Karlsruhe Institute of Technology

Institute for Applied Materials

Diagnostics in All-Vanadium Redox-Flow Batteries

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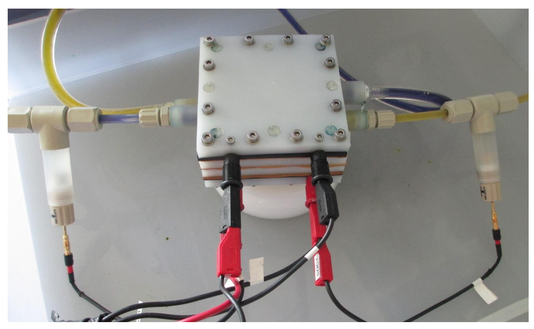
Introduction

Motivation:

- Redox-flow batteries (RFB) are a potential energy storage technology for electronic grid integration of renewables
- In RFB energy and power can be scaled independently
- All-Vanadium redox-flow batteries (VRB) offer the additional advantage that cross-over is not a problem and the energy is completely stored in the liquid electrolyte
- Currently used carbon based electrodes still show high overpotentials
- E/i-curves can give valuable information to distinguish the source of losses

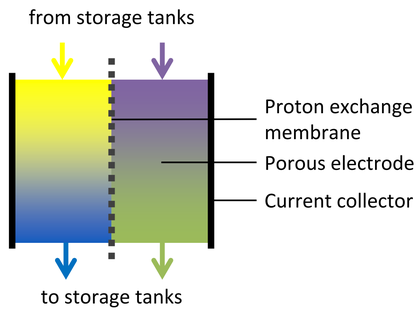
Different Oxidation states of Vanadium



Single Test Cell

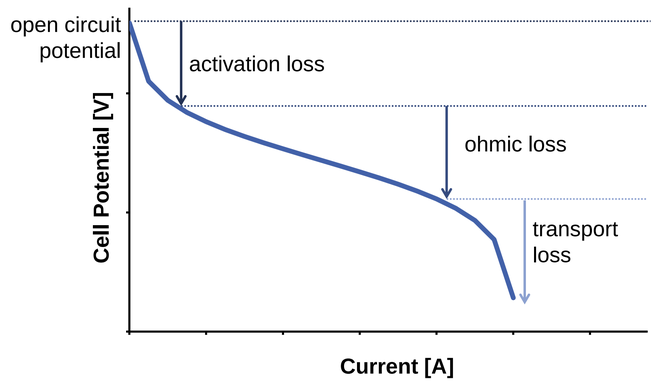
Cell Scheme

The VRB consists of two storage tanks for the electrolyte and the electrochemical cell. The latter consists of two carbon based porous electrodes, which are separated with a proton exchange membrane (Nafion 117). They are encased in graphite current collectors. Those can be used either with or without a flow field for the even distribution of the electrolyte.



Electrolyte: 0.5M $VOSO_4$ in 3M H_2SO_4
Flow rate: 100 mL/min
Membrane: Nafion 117
Electrode: Freudenberg [carbon nonwoven]
Single Cell: 25 cm² [flow through]

$$VO_2^+ + 2H^+ + e^- \underset{charge}{\overset{discharge}{\rightleftharpoons}} VO^{2+} + H_2O \qquad V^{2+} \underset{charge}{\overset{discharge}{\rightleftharpoons}} V^{3+} + e^-$$



E/i-Curves

- With E/i-curves it is possible to determine the major losses of an electrochemical cell.
- Activation loss arises from reaction mechanism itself.
- Ohmic losses come from charge transfer through the electrode and the membrane.
- Transport loss arises from diffusion limitations

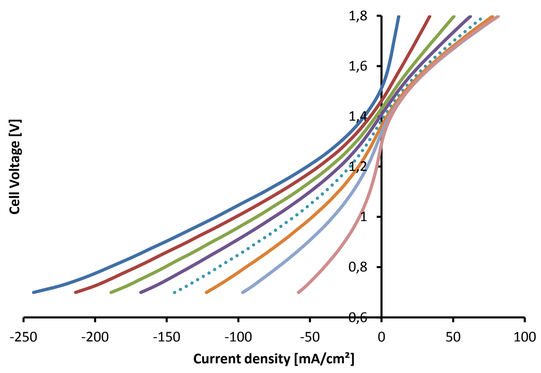
Experimental

Influence of State of Charge (SOC)

The open circuit potential of the VRB depends highly on the SOC (i.e. Nernst equation).

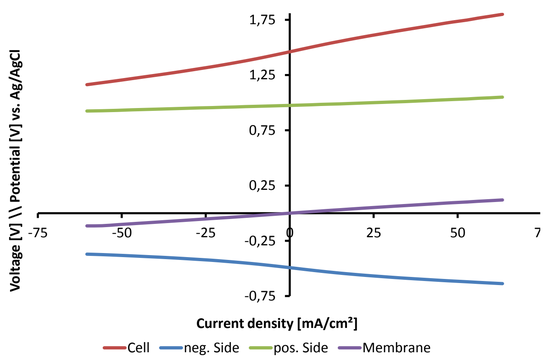
- ➢ This leads not only to a shift of the polarization curve to lower potentials but also increases the transport losses due to starvation.
- ➢ At 50% SOC (dotted curve) the charge and discharge curve are similar as expected.
- ➢ At lower SOC the charging process does not become as efficient as the discharge process at the corresponding higher SOC.

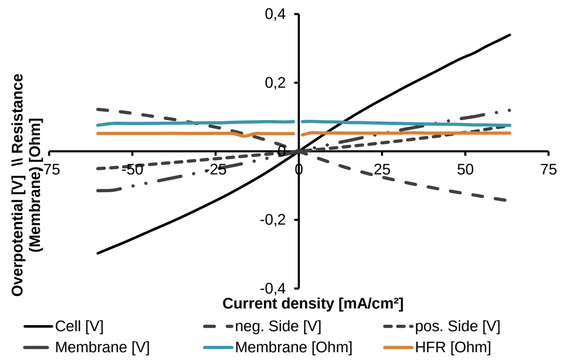
$$E = 1{,}26\ V + \frac{RT}{F}\ ln\left(\frac{c[VO_2^+]\,c[V^{2+}]}{c[VO^{2+}]\,c[V^{3+}]} \cdot \left(\frac{c^+[H^+]}{1}\right)^2 \cdot \frac{c^+[H^+]}{c^-[H^+]}\right)$$



Determination of the Ohmic Losses

One approach is the High Frequency Resistance (HFR) at 10 kHz. Another one is to use reference electrodes on both sides of the membrane. By subtracting both half-cell overpotentials from the cell overpotential, the ohmic and diffusion losses remain.
The results are in good agreement. Differences arise from uncertainties of both approaches (e.g. inhomogeneous potential distribution over the electrode, further potential losses over the membrane (diffusional, Donnan).

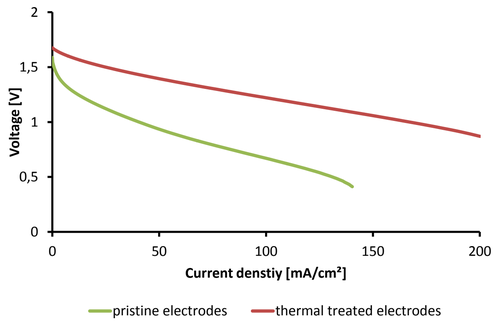


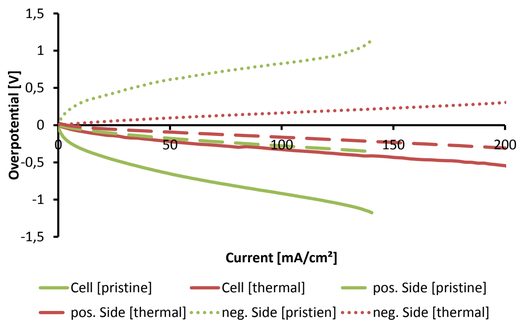


Thermal Treatment

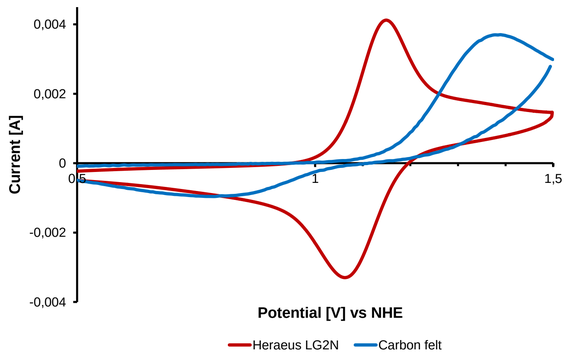
Oxidation of the carbon felt leads to an increase of the wettability towards the electrolyte and a performance gain.

- ➢ Reference electrodes show that both half-cells contribute to this effect
- ➢ Negative half-cell shows the higher improvement





Electrochemical Activity



Cyclic Voltammetry in a three electrode setup was used to evaluate the activity of different carbon based materials. Used Electrolyte was 0.1M $VOSO_4$ in 3 M H_2SO_4

- ➢ Carbon felt (used electrode material) has to be improved
- ➢ LG2N from Heraeus shows very good electrochemical characteristics and is a promising candidate for a composite electrode material

Conclusions

Summary

- Proposed setup with reference electrodes enables another approach to distinguish different potential losses
- Performance of the cell depends strongly on the SOC
- Different loss mechanisms are a function of the SOC
- Thermal treatment improves mainly the negative half-cell reaction
- Electrochemical characteristics can be improved by other carbon materials
  - ➢ Composite electrode

Future Plans

- Evaluate different carbon felts and effects of chemical or thermal oxidation (wettability, catalytic improvements) (XPS, BET, NEXAFS)
- Evaluate further materials (Carbon Black, Graphite, CNT) for composite electrodes
- Design composite electrodes
  - Enhance surface area, better electrochemical behavior
- Investigate the composite electrodes 3D structure (Hg-Porosimetry, SEM, FIB-SEM)

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