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Development of Carbon Composite Bipolar Plates for Vanadium Redox Flow Batteries

Nam Jin Lee,[†,‡] Seung-Wook Lee,[†] Ki Jae Kim,[†,*] Jae-Hun Kim,[†] Min-Sik Park,[†] Goojin Jeong,[†] Young-Jun Kim,[†] and Dongjin Byun[‡]

[†]*Advanced Batteries Research Center, Korea Electronics Technology Institute, Gyeonggi 463-816, Korea*
[*]*E-mail: kijaekim@keti.re.kr*
[‡]*Department of Materials Science and Engineering, Korea University, Seoul 136-713, Korea*
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Carbon composite bipolar plates with various carbon black contents were prepared by a compression molding method. The electrical conductivity and electrochemical stability of the bipolar plates have been evaluated. It is found that the electrical conductivity increases with increasing carbon black contents up to 15 wt %. When the carbon black contents are greater than 15 wt %, the electrical conductivity decreases because of a poor compatibility between epoxy resin and carbon black, and a weakening of compaction in the carbon composite bipolar plate. Based on the results, it could be concluded that there are optimum carbon black contents when preparing the carbon composite bipolar plate. Corrosion tests show that the carbon composite bipolar plate with 15 wt % carbon black exhibits better electrochemical stability than a graphite bipolar plate under a highly acidic condition. When the optimized carbon composite bipolar plate is applied to vanadium redox flow cells, the performance of flow cells with the carbon composite bipolar plate is comparable to that of flow cells with the graphite bipolar plate.

Key Words : Redox flow battery, Bipolar plate, Carbon composite, Electrical conductivity, Electrochemical stability

Introduction

With increasing demands for energy due to the global economic development, electrical energy storage systems have attracted much attention. Redox flow batteries are one of promising energy storage systems owing to moderate cost, long cycle life, flexible design, and fast response time.[1] Redox flow battery, which was first proposed by Thaller in 1975,[2] stores energy by using two soluble redox couples which are oxidized and reduced. Several kinds of redox couples such as iron/chromium,[2] soluble Pb battery,[3] zinc/cerium,[1] zinc/bromine,[4,5] and vanadium/vanadium[6,7] have been proposed. Among the flow batteries, all vanadium redox flow batteries have been widely investigated due to their low ion cross-over by use of the same element in both half-cells.[1] In the flow batteries, bipolar plate (BP) is one of the main components, which might contribute up to 30% of the total cost of the batteries.[8] The main functions of the BP are connection of each cell, conduction of current from cell to cell, and prevention of electrolyte leakage. Thus, the BP should be highly conductive and chemically stable in the highly acidic environment inside the flow batteries.

One of the most used materials for BP is graphite because it is electrically conductive and easy to machine. However, the graphite BP has been reported to have several major disadvantages such as high cost to handle and difficulty to assemble due to a brittle nature of graphite.[9] Many researchers have attempted to improve the performance and to reduce the cost of the graphite BP by using graphite composites including some reinforcing materials by the compression molding method.[10,11] However, the BPs have been developed for use in fuel cell applications and no detailed data on BPs for vanadium redox flow batteries (VRFBs) have been disclosed so far. The BPs for fuel cells could not be directly applied to flow batteries because the operating environment is highly acidic states in comparison with that of fuel cells. If the BPs are used in flow batteries, the graphite particles of the BP can be dissolved into the electrolytes. Those particles may be piled up in the flow path, leading to the change of the flow rate and the electrochemical performance degradation. Therefore, there are needs to develop the BPs which have high durability under highly acidic environment for vanadium redox flow batteries.

In this study, carbon composite bipolar plates for vanadium redox flow batteries were prepared by a compression molding method. To verify their potential for use in VRFBs of highly acidic conditions, the electrical conductivity and corrosion resistance of the BPs have been investigated using electrochemical techniques and the cell performance of VRFBs employing the BPs is demonstrated.

Experimental

The materials employed for carbon composite bipolar plates were graphite (Morgan Korea), carbon black (Super-P), resin (Epoxy, Tohto Kasei), hardening agent (TAMANOL 758, Arakwa Chemical), and hardening accelerator (Triphenylphosphine, Arkema). The materials were uniformly mixed together for 2 min using an M20 universal mill (IKA) with a weight ratio 79-x:x:13:7:1 (graphite:carbon black:resin:

hardening agent:hardening accelerator). To optimize the composition of the carbon composite BPs, contents of the carbon black were changed from 1 to 20 wt %. After mixing, the mixture was placed into a steel mold frame with inner dimensions of 100 × 100 mm. The steel mold was hot-pressed at 100 °C with a pressure of 100 kgf cm^{-2} for 10 min and at 190 °C with a pressure of 200 kgf cm^{-2} for 40 min in sequence.

Electrical conductivity of the carbon composite BPs was measured using a 4-point probe technique (Loresta GP, Mitsubishi Electric).[12] The morphologies of the BPs were examined by a field emission scanning electron microscope (FE-SEM, JEOL JSM-7000F) after Pt coating. Especially, cross sectional images of the BPs were obtained after preparation of samples by cross sectional polishing with Ar ion beam (JEOL SM-0901). To analyze corrosion characteristics of BPs, potentiodynamic polarization tests were carried out using a potentiostat/galvanostat (VMP-3, Bio-logic) in a three-electrode cell consisting of the BP working electrode, platinum mesh counter electrode, and a saturated calomel electrode (SCE) as a reference. The tests were performed from 1.0 to 2.0 V *vs* SCE in 2.5 M H_2SO_4 solution at room temperature with a scan rate of 5 mV s^{-1}.

For VRFB cell test, electrolytes were prepared by dissolving 2 M $VOSO_4$ (Aldrich, 99.5%) in 2.5 M H_2SO_4 solution (Aldrich, 99.9%). Commercial carbon felt (GF-3F, Nippon carbon) was used for both electrodes and a Nafion separator (N117, Dupont) was used as an ion exchange membrane. The test cells were charged and discharged between 1.7 and 0.8 V at a current density of 40 mA cm^{-2}. The flow rate was fixed at 1.37 mL s^{-1}.

Results and Discussion

Figure 1 shows the electrical conductivity variation of the carbon composite BPs with various carbon black contents. The electrical conductivity increases with increasing carbon black contents up to 15 wt %. It could be explained by noting that the carbon black is acting as a conductive agent between graphite particles because the particle size of the carbon black is much smaller than that of graphite. On the other hand, when the carbon black contents are greater than 15 wt %, the electrical conductivity decreases. The result implies that there is an optimum point in carbon black

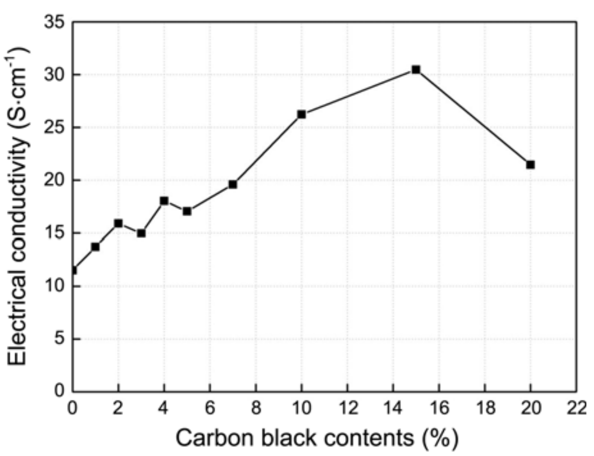

Figure 1. Electrical conductivity of the carbon composite BPs with various carbon black contents.

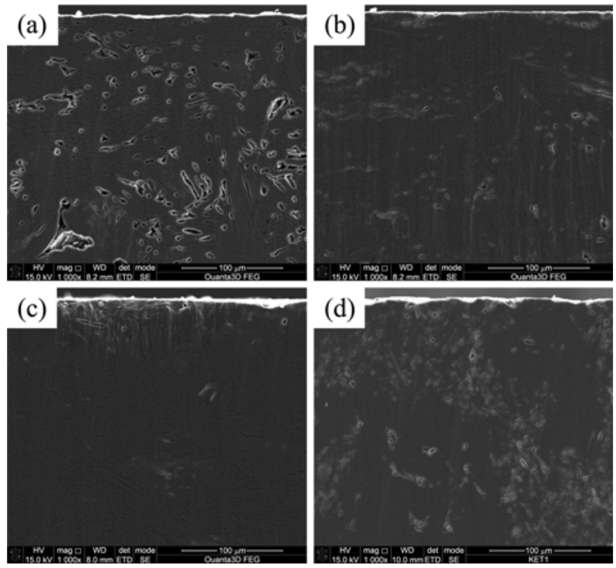

Figure 2. Cross-sectional SEM images of the carbon composite BPs with (a) 0%, (b) 5%, (c) 15%, and (d) 20 wt % carbon black contents.

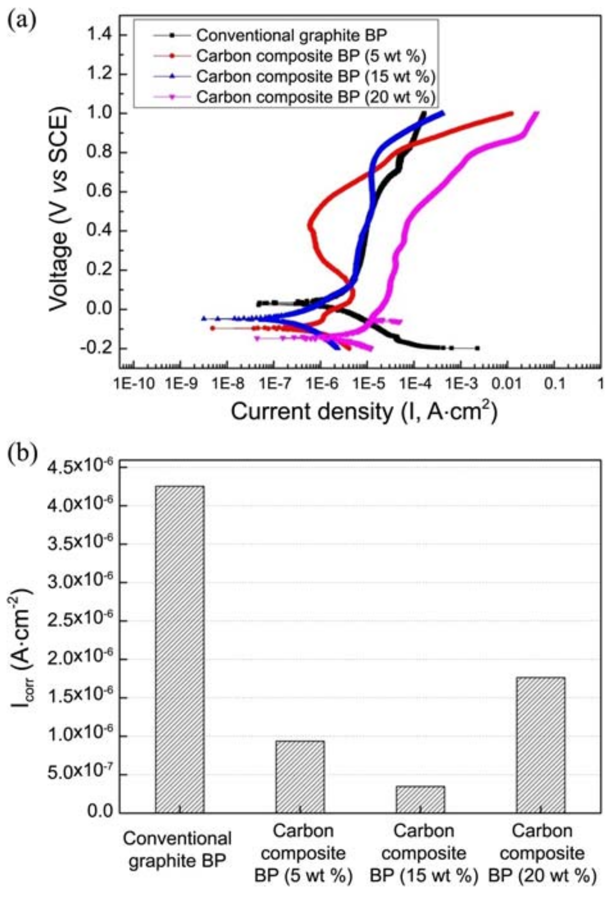

Figure 3. (a) Polarization curves of the carbon composite BPs and (b) corrosion current densities obtained using an extrapolation analysis from Tafel plots.

contents. Figure 2 presents the cross-sectional images the carbon composite BPs with carbon black of 0, 5, 15, and 20 wt %, respectively. It is observed that the carbon composite BP prepared without carbon black is not compact and there are lots of pores inside it (Fig. 2(a)). As the carbon black content increases, the BPs becomes more compact and the number of pores inside it tends to be reduced (Fig. 2(b) and (c)). In the case of the BP with the carbon black contents greater than 15 wt % (Fig. 2(d)), some pores begin to appear again inside of the BP. This would be explained by a poor compatibility between epoxy resin and carbon black, and a weakening on compaction of the BP. These observations support that the electrical conductivity first increases with increasing carbon black contents and an optimum point of carbon black contents exists.

To investigate the corrosion behavior of the carbon composite BPs with various carbon black contents, polarization tests were carried out in 2.5 M H_2SO_4 solution at room temperature and polarization curves and corrosion current densities are shown in Figure 3. The corrosion current density (exchange current density, I_{corr}) and potential were obtained using an extrapolation analysis from Tafel plots (log *i vs* potential, *i*=current density).[13] It is clearly seen that the carbon composite BP has much lower corrosion current density when compared to a conventional graphite BP. This result would be owing to the high electrochemical stability of the epoxy resin in the composite material. In other words, epoxy resin would protect graphite and carbon black against highly concentrated sulfuric acid. When the carbon contents are greater than 15 wt %, over the entire range of potential, current density is higher than that of the conventional graphite BP. As carbon black contents exceed the optimum point, compatibility between carbon black and epoxy resin is getting poor, so that bare carbon black and graphite could be exposed to the strong acid electrolyte. Therefore, it is concluded that the optimized carbon composite BP has better electrochemical stability in the VRFB environments.

Based on the electrical conductivity and corrosion test results, the carbon composite BP with 15% carbon black appeared to be the optimized BP, which was used in VRFB cell tests. Figure 4(a) shows a comparison of voltage profiles of the VRFB cells for the first cycle. The cells employing the conventional graphite BP and the carbon composite BP with 15 wt % carbon black, respectively, show almost the same charge and discharge profiles even though conventional graphite BPs have better electrical conductivity (around 3 × 10^2 S cm^{-1}) than the carbon composite BP with 15 wt % carbon black. This result implies that the critical resistivity of BPs affecting the cell performances may exist. Coulombic, voltage, and energy efficiency results of the VRFB cells are demonstrated in Figure 4(b)-(d). According to the comparison, coulombic efficiency of the carbon composite BP with

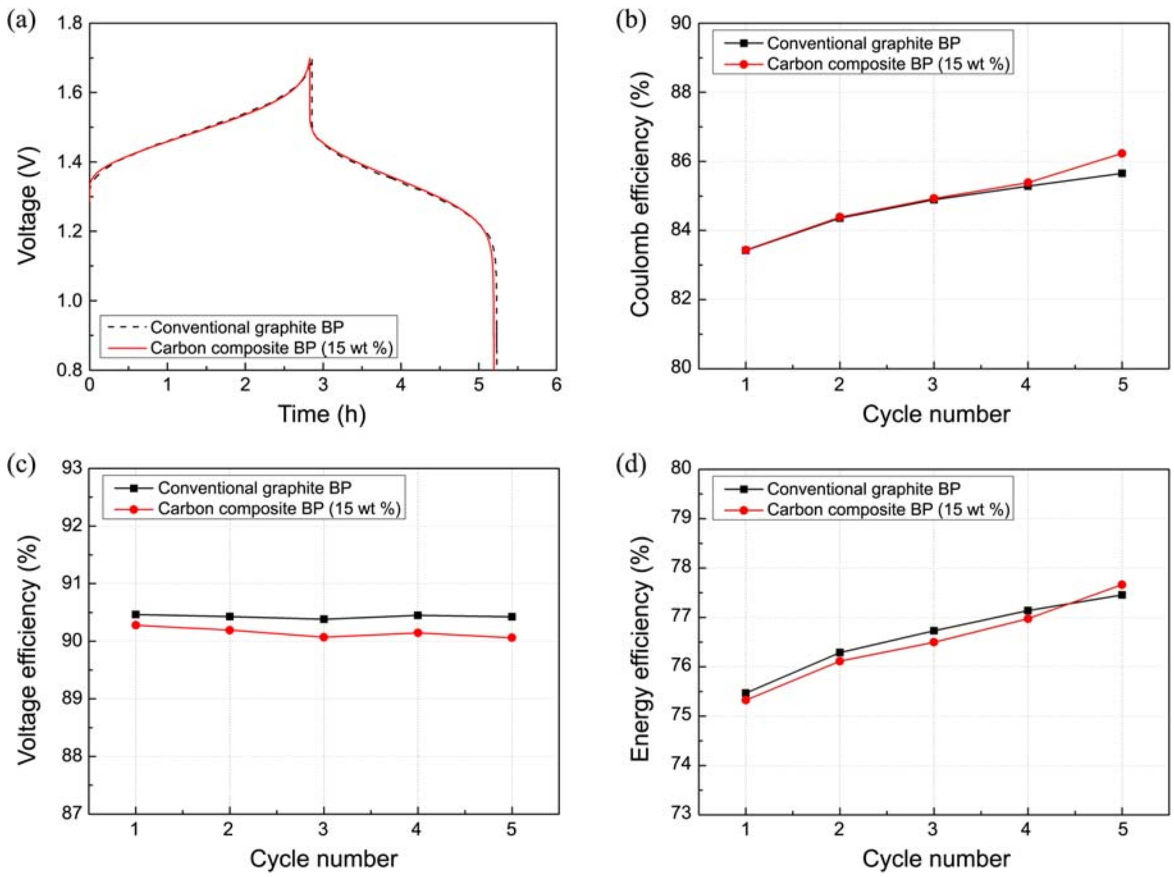

Figure 4. Electrochemical performances of VRFB cells employing the carbon composite BP with 15 wt % carbon black and the conventional graphite BP; (a) voltage profiles for the first cycle, (b) coulombic, (c) voltage, and (d) energy efficiencies.

15 wt % carbon black is slightly higher than that of the conventional graphite BP from the forth cycle (Fig. 4(b)). On the other hand, it is observed that voltage efficiency of the conventional BP is slightly higher than the carbon composite BP with 15 wt % carbon black because it has higher electrical conductivity. Overall, both BPs show almost similar energy efficiency. From the results, it is concluded that the carbon composite BPs with an optimized carbon content have a considerable potential as BPs for VRFB systems because the electrochemical performance is comparable to the conventional graphite BPs and the carbon composite BPs have relatively high electrochemical stability.

Conclusions

The properties of carbon composite BPs with various carbon black contents have been investigated in terms of electrical conductivity and electrochemical stability. The carbon composite BP with 15 wt % carbon black exhibited a reasonable electrical conductivity and increased electrochemical stability in highly acidic environments of VRFBs. Moreover, this carbon composite BP showed competitive performances under both anodic and cathodic conditions of VRFB cells. Therefore, it is suggested that the carbon composite BPs with an optimized carbon black content have a considerable potential for the VRFB applications.

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