

# REDOX FLOW ENERGY STORAGE FOR FLUCTUATING RENEWABLE ENERGIES

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## OVERVIEW

A prototype of a redox flow cell has been developed. This enables the flexible testing of various electrode materials, membranes and electrolytes. Different redox flow systems have been compared in this test design, showing the main advantages and disadvantages of the different types of redox systems.

## INTRODUCTION

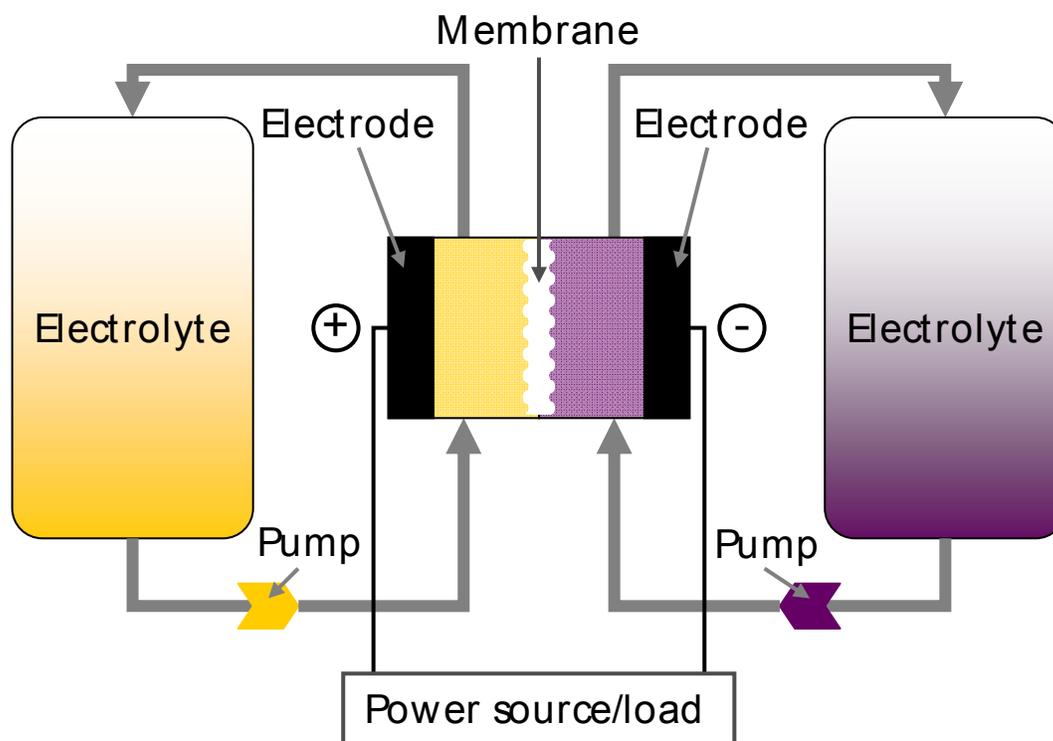
The amount of energy generated in wind and solar energy plants fluctuates and often falls short of requirements. As a result, the storage of electrical energy has become a key technology and one of the greatest challenges faced by the energy technology sector. To compensate the increasing number of temporary imbalances between generation and demand, innovative solutions are required in network construction and in the power output and balancing energy reserves. A better adjustment of the capacity of the reserves to the changing demands is possible when decentralized storage devices are applied, as they are scalable in terms of power output and the amount of energy stored.

Redox flow batteries (RFB) are based on the principle of chemical energy storage, in the form of dissolved redox couples in external tanks. Electricity is converted in a separate power module. During discharge the electrodes are continually supplied with the dissolved substances from the tanks, and once they are converted the resulting product is removed to the same or another tank. Depending on whether a two or four -tank configuration is used, only the current flow or the pumping direction of the electrolyte is reversed to recharge the battery. The storage capacity of the electrolyte solution is largely dependent on the size of the tank, and the energy efficiency is up to 80 %. This type of storage has potential for large-scale application.

## EXPERIMENTAL

As shown in fig. 2 a test-cell was built. One cell consists of two half cells which are separated by an ion conducting membrane. Each half cell consists of a metallic current collector, a graphite sheet or a polymeric composite graphite plate, a graphite felt and a flow frame. The graphite felt is embedded into the flow frame, allowing the electrolyte to flow uniformly through the graphite felt. Two stainless steel end plates are necessary for the mechanical stability of the cell. One endplate has connectors for inlets and outlets for both electrolytes. In addition several gaskets are necessary to prevent leaks. For electrical isolation purposes, rubber sheets are fitted between the endplates and the current collectors. The cell was constructed to give a geometrical active area of 51 cm<sup>2</sup>. With this construction it is easily possible to test a wide range of different electrolytes, membranes and electrodes. By adding additional half cells the assembly can easily be extended to a stack, where the voltage is the sum of single cells. Electrolyte flow is parallel through the cells.

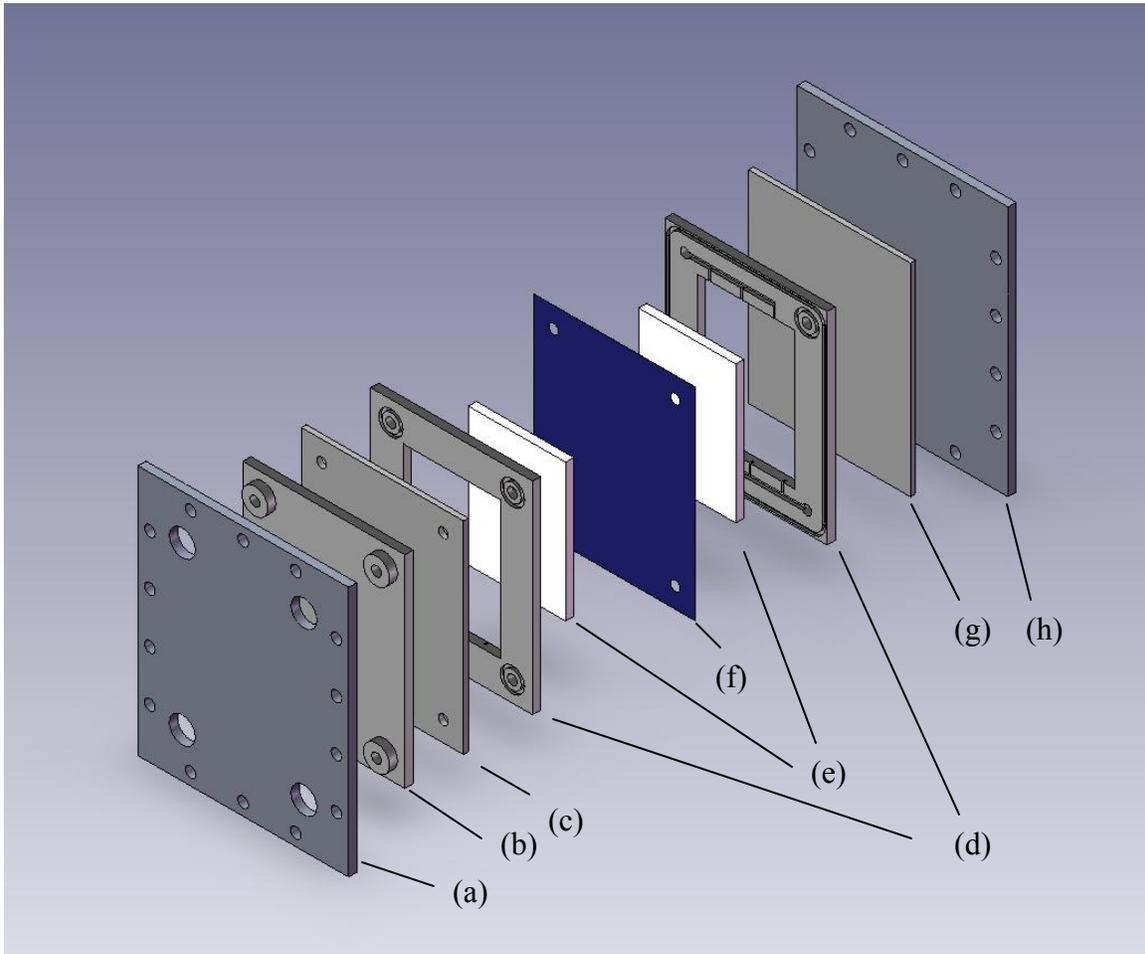
The flow frames were made of polyvinylidenechloride (PVC) in a VRFB and in an iron/chromium redox flow (Fe/Cr-RFB) system. Because of the significant corrosion at the PVC flow frame in a bromine half cell, the flow frames were made of polytetrafluoroethylene (PTFE) in a zinc/bromine redox flow cell. A flow frame consists of diagonally arranged electrolyte inlets and outlets. One electrolyte passes the flow frame through the graphite felt. The other electrolyte passes the flow frame directly to the other half cell. This half cell is a mirrored flow frame. Graphite felts were used because they have a significantly higher surface area than plain graphite electrodes. This, and a more turbulent electrolyte flow, leads to higher power densities.



**Figure 1. Redox flow battery principle**

The graphite felts were GFD5 (SGL-Carbon Group, Germany) with a thickness of 5 mm. The felts were treated in conc. H<sub>2</sub>SO<sub>4</sub> for 5 hours [2], thoroughly rinsed with de-ionized water and then 30 h heat treated at a temperature of 400 °C [3]. A graphite bipolar plate is fitted directly on the flow frame providing better mechanical stability, electrical contact to the felt and a sealing of the half cell. Bipolar plates should have a low electrical resistance and a high mechanical stability. The graphite bipolar plates used were FU-4369 (Schunk Kohlenstofftechnik, Germany) with a thickness of 3 mm. The whole experimental setup consisted of a peristaltic pump with 2 channels, 2 electrolyte reservoirs, 2 magnetic stirrers and battery test system (cell test 1470E, Solartron Analytical, USA)

The different battery systems were charged and discharged in a climate chamber at different temperatures at a humidity of 50 %. The charging of the batteries was first carried out galvanostatically with a current density of 20 mA/cm<sup>2</sup> up to a voltage dependent on the battery system. Afterwards the battery was charged potentiostatically down to a current density of 10 mA/cm<sup>2</sup>. Discharging was carried out galvanostatically at 20 mA/cm<sup>2</sup> down to a voltage dependent on the battery system followed by potentiostatic discharging down to current density of 10 mA/cm<sup>2</sup>. To characterize the different systems, 20 charge and discharge cycles were completed, and then the open circuit voltage of a fully charged battery was measured for 24 h.



**Figure 2. Redox flow battery test-cell; a) Steel plate, b) Isolation plate, c) Flow-through graphite electrode, d) Flow frame, e) Graphite felt, f) Membrane, g) Graphite electrode, h) Steel plate**

From measured voltage, current, time and charge, additional values were calculated. These are electrical power, energy efficiency (EE), coulomb efficiency and voltage efficiency.

Average electrical power:

$$\bar{P} = \frac{1}{t} \int_{t_1}^{t_2} U(t) \cdot I(t) dt \quad [1]$$

Energy efficiency (EE)

Energy efficiency is the energy effectiveness of the energy conversion without peripheral devices. Energy efficiency is delivered energy divided by input energy  $W_{el}$ :

$$\eta_{EE} = \frac{W_{dc}}{W_c} \quad [2]$$

Voltage efficiency (VE)

Voltage efficiency is the ratio of voltage at discharge and voltage at charge:

$$\eta_{VE} = \frac{V_{dc}}{V_c} \quad [3]$$

Coulomb efficiency (CE)

Coulomb efficiency is the charge carrier efficiency. That means the ratio of delivered charge carrier and input charge carrier.

$$\eta_{CE} = \frac{Q_{dc}}{Q_c} \quad [4]$$

### Vanadium/Vanadium-RFB

A commercial electrolyte was used to measure the VRFB (Treibacher Industrie AG, Austria) which was a mixture of 0.4 mol/L  $V_2(SO_4)_3$ , 0.8 mol/L  $VOSO_4$ , 2 M  $H_2SO_4$  and 0.05 M  $H_3PO_4$  according to a formal concentration of 1.6 mol/L  $V^{3,5+}$  and a state of charge at -50 %. An electrolyte volume of 60 mL was used in both half cells for measurements at a single cell according to a theoretical capacity of 2.6 Ah. An anion-conducting membrane was used as ion exchange membrane (Fumasep FAP, Fumatech GmbH, Germany). The upper limit of voltage during charge was 1.65 V. The lower limit during discharge was 0.8 V.

### Iron/Chromium-RFB

The electrolyte was a 1 M  $CrCl_3$  solution in 2 M HCl as anolyte and a 1 M  $FeCl_2$  solution in 2 M HCl as catholyte. The same anion-conducting membrane was used as was used for testing the VRFB (Fumasep FAP, Fumatech GmbH, Germany). Charge and discharge cycles were carried out in the upper limit of 1.4 V and a lower limit of 0.2 V.

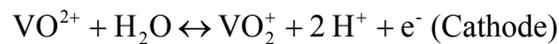
### Zinc/Bromine

Anolyte and catholyte were the same electrolyte [7]. The electrolyte was a solution of 0.5 mol/L  $ZnBr_2$ , 1.5 mol/L  $ZnCl_2$ , 3.0 mol/L KCl and 2.0 mol/L KBr. In the cathodic half cell a graphite felt was used. The anodic half cell was left without a felt. A microporic separator was used (Daramic Inc., USA).

## RESULTS AND DISCUSSION

### Vanadium redox flow battery

The chemical reactions of a VRFB are the following:

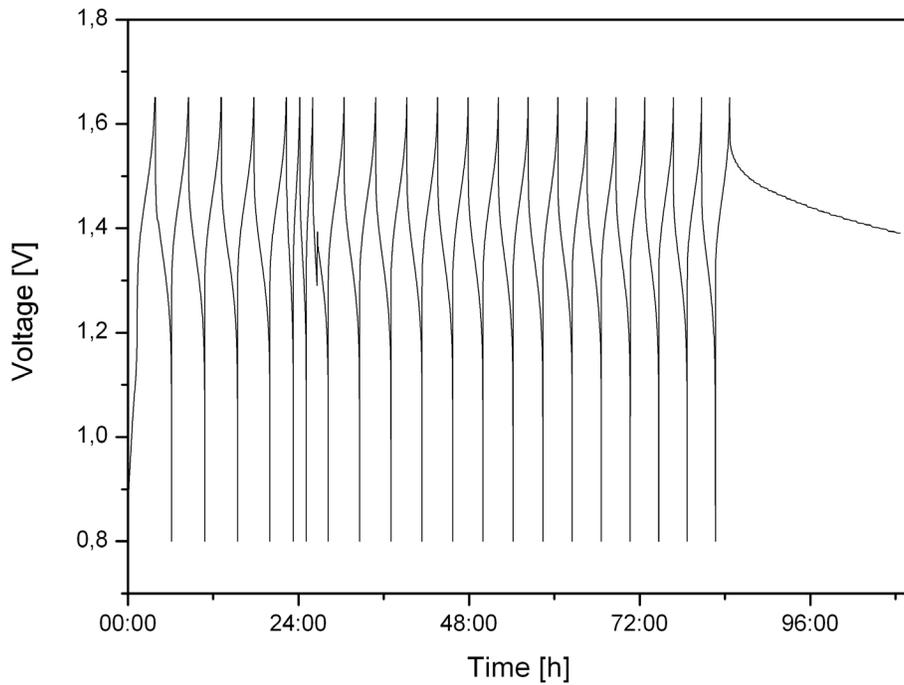


$$E^0 = +1.00 \text{ V vs. SHE}$$



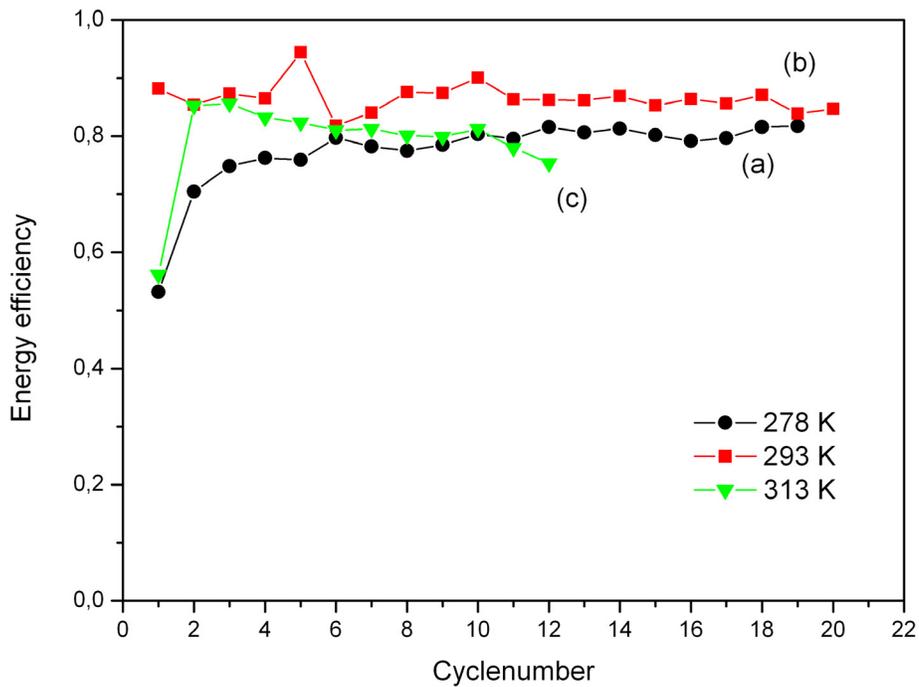
$$E^0 = -0.26 \text{ V vs. SHE}$$

Fig. 3 shows the charge and discharge curves of a VRFB at a temperature of 20 °C. Some irregular cycles at cycle number 6 and 7 can be clearly seen where, due to a technical error, the electrolyte was not pumping through the cell, so charge and discharge could only occur with the electrolyte left in the cell. After recovery, the capacity and power were nearly the same as before. The measurement of the open circuit voltage shows a voltage of 1.4 V after 24 hours, which suggests a relatively low vanadium crossover.



**Figure 3. VRFB; voltage**

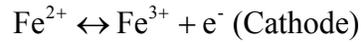
Fig. 4 shows energy efficiencies at different temperatures. The energy efficiency is lowest at 278 K, highest at 293 K, and at 313 K the energy efficiency decreases with increasing cycle number. Heavy exfoliations could be seen at the cathode at this temperature so the flow channels were blocked. This is a weakness of the construction of the cell with a flow through the bipolar plate. In addition, a current flow over the bipolar plate can be seen. Despite these disadvantages, high energy efficiencies of over 85 % and a decrease of vanadium crossover compared to NAFION could be achieved [9].



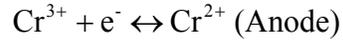
**Figure 4. VRFB; Energy efficiency at 5 °C (a), 20 °C (b) and 40 °C (c)**

### Iron/Chromium-RFB

The chemical reactions of a Fe/Cr-RFB are the following:

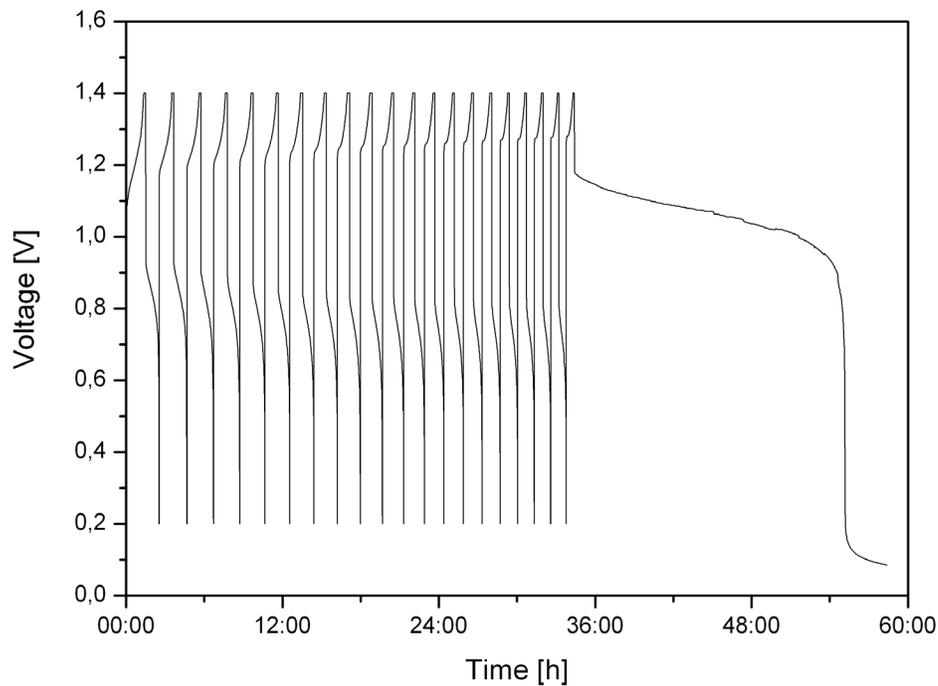


$$E^0 = +0.77 \text{ V vs. SHE}$$



$$E^0 = -0.41 \text{ V vs. SHE}$$

Charge and discharge curves are shown in fig. 5. With an increase in cycle number, a decrease in voltage efficiency is visible as capacity on shorter cycle time also decreases. After a few cycles a discoloration of both electrolytes can be observed. Measurement of open circuit voltage also indicates a higher iron and chromium crossover than the tested VRFB system. Energy efficiencies as shown in fig. 6 illustrate a slight decrease with increasing cycle number, with the highest values at a temperature of 40 °C.



**Figure 5. Fe/Cr-RFB; Voltage**

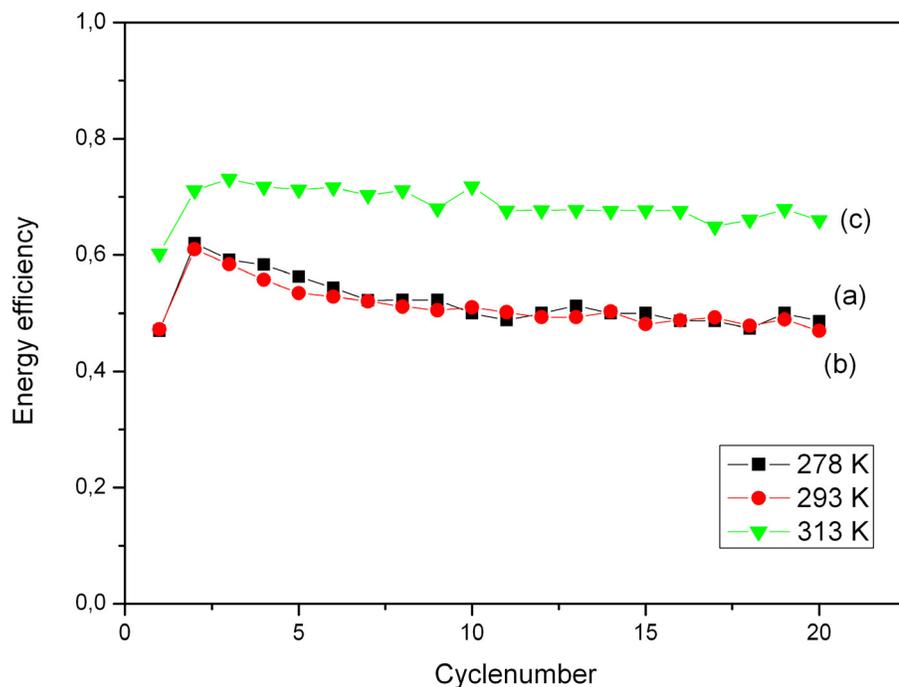
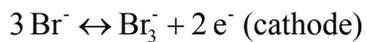


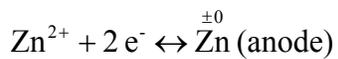
Figure 6. Fe/Cr-RFB; Energy efficiency at 5 °C (a), 20 °C (b) and 40 °C (c)

### Zinc-Bromine

At the catholyte of a Zn/Br-RFB dissolved bromide reacts to form bromine which combines with bromide to form soluble tribromide. A part of this bromine is also gaseous above the solution. At the anolyte dissolved zinc ions react to form metallic zinc which deposits on the graphite anode. The chemical reactions are the following:



$$E^0 = +1.09 \text{ V vs. SHE}$$



$$E^0 = -0.76 \text{ V vs. SHE}$$

As shown in fig. 7 a high polarization is clearly visible in this system. Unlike in the previous systems, the charge and discharge curves illustrate a slight decrease of voltage during a charge step. With an increase of deposition of metallic zinc voltage first decreases and then increases.

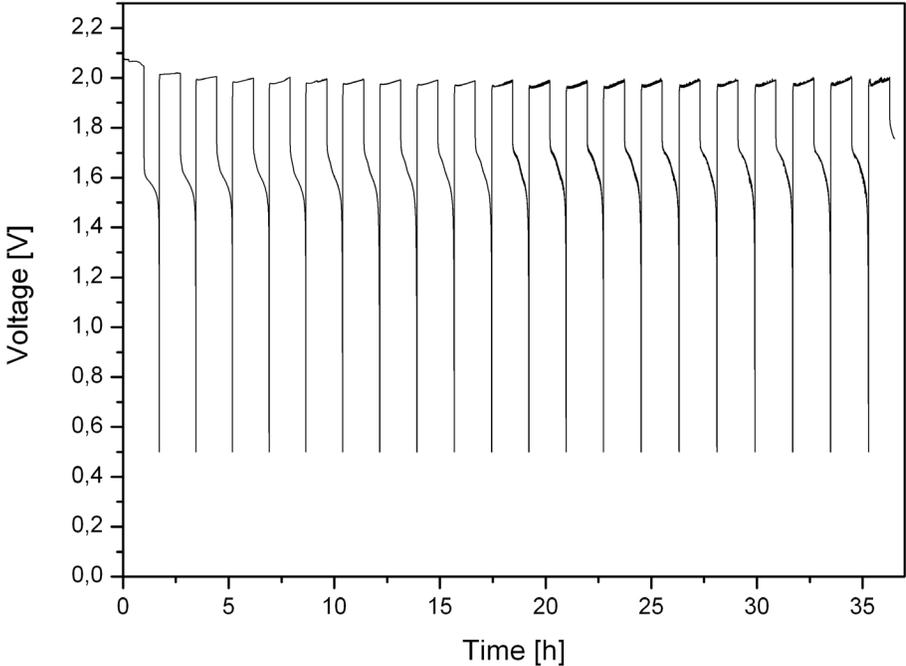


Figure 7. Zn/Br-RFB; Voltage

As shown in fig. 8 energy efficiencies show a clear dependence on temperature. The energy efficiency at a temperature of 20 °C is nearly twice as high as at 5 °C. With an increase in cycle number energy efficiency slowly increases.

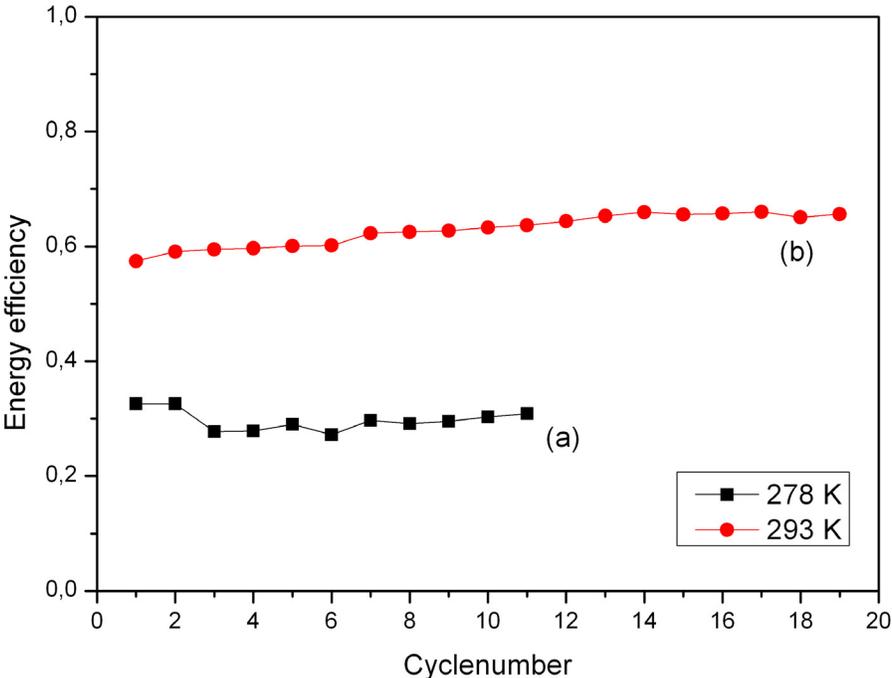


Figure 8. Zn/Br-RFB; Energy efficiency at 5 °C (a) and 20 °C (b)

An increase in voltage efficiency with an increase in cycle number is also visible in fig. 7. During charging, with increasing formation of bromine a brown coloration of the transparent electrolyte is visible, suggesting a relatively strong crossover of bromine. After a first charge step the cell was opened to identify the distribution of zinc deposition on the anode. Zinc deposition is v-shaped over the electrolyte inlets, suggesting an inadequate distribution of zinc so that power and capacity could not reach their ideal values in this cell.

### Comparison of systems

For a significant comparison not only power and energy efficiency are necessary. This test cell was built as a vanadium redox-flow system, which would be expected to have higher power and energy efficiency.

**TABLE I. Single cell**

<b>Redox flow system</b>	<b>P<sub>charge</sub> [mW/cm<sup>2</sup>]</b>	<b>P<sub>discharge</sub> [mW/cm<sup>2</sup>]</b>	<b>CE</b>	<b>VE</b>	<b>EE</b>
V-V 278 K	25	22	0.95	0.61	0.77
V-V 293 K	25	25	0.98	0.88	0.87
V-V 313 K	26	25	0.86	0.78	0.79
Fe-Cr 278 K	23	13	0.94	0.53	0.49
Fe-Cr 293 K	25	13	0.92	0.51	0.51
Fe-Cr 313 K	23	18	0.90	0.68	0.69
Zn-Br 278 K	39	31	0.78	0.61	0.63
Zn-Br 293 K	48	20	0.73	0.31	0.30

**TABLE II. Two cells**

<b>Redox flow system</b>	<b>P<sub>charge</sub> [mW/cm<sup>2</sup>]</b>	<b>P<sub>discharge</sub> [mW/cm<sup>2</sup>]</b>	<b>CE</b>	<b>VE</b>	<b>EE</b>
V-V 278 K	54	40	0.90	0.83	0.77
V-V 293 K	53	46	0.64	0.74	0.78
V-V 313 K	54	44	0.84	0.87	0.70
Fe-Cr 278 K	44	22	0.94	0.45	0.43
Fe-Cr 313 K	39	30	0.89	0.71	0.64

## CONCLUSIONS

Redox flow energy storage provides a simple possibility for stationary energy storage with high energy efficiency. In terms of energy efficiency, a simple electrolyte, full scalability and crossover resistance, the VRFB is superior to the other two systems. Further research has significant potential to increase power density and energy density. The Zn/Br-RFB has higher energy and power density but is not fully scaleable and is associated with certain problems due to toxic and aggressive bromine. The Fe/Cr-RFB uses simple electrolytes but has the disadvantage of ion crossover so that only low capacity retention is expected.

## REFERENCES

1. W. Kangro, H. Pieper, "Zur Frage der Speicherung von elektrischer Energie in Flüssigkeiten", *Electrochimica Acta*, **7**, 435, (1962)
2. B. Sun, M. Skyllas-Kazacos, "Chemical modification of graphite electrode materials for vanadium redox flow battery application – II Acid Treatment", *Electrochimica Acta* **37**, No 13, 2459, (1992)
3. B. Sun, M. Skyllas-Kazacos, "Modification of graphite electrode materials for vanadium redox flow battery application – I Thermal Treatment", *Electrochimica Acta*, **37**, No 7, 1253, (1992)
4. M. Skyllas-Kazacos, R. Rychcik, R. Robins, A. Fane, M. Green, "New All-Vanadium Redox Flow Cell", *J. Electrochem. Soc.*, **133**, 1057, (1986)
5. L.H. Thaller, "Electrically rechargeable redox flow cells", *Proc. 9th Intersoc. Energy Conv. Eng. Conf.*, San Francisco, CA, 26-30 August, 1974; NASA TM X-71540, p. 924, (1974)
6. Maria Skyllas-Kazacos, "Novel vanadium chloride/polyhalide redox flow battery", *Journal of Power Sources*, **124**, 299, (2003)
7. A. Leo, G. Albert, M. Bilhorn, C. Chi, W. VanSchalkwijk, „Development of zinc-bromine batteries for stationary energy storage applications”, *Proc. Intersoc. Energy Convers. Eng. Conf.* 21St 2 (1986) 992, (1986)
8. Peng Qian, Huamin Zhang, Jian Chen, Yuehua Wen, Qingtao Luo, Zonghao Liu, Dongjiang You, Baolian Yi, "A novel electrode-bipolar plate assembly for vanadium redox flow battery applications", *Journal of Power Sources* **175**, 613-620, (2008)
9. Jingyu Xi, Zenghua Wu, Xiangguo Teng et. Al., "Self-assembled polyelectrolyte multilayer modified Nafion membrane with suppressed vanadium ion crossover for vanadium redox flow batteries", *J. Mater. Chem.* **18**, 1232 – 1238, (2008)