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The influence of compressed carbon felt electrodes on the performance of a vanadium redox flow battery

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ABSTRACT

Compressed carbon felt electrodes with various percentages of compression are prepared by stacking pieces of PVC gaskets; the performance of VRFB cells prepared using these electrodes is evaluated in order to better understand the influence of the compressed electrodes on the fundamental properties of VRFBs. It is found that the specific resistance and porosity of the electrodes decreases with increase of the percentage of electrode compression. In addition, as the percentage of electrode compression increases, the discharge time and maximum power of the VRFB cells gradually increase due to the increased electron transfer. The energy efficiency of the cell increases with the increase of the percentage of electrode compression up to 20%. When the percentage of electrode compression is greater than 20%, the energy efficiency decreases due to the combined effects of reduced cell resistance, poor electrolyte transport, and longer charge/discharge time. Based on our results, it can be concluded that compressed electrodes have a positive effect on cell performance; however, their inevitable reduced porosity is detrimental to electrolyte transport, thereby resulting in a decrease of energy efficiency. Consequently, it is suggested that carbon felt electrodes with an optimized percentage of compression have considerable potential for use in VRFB applications without incurring additional cost.

1. Introduction

Globally accelerating concerns about environmental pollution from the burning of fossil fuels and energy shortage have provoked great interest in the generation of electrical energy from renewable sources such as wind and solar [1–3]. However, the random and intermittent nature of these power sources induces low-quality output electricity, which affects the stability of the grid. Because energy storage systems (ESSs) can efficiently balance between power generation and consumption of renewable energy sources through load-leveling and peak-shaving strategies, they have emerged as a key technological challenge. The redox flow battery (RFB) has been considered to be one of the most promising large-scale ESSs, owing to its attractive features such as flexible design, high safety, high efficiency, and long cycle life. Unlike traditional batteries that store energy in electrode materials, RFBs are a rechargeable battery system in which an electrolyte containing one or more dissolved electroactive materials flows through an electrochemical cell that directly converts chemical energy to electrical energy. Among the various types of RFBs, the all-vanadium redox flow battery (VRFB), due to its nature of reduced cross-contamination by enlisting the same element, vanadium, in both electrolytes, is one of the most advanced RFBs and has reached the demonstration stage [4]. This VRFB is an electrochemical system capitalizing on reactions between two redox couples of V^{2+}/V^{3+} in a negative half-cell and VO^{2+}/VO_2^{+} in a positive half-cell to perform a reversible conversion between electrical energy and chemical energy.

As one critical component in a VRFB stack, the electrode, does not take part in the electrochemical reaction directly, but provides proper electrochemical reaction sites for the active substances. In addition, the electrode contributes to the stack polarization through the ohmic resistance and charge transfer polarization, because the redox reaction takes place on the electrode surface. The typical VRFB electrode materials, because of their stable three-dimensional network structure, relatively low cost, large surface area, high conductivity, and good chemical/electrochemical stability, are carbon felts. However, modification of the electrode materials is still necessary in order to enhance the kinetic reversibility and electrochemical activity. Many researchers have attempted to enhance the VRFB performance using heat treatment [5] and by depositing conductive metals such catalysts like Pt, Au, Ir, Pd, Ru,

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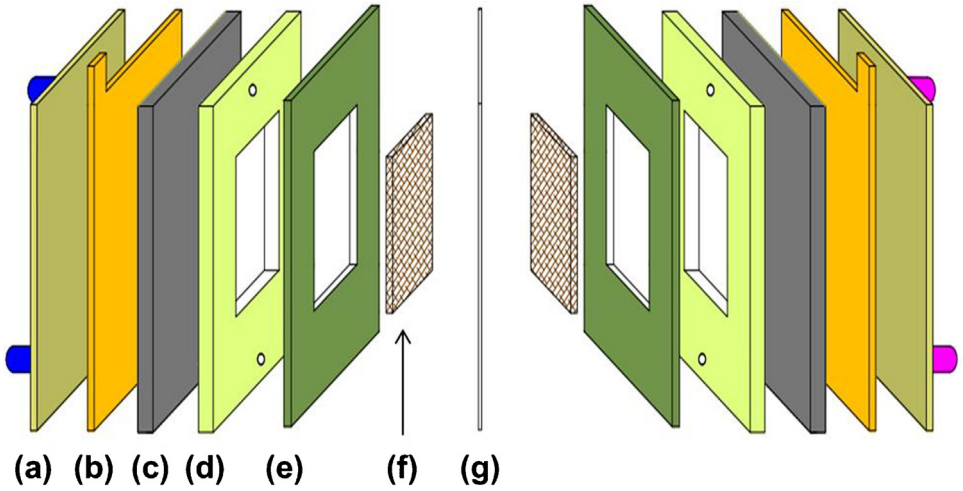

Fig. 1. Schematic diagram of a single flow cell: (a) acrylic endplate, (b) copper current collector, (c) graphite polar plate, (d) polypropylene manifold frame, (e) PVC gasket, (f) carbon felt electrode, and (g) ion exchange membrane.

Mn_3O_4, WO_3, and Bi [6–13], which reduce the activation barrier for the redox conversion. It was found using cyclic voltammetry and charge/discharge cycling measurements that the electrode with the best electrochemical behavior was one that was modified with Bi. In this regard, modification of the electrode materials is an effective way to enhance the RFB performance.

Another method to enhance the RFB performance without incurring additional cost is electrode compression. The compression of an electrode such as one made of carbon felts effects the RFB performance because this performance depends heavily on the cell resistance and the mass transport property. There is a tradeoff between these two fundamental parameters with electrode compression, through which the RFB performance can be optimized for electrode compression. Despite the importance of this process, few studies have been performed to understand the role of electrode compression in RFB performance. Recent research done by Chang et al. has shown that the compression of a carbon felt electrode effects the electrical, mechanical, and morphological properties in VRFB [14]. However, research into VRFB performance, including charge/discharge behavior, has not been performed. Therefore, the objective of this work is to investigate the influence of the compression of carbon felt electrodes on their VRFB performance, including charge/discharge behavior, cell resistance, coulombic efficiency, voltage efficiency, and energy efficiency as well as to determine their porosity and specific resistance.

2. Experimental

Specific resistance measurements of carbon felt electrodes have been done with a Source Meter (Agilent, 34401A digital multimeter); this device includes two copper foil tapes to maintain the samples. The compression of carbon felt electrodes was adjusted by stacking the pieces of PVC gasket, which were used as spacers. Resistance measurements were done during this process, so the only results available for the moment represent the addition of the bulk resistance of the electrode sample and the two types of contact resistance between the samples and the copper plates. In order to measure the relatively large porosity of the electrode samples, the pycnometer method (pycno) was used to study the porosity change under various percentages (0, 10, 20, 30%) of electrode compression [16].

The VRFB cell performance was tested using an in-house designed flow cell system, which consists of a single cell connected with two Pyrex® glass beaker reservoirs through a peristaltic Masterflex pump (Cole-Parmer instrument Co., Chicago, IL, USA) and Viton® tubing. As shown in Fig. 1, the VRFB single flow cell was composed of a symmetric cell consisting of two copper current collectors, two graphite polar plates (5 mm, SK507, Morgan Korea Co., Ltd.), two polypropylene frames, PVC gasket materials, two carbon felt electrodes (4 mm, XF-30A, Toyobo Co., Ltd.) with effective reaction area of 30 cm^2, and a Nafion® 117 membrane (Dupont, USA). The compression of carbon felt electrodes was adjusted in the range of 0–30% by stacking the pieces of PVC gaskets. Before the cell assembly, the Nafion® 117 membrane was rinsed using 3% H_2O_2, followed by soaking in 0.5 M H_2SO_4 for 8 h at 80 °C; the membrane was then stored in pure water. The VO^{2+} solution was prepared by dissolving $VOSO_4{\cdot}3.5H_2O$ (99.9%, Wako Pure Chemical Industrials, Osaka, Japan) in 2.0 M of H_2SO_4 solution. The V^{3+} solution was prepared by the electrochemical reduction of the VO^{2+} solution. 50 mL of 2.0 M VO^{2+} and V^{3+} in 2.0 M H_2SO_4 solutions were used as initial positive and negative electrolytes, respectively. Each electrolyte was circulated at a flow rate of 50 mL min^{-1}.

The charge/discharge test was conducted between 0.8 V and 1.6 V under a constant current mode at current densities varying from 20 to 70 mA cm^{-2} at 25 °C using a battery cycler (Maccor 4000 Series). The charge/discharge of the cell underwent each of 7 cycles at the same current density. The coulombic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE) of the cell were calculated as in the following equations [15]:

$$CE = (\text{discharge capacity}/\text{charge capacity}) \times 100 \quad (1)$$

$$VE = (\text{middle point of discharge potential}/\text{middle point of charge potential}) \times 100 \quad (2)$$

$$EE = CE \times VE \quad (3)$$

The cell resistance was calculated from Eq. (4) for the discharge obtained from the cell potential and the open circuit potential (OCP) [17];

$R_D = (E_M - E_D)/I_D$ (4) where R_D [Ω] is the cell resistance for discharge, E_M is the OCP at the rest time between charge and discharge,