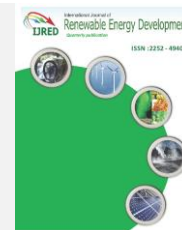




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Improvement of the Performance of Graphite Felt Electrodes for Vanadium-Redox-Flow-Batteries by Plasma Treatment

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ABSTRACT: In the frame of the present contribution oxidizing plasma pretreatment is used for the improvement of the electrocatalytic activity of graphite felt electrodes for Vanadium-Redox-Flow-Batteries (VRB). The influence of the working gas media on the catalytic activity and the surface morphology is demonstrated. The electrocatalytical properties of the graphite felt electrodes were examined by cyclic voltammetry and electrochemical impedance spectroscopy. The obtained results show that a significant improvement of the redox reaction kinetics can be achieved for all plasma modified samples using different working gasses (Ar, N₂ and compressed air) in an oxidizing environment. Nitrogen plasma treatment leads to the highest catalytical activities at the same operational conditions. Through a variation of the nitrogen plasma treatment duration a maximum performance at about 14 min cm⁻² was observed, which is also represented by a minimum of 90 Ω in the charge transfer resistance obtained by EIS measurements. The morphology changes of the graphitized surface were followed using SEM.

Keywords: air plasma, carbon felt electrode, graphite surface modification, vanadium-redox-flow battery

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1. Introduction

All-Vanadium-Redox-flow batteries (VRB) received recently significant attention, due to their long life, high reliability, flexible design and fast response times. The VRB is suitable for a wide range of energy storage applications such as enhanced power quality, UPSs, peak shaving, increased security of supply and integration with renewable energy sources (Skylas-Kazacos 2009; Dunn & Kamath *et al.* 2011; Skylas-Kazacos *et al.* 2011). The power output is determined by the converting unit (cell stacks) and energy capacity is defined by the size of the electrolyte tanks, giving the VRB a high degree of design flexibility. In general VRB is based on reversible redox reactions of vanadium (V) species with different oxidation states, dissolved in acidic media (cathode: V⁵⁺/V⁴⁺; anode: V²⁺/V³⁺). The vanadium containing electrolytes are fed from external storage tanks using pumping equipment into a

converting unit, where the redox reactions take place. As electrodes graphite based felt materials with high surface area and chemical stability are used. However carbon based electrodes are hydrophobic and show poor kinetics reversibility for the vanadium redox reactions. Several physical, chemical and electrochemical surface modification methods are used in order to increase the activity of the graphite surface toward the vanadium redox reactions (Sun & Skylas-Kazacos 1991; Sun & Skylas-Kazacos 1992a, b; Wang & Wang 2007). Sun & Skylas-Kazacos 1992a, b propose that the vanadium redox reactions take place preferentially on active sides on the graphite surface, containing hydroxyl and carbonyl functional groups. The authors report that optimized chemical and thermal oxidative treatment can significantly improve the performance of the VRBs. According to the authors treating the graphite felt at 400°C for 30h reduces significantly the cell resistance and improves the-

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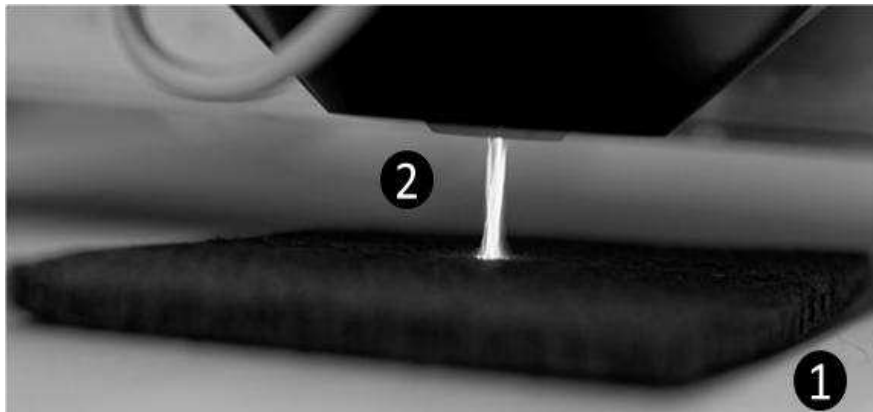


Fig. 1 Example of the plasma treatment set up: 1–graphite felt with 5mm thickness; 2–plasma discharge at 15 kV and 25 L/min compressed air as working gas

-efficiency of the VRB. Similar improvements provide graphite felt electrodes treated for several hours in hot mixture of concentrated sulphuric and nitric acids. Recently it was shown, that nitrogen doped mesoporous carbon has enhanced electrocatalytic activity towards the vanadium redox reaction and improved wetting properties (Shao *et al.* 2010).

Surface modification of carbon based materials via different plasma treatments has become widely used on laboratory and industrial scale (Bismarck *et al.* 1999; Rousseau *et al.* 2003; Kimura, Yamamuro *et al.* 2007). According to the literature using oxygen plasma treatment hydroxyl or keto-enol functional groups can be introduced on the surface of pyrolytic graphite [Nakahara & Sanada 1993; Nakahara & Sanada 1994; Cvelbar, *et al.* 2006]. Thereby the reported microscopy studies on plasma treated carbon based samples reveal changes in the topographies propagating with increasing treatment durations (Brown, *et al.* 1998; Paredes *et al.* 2000; Elersic *et al.* 2011).

In the present contribution dielectric barrier plasma discharge was used to modify the surface of graphite felt electrode, common in VRB, in order to improve the vanadium redox reaction kinetics. The influence of different working gases (N_2 , Ar, compressed Air) on the performance and the properties of the electrodes were investigated via conventional electrochemical techniques and SEM-EDX. The plasma treatment was performed in atmospheric environment at different operational conditions such as treatment duration.

2. Experimental Methods

The surface of graphitized carbon felts (1cm² sized, thickness: 5 mm, SGL Carbon, Sigratherm GFD5) was treated with a dielectric hindered plasma (n.transfer GmbH). Therefore, different working gases (N_2 , compressed air and Argon) were used varying the treatment duration from 3 to 30 minutes. The flow rate of the working gasses was kept constant at 25 L/min.

The input voltage and frequency of plasma discharge were also maintained constant and equal to 15 kV and 1.3 kHz, respectively. All the measurements were performed in air environment. Brief example of the plasma treatment set up is shown in Fig. 1. The cyclic voltammetry (CV) and the electrochemical impedance spectroscopy (EIS, 300 kHz-50 mHz, amplitude = 10 mV, DC level 0.8V) measurements were performed in a 0.1 M H_2SO_4 + 0.01 M $VOSO_4$ aqueous solution using a ModuLab potentiostat/galvanostat (ModuLab, Solatron analytical). All measurements were carried out at 20°C using a conventional three electrode arrangement with an Ag/AgCl reference- and a platinum-counter-electrode. The carbon felts were attached to a platinum wire and used as working electrode. Before each experiment, the electrolyte was deoxygenized by leading N_2 -gas through the solution for 15 minutes. The surface morphologies of the graphite felt were studied using scanning electron microscopy (SEM, NEON 40). Additionally, computer tomography (CT) measurements were performed employing a micro-CT (Skyscan, resolution: <0.7 μm /px to 25 μm /px), which enables a three dimensional analysis of the felt structure.

3. Result and Discussion

In Fig. 2 is shown the electrochemical behavior of a pristine sample in a 0.1 M H_2SO_4 + 0.01 M $VOSO_4$ aqueous solution. It can be seen from the cyclic voltammogram that the vanadium reaction takes place at very high overpotentials and has poor reversibility. A very large overall impedance in the range of several k Ω s for the V^{4+}/V^{5+} redox reaction can be observed from the performed EIS measurements at 0.8V (see inset). As expected the pristine graphite felt electrode shows poor electrocatalytic activity toward the vanadium redox reactions.

Plasma treatment, using different working gases, was performed in order to modify the surface of the graphite felt. The electrocatalytic response of samples treated with compressed air, argon and nitrogen at the -

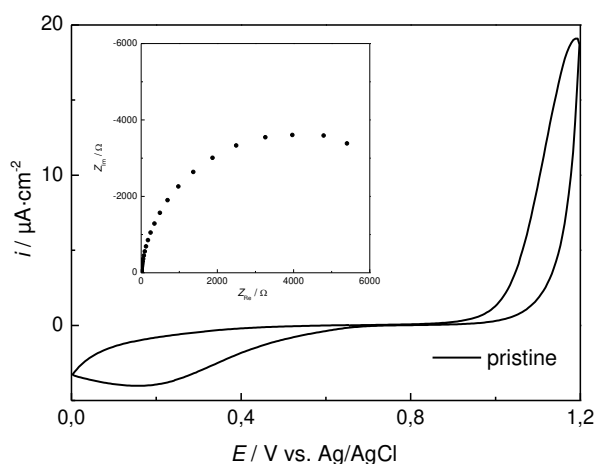


Fig. 2 Cyclic voltammogram ($dE/dt = 5\text{mV}\cdot\text{s}^{-1}$) and EIS (inset) at 0.8V in 0.1 M $\text{H}_2\text{SO}_4 + 0.01\text{ M VOSO}_4$ electrolyte on pristine electrode

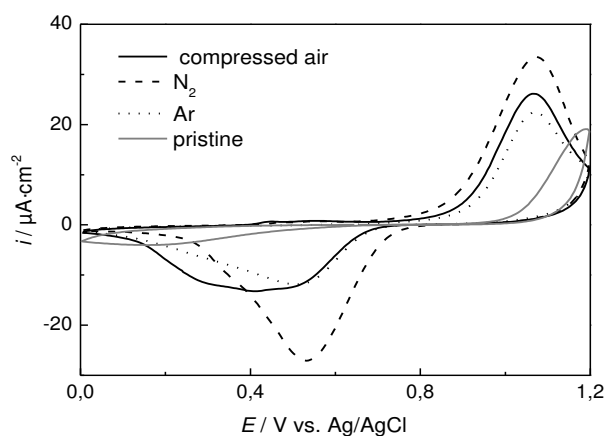


Fig. 3 Cyclic voltammogram ($dE/dt = 5\text{mV}\cdot\text{s}^{-1}$) in 0.1 M $\text{H}_2\text{SO}_4 + 0.01\text{ M VOSO}_4$ electrolyte on differently plasma treated samples in comparison to pristine electrode

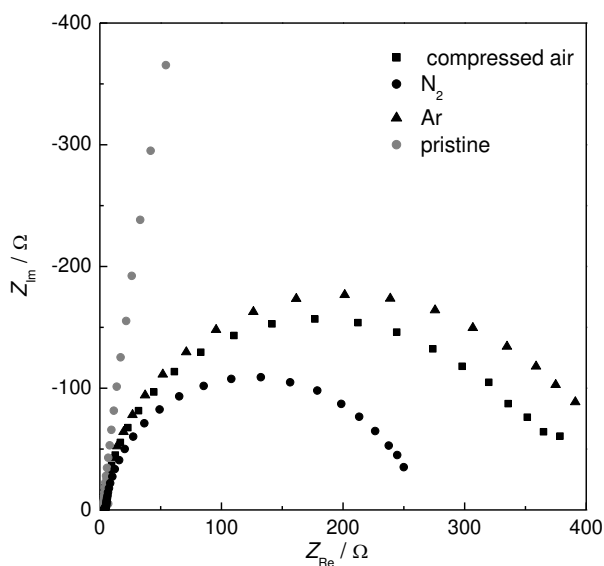


Fig. 4 EIS at 0.8V in 0.1 M $\text{H}_2\text{SO}_4 + 0.01\text{ M VOSO}_4$ electrolyte on differently plasma treated samples in comparison to pristine electrode

-same operational conditions in comparison to an untreated one is shown in Fig. 3. A significant enhancement of the reversibility of the reaction can be observed for all modified samples in contrast to the pristine electrode. In addition the vanadium redox reaction appears at much lower overpotentials for the treated samples, revealing an increased electrocatalytic activity. Dramatic improvement of the reaction kinetics at the modified samples can be also observed from the performed EIS measurements (Fig. 4). Substantial decrease of more than one order of magnitude in the overall impedance for the modified samples was estimated.

The observed enhanced performance for all samples modified with different working gases is most probably due to increased number of active sites induced by the plasma irradiation. However during dielectric barrier discharge in oxygen presence under atmospheric pressure various reactive species such as O_3 , O and their excited states are formed, which can react with the graphitized surface to form various oxygen containing sites.

In addition the air humidity may play an important role due to formation of H , OH , or HO radicals. According to the literature by air plasma exposure an oxidation of graphite surface occurs mainly by inducing alcohol type functionalities (Jones & Sammann 1989). This can explain the improved performance towards redox activity of the compressed air treated sample. The argon treated electrodes show comparable behavior as the air treated ones. Similar species are most probably formed on the graphite surface during argon plasma irradiation, since it is known, that the argon plasma treatment creates a highly active carbon surface which reacts with any oxygen present in the system (Jones & Sammann 1989).

One should also consider that under air conditions nitrogen ions N^+ , N_2^+ , atoms and excited atomic nitrogen oxide species (NO , N_2O , NO_2 , NO_3 , and N_2O_5) are generated, adding to the complexity of the reaction system (Kogelschatz 2003). In general, nitrogen plasmas is known to introduce C/N functionalities on carbon based surfaces increasing the hydrophilicity (Jones & Sammann 1989). According to the literature a nitrogen plasma treatment can nitride the graphite by inducing C-N bonds (Kimura *et al.* 2007).

It was previously shown, that via nitrogen plasmification of graphene pyridinic-N, pyrrolic-N, quarternary-N and pyridinic N-oxides are formed on the surface, which can significantly contribute to the electrocatalytic activity of carbon based materials towards the $\text{V}^{4+}/\text{V}^{5+}$ redox reaction (Abbas *et al.* 2007; Shao, *et al.* 2010; Shao *et al.* 2010). In addition nitrogen plasma treatment can also create structural defects, such as unsaturated carbon atoms at graphene edge sites which are very active to react with oxygen and form oxygen-containing groups when exposed to air (Abbas *et al.* 2007). Therefore, it can be assumed, that -

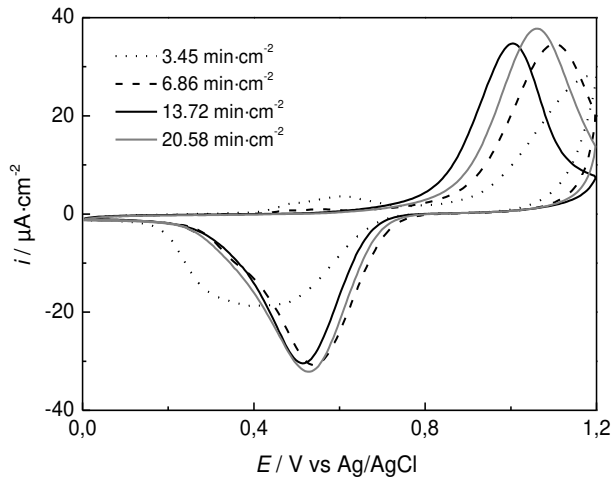


Fig. 5 Cyclic voltammogram ($dE/dt = 5\text{mV}\cdot\text{s}^{-1}$) in $0.1\text{ M H}_2\text{SO}_4 + 0.01\text{ M VOSO}_4$ electrolyte on samples treated by nitrogen plasma at different exposure times

-the higher performance of the sample modified with nitrogen plasma is a superposition of the described effects. However further experiments; including XPS should be performed in order to clarify the surface chemical composition.

In Fig. 5 cyclovoltammograms of graphite electrodes modified with nitrogen plasma varying the treatment duration are shown. As one can see, with increasing time the electrocatalytic activity rises. However, at very long exposure times the performance seems to decrease again.

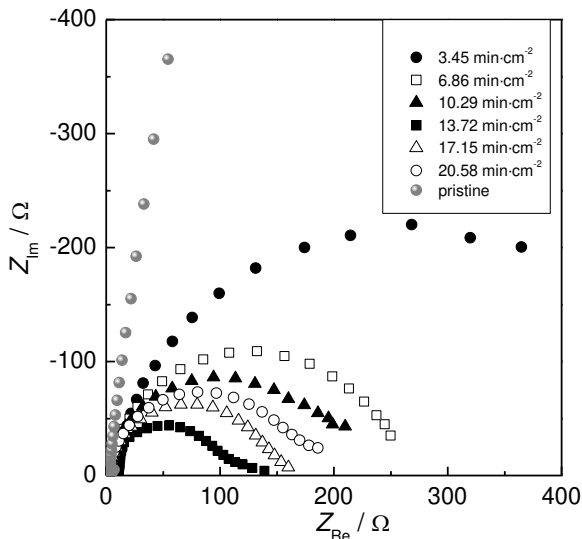


Fig. 6 EIS at 0.8V in $0.1\text{ M H}_2\text{SO}_4 + 0.01\text{ M VOSO}_4$ electrolyte on samples treated by nitrogen plasma at different exposure times in comparison to pristine electrode

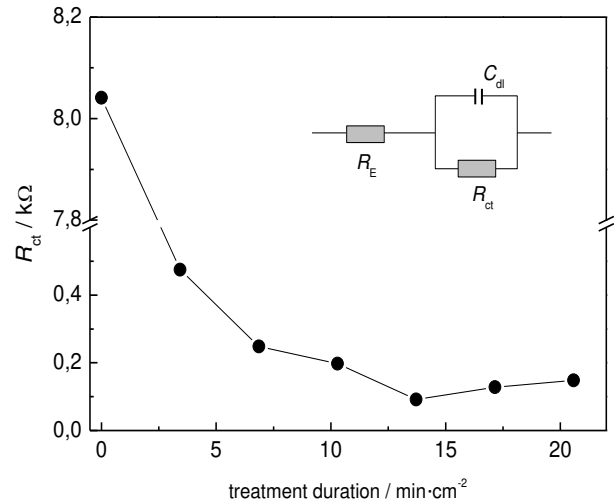


Fig. 7 Dependence of the charge transfer resistance of the $\text{V}^{4+}/\text{V}^{5+}$ redox reaction on the nitrogen plasma treatment duration; inset - equivalent circuit diagram for estimation of the charge transfer resistances values

The overall impedance follows the same trend (Fig. 6) revealing an optimal treatment duration of about $14\text{ min}\cdot\text{cm}^{-2}$. This can be more clearly observed by quantitative analysis of the EIS spectra using the electric circuit, shown in the inset plot of Fig.7, where R_E is the resistance of the electrolyte, C_{dl} is the capacity of the double layer and R_{ct} the charge transfer resistance of the $\text{V}^{4+}/\text{V}^{5+}$ redox reaction. The charge transfer resistance of the reaction decreases dramatically in comparison to the untreated samples, even at the shortest treatment duration. It reaches its minimum of $90\ \Omega$ at about $14\text{ min}\cdot\text{cm}^{-2}$ and starts to rise slightly again for higher exposure times. The changes in morphology could be the reason for this behavior.

In Fig.8 SEM images of samples treated with different duration are compared to a pristine one. With short treatment times craters with random size distribution are visible. This morphology change could be caused by etching via formation of CO radicals and CO₂ molecules, as already observed earlier (Brown *et al.* 1998; Elersic 2011). With increasing exposure time roughening of the fiber surface occurs giving rise most probably to higher catalytic surface area (Fig. 8c). However further treatment elongation can lead to significant surface destruction of the graphite surface and material losses which could explain the slight decrease in performance. Similar behavior is observed for thermal activation of graphite felt electrodes (Sun & Skyllas-Kazacos 1992b).

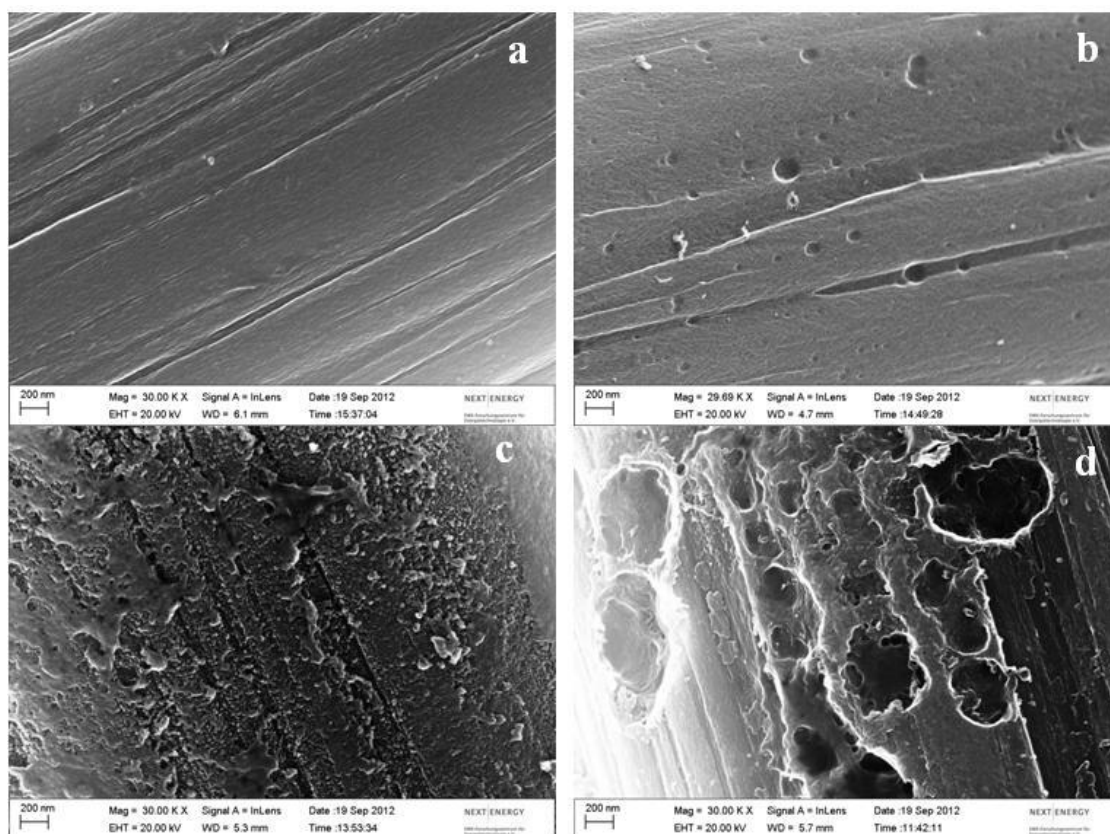


Fig. 8 SEM images of samples treated by nitrogen plasma at different exposure times in comparison to pristine electrode: a) pristine; b) 3.45 min-cm⁻²; c) 6.86 min-cm⁻²; d) 14 min-cm⁻²

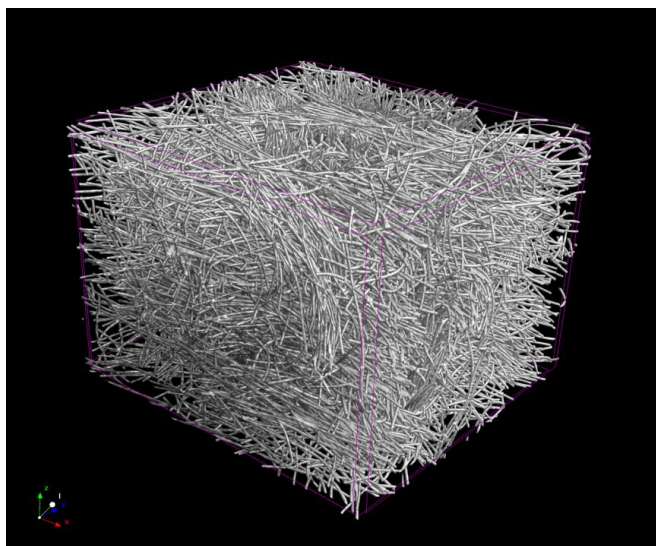


Fig. 9 Computer tomogram of pristine graphite felt electrode

However, it should be noted, that due to the complex architecture (see Fig. 9) of the electrode felt and the filamentary character of the dielectric barrier plasma inhomogeneous morphology changes of the fiber surface are present. Therefore it is to be expected, that the severe destruction of the surface appear more

likely in the external parts of the felt, whereas the internal parts are most probably only attacked by the active species induced by plasma.

4. Conclusion

In the present contribution for the first time dielectric barrier plasma discharge treatment was successfully applied to activate the surface of graphitized felts towards the V⁴⁺/V⁵⁺ redox reaction. Compressed air, argon and nitrogen were used as working gasses for the plasma discharge in an oxidizing environment. Using cyclic voltammetry and electrochemical impedance spectroscopy the electrochemical behavior of differently treated graphite felt electrodes was characterized in vanadium containing electrolyte. A significant improvement of the redox reaction kinetics is observed for all modified samples essential for the overall efficiency of the vanadium-redox-flow-batteries. A comparison of the electrocatalytical performance of samples treated with different working gases shows that a nitrogen plasma treatment leads to the highest catalytical activities at the same operational conditions. Through a variation of the nitrogen plasma treatment duration a maximum

performance at about $14 \text{ min}\cdot\text{cm}^{-2}$ appears, also represented by a minimum of 90Ω in the charge transfer resistance obtained by EIS measurements. A further increase of the exposure time is accompanied by a slight decrease in the electrocatalytical performance. The obtained results are competitive compared to other activation techniques, like thermal and chemical treatment.

All plasma experiments lead to significant morphology changes not apparently depending on the working gas, whereas prolonged exposure provokes stronger roughening and subsequent destruction of the surface. Most probably morphology changes are related to an increase in the catalytical performance due to a higher catalytic surface area. However, further experiments, including XPS should be performed in order to clarify the surface chemical composition of the felts to better understand the catalytical effects. Additionally, the influence of humidity on the catalytic activity has to be investigated. However, the presented results reveal that the plasma pretreatment is a promising technique for easily implementation of a plasma pretreatment of carbon felt electrodes into large scale industrial processes in order to enhance the overall performance of vanadium-redox-flow-batteries. The plasma treatment could allow decreasing of the activation durations and avoiding the use of highly oxidative and dangerous substances such as hot concentrated acids.

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