29TH SEMPTEMBER 2021

UNIVERSITY OF
CHEMISTRY AND TECHNOLOGY
PRAGUE

AUTUMN FLOW BATTERY MEETING 2022

BOOK OF ABSTRACTS

UNIVERSITY OF CHEMISTRY AND TECHNOLOGY PRAGUE
DEPARTMENT OF CHEMICAL ENGINEERING
Laboratory of Energy Storage
kosekgroup.cz

Autumn flow battery on-line meeting 2022

UNIVERSITY OF
CHEMISTRY AND TECHNOLOGY
PRAGUE

Dear colleagues,
we would like to kindly invite you for the on-line ***Autumn flow battery on-line meeting*** which will be held on Thursday **29th September 2022** by our Energy storage research group on University of Chemistry and Technology Prague. The aim of the workshop is to share the actual scientific ideas, experiences and knowledge in the field of research and development of flow electrochemical energy storages. The workshop aims to focus on the following topics:

- Redox flow batteries (metallic and organic)
- Hybrid flow batteries, fuel cells and electrolysers
- Advanced concepts (capacity boosters, suspension batteries)
- Other systems (solid state batteries, electrosynthesis)

The workshop will be free of charge and open for the broad audience. Both representatives from academic research as well as from battery manufacturers are invited to discuss the actual challenges in the field.
We would be honoured if you could also actively participate in the meeting! In case of interest please send us a title of your contribution and a short abstract to our email address: mazurp@vscht.cz.

On behalf of the organization team,
Dr. Petr Mazúr
Department of Chemical Engineering
University of Chemistry and Technology Prague
Technicka 5
166 28 Prague
Czechia

More info about organizer here: http://www.kosekgroup.cz/research/energy-storage/

The seminar is organized within 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.

EUROPEAN UNION
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MINISTRY OF EDUCATION, YOUTH AND SPORTS

Thursday 29th September 2022

	Presenter	Presentation title	Starting at (CEST)
		Welcome and info	**9:00**
	Section 1: Organic RFB (9:15 - 10:30)		
S1-1	Petr Mazúr	Organic redox compounds for cheaper and greener flow batteries – a critical view	9:10
S1-2	Juan Asenjo	Design of new triazine electrolytes for multiple-electron storage	9:30
S1-3	Maddalen Agirre	Study of the behaviour of 2,2´-bipyridines in Aqueous Organic Redox Flow Batteries	9:50
S1-4	Maël Penhoat	From biomimetic mediated formate flow fuel cells to redox flow batteries	10:10
		Coffee break (10:30 - 11:00)	**10:30**
	Section 2: Mathematical modelling (11:00 - 12:00)		
S2-1	Gael Morouga	The potential of physics-based modelling for improved flow battery management	11:00
S2-2	Roman Pascal Schärer	Effective Transport Parameters for Porous Electrodes in Flow Batteries	11:20
S2-3	Martin Bureš	Predicting properties of carbon felt electrodes by mathematical modelling and μ-computed tomography	11:40
		Lunch break (12:00 - 14:00)	**12:00**
	Section 3: Electrode performance and stability (14:00 - 15:00)		
S3-1	Přemysl Richtr	Influence of static mixers on zinc electrodeposition in alkaline zinc-air flow battery	14:00
S3-2	Jindřich Mrlík	Study of deactivation of vanadium redox flow battery negative graphite felt electrode in symmetric-cell	14:20
S3-3	Petr Mazúr	Performance stability of graphite felt electrodes in SPr_2V-Ferrocyanide flow battery using double half-cell approach	14:40
		Closing of the Autumn flow battery on-line meeting	**15:00**

The seminar will be available for free via Teams:
https://teams.microsoft.com/l/team/19%3a5jIRT1gzQiNxWxItFz4iMHZHLUzwSYLPFnMWusSdyFg1%40thread.tacv2/conversations?groupId=eb156201-8e6c-4852-9744-fbf3edcc8d21&tenantId=a5085469-d927-486a-966e-f350bf2fe08a

Organic redox compounds for cheaper and greener flow batteries – a critical view

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Redox flow batteries (RFB) represent safe, reliable and long-lasting energy storage technology for stationary applications. The currently most matured system based on vanadium is being commercially deployed worldwide by several companies such as CellCube (AUT), Invinity Energy Systems (GB), Sumitomo Electric (JAP), Volterion (GER) or Pinflow Energy Storage (CZE). However, the high price, limited accessibility and negative environmental aspects of use of vanadium and other metals motivates the search for alternative redox compounds, very often from organic chemistry.[1, 2]

In our contribution, we will provide the overview of currently investigated and employed organic redox couples for aqueous RFB electrolytes including representatives of quinone, viologen, ferrocene groups. The most promising organic chemistries will be compared with the benchmark inorganic RFB based on vanadium ions with respect to the technical and economical parameters using our own experimental data. The directions towards industrially suitable solutions will be outlined.

Acknowledgments:

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. The research leading to these results has received funding from the European Union under Grant Agreement no. 875913.

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References:

1. Fischer, P., P. Mazúr, and J. Krakowiak, *Family Tree for Aqueous Organic Redox Couples for Redox Flow Battery Electrolytes: A Conceptual Review.* Molecules, 2022. **27**(2): p. 560.
2. Sánchez-Díez, E., et al., *Redox flow batteries: Status and perspective towards sustainable stationary energy storage.* Journal of Power Sources, 2021. **481**: p. 228804.

Design of new triazine electrolytes for multiple-electron storage

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The development of renewable energies has emerged as an imperative due to the critical consequences of climate change. However, the intermittent nature of some of these renewable energies constitutes a significant drawback in the context of massive-scale integration. Redox Flow Batteries (RFB) have surfaced as promising alternatives for energy storage systems to solve this problem. Indeed, the use of cheap and easily tunable water-soluble organic molecules as redox active material stands as a promising strategy for future RFBs. Aqueous Organic Redox Flow Batteries (AORFB) combine the positive advantages of the aqueous media (safe, highly conductive, and economical) with highly tunable redox active materials to deliver optimal properties [1]. Almost all the organic molecules described in the literature are capable of storing one electron without compromising the stability.

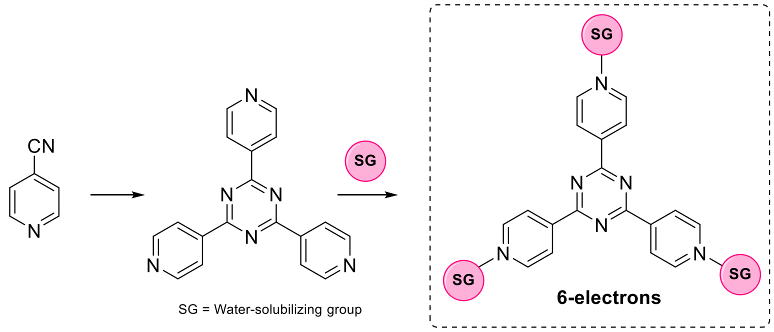

Figure 1: Synthesis of the triazine derivative.

Recently, *Zhang et al.* have described a triazine derivative which is able to store up to 6 electrons [3]. The synthesis of this molecule includes 6 steps and requires a triple exchange of the counterion. Herein, we present easily scalable synthesis of a new triazine derivative as promising anolyte for Aqueous Organic Redox Flow Batteries (AORFB). The synthetized triazine is able to store up to six electrons. By using RDE measurements the redox kinetic constants and diffusion coefficients have been measured. The Pourbaix diagram shows three redox process which involve two electron one proton reactions. In order to explain the mechanism of the consecutive reductions of this molecule, DFT calculations have been carried out. Furthermore, this molecule has been paired with potassium ferrocyanide showing good stability in single cell. This work represents a significant step in the transition from fossil fuels to renewables energies.

References

[1] E. Sánchez-Díez, *et al. J. Power Sources*, Cambridge, **2021**, *481*, 228804.

[2] J. Huang *et al. Angew. Chem. Int. Ed.* **2021**, *60,* 20921.

Study of the behaviour of 2,2´-bipyridines in Aqueous Organic Redox Flow Batteries

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In the current scenario of energy transition, the deployment of environmentally friendly, safe and low-cost energy storage technologies is needed [1]. In this context, Redox Flow Batteries (RFBs), relying on their particular architecture alternative to that of static batteries, have emerged as relevant candidates to tackle the sustainable energy generation. Their modular design allows decoupling of power and energy and makes them a suitable option for grid-scale stationary applications, in terms of scalability, moderate maintenance cost and recyclability [2]. Moreover, those batteries based on highly stable redox active materials, show long cycle life (>10.000 cycles) and calendar life (10-20 years), as components can be independently replaced. However, this technology presents a series of limitations, mainly linked to the vanadium chemistry, currently defining the state-of-the-art [3]. The use of chemistries based on ubiquitous elements, such as C, N, H, O, S, or earth abundant metals arises as alternative to overcome the hurdles of VRFBs, due to their abundance and the high tunability of their properties [4]. Amid the variety of chemistries proposed as anolyte-directed active materials for AORFB, viologens have gained increased interest as for their high water solubility, low-cost, low redox potential and fast electrochemical kinetics [5]. Herein, the study of both the physico-chemical and electrochemical properties of a family of anolyte-directed seven-membered 2,2'-bipyridinium derivatives is presented, comparing their stability by cell testing performance.

Acknowledgements

We gratefully acknowledge financial support from the European Union under the HIGREEW project: Affordable High-performance Green Redox Flow batteries (Grant agreement no. 875613). H2020: LC-BAT-4-2019.

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From biomimetic mediated formate flow fuel cells to redox flow batteries

Maël Penhoat, Miniaturization for Synthesis Analysis and Proteomics UAR CNRS 3290, University of Lille, France

Water soluble biomimetic models of Riboflavin (B2 vitamin) and Folic acid (B8 vitamin) demonstrated to be good oxidant of formic acid at various pH. Their usage as anolyte mediators in a flow fuel cell to convert formic acid (or formate) into electricity is validated with measured power densities up to 16 mW cm^{-2} . These preliminary optimum conditions demonstrated a volumetric energy density of 0.68 Wh L^{-1} when operating at 5 mA.cm-2 and neutral pH. These new conditions inspired from redox flow batteries processes permit to remove noble metals at both sides of the formate flow fuel cell.

Furthermore, these new molecules have been evaluated as catholytes versus potassium ferrocyanide anolyte and appeared particularly promising with preliminary observed power densities in the range of 50 mW cm^{-2}. Nevertheless high resistance are observed and further work is still necessary to improve the performances of these systems.

The potential of physics-based modelling for improved flow battery management

Gael Morouga, Zürcher Hochschule für Angewandte Wissenschaften
Institute of Computational Physics, Technikumstrasse 71, 8400 Winterthur, Switzerland

Physics-based modelling is a useful tool to predict battery outputs as a function of operating conditions and battery design, and is therefore helpful in optimising the return on investment of battery systems.

This talk will focus on introducing the improved business case of flow batteries in the modern European electricity market, and illustrate how physics-based battery management systems may be the next step in improving the competitivity of flow batteries in stationary storage applications.

Effective Transport Parameters for Porous Electrodes in Flow Batteries

Roman Pascal Schärer, Zürcher Hochschule für Angewandte Wissenschaften
Institute of Computational Physics, Technikumstrasse 71, 8400 Winterthur, Switzerland

Porous electrodes constitute a key component of flow batteries as they provide the reaction surface for the heterogeneous electrochemical reactions. We are interested in homogenized transport descriptions of the coupled processes of mass transport and heterogeneous reactions in porous electrodes for macroscopic cell models. Homogenized transport equations capture the subgrid-scale effects by the use of effective parameters, such as the dispersion tensor or the effective reaction rate. Specifically, the pore-scale morphology and surface properties of the electrode, as well as the applied operating conditions, such as the flow rate or electrolyte composition, can strongly impact the macroscopic transport properties. Quantifying the impact of the pore-scale properties on the macroscopic transport properties is important for optimizing operating conditions and designing next-generation porous electrode structures with improved performance metrics.

In the current study, we investigate the impact of several simplified periodic pore-scale geometries on macroscopic transport parameters. We apply the method of volume averaging for upscaling the pore-scale transport problem to obtain effective macroscopic descriptions. To allow for an efficient simulation of the macroscopic transport equations, we construct simplified surrogate models for the effective parameters, which can be used in place of empirical or simplified analytical models. By applying the determined effective parameters to a simplified one-dimensional transport problem, we compare the efficiency of different pore-scale structures in terms of the resulting reaction and energy dissipation rates.

Predicting properties of carbon felt electrodes by mathematical modelling and µ-computed tomography

Martin Bureš[a], Zbyněk Tomiška[a],Alexandr Zubov[a], Jiří Charvát[a], Petr Mazur[a], Miloš Svoboda[b], Juraj Kosek[a,b]
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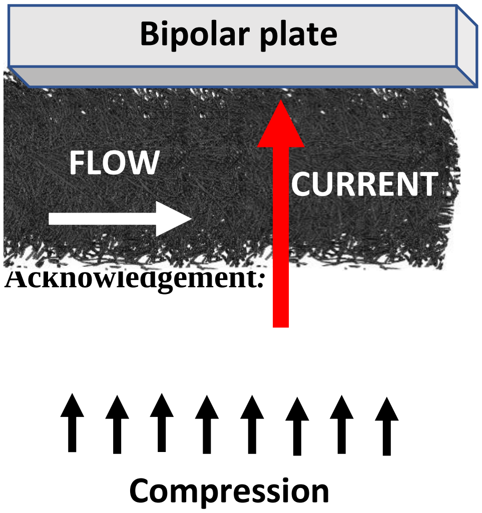
Redox flow batteries of various chemistries are potential electrochemical energy storages for residential accumulation and grid stabilization. Decoupled power and capacity represent the main advantages of the technology. The key component of the battery, the carbon felt electrode, does not participate in the electrochemical reaction directly, but it provides active sites for the electrochemical reaction of electroactive ions. In addition, the electrode contributes to the battery stack polarization through the charge transfer, ohmic and mass transport resistances and increases the hydraulic resistance of the battery stack and resulting pumping losses associated with the electrolyte circulation.

In this contribution, a mathematical model was developed to evaluate geometrical parameters and simulate the effective electric conductivity and hydraulic resistance of two commercially available carbon felt electrodes using their micro-tomography images. These were preprocessed and binarized into a reconstructed computation domain. Geometric descriptors, such as a porosity, specific surface area and fiber spatial orientation, were calculated using in-house developed algorithms. The area specific resistance and hydraulic resistance were then estimated and validated against our own experimental data, which were measured for both felts under six different relative compressions.

The results suggest that with increasing felt compression the orientation of fibers in carbon felt is changing. This affects the development of electric conductivity and hydraulic resistance development upon the felt compression. Interestingly, Carman-Kozeny constant values also decrease with increasing compression due to fiber reorientation. The developed model can be further used to optimize the textural properties of 3D fibrous electrodes from hydraulic and ohmic point of view, within the development of flow electrochemical reactors.



Acknowledgement:

Influence of static mixers on zinc electrodeposition in 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 battery (ZAFB) is a promising technology due to high theoretical energy density, low capacity costs and eco-friendliness. However, ZAFB is in an early stage of development and successful commercialization is obstructed by several technical issues, such as instability of air electrodes and deposition of zinc in unwanted morphologies. Zinc can be deposited in 4 main morphologies (layer-like, mossy, crystalline and dendrites), crystalline being the desired one [1]. Evolving morphologies depends on battery operation conditions such as state of charge, hydrodynamic conditions close to electrode surface and current load. The ratio between applied and limiting current density can be used as morphology indicator. To enhance mass transfer of zincate ions to electrode surface and thus to increase limiting current density, the use of turbulence promoters can adopted e.g. from electrodialysis field [2]. However, static mixers increase pressure drop and, in batteries with metal deposition, lowers the capacity of cell.

The aim of this work is to study influence of static mixer geometry on zinc deposition in alkaline ZAFB. We used computational fluid dynamics CFD to model the electrolyte flow in the gap between battery electrodes with and without use of turbulence promoters. We studied influence of static mixer geometry on relevant parameters such as pressure drop, distribution of electrolyte flow and mass transfer of electroactive spices. To validate the model we performed systematic series of experimental measurements of pressure drop and zinc deposition under selected hydrodynamic conditions. Deposition tests were run in a lab-scale flow single-cell in 3-electrode set-up using suitable cabon-based substrate for deposition, oxygen evolution as a counter reaction and reference electrode to control. The series of galvanostatic depositions with optimised static promoters was performed with subsequent deposit morphology characterization by SEM to identify the current density window for the desired the crystalline morphology deposition.

Acknowledgement

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Study of deactivation of vanadium redox flow battery negative graphite felt electrode in symmetric-cell

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For long term efficient operation of vanadium redox flow battery is vital stable catalytic activity of its carbon felt electrodes, especially the negative one. To study its deactivation we used symmetric-cell, which provides posibility of tests under defined conditions (SoC of electrolyte, just oxidation or reduction on one electrode), instead of standard charge-discharge cycling alterations of conditions during each cycle. We have observed that the main source of negative electrode felt deactivation is purely chemical deactivation due to negative electrolyte without current load with negligible changes due different SoC (+25 – +95 %) and that mild acceleration of deactivation takes place on reduction felt, wheareas a bit stronger deceleration on oxidation felt under current density loads (150 – 500 mA cm^{-2}) compared to purely chemical conditions.

Performance stability of graphite felt electrodes in SPr_2V-Ferrocyanide flow battery using double half-cell approach

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In last decade, organic aqueous redox flow batteries were dominating the attention of the R&D community. Whereas the main attention was focused on identification of new molecules and chemistries and related structure-property investigations and the evaluation of the electrochemical stability of the redox species under the relevant conditions, significantly less effort was dedicated to the topic of carbon felt electrode performance and stability.

In our contribution, we study the effect of carbon felt activation on the performance of the single-cell using sulfopropylviologen-based negolyte and ferrocyanide posilyte . The experiments were conducted in two setups: i) std. single-cell and ii) double half-cell, which enabled us to identify the most significant contributions to the cell performance deterioration.

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