



2022 Winter School in Copenhagen – Book of Abstracts

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Redox Flow Battery Technology: From Vanadium Flow Battery to Next Generation Systems

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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.

Selective Transport through Flow Battery Separators: Fundamentals and Design Principles

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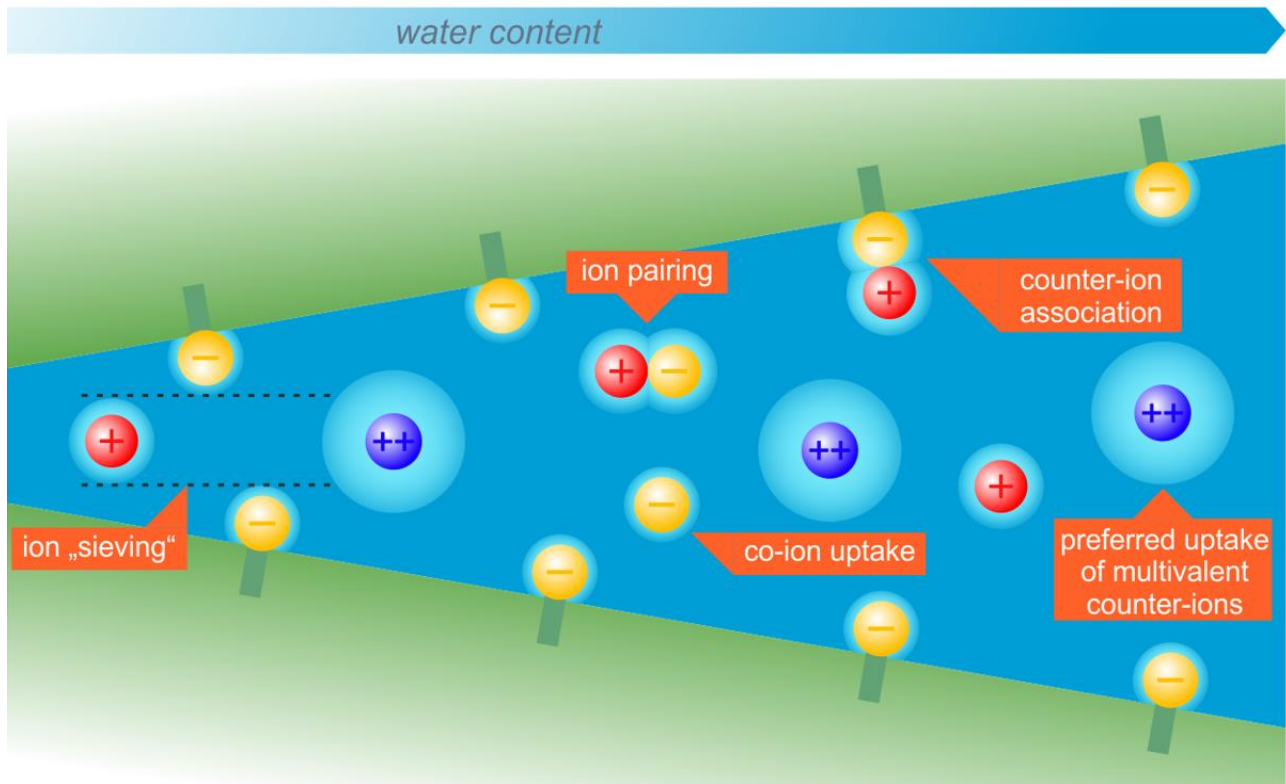
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Separator membranes in electrochemical energy conversion and storage devices need to conduct specific types of ions for mediating the electrochemical reactions taking place at anode and cathode while efficiently separating the electrochemically active species. Separators used in flow batteries typically conduct H^+/OH^- and/or anions such as HSO_4^-/SO_4^{2-} while transport of solvent (e.g. water) and any neutral and charged species participating in the electrochemical (redox) reactions (e.g. vanadium containing species in VRFBs) is highly unwanted. Since wanted and unwanted parasitic transport take place along the same pathways within the separator (aqueous ionic domains), these must be designed in a controlled way. Efficient design principles are based on a quantitative understanding of the effects **charge distribution**, **specific chemical interactions** and **morphological features** have on uptake and transport of relevant species.

In this lecture, I will lead the students through the fundamentals in an attempt to provide answers to specific questions such as:

- Is there anything we can learn from high and selective ion transport in biological systems?
- Can specific chemical interactions be exploited for enhancing selectivity?
- Which parameters control the preferential uptake and transport of cations over anions and *vice versa*?
- What is the relation between nano-phase-separation and selective transport?

Finally, I will discuss the tradeoffs between selectivity and transport rates and make suggestions for choosing, optimizing and developing separators especially for **vanadium-redox-flow batteries**. Because of the importance of “sieving effects”, this discussion comprises not only ion-exchange-membranes (IEM) but also uncharged microporous membranes (e.g. polybenzimidazole) with controlled morphology.



K. D. Kreuer and A. Muenchinger: *Fast and Selective Ionic Transport: From Ion-Conducting Channels to Ion Exchange Membranes for Flow Batteries* Annual Review of Materials Research **51**: 21-46 (2021)

J. P. Melchior, G. Majer, K. D. Kreuer: *Why do proton conducting polybenzimidazole phosphoric acid membranes perform well in high-temperature PEM fuel cells?* Physical Chemistry Chemical Physics **19**(1): 601-612 (2017)

Synthetic strategies for ion exchange-membranes

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Most energy-related electrochemical applications such as flow batteries, fuel cells and electrolyzers critically rely on thin multifunctional polymeric ion-exchange membranes tailored for high chemical and thermal stability, fast and selective ion transport, and high mechanical strength.¹⁻⁴ These ion-exchange membranes typically consist of polymer backbones with covalently attached ions, either pendant or in-chain. Alternatively, cationic or anionic groups may form through protonation or de-protonation of the polymer as the membrane comes in contact with an acidic or basic electrolyte solution, respectively. Important structural features include the molecular structure and molar mass of the polymer backbone, the character and concentration of the attached ions, as well as how the ions are incorporated in the polymer structure (e.g., together or individually). These molecular parameters determine, together with the casting conditions, the morphology, stability and transport properties of the membranes.

The present lecture will not focus specifically on flow battery membranes, but will rather highlight some general principles on how the polymer structure can be designed to influence and control morphology, chemical stability and conductivity of both cation- and anion-exchange membranes.

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Life Cycle Assessment of flow batteries: how to make the best out of it ?

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Life Cycle Assessment (LCA) is recognized as the foremost tool to analyze the potential environmental impacts and to rate the sustainability of a system, whether it is a product, a process, an activity or a service. In the case of a product, such as flow batteries, LCA considers its life cycle (i.e. cradle-to-grave) from raw materials acquisition through production, use, disposal and recycling. The basics of LCA and the points of attention will be presented before the description of its application to flow batteries. Flow batteries are rechargeable batteries based on the concept of the conversion of chemical energy into electricity. It the vanadium redox flow battery (VRFB) is the most well-known, other chemistries have been proposed. The key element of flow batteries is the electrolyte but the full inventory includes also electrodes, membrane, tanks, pumps, etc. Finally, the LCA of VRFBs will be detailed and guidelines for generalization to other flow batteries will be provided.

A redox flow battery based on the fungal produced anolyte phoenicin

Jens Laurids Sørensen

The fungal kingdom is full of colorful pigments with a quinone structure, which are used as protective agents against oxidative stress and competing microorganisms. Besides their natural biological role, quinones are gaining increased interest as promising electrolytes in organic redox flow batteries (RFBs) that can be used to store energy from solar and wind power plants. However, the current quinones used in RFBs have been chemically synthesized from crude oil, which is not aligned with the sustainable thinking behind renewable energy.

Here I will present our work in developing a RFB based on the bibenzoquinone phoenicin, which is produced by several *Penicillium* species. The wildtype *P. atrosanguineum* strain produced approximately 3 g/L phoenicin in a week, which was then used to generate a RFB with a cell voltage of 0.86 V and an initial capacity of 11.75 Ah/L. The electrochemical properties of phoenicin are similar to the published petro-quinones, which demonstrates that fungal biosynthesized quinones provide a sustainable solution for energy storage.

Polybenzimidazole membrane for vanadium flow battery applications

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The vanadium redox flow battery (VRFB) is one of the most promising secondary batteries as a large-capacity energy storage device for storing renewable energy.¹ Perfluorinated-based ion exchange membranes such as Nafion are the most widely used membranes in VRFB due to their high proton conductivity. However, the extremely high cost and low ion selectivity of Nafion have limited their further application in VRFB. Among the aromatic hydrocarbon-based membranes that combine both high ion selectivity and high proton conductivity, polybenzimidazole-based membranes have served as one of the most promising alternatives to Nafion due to their excellent chemical and mechanical stability and low cost.²

m-PBI membranes by varying thickness are prepared, their properties and VRFB performances are compared. The voltage efficiency (VE) increased with decreasing membrane thickness because of the decreasing ohmic resistance. The excellent current efficiency (CE) of VRFBs using meta-PBI based membranes is attributed to the negligible vanadium crossover observed in ex-situ permeability tests.

The chemical stability of PBI membranes is analyzed after immersion of the PBI samples in various highly oxidizing and reducing sulfuric acid-based vanadium and cerium solutions. The membranes stay unchanged for more than 4 months. This result suggests that the PBI membranes demonstrate excellent ex-situ chemical stability in the harsh acid, oxidizing and reducing conditions.

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Engineering Porous Electrodes and Electrochemical Reactors for Redox Flow Batteries

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Redox flow batteries are a promising option for large scale and multi-hour energy storage, but widespread deployment is challenged by elevated costs. One effective strategy to reduce the capital costs is by increasing the power density of the electrochemical stack. To this goal, engineering porous electrodes and electrochemical reactors is a promising avenue to reduce cell overpotentials, minimize pumping losses, and improve durability. In this lecture, I will first introduce the fundamentals of flow battery electrochemical reactors. Second, I will discuss the basic principles of porous electrodes and review existing technology with a focus on understanding the role of porous electrode microstructure and surface chemistry. I will also describe some emerging approaches for electrode engineering and functionalization strategies during the talk. Then, I will discuss engineering aspects of the electrochemical cell and the interaction between flow field geometries and porous electrodes. Finally, I will review diagnostic techniques that enable characterization of reactor performance and isolation of cell overpotentials.

From Idea to a Company

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Starting a company in the flow battery industry in a relatively immature market offers opportunities and challenges. How does one discern whether an idea can become the basis for a company and how can one navigate the ups and downs of startup life? These questions and more will be presented.

Challenges of developing a Membrane Electrode Assembly for HBr Redox Flow Batteries

Vignesh Balasubramanian

Large-scale electricity storage is a missing link in the green energy transition. Elestor is developing and manufacturing cost-effective, large-scale electricity storage based on hydrogen bromide flow battery technology. The technology selection is based on its upscaling potentials: abundant raw material, high kinetics, and the decoupling of power (MW) and energy (MWh). Currently, Elestor is working closely on the development process of the “Membrane Electrode Assembly (MEA)” to build the “Minimum Viable Product (MVP)”, as is described in the business plan. Surely, we foresaw and faced a few upscaling challenges. The lecture will dive into 1 challenge faced in each section of the MEA during the development stage, namely the hydrogen electrode (ionomer influence on flooding), bromine electrode (mechanical fatigue analysis) and the membrane (MEA Lamination). Through the interactive session, we will systematically discuss the challenge, design of experiments and outcomes along with overall insights obtained from these experiences.

Zwitterionic Membranes for all-Vanadium Redox Flow Batteries

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Ion exchange membrane (IEM), as the key component in redox flow batteries (RFBs), has significant effects on the total costs and energy efficiency of the system. Therefore, the development of sustainable IEMs with more advantageous properties is essential. In the current work, a series of zwitterionic membranes using poly(*p*-terphenyl) backbone were synthesized and their potential application was investigated for vanadium redox flow batteries (VRFBs). Membranes were partially quaternised with a sulfonated alkyl chain to improve membrane selectivity and ionic conductivity. Also, different zwitterionic (sulfonic acid and piperidinium) contents of 40%, 50% and 60% were used to find out the optimum value. The membranes showed competitive performance in a VRFB system compared to Nafion 212 regarding ionic conductivity and capacity retention. Among zwitterionic membranes, the VRFB using the membrane with the highest zwitterionic content (60%) showed the best performance. The self-discharge time of VRFB using ZW60% was promising with more than 7000 h. Moreover, the VRFB showed over 95% average capacity retention for the first 50 charge/discharge cycles at a current density of 130 mA cm⁻² compared to Nafion® 212 [1,2]. Our results represent a critical step for the development and understanding of new and competitive formulations of ion exchange membranes for VRFBs.

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A Hydroxylated Tetracationic Viologen based on Dimethylaminoethanol as a Negolyte for Aqueous Flow Batteries

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Organic flow batteries receive much consideration as future alternatives to the costly vanadium chemistry. [1] 4,4'-Bipyridilium derivatives, also known as viologens, are promising redox-active molecules for the negative electrolyte of aqueous, organic flow batteries. [2] What makes this class of compound attractive, besides their three stable redox states, is the tunability of the nitrogen substituents, mainly via the S_N2 reaction. [3,4] Such substituents dramatically affect the chemical stability, electrochemical properties, compatibility with ion exchange membranes and solubility of the compounds.

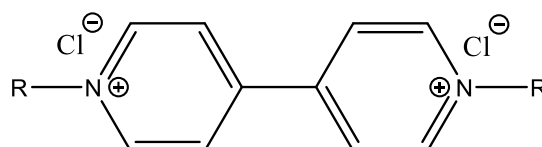


Figure 1. 4,4'-Bipyridilium derivatives for organic flow batteries.

Among the most interesting substituents studied in recent years, pendant-charged groups have gained particular attention. Specifically, the use of positively-charged ammonium groups has led to tetracationic species, virtually allowing the storage of two electrons per molecule. [5,6] In principle, this would imply doubling the charge capacity of the battery and significantly increasing the possibilities for commercial development. However, not so much has been done in terms of different positively-charged groups and the scope of the substituents remains to be exploited. Concerning this, bifunctional compounds such as amino-alcohols (e.g., ethanolamines) seem to be ideal candidates.

This work presents a new hydroxylated tetracationic viologen developed for high aqueous solubility, improved stability and superior battery performance. The new derivative was characterised chemically and electrochemically. The effect of the hydroxylated permanently charged moieties is discussed in terms of enhanced solubility and DFT calculations. A proof-of-concept battery is also reported by pairing the new negolyte with TEMPOL, a well-known commercially available posolyte.

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Further observations of 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 static mixers can adopted e.g. from electrodialysis field [2]. However, static mixers in batteries with metal deposition lowers the capacity of cell. The zinc electrodeposition is also affected by temperature (see Figure 1). With increasing temperature, the viscosity is decreased which lowers the thickness of the boundary layer, hence the transport of zincate ions is faster.

Deposition tests were run in a lab-scale flow single-cell in 3-electrode set-up using various substrate materials for deposition, oxygen evolution as a counter reaction and reference electrode to control. The series of galvanostatic depositions (charging experiments), discharging experiments as well as cycling experiments for various deposition substrates was performed. Subsequently, all depositions were characterized by SEM to identify the current density window for the desired the crystalline morphology deposition.

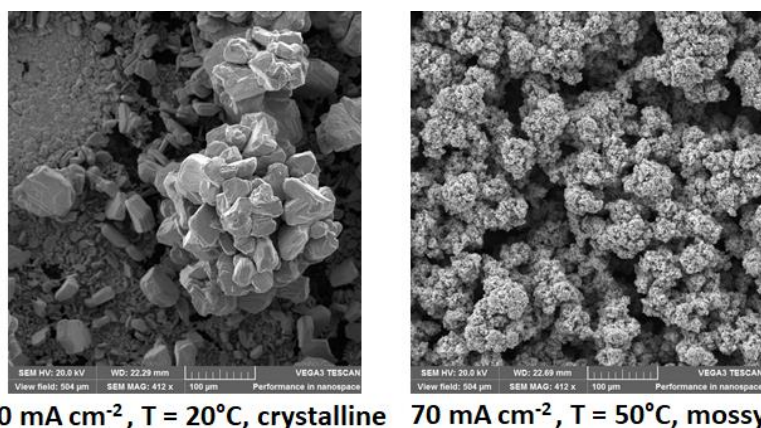


Figure 1 - SEM images of Zn deposition from alkaline electrolyte on composite A substrate at different temperatures.

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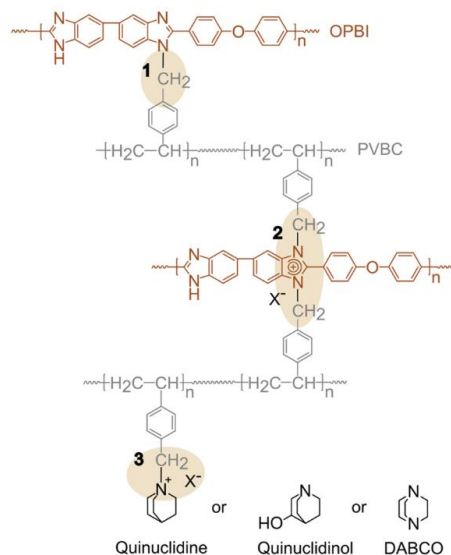
Performance of Quaternized Polybenzimidazole-Cross-Linked Poly(vinylbenzyl chloride) Membranes in VRFB

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Energy storage has been identified as a major enabling component for expanding and integrating renewable energy systems such as wind and solar [1]. Electrochemical energy storage in the form of redox flow batteries can deliver the energy capacity needed owing to their inherently decoupled energy and power, and the resulting diminishing storage cost with increasing discharge times. Vanadium redox flow battery consist of V^{2+}/V^{3+} and VO^{2+}/VO_2^+ for the negative and positive side respectively. An ion exchange membrane (IEM) separates the two compartments. The ideal IEM should deliver high ion conductivity while block vanadium crossover, be chemically and mechanically stable with high lifetime and have low cost. Polybenzimidazoles (PBI) is a group of polymers containing benzimidazole units. These polymers have excellent thermomechanical properties. They also present ion conducting properties when immersed in acidic or alkaline solutions [2], which has led to their application in VRFB. Pristine PBI membranes show excellent barrier properties in regards to vanadium crossover but lack in terms of conductivity. Blending of PBI with other polymers can lead to mechanically stable membranes retaining the barrier properties of PBI while increasing the conductivity. In this work we present the battery performance of VRFB single cells of different blends of poly[2,2'-(4,4'-oxybis(1,4-phenylene))-5,5'-bibenzimidazole] (OPBI) crosslinked with poly(vinylbenzyl chloride) (PVBC) and quaternized with three amines (1,4-diazabicyclo(2.2.2)octane (DABCO), quinuclidine and quinuclidinol).



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Development of oxygen reduction and oxygen evolution electrodes for alkaline zinc-air flow battery

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Zinc-air flow battery (ZAFB) is a promising technology due to high resources of abundant zinc and eco-friendliness. However, ZAFB is in an early stage of development and successful commercialization is limited by several technical issues, such as instability of air electrodes and deposition of zinc in unwanted morphologies. Our approach for ZAFB is three-electrode set-up. In this study we focused on oxygen evolution and reduction electrodes.

The aim of first research area is to develop improved oxygen evolution electrode OEE. Where we compared catalytically activated by NiCo₂O₄ with bare nickel electrodes. We also performed the preliminary study of electrodes with modified surface by laser. In second phase we studied temperature effect on overpotential of bare nickel electrodes. The prepared electrodes were electrochemically tested with following methods: electrochemical impedance spectroscopy, load curve measurements and galvanostatic load.

The second area of interest is focused on development of gas diffusion electrode (GDE) providing high performance and low permeability for the electrolyte. We performed systematic study of oxygen reduction electrodes with different content of PTFE, (from 30 up to 80 wt.%) in catalytic layer. The prepared electrodes were electrochemically tested with following methods: electrochemical impedance spectroscopy, load curve measurements and galvanostatic load.

Acknowledgement

This work was supported by TAČR, program THÉTA2, project no. TK02030001.

This work was supported from the grant of Specific university research – grant A1_FCHI_2022_005 and A2_FCHI_2022_037.

Organic input for flow battery and e-refinery

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A flow device, battery or electrolyzer, comprises electrodes, redox reactants, and (more often than not) a selective membrane or separator. In this communication, the possibilities we are working at to use organic materials for all these components will be discussed.

Quinols/quinones are among the aromatic redox active molecules chosen by nature and also constitute the building blocks for one of the most abundant wood-based biopolymers, lignin. Conducting polymers, such as PEDOT, due to their mixed ionic and electronic conductor properties, can serve as appropriate electrode material for redox transformations involving ions [1]. We studied the performance of ionic quinone-based aqueous RFB with PEDOT modified electrodes.

PEDOT is also notorious for driving oxygen reduction predominantly to the 2e pathway resulting in hydrogen peroxide production, rather than to thermodynamically more favorable 4e reaction leading to water [2]. We therefore used PEDOT cathode for producing hydrogen peroxide in a flow reactor. The anodic reaction in such electrolyzer could be water splitting at metal oxides [3] but also the same quinol oxidation as in the RFB we studied previously [4].

In addition to commercial synthetic polymer based ion exchange membranes, we prepared cellulose-based selective membranes and tested their behavior in our aqueous organic RFB, with promising results [5, 6].

Unresolved problems and challenges we are facing related to the use of organic materials in aqueous flow devices will also be discussed.

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Wood-derived ion-selective membranes

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Wood-derived cellulose nanofibrils (CNFs) are high aspect ratio nanoparticles with hydroxyl rich surfaces which are feasible to chemically modify with both anionic and cationic groups. These groups facilitate both the liberation of the CNFs from the parent structure, the wood fibre, while also providing the materials prepared from the CNFs with fixed ionic groups which can be used to prepare e.g. ion-exchange materials and for inducing ion selectivity and conduction properties in membranes prepared from the CNFs. By assembling CNFs into paper-like sheets will the highly crystalline core of the CNFs result in a significant portion of the volume being excluded while at the same time form nano-sized pores which contains the fixed ionic groups on the surfaces of the CNFs, thus forming the basis of an ion-selective membrane. Membranes prepared from two different types of CNFs, one functionalized with weak carboxylic acids and one with strong sulfonic acids, were prepared and the effect of degree of modification and crosslinking chemistry were evaluated. The membranes modified with weak carboxylic acids displayed good wet-strength with no excessive swelling in water and displayed optima in pore-size (1.4 nm), ion-selectivity ($t_+ = 0.87$) and conductivity (8 mS/cm in 0.1M KCl) at a moderate degree of crosslinking. The ionic conductivity was also demonstrated to be affected by pH showing higher conductivity at pH values above 4.¹ CNFs membranes containing sulfonic acid and aldehyde functionalities were prepared by sequential aqueous periodate oxidation and sulfonation reactions. The sulfonic acids provide the ionic selectivity and conduction while the aldehydes provide the possibility for chemical crosslinking through hemiacetals inducing wet stability. By tuning the reaction conditions and preparing CNFs with different degrees of modification could the ion exchange capacity, the ion conductivity and selectivity of the membranes be tuned. A larger amount of fixed sulfonic acids formed membranes with greater water uptake as well as ion conductivity and selectivity.² The performance of the sulfonated membranes was also evaluated in an aqueous organic redox flow battery where the sulfonated CNF-membrane demonstrated superior performance, a higher capacity retention, compared to a commercial synthetic ion-exchange membrane.³ Post treatments of the sulfonic acid containing membranes to reduce their water uptake and pore size were also shown to lower the passive crossover of redox active species and therefore in the end also improve the overall flow battery performance.

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Polyfluorenes functionalized with pairs of alicyclic quaternary ammonium cations as anion exchange membranes

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Anion exchange membranes (AEM)s are crucial components in many electrochemical energy devices where the performance is strongly influenced by the ionic conductivity, mechanical robustness, and thermochemical stability of the materials.¹ For example, one considerable challenge is to develop AEMs by molecular designing and synthesizing cationic polymer materials combining high hydroxide ion conductivity at low water uptake with high long-term stability for use in fuel cells and electrolyzers.^{2,3} In this respect, ether-free polymer backbones carrying piperidinium cations have shown high ion conductivity and long-term chemical stability.^{4,5} This class of AEM polymers are also be interesting for use in vanadium flow batteries.⁶

Here, we report the preparation of a series of ether-free polymers derived from a new diphenylfluorene monomer functionalized with dual *N,N*-dimethylpiperidinium (DMP) cations attached via methylene links (Figure 1). The monomer was copolymerized with a non-ionic diphenylfluorene monomer in superacid-mediated polyhydroxyalkylations to produce high-molecular weight poly(diphenylfluorene alkylene)s with well-controlled ionic contents. Compared to our previous study⁷, the ionic conductivity was enhanced after tethering the piperidinium rings in the 4-position instead of the 1(*N*)-position. For example, a membrane with an ion exchange capacity of 2.0 meq. g⁻¹ reached OH⁻ and Br⁻ conductivities of 49 and 4 mS cm⁻¹, respectively, at 20 °C under fully hydrated conditions.

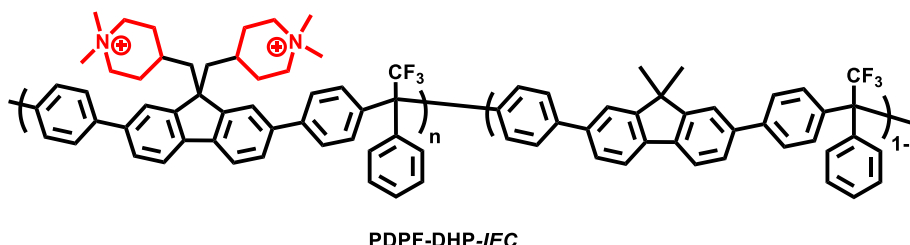


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Titanium Catechol Complexes as Anode Material for Redox Flow Batteries

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Alkaline redox flow batteries (RFB) have become of significant interest for stationary energy storage due to their low cost, high efficiency, and long cycle life. The most exploited and commercialized type of RFBs is the all-vanadium redox flow battery (VRFB) in strongly acidic solutions. However, numerous studies have been conducted to demonstrate the advantages and applications of alkaline RFBs. Most studies use potassium ferrocyanide as the posolyte, however different studies have examined a variety of candidates for the negolyte. In this study, the Ti(IV) tris-catecholate complex (Ti(cat)₃) is investigated as a promising negolyte for alkaline RFBs. Herein, the synthesis of the Ti(cat)₃ complex and the extremely low redox potential (-1.16 V vs. SHE) of the complex are reported.

The Ti(cat)₃ complex has been proven to be extremely air sensitive due to the high reactivity of the catechol ligands. The RFB consisting of potassium ferrocyanide (catholyte) and Ti(cat)₃ complex (anolyte) was cycled at different pH-values. The best performance of the Ti(cat)₃ complex was obtained at high pH values (pH 10-12) as low pH values (pH 7-10) resulted in significant amount of unwanted hydrogen evolution. The oxygen concentration in the desiccator was maintained below 1%, which provided a coulombic efficiency of 94%. This study demonstrates the potential of the Ti(cat)₃ complex for large scale stationary energy storage

Development of the aqueous all-copper redox flow battery

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While the adoption of renewable energy sources has significantly increased in recent years to distance our energy supply from fossil fuel sources the adoption has been severely hampered by the lack of large-scale energy storage to accompany the new energy sources. This is mainly due to the intermittent nature of renewable sources such as wind power and solar power generation, where energy storage is required to store energy during high production periods for use in low production periods. With the large energy storage method being employed being pumped hydro storage, however, pumped hydro storage is not suitable for all geographical locations. Therefore, of late using large scale chemical energy storage has been investigated to diversify energy storage. The most common of the chemical energy storage being vanadium redox flow batteries (VRFBs), iron chromium redox flow batteries (ICRFBs), and traditional batteries such as lithium-ion battery installations.[1] However, due to the large scale of energy storage required to transition fully to renewable energy further diversification of large-scale energy technology is required, with an emphasis on the technology to be ecologically and economically sustainable itself.

One such alternative to these technologies being the aqueous all copper redox flow battery (CuRFB), which exploits the single element nature to provide an easy to use, recycle, and maintain redox flow battery.[2] As with the CuRFB the electrolyte is recyclable using existing copper recovery techniques, and the mild copper electrolyte allowing for the use of inexpensive and greener membrane alternatives. However, the CuRFB is still understudied as a complimentary energy storage technology, therefore under the European Union's Horizon 2020 program research was undertaken to better understand the CuRFBs' operation, improve its performance, and raise the technological readiness level through the construction of a 5-kW demonstration plant in 2023. With the research conducted thus far improving the CuRFBs energy efficiency, reducing capacity loss rate, and showing the ease of electrolyte rebalancing after electrolyte imbalances have occurred. With the single element nature resulting in a greatly simplified electrolyte maintenance procedure compared to VRFBs and ICRFBs which require extensive rebalancing cells.

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Modelling AORFB: from cell to system management

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The HIGREEW project (Affordable High-performance Green Redox flow batteries) aims to design, develop and validate an advanced redox flow battery, based on novel aqueous organic electrolytes. This project is just an example of the fact that redox-active organic species [1] are becoming a real alternative to metal-based redox species due to benefits such as abundance and sustainability. Besides, they also offer a high molecular tunability enabling the research of derivatives that could provide wider cell voltages, higher solubilities, faster reaction kinetics, reduced crossovers or improved chemical and thermal stabilities. However, these new electrolytes entail new challenges on the commercialization and consolidation of the RFB technology in the current and future markets.

For instance, in the case of the HIGREEW prototype [2], it has been observed that the viologen based electrolyte is sensitive towards oxygen exposure in its charged state, and therefore, the prototype is equipped with an inertization system in its storage tanks to minimize capacity losses. Moreover, since the thermal stability window of the electrolyte is limited between 10°C and 45°C, the prototype design also has different equipment aimed for the container temperature control. In addition, it has been further observed that the viscosity of the aqueous organic electrolyte formulation plays a key role in the overall battery performance too. The viscosity changes experienced by the flowed material in correlation with the state of charge and temperature variations can cause the increment of the pressure losses across the stacks, rising some practical issues. For instance, an excessive pressure at the stack individual inlets may compromise the structure of the stack, or a certain pressure difference between hydraulic halves at the stack inlets may cause membrane ruptures disbalancing the system. In HIGREEW, this last issue is addressed by implementing a control algorithm that always establishes a safe flow rate for the anolyte side, as it is the most viscous one, while the catholyte is controlled in such a way to minimize the pressure difference, imposing a slightly higher flow rate as the differences in viscosity arise.

With the objective of diving more into the above hot topics connected to the relatively wide viscosity range at which organic electrolytes operate, a three-dimensional fluid-dynamic model aimed for RFBs [3] has been implemented and simulated using a Computational Fluid Dynamic (CFD) approach in ANSYS. The model is validated against pressure differences measured at a 20 cm² cell with flow-through configuration in the range of 10-80 mL min⁻¹ flow rates and for compounds with viscosities in the range of 0-10 cP. Furthermore, beside the accuracy of the simulation results, the computational performance of the model has been analyzed and optimized by controlling the quality and the density of the mesh in the different regions of the studied control volume.

Acknowledgements:

This work is financially supported by the project HIGREEW, under the European Union's Horizon 2020 Program (Grant Agreement no. 875613). Besides, Aitor Beloki acknowledges the support from the Basque Government (GV-ELKARTEK-2022 KK-2022/00043 and fellowship).

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Scaling up electrode manufacturing with the non-solvent induced phase separation technology

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Abstract

Grid-scale energy storage technologies must be deployed at a massive scale to balance the mismatch between energy generation using renewable technologies and demand. Redox flow batteries are an emerging technological option for large-scale and multi-hour electrochemical energy storage due to their ability to decouple energy and power¹. Despite their intrinsic advantages, their current elevated costs hinder commercialization². To improve cost competitiveness, research efforts have focused on developing novel electrolyte chemistries and engineered reactor concepts. To the latter, optimizing the porous electrode microstructure and surface chemistry offers a promising pathway to increase the performance of flow batteries. However, porous electrode design is challenging as they must fulfil contradictory requirements such as providing high surface area for electrochemical reactors, facilitating mass transport of reactive species, and maintaining low operational pressure drop. Furthermore, state-of-the-art porous electrodes have been repurposed from other mature electrochemical technologies, but have not been tailored for the unique requirements of redox flow batteries³.

We propose to apply non-solvent induced phase separation (NIPS) to manufacture porous electrode microstructures for redox flow batteries. We draw inspiration from membrane fabrication techniques and we reengineered the method for the synthesis of porous electrodes for implementation in redox flow batteries. Polyacrylonitrile (PAN) was chosen as carbon precursor and polyvinylpyrrolidone (PVP) as pore-forming agent. By varying several parameters (e.g. polymers, solvent, temperature, etc.) a variety of different microstructures (e.g., macrovoids, isoporous or porosity gradient) can be achieved without involving complex steps. The combination of large macrovoids and high surface area is highly beneficial as it reduces convective transport and kinetic losses. The porous electrodes synthesized with NIPS were tested in a single-electrolyte cell configuration and then in a vanadium redox flow battery and the performance exceeds that of commercial fibrous carbon materials^{4,5}. Current work focuses on scaling up the method to manufacture electrode materials at industrial scale.

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A long cycle life zinc-iodide flow battery enabled by a multifunctional low cost supporting electrolyte

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High energy density and cost-effective zinc-iodide flow battery (ZIFB) offers great promise for future grid-scale energy storage. However, their practical performance is hindered due to critical challenges such as poor cyclability, capacity fading because of irreversible zinc plating and stripping, slow kinetics of the redox reactions, and insoluble iodine (I_2) precipitation. In this study, we report NaCl-supported electrolyte chemistry to address these issues simultaneously. The addition of NaCl improved the redox reversibility of Zn/Zn²⁺. Experimental results depict that the coordination interactions between Zn²⁺ and Cl⁻ in the formation of soluble chloride anions, are the key factor for the improvement of Zn/Zn²⁺ redox reversibility. While the formation of soluble I_2Cl^- complex stabilizes the battery from solid I_2 precipitation, participation of Na⁺ and K⁺ as main charge balance carriers passing through cation exchange membranes, restricts migration of large, solvated Zn²⁺, thus, blocking the electrolyte crossover. A ZIFB with the improved electrolyte delivers high-energy efficiency, stable discharge capacity, and long cycle life (100 cycles) at 20 mA·cm⁻² while a conventional ZIFB shows the trend of capacity fade right from 10 cycles. These encouraging results indicate that the addition of a cost-effective salt, NaCl, enlightens great prospects for high-performance ZIFB applications.

Keywords: Zinc-iodide flow batteries, Supporting electrolyte, Zinc chloride complexation, Redox reversibility

Development of a scalable test platform for organic and semi-organic flow batteries

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The expansion of renewable energies increases the need for energy storage facilities. One of the suitable technologies for this purpose is the flow battery concept. An advantage of flow batteries is the independent adaptation to the demand of power and storage capacity [1]. In particular, iron-based systems are an interesting option as they are based on inexpensive and abundant resources. Recent interest focuses on the stabilization of iron species by incorporating them into organic ligands. Such new systems are often tested at a small laboratory scale and only a few parameters are measured. As a result, we here present a scalable test platform that challenges previous practice and aims to monitor the evaluated flow batteries extensively. As shown in Figure 1, the experimental arrangement offers enough space and power to operate cells with different power ratings. The capacity is also variable, in that the diameter of the tanks and thus the tank volume can be adjusted.

A test platform is benchmarked on the accuracy of the data that can be recorded and on its flexibility. Equally important is the ease of operation and low cost. To meet the first requirement, the flow velocity and the fill level of the tanks are continuously monitored with sensors in an automated manner. In addition to the potential during operation of the cell, the resting potential of the half cells are be measured individually. The data will be supplemented by the temperature of the electrolytes at the outlet of the cell. Flexibility is provided by the fact that different cell sizes can be used as well as different and flow rate of the electrolytes independent of each other. The control and measurement data output are done via a graphical user interface in LabVIEW in junction to a BaSyTec battery analyser. The communication with the sensors is done via an inexpensive Arduino microcontroller. Results are presented for the investigation of an alkaline iron flow battery with hexacyanoferrate on the positive half-cell and a complex of iron-DIPSO in the negative half-cell [2].

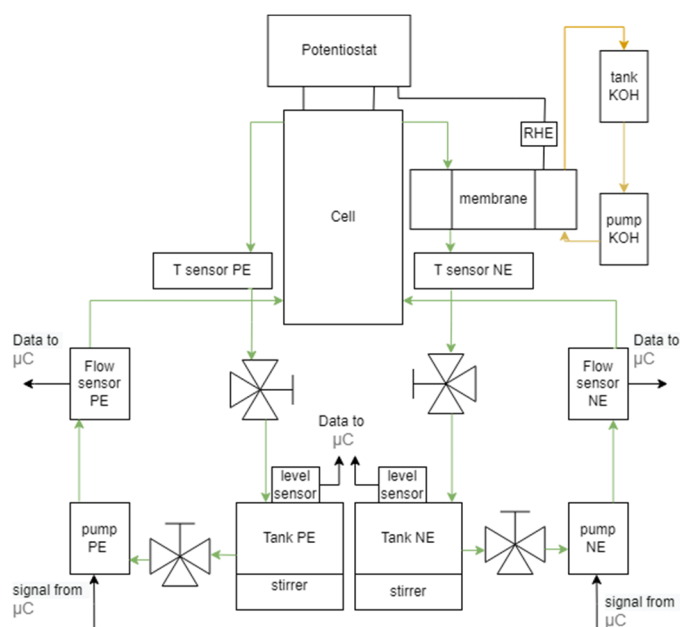


Figure 1: Flow chart of the test platform for novel flow batteries.

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Elucidating the influence of electrolyte composition on iron electroplating performance for high-power iron-based flow batteries

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Pressing environmental concerns and economic growth have motivated a transition to a renewables-based energy economy. In this new paradigm, large-scale energy storage will play a central role in the integration of renewable energy technologies, such as wind or solar. Among the options, redox flow batteries (RFBs) are promising candidates to overcome their main challenges, such as variability for both energy supply and demand at grid level. The widespread deployment of RFBs is currently restricted by material availability and costs. Aqueous all-iron redox flow batteries rely on earth-abundant active materials, and environmentally friendly and abundant water as solvent, offering potential for low cost and high-performance systems. However, the performance and durability of these electrochemical reactors is severely hampered by poorly reversible iron plating kinetics, competitive hydrogen evolution or uneven coating distributions, among others [1]. Therefore, a deeper level of fundamental understanding about the interactions of Fe^{2+} ions with electrolyte components and the electrode surface is paramount to engineer high-performance and durable iron-based flow batteries.

In this research program, we aim to gain fundamental insight into the poorly understood underlying mechanisms of nucleation and growth of iron electroplating. We employ a suite of electrochemical techniques, coupled with parameter fitting to pre-existing physical models [2], modified and adapted the iron-based chemistry, to study the formation, growth and dissolution of metallic iron. Chelating agents were investigated as a route to regulate plating kinetics and spatial distribution of the iron coating, which was further corroborated by microscopic techniques and galvanostatic charge discharge cycling of a symmetric Fe||Fe microcell. Our research provides deeper understanding of the iron electrodeposition process by electrolyte modification over a full range of potentials practical to iron-based battery operation. We elucidate the influence of electrolyte additive on iron plating kinetics. We quantify the nucleation rate and spatial distribution of iron active centers and their effect on reaction specificity and faradaic efficiency. Furthermore, we find that highly stable complexes, such as the iron-borate chelate, increase battery cyclability by nearly 50%. Further efforts will explore new ligands of both organic and inorganic nature, with different moieties to further tailor coating structure and activity. With this research we hope to shed light onto the control of ion-ion and solid-liquid interactions. This will aid the design of tailored electrolytes as a key step toward the realization of next generation, power-dense energy storage systems.

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A dual-layer electrode assembly for improved flow distribution in a symmetric vanadium battery configuration

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Recognizing the urgent need of further cost reduction to drive wider adoption of redox flow batteries (RFBs), it is critical to improve the reactor performance, which has been regarded as a key approach to reduce the stack size as well as the high capital cost [1]. As one of the main contributors to reactor internal resistance, porous electrodes with properly designed structure and optimized physiochemical properties offers a pathway to reduced voltage losses, including kinetic, ohmic, and mass transport overpotentials [2]. Recently, carbon cloth electrodes have been explored in flow battery applications owing to their bimodal pore size distributions [3-5], which opens a potential opportunity for improved mass transport behavior. Although the unique woven structure of cloth provides some flexibilities in electrode designs, it is still a barrier to strike a trade-off between the electrolyte penetration pathways and abundant active surface area.

In this study, we propose a novel dual-layer electrode assembly as an advanced hierarchical architecture to meet the requirement of high active surface area and low mass transport resistance. Carbon cloth was placed close to the flow plates and served as a flow distribution layer with a carbon paper sub-layer near the membrane to provide sufficient reaction sites. The electrochemical measurements were conducted in a symmetric vanadium flow battery setup, and the performance gain and quantitative analysis of contribution from each type of polarizations were investigated under both sluggish redox couples (i.e., V^{2+}/V^{3+}) and fast kinetic couples (i.e., VO^{2+}/VO_2^+). The Lattice Boltzmann Method (LBM) was considered to be adopted in this study to provide insights of flow patterns and velocity distributions in this electrode assembly. The results show that compared to the single-layer carbon paper/cloth, the overall voltage losses of the dual-layer structure are decreased. The strategy proposed here can be regarded as a promising approach for boosting battery performance.

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Flow battery research at University of Turku

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We will give a short overview of our work in the field of flow batteries, including discovery of novel organic molecules or metal complexes for flow batteries, measurement system development of lab scale flow batteries and comparative testing of flow batteries. Discovery of novel materials for flow batteries is carried out with collaborators employing state of the art computational tools such as density functional theory calculations and machine learning. In some cases also high-throughput synthesis and electrochemical testing is feasible realized with a pipetting robot.

We will also present our work on the concept of solid boosters, where the charge is stored in solid redox active materials in the tank by a chemical charge transfer reaction with the redox mediator. Additional concepts include bipolar membrane based and biphasic systems, as well as lignin based polymer systems. The aim is to develop measurement techniques and evaluate the opportunities and challenges offered by these concepts.

Hybrid Hydrogen-Manganese Redox Flow Battery

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Abstract

The intermittent nature of renewable energies (e.g., solar, wind) and their increasing contribution to electricity generation require efficient energy storage systems to be developed. Among different available technologies, redox flow batteries (RFBs) are particularly suited for renewable energy storage. There are different chemistries for RFB, and up until now, several systems have been upscaled from lab or pilot scale to commercial scales, such as all-Vanadium and zinc-bromine RFBs. However, to provide a better fit to the grid, there is still a lot of room for improvement in the sustainability of RFBs. A hybrid Hydrogen-Manganese RFB using hydrogen gas on the negative and acidic manganese (Mn^{2+}) electrolyte together with titanium (Ti^{4+}) which is used to avoid the precipitation of MnO_2 on the positive side, is a promising and sustainable system [1]. Manganese is a low-cost and abundant material. Moreover, the cell potential of Hydrogen-Manganese RFB (1.51 V) is higher than all-Vanadium (1.26 V), thanks to the high standard potential of manganese.

In the current work, we have through different electrochemical characterization methods, estimated the kinetic parameters of the electrolyte in the cell. Further, we have tested the performance of the RFB system for 50 cycles at low and high concentrations of manganese. The low-concentration tests were successfully carried out at 15 mA/cm² current density with an average coulombic efficiency of 95%, while the high-concentration tests were performed at 70 mA/cm² with an average coulombic efficiency of 99.8%.

Ref: [1] Rubio-Garcia, J., et al., *Hydrogen/manganese hybrid redox flow battery*. Journal of Physics: Energy, 2018.

Microstructural description of modified ion exchange membranes based on thermodynamical approach

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Modification on ion exchange membranes (IEMs) are of interest in scientific community due to the overall benefits that the resulting material can provide. Such modifications can enhance the conductivity of the membrane, to limit the crossover of the active redox compounds in the redox flow battery technology, as well as the mechanical properties of the starting material. In this work, we proposed a pyrrole polymerization in the microcavities of some commercially available IEMs (both cationic and anionic) [1]. However, the chemical procedure used produces more effects than simply filling the micropores of the pristine membrane. The properties of the membrane, as well as the transport ions through the resulting material, may considerably change. To this end, we have explored the insight of membranes by structural and generalized conductivity considerations [2-4]. The transport structural parameters (TSP) have been obtained from the electrolyte concentration dependencies (NaCl, in this work) using the so-called two-phase model. AEMs successfully increased their specific conductivity (between 2.5 and 3.9 times) whereas CEMs slightly decreased (between 1.3 and 2 times). AEMs increased almost twofold while CEMs decreased doubled their internal microphase arrangement in terms of structural parameter (α). Finally, based on TSP obtained we proposed a microstructural description for the IEMs studied in this work with the aim of elucidating the possible transport mechanisms in these materials.

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Gamma-aminobutyric acid-functionalized naphthalene diimide for aqueous organic flow batteries

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Aqueous organic flow batteries (AOFBs) are one of emerging electrochemical systems for large scale energy storage systems. One attractive molecule that has recently gained attention towards itself to be used in AOFBs is a family of organic molecules known as 1,4,5,8-naphthalene diimides (NDI). NDI is a molecule similar to quinone with two imide groups attached to a naphthalene core.¹ NDI undergoes two electron reduction reaction that makes it desirable as it can double the charge density of the RFB. NDI molecule has been studied for use in photovoltaics, sensors, semiconductors, electrocatalysts, and lithium-ion batteries, while it is not investigated thoroughly for utilization in AOFBs.² In this work, we synthesized GABA-NDI, an NDI molecule bearing negative charges with higher solubility of approximately 250 mM in 1 M ammonium chloride than the previous negatively charged NDI molecules in aqueous solutions and studied its performance in a flow battery. Our battery was built using 10 mL of 200 mM GABANDI as negolyte and 25 mL of 200 mM ammonium ferrocyanide as posolyte in the buffered supporting electrolyte and exhibits an average voltage of 0.76 V. The flow battery consisting of the mentioned couple in a buffered electrolyte is stable for over 200 cycles and gave a coulombic efficiency of 99.96% and a high energy efficiency of 80.9% at 60 mA/cm². The high energy efficiency in the batteries is an indication of fast kinetics of the molecule and a low ohmic resistance of the cell. Moreover, 95% of the theoretical charge capacity of the GABA-NDI was accessed when cycling the battery galvanostatically at 60 mA/cm². According to the cycling results, GABA-NDI has good cycling stability, but a higher solubility would be needed for it to be feasible in industrial applications. However, the one-step easy synthesis makes this molecule desirable for mass production at a low cost.

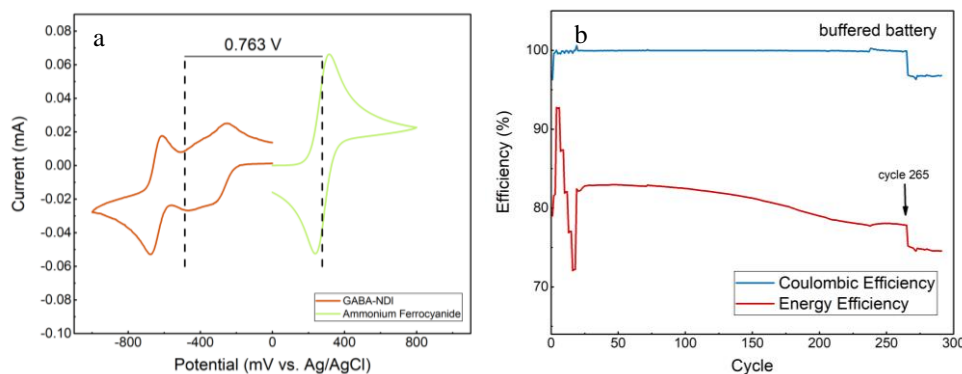


Figure 1. a) Average voltage between GABA-NDI and ammonium ferrocyanide. b) Coulombic efficiency and energy efficiency of the battery

References

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The Preliminary Study on Ionic-liquid-based Redox Flow Battery Systems for Cold-climates

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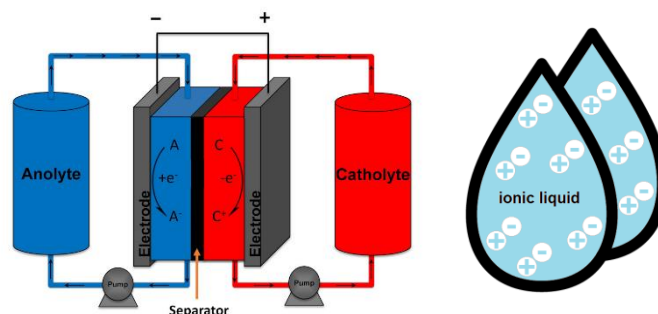
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Energy storage serves as a vital link between intermittent renewable energy sources and energy consumption. Energy storage solutions that are both affordable and efficient are required for the widespread and deep penetration of renewable energy. Renewable energies are highly intermittent, necessitating the development of reliable energy storage devices to store intermittent energy during peak times and compensate for demand over time.

Redox flow batteries (RFBs) are one amongst promising energy storage technologies for large-scale applications. Both energy and power can be easily adjusted from a few hours to days for storage depending on the application, which is an important advantage for renewable integration of energy management.

Ionic liquids (ILs) are salt-like materials as a class of non-molecular compounds that are composed solely of organic cations and inorganic or inorganic anions. Ionic liquids are molten, which exist in the liquid state at relatively low temperatures as low as minus 90°C. The chemical-physical properties of ionic liquids can be adapted very well to given technical objectives. Their characteristic features include almost no vapor pressure (remain liquid even at high temperatures), non-flammability, high thermal stability, wide temperature ranges for being liquids, and high ionic conductivity.



The goal of the project is mainly focused on the operation conditions at low temperatures. The used commercial systems in our daily life encounter some difficulties at cold temperatures and such cases lead into inefficiency. Especially in Nordic countries, Russia, Canada and USA where face extreme low temperature during the year.

In this study, we performed some preliminary electrochemical experiments for few inorganic, organometallic and organic compounds to understand their redox properties in ionic liquids. We will further study our selected systems to develop a suitable system for cold-climate.

Acknowledgment

This work is partly supported by Proionic GmbH and Academy of Finland (Funding No 334828).