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REDOX FLOW BATTERIES — PERSPECTIVE MEANS OF ELECTROCHEMICAL ENERGY STORAGE

У статті представлено огляд технології так званих проточних редокс батарей. Наведено принцип їх роботи, а також приклади їх практичного використання, переваги та недоліки. Обговорюється сучасний стан наукових досліджень, що стосуються проточних редокс батарей. Перелічено редокс пари та електродні матеріали, що використовуються в проточних редокс батареях. Запропоновано шляхи їх подальшого вдосконалення.

Ключові слова: зберігання електроенергії, батарея, електроліт, електрод, каталітична активність, сплав

1. Introduction

In recent years a lot of attention was given to renewable sources of energy such as wind and solar. It is known that those are able to provide significant energy supply but at the same time are intermittent and to a large extent unpredictable. In order to make use of before mentioned energy sources they should be collected into means of storage in order to be used afterwards. Another example when energy storage would be beneficial is balancing the grid load over time: storing the excessive energy at night and giving it away during the day peak loads.

Electrochemical means of energy storage (EMES) offer a lot of flexibility and control over the process of energy collection and release. Lately among all kinds of EMES such as batteries, capacitors, and fuel cells so-called redox flow batteries (RFBs) emerged as a promising means of large scale energy storage. The whole concept of RFBs has been known since 1970s from NASA's study and recently attained attention again. These RFBs differ from traditional lithium-based batteries (LBB) by the fact that electroactive materials are not stored inside of a RFB at all times but rather in special tanks outside of power conversion device and are introduced during device operation only. Thus, RFB is easy to scale up for any given situation.

Another difference between a RFB and a LBB is that the latter uses electrode material as a part of electrochemical fuel while in RFB electrode materials usually do not participate in reactions. In a LBB electrodes would suffer from physical and chemical changes and be eventually all used up. Besides, since all electroactive material is situated inside a LBB, the attempt of increasing power and energy density would inevitably result in the increased number of identical battery modules. In a RFB the higher performance characteristics can be achieved by simply increasing the volume of tanks for electrolytes.

2. Literature review

Among RFBs there might be distinguished true and hybrid ones. True RFBs indeed have all electroactive species (liquid or gas) outside while hybrid RFBs have at least one electroactive component inside the cell. The

majority of true RFBs utilizes two solutions — one for positive electrode reactions and another for negative electrode ones [1]. These solutions might consist of the same nature species but in different oxidation states, for example all-vanadium RFBs, or different nature species, such as iron-chromium RFBs (Fig. 1). Electrolytes need to be separated by an ion selective membrane to prevent electroactive particles mixing.

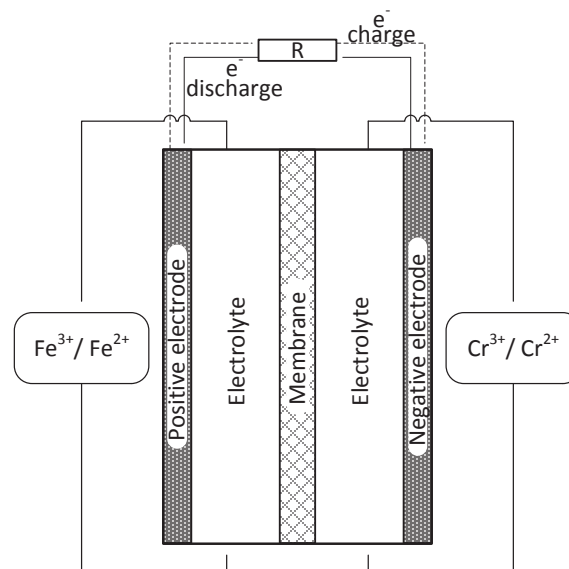


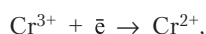
Fig. 1. Schematic of a RFB. Electrodes shown in a charge mode

In other words, the initial solutions of positive and negative electrolytes consisting of CrCl_3 and FeCl_2 should be charged by external electricity to store the electric energy converting Fe^{2+} into Fe^{3+} and Cr^{3+} into Cr^{2+} . During the charge process the electrolytes are pumped through the cell undergoing electrochemical change until all electroactive species are converted into their charged forms. When it is time to release the energy the direction of the process is reversed and the particles of Fe^{3+} and Cr^{2+} go back to their initial oxidation states, i. e. Fe^{2+} and Cr^{3+} giving energy in the form of electricity away.

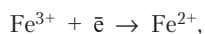
The RFBs exhibit a number of advantages over other electrochemical energy sources. As mentioned above, electrodes in RFBs themselves do not participate in the electrochemical reactions thus providing more stable and reliable performance. Furthermore, to increase the energy capacity of a RFB it is enough to use bigger volume tanks with more electrolytes without changing the cell size. This leads to easily scaled up cell design and smart materials utilization (i.e. electrodes, membranes, etc.). Another big advantage of a RFB is its inherent safety coming from the fact that most of the time energy storing species is spatially separated from the point of reaction. High efficiency (electricity to electricity conversion) and energy density, low maintenance and easiness of operation, resistance to overcharge and overdischarge along with the ability for deep discharge complement the list of RFB strengths. Among their shortcomings there is necessity of using pumps and flow sensors as well as low power density.

For the iron-chromium RFB, reactions occurring during charge-discharge are:

– charge:



– discharge:



The concept of RFB is relatively new and very few of them have been commercialized so far. There are a number of limitations to overcome for RFBs to become more suitable and effective for industrial purposes [1]:

- stable, low-cost and environmentally friendly redox couples with high solubility and fast kinetics need to be found;
- membranes possessing high selectivity and durability are to be developed;
- cell design should provide minimal transport losses;

- efficient, stable, and low-cost material electrodes are to be synthesized;
- integration into the traditional electric grid system is to be performed.

Among these limitations our group has been focusing on the electrochemical synthesis of catalytically active electrode materials with properties optimal for highly performing RFBs. Previous studies have shown that catalytic electrolytic nanostructured deposits of binary CoW and NiW alloys can be utilized as electrode materials [2]. Along with V, such elements as W and Mo are soluble in several oxidation states and thus in principle can be considered as redox couples for RFB electrolytes [3]. If so, CoW and NiW might offer additional benefits in terms of their functional properties when utilized as electrodes in RFBs.

A number of redox couples have been investigated for use in RFBs (tabl. 1). All-vanadium RFB are considered to be the most commercially attractive but limited availability of vanadium and poor solubility of its sulfate results in the need of search for more available, affordable, and effective substitutions for vanadium redox couples. Also, because of the high possibility of cross-contamination between positive and negative electrolytes of a cell during long time operation leading to lost capacity and lowered efficiency it is beneficial to consider electrolyte with the common elements in both half-cells. Other examples of elements examined for their use in RFB as electroactive species in electrolyte include nickel, lead, neptunium, uranium, and ruthenium. The search of affordable, efficient, abundant and environmentally friendly redox couples is one direction of further RFB development.

One recent study focused on Cu(II)/Cu(I) redox couple as a half-cell electrolyte for RFBs [4]. The effect of chlorides as complexing agents to stabilize Cu(I) has been studied. From the paper, high concentration of chlorides allowed for achieving the desired degree of reversibility and employing Cu(II)/Cu(I)-based solutions as positive electrolyte performing nearly as considered cheap iron electrolytes. Thermal stability of Cu(II)/Cu(I) system allowed its usage at up to 60 °C which was higher than that of

Table 1

Characteristics of selected redox flow batteries (adapted from [9])

Redox couple	Electrolytes	Charge/discharge reactions	Voltage, V	Efficiency, %
Iron-chromium	1 M CrCl ₃ (negative side) and 1 M FeCl ₂ (positive side) in 2 M HCl	$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \bar{e}$ $\text{Cr}^{3+} + \bar{e} \rightarrow \text{Cr}^{2+}$	1,18	95
Iron-titanium	1 M FeCl ₃ + 3 M HCl (positive side) 1 M TiCl ₃ + 3,5 M HCl (negative side)	$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \bar{e}$ $\text{Ti}^{4+} + \bar{e} \rightarrow \text{Ti}^{3+}$	1,19	44–50
All-vanadium	1,6–2 M V ₂ (SO ₄) ₃ in H ₂ SO ₄ (both sides)	$\text{VO}^{2+} + \text{H}_2\text{O} \rightarrow \text{VO}^{2+} + 2\text{H}^+ + \bar{e}$ $\text{V}^{3+} + \bar{e} \rightarrow \text{V}^{2+}$	1,6	80
Vanadium-bromine	1–3 M VBr ₃ in 7–9 M HBr + 1,5–2 M HCl (both sides)	$2\text{VBr}_3 + 2\bar{e} \rightarrow 2\text{VBr}_2 + 2\text{Br}^-$ $2\text{Br}^- + \text{Cl}^- \rightarrow \text{ClBr}_2^- + 2\bar{e}$	1,4	74
Manganese-vanadium	0,3 M Mn(II)/Mn(III) in H ₂ SO ₄ (positive side) V(III)/V(II) in 5 M H ₂ SO ₄ (negative side)	$\text{Mn}^{2+} \rightarrow \text{Mn}^{3+} + \bar{e}$ $\text{V}^{3+} + \bar{e} \rightarrow \text{V}^{2+}$	1,66	63
Zink-cerium	0,3 M Ce ₂ (CO ₃) ₃ + 1,3 M ZnO in methane sulfonic acid (positive side); 0,36 M Ce ₂ (CO ₃) ₃ + 0,9 M ZnO in methane sulfonic acid (negative side)	$2\text{Ce}^{3+} \rightarrow 2\text{Ce}^{4+} + 2\bar{e}$ $\text{Zn}^{2+} + 2\bar{e} \rightarrow \text{Zn}_0$	2,45	98
All-chromium	0,2 M chromium EDTA complex in HCl (both sides)	$[\text{Cr(III)EDTA(H}_2\text{O)}]^- \rightarrow [\text{Cr(V)EDTA(H}_2\text{O)}]^+ + 2\bar{e}$ $2[\text{Cr(III)EDTA(H}_2\text{O)}]^- + 2\bar{e} \rightarrow 2[\text{Cr(II)EDTA(H}_2\text{O)}]^{2-}$	2,11	15

vanadium ones. The Cu(II)/Cu(I) couple can be considered for application as a negative half-cell electrolyte as well.

Water based electrolytes have potential window limited by the electrochemical water decomposition (see the table below). Solutions based on or containing organic compounds, for instance, methane sulfonic acid, would a priori offer wider range of possible cell voltages (2,45 V for the zink-cerium system in the tabl. 1) but at the same time would be more expensive and difficult to operate due to the safety issues. Also, for the aqueous electrolytes the rate of electrode corrosion would be significant, especially taking into account that environment is mostly highly acidic.

Vast majority of RFBs employed carbon based electrode materials: carbon or graphite felt, foil, or fiber cloth, graphite plates, and glassy carbon sheets [5–8]. Some reports suggest that platinum, platinized titanium mesh, carbon on gold, titanium, and iridium oxide coated titanium, reticulated nickel, and nickel foam, porous nickel sulphide, nickel oxide, sintered nickel, and lead were utilized as electrode materials in RFBs. Some elements were mentioned to catalyze the electrode reactions. For instance, in the bromine/poly sulphide RFB (2 M Na₂S₂ negative electrolyte, 1 M Br₂ dissolved in 2 M NaBr positive electrolyte) nickel catalyst supported on carbon was employed for negative electrode reaction and platinum on carbon – for positive one. The search of effective electrode materials or/and catalysts which would speed the electrode reactions up should be under investigation.

3. Conclusion

To summarize, RFBs is a promising technology of electrochemical energy storage. If integrated into the traditional grid they would allow for balancing the load out over time by storing the electricity during low-load hours and giving it away during the peak-load ones. One way to improve RFB performance is to introduce novel electrode materials that would speed up the reactions of interest, for example by catalysis, and provide high overpotential of hydrogen and oxygen evolution. Such materials on the bases of binary catalytic alloys can be electrochemically synthesized which constitutes the subject of our future research [10].

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ПРОТОЧНЫЕ РЕДОКС БАТАРЕИ — ПЕРСПЕКТИВНЫЕ ЭЛЕКТРОХИМИЧЕСКИЕ ИСТОЧНИКИ ЭНЕРГИИ

Статья представляет собой обзор технологии так называемых проточных редокс батарей. Приведен принцип их работы, а также примеры практического использования, достоинства и недостатки. Обсуждается современное состояние научных исследований касательно проточных редокс батарей. Перечислены редокс пары и электродные материалы, используемые в проточных редокс батареях. Предложены пути их дальнейшего совершенствования.

Ключевые слова: хранение электроэнергии, батарея, электролит, электрод, каталитическая активность, сплав.

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