Journal of Power Sources 263 (2014) 104–109

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Microwave-treated graphite felt as the positive electrode for all-vanadium redox flow battery

Xiaoxin Wu, Hongfeng Xu*, Pengcheng Xu, Yang Shen, Lu Lu, Jicheng Shi, Jie Fu, Hong Zhao

Liaoning Provincial Key Laboratory of New Energy Battery, Dalian Jiaotong University, Dalian 116028, Liaoning Province, PR China

HIGHLIGHTS

- Graphite felt treated by microwave method works as positive electrode of VRFB firstly.
- The microwave-treated graphite felt carries more hydrophilic groups on its defects.
- Graphite felt treated via microwave exhibits excellent electrochemical activity.
- The single cell performance is improved remarkably with the use of modified electrode.

ARTICLE INFO

Article history:
Received 5 December 2013
Received in revised form
3 March 2014
Accepted 7 April 2014
Available online 18 April 2014

Keywords:
Vanadium redox flow battery
Microwave treatment
Graphite felt
Hydroxylated-functionalization

ABSTRACT

An environmental, economic, and highly effective method based on microwave treatment was firstly used to improve the electrochemical activity of graphite felt as the positive electrode in all vanadium redox flow battery (VRFB). The graphite felt was treated by microwave and characterized by Fourier transform infrared and scanning electron microscopy. The electrochemical performance of the prepared electrode was evaluated with cyclic voltammetry and electrochemical impedance spectroscopy. Results show that graphite felt treated by microwave for 15 min at 400 °C exhibits excellent electro-catalytic activity and reactive velocity to vanadium redox couples. The coulombic, voltage, and energy efficiency of the VRFB with as-prepared electrodes at 50 mA cm^{-2} are 96.9%, 75.5%, and 73.2%, respectively; these values are much higher than those of cell-assembled conventionally and thermally treated graphite felt electrodes. The microwave-treated graphite felt will carry more hydrophilic groups, such as −OH, on its defects, and rough degree of the surface which should be advantageous in facilitating the redox reaction of vanadium ions, leading to the efficient operation of a vanadium redox flow battery. Moreover, microwave treatment can be easily scaled up to treat graphite felt for VRFB in large quantities.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Redox energy storage systems proposed by Sum et al. [1] have unique advanced characteristics, namely, low operation and maintenance costs, long lifecycle, deep-discharge capability, flexible design, high reliability, and efficient generation of electricity [2–4]. In particular, the all-vanadium redox flow battery (VRFB) is a promising candidate for storing electrical energy. VRFB offers the advantage of low contamination of metal cations by employing the same element in both electrolytes [5]. VRFBs have been significantly improved, but these improvements are insufficient for VRFBs to replace the current internal combustion engines. Therefore, the energy efficiency (EE) of VRFBs must be improved prior to commercialization. The EE of a VRFB depends largely on the physicochemical properties of its electrodes, because the electrochemical reactions of vanadium ions occur on the electrode surface [6,7]. In VRFB, carbon-based materials are widely used in the electrodes to catalyze reactions [8–11]. Graphite felt with a large surface area is an appropriate material, because it provides abundant redox reaction sites and maintains good electronic conduction and mechanical stability during cycles. A typical electrode material for VRFB is graphite felt, which exhibits good stability in highly acidic solutions and provides a large reactive surface area for a sufficient number of redox reaction sites [12]. However, graphite felts must be subjected to surface treatments before being utilized as electrodes to ensure that

* Corresponding author. Tel./fax: +86 411 84106713.
E-mail address: hfxu@fuelcell.com.cn (H. Xu).

http://dx.doi.org/10.1016/j.jpowsour.2014.04.035
0378-7753/© 2014 Elsevier B.V. All rights reserved.

their electrochemical activity and wettability originated from a hydrophobic surface [13,14].

In the past, much attention has been paid to the improvement of the electrochemical properties of graphite felt electrodes. Considerable studies about the modification of electrode materials have been carried out to enhance their electrochemical performance; those methods include electrochemical oxidation [15], thermal activation [16,17], acid treatment [18,19], nitrogen modified [20], and metal modified [21,22]. An effective way to achieve enhanced electrochemical performance is by the thermal treatment of graphite felts to increase the surface functional groups of C—O and C═O dramatically, particularly C—OH that was expected to electrochemically catalyze the electrode reaction [23,24]. B. Sun and M. Skyllas Kazacos [16] also showed that graphite felt thermally heated at 400 °C exhibited the greatest improvement in terms of the performance of the vanadium cell.

Much attention has been paid to the surface hydroxylated function of carbon material [25–27]. However, the conventional thermal treatment for graphite felt electrodes is known to be energy or time-consuming or harmful to the environment.

Microwave efficiently heats the preform from the inner part to the surface and produces an inverted temperature gradient because of the convective and radiative heat loss on surface [28,29]. Meanwhile, microwave has the advantage of rapid heating and low energy consumption. In general, carbon materials are good absorbent of microwaves, i.e., they are easily heated by microwave radiation. This characteristic allows them to be transformed by microwave heating, giving rise to new carbons with tailored properties to be used as microwave receptors [30]. Previous work has demonstrated that activated carbons from different carbon sources can be prepared by microwave-assisted heat treatment [31,32], which proves that microwave heating is better than conventional methods of heat treatment because of certain advantages, such as high heating rate, easy control of the heating process, and no direct contact between the heating source and the materials [33]. The temperature of the reaction system is homogeneous to the process because of the penetrability of microwave [34]. Menéndez et al. claimed that carbon materials are generally a good absorbent of microwaves, i.e., they are easily heated by microwave radiation [30].

Thus, we proposed using microwave-treatment to improve the electrochemical activity of graphite felt electrodes in VRFB at 400 °C. In our research, the positive electrode for VRFB was mainly studied. In order to eliminate the influence of the negative electrode on cell potential, we used the graphite felt treated by microwave as the positive electrode and used the hydrogen electrode and H_2 to replace the graphite felt and V^{2+}/V^{3+} couple in the negative electrode in the VRFB performance test.

2. Experimental

2.1. Preparation and characterization of microwave-treated graphite felt

2.1.1. Preparation of microwave-treated graphite felt

Commercial graphite felt was used particularly for this study (3 mm thickness PAN-based graphite felt, <16 mΩ cm^2, Hongwei Co., Gansu). The graphite felt was microwave treated with a NJZ4-3A microwave sintering oven (Jiequan Microwave Development Co., Ltd., Nanjing) which contains an infrared temperature measuring instrument to measure the temperature of the samples and then with a different microwave program. The graphite felt was put in a silicon carbide crucible and placed inside another larger silicon carbide crucible, which was stuffed with glass wool. Glass wool is mainly used to avoid breaking and cracking the quartz turntable in the microwave sintering oven by minimizing the heat transfer to the turntable. The whole assembly was kept at the center of the turntable. At 400 °C under atmospheric conditions, the graphite felt was homogeneously exposed to microwave radiation for various exposure times, i.e., 10 min, 15 min, and 20 min and designated as graphite felt-10 min, graphite felt-15 min, and graphite felt-20 min, respectively.

Another graphite felt, which was heated by conventional thermal treatment in a muffle oven at a constant temperature of 400 °C for 30 h, was prepared for comparison (referred to as graphite felt-30 h) as described in Ref. [16].

2.1.2. Characterization of microwave-treated graphite felt

2.1.2.1. SEM for microwave-treated graphite felt. The morphology of the materials was analyzed with a JSM-6360LV microscope (JEOL, Japan) at an accelerating voltage of 20 kV. The microscope was also utilized to examine the appearance of the microwave-treated graphite felt at 20 kV and the magnification of 15,000.

2.1.2.2. FT-IR for microwave-treated graphite felt. The Fourier transform infrared (FT-IR) spectra of the samples were recorded in an FT-IR spectrometer (FTIR430, Jasco Co., Japan). First, graphite felts were millinged to be powder. Second, 1 mg of the powder was mixed with 50 mg of KBr. The mixture was pressed to form disks as the determinant.

2.1.2.3. Cyclic voltammetry and electrochemical impedance spectroscopy for microwave-treated graphite felt. The electrochemical activity of the as-prepared electrodes was evaluated through cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). CV and EIS results were obtained in the electrochemical workstation, Autolab PGSTAT302N, (Ecochemie Co., Netherlands) in 0.5 M $VOSO_4$ + 3 M H_2SO_4 solutions at room temperature. A three-electrode system was utilized in the electrochemical test with microwave-treated graphite felt as the working electrode; saturated calomel electrode (SCE) and Pt foil were employed as the reference and counter electrode, respectively. Salt bridge with Rudin capillary was used to connect the reference and working electrodes. The scanning range of CV was limited from 0 V to 1.6 V (vs. SCE), and the scanning rate was 2 mV s^{-1}. Impedance spectra were obtained by sweeping various frequencies in the range of 10^{-2} Hz to 10^5 Hz. The potential was fixed at 0.79 V in all EIS measurements to ensure similar polarization.

2.2. Single cell evaluation

Constant current charge—discharge tests were performed with a single cell and CT2001D LAND battery test system (LAND Electronics Co., Wuhan). A piece of microwave-treated graphite felt with an active area of 12 cm^2 (3.0 cm × 4.0 cm) was used as a positive electrode. Nafion 212 ion exchange membrane was utilized as the separator. A graphite plate with a serpentine flow field on its surface served as the current collector. The cell was sealed with rubber washers. The initial positive electrolyte was 100 mL 0.5 M V (IV) + 1 M H_2SO_4 solution, which was stored in tanks outside the cell. The electrolytes were pumped into the compartments as flowing liquid during cell operation. The upper limit and lower limit of discharge voltage were 1.7 V and 0.8 V, respectively. The hydrogen electrode and H_2 replaced the graphite felt and V^{2+}/V^{3+} couple in the negative side. Another single cell with graphite felt-30 h as a positive electrode was prepared for comparison.

Download English Version:

https://daneshyari.com/en/article/1286511

Download Persian Version:

https://daneshyari.com/article/1286511

Daneshyari.com