadium redox flow battery: Double half-cell set-up experiments”, J. Mrlík (University of Chemistry and Technology Prague), Mazúr Petr, Pocedič Jaromír, Vrána Jiří, Dundálek Jan, Charvát Jiří, Kosek Juraj

15:20 *Flash presentation* “Mitigation of capacity and efficiency fade in Vanadium redox flow batteries”, *Martin Bureš (University of Chemistry and Technology Prague), Petr Mazur, Jiří Charvát, Jaromír Pocedič, Juraj Kosek*

15:25 *Break*

Chair: David Pasquier

15:45 “Determining charge transfer kinetic constants for fast reversible systems on porous electrodes using Electrochemical Impedance Spectroscopy”, *Vincent Feynerol (Université de Lorraine), Liang Liu, Oihane Zugazua, Maddalen Agirre, Ana Catarina Lopes, Eduardo Sánchez-Díez, Mathieu Etienne*

16:05 “0D modeling to help development of new ORFB electrolytes”, *Quentin Cacciuttolo (IFPEN), Martin Petit, David Pasquier*

16:25 “Exploring the thermodynamics of the bromine electrode in concentrated solutions for improved parametrisation of the hydrogen-bromine flow battery models”, *Jakub Włodarczyk (ZHAW), Michael Kuettinger, Andreas Friedrich, Jürgen Schumacher*

16:45 “Towards concentrated solution theory in flow battery modelling: measuring the chemical activity of aqueous electrolytes via Differential Scanning Calorimetry”, *Gaël Mourouga (ZHAW), Matthieu Courty, Emmanuel Baudrin, Juergen O. Schumacher*

17:05 “Water transport in VRFB: experiments and simulations”, Gvozdik Nataliya (Skolkovo Institute of Science and Technology), Ryzhov Alexander, Panin Igor, Pugach Mikhail, Vlasov Valentin, Stevenson Keith

17:25 “©FlowBat – redox flow battery simulator”, Pugach Mikhail (Skolkovo Institute of Science and Technology), Panin Igor, Ryzhov Alexander, Stevenson Keith

17:45 closing remarks

Abstracts

What kind of flow battery chemistry has the potential to replace the all-vanadium flow battery in the future?

Peter Fischer (1), Jens Tübke (1)
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Abstract

Vanadium flow batteries are widely acknowledged as long duration storage for stationary applications. Nevertheless, a huge variety of flow battery technologies have been published in literature during the last four years.

In this talk the advantages and disadvantages of vanadium flow battery technology will be presented. The conventional VRFB will be contrasted with different new emerging flow battery systems. Examples of current research at Fraunhofer ICT will be presented.

Anthraquinone and viologen derivatives for aqueous redox flow battery electrolytes

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Vanadium redox flow batteries, with several MWh-scale installations worldwide[1], proved to be a safe, reliable and long-lasting energy storage technology. However, high and fluctuating price of vanadium stimulate the seek for alternative active compounds. Organic redox couples are particularly attractive[2, 3] as their relevant properties can be tailored by modification of their chemical structure. Moreover, they can be produced at high volumes and low costs e.g., from oil residues.

In our study a series of organic redox active compounds based on bipyridine or anthraquinone was synthesized and characterized with respect to their application in redox flow battery as active compound of negative electrolyte. General electrochemical characterization was assessed from voltammetric experiments using glassy carbon rotating disc electrode at different pH of electrolyte. Selected molecules were tested in a flow electrolysis cell using carbon felt electrodes to evaluate their electrochemical stability under conditions of application. The change in chemical structure of the redox molecules due to cycling was evaluated by NMR analysis of the electrolytes.

References:
[1] USA, D.o.E.o., www.energystorageexchange.org/projects. 2015, Sandia Corporation.

[2] Leung, P., et al., Recent developments in organic redox flow batteries: A critical review. Journal of Power Sources, 2017. 360: p. 243-283.

[3] Winsberg, J., et al., Redox-Flow Batteries: From Metals to Organic Redox-Active Materials. Angewandte Chemie International Edition, 2017. 56(3): p. 686-711.

The work was supported from European Regional development Fund-Project "Organic redox couple based batteries for energetics of traditional and renewable resources (ORGBAT)" No.CZ.02.1.01/0.0/0.0/16_025/0007445.

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Aqueous Organic Redox Flow Batteries: challenges and achievements

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Redox Flow Batteries[1] stand for one of the most reliable emerging candidates as stationary ESS. Among many advantages, one can cite that: (i) it can deliver above 3-4 hours of storage durations while increasing its cost competitiveness; (ii) it can propose low capex and opex thanks to the use of standard component and the high durability of the molecules; (iii) and it's one the safest ESS solution (specifically water-based RFB) thanks to its inability to catch fire or to explode. Also, depending on the active materials synthesis process, their physicochemical properties and their stability, there is room (iv) for developing low carbon footprint productions and (v) for recovering them after their cycling life in closed-loop recycling.

However, some drawbacks do not allow RFBs to deliver all of its expected key features at the same time. As an example, most developed RFBs to date use corrosive electrolytes and toxic active species, generating reliability, safety and environmental issues. They also usually suffer from cross-contamination, membrane fouling, poor energy efficiency, raw material costs fluctuation, vulnerability to impurities, precipitation, etc. Alternative chemistries, like organic- and organometallic- based electrolyte, are currently under development at different stages of technological maturity. Considering the state-of-the-art academic publications, a lot of different chemistries appear to be very promising but the majority of the exhibited battery tests are conducted in ideal conditions. These tests tend to shield unwanted secondary reactions that shall appear at real-size scale. In addition, most of the time, great performances in terms of energy density, power density and durability are demonstrated, but they are rarely achieved at the same time, which is what is required in the full-size system.

In this context, Kemiwatt has developed a set of characterization tools, namely batteries with specific design features and adapted process components, allowing to diagnose the system's achievements in close-to-real conditions. This validation equipment allows to identify the physical and chemical limits that shall be reached in upper scales. Besides, it saves us significant time on the development process. A specific example of a reproducible test at different scales will be presented to illustrate this statement.

In parallel, commercially available quinones were tested up to the system's scale, showing honorable results during demonstration phases. However, developing a competitive commercial product requests to develop more effective redox active molecules. Thanks to the versatile nature of organic materials, we have selected a proprietary quinone (in the negolyte) used in combination with a ferrocyanide salt (in the posolyte). Specific battery components have also been selected. In this presentation, we will also disclose typical battery performances and initiate discussion about the challenges and the expected optimization roads to cover.

[1] K. Mongird *et al.*, "Energy storage technology and cost characterization report" *Pacific Northwest Natl. Lab.* n° July (2019) pp. 1–120

Organic redox active materials: on the importance of the structure and counterion design

Sánchez-Díez, Eduardo[1], Lopes, Ana Catarina [1], Zugazua, Oihane [1], Agirre, Maddalen[1], Armand, Michel[1], Ferret, Raquel[1]
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Redox flow batteries will play a key role in the energy transition. Based on independent power and energy scaling, they are well suited for stationary energy storage. Vanadium stands as the most popular active material and represents the state-of-art of the technology. Good performance, the use of a single species for both anolyte and catholyte and demonstrated long stability are main features of VRFBs. However, limitations of this technology, resulting from the volatile price of V_2O_5 raw material,[1] have triggered a constant search for new redox chemistries. Organic redox active materials, based on earth-abundant elements that will result in lower environmental impact while avoiding any concern for truly large scale required for grid storage, are advocated to replace inorganic materials.[2]

Aqueous organic redox flow batteries combine positive advantages of the aqueous media (safe, highly conductive, economical) with highly tunable redox active materials to deliver desired properties. Recently, several examples of systems that successfully operate at neutral pH have been reported. Despite the good stability[3] and low corrosivity shown by those electrolytes, neutral electrolytes are generally less energy efficient and less powerful than their alkaline and acid counterparts. High battery resistance would be responsible for this problematic for neutral AORFBs and work on membrane and electrolyte formulation has turned to be essential to increase conductivity among other parameters.[4]

In line with these reports, a detailed fundamental study on the impact of both structural modifications and counterion selection on different parameters as solubility, conductivity, viscosity and kinetics is provided. Thus, application oriented design of redox active materials should not only aim for tuning of redox potential and solubility. In comparison to deeply studied vanadium electrolytes, there is still room to improve recently reported chemistries and prove the potential of AORFBs.

References:

1. a) https://www.vanadiumprice.com/; b) Weber, A. Z *et al.* Redox Flow Batteries: A Review. *J. Appl. Electrochem*, *41*, **2011**, 1137.
2. Schubert, U. S. *et al.* Redox-Flow Batteries: From Metals to Organic Redox-Active Materials. *Angew. Chem. Int. Ed*. *56*, **2017**, 686.
3. a) Liu, Y. *et al.* A Long-Lifetime All-Organic Aqueous Flow Battery Utilizing TMAP-TEMPO Radical. *Chem. 5*, **2019**, 1861; b) Hu, B. et al. Long-Cycling Aqueous Organic Redox Flow Battery (AORFB) toward Sustainable and Safe Energy Storage. *J. Am. Chem. Soc. 139*, **2017**, 1207. c) Beh, E. S. *et al.* A Neutral pH Aqueous Organic−Organometallic Redox Flow Battery with Extremely High Capacity Retention. *ACS Energy Lett. 2*, **2017**, 639.
4. a) Hu, B. *et al.* Boosting the energy efficiency and power performance of neutral aqueous organic redox flow batteries. *J. Mater. Chem. A*, *5*, **2017**, 22137. b) Luo, J. *et al.* Unprecedented Capacity and Stability of Ammonium Ferrocyanide Catholyte in pH Neutral Aqueous Redox Flow Batteries. *Joule*, *35*, **2019**, 1.

Acknowledgements
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Lignin-based electrolytes for organic RFBs

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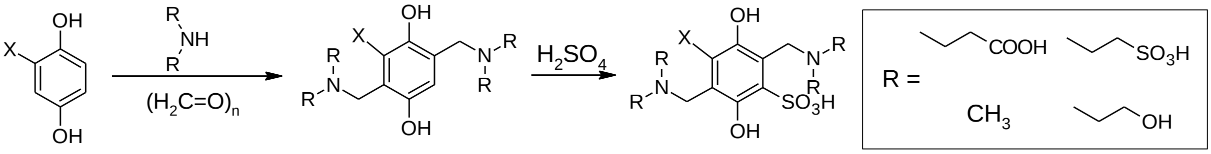
CMBlu is a pioneer and market leader in the area of Organic Flow Batteries, which can be used flexibly as stationary energy storage systems in the entire energy value chain and help to balance energy generation and consumption. In cooperation with leading university groups and industrial partners, CMBlu is developing the key technology for an environmentally friendly and sustainable energy transition since 2014. The goal is to make a substantial contribution to a secure, efficient and sustainable power supply worldwide. In addition to the management board and 70 employees, a prototype production and one of the largest R&D centers for Organic Flow Systems globally are located in Alzenau, which is close to Frankfurt/Main in Germany.
Organic Flow Batteries of CMBlu are characterized by an organic storage medium – the electrolyte – which can be derived from the natural substance Lignin. Lignin is a naturally renewable source and occurs in pulp and paper production as a waste product on a million-ton per year scale. This guarantees a permanently available source for large-scale energy storage. Here we present our studies on the synthesis of hydroquinone derived electrolytes and investigations of their electrochemical properties.



Synthesis of hydroquinone derivatives studied in organic RFBs

References:
[1] Krawczyk, Nastaran; Moeller, Alexander; Geigle, Peter; Larionov, Evgeny; Hartwig, Jan; Production of lignin-derived low molecular weight products for use as redox flow battery electrolytes at large scale with reduced cost *WO2018146344*
[2] Geigle, Peter; Hartwig, Jan; Larionov, Evgeny; Baal, Eduard; Lignin-derived redox-active compounds for redox-flow battery electrolytes *WO2020035138*

In situ study of ORFB using NMR/MRI and additive manufacturing

Borja *Caja Munoz (CEA Saclay)*

The present thesis project aims to study operating cells taking advantage of integrated dynamic nuclear magnetic resonance systems combined with the progress in additive manufacturing technologies. The recent advances enable the development of an innovative battery real-time monitoring device for the identification of different molecular species and migrations generated during the operation of an organic redox flow battery (ORFB).

For this purpose, several 3D-printed mini-battery prototypes have been designed optimizing parameters such as size, geometry, compartments volume and electrodes material. A vertical super wide bore magnet is available to perform spatially resolved imaging and localized spectroscopy in different positions of the battery during in situ or in operando experiments, with the main goal being to understand the degradation mechanism of the redox molecule (anthraquinone derivatives) during cycling. Moreover, the main challenge to make this system work lies in overcoming operational constraints such as voxel size limitations, radiofrequency interferences or magnetic field and spectral homogeneities.

On the other hand, micro-fluidic and NMR micro-detection devices are designed with different probe head coil geometries (solenoid, saddle coil) and plugged in standard microimaging or other liquid-NMR probes. The 18 mm 3D-printed insert, so-called “half-cell”, is coupled with an airlift pump were the gas bubbles set the solution in motion, allowing the liquid to circulate in a small fluidic loop. Thus, displacement mechanisms of molecular species can be studied by means of this high-sensitivity system, notably the effect of self-diffusion and the effect of the group flow velocity.

Finally, the behavior of several electrolytes is studied during the redox reaction at different conditions of concentration and pH in order to identify a reversible redox quinone with optimal working potential (Wh/L) and ionic conductivity (W/L).

Synthesis, Characterization and DFT Calculation of New Bipyridine-type Electrolytes for Aqueous Redox Flow Batteries.

Asenjo-Pascual, Juan[a]; Salmerón-Sànchez, Ivan[a]; Sánchez-Díez, Eduardo[c]; Mauleón, Pablo[b]; Avilés, Juan Ramón[a]; Ocón, Pilar[a]
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[c] CIC Energigune. Parque Tecnológico de Álava, Albert Einstein 48, 01510 Miñano, Álava (Spain)

Abstract

The use of renewable energies has emerged as an imperative due to the critical consequences of climate change. However, the intermittent nature of some of these renewablee energies constitutes a significant drawback in the context of massive-scale integration. Redox Flow Batteries (RFB) have surfaced as promising energy storage systems to solve this problem [1]. Indeed, the use of cheap and easily tunable water-soluble organic electrolytes stands as a promising strategy for future RFB. Along the organic electrolytes, Methyl Viologen derivatives have been widely studied showing low capacity retention due to bimolecular annihilation [2].

Herein, we present a family of non-planar bipyridines as promising electrolytes for Aqueous Organic Redox Flow Batteries (AORFB). The synthesis of these compounds by conventional microwave radiation is easy, cheap and eco-friendly. Once prepared, we have evaluated physical and electrochemical properties of these compounds: in particular, two of them (**BP6** and **BP7**) show high solubility in water and highly reversible redox process with fast kinetics and high diffusion coefficients. *In situ* measurements using Raman spectroscopy confirm the presence of the reduced species. Also, in order to better understand the structural and electronic behaviour of this family of compounds, DFT calculations have been performed on the structure of the redox pair which show that the dihedral angle plays a key role in the reversibility of the redox process. Moreover, NBO and AIM analysis help understand this fact in terms of electronic delocalization and non-covalent interactions.

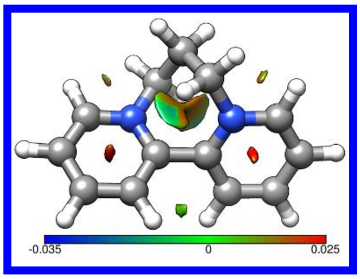

Figure 1: Atom in Molecule analysis of the **BP7**

Plans for the near future include the use of these compounds as organic electrolytes in Redox Flow Batteries. Additionally, we will conduct theoretical and experimental characterization of different derivatives in order to improve their behaviour as electrolytes.

Acknowledgements

This work has been supported by the European Union under HIGREEW, Affordable High-performance Green Redox Flow batteries (Grant Agreement no. 875613)

References
[1] (a) Z. Yang, Z.; Zhang, J.; Kintner-Meyer, M. C. W.; Lu, X.; Choi, D.; Lemmon J. P.; Electrochemical Energy Storage for Green Grid. *Chem. Rev*. 111 (2011) 3577.
[2] (a) Hu, B.; Tang, Y.; Luo, J.; Grove, G.; Guo, Y.; Liu, T. L.; Improved radical stability of viologen anolytes in aqueous organic redox flow batteries. *Chem. Commun.* 54 (2018) 6871.

Use of the dye 3,4-dihydroxy-9,10-anthraquinone-2-sulfonic acid in alkaline AORFB : a case study

Solène Vacher-Guiheneuf [a], Florence Geneste[a], Didier Floner[a], Jean-Marie Fontmorin[a],
Thibault Godet-Bar [b]
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[b] Kemiwatt, 11 allée de Beaulieu - CS 50837, F-35708 Rennes cedex 7, France

To make a water-based redox flow battery competitive with respect to traditional batteries for the storage of intermittent energy, it must comply with a number of demanding specifications in terms of performances (energy density > 10 Wh/L, voltage > 1 V), durability (capacity loss < 20% after 4 000 cycles) and cost (price of electrolyte < 110 €/kWh). To achieve this goal, a large variety of electrolyte solutions have been studied. Quinones and particularly anthraquinones have been considered as interesting negolyte in AORFB owing to their reversible two-electron redox system. In this work made in collaboration with the Kemiwatt Company, we report the performances of anthraquinonoid derivatives in redox flow batteries. We studied the overall process from their synthesis to their stability in operating systems, evaluated over several months of cycling.

We used the commercially available dye 3,4-dihydroxy-9,10-anthraquinone-2-sulfonic acid *versus* ferrocyanide in alkaline medium, whereas it has been previously used in neutral and acidic conditions [1,2]. Advantageously, the presence of phenolate groups on anthraquinone shifted negatively its potential, leading to a high potential window of 1.2 V. It also improved its solubility compared to the 9,10-anthraquinone-2-sulfonic acid, depending on the nature of the cations. Indeed, the cation associated to the sulfonate moiety is a critical parameter to improve solubility [1]. A high solubility of 0.5 M was obtained and a demonstrated energy density up to 13 Wh L^{-1} could be reached using the highly soluble potassium salt of ARS. The hydroxide concentration is also determinant concerning both solubility and viscosity. The influence of ARS purity, the applied current and the cations on the performances of ARS in a redox flow battery of 25 cm^2 were studied. Despite a rapid capacity loss in the early stage (100 first cycles), it represented less than 0.02% of the theoretical capacity per cycle. The evolution of the electrolyte composition was studied on 4000 cycles, using cyclic voltammetry, NMR, mass spectrometry and ion chromatography analyses. ARS slowly degraded into a reversible electroactive compound. This product was then synthetized and evaluated in a 25 cm^2 cell, showing a high chemical stability over several hundred cycles.

References (Times New Roman, 10 points) :
[1] J. Carretero-Gonzaical, E.Castillo-Martinez, M. Armand. Highly water-soluble three-redox state organic dyes as bifunctional analytes *Energy Environ. Sci.* (9) (2016), 3521.
[2] Shu Zhang, Xin Li, Dandan Chu. An Organic Electroactive Material for Flow Batteries. *Electrochim. Acta* (190) (2016), 737.

Aqueous solubility of Organic compounds for flow Battery applications

Sergio Navarro Garcia[a], Denes Konya[a]
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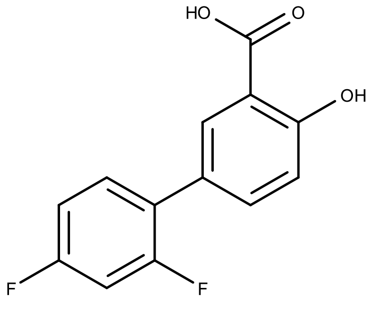
Organic compounds, based on abundant elements, are appealing alternative as electrolyte for redox flow batteries. The straighforward scalability, the independence of material sources and the potencially attractive price, pushes researchers to investigate this technological area. Organic compounds however tend to be soluble rather in organic solvents. Organic solvents are usually flammable, toxic and expensive for stationary applications. Water as solvent is cheap, not flammable, safe, so a much desirable option. Unfortunately most of organic compounds are poorly soluble in water. In this presentation a rough estimation is given for the minimal solubility needed to build a fully organic redox-flow battery on an economic way and some important factors of solubility is highlighted. In the shed of these factors, a short explanation is given about the difficultiness of predicting aqueous solubility of organic compounds.



(Diflunisal)

Pharma and ORFBresearch: concerning solubility predictions, we are all in the same boat!

Characterization of Ion-Exchange Membranes for Aqueous Redox Flow Battery Application

Salmeron-Sànchez Ivan[a], Asenjo-Pascual Juan[a], Mauleón Pablo[b], Avilés-Moreno Juan Ramón[a], Ocón Pilar[a]
[a] Departamento de Química Física Aplicada, [b] Departamento de Química Orgánica, Universidad Autónoma de Madrid, C/ Francisco Tomás y Valiente 7, 28049, Madrid (Spain).

Aqueous Redox Flow Batteries are considered the best option to store electricity from medium to large scale applications, performing in a sustainable and highly efficient way. Many prototypes have been developed such as all-vanadium that has been extensively studied.[1,2] One of the key components of these systems is the ion exchange membrane (cationic and/or anionic) Figure 1. The function of the membrane is to prevent cross mixing of the positive and the negative electrolytes and the short-circuit of the two half cells. Additionally, they should offer good ionic conductivity and present an economic viability as an alternative to the most widely used membrane, the Nafion® membrane.

The properties of these membranes differ depending on the following characteristics: polymeric matrix, the functional group that allows the exchange of ions, the homogeneity at the microstructure phase[3] and especially the membrane-electrolyte interaction.[4,5] All this attributes directly affects the performance of the battery, e.g. its capacity and energy efficiency.

In this work we performed a comparative study of the physicochemical properties (water uptake, swelling ratio, ion exchange capacity, crossover and conductivity) and the evaluation of the electrical response by chronopotentiometry of commercial ion exchange membranes. Those selected will be susceptible to modify and tested in electrochemical cycling tests to evaluate the energy efficiency for battery application for the HIGREEW project.

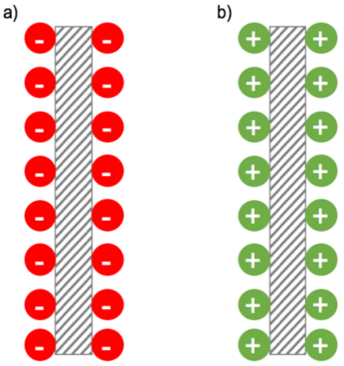


Figure 1. Types of polymeric ion-exchange membranes with functional groups : a) cationic and b) anionic.

Acknowledgements:
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Correlation study of polymer structure, membrane properties and cell performance in an aqueous organic redox flow battery

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Neutral aqueous organic redox flow batteries (AORFBs) are a promising alternative for large-scale electrochemical energy storage due to their sustainable, noncorrosive and environmentally friendly nature[1]. AORFBs employing water-soluble dimethyl viologen chloride (MV) and *N*,*N*,*N*-2,2,6,6-heptamethylpiperi-dinyl oxy-4-ammonium chloride (TMA-TEMPO) was demonstrated as a stable and high performance flow battery.[2] The lifespan, performance and cost of the battery depends on the chemical composition and properties of the employed membrane. Therefore, synthesis of a suitable membrane, which shows a high ion conductivity, selectivity, optimized water uptake and adapted mechanical strength, is required[3].

In the present work, five anion-exchange membranes employing poly(p-phenylene oxide) grafted with poly(diallylpiperidinium chloride) were prepared via a rapid UV irradiation method. The correlations of polymer structure, membrane properties and cell performance in a TMA-TEMPO/MV-based AORFB were investigated. The trend in available capacity after 100 cycles at 80 mA/cm^2 was closely related to the initial resistance of the membranes and degree of cross-contamination. The capacity fade was attributed to the cross-contamination of TMA-TEMPO and MV, which strongly depends on the water uptake of the membrane. The best-resulting battery exhibited excellent coulombic efficiency (>99%) and high power density (258 mW/cm^2). Our results provide insights in guiding the selection and preparation of suitable membranes to improve the cycling stability and performance of AORFBs.

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Pathways Towards Next Generation Energy Storage Technologies Based on Redox Flow Batteries: Aqueous Organics and Solid Boosters

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Redox flow batteries offer interesting options for electrochemical energy storage and even for heat-to power conversion. In the first part of the talk, we will discuss the possibilities offered by organic redox couples in aqueous solutions [1],
report some recent examples from our lab, and describe our collaborative efforts for computational screening of organic redox couples within CompBat H2020-project. In the second part of the talk, we shall introduce the concept of solid boosters for flow batteries. The advantage of such systems is that it allows relaxing the requirement for high solubility of the redox couple, significantly increasing the number of redox couples available for flow batteries. Wang et al. First suggested this concept, where the electrolyte tank is filled with solid redox active mm-sized beads forming a backed-bed type system, in 2013 [2]. Firstly, the redox mediator is charged in the electrochemical cell and pumped back into the storage tank. The charge is then transferred into the solid material in a chemical reaction with the mediator, similarly to "molecular wiring" used, for example, in electrochemical enzymatic glucose sensors [3]. The redox mediator can then be further charged in the electrochemical cell. We and others have shown that significant amount of the charge storage capacity of the solid materials can be used with a single mediator, if the redox potentials of the solid and soluble materials match well enough. [4-7] Since charge storage density is much higher in solids, lower concentration of the mediators can be utilized as the capacity of the flow battery boosted with solids is mostly due to the solid only.

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Synergic effects between carbon nanofluids and redox couples dispersed in O_2 reduction electrolytes

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Carbon materials have a high electronic conductivity and low density, which make them essential additives in electrodes for electrochemical storage devices[1]. However, the use of nanocarbon material suspensions in the electrolyte of such devices is also attractive for two aspects: increasing total electrode active surface area and/or building percolation networks for electrons[2]. For these reasons, nanocarbons have been considered as components in semi-solid electrolytes, which can be considered one class of nanofluids.
Furthermore, the introduction of multiredox couples dispersed in the electrolyte can also lead to remarkable improvements, as seen in Li/air batteries[3]. These redox couples can act both as redox mediators and catalysts for the oxygen reduction or evolution reactions (ORR, OER) that take place during the battery cycling. Polyoxometalate clusters or other nanoparticles such as IrOx are already known by their catalytic activity in O_2 reduction and reoxidation processes[5].

In this work we show the influence of carbon black and redox couples in organic media for the cathode of metal-air batteries, *i.e.* O_2 reduction electrolytes. The addition of nanocarbons or mediators separately does not result on an impedance decrease or a clear effect on terms of current densities and overpotentials. Nevertheless, we observe a synergy between the redox and the conducting components added simultaneously, giving rise to enhanced currents, lower overpotentials and lower impedances for the charge transfer and diffusion processes. The relevant parameters and hypothesis for a mechanism will be discussed based on impedance analysis.

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Experimental aspects of the redox-targeting reaction of $LiFePO_4$-with ferri/ferrocyanide in aqueous posolyte

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In a Redox Targeting Redox Flow Batteries (RT-RFB), solid insertion materials react with soluble flowing active species (redox mediators) [1]. Such an approach is challenging namely in finding couples of mediators and insertion materials having similar electrochemical potentials, and in optimizing the interaction between the solid and the flowing electrolyte. First, we studied and optimized a $LiFePO_4$ (LFP) - ferri/ferrocyanide posolyte playing with the DMSO/water solvent ratio to adjust the potentials, and we assessed the thermodynamic and kinetic of the reaction. Secondly, we had to optimize the experimental setup. Indeed, first attempts using LFP powder were unsuccessful. Much better results were obtained using i) LFP particles shaped as dense pellets with controlled total porosity, obtained by Spark Plasma Sintering with NaCl microcrystals as hard template and ii) an extra-tank localized between the cell and the electrolyte reservoir and containing the pellet(s). We first tested LFP pellets with 30 % porosity (LFP30) and indeed observed a related increase in capacity compared to the sole mediator-based electrolyte (Figure 1.a), but the coulombic efficiency was low with difficulties to re-insert Li^+ during the reduction. Hence, LFP pellets with larger porosity were prepared (40%). In that case, much higher capacity and reversibility were achieved (Fig. 1.b). At low current density (0.25 $mA.cm^{-2}$) full capacity is spotted for both the mediator and the solid material, with a first-cycle reversibility of 99 %, and a doubling of the capacity with only 1 vol % of added $LiFePO_4$ in the electrolyte.

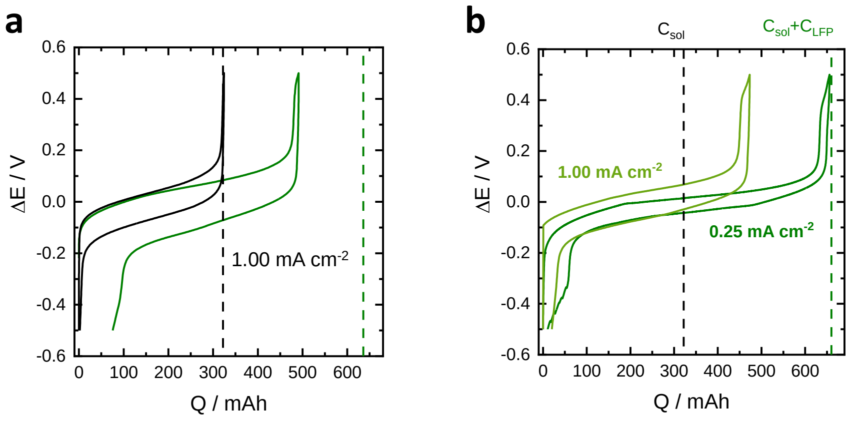

Figure 1: Galvanostatic cycling (a) $K_4Fe(CN)_6$ as posolyte (black) and after adding LFP30 (green). (b) Same after adding LFP40, obtained at 1.00 (light green) and 0.25 (dark green) $mA·cm^{-2}$

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Composite Anion Exchange Membrane Proposed for RFBs.

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A novel, composite membrane consisting of a PVC/Silica porous substrate coated with a thin layer of an anion-exchange polymer has been prepared and characterized for application in Redox Flow Batteries (RFBs) (Fig 1a). The composite membrane is formed in a two-step process. Blade coating technique can be used to apply poly(vinyl pyrrolidone) (PVP) – a well-known commodity ionomer mixed with radically reactive precursors and an initiator onto the porous substrate. During the second step, UV curing, a strong polymeric backbone is formed immobilizing PVP in an interpenetrating polymeric network (IPN). The crosslinked matrix of IPN prevents dissolution and excessive swelling of the highly hydrophilic ionomer enabling its use in aqueous electrolyte. Furthermore, by changing the amount of PVP in the coating one can easily tune ion conductivity and perm selectivity which have a significant impact on the final performance of the membrane in an RFB cell or stack.

The innovative fabrication process allows to obtain the material starting with low-cost commodity chemicals (such as N-[3-(Dimethylamino)propyl]methacrylamide or *N*-Hydroxyethyl acrylamide) in a straight forward process. The mechanically robust porous substrate allows considering a wider range of ionomers and precursors including those that do not form self-supported films. This can be seen as a practical advantage over the methods used for making of commercially available dense ion-exchange membranes [1].

The dependence between the composite membrane's characteristics and the content of PVP in the coating can be also observed in the cycling results. To evaluete performance of the membranes in RFB, the membrane was assembled in a Vanadium RFB test cell (20 cm^2 of active area). Fig. 1.b shows that at 80mA/cm^2 the membrane consisting of 14 wt. % PVP in the coating exhibited energy efficiency close to that of Nafion N115 (74.9% versus 75.5%). Comparing the performance with two other membranes (8% and 11% PVP) it can be observed that higher wt.% of PVP leads to improved hydrophilicity and ion conductivity, resulting in the increase of voltage efficiency. Following that trend coulombic efficiency decreases.

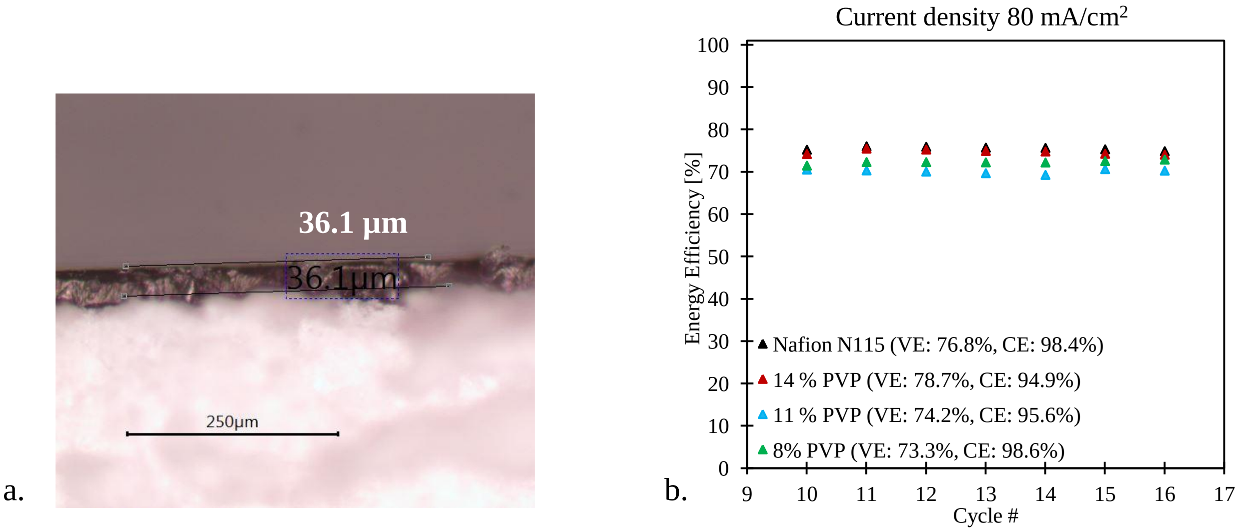

Figure 1. a. microscope picture of the crosss section of the membrane
b. Energy efficiency of the tested membranes a. current density 80 mA/cm

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Composite polymer-ceramic ion-conducting membranes based on LATP and LAGTP ceramics for novel all-organic redox-flow batteries

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Redox-flow batteries (RFBs) are perspective next-generation electrochemical energy storage devices due to independent power and capacity control, high energy efficiency (up to 90%), and ease scalability [1]. Although higher energy density and working potential distinguish all-organic RFBs beneficially from aqueous ones, high resistance and crossover rate of the contemporary membranes (e.g. Neosepta AHA) reduce the RFB energy efficiency and cycle life significantly [2]. Li-conductive ceramics were recently shown to be a perspective solution to these issues due to high ionic conductivity (up to 10^{-3} S/cm) and suppressed crossover [3]. Unfortunately, along with such essential advantages, ceramics do possess certain limitations, such as mechanical fragility that shortens the whole battery's life cycle. In order to overcome the highlighted challenges, here we investigate the composite Li-conductive polymer-ceramic membranes that combine the high ionic conductivity of ceramic superionic conductors and high mechanical flexibility and wide electrochemical stability window typical for polymers.

For this purpose we selected the $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP) and $Li_{1.4}Al_{0.4}Ge_{0.2}Ti_{1.4}(PO_4)_3$ (LAGTP) as a ceramic filler and polyvinylidene fluoride (PVdF) as a polymer binder, optimized the membrane fabrication route, and studied its performance. The studies by the electrochemical impedance spectroscopy (EIS) revealed the membranes possessed the ionic conductivity of $0.6\text{-}2\cdot10^{-5}$ S/cm at 23 °C in dry form and $1\text{-}2\cdot10^{-4}$ S/cm at 23 °C after being soaked in supporting electrolyte solution. The electronic conductivity studied by the DC polarization was about 10^{-10} S/cm. The linear sweep voltammetry (LSV)-based electrochemical stability window tests resulted in the value 1.9-4.7 V vs. Li^+/Li. Finally, the application of fabricated membranes in viologen-triarylamine-based h-cells and their further cycle testing revealed the current efficiency exceeds 95%. The volumetric capacity was 53.6 mAh/L after the first cycle (86% of the redox couple's theoretical value) and stabilized on the level of 42 mAh/L (65% of the theoretical value) after 50 cycles.

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Effect of membrane properties on the performance of vanadium oxygen fuel cell

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Vanadium redox flow battery is one of the most developed type of stationary energy storage technology but it has some disadvantages such as low energy density and relatively high price. A vanadium oxygen fuel cell (VOFC), where the positive electrolyte (VO^{2+}/VO_2^+ couple) is replaced by oxygen reduction, could significantly improve energy density and reduce costs of capacity as only negative electrolyte is used. Moreover, concentration of vanadium electrolyte can be substantially increased when compared to standard vanadium redox flow battery where the stability of positive electrolyte limits the concentration to 1.6 – 2.0 mol dm^{-3}.

In this work, the effect of membrane properties such as thickness and ion-exchange capacity on the performance and mid-term stability of VOFC is systematically studied for a broad range of ion-exchange membranes. Innovative incorporation of vanadium-oxygen flow electrolyser into the testing set-up enabled us to study the performance stability at constant and defined state of charge of vanadium electrolyte. In general, stable and efficient operation at higher current densities (up to 100 mA cm^{-2}) is achieved with membranes of higher ion-exchange capacity and reduced thickness. In contrast to the most of the previous studies, our results reveals that vanadium permeation across the membrane does not significantly contribute to the performance decay of the fuel cell, but the optimisation of water management in the catalyst layer of gas diffusion cathode is crucial for efficient and stable performance of the fuel cell.

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Highly Conductive and Selective Anion Exchange Membranes for High Performance TMA-TEMPO/MV-based Neutral Aqueous Organic Redox Flow Battery

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Neutral aqueous organic redox flow batteries (AORFBs) employing water-soluble dimethyl viologen (MV) and *N,N,N*-2,2,6,6-heptamethylpiperi-dinyl oxy-4-ammonium chloride (TMA-TEMPO) molecules has been demonstrated as stable system with high electrochemical energy storage performance[1]. As a key component, the membrane allows the transport of the charge carriers while preventing the intermixing of the redox-active molecules in the electrolyte solutions, despite of which, appropriate membranes designed for the system are usually overlooked in many studies[2].

In this work, a series of flexible and conductive anion-exchange membranes (AEMs) composed of PPO with six carbon side chain ended with quaternary ammonium (Diazabicyclo[2.2.2]octane)-DABCO or Trimethylamine - TMA) were fabricated via casting and tested in the TMA-TEMPO/MV–based AORFB single cell. The PPO-DABCO AEM exhibited much higher peak power density than a well-performing commercial membrane (FAA-3-50®, Fumatech) (388 vs 244 mW/cm^2) (Figure 1). Moreover, our membrane permitted to obtain excellent coulombic efficiency (>99%) and a high energy efficiency (80% vs. 78%) than the commercial membrane. Our results show an excellent membrane candidate to improve the cell performance of AORFBs.

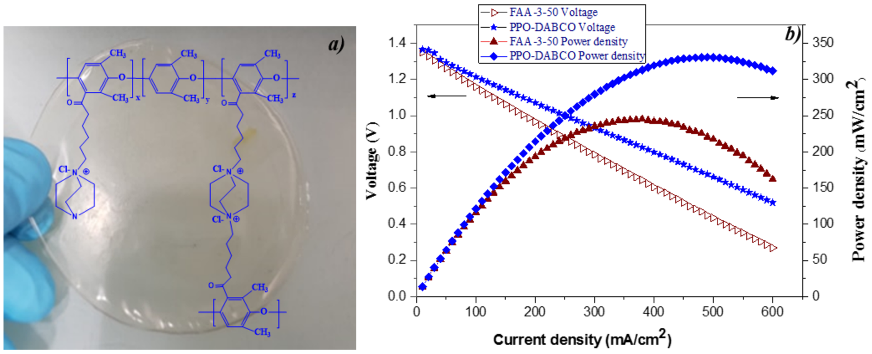

Figure 1: a) Schematic representation of the prepared membrane structure and b) polarization curve of FAA-3-50 and PPO-DABCO membranes

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Chemical compatibility of commercial seals in next generation redox flow batteries.

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A semi objective way to generate an overview on the mechanical properties of an elastomer after a ISO 1817 submersion, is with an elastomer compatibility index (ECI). This creates a baseline to evaluate the effects of the electrolyte on the elastomer materials, which are used as sealing elements. On slightly elevated temperatures, the ISO 1817 submersion test provides insight on long-term chemical corrosion effects. The ECI gives a relative overview of the change on the following elastomer properties: hardness, volume swell/shrink, tensile strength and strain at break. In the FlowCamp project, this method is applied on various sealing materials with electrolytes for Hydrogen-Bromine, Zinc-Air and organic next generation redox flow battery (RFB) systems. There is not one unique sealing material which can cover all these different RFB systems. Therefore, it is necessary to investigate the chemical compatibility of sealing materials for each battery system separate. Even within one specific sealing material class, such as fluorinated elastomers (FKM), there are distinct differences in elastomer composition that drastically affect the chemical compatibility.

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Overcoming the limitations of membranes: high performant anionic exchange membranes for aqueous organic redox flow batteries

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The main challenge in organic redox flow batteries (ORFBs) is the development of novel redox-active species and high conductive membrane materials. The overall performance of the ORFBs is mainly limited by two factors: the resistance of the membrane, *i.e.* the ion conductivity and the mass-transport properties of the redox-active molecules at the electrodes. In this work, we present an optimized TMA-TEMPO/MV ORFB system (*Figure 1*) where the membrane limitations have been overcome, hence showing better cell performance compared to the previously reported one[1].

A new series of anionic exchange membranes (AEMs) based on aromatic multiblock copolymers were synthesized by controlling the ratio between the monomers and reaction time. The anion conducting multiblock polysulfones bearing trimethyl quaternary ammonium (TMA) groups were designed to enhance the transport properties with well-defined hydrophilic/hydrophobic phase separated morphology. The molar mass (M_w) and the substitution degree (DoF) of the polymers (In1515TMA) were tuned in a wide range (M_w: 58~138 kg/mol, DoF: 50~100%).

Among the tested In1515TMA membranes, M1 displayed the best overall performance, with excellent coulombic efficiency (>99.5%), capacity retention (89% at 80 $\mathrm{mA \cdot cm^{-2}}$ after 128 cycles) and higher peak power density (272 vs. 254 $\mathrm{mW\ cm^{-2}}$ at 16 $\mathrm{mL \cdot min^{-1}}$) comparing to the state-of-the-art commercial membrane FAA-3-50® (Fumatech) for this system. In particular, when the flow rate increased to 24 $\mathrm{mL \cdot min^{-1}}$, the peak power density of M1 reached 324 $\mathrm{mW \cdot cm^{-2}}$. The significant increase in power density at higher flow rate (*i.e.*, faster exchange of redox-active materials) suggested that the In1515TMA membrane breaks through the limitation of the membrane to the cell performance of this ORFB system. These findings indicated that by the rational design of optimized polymer architecture, it is possible to push further the upper limit of cell performance in ORFBs.

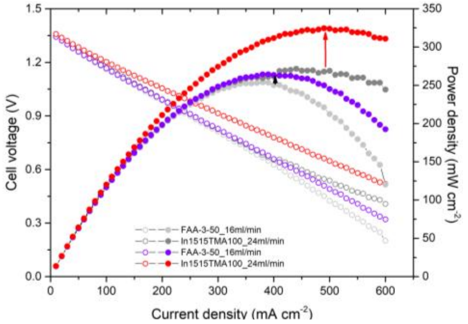

Figure 1. Polarization curves of M1 and FAA-3-50 in TMA-TEMPO/MV based ORFB system.

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Effect of operation conditions on the performance of alkaline Zinc-air flow battery

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Ongoing decarbonization of the energy sector leads to the growth of energy production from renewable sources. The fluctuating production of electricity from renewable resources can be stabilized using stationary energy storages, nowadays mainly based on Li-ion batteries, hydrogen technologies or vanadium redox flow batteries. However, these technologies are limited by the availability of mineral resources, low efficiency or potential safety risks of operation, and therefore other electrochemical systems are intensively investigated and developed. Zinc-air flow batteries are promising alternatives due to their high theoretical energy density, safety and eco- friendliness. However, these batteries are in an early stage of development and successful commercialization is limited by several technical issues, such as dendritic growth of metal zinc on the negative electrode and long-term instability of air electrodes.

The aim of this work was to study the influence of operating conditions on efficiency and performance stability of laboratory zinc-air flow battery. For our study we developed laboratory flow single-cell using three-electrode set-up. Zinc was deposited from alkaline zincate solution on a flat composite carbon plate, nickel mesh served for oxygen evolution and gas diffusion electrode (GDE) with a spinel based cobalt oxide electro-catalyst was used for oxygen reduction. We systematically studied the effect of various charging conditions: mode (galvanostatic vs. pulse), current density (20-50 mA cm^{-2}) and applied charge on the cycle efficiency and capacity retention. Moreover, we performed electrochemical impedance spectroscopy and load curve measurements at various conditions to identify the main sources of voltage inefficiency of the battery and to assess the mid-term stability of the battery.

Galvanostatic method turned out to be more suitable charging technique providing higher coulombic efficiency of the cycle at tested effective current density when compared to the tested pulse methods. The zinc dendrites formation can be prevented by operation below limiting current density, which was found to be dependent on zincate concentration and electrolyte flow rate. The leak of electrolyte through the GDE and related flooding of catalyst layer of GDE was identified as the main issue limiting the performance stability.

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GRAPHENE-BASED MATERIALS AS ELECTRODES IN VANADIUM REDOX FLOW BATTERIES

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Vanadium redox flow batteries (VRFB) are ideal candidates for large scale energy storage. However, their cost is still too high to be widely implemented. Using advanced carbon materials as electrodes can increase their performance, lowering the cost. The VRFB electrodes contribute to the performance of the battery by determining the power density and energy efficiency since electrochemical reactions take place on the electroactive surface of the electrodes (due to their electronic transport capacity) [1]. The present works aims at obtaining nitrogen-doped reduced graphene oxide and investigating its performance as both positive and negative electrodes in vanadium redox flow batteries.

Graphene oxide (GO) was obtained by exfoliation of commercial powder graphite by a modified Hummers method [2, 3]. Doping with N was carried out by mixing the GO with urea and heat treating it under N_2 atmosphere at 500 °C, 600 °C, 700 °C, 800 °C and 900 °C. [3] The composition of the obtained materials, analysed by elemental analysis, shows a nitrogen concentration of up to 33% in mass after heat treatment with urea. The samples obtained were analysed by XRD where the loss of the peak corresponding to graphene oxide ($2\theta = 11^o$) and the appearance of a peak at $2\theta = 25^o$, indicative of the reduction of graphene oxide.

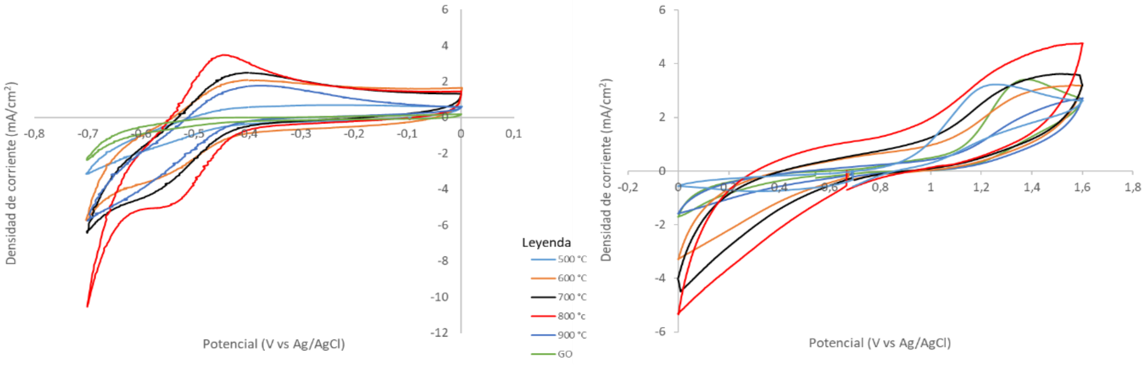

Figure 1. Cyclic voltammetry at 20 mV/s for the negative electrode (V^{2+}/V^{3+}, left) and positive (VO^{2+}/VO_2^+, right)

Materials were electrochemically studied in 3-electrode cell. Cyclic voltammetries show a clear influence of the temperature of the heat treatment. A progressive improvement of the current can be observed by increasing the temperature of the thermal treatment, obtaining the best result in the material treated at 800 °C, which shows the peak with the highest current intensity both in the oxidation and reduction processes for both electrodes.

In conclusion, the temperature of the heat treatment plays a fundamental role in the reduction and doping of graphene, determining its performance as an electrode.

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Development of safe and performant bromine based electrolytes for hydrogen/bromine redox flow batteries

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Redox flow batteries (RFB) can be one solution for stationary large energy storage [1]. Hydrogen/bromine RFBs (H_2/Br_2-RFB) are in the system development phase [1]. In H_2/Br_2 RFB theoretical volumetric energy densities up to 250 Wh L^{-1} in bromine catholytes can be achieved. The application of bromine as an energy storage medium in aqueous solutions poses challenges to the safety. Bromine is volatile and toxic by inhalation. To reduce its vapour pressure, bromine complexing agents (BCA) are used and bind the bromine in the solution in a second liquid phase as fused salt [2]. Mainly quaternary ammonium bromides reduce the vapour pressure of bromine in aqueous solutions. Prominent BCAs are [MEP]Br or [MEM]Br used in zinc/bromine RFB [3]. In H_2/Br_2 RFB, however, electrolytes are based on hydrobromic acid.

In this work we define requirements and present physical and chemical properties of those electrolytes for H_2/Br_2 RFB cathodes for safe and performant operation. Extensive ex situ experiments (Br_2 concentrations, BCA concentration, conductivity, polybromide distribution) and single cell tests based on 1-alkylpyridin-1-ium bromide BCAs will be discussed.

As a result electrolytes with 80 mol% of Br_2 stored in the fused salt phase were reached, leading to reduced vapor pressure from the aqueous electrolyte phase. Length of the alkyl side chain of the investigated BCAs influences the complexation strength strongly. Long side chains ([C6Py]Br) bind the bromine stronger in the fused salt then short side chain BCAs ([C2Py]Br) as can be already depicted by the change of color in the solutions in fig. 1. A strong influence of the state of charge of the electrolyte (SOC) is given (fig. 1). Low concentration of Br_2 on the other hand leads to a weak discharge performance of the bromine cathode in the cell by mass transport limitation. In addition, the BCAs solved in aqueous solution lead to higher membrane resistances in PFSA membranes. Both issues could be solved by further electrolyte development. In addition, fused salt phase shall be avoided during operation due to its low conductivities < 100 mS cm^{-1}, while the aqueous phase offers electrolyte conductivities between 300 and 700 mS cm^{-1}. We give a comprehensive overview of electrolyte development for this RFB battery.

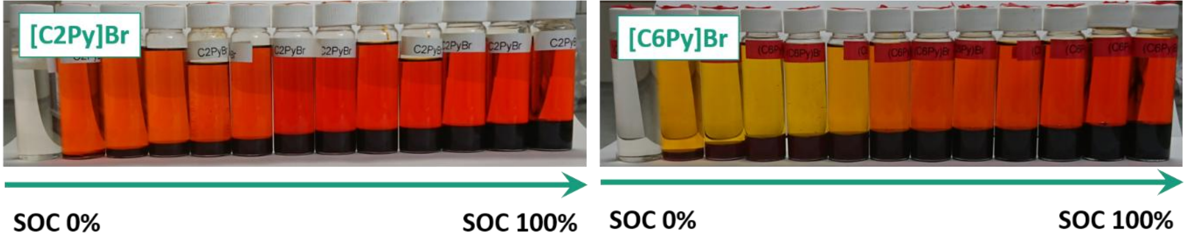

Figure 1 : HBr/Br_2 electrolyte at various SOC for the BCAs [C2Py]Br and [C6Py]Br.

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Redox Flow Battery Application to Salt Cavern

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Rechargeable batteries have long been studied and recognized as promising candidates for stationary energy storage due to their ability to convert and store electrical energy. Among these batteries, redox flow batteries (RFB) which have been developed for over 40 years, have been identified as one of the ideal choices for large-scale energy storage due to their safety, high reliability and long-life expectancy.

The use of salt cavern as a container for electrolyte for redox flow batteries has several advantages. The biggest advantage is the very large volume of electrolyte which offers high electrical storage capacity (available volume between 90 000 and 600 000 m^3). In addition, the salt caverns provide an electrolyte saturated with salt, which could solve the problem of the chemical instability of the water and avoids the production of side reactions (decomposition of water). Finally, the underground temperature (between 40 and 45°C) also improves the solubility of the redox couples to be stored in the electrolytes.

Based on these advantages, the feasibility of using salt cavern for RFB was deepened on three thematics :

- Find an electrolyte that is compatible with saturated brine in a convenient concentration
- Estimate the energy yield and the costs for such a system
- Guarantee the absence of contamination of redox species into the underground

The first works carried out demonstrated that some organic redox species are soluble in salt cavern. Furthermore, their addition in the brine does not increase the viscosity of the fluid, which is satisfactory. However, the solubility of redox species in brine found during these first works did not outreach 2.10^{-2} mol/l.

With such a concentration, the energy yield would be too low to be interesting. As a matter of fact, the RFB application to Salt Cavern consumes a lot of energy due to the pumping of electrolyte at about 400 meters deep.

To get an energy yield of 0.5, with a flowrate of 1000 m^3/h, a minimum concentration of 0.11 mol/l of redox species is necessary. Additional redox species could be tested to find a better solubility. The help of additive as hydrotropic species is also targeted.

Concerning the cost, RFB applicated to Salt Caverns was estimated between 180 and 640 €/kWh depending on flowrate, redox species concentration and loading time.

Understanding the vanadium redox-flow battery: an in-depth study using the distribution of relaxation times analysis

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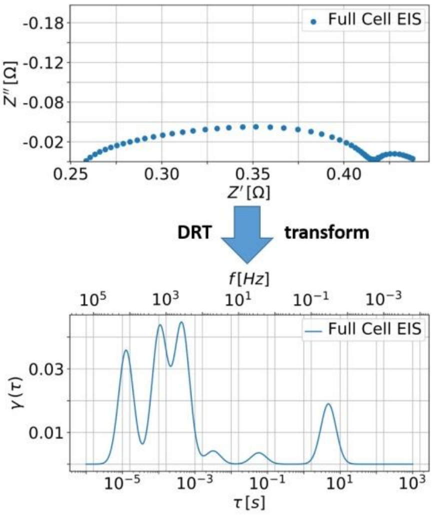
Abstract:

Significant cost optimization is needed in order to achieve a commercial break-through in vanadium redox-flox battery (VRFB) technology. Driving this development in a rationality-based fashion requires a profound understanding of the number, nature and time scales of processes contributing to losses during operation of the battery. Non-invasive electrochemical impedance spectroscopy (EIS) can, if conducted properly, yield these insights. However, distinguishing processes of comparable time scales is often not possible using the standard complex non-linear least-squares (CNLS) fitting of electrical circuit models (ECM) to experimental data. Furthermore, finding a suitable ECM in the first place can be treacherous due to the inherent ambiguity of EIS (different models may fit the same data set equally well).



These challenges can be overcome by applying distribution of relaxation times (DRT) analysis. Using this approach, we are able to deconvolute impedance spectra with respect to the underlying characteristic time constants. This enables processes that overlap in the classical Bode- and Nyquist-representation to be displayed as distinct peaks, thus greatly enhancing resolution.

In the present contribution, we showcase the application of DRT analysis to single cell VRFB impedance data. Aiming at an EIS-based online state-of-health monitoring, we outline our strategy to unravel the physical nature of processes related to the individual signals found in the DRT spectrum. By combining varied experimental conditions and theoretical considerations, we ultimately display loss processes in terms of their individual time scales and link them to the respective cell components.

Keywords: electrochemical impedance spectroscopy; distribution of relaxation times; deconvolution; vanadium redox flow battery

Deactivation of negative felt electrode of vanadium redox flow battery: Double half-cell set-up experiments

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The vanadium redox flow battery is one of the most promising technologies for storing of electric energy from renewables. Its advantages are power and capacity independency, high efficiency and outstanding lifetime.

In previous work, we observed energy efficiency decay by 15% during 2000 charge-discharge cycles when using as received carbon felt negative electrode, whereas it decreased only by 1% with thermally treated felt.[1] Nonetheless, even the slow decrease could be a problem on ten years scope.

Thus, here we study influence of operating conditions such as current load (0 and 150 mA cm^{-2}) and SoC of negative electrolyte (+25 to +95%) on deactivation rate of as received felt using modified double half-cell setup[2] with single negative electrolyte to evaluate the effect of these well defined conditions for real battery operation and accelerated lifetime testing. Both full-cell and half-cell polarization at 25 mA cm^{-2} and electrochemical impedance spectroscopy at OCV were used for deactivation evaluation. Before and after 6-days experiments under given conditions characterization in +50% SoC was performed to compare the performance under identic conditions.

Results showed us that used felt electrodes have significantly different initial performance (charge-transfer resistances) and also initial phase of deactivation process is very variable for individual pieces of the same felt material. From these data it seems that current load neither electrolyte SoC does not have huge effect on the deactivation rate. The developed method can be easily adopted for stability evaluation of electrode materials for redox flow batteries of versatile chemistries.

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EVROPSKÁ UNIE
Evropské strukturální a investiční fondy
Operační program Výzkum, vývoj a vzdělávání

MINISTERSTVO ŠKOLSTVÍ, MLÁDEŽE A TĚLOVÝCHOVY

Mitigation of capacity and efficiency fade in Vanadium redox flow batteries

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Actual increase of energy from renewable sources requires a safe and reliable stationary energy storage due to their intermittent production. Among other options, Vanadium redox flow battery (VRFB) is a promising stationary energy storage. It uses vanadium salts dissolved in acidic electrolytes. The electrolytes are pumped through the battery stacks where energy is stored or released via electrochemical reactions. Membrane is an important component of VRFB stack transferring charge between the half-cells while preventing electrolytes from mutual cross mixing. However, in real VRFB, electrolyte constituents permeate through the membrane by diffusion, migration and osmosis mechanisms. These phenomena have negative effect on battery performance (efficiency and available capacity).

Using mathematical model, we simulate the performance of VRFB and test different selected strategies and control methods for mitigation of capacity and efficiency losses. The model simulates dynamic battery behaviour during charge-discharge cycling taking into account electrochemical and chemical reactions of vanadium ions, permeation of all ions across ion-exchange membrane, osmotic pressure and osmotic flux. The model was developed and validated using our original experimental data for a representative cation-exchange membrane (CEM) and anion-exchange membrane (AEM).

The hydraulic shunt, i.e. connection of electrolyte tanks via a thin capillary was identified as the most promising operation strategy among tested, reducing the capacity fade by 69% vs. standard VRFB operation in the tested interval of 150 cycles (for CEM), with only small decrease of coulombic efficiency. Moreover, when combined with periodic electrolyte rebalance the amount of stored energy for AEM can be increased by 80% comparing to standard VRFB operation with CEM. Our model can be further used to optimize construction and maintenance of the battery and easily adopted to other RFB chemistries, including organic-based.

The work was supported from European Regional development Fund-Project "Organic redox couple based batteries for energetics of traditional and renewable resources (ORGBAT)" No.CZ.02.1.01/0.0/0.0/16_025/0007445.

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Determining charge transfer kinetic constants for fast reversible systems on porous electrodes using Electrochemical Impedance Spectroscopy

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Among the possible electrolytes suggested as substitutes for vanadium-based ones in redox flow batteries, aqueous organic based electrolytes have recently attracted high interest. These electrolytes are organic compounds presenting relatively high solubility in water. Molecules such as Indigo Carmine, Viologen and TEMPO, can then provide very fast charge-transfer reaction kinetics in neutral or mildly acidic or basic aqueous electrolytes. The resulting electrolytes may have less environmental concerns and possibly lower production cost than vanadium electrolytes, while showing higher reversibility and energy density. Although the charge transfer kinetics of these molecules on simple electrodes such as glassy carbon can be readily acquired by classical methods, other methods are desired for studying them on carbon felt electrodes which are commonly used in industrial applications. Electrochemical Impedance Spectroscopy is considered to be an appropriate analytical measurement. However, it faces two challenges for deriving reliable kinetic data for two reasons: First, the complicated porous structure of the carbon felt electrode requires an adapted analytical model that differs from planer electrodes. Second, the very fast kinetics of the electrolyte ($k_0 \sim 10^{-2}$ cm·s^{-1} on glassy carbon) result in very low impedance values. Here we present our work on the kinetic study of organic aqueous electrolytes developed in HIGREEW project by EIS, on glassy carbon as a first approach, and then on different commercial carbon felts. Apparent kinetic constant (normalized to the geometric surface area of the porous electrode) is derived by fitting the impedance spectra using equivalent circuit models as a first approach. Prospects of using more complex physical models from the literature are discussed.

Acknowledgements
This work has been supported by the European Union under HIGREEW, Affordable High-performance Green Redox Flow batteries (Grant Agreement no. 875613).

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0D modeling to help development of new ORFB electrolytes

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The need of efficient energy storage solutions is increasing to support the integration of intermittent electricity producers in the electrical grid. IFPEN, a French applied research institute in the fields of energy, transport and the environment, is notably working on different energy storage solutions (CCUS, Hydrogen, Li-ion battery, Flow battery (FB), Energy management system…). The Redox Flow Battery (RFB) is earmarked as a key technology in stationary energy storage applications thanks to its high energy capacity and the intrinsic ability to decouple energy and power outputs. Nowadays great attention is given to organic electrolytes using only earth-abundant element, as a promising way to lower the cost of flow batteries [1].

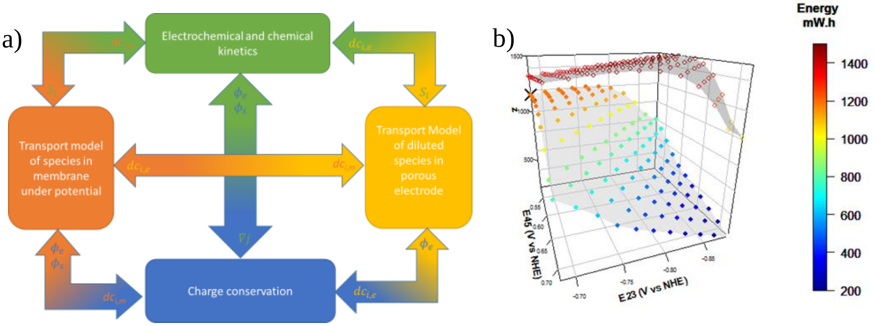

Figure 1 : a) schematic description of the different physics of IFPEN 0D model, b) simulated energy stored in an ORFB depending of potential of negolyte (E23) and posolyte (E45) with U_{min}=0.6/U_{max}=1.6 (♦) and U_{min}=0.8/U_{max}=1.8 (◊).

In order to help the development of new electrolytes, IFPEN has developed a single cell 0D physical model of organic RFB (ORFB). This model takes into account the electrochemical reactions, depending of the electrolyte flow rate, the diffusion of the electroactive molecules from the bulk to the reaction sites, the cation transfer through a cation exchange membrane and the ohmic losses. Furthermore, it has the specificity of taking into account side reactions such as HER and OER. It has been calibrated with a well-known 2,6 DHAQ/Ferrocyanide system [2]. The presentation will focus on the exploitation of this model as a tool for optimizing operating conditions and to help with the choice of new electrolytes in terms of potential and kinetics.

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Exploring the thermodynamics of the bromine electrode in concentrated solutions for improved parametrisation of the hydrogen-bromine flow battery models

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In flow battery systems, high energy density is achieved by increasing the concentration of active redox species in the electrolyte or compressing gas in hybrid systems, such as the hydrogen-bromine redox flow battery (HBRFB) [1]. High electrolyte concentration, although favourable from the practical perspective, poses serious difficulties in modelling and simulation aspects. Some models simply revert to complicated, empirical formulae [2]. The presented work describes computational methods useful for predicting the physiochemical, thermodynamic and electrochemical properties of the posolyte used in practical HBRFB.

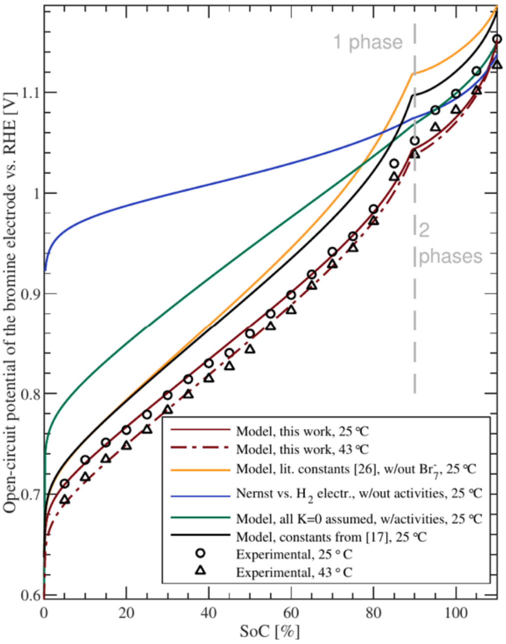

Figure 1. OCP prediction using the presented model for different equilibria scenarios and for various model scenarios

The study first comprises of an analysis of a standard method of measuring the open-circuit potential (OCP) using a reference electrode (e.g. Ag/AgCl) and glassy carbon electrode at which the redox reaction $Br_2 + 2\ e^- \Leftrightarrow 2\ Br^-$ occurs. Typical experimental difficulty in such systems is the liquid junction potential (LJP) forming in the porous electrolytic junction because of the complexity in its theoretical description. This fact adds high uncertainty to the data points used for model validation. Next, an alternative experimental approach without LJP is presented and an OCP model is formulated which provides a tool for extraction of polybromides stability constants. By comparison with the results from the improved experiment, it was found that the formation constants available in the literature (for very diluted solutions) are too low (Fig. 1). In combination with other experimental techniques the missing constants are evaluated which are the key to successful prediction of the OCP in the practical HBRFB systems by means of numerical simulation.

The work is performed within the FlowCamp** project, a part of Maria Skłodowska-Curie Actions from the EU Horizon 2020 programme.

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Concentrated solution theory for organic redox flow batteries: Measuring the chemical activity of aqueous electrolytes via Differential Scanning Calorimetry

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The energy density of aqueous flow batteries is known to be low [1] compared to other battery technologies. One way to increase the energy density is to use more concentrated solutions, but this also increases the non-ideal behaviour of the electrolytes, and makes it harder to predict the battery performances via equations featuring dilute solution hypothesis. As an example, the Nernst equation used for voltage predictions gives better results when parametrized with chemical activity rather than concentration [1].

This paper aims to provide a facile and universal measurement method for the chemical activity of aqueous electrolytes used in organic flow batteries.
Measurements of the freezing point depression and the enthalpy of fusion via Differential Scanning Calorimetry allow to accurately predict the activity of water in the electrolyte, which is converted to activity coefficient of the solute via the Pitzer equations [2].

The accuracy of the method is demonstrated on common salts (NaCl, CaCl2) and applied to organic electrolytes used in aqueous flow battery technologies.

Gibbs-Duhem equation:

$$\frac{\partial \ln a_w}{\partial T} = \frac{H}{RT^2}$$

Pitzer equation for the osmotic coefficient:

$$\phi - 1 = |z_+ z_-| f^\phi + 2m\left(\frac{pq}{p+q}\right) B^\phi + 2m^2\left(\frac{\sqrt[3]{pq}}{p+q}\right) C^\phi$$

Pitzer equation for the activity coefficient:

$$\ln \gamma_\pm = |z_+ z_-| f^\gamma + 2m\left(\frac{pq}{p+q}\right) B^\gamma + 2m^2\left(\frac{\sqrt[3]{pq}}{p+q}\right) C^\gamma$$

a_w: activity of water
H: enthalpy (J/g)
T: temperature (K)

φ: osmotic coefficient
γ: activity coefficient
f: Debye-Hückel term
B, C: Pitzer parameters

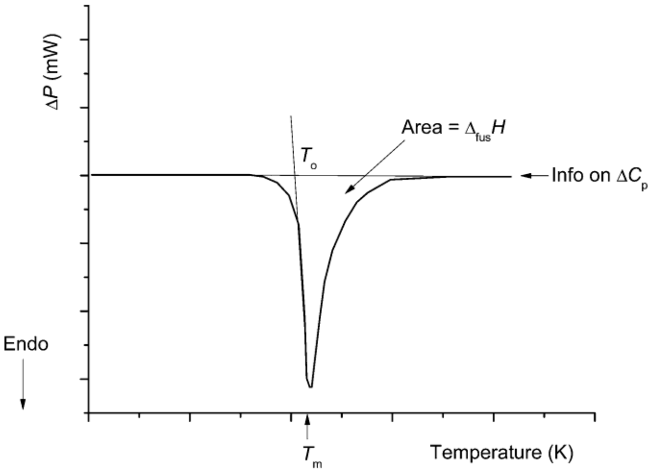

Figure 1. Model equations and typical DSC spectrum used for measurement of the parameters

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Water transport in VRFB: experiments and simulations

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Wind and solar farm power are infrastructures that currently attract huge investments [1]. Redox Flow Batteries (RFB) currently become a unique solution for these types of generation smoothing, as it is intrinsically scalable in power and capacity through variations in stack size and electrolyte volumes and is several times cheaper than other alternatives [2]. The technology becomes more mature as much attention has been paid to its improvements. However, some aspects are still poorly understood.

In the present work, we study the effect of imbalance [3] of RFB on the example of a small-scale Vanadium RFB via experiments and simulations using a zero-dimensional transport and electrochemical model. We showed using long-lasting cycling how volumes in tanks change in time (see fig.1), leading to capacity fade. We performed cycling on 5 cm^2 single cell prototype with starting volume of 30 ml at 60 mA/cm^2 current density. We built the mathematical model that described the VRFB operation, taking into account vanadium ion crossover and water transport through the membrane [4, 5] due to osmotic pressure, the pressure difference in half cells, and electro-osmosis. Nafion 115 membrane study was performed as a widely used membrane to validate the model. Further extension of the model for new types of membranes is ongoing. We believe that such an engineering model will be a useful tool for the development battery management algorithms.

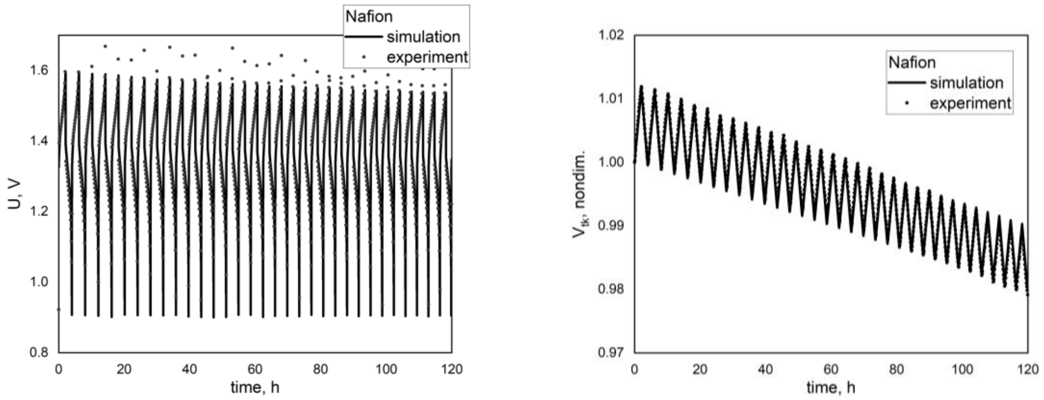

Figure 1. Potential and electrolyte volume change for Nafion membrane.

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©FlowBat – redox flow battery simulator

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The simulation of Redox Flow Batteries (RFB) is the crucial element for designing reliable RFB systems. It allows modeling these batteries under real operating conditions and thus estimating and optimizing their performance for different applications before constructing expensive experimental facilities. There are many different approaches for RFB modeling, but most of them are the in-house software that is not widespread. Thus, many researchers have to develop their computer programs for investigation of RFB systems while it is not the subject of the primary research. Therefore, we decided to develop FlowBat – a redox flow battery simulator that provides researchers with powerful tools for investigating and developing RFB systems. FlowBat aggregates the modeling approaches presented in our previous papers, further improving them for practical application. The core of FlowBat is our RFB model [1], which is based on the general conservation principles of charge and mass transfer; hence it can simulate a wide range of RFB systems with different sizes and specifications. The key feature of the model is the accurate simulation of internal processes based on analytical solutions. Such an approach allows obtaining high accuracy while having low computational complexity simulating dynamic RFB behavior in real-time. FlowBat has three main blocs (Fig. 1):

1) **Battery identification** is the bloc where the physical properties of each internal component of the RFB system can be specified.

2) **Battery simulation** is the bloc that simulates the dynamic behavior of the specified RFB system under different operating conditions. One of the key features is parametric sweep calculations, when the simulations can be automatically run for a set of operating conditions (e.g., different loading currents, input/output powers, SOC ranges) and further compared and analyzed.

3) **Battery analytics** is the bloc that analyzes the results of simulations, elucidates the effect of internal processes, and provides recommendations for optimizing the RFB system.

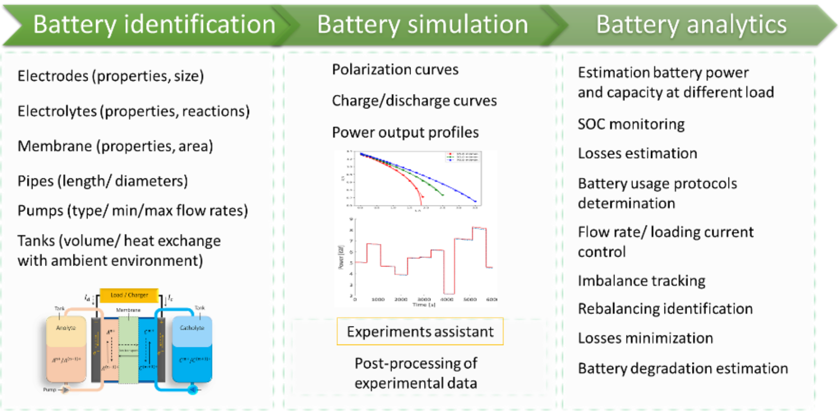

Figure 1: FlowBat structure.

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