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Short Communications

Carbon Felts Electrode Treated in Different Weak Acid Solutions through Electrochemical Oxidation Method for All Vanadium Redox Flow Battery

Yue Men[1,2], *Ting Sun*[1,*]

[1] College of Science, Northeastern University, 3-11 Wenhua Road, Shenyang, 110819, China
[2] Shenyang TV University, 7 Fourteen Road 110003, Shenyang, China
[*]E-mail: michelle7588@sina.com

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Electrochemical oxidation method in different weak acid (citric acid, oxalic acid and ethylene diamine tetraacetic acid) solutions was used to modify the carbon felts (CFs) electrode for all vanadium redox flow battery (VRFB). The CFs electrode was investigated through scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), cyclic voltammetric (CV) and linear sweep voltammetry (LSV). The electrochemical activity of the CFs was improved with little morphologies changing after it was treated in the weak solutions. Single cell was assembled to test the battery performances and the energy efficiency (EE) increases from 81.4% to 85.4% after the CFs was oxidized in ethylene diamine tetraacetic acid for 2 h. The enhanced electrochemical activity was ascribed to the increase of oxygen content on the surface of the treated CFs. The treated CFs are supposed to be used in the VRFB and improve the storage efficiency.

Keywords: Vanadium redox flow battery; Carbon felts; Mild Oxidation; Electrochemistry

1. INTRODUCTION

The All vanadium redox flow battery (VRFB) [1-2] is considered a efficiency storage application for electric network peak shaving and intermittent renewable power sources storage because of its excellent performances such as long-life cycle, low cost, deeply charge and discharge and environmental friendly. It uses VO_2^+/VO^{2+} and V^{2+}/V^{3+} redox couples insulphuric acid as the positive and the negative half-cell electrolytes, respectively, and exhibits an open circuit voltage of approximately 1.26 V at 100% state of charge [3]. Carbon felts (CFs) are used as electrode for VRFB extensively because of high specific surface areas and stability in the strong acid solutions. But the poor electrochemical activity to electrode reactions needs to be improved and lots of investigations have already been done to enhance its electrochemical activity [4-8]. The oxygen-containing functional groups on the electrode surfaces were supposed to be the catalytic active points for the VO_2^+/VO^{2+} and V^{2+}/V^{3+} redox couples [9, 10]. Being oxidized in the air or electrochemically oxidized in the strong acid [9, 11] were supposed to be a promising method to modify the CFs, but with the physical performances reducing. So in this paper, some weak acids solutions were used as electrolytes to oxidize the CFs in order to preserve its physical performances and improve its electrochemical activity.

2. EXPERIMENTAL

2.1. Surface treatment of carbon felts

Polyacrylonitrile (PAN) based carbon felts manufactured by Shanghai Xinka (55 cm thick) were employed for this study. 1 M citric solution, 1 M oxalic acid and 0.2 M ethylene diamine tetraacetic acid (EDTA) solution were used for the anodic oxidation of carbon felts. The CFs were oxidized at the current density of 40 mA cm^{-2} for 1 h and this was precisely controlled by a glavanostat. After oxidation, the CFs were extensively washed with deionized water until the PH=7, then dried at 100 ^{o}C in the vacuum condition.

2.2. Samples characterization

The sample structure was characterized by scanning electron microscopy (SEM, XL30FEG). X-ray photoelectron spectroscopy (XPS) was carried out using ESCA-LAB250 surface analysis system (Al K_α X-ray source generated at 15 kV and 10mA, ultra-high vacuum condition). The CFs were milled into powders before the XPS measurement. The cyclic voltammograms (CVs) were obtained using a three electrode electrochemical cell on a Princeton Applied Research EG & G potentiostat model 273. Carbon felts (1.5 cm × 1.5 cm × 1.0 cm in size), Pt electrode and saturated calomel electrode were used as working electrode, counter electrode and reference electrode, respectively. The electrolyte used in the measurement is 0.3 M $VOSO_4$ + 2 M H_2SO_4 solution and a salt bridge was employed to eliminate the liquid junction potential.

2.3. Single cell test

The single cell for testing was constructed with carbon felts, an ion exchange membrane (Dupont N115) and bipolar plates. The anodic electrolyte was 160 mL of 1.5 M VO^{2+} in 2 M H_2SO_4 solution and the cathodic electrolyte was 80 mL of 1.5 M VO^{2+} in 2 M H_2SO_4 solution. They were pumped through the cell unceasingly during the test at room temperature. The effective area of the membrane was 28 cm^{-2}, and the cells were galvanostatically charged and discharged in a voltage range of 1.0-1.7 V with a current density of 50 mA cm^{-2}.

3. RESULTS AND DISCUSSION

The surface morphologies of the CFs were observed before and after treatment and the SEM images are shown in Fig. 1. The surfaces of the CFs are still smooth and no visible changes are detected after mild oxidation in the different weak acids, suggesting no deformation is induced by the mild electrochemical oxidation. The physical properties of the CFs can be preserved that is helpful to be used as electrode materials for VRFB.

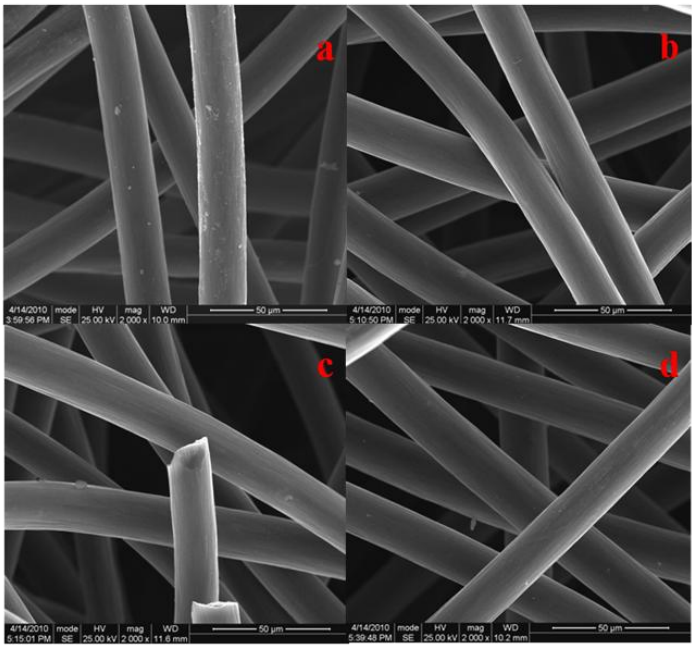

Figure 1. SEM images of untreated CFs (a), treated in citric acid (b), oxalic acid (c) and EDTA solution (d).

Table 1. C/O ratios and functional groups obtained from C1s spectra peak fitting of samples (%)

Sample	O/C ratio	C=C/C-C 284.5eV/285.5eV	C-OH 286.3eV	C=O 288.3eV	COOH 289.8eV
untreated	0.097	90.2	5.8	1.3	2.7
Treated in citric acid	0.16	80.3	8.2	2.4	9.1
Treated in oxalic acid	0.17	79.5	8.7	2.6	9.2
Treated in EDTA acid	0.19	78.2	8.7	3.3	9.8

For further investigations, an XPS study has been conducted to exactly identify their surface chemical state before and after the surface modifications. Table 1 shows the XPS results of C and O element percentages for the untreated and modified CFs, the O/C ratio increases from 0.097 to 0.19 (treated in the EDTA solution), indicating more oxygen atoms are introduced on the surface of CFs. In order to investigate the percentages of the oxygen-containing functional groups, The C1s spectra have been fitted by the de-convolution of each obtained peak. As regard to the C1s peak, it can be fitting by five peaks [12]: sp^2 C=C (284.5), sp^3 C–C (285.5 e V), C–OH (286.3 e V), C=O (288.3 e V), and COOH (289.8 e V) and the results are also listed in the Table 1. The oxygen-containing functional groups are supposed to be the active points for the electrode reactions for VRFB [12, 13], so the CFs treated in EDTA for 1 h are supposed to have enhanced electrochemical activity compared with the untreated CFs.

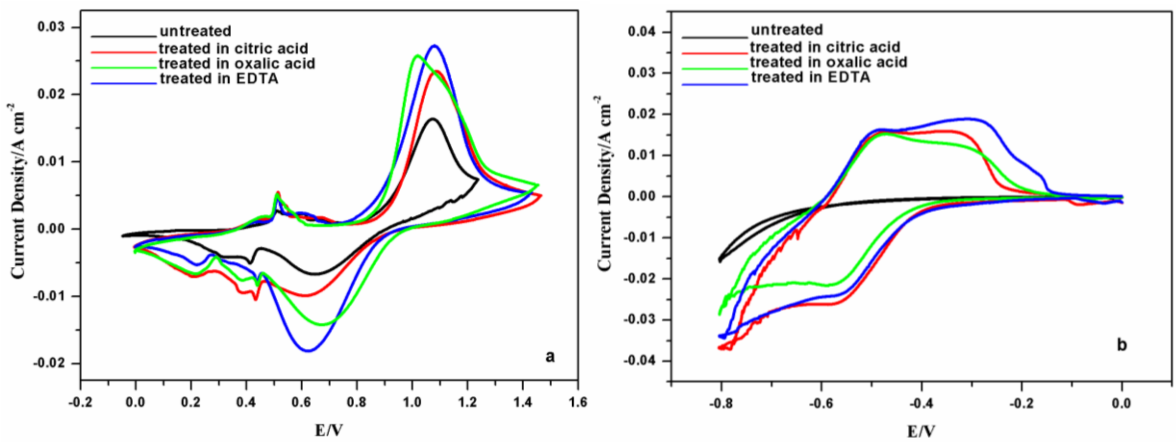

Figure 2. Positive and negative CVs of untreated and modified CFs in 0.3 M $VOSO_4$ +2 M H_2SO_4 solution at a scan rate of 2 mV s^{-1}.

The CVs of the VO_2^+/VO^{2+} and V^{3+}/V^{2+} redox couples, measured at a scan rate of 2 mV s^{-1} on the CFs samples, are shown in Fig. 2. The four samples exhibit an anodic peak associated with the oxidation of VO_2^+/VO^{2+}, and a cathodic one associated with the reverse reaction. The peak current densities of the oxidation and reduction processes for untreated CFs is 16.4 mA cm^{-2} and -6.7 mA cm^{-2}, respectively (Fig. 2a). After being treated in the weak acids solution, the electrochemical activity enhances significantly. The oxidation and reduction peak current densities are 27.1 mA cm^{-2} and -18.1 mA cm^{-2}, respectively, for the CFs treated in the EDTA for 1h. No obvious peak can be seen during the cathodic process when the untreated CFs is used as working electrode, suggesting very poor electrochemical activity to the V^{3+}/V^{2+} redox couple. All of the treated CFs show excellent electrode performances for the cathodic reactions. For example, the peak current densities of the oxidation and reduction reaction for CFs treated in the EDTA solution are 16.3 mA cm^{-2} and -23.9 mA cm^{-2}, respectively, and the peak potential separation is only 83 mV indicates that the reaction is electrochemically quasi-reversible on this type of electrode. According to the literatures [9,10], the oxygen-containing functional groups are supposed to be the catalytic active points for the electrode reactions for the vanadium ions and these functional groups could facilitate the electrons and oxygen atom transfer. The CFs oxidized in the EDTA solution possess plentiful oxygen-containing functional groups and show the excellent electrochemical activity, the XPS results identify with the CVs results.

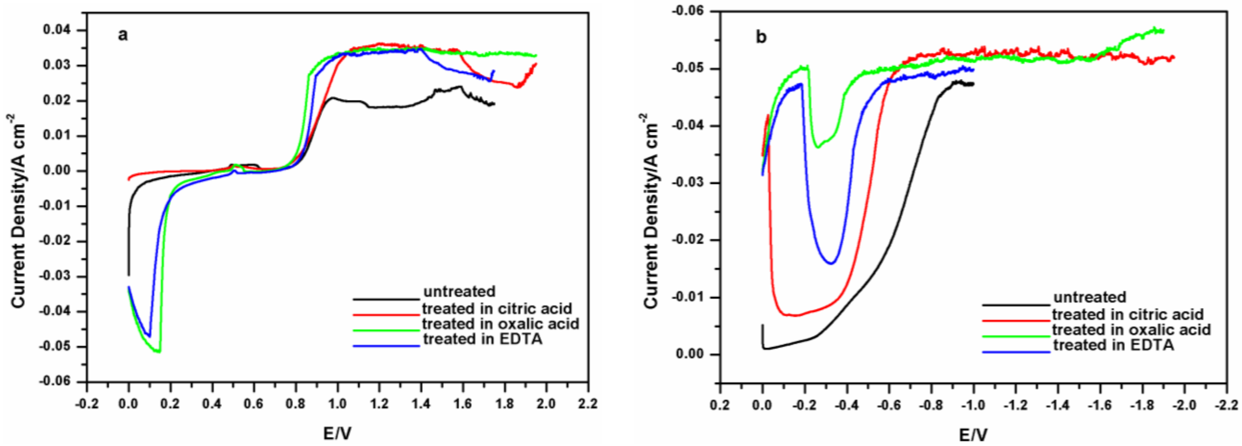

Figure 3. Negative and positive linear sweep voltammograms for the untreated and oxidized CFs in in 0.3 M $VOSO_4$ +2 M H_2SO_4 solution at a scan rate of 0.5 mV s^{-1}.

The LSV curves of oxidation reaction for VO_2^+/VO^{2+} are shown in Fig. 3a, the reaction range is from 0.65 V to 1.0 V. But with the potential increasing, the oxygen evolution reaction will occur. The limit diffusion current densities are 21.0 mA cm^{-2}, 33.5 mA cm^{-2}, 34.8 mA cm^{-2} and 35.6 mA cm^{-2} for the untreated CFs, CFs treated in citric acid, oxalic acid and EDTA solutions, respectively. Large limit diffusion current density means the treated CFs can meet the large current charge-discharge condition. The reaction range for V^{3+}/V^{2+} reduction process is about -0.25 V—0.6 V, no hydrogen evolution reaction is observed when the oxidized CFs are used as working electrodes, suggesting the modified CFs are more stable than the untreated CFs during the reduction reaction.

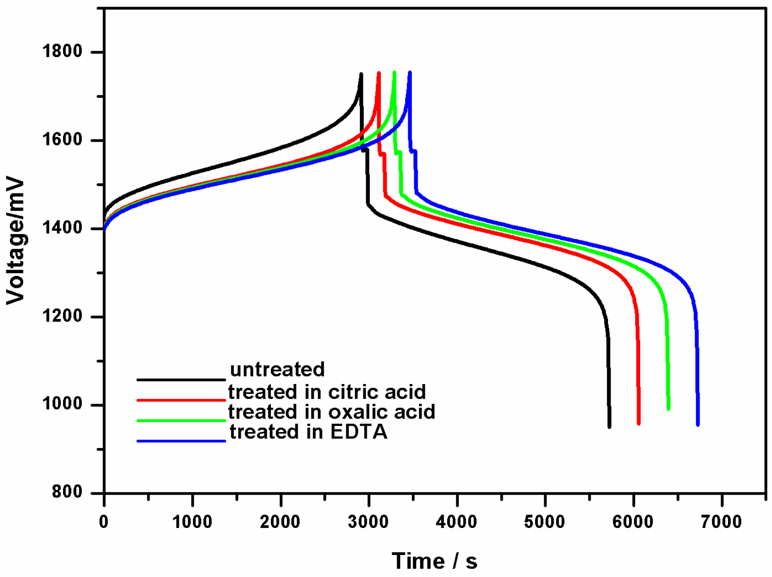

Figure 4. The charge-discharge curves for single cell with untreated and modified CFs as working electrodes at the current density of 50 mA cm^{-2}.

VRFB performances for the untreated CFs and oxidized CFs are compared and the charge-discharge curves are shown in Fig. 4. The initial charge potentials of treated carbon felts are lower and the initial discharge potentials are higher than those of the pristine carbon felts, suggesting the heat treatment reduces the polarization resistance during the charge-discharge process. The columbic efficiency (CE), voltage efficiency (VE) and energy efficiency (EE) for different CFs are listed in table 2. The EE is about 85.4% when the CFs treated in EDTA employed as working electrodes and the EE value can meet the need of practical applications.

Table 2. The values of CE (%), VE (%) and EE (%) for the untreated CFs and oxidized CFs used as electrodes.

	CE	VE	EE
untreated	94	86.6	81.4
treated in citric acid	93.5	84.3	90.2
treated in oxalic acid	93.6	85	90.8
treated in EDTA	93.4	85.4	91.4

4. CONCLUSIONS

CFs were electrochemical oxidized in the week acids solutions and used as electrodes for VRFB. Different from the strong oxidizing process, no obvious etch was observed on the surface of the carbon fiber, so this mild method could perverse the physical performance and enhance the electrochemical activity of the CFs. The CFs treated in EDTA solution for 1 h exhibits the best electrochemical performances and EE is about 85.4 %, suggesting the modified CFs could meet the demand of practical applications.

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