The redox flow cell 2.0
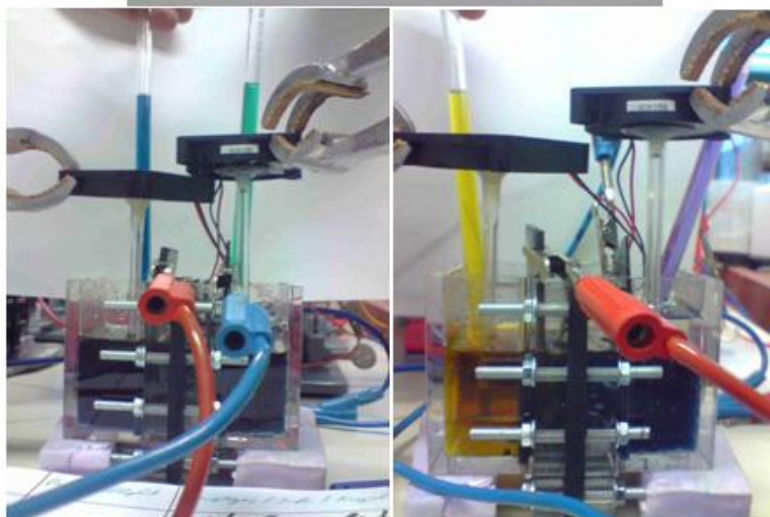

A research project by

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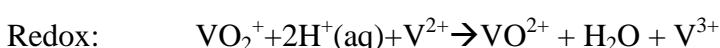
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1. Abstract

The redox flow cell is an energy-storage-system without self-discharge and memory effect. Therefore it is perfect for storing energy for a long time. The storage medium consists of a liquid electrolyte. The long lifetime (over 40 years) of redox flow cells is due mainly to the fact that the electrode is not changed in structure during the charging and discharging process. Another advantage is the size independence of the system, which allows storing a lot of energy in large tanks at a low cost. In our research project we developed a new design for a redox flow cell based on a vanadium/vanadium-battery. We solved several problems, at low cost e.g. the problems of leakage and oxidation protection. In addition we boosted the power of our cell by using a special design for our electrode.
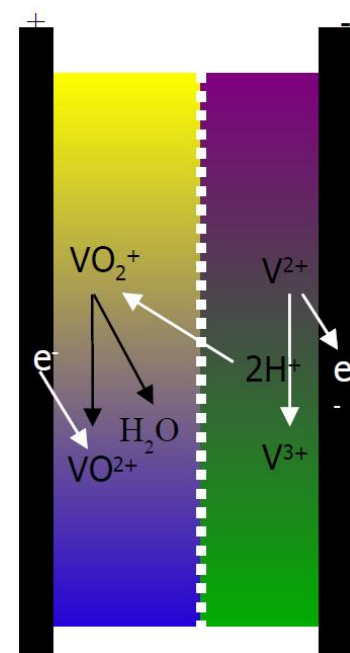
2. State of the art

The redox flow cell is an energy-storage-system with great potential for the future. Redox flow cells are not self-discharging and have no memory effect. That is why they are predestined to store renewable energies. The energy is stored in liquid electrolytes which allow to "charge" the cell by just replacing the electrolytes. This makes the redox flow cell attractive for use in electric vehicles. However, using redox flow systems with state of the art technology turns out to be difficult, because of the low energy-density of today's vanadium based redox flow systems (20Wh/kg and 25Wh/L2). Redox flow batteries have an extremely long lifetime because the electrodes are not changed structurally during the charging/discharging process. Electricity can be stored in big tanks at a low cost. With redox flow cells the power and energy supply can be scaled independently from each other.

3. Functionality of a redox flow cell

The redox flow cell is a galvanic cell that uses ions dissolved, usually in an acidic solvent (e.g. sulfuric acid), as electrolytes. So the energy is stored in fluids. The redox flow system consists of a reaction unit (which is the cell itself), tanks containing the fluids, and pumps as well as tubes in order to connect the cell with the tanks. The cell is separated by an ion exchange membrane permeable for H3O+ Ions but not for metal-ions. The tank size can be adapted to the energy which has to be stored. When the system is fully charged, one tank contains V2+ ions (Vanadium(II)) whereas the other tank contains VO2+ ions (Vanadium(V)) Both are dissolved in battery acid (38wt% sulfuric acid). During discharge the ions react as follows:

Reduction: $VO_2^+ + 2H^+(aq) + e^- \rightarrow VO^{2+} + H_2O$

Oxidation: $V^{2+} \rightarrow V^{3+} + e^-$

Redox: $VO_2^+ + 2H^+(aq) + V^{2+} \rightarrow VO^{2+} + H_2O + V^{3+}$

Since vanadium is used in both half-cells the cell is not affected by cross-over effect.

Ill.3.1: the discharge-reaction in the cell

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Therefore the vanadium/vanadium battery has a very long lifetime. The different oxidation states have different colors. Therefore the state of charge can be roughly identified by the color of the electrolyte. (V(V) is yellow V(IV) is blue V(III) is green and V(II) is gray to violet). The Voltage of the cell can be calculated from the standard potential of the redox couples:

$$V^{2+} \rightarrow V^{3+} + e^- \qquad E_0 = -0.26V$$

$$VO_2^+ + 2H^+(aq) + e^- \rightarrow VO^{2+} + H_2O \quad E_0 = +1.00V$$

Ill.3.2: the four different oxidation states (V(V) to V(II) from left to right
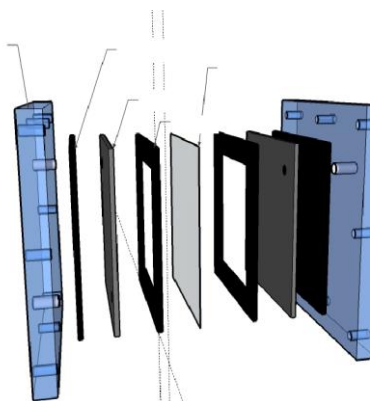
However, the material of the electrode and the concentration of vanadium play a major role for the voltage as well. The maximum voltage of a single cell is limited to 1.7V, since the water in the redox flow cell starts to decompose at this voltage.

4. Safety

The battery acid we used is very corrosive, so we had to use safety goggles and safety gloves. vanadiumpentoxide, which we used to prepare the electrolyte is toxic and ecologically harmful. So we had to work under a hood. We also tested all materials used for our cell of their resistance to acids. In order to limit the effects of leakages we put the whole system in an acid resistant plastic box.

5. The redox flow cell 1.0

5.1 Setup

Ill. 5.1: Setup of our first redox flow cell

The redox flow cell is a sandwich construction, containing two layers of rubber plates and one layer of an acrylic plate per half-cell. Between the half cells there is a membrane separating the half-cells.
The membrane is made of a sulfonated tetraflouoethylene (e.g. Nafion), which is permeable for oxonium-ions (H3O+). The membrane layer is followed by a rubber frame forming the reaction cell between the membrane and the electrodes. The electrodes as well as both following layers have two ports, enabling the electrolyte to flow through the cell. Another layer of rubber plate used as gasket and the acrylic plates complete the cell. This setup is pressed together by threaded rods. The electrolyts are stored in external tanks. They get into the cell via a peristaltic pump. The Voltage supply for charging is provided by thin copper plates between the electrode and the outer rubber plate.

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5.2 Problems

This setup of the redox flow cell is a common setup. However, it causes many problems. Leaks were one of the largest problems. Especially at the links from cell to tube and in the peristaltic pump. Another problem is the oxidation of V2+ in contact with air. This problem is usually solved by using nitrogen as shielding gas, which is expensive in long term use. Another problem is the expensive and ineffective peristaltic pump.
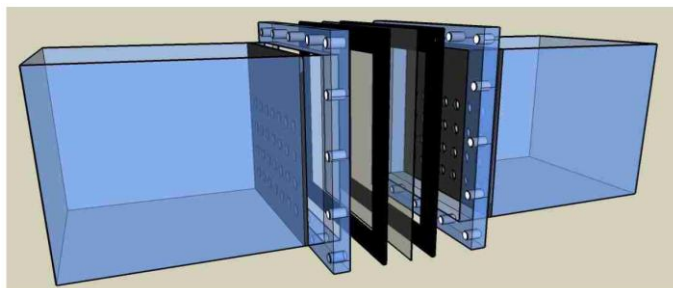

Ill.5.2: Our redox flow cell (left) and the complete setup of the redox flow system

6. The redox flow cell 2.0
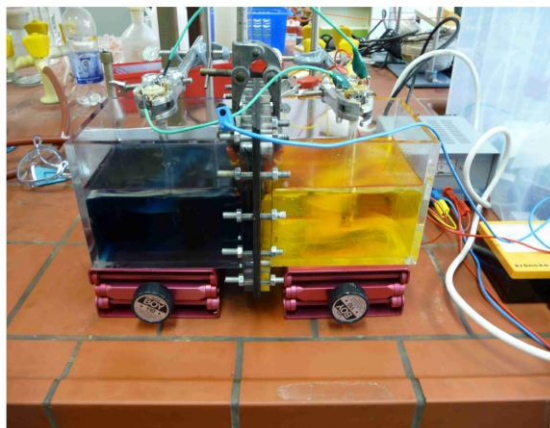
6.1 Setup of the new redox flow cell

In order to solve the problems of our first redox flow cell we decided to design a completely new setup of a cell. This setup should not have the problems of the common cell design, we used before. The most problems concerning leaks were at the ports from tube to cell and in the peristaltic pump which we need to change the ions at the electrodes. Finally we developed a new cell design with integrated tanks (cf. Illustration...). Instead of a pump we use agitators to agitate the electrolyte. Therefore the half-cells had to be open to the top which is another problem because of the oxidation of vanadium(II). But in order to protect the electrolytes from evaporating and the vanadium(II) from oxidizing we used paraffin which can be compared with oil.

Ill.6.1: The setup of the new redox flow cell

The new cell consists of two half-cells with integrated tanks and two rubber gaskets and the membrane hold together by threaded rods. We inserted the electrodes that are perforated in order to let the electrolyte flow through them, from the top near the membrane.

Ill.6.2: the new redox flow cell at work

6.2 Advantages of our new setup

In contrast to our first redox flow cell, the new one does not have leaks. Also due to the new oxidation protection and the abandonment of the peristaltic pump it is cheaper than the old setup. After thoroughly investigating whether paraffin was already being used as oxidation protection for redox flow cells and finding out that our invention was revolutionary, we have filed a patent. Due to our improvement the redox flow cell can be operated at lower cost.
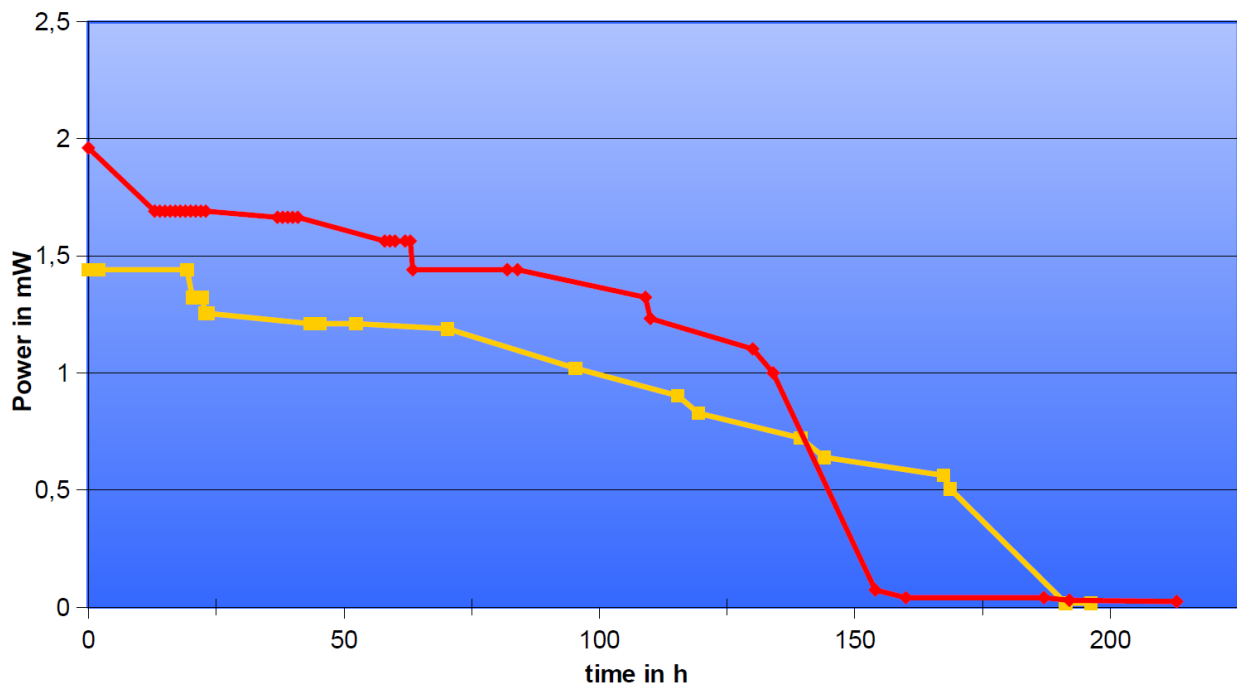
6.3 Experiments to boost the power of our cells

In order to compare different electrode structures we constructed smaller cells, which were 6cm high, 4.5cm wide and 4cm deep at the inner side. The cells were not filled completely, so we calculated with a fill level of 4cm. This gives an active membrane surface of 18cm2. As agitators we used old computer fans with glass tubes. In order to improve the power of our redox flow cell we tried to boost the current that is supplied by the cell. Two factors are limiting the current: the ions at the electrode surface and the maximum current-density of the membrane. The maximum current-density of the Nafion-membrane we used is 80mA/cm². While the maximum current of our little cell is 1.5A, we decided to investigate a way to enlarge the electrodes surface to get a better current and power supply. Searching a graphite material with a large surface that we had at school, we found activated carbon. It has a very large internal surface, and consists of graphite. Of course we had to prove the advantage of activated carbon, so we filled two of our little cells with 100ml of electrolytes and prepared one with 7g activated carbon and the other with a normal electrode. Then we charged the cell with 1.7V. Using two ampere-meters we measured the current of every cell. The cell prepared with activated carbon was charging with 160mA whereas the other cell was charging with 10mA. In order to find out what effect different amounts of activated carbon at the electrode have we tested the other cells with several amounts of activated carbon. As you can see in the diagram below, the current increases linearly with the amount of activated carbon. Now we wanted to test the discharge performance of the new electrode. After putting the activated carbon in a fully charged cell the vanadium(V) was instantly reduced to vanadium(IV). But what was oxidized? After some investigation we found out, that activated carbon contains traces of metals like zinc, which is able to reduce the vanadium-ions. So we had to think about another way to enlarge the surface of our electrodes. We get the idea of using small pieces of the graphite plates which forms our normal electrode. We put the graphite between the electrode plate, so that it is connected to our electrode.

We charged now one cell with the modified electrodes and the other with the normal electrodes. The next morning we found the modified cell fully charged whereas the other cell was not ready yet. In order to investigate the power of the modified cell compared to the normal cell we start a measurement. We discharged two cells (one unmodified and one with graphite particles) via a resistor of 1kΩ.

6.4 Analysis

The power of our cells with different electrodes

As you can see from the graph above our experiments were running for about 200 hours. The power of the modified cell at the beginning of the measurement was 1.96mW this is an increase of around 36% compared with the normal cell starting with 1.44mW. The power of the modified cell is better than the power of the normal cell during the first 137 hours. Then the modified cell is discharged and the power declines. The normal cell is discharged 34 hours later.

All in all the experiments result shows that due to the modified electrode the power increases of around 25%.

6.5 Specifications of our redox flow cell

Finally we identified important specifications of our redox flow cells. We calculated the energy density from our discharge-experiments. The area under the graph of the p-t-diagram is the energy divided by the volume of our electrolyte it gives the energy-density. The energy-density depends on the concentration of the vanadium ions in the cell. We found out an energy-density of 9.3Wh/mol vanadium. Our cells have an efficiency of around 66%. The maximal power output was 100mW by discharging the cell over a 22Ω resistor.

7. Safety for mobile use

Ill.7.1: zeolite reacts with the acid creating a plug

The redox flow system is only used in stationary applications today. If the energy-density increases, it is able to use this system in mobile applications such as electric vehicles. But there is another problem using the redox flow system in electric vehicles; safety! The sulfuric acid and the vanadium may not get into environment even in case of an accident. In order to prevent the release of the electrolyte we searched a material absorbing the liquid. First we experiment with superabsorbent polymer. But the concentration of ions in the electrolyte was too high, so it was not absorbed. Investigating other materials we found out, that zeolite may be able to react with the electrolyte. Zeolite consists of AlO4 and SiO4-tetrahedras. An alkaline or an alkaline earth cation is connected to the AlO4. This cation is replaced by the H+ ion from the acid. The resulting salts can block the leaks and prevent the tank of leaking. In our experiments with a hopper this plug stayed close for around five hours.

8. Conclusion

In this Project we developed a new setup of a redox flow system. We improved the safety of the redox flow system and we succeeded in creating a low cost redox flow cell. But we can increase the power of our redox flow cell by using graphite felts instead or additionally to the graphite debris. The new setup gives us the possibility to use more viscous electrolytes enabling a better energy density.

9. Acknowledgments

10. Literature and links

[1] http://www.cellstrom.com/Technology.7.0.html?&L=1

[2] http://en.wikipedia.org/wiki/Vanadium_Redox_Flow_Battery