Journal of Power Sources 341 (2017) 270–279

Contents lists available at ScienceDirect

Journal of Power Sources

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

Water-activated graphite felt as a high-performance electrode for vanadium redox flow batteries

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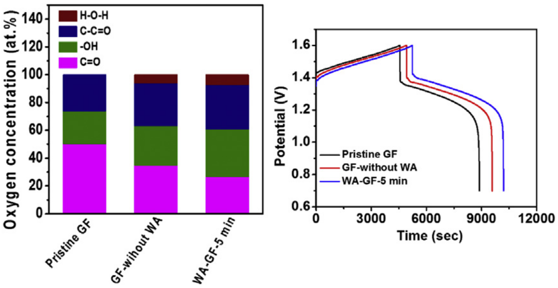
HIGHLIGHTS

- The effect of water activation on the electrochemical activity of GF is investigated.
- A high content of oxygen-containing groups improves the performance of VRFB.
- Improved wettability due to increased surface-active oxygen functional groups.
- WA-GF-5 min improves battery energy efficiency from 69.84% to 78.12% at 80 mA cm^{-2}.
- WA-GF-5 min acts as more powerful positive electrode for the VO^{2+}/VO$_2^+$ redox couple.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 August 2016
Received in revised form
28 November 2016
Accepted 2 December 2016
Available online 9 December 2016

Keywords:
Vanadium redox flow battery
Electrode
Electrochemical activity
Water activation
Water vapor

ABSTRACT

A simple, green, novel, time-efficient, and potentially cost-effective water activation method was employed to enhance the electrochemical activity of graphite felt (GF) electrodes for vanadium redox flow batteries (VRFBs). The GF electrode prepared with a water vapor injection time of 5 min at 700 °C exhibits the highest electrochemical activity for the VO^{2+}/VO$_2^+$ couple among all the tested electrodes. This is attributed to the small, controlled amount of water vapor that was introduced producing high contents of oxygen-containing functional groups, such as —OH groups, on the surface of the GF fibers, which are known to be electrochemically active sites for vanadium redox reactions. Charge—discharge tests further confirm that only 5 min of GF water activation is required to improve the efficiency of the VRFB cell. The average coulombic efficiency, voltage efficiency, and energy efficiency are 95.06%, 87.42%, and 83.10%, respectively, at a current density of 50 mA cm^{-2}. These voltage and energy efficiencies are determined to be considerably higher than those of VRFB cells assembled using heat-treated GF electrodes without water activation and pristine GF electrodes.

1. Introduction

Redox flow batteries (RFBs) are considered one of the most effective grid-scale electrochemical energy storage systems currently available because of their design flexibility, uncoupled energy and power capacities, high safety, quick response, low maintenance cost, long life cycle, and high energy efficiency [1–6]. In RFBs, energy is stored entirely within electrolytes rather than in electrode materials [7]. They store electrical energy through the chemical reaction of a

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http://dx.doi.org/10.1016/j.jpowsour.2016.12.004
0378-7753/

pair of reduced and oxidized species dissolved in two separate liquid electrolytes [8]. Among the various types of RFBs, all-vanadium redox flow batteries (VRFBs) have attracted considerable attention because they use active species of the same element as the positive electrolyte (VO^{2+}/VO_2^+) and negative electrolyte (V^{2+}/V^{3+}), which substantially minimizes the problem of active component crossover contamination across the ion exchange membrane [9,10]. A standard cell potential of 1.255 V is produced through the following electrochemical reactions in a VRFB:

$$\text{Positive electrode}: \ VO^{2+} + H_2O \leftrightarrow VO_2^+ + 2H^+ + e^- \quad E^0 = +1.00\,V \tag{1}$$

$$\text{Negative electrode}: \ V^{3+} + e^- \leftrightarrow V^{2+} \ \ E^0 = -0.255\,V \tag{2}$$

Because the redox reaction of vanadium ions occur at the electrode surface in each half cell, the energy efficiency of a VRFB mainly depends on the physicochemical properties of the electrode materials, which thus must be selected carefully. Graphite felt (GF) is a typical VRFB electrode material because of its wide range of operating potentials, corrosion resistance in the acidic solution, good electrical conductivity, high mechanical and chemical stability, porous three-dimensional network structure, and low cost [11–13]. However, GF without modification has a naturally hydrophobic surface and low specific surface area, which results in poor electrochemical activity in the VRFB [14,15]. Therefore, modifications are required to enhance the performance of GF [16]. Various methods have been reported by several groups, including acid treatment, electrochemical oxidation, thermal treatment, modification using nitrogen doping, and modification using metals [10,12,16–18]. The main aim of these methods was to increase the number of active sites at which the $VO^{2+}/VO_2{}^+$ redox reaction could occur by introducing more nitrogen- or oxygen-containing functional groups onto the GF surface, such as hydroxyl (−OH), carbonyl (−CO), and carboxyl (−COOH), which facilitates electron transfer and thus reduces the overpotential. However, these methods are unsuitable for commercial application because they use precious metals or dangerous concentrated acids, or involve difficult and time-consuming processing steps [19,20]. Thus, a new, simple, and time-efficient modification method with a reasonable cost is required to produce robust and abundant oxygen-containing functional groups. Previous studies have demonstrated that introducing a small, controlled amount of water vapor into the tube furnace enhances the catalytic activity of the materials because H_2O produces large numbers of oxygen containing functional groups, such as −OH groups on the surface of the GF fibers [21–28]. Moreover, using an optimal amount of water vapor led to the elimination of impurities adhered to the surface.

In this work, we report a simple, green, novel, time-efficient, and potentially cost-effective water activation (WA) method for improving the electrochemical activity of GF for use in VRFBs for the first time. Within 5 min water activation of the GFs, the VRFB

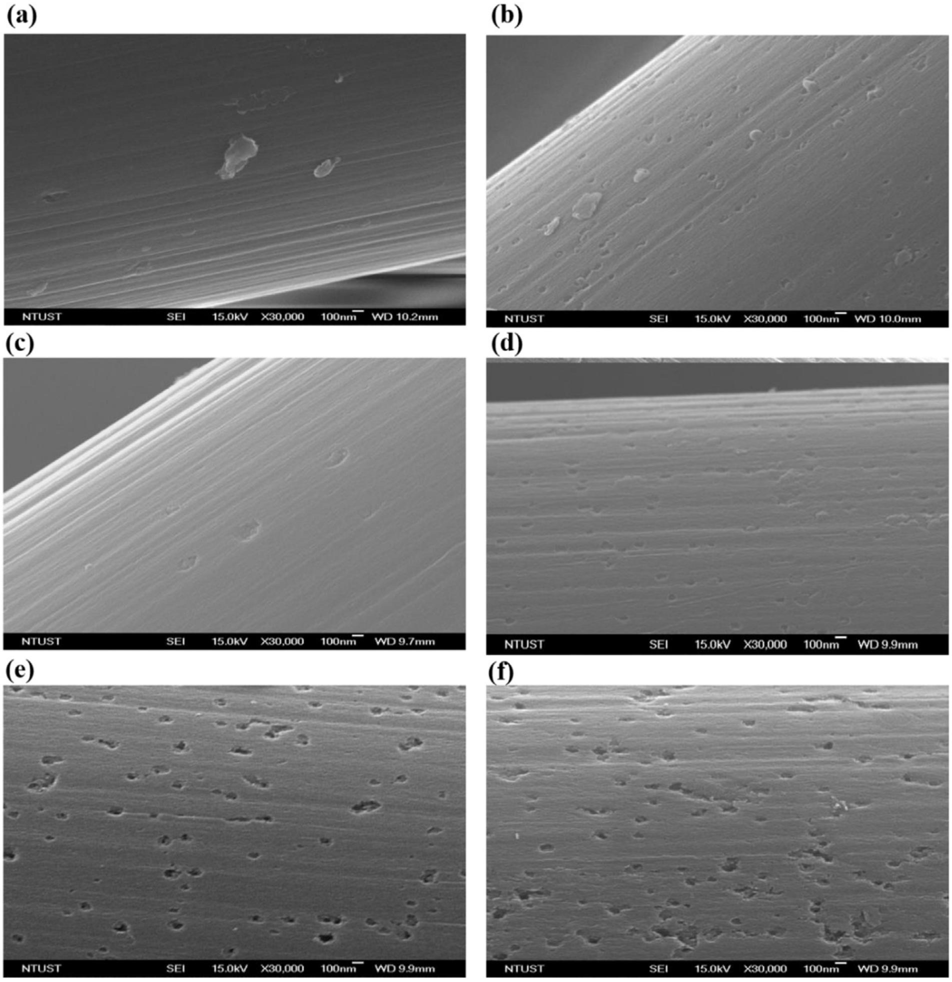

Fig. 1. SEM images at high magnification of (a) pristine GF, (b) GF-without WA, and WA-GF with the water vapor injection time of (c) 1 min, (d) 3 min, (e) 5 min, and (f) 10 min.