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KOH etched graphite felt with improved wettability and activity for vanadium flow batteries

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ABSTRACT

In this work, a simple and effective method to activate graphite felt (GF) electrode by using KOH as etching agent is studied for vanadium flow battery (VFB) application. The surface of GF is etched by KOH at 800 °C to generate micropores and attain oxygen-containing functional groups, resulting in greatly improved electrolyte accessibility. Surface morphology, oxygen distribution and microstructure of the KOH etched graphite felts (eGFs) are characterized by SEM, EDX, XPS, XRD and Raman techniques. Due to the abundant exposed edge carbon sites and oxygen-containing functional groups introduced by KOH activation, electrochemical activity of eGFs towards both VO^{2+}/VO_2^+ and V^{2+}/V^{3+} redox couples are remarkably improved comparing with GF. In particular, eGF-2 (mass ratio of KOH/GF = 1.25) exhibits the best electrochemical activity and VFB performance among all eGFs. Moreover, the VFB with eGF-2 electrode can run at current density up to 250 mA cm^{-2} with the energy efficiency of 64%. Long-term cycle life test at higher current density of 150 mA cm^{-2} confirms the outstanding stability of eGF-2 electrode.

1. Introduction

The storage of intermittent renewable energy sources such as solar and wind power has attracted tremendous attention with the development of large-scale energy storage technologies. Vanadium flow battery (VFB) is a promising candidate due to its outstanding features such as long cycle life, eco-friendly, low cost and safety [1–5]. VFBs employ four different oxidation states of vanadium ions, i.e. VO^{2+}/VO_2^+ redox couple in positive electrolyte and V^{2+}/V^{3+} couple in negative electrolyte, which are sealed in two isolated tanks. Owing to the innate advantage that VFB employs the same element in both electrolytes, crossover contamination caused by the diffusion of different metal ions across the membrane is thus eradicated [1].

Since electrode is the key factor of power density and energy density of VFB, it is crucial to introduce an electrode with good stability and electrochemical activity [6–8]. Carbonaceous material, in particular graphite felt (GF) is widely applied in VFBs in consideration of its favorable physicochemical properties including high conductivities and corrosion resistance in strong acid [6]. However, GF still suffers from severe drawbacks such as inferior hydrophilic, low surface area as well as poor kinetic reversibility and electrochemical activity [7–9], resulting in poor battery performances of VFBs.

To address these issues, comprehensive researches have been conducted on GF to enhance its wettability and electrochemical activity toward VO^{2+}/VO_2^+ and V^{2+}/V^{3+} redox reactions. Noble metals (such as Pd [10], Ir [11], Bi [12]) and metal oxides (such as CeO_2 [13], ZrO_2 [14], Nb_2O_5 [15]) were deposited on the surface of the GF electrode as a catalyst to reduce the electrochemical activation barrier for the redox conversion. However, the high cost and inferior mechanical instability of noble metals hindered them from further commercial application [16]. Moreover, undesirable hydrogen evolution could be triggered by noble metal decoration due to the improved catalytic activity toward water splitting process, thus leading to a decline of energy efficiency in VFB performance [17]. Carbon nanomaterials, such as single-walled carbon nanotubes [18], multi-walled carbon nanotubes [19], electrospun carbon nanofibers [20], graphene [21] and nitrogen-doped carbon nanospheres [22], have also attracted growing interest recently due to their unique properties like high electrical conductivity, chemical stability and large surface area which can accommodate more active sites for vanadium redox couples [8]. However, how to keep these nano electrocatalysts stable on the GF

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during the long-term operation of VFB still remains great challenges [7,8]. Hence, activation GF itself would be the most reliable method to maintain its stability in the flowing vanadium electrolyte. Thermal activation [23], acid treatment [24] and electrochemical oxidation [25] strategies were reported as effective methods to introduce defects and oxygen-containing functional groups (e.g. hydroxyl and carboxyl) onto the surface of GF. Despite the obviously enhanced performance of VFB, the specific surface area of GFs improved little and even decreased caused by chemical oxidation [7,26].

KOH etching is a well-established method to develop particular pore sizes on the surface of carbon materials, such as carbon nanotubes, carbon fibers and graphene [27–31]. In this work, KOH was used as etching agent to generate micropores and attain oxygen-containing functional groups on the surface of GF fibers. The effect of KOH/GF mass ratio on the surface morphology, microstructure and wettability of eGFs are studied by SEM, XRD and Raman characterization as well as the electrolyte accessibility test. Electrochemical activity of eGFs towards VO^{2+}/VO_2^+ and V^{2+}/V^{3+} redox couples is evaluated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) methods. eGF electrode demonstrates high efficiency and excellent stability through VFB single cell test at current densities from 50 to 250 mA cm^{-2}.

2. Experimental

2.1. Materials

PAN based GF (Gansu Haoshi Carbon Fiber Co., Ltd.) was rinsed in ethanol and deionized water binary solution (volume ratio = 1:1) under ultrasonic wave to remove impurities before use. Nafion 115 membrane was purchased from DuPont Company and was treated by standard acid boiling procedure before use [32]. KOH and all other reagents were of analytical grade and used without further purification.

2.2. Electrode preparation

GFs were immersed in high concentration KOH solution in a PTFE container to form a uniform KOH crust on the surface of GF fibers, followed by vacuum drying at 90 °C for 10 h. The mass ratio of KOH/GF was adjusted by changing the concentrations of KOH solutions. Afterwards, KOH/GFs were preheated at 200 °C for 0.5 h, and subsequently calcined at 800 °C for 2 h. All the procedures were operated under N_2 atmosphere in a horizontal furnace. The resulting etched GFs (eGFs) were rinsed thoroughly with diluted HCl and deionized water to eliminate the residual potassium species. The eGFs applying mass ratio of 0.50, 1.25, 2.00 and 2.75 were labelled as eGF-1, eGF-2, eGF-3 and eGF-4, respectively. As a reference, a pristine GF was heated at 200 °C for 0.5 h and then at 800 °C for 2 h under nitrogen atmosphere without KOH etching and denoted as GF.

2.3. Electrode Characterization

The surface morphology of eGFs was characterized by scanning electron microscopy (SEM) on a ZEISS SUPRA 55 instrument at the acceleration voltage of 5 kV and the element content was analyzed by energy dispersive X-ray spectroscopy (EDX). The samples were analyzed by X-ray photoelectron spectroscopy (XPS) using a PHI Quantera SXM spectrometer (ULVAC-PHI) equipped with a hemispherical electron analyzer and a Al Kα X-ray source. The pressure in the measurement chamber was below 1.0×10^{-7} Torr. Nitrogen adsorption isotherm of eGFs was measured on ASAP 2020 micromeritics at −195.88 °C and the specific surface area was calculated by BET formula. The crystallographic data of the eGFs was collected with an X-ray diffractometer (XRD, D/max-2500 PC, Rigaku) in the range from 10° to 90° with a scan rate of 5° min^{-1} at a step size of 0.02°. Samples were analyzed utilizing Bragg-Brentano geometry at tube voltage of 40 kV and tube current of 100 mA. Raman spectra was measured by a LabRam HR800 Raman spectrometer with 532 nm YAG laser as the excitation source.

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were conducted on PARSTAT 2273 electrochemical workstation. A three-electrode cell was used with the eGF (1 cm × 1 cm) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a graphite plate as the counter electrode, respectively. CV was performed in 0.1 M VO^{2+} + 2 M H_2SO_4 solution from 0.4 V to 1.4 V and in 0.1 M V^{3+} + 2 M H_2SO_4 solution from −0.9 V to 0 V respectively, with a scan rate of 1 mV s^{-1}. EIS was carried out under 0.75 V in 0.1 M VO^{2+} + 2 M H_2SO_4 solution and −0.3 V in 0.1 M V^{3+} + 2 M H_2SO_4 solution respectively, with an excitation signal of 5 mV in the frequency range of 100 kHz to 10 mHz.

2.4. VFB single cell test

The VFB single cell was assembled by sandwiching the Nafion 115 membrane (7 cm × 7 cm) [33] between two pieces of eGF electrodes (5 cm × 5 cm × 0.5 cm) and then clamping the sandwich between two graphite polar plates as reported previously [34,35]. Two 50 mL solutions of 2 M $V^{3.5+}$ (VO^{2+}/V^{3+} = 1:1) with 2 M free sulfuric acid were applied as positive and negative electrolytes, respectively. The electrolytes cycle was driven by peristaltic pumps (BT00-300T) with a flow rate of 60 mL min^{-1}. The cell test was performed on CT-3008W-5V10A (Neware) battery testing system with the potential range from 0.8 V to 1.65 V. The charge-discharge test was carried out at current densities from 50 to 250 mA cm^{-2}, while the cycle life test was conducted at a constant current density of 150 mA cm^{-2}. The coulombic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE) were calculated as reported previously [36].

3. Result and discussion

3.1. Morphology Characterization

SEM and EDX images of GF and eGFs are shown in Fig. 1. Differences can be hardly found between GF and KOH activated GFs in low magnification SEM images (left column of Fig. 1) since the diameters of micropores on eGF fiber surfaces are mostly less than 2 nm. eGFs show rough and porous texture on its fiber surface compared to GF, as shown in the high magnification SEM images (right column of Fig. 1). Micropores generated in KOH activating can provide more active sites for the redox reactions between different valence vanadium ions. O mapping results qualitatively indicate that eGFs retain more oxygen-containing functional groups, which are considered as essential active site for both VO^{2+}/VO_2^+ and V^{2+}/V^{3+} redox reactions on electrode surface [7]. eGF-2 owns the highest O/C ratio among all eGFs. The introduction of oxygen-containing functional groups can be ascribed to the hydroxide reduction and carbon oxidation by KOH activating [37,38]. To further identify the accurate molar ratio of O and C elements, the XPS wide scan spectra in the binding energy range of 0–1200 eV was performed on GF and eGF-2 as shown in Fig. 2. The atomic oxygen content on the surface increases dramatically after KOH activation (from 3.32 at.% for GF to 7.14 at.% for eGF-2).

BET surface area of GF and eGF-2 is 1.1 m^2 g^{-1} and 17.6 m^2 g^{-1}, respectively. The surface area increase of eGF-2 could be ascribed to broadening of graphene layer interstices and consumption of graphene [29]. The exposed edge carbon sites generated in the