

# Redox flow batteries as the means for energy storage



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## ABSTRACT

As the deployment of solar and wind electrical energy increases, the intermittency of these power plants necessitates some means of energy storage for rebalancing the load and the supply. Storage of excess produced energy in electrochemical cells (batteries) is an obvious choice, and perhaps even the most practical method. However, the challenge is to find batteries that would be reliable, widely available, effective and cost-attractive. Within electrochemical storage the redox flow batteries constitute an important subgroup of storage and both the concepts and a number of redox systems is discussed here. The possible chemistries cover the more traditional vanadium redox flow cell. The modern trends are covered in the bromine-hydrogen, flow-through lead, zinc-bromine, cells with organic electrolytes and chemically regenerated redox fuel cells. A table comparing these systems is included.

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## 1. Introduction. What are the benefits of redox flow batteries?

Storage of electrical energy, which may be produced temporarily in excess, is a challenging problem of modern electrical distribution networks that largely draw power from wind or solar radiation, predictably unsteady resources, which are intermittent due to volatile nature of wind and sunlight. So far, the most efficient means of storage are systems based on mechanical principles. Two of the best are pumped storage hydroelectric power and compressed air [1]. However, in order to achieve high efficiency, these systems require large-scale deployment and thus considerable initial investment. Not every location is suitable for their construction nor it is always feasible or even desirable to build a large-scale system. Therefore, storage of excess produced energy in electrochemical cells (batteries) is an obvious choice, and perhaps even the most practical method. However, the challenge is to find batteries that would be reliable, widely available, effective and cost-attractive. This article focuses on electrochemical aspect of these backup sources.

## 2. Principles and general advantages and disadvantages

One possible electrochemical energy storage technology is based on the so-called redox flow cells (or often called batteries). The fundamental principle is the same as in any galvanic cell. Two

chemical reactions, oxidation and reduction, running separately, cause current flow in the electrochemical cell in the form of ion flux, and in the outer electrical circuit as electric current in the form of electrons. This electric current can then deliver power where it is needed. Compounds which undergo oxidation or reduction are the sources of chemical energy. After reacting and releasing their energy, these substances will render the electrochemical cell discharged. For rechargeable cells an opposite process can reverse the process of discharging and the cell can be recharged via an external power supply. The reacted, depleted, substances are converted during charging to their original form. Flow redox cells differ from the more common electrochemical cells in that the reactive material is not part of the structure's own body, but is supplied from external storage tanks in the form of a fluid phase during cycling passes from the storage containers. The total energy capacity of the system is then proportional to the amount of electrolyte in the external containers, while the output power is dependent on the electrode arrangement (electrode area of the system). A schematic diagram of the flow cell arrangement is the following picture (Fig. 1).

### 2.1. Advantages and disadvantages

The biggest advantage of the redox flow cells (RFB – Redox Flow Batteries) is based on their physical arrangement, in which the defining parameters of power and energy are separated. Their design can then be based on needs and the applications can be highly variable. Increasing the capacity of the cell can be solved by “mere” exchange of tank of the electrolyte with a larger one.

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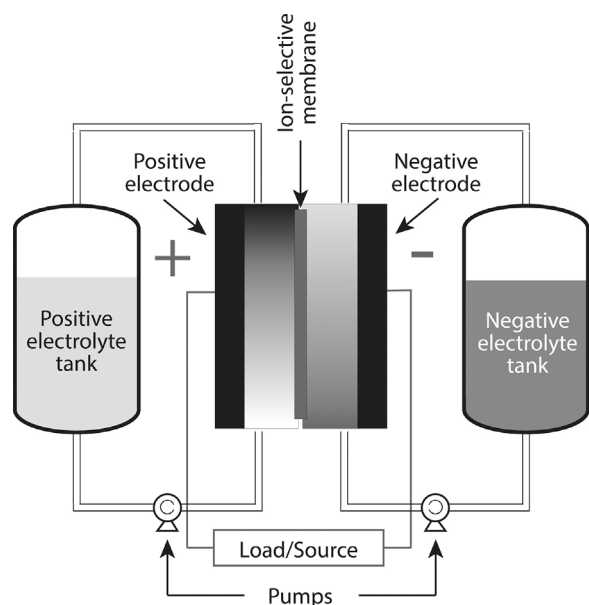


Fig. 1. Diagram of the principle of a redox flow-through cell.

Similarly, replacing the electrolyte can quickly accomplish “charging.” If one plans to settle for lower power, than smaller cell size is sufficient. For larger power it is then possible to design battery with more cells or to combine several smaller modules. Because the cell electrodes remain during charging and discharging chemically unchanged, and the electrolytes undergo only reversible processes, the batteries have, at least in theory, infinite cyclability. Other benefits include the ability to respond very rapidly to network demands, minimum maintenance and zero emissions. These cells are also known to tolerate a short term overload and can be “recharged” by resupply of electrolytes. The needed voltage, which is low from a single cell, is increased, as in other electrochemical sources, by linking several cells in series, thus creating a flow battery.

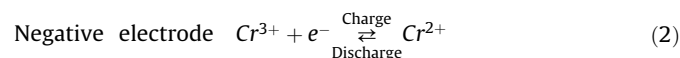
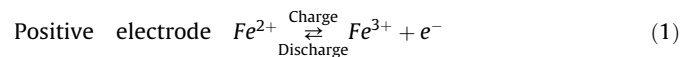
Compared with other types of batteries (e.g., Li-ion) the power density and energy of RFB is very low. This makes the cells unsuitable for mobile and traction applications. To increase the nominal current, the active area of the electrodes can be increased. It then causes high transverse gradient in solutions flowing through the cell, which thus reduces the average current density. Compared to conventional batteries, the flow cells are rather complicated and require a lot of ancillary equipment such as pumps, sensors, control units, fuel tanks and the like. In general, the flow through batteries are not just electrochemical cells; they are also engineering systems. To this end a comprehensive review was given recently in *this journal* by Arenas et al. [2].

### 3. Brief history, evolution, directions, and early systems

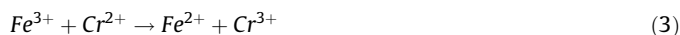
Conceptual design flow battery was first mentioned in 1933 in a patent by P. A. Pissort which, inter alia, also described the use of a vanadium redox couple [3].

Based on the concept of flow sections as described by L. H. Thaller in U.S. Patent 3,996,064 (1976) [4], NASA space program carried out in the late 1970s a systematic study on this subject. Many potentially suitable redox couples were considered from which were eventually selected and developed more promising systems of redox couples mainly Fe-Cr [5] and Fe-Ti [6] (soluble salts of Fe, Cr, Ti in an aqueous HCl solution). The main criterion for selection of a redox couple has been its low price and ready availability.

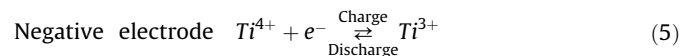
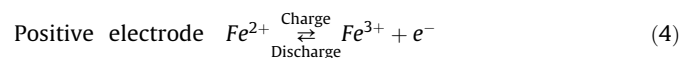
The Fe-Cr system is using  $1.0 \text{ mol dm}^{-3}$   $\text{CrCl}_3$  solution in  $2.0 \text{ mol dm}^{-3}$  HCl on the negative side and  $1 \text{ mol dm}^{-3}$   $\text{FeCl}_2$  solution in  $2.0 \text{ mol dm}^{-3}$  HCl on the positive side of the flow through cell. The electrodes are made from carbon felt. Considering the slowness of the reactions of chromium compounds on majority of electrode surfaces, the negative electrode was doped by traces of lead ( $100\text{--}200 \text{ mg cm}^{-2}$ ) and gold ( $12.5 \text{ mg cm}^{-2}$ ) [7]. The electrode compartments are separated by an ion-exchange membrane. The half-cell reactions proceed as follows:



and the spontaneous overall discharge reaction is



The open circuit potential (OCP) of the cell is 1.18 V. The current density was about  $20 \text{ mA cm}^{-2}$ . The half-cell reactions of the second mentioned process [6] can be described as:



with the spontaneous discharge reaction



It may be of interest to note that the above reaction in an example of titanometric redox determination, a standard when redox reaction were the mainstay of analytical chemistry [8].

While the cell equilibrium potential for reaction (6) is 0.782 V, authors [9] achieved for the iron-titanium system OCP higher, about 1.19 V, due to using lead granules and graphite foil as a current collector for the cathode. But the achieved current density was smaller than for the chromium-iron system, only about  $14 \text{ mA cm}^{-2}$ . This type of the cell is using solution of  $1.0 \text{ mol dm}^{-3}$   $\text{TiCl}_4$  in  $3.5 \text{ mol dm}^{-3}$  HCl on the negative side and  $1.0 \text{ mol dm}^{-3}$   $\text{FeCl}_2$  in  $3.0 \text{ mol dm}^{-3}$  HCl on the positive side. The electrode compartments are again separated by an ion exchange membrane. The work of Savinell et al. [6] compares in the regard to this system the use of a graphite foil for electrodes with a platinumized platinum foil. As the ion-exchange membrane was used Ionac MA-3745.

The NASA program in redox flow batteries was terminated in 1984. It was focused on the iron/chromium system [4,5,10]. Other older systems involved also for example zinc-bromine [11]. None of these systems, however, has been exploited for commercial use due to low energy density and slow reaction kinetics at the negative electrode. In the case of the experiments using electrolytes based on titanium salts the electrode kinetics was successfully increased using palladium catalyst, which has led, however, to a rapid increase in the cost and potentially unsalable system.

#### 3.1. Present state – the classics: vanadium systems

In 1978 A. Pellegrini and P. M. Spaziante stated in a patent application the idea of using vanadium redox salts [12], unfortunately, however, without further significant developments. The first known successful demonstration of a commercially exploitable vanadium cell was presented by a group of Australian scientists led by M. Skyllas-Kazacos from the University of New

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