Important Factors in Redox Flow Battery Design for Application in Public Spaces

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Friday 25 august 2017 14:00h

Content

Introduction

As the need for renewable energy is growing, so is the demand for stable energy storage on a large scale. The fluctuating energy supply is a feature of common renewable energy sources like solar energy and wind energy. This fluctuation is not matching the energy demand on the side of the costumer. A steady energy supply can only be guaranteed if large amounts of energy can be stored, bridging the energy generation and consumption. This storage could be limited only to large power plants, or can be expanded to small scale energy storage at home. In recent years, interest in the use of redox-flow batteries (RFB) for this purpose has increased [1].

Operation of RFBs

A RFB works following the same general principle as a galvanic cell. Two compartments contain a different redox-active species and are separated by a membrane (Figure 1).
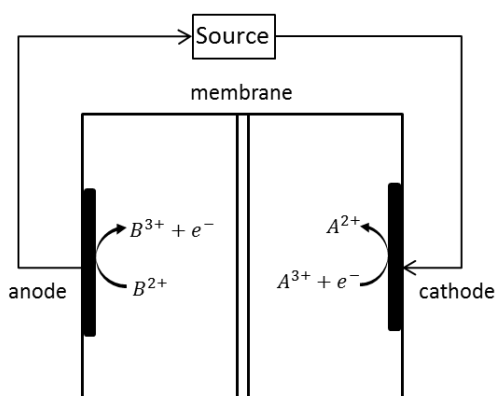

Figure 1: An electrochemical cell during charging.

The purpose of the membrane is to prevent mixing of the solutions and to let only certain ions (e.g. H^+) through. Depending on the redox active species, the membrane can be either exchanging cations or anions. An electrode is placed in each of the compartments. In the charging mode of the battery, a voltage is applied and the redox element in compartment A is reduced (Eq. 1.1) while the redox element in compartment B is oxidised (Eq. 1.2).

$$A^{3+} + e^- \rightarrow A^{2+} \qquad \text{(eq. 1.1)}$$
$$B^{2+} \rightarrow B^{3+} + e^- \qquad \text{(eq. 1.2)}$$
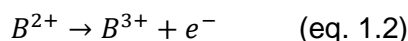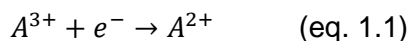
The opposite occurs when the battery is discharged: compound B will be reduced (Eq. 1.3) while compound A is oxidised (Eq. 1.4). The discharge process is the reverse of the charging process (Figure 1) i.e. with all reactions and currents reversed. A single charge-discharge cycle is represented in Figure 2 where cyclic voltammograms of an iron complex (catholyte) and a cobalt complex (anolyte) are shown.

$$B^{3+} + e^- \rightarrow B^{2+} \qquad \text{(eq. 1.3)}$$
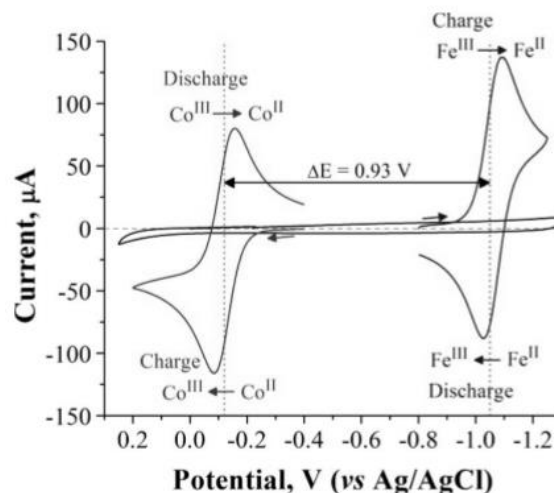$$A^{2+} \rightarrow A^{3+} + e^- \qquad \text{(eq. 1.4)}$$
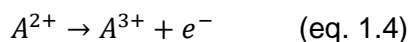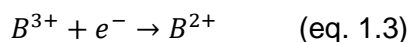

Figure 2: Cyclic voltammograms of a redox active species set in a single charge-discharge cycle. Reproduced from ref [2]. Copyright ECS (2015)

A difference with a galvanic cell is that in a RFB the catholyte and anolyte are in a cycling flow through the electrochemical cell to

two separate storage tanks (Figure 3). The ability to scale up the volumes of these storage tanks gives a potential to store large amounts of energy in a single battery. In the case of an excess in available energy, the flowrate of the electrolytes through the electrochemical cell can be increased accordingly.
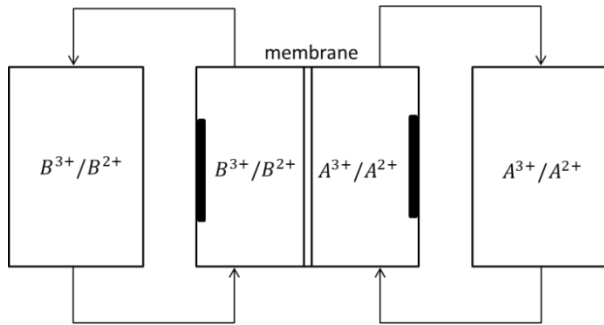

Figure 3: A redox flow battery (RFB) with an electrochemical cell (middle) and two storage tanks for both electrolytes (left and right).

In designing a RFB, a major factor is to achieve a high efficiency and lose the least amount of energy as possible. Two points of energy loss are described by the coulombic efficiency (CE) and the voltage efficiency (VE). Coulombic efficiency gives the efficiency in the actual charge transfer; if side reactions take place or a redox active species crosses the membrane the CE drops. Voltage efficiency is determined by energy losses due to applied overpotential. Activation energy for electron transfer, concentration depletion of the redox active species or gas evolution at the electrode, can all contribute in the need for a slight overpotential. This extra energy is mostly converted into heat. The product of CE and VE describes the overall energy efficiency (EE) of a battery.

Over the last 40 years interest in RFBs has fluctuated. In the course of these years many different types of RFB have been developed. Inorganic metal species based on iron [3][4][5], chromium [6][7][8], vanadium [7][9], copper [10][11] and boron [12] as well as organic molecules[13][14] have been deployed as redox-active elements in RFBs. Possibilities for these RFB range from all-soluble to hybrid (involving metal plating), in aqueous or non-aqueous media and in acidic, alkaline or neutral environment. And recent research from Wedege et al. demonstrates an alkaline aqueous RFB which is able to charge directly from solar radiation [15]. Tough still not competitive with a low efficiency, it opens up new possibilities for energy storage in RFBs.

The aim of this colloquium is to evaluate important factors in RFB design to achieve a high total energy capacity for application in public spaces (e.g. at home). In the first place, all-soluble RFBs have a major advantage over hybrid RFBs. In hybrid RFBs solid metal particles have to be stored and on a larger scale it becomes increasingly more difficult to keep particles flowing. Clogging in pipes or pumps and deposition of solid particles reduce the flexibility. Secondly, inorganic redox active species provide more flexibility to change the properties by variations to the ligands than organic redox active species. Other considerations are the costs and safety. By using more abundant metals, costs can be reduced significantly. The abundance of iron is much higher than that of cobalt, chromium, vanadium, boron and copper [16] and is the most promising. The toxicity of vanadium and chromium [17] species increases the safety demands in their use in public spaces. Organic solvents hold the same problem giving aqueous

media a preference. The potential range in aqueous solutions is limited by gas evolution reactions. At a high potential oxygen evolution occurs and at a low potential hydrogen evolution. Depending on the pH there is a shifting potential range of 1.23 V in which neither of these gas evolution reactions takes place. This range is plotted in the Pourbaix diagram in Figure 4.
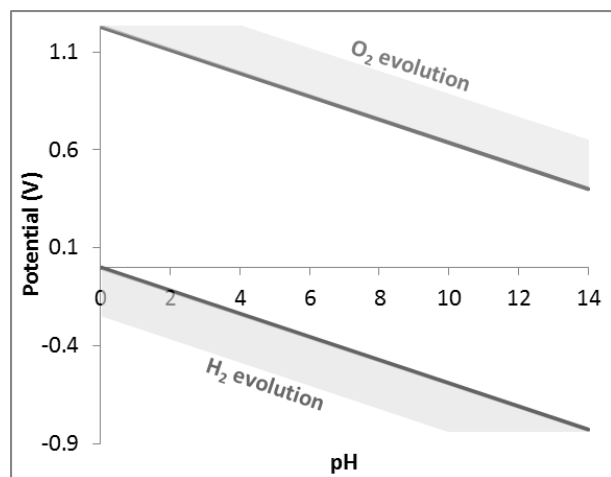

Figure 4: Pourbaix diagram of the water stability.

Giving the considerations above, the scope of this colloquium is on metal-based, non-toxic and earth-abundant redox-active species for the use in aqueous all-soluble redox-flow batteries.

Inorganic electrolytes

An early example of metal ion coordination compounds for the use in flow cells was presented by Chen et al. in 1981 [18]. They describe Fe(III)/Fe(II) complexes with several o-phenanthroline and bipyridine ligands and noted how the coordination of the ligands affects the redox potential. In 2016 an all-iron based aqueous RFB was developed by Gong et al. [19] considering a list of already known redox potentials of soluble iron complexes from literature (Figure 5).
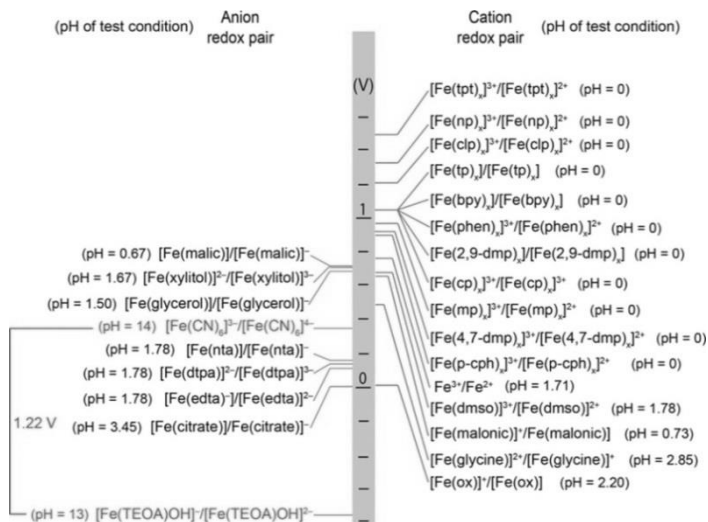

Figure 5: Selection of iron complex redox couples for application in RFBs. Reproduced from ref [19]. Copyright ACS (2016)

They found that the combination of an iron-triethanolamine complex ($[Fe(TEOA)OH]^{2-/-}$ or **Fe-TEOA**) at the cathode and iron-hexa-cyanide ($[Fe(CN)_6]^{3-/4-}$ or **Fe-CN**) at the anode (Figure 6) could provide a high cell voltage of 1.22V. Therefore, they selected this redox couple to test in a RFB setup.
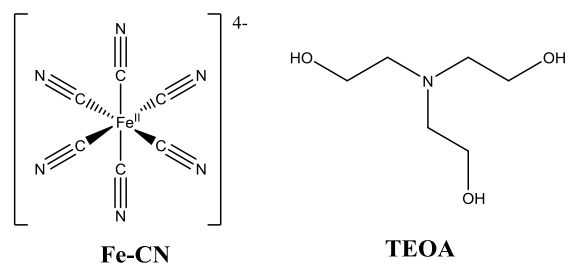
*Figure 6: Structures of **Fe-CN** and **TEOA** ligand.*

Several other groups have considered the use of triethanolamine as a ligand. Bechtold et al. have shown that organic compounds with a N-(2-hydroxyethyl)amino group show iron-binding capacity [20]. Wen et al. describe the solubility of **Fe-TEOA** complexes with different metal to ligand ratios (1/1 to 1/10) with an optimal solubility of 0.4-0.6 M for **Fe(III)-TEOA** at a ratio of 1/6 [21]. A different approach was taken by Saalfrank et al. who synthesised several **Fe-TEOA** clusters centred around

different metal ions [22]. Overall it is apparent that iron triethanolamine clusters are formed, but they have not been characterized in detail yet. Like **Fe-TEOA** the maximum solubility for **Fe-CN** is around 0.5 M [23]. An advantage of this electrolyte combination is the relative redox flow potential. Half-cell potentials of 0.48 V vs SHE for **Fe-CN** and -0.86 V vs SHE for **Fe-TEOA** give a standard cell voltage of 1.34 V. Using these two electrolytes, Gong et al. assembled a redox flow battery with a Nafion-212 as cation-exchange membrane.
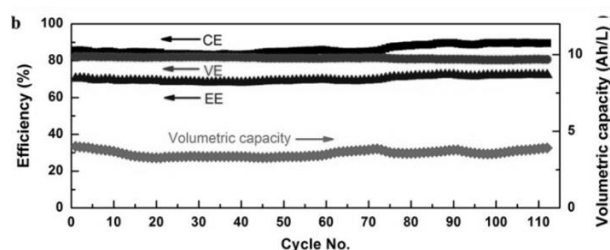

*Figure 7: Efficiencies though charge-discharge cycles in a **Fe-TEOA/Fe-CN** RFB. Reproduced from ref [19]. Copyright ACS (2016)*

A single charge-discharge cycle proceeded in a coulombic efficiency (CE) of 93%, a voltage efficiency (VE) of 78% and an energy efficiency (EE) of 73%. In a 110-cycle test, the CE stayed between 80 and 90% and the VE was constant around 80% resulting in an EE of roughly 70% (Figure 7). A reason why only a CE of 80-90% is achieved could be the

crossover of TEOA across the membrane. When TEOA crosses the membrane, it could be oxidised in two ways: at the electrode or by **Fe-CN** itself (Figure 8). The oxidation products have both been identified in solutions containing **Fe-TEOA** and **Fe-CN**. In RFB setup, a crossover concentration of 6 mM was observed for TEOA after 4 h.

Arroyo-Curras et al. used the same **Fe-TEOA** complex as catholyte in a RFB [2], only as anolyte they used a **Co-mTEOA** complex (mTEOA = 1-[Bis(2-hydroxyethyl)amino]-2-propanol) (Figure 9). With half-cell potentials of -1.05 V (**Fe-TEOA**) and -0.12 V (**Co-mTEOA**) a cell potential of 0.93 V was achieved.
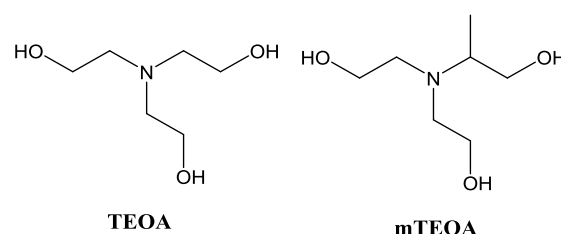
*Figure 9: Structures of **TEOA** and **mTEOA** ligand.*

This RFB was operated under alkaline conditions (5 M NaOH) with 0.5 M **Co-mTEOA** and 0.25 M **Fe-TEOA**. The battery was tested for 30 cycles averaging a coulombic efficiency of 99% per cycle and a total energy efficiency of 71% per cycle (Figure 10). During this operation no precipitation or gas evolution of
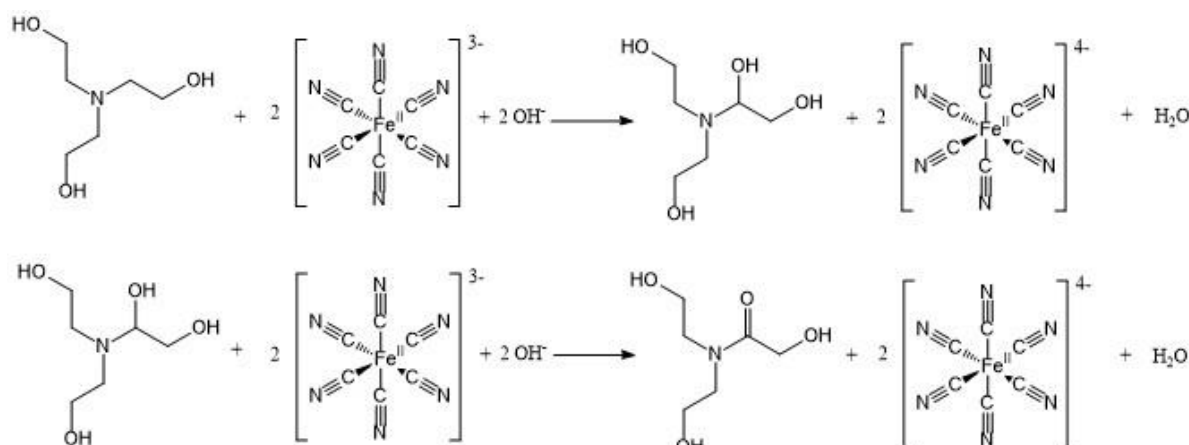

*Figure 8: Two possible oxidation routes of TEOA ligand by **Fe-CN***

hydrogen or oxygen was observed. The Nafion-112 membrane is a limitation of the efficiency due to poor conductivity of Na^+ in NaOH. The resistance of the membrane multiplied by the current density (30 mA cm^{-2}) accounts for 0.2 V overpotential needed. Besides the resistance of the membrane, also concentration crossover is an important factor. For this RFB a concentration crossover below 4% is reported after 20 h. This accounts for 20 mM crossover concentration in 20 h.
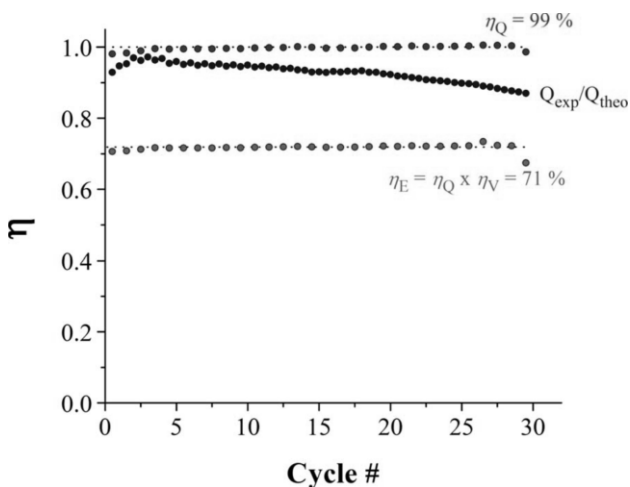

Figure 10: Coulombic (η_Q) and energy efficiency (η_E) for a **Co-mTEOA/Fe-TEOA** RFB. Reproduced from ref [2]. Copyright ECS (2015)

Combination of organic with inorganic electrolytes

Instead of using two inorganic electrolytes, there is also a possibility to use a combination of organic and inorganic electrolytes. Hu et al. reported a neutral aqueous redox flow battery with a substituted ferrocene as catholyte and methyl viologen (**MV**) as anolyte [24].
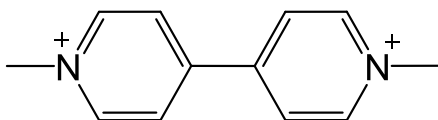

Figure 11: Structure of methyl viologen.

Ferrocene is insoluble in water [25] and ferrocene compounds functionalized with hydrophilic groups (ferrocenecarboxylic acid, 1,1'ferrocenedicarboxylic acid and 1,1'ferrocenedimethanol) are only soluble up to 100 mM. Hu et al. introduced a trimethylammonium group (**FeNCl**) that increased the solubility to 4.0 M in water and 3.0 M in 2.0 M NaCl. The addition of a second ammonium group (**FeN$_2$Br$_2$**) (Figure 12) increased the solubility to 3.1 M in water and 2.0 M in 2.0 M NaCl.
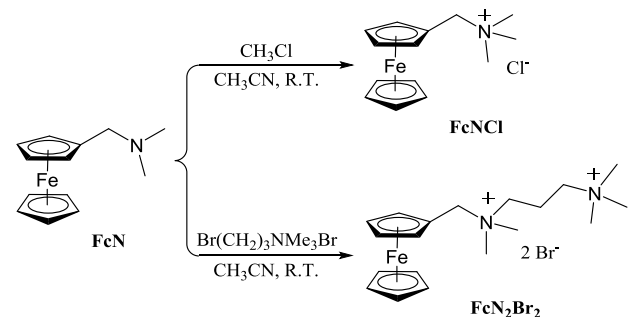
Figure 12: Synthesis of **FeNCl** and **FeN$_2$Br$_2$**.

From cyclic voltammetry, a reversible Fe^{3+}/Fe^{2+} redox wave is seen at 0.61 V (vs NHE) for both **FeNCl** and **FeN$_2$Br$_2$**. This is slightly more positive than the redox wave of **FeN** at 0.40 V (vs NHE). The similarity between redox potentials of **FeNCl** and **FeN$_2$Br$_2$** show that the addition of an extra ammonium group has little influence. However by increasing the redox potential of both ferrocene moieties a cell voltage of 1.06 V can be achieved when paired with methyl viologen (**MV**, -0.45 v vs NHE) in a redox flow cell. The high solubility of **FeNCl/MV** and **FeN$_2$Br$_2$/MV** give that theoretical energy densities in a RFB of 45.5 and 35.8 Wh L^{-1} respectively could be achieved. When tested in a flow cell under nitrogen, a capacity retention of 91% after 700 cycles for **FeNCl/MV** at 60 mA/cm^2 was

observed, corresponding to an average 99.99% capacity retention for a single charge/discharge cycle. Beh et al. investigated a similar redox couple in a RFB setup [26]. They functionalised ferrocene and viologen with two bis(trimethylammoniopropyl) groups to give bis((3-trimethylammonio)propyl)-ferrocene dichloride (**BTMAP-Fc**) and bis(3-trimethylammonio)propyl viologen tetrachloride (**BTMAP-Vi**) (Figure 13).
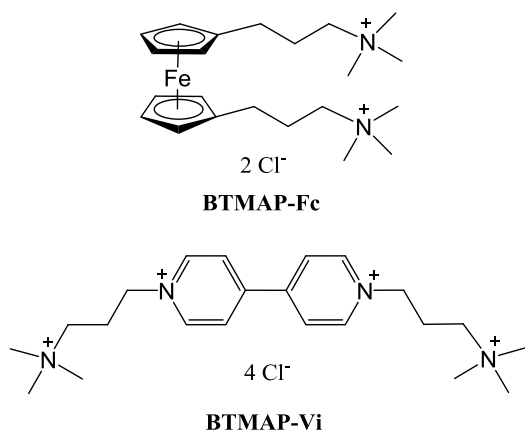

BTMAP-Fc

BTMAP-Vi

*Figure 13: Structures of **BTMAP-Fc** and **BTMAP-Vi**.*

With these additional hydrophilic groups, a solubility of 1.9 M for **BTMAP-Fc** and 2.0 M for **BTMAP-Vi** in water was achieved. In comparison to the study by Hu et al. [24], the redox flow potentials are nearer to each other, -0.36 V vs SHE for **BTMAP-Vi** and 0.39 V vs SHE for **BTMAP-Fc**, giving a lower potential cell voltage of 0.75 V. When tested in a flow cell under nitrogen, the cell capacity dropped to 98.6% after 250 cycles at a concentration of 1.3 M for both redox species, giving a capacity retention of 99.9943% per cycle. Higher capacity retentions could be achieved by lowering the concentrations of **BTMAP-Fc** and **BTMAP-Vi**. When the RFB was operated in a more oxygen rich environment, the cell capacity dropped very quickly (Figure 14).
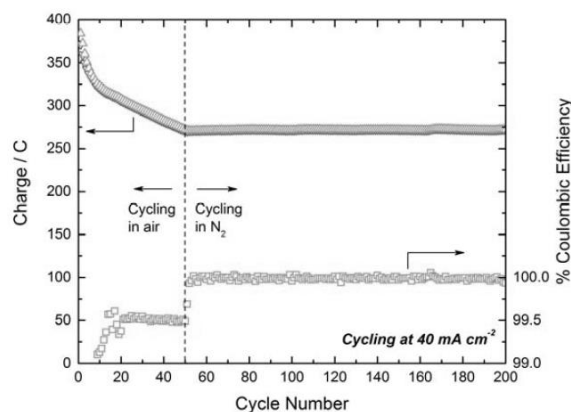
*Figure 14: Cell capacity of a **BTMAP-Fc/BTMAP-Vi** RFB operated in air and in N_2. Reproduced from ref [26]. Copyright ACS (2017)*

A different approach was taken by Lin et al. [23] by choosing two commercially available electrolytes: potassium ferrocyanide (**K₄Fe(CN)₆**) as catholyte and 2,6-dihydroxyanthraquinone (**2,6-DHAQ**) as anolyte (Figure 15). Anthraquinone itself is insoluble in water, but the addition of two hydroxy groups and the use of an alkaline solution (1M KOH) give a solubility of 0.6 M which is also similar to the solubility of **K₄Fe(CN)₆**.

$[Fe^{II}(CN)_6]^{4-}$ **2,6-DHAQ**

*Figure 15: Structures of $[Fe^{II}(CN)_6]^{4-}$ and **2,6-DHAQ***

Interestingly, the reduction potential of **2,6-DHAQ** can be tuned by changing the pH. An increase of the pH from 10 to 12 fully deprotonates **2,6-DHAQ** and shifts the reduction potential from -0.6 V vs SHE to -0.68 V vs SHE (Figure 16). Further increase of the pH above 12 has no influence on the reduction potential.

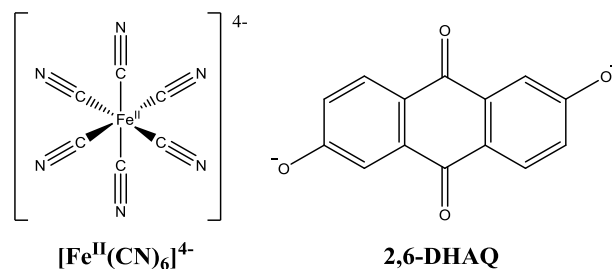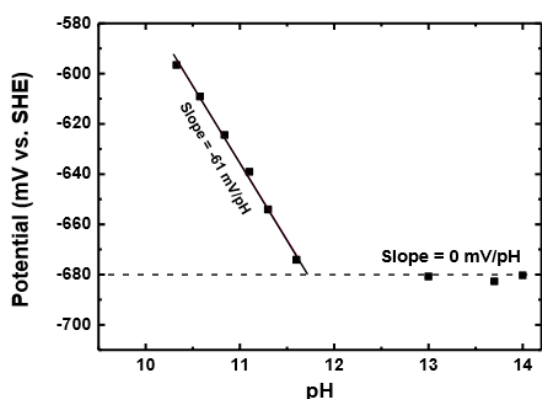*Figure 16: Redox potential **2,6-DHAQ** vs. pH. Reproduced from ref [23]. Copyright AAAS (2015)*

The redox couple of **2,6-DHAQ** with $K_4Fe(CN)_6$ (redox potential of 0.5 V vs SHE) gives a potential cell voltage of 1.2 V. Testing of the flow cell setup was performed with a current density of 0.4 A cm^{-2} for 100 cycles and gave an coulombic efficiency above 99% and an energy efficiency of 84% per cycle. An average cell capacity loss per cycle of 0.1% was observed over the 100 cycles. Three different mechanisms were investigated: Chemical decomposition, electrolyte crossover and leakage from the pump system. Chemical decomposition is ruled out since no degradation products (at a sensitivity level of 1%) are observed after heating **2,6-DHAQ** at 100°C for 30 days. Membrane crossover is also eliminated because cyclic voltammetry measurements of the **$K_4Fe(CN)_6$** electrolyte show no presence of **2,6-DHAQ**. Leakage of the pumping system was observed in a minor amount (unquantifiable). This leakage is expected to become negligible when the system is scaled up.

Discussion

This colloquium highlighted several possibilities in RFB design using inorganic

redox active species. Gong et al. have listed the redox potentials of several iron complexes (Figure 5) [19]. However, the performance of these redox active species in a RFB has not been investigated extensively up to now. An important factor of the energy capacity of a RFB is the total cell potential from a combination of anolytes. In aqueous solutions, a limited potential range of 1.23V between H_2 evolution and O_2 evolution, is available. Gong et al. selected redox active species (**$Fe(CN)_6$** and **Fe(TEOA)**) to give a high cell potential of 1.34 V, which is higher than possible within the limits of an aqueous RFB. With no mention of H_2 evolution or O_2 evolution, this limitation is not considered. Not only the cell potential is of importance on the energy capacity, also the solubility of the redox active species is. A low solubility reduces the amount of energy that can be stored in a certain volume. Studies by Beh et al., Hu et al. and Lin et al. all added hydrophilic groups on redox active species to increase the solubility and therefore also the total energy capacity of a RFB. The solubility of anthraquinone in water is increased from 0 to 0.6 M by the addition of two hydroxy groups, but the solubility of ferrocene in water is increased even more from 0 to 4 M by addition of large hydrophilic groups. Although the solubility of a single electrolyte could be increased, the coupling with the other electrolyte matters for the total energy capacity. If the concentration of the redox active species is significantly different, the capacity will be limited by the least soluble species. However, with only a high energy capacity, there is no guarantee for the use on a long term. One of the major factors in capacity retention is the

separation of the redox active species by a membrane. A re-occurring theme in these RFB studies is the crossover of redox active species across the membrane. Concentration crossover can be reduced significantly by separating two anionic electrolytes with a cationic membrane or two cationic electrolytes with an anionic membrane. However even with such a setup, Gong et al. and Arroyo-Curras et al. observed concentration crossover. They used two different types of Nafion membranes with a different ion exchange capacity, but in both studies concentration crossover of redox active species is observed. This tells that the development of membranes is also of major importance for the improvement of the energy capacity of a RFB. Nafion is a perfluorosulfonic membrane developed by Dupont de Nemours in 1962 [27]. In the studies with viologen and ferrocene derivatives as redox active species, a Selemion membrane is used instead of Nafion. Selemion consists of a copolymer of sulfonated styrene and divinylbenzene with a varying ratio of monomers [28]. The properties of these membranes (e.g. exchange capacity and conductivity) are dependent on membrane composition, membrane thickness but also the ions in question. Minimization of crossover of redox active species across the membrane can be a large contributor to the capacity retention. A recent study by Winsberg et al. showed the use of a single organic compound as catholyte and anolyte in the same battery [29] which would eliminate problems with concentration crossover. Two redox active materials (TEMPO and Phenazine) were connected with TEG (triethylene glycol) linkers. A disadvantage is that this approach limits the freedom of choice

of redox active species. Besides concentration crossover, also the decomposition of redox active species can reduce the capacity retention. Lin et al. did not detect any decomposition products of **2,6-DHAQ**. Most studies on RFB do not include any observations about decomposition products of redox active species, but this is something that should be taken in account. Another consideration for the introduction of RFB for public use (e.g. at home) is safety, hence the use of non-toxic redox active species and aqueous solutions. Finally, the costs of RFB production are taken in account, limiting this colloquium to earth abundant metal based redox active species like the commercially available potassium ferrocyanide.

Conclusion

Application of RFBs in public spaces (e.g. at homes) give the need for safe and cheap redox active species. However from the large amount of research on redox active species in RFBs, only a minority is focussed on earth-abundant non-toxic metal-based species in aqueous all-soluble RFBs. The examples of non-toxic, earth-abundant metal-based redox active species that are described in this colloquium show that the flexibility of metal complexes can be used to influence the cell voltage and the solubility. Good energy efficiencies are achieved, in some cases over a large amount of charge-discharge cycles. The importance of membrane development and minimization of crossover of redox active species is also addressed.

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