Modification of Graphitization Degree of Carbon Based Electrodes in Vanadium Redox Flow Batteries

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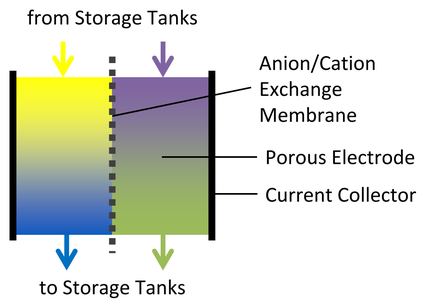
Motivation

- Redox-flow batteries (RFB) are a potential energy storage technology for electric grid integration of renewables.
- In RFB capacity (electrolyte volume) and power (stack size) can be scaled independently.
- Vanadium redox flow batteries (VRFB) offer the additional advantage that cross-contamination of the electrolyte active species by diffusion through the membrane is not a problem.

- In this work we investigated the electrode material with the focus on the surface structure of pristine (P) and thermally oxidized (T) PAN-based fibers. For this purpose, XPS and NEXAFS were used.
- The PAN-based felts were graphitized at 1500 and 2000 °C under argon atmosphere. Thermal treatment was carried out under air at 500 °C for 10 hours to improve the reversibility for the $V^{4+/5+}$ reaction.

How does a VRFB work

The VRFB consists of two storage tanks for the electrolyte and the electrochemical cell. The latter contains two carbon based porous electrodes, which are separated by an anion or cation exchange membrane. They are encased in graphite current collectors.

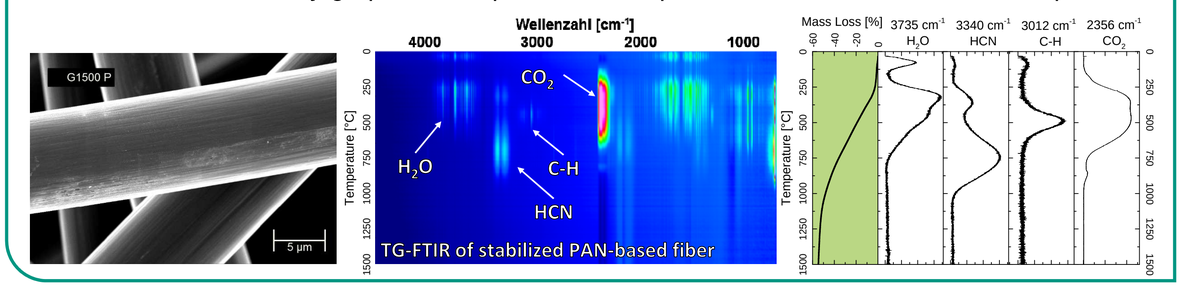


$$VO_2^+ + 2H^+ + e^- \underset{charge}{\overset{discharge}{\rightleftharpoons}} VO^{2+} + H_2O \qquad V^{2+} \underset{charge}{\overset{discharge}{\rightleftharpoons}} V^{3+} + e^-$$

E^0 = 1.0 V vs. RHE E^0 = -0.26 V vs. RHE

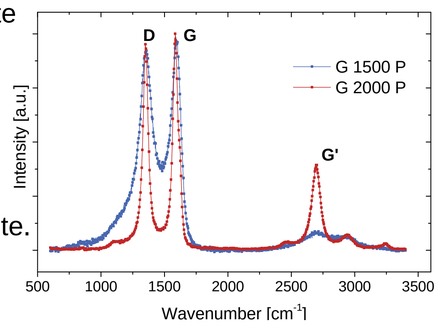
Analysis of Electrode Preparation

- The fiber surface appears homogeneous in the SEM.
- TG-FTIR measurement shows evolution of H_2O, CO_2 HCN and some aliphatic species.
- Mass loss is around 55% for G1500 and 56% for G2000.
- Above 1500 °C only graphitization process takes places and reaction of PAN is completed.



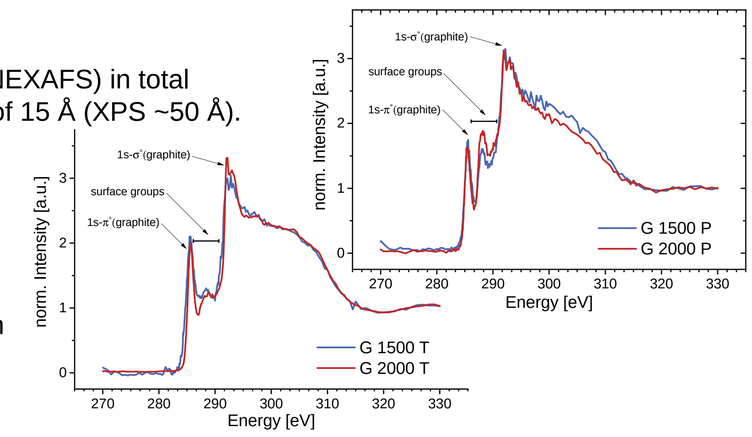
Raman-Spectroscopy

- D- and G-band from graphite are clearly visible.
- G1500 shows very broad features and the G'-band is indistinct
  - This is assigned to the c-stacking order of graphite.
- G2000 spectrum has much more distinct features; especially the G'-band.



NEXAFS

- Near Edge X-Ray Absorption Fine Structure (NEXAFS) in total electron yield setup has an information depth of 15 Å (XPS ~50 Å).
- sp^2-carbon content of the pristine samples (upper right figure) is very low.
- This is due to a amorphous/aliphatic carbon layer on the surface which is removed by the heat treatment (lower left figure).
- Remarkable is the close resemblance between the fiber surfaces in terms of sp^2-carbon content.

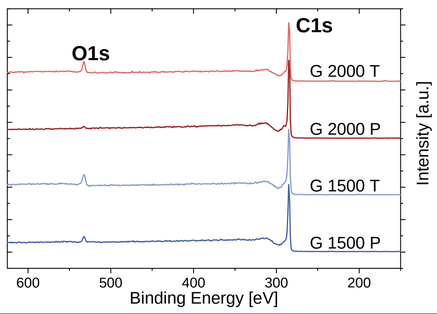


X-Ray Photoelectron Spectroscopy

- Besides carbon XPS measurements also show the presence of oxygen and traces of nitrogen. G2000 contains a lower fraction of heteroatoms.
- A difference in graphitization degree is also clearly seen between G1500 and G2000.
- Thermal oxidation leads to a higher oxygen content and the graphite fraction is reduced.
  - Both samples take up an additional 3 at% of oxygen.

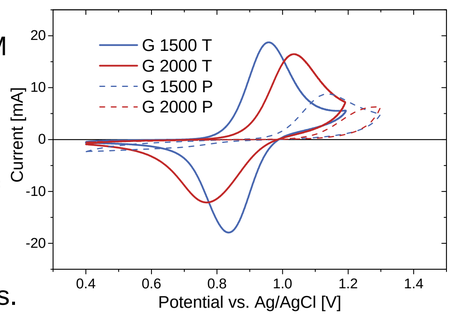
Atomic Fractions from C1s peak

Sample	C graphitic	C-H, C-C	C-O	C=O
G1500 P	67.0	17.6	2.8	2.0
G1500 T	61.5	17.0	3.9	3.9
G2000 P	83.0	6.8	0.5	0.8
G2000 T	74.0	11.5	1.9	2.1



Cyclic Voltammetry

- Cyclic voltammetry was performed with 5 mV/s in 0.1 M $VOSO_4$ and 2 M H_2SO_4 in a three electrode setup.
- Both pristine samples do not show a reduction peak of V^{5+} in the potential window. It appears around -0.2 V vs. Ag/AgCl.
- Thermal treatment dramatically increases the reversibility and activity of the $V^{4+/5+}$ redox reaction as shown in many other publications.
- G1500 pristine sample performs with a higher reversibility compared to G2000 T although they have the same amount of oxygen surface groups.



Conclusions

- Graphitization degree of G2000 sample is much higher as for the G1500 (Raman and XPS). However, NEXAFS measurement show that, the surface of G1500 and G2000 are very similar in terms of sp2-carbon for the pristine and treated sample.
  - This is neither shown by Raman nor XPS as they are not surface sensitive enough.
- NEXAFS reveals a very thin amorphous carbon layer on the pristine fibers. The origin could be residuals from graphitization process. The surface cleaning from the amorphous residuals by thermal treatment increases the activity of both materials.
- However although both thermal treated sample G1500 T and G2000 T have a similar sp^2-carbon content at the surface they show a different electrochemical behavior.
  - This difference in the activity correlates with the amount of oxygen functional groups, as revealed by NEXAFS and XPS.

Acknowledgment

The financial support of the BMBF within the project "Flow 3D" (03EK3011D) is gratefully acknowledged.
Freudenberg New Technology is acknowledged for providing stabilized PAN-based felt.

SPONSORED BY THE
Federal Ministry of Education and Research
Freudenberg