Influence of the carbonization degree of carbon nonwoven electrodes in vanadium redox flow batteries

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Introduction:

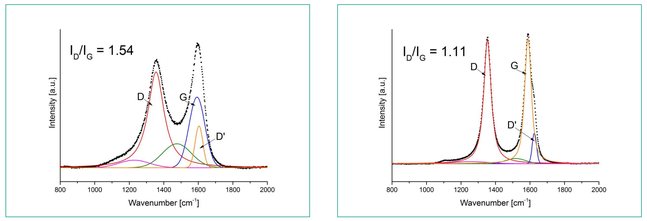
Various carbon based electrodes for vanadium redox flow batteries are widely used and treated with different methods to functionalize the surface for higher energy efficiencies. Besides surface groups containing oxygen or nitrogen the fibers of the electrodes are decorated with carbon nanotubes to achieve higher reversibility of the redox-reaction or increase the surface area.
This work is part of a BMBF project (“Flow 3D”) with the aim to optimize the 3D-structure of carbon based electrodes.

Objective:

In this work we varied the carbonization temperature and conditions to keep the macroscopic structure of the electrode nonwoven and vary the carbonization degree. As it is known from literature, functional groups at the surface are required to increase the wettability and improve the redox behavior. Here, this was done by thermal oxidation under ambient air and pressure. The electrodes were investigated by Raman, SEM, XPS and cyclic voltammetry.
As template material a nonwoven made out of PAN fibers was used and carbonized at 1500 and 2000°C under argon for 1 hour.

Raman Spectroscopy

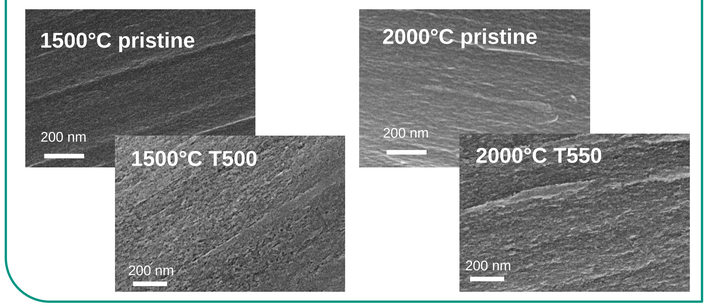
Raman spectra show clearly D and G bands for all materials. For the fit of the 1500°C sample data, additional contributions are required due to a high amorphous carbon fraction. This is not taken into account by the I_D/I_G ratio as this gives only a grade of defects in graphitic structures (i.e. graphite crystal size).
As expected a higher temperature leads to a higher fraction of graphitic carbon.



Raman spectra and fits of the 1500 °C and 2000 °C pristine sample. Besides the D, G and D’ band two additional bands were needed to take the amorphous features into account.

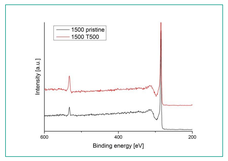
Thermal Oxidation

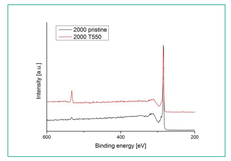
The oxidation treatments of the different samples were varied from 400 to 600 °C under ambient atmosphere for 10 hours each time.
The SEM pictures of the freshly carbonized samples show an almost smooth surface of the fibers. After the oxidation treatment a roughening is observed. Its extent mainly depends on oxidation temperature but also on the degree of carbonization.



Surface Analysis - XPS

To determine the surface composition the carbon nonwovens,were investigated by XPS.
The freshly carbonized sample at 2000°C contains less oxygen than the 1500°C sample and a higher sp^2-content.
After the oxidation treatment both series show a slight decrease in sp^2 hybridized carbon. The oxygen content increases steadily with oxidation temperature except for the 600°C sample of the 2000°C series.

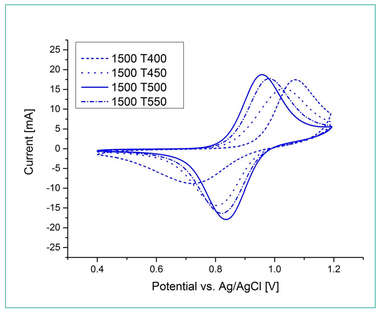




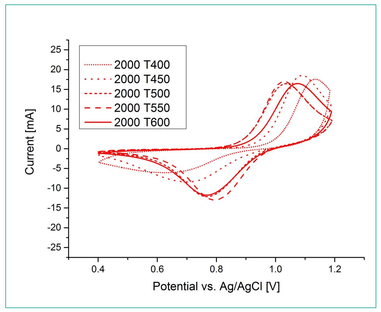
	sp^2- Content [%]	O-Content [%]
1500 pristine	91,2	4,2
1500 T400	88,6	5,0
1500 T450	90,0	6,2
1500 T500	**88,7**	**8,0**
1500 T550	87,2	10,1
2000 pristine	94,0	1,3
2000 T400	91,7	4,2
2000 T450	91,8	4,5
2000 T500	91,6	4,0
2000 T550	**87,0**	**7,5**
2000 T600	90,1	5,7

Cyclic Voltammetry

The samples were electrochemically characterized for the Vanadium 4+/5+ redox reaction via a three electrode setup.
The redox behavior improves with increasing oxidation temperature up to 500 °C (1500 °C series) and 550 °C (2000 °C series) and then starts to decrease again.
The 1500°C sample shows complete reversibility at 500 °C (peak separation is 60 mV) while the 2000°C series does not reach such a reversible behavior at any temperature. Further the onset of the oxidation peak is shifted to higher potentials.
Comparing this behavior to the XPS data a correlation can be observed in the oxygen content up to a certain amount (8 %). As the same oxygen content in 1500°C and 2000°C does not lead to the same cyclovoltammogramm other influences play also an important role.



Cyclovoltammogramms of the 1500°C series oxidized at different temperatures. Measurement was performed in 0.1 M $VOSO_4$ and 2 M H_2SO_4 at a scan rate of 5 mV/s.



Cyclovoltammogramms of the 2000°C series oxidized at different temperatures. Measurement was performed in 0.1 M $VOSO_4$ and 2 M H_2SO_4 at a scan rate of 5 mV/s.

Summary

Two different carbonization degrees of a carbon nonwoven were synthesized and characterized. To enhance the electrochemical behavior for the Vanadium 4+/5+ redox reaction the felts were heat treated at different temperature to increase the oxygen amount on the surface.
A clear correlation between oxygen amount in the surface layer and the reversibility of the redox reactions was observed. It was also observed that the same amount of oxygen at different carbonization degrees does not lead to the same electrochemical behavior.

Acknowledgment

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