



Influence of Fenton's reagent treatment on electrochemical properties of graphite felt for all vanadium redox flow battery

Chao Gao^a, NanFang Wang^b, Sui Peng^a, SuQin Liu^{a,*}, Ying Lei^a, XinXing Liang^a, ShanShan Zeng^a, HuiFang Zi^a

^a Key Laboratory of Resources Chemistry of Nonferrous Metals, Ministry of Education, College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, China

^b School of Chemistry and Chemical Engineering, Hunan Institute of Engineering, Xiangtan 411104, China

ARTICLE INFO

Article history:

Received 8 August 2012

Received in revised form 7 October 2012

Accepted 8 October 2012

Available online 16 October 2012

Keywords:

Fenton's reagent

Hydroxylated-functionalization

Graphite felt

Vanadium redox flow battery

Electrochemical activity

ABSTRACT

An environmental, economic and highly effective method for carbon fiber hydroxylated-functionalization based on Fenton's reagent treatment is used to improve the electrochemical activity of graphite felt (GF) as the positive electrode in all vanadium redox flow battery (VRFB). The effect of H₂O₂ content in Fenton's reagent on the structure and electrochemical properties of GF is investigated. The scanning electron microscope (SEM) indicates that the surface of the treated GF is etched increasingly with the content of H₂O₂. The Fourier transformation infrared (FTIR) spectroscopy shows that the peak intensity of hydroxyl groups on the treated felt is increased with the H₂O₂ concentration, which is further verified by X-ray photoelectron spectroscopy (XPS). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) show that the treated sample exhibits a higher electrochemical activity. A VRFB with the treated GF as electrodes exhibits higher coulombic, voltage and energy efficiency (98.8%, 75.1% and 74.2%) than that with the untreated GF (93.9%, 72.1% and 67.7%) at 60 mA cm⁻², and this method is even superior when compared with the reported methods.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

The vanadium redox flow battery (VRFB), proposed by Skyllas-Kazacos et al. in 1985, is emerging as a potential candidate for grid scale energy storage systems, owing to its flexible design, high reliability, separated battery capacity, long cycle life, low cost of maintenance and environmental friendship [1–5]. It employs the V(IV)/V(V) and V(II)/V(III) redox couples in sulfuric acid as the positive and negative half-cell electrolytes, respectively [6].

Because the positive and negative half-cell reactions occur on the inert electrodes [4,7,8], the electrochemical activity of the electrodes is vital to energy conversion of VRFB. It is known that the negative half-cell reaction (V(II)/V(III) couple) is more reversible and faster than the positive one (V(IV)/V(V) couple) because the latter one involves at least three elementary steps [9], therefore, it is important to enhance the electrochemical property of positive electrode toward V(IV)/V(V) couple. Carbon fiber materials, especially the polyacrylonitrile (PAN)-based graphite felt (GF) is commonly used as electrode material in VRFBs, due to their wide potential

range, acid resistance, high specific surface and reasonable cost [5,7,10]. However, the low electrochemical activity of commercial GF, due to the poor kinetics reversibility, greatly limits their wide-spread use in VRFBs [11]. In recent years, a great deal of attention has been directed toward the improvement of electrochemical properties of carbon fiber. Chemical modifications such as electrochemical oxidation [12], thermal activation [13,14], treatment with acid [15,16], metal modified [11,17–19], nitrogen modified [20], multi-walled carbon nanotubes (SWCNT) coated [21,22], etc. [13] have been introduced with the aim of enhancing the wettability toward the electrolyte or providing more active sites for electron transfer of the electrode for VRFB. However, note that such methods are either high energy-consuming, time-consuming or harmful to the environment. Since the oxygen-containing groups like C–OH and C=O, particularly C–OH were expected to electrochemically catalyze the electrode reaction [12,23,24], much attention has been paid to the surface hydroxylated-functional of carbon material [25–29], as well as the activation of VRFB electrode materials [12,15,30], but these modifications are not advantageous to commercial application because they are dangerous for environment and workers, and involve high cost or tedious procedures.

Fenton's reagent (Fe²⁺ + H₂O₂ + H⁺), as one of the oldest advanced oxidation processes, has been widely used to treat

* Corresponding author. Tel.: +86 0731 88879850; fax: +86 0731 88879850.

E-mail address: sqliu2003@126.com (S. Liu).

extremely polluted wastewaters, because it is cheap, non-toxic, catalytically homogeneous, technologically simple, and has a high oxidation potential. The oxidation power of Fenton' reagent (up to 2.8 V vs. standard hydrogen electrode) is attributed to the generation of hydroxyl radical ($\cdot\text{OH}$) during the iron-catalyzed decomposition of hydrogen peroxide in acid medium [31–34]. Compared to the above hydroxylated methods, Fenton's reagent treatment is completed in only one step, working under ambient conditions rather than under elevated temperature or high pressure. More importantly, it will never produce any toxic gas. Consequently, it is extremely economic, and is friendly to workers and the environment. To the best of our knowledge, GF treated by Fenton's reagent for electrode materials of VRFB has not been reported yet. In the current study, Fenton's reagent hydroxylated-functionalized GFs were used as the electrode and their performance was investigated for V(IV)/V(V) redox couple for VRFB.

2. Experimental

2.1. Materials

In this experiment, the GF (6 mm thickness PAN-based graphite felt, cubic resistance $0.1 \Omega/25 \text{ mm}$, Shenhe carbon fiber Materials Co. Ltd., Liaoning, China) was used as an electrode material. The V(IV) electrolyte solutions were prepared by electrolytic dissolution of V_2O_5 (>99.95%, Dadi Vanadium Research Institute, Chongyang, Hubei, China) in $3.0 \text{ M H}_2\text{SO}_4$ supporting electrolyte in a two-compartment electrolysis cell [35]. The V(III) electrolyte solution was prepared by charging the prepared V(IV) solution in a flow single cell at 60 mA cm^{-2} . The prepared solution was analyzed by potentiometric redox titration to determine the valence and concentration of the vanadium ions using a standardized potassium permanganate solution [36].

2.2. Treatment of GF

Each piece of GF ($5 \text{ cm} \times 6 \text{ cm}$) was soaked in ethanol water solution (70%) under ultrasonication for 0.5 h to remove impurities in the fibers, rinsed with deionized water and dried in an oven at 50°C for 10 h. His purified GF was denoted as an untreated sample for comparison. The purified GFs were dipped in four beakers containing 20 mL, 0.02 M ferrous solutions (adjust $\text{pH}=3$) for 1 h under ambient conditions, respectively. Then, 5, 10, 15 and 20 mL H_2O_2 (30%) were added into the beakers and each solution was diluted to 40 mL with deionized water, respectively, and GF was treated until no gas evolution was observed (0.5–2 h). The treated samples were immersed in $0.1 \text{ M H}_2\text{SO}_4$ under ultrasonication for 30 min to remove the attached $\text{Fe}(\text{OH})_3$, washed with deionized water until the pH of washed water became neutral, and dried in an oven at 50°C for 10 h.

2.3. Characterization of GF

FTIR (Thermo Nicolet Corporation, Nicolet 6700, USA) was used to characterize the oxygen-containing groups in carbon fibers. Carbon fibers were firstly milled to be powder, and then 1 mg of the powder was taken to be mixed with 50 mg of dried potassium bromide. The mixture was pressed to be disks as the determinant. XPS measurements were performed on a K-Alpha 1063 (Thermo Fisher Scientific, UK) in an ultra-high vacuum set-up equipped with Al K α X-ray source generated at 12 kV and 6 mA, employing Thermo Advantage survey and analysis system. The base pressure in the measurement chamber was about 10^{-9} mbar. The surface morphology of the samples was characterized with a scanning electron microscopy (JEOL, JSM-6360LV, Japan) at an acceleration

voltage of 25 kV. For CV and EIS measurements, a three-electrode cell was used at room temperature. The cell was composed of a GF as the working electrode ($1.0 \text{ cm} \times 1.0 \text{ cm}$), a saturated calomel electrode (SCE) as the reference electrode, and a Pt electrode ($2.0 \text{ cm} \times 2.0 \text{ cm}$) as the counter electrode. The GF piece is sandwiched by two pieces of conductive plastics, except the active area, and the side of conductive plastic and graphite felt, as well as the back of conductive plastic were all sealed by wax. The CV tests were performed on the electrochemical workstation (Shanghai ChenHua Instrument Co. Ltd., China). EIS was measured on Princeton workstation (PARSTAT2273, EG&G, US) by applying an alternating voltage of 5 mV over the frequency range from 10^{-2} to 10^5 Hz.

2.4. Single cell test

A VRFB single cell was fabricated by sandwiching a membrane (Nepem-Nepem-1110, Best Industry & Trade Co., Ltd) between two pieces of the GF with the size of $5 \text{ cm} \times 6 \text{ cm}$, which served as the electrodes, and two conductive plastic parts were used as the current collectors. The initial electrolyte was 150 mL $1.5 \text{ M V(IV)}/3.0 \text{ M H}_2\text{SO}_4$ solution for catholyte and 150 mL $1.5 \text{ M V(III)}/3.0 \text{ M H}_2\text{SO}_4$ solution for anolyte. The two electrolytes were cyclically pumped into the corresponding half-cell by two magnetic pumps (MP-10RN, Shanghai Xinxishan Industrial Co. Ltd., China) with a flow rate of 50 mL/min. The single cell was charged and discharged by a CT2001C-10V/10A battery test system (Wuhan Land Co. Ltd.) with a constant current density of $20\text{--}60 \text{ mA cm}^{-2}$. To avoid the corrosion of the carbon felt electrodes and conductive plastic, the voltage of charge and discharge range from 0.7 to 1.7 V.

3. Results and discussion

3.1. Characterization of GF treated by Fenton

Fig. 1 illustrates the surface morphology of the treated GF. There are some particles on the surface of the untreated sample (Fig. 1a), due to the impurities adhering to the surface even after purification procedure, which can hinder the approach and adsorption of the vanadium ions and the electron transfer [14,16]. The SEM micrographs of GF samples (Fig. 1b–e) treated by various H_2O_2 concentrations in Fenton reveal modification of the surface compared with the untreated GF. At low concentration of H_2O_2 , the particles on the surface of GF become less (Fig. 1b) and vanish (Fig. 1c), besides, the surface was etched and slightly rough. With the H_2O_2 concentration increasing further, the GF surface was more sculptured and rougher (Fig. 1d). When H_2O_2 reaches 20 mL, the fibers become slender and are corroded like tree root as Fig. 1e shown, indicating that some carbon fibers have been shed from the felt body, accordingly, the mechanic strength should be deteriorated. It reveals that the oxidation process could remove the surface contamination or the inhibitory layer and slightly destroy the surface of the GF.

Fig. 2 displays FTIR spectra of GF samples. The peak at 3433 and 1382 cm^{-1} is assigned to the O–H stretching vibration and bending vibration. The peaks at 1117 cm^{-1} is attributed to C–O stretching vibration [37]. The stretching mode of –OH groups in the enol (C=C–OH) appears at around 1620 cm^{-1} [38] and the peak at 1756 cm^{-1} is attributed to C=O groups in ketone, aldehyde, or lactone groups [39]. The intensity of O–H peak is increased with the H_2O_2 concentration, indicating that the oxygen containing groups were successfully introduced to the surface of carbon fibers.

To identify the surface elements and carry out a quantitative analysis, the XPS wide scan spectra in the binding energy range

Download English Version:

<https://daneshyari.com/en/article/187692>

Download Persian Version:

<https://daneshyari.com/article/187692>

[Daneshyari.com](https://daneshyari.com)