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Effect of oxygen plasma treatment on the electrochemical performance of the rayon and polyacrylonitrile based carbon felt for the vanadium redox flow battery application



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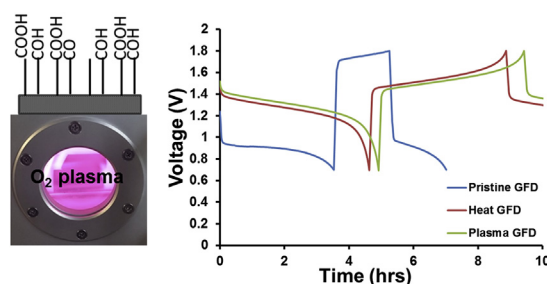
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HIGHLIGHTS

- Activation of commercial carbon felts using oxygen plasma treatment.
- Almost 20% increase in functional group on the surface by plasma treatment.
- Performance increase purely attributed to increase in functional groups.
- Importance of having uniformly activated electrodes in VRFB.

GRAPHICAL ABSTRACT



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ABSTRACT

Oxygen plasma treatment was applied on commercially available graphite felt electrodes based on rayon (GFA) and polyacrylonitrile (GFD). The formation of functional groups on the surface of the felt was confirmed by X-ray photoelectron spectroscopy measurements. The BET studies of the plasma treated electrodes showed no significant increase in surface area for both the rayon as well as the PAN based felts. Both plasma treated electrodes showed significantly enhanced V^{3+}/V^{2+} redox activity compared to the pristine electrodes. Since an increase of the surface area has been ruled out for plasma treated electrode the enhanced activity could be attributed to surface functional groups. Interestingly, plasma treated GFD felts showed less electrochemical activity towards V^{5+}/V^{4+} compared to the pristine electrode. Nevertheless, an overall increase of the single cell performance was still observed as the negative electrode is known to be the performance limiting electrode. Thus, to a great extent the present work helps to preferentially understand the importance of functional groups on the electrochemical activity of negative and positive redox reaction. The study emphasizes the need of highly active electrodes especially at the negative electrode side as inactive electrodes can still facilitate hydrogen evolution and degrade the electrolyte in VRFBs.

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1. Introduction

Vanadium redox flow batteries (VRFB) are now considered to be one of the most promising candidates for large scale stationary energy storage applications. Apart from the advantage that the energy as well as the capacity can be independently tuned for flow batteries, VRFB's are exceedingly attractive as they employ only a single redox-active chemical species and therefore cross-contamination problems associated with other redox flow systems like Cr–Fe are often eliminated [1]. However, the VRFB system still suffers from a severe irreversible capacity fade due to an imbalance of the state of charge (SOC) of the redox species in catholyte and anolyte [2,3]. In an ideal VRFB system the amount of V^{2+} ions in the anolyte should be equal to the amount of V^{5+} in the catholyte. The same applies to the amount of V^{3+} and V^{4+} ions, respectively. However, due to parasitic reactions, mainly hydrogen evolution reaction, the balance of the active species is hampered and leads to an irreversible capacity loss [4,5]. An irreversible capacity loss means that the cell cannot be reactivated by just intermixing the anolyte and catholyte, but that additional chemical or electrochemical activation processes are needed. One way to reduce side reactions, especially hydrogen evolution reaction, is to use optimized electrode materials on the negative side, which can push the hydrogen evolution reaction to lower potentials [6,7]. This requires a uniform coverage of the electrode with functional groups which are more kinetically selective to the V^{3+}/V^{2+} redox process. The functional groups preferentially bond to the V^{3+}/V^{2+} species and inhibit hydrogen evolution. Typically, thermal activation in air or oxygen atmosphere is often required to activate graphite felts especially for the negative redox reaction [6,8]. However, thermal treatment processes seldom produce a homogenous surface functionalization of the graphite felt [9]. Moreover, thermal activation processes have a poor selectivity for the functional groups formed on the surface of the graphite felt. Hence, it is important to choose those activation steps which offer both, a selectivity and uniformity of functional groups. Furthermore, thermal treatments not only introduce functional groups but also simultaneously increase the surface area of the electrode. Therefore, it is often difficult to distinguish between the positive benefit obtained from an increase in surface area and functional groups [10]. In addition, the formation of functional groups on the surface of the electrode enhances its wettability and apparently increases the electrochemically active surface area. Many different methods such as chemical activation, plasma treatment, gamma-ray irradiation, microwave treatment, corona discharge, etc. have been used to activate VRFB electrodes [11–14]. However, simultaneous and detailed investigation of the electrochemical processes taking place at both negative and positive electrodes is lacking as the activity of the positive as well as negative redox reactions are greatly influenced by specific surface properties of the electrode [15,16]. For e.g. Manahan et al. showed that addition of nanoporous layer preferentially increases the performance of the negative electrode [16]. More recently Fink et al. clearly showed that even when the hydroxyl, carbonyl or the carboxyl group catalyze the V^{2+}/V^{3+} redox reaction the same functional group impede the V^{4+}/V^{5+} reaction [17]. Finally depending on the nature of the carbon felt extent of functionalization or activation may also vary. In the work done by Kim et al. in 2011, influence of different surface treatments on the electrochemical performance of PAN-based commercial carbon felt in VRFBs is reported. They have observed that the surface treatments including mild Oxygen plasma treatment give rise to an improved energy efficiency of the cell [12]. In 2015, Chen et al. reported a work on the modification of commercial graphite felt with atmospheric pressure plasma jets. An improvement in the energy efficiency and discharge capacity was observed for the

treated electrodes which was attributed to the increased wettability due to the presence of oxygen-containing functional groups and lowered barrier for carrier transport [18]. However, no separate investigations, to understand the influence of surface-modified electrode on positive and negative electrode activities were conducted in these works which are important to understand for tailoring the electrode properties.

In this work an oxygen plasma treatment process was applied to Rayon as well as PAN based graphite felts and its effect on the negative as well as the positive half-cell reactions is investigated. The Rayon and PAN based felts, which are commonly used as electrode material, differ a lot in their graphitic nature. As a consequence, any activation process can result in a different extend of surface functionalization and surface area changes. For e.g. PAN based materials, which are much more graphitic than those based on rayon, often need higher activation temperatures to obtain a reasonably good electrochemical activity. At the same time, rayon based felts suffer higher weight losses under the same thermal conditions compared to the PAN based felt. In the present work, the electrochemical performance enhancement achieved through plasma treatment is correlated with the amount of functional groups. Finally, it was possible to distinguish between the effects caused by the increase in surface area and functional groups, respectively, on the electrochemical activity of negative as well as positive electrodes' redox reaction.

2. Experimental

2.1. Materials

Carbon felts GFA 3 EA (Rayon) and GFD 3 EA (PAN) from SGL, each having a thickness of 3 mm, was used as electrode materials. An anion exchange membrane, VX 20 from Fumatech was used for all single cell experiments.

2.2. Heat treatment process

The GFA and GFD materials were annealed at 400 °C in air with a heating rate of 5° C/min in a muffle furnace to generate the heat treated materials.

2.3. Plasma treatment process

Plasma functionalization was carried out in a radiofrequency (rf) 13.56 MHz plasma setup (Femto, Diener electronic GmbH, Germany) [19,20]. The power rating of the rf generator is 300 W (max. rf power limited to 200 W). 5 cm × 5 cm felts were loaded into the plasma chamber which was subsequently evacuated to a pressure below 0.2 mbar before the chamber was filled with about 0.8 mbar of oxygen. All plasma treatments were carried for 4 min at 20% maximum power.

2.4. X-ray diffraction

X-ray diffraction (XRD) was performed on the pristine, heat-treated and plasma-treated GFD and GFA materials to investigate any differences in the crystallinity of the bulk. The diffraction experiments were conducted using a STOE STADI/P powder diffractometer [Cu K α radiation, $\lambda = 1.5406 \text{ \AA}$, Dectris Mythen 1K Silicon strip detector, curved Ge(111) monochromator, step width 0.015° (2 θ)] in flat-sample transmission mode.

2.5. Scanning electron microscopy (SEM)

The carbon surface fiber morphology was investigated in a Zeiss

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