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Durability of graphite coated carbon composite bipolar plates for vanadium redox flow batteries



COMPOSITE

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ABSTRACT

Composite bipolar plates for vanadium redox flow batteries (VRFBs) and fuel cells are coated with expanded graphite to decrease the interfacial contact resistance of the carbon composite. The bipolar plates of vanadium redox flow batteries are exposed to electro-chemical corrosion, which might degrade the graphite coating layer. From two types of graphite foil, i.e., pyrolytic graphite and expanded flake-type graphite, the former has higher durability because its graphene sheets are crystallized in a planar direction with a highly oriented structure, which has a stronger van der Waals bonding.

In this study, the characteristics of the pyrolytic graphite and expanded flake-type graphite are investigated with respect to the porosity of graphite. The durability of the graphite coating of the carbon/epoxy composite bipolar plate during the electrochemical reaction in vanadium electrolytes, based on highly concentrated sulfuric acid, is investigated. The areal specific resistances (ASRs) of the bipolar plates coated with pyrolytic graphite are measured, from which the ASR is expressed in terms of modulus of the graphite based on the Hertzian contact model. A single cell test is performed to evaluate the performance of the developed bipolar plate.

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1. Introduction

Recently, electric power management has become an important issue as power consumption has been increased, but the construction of new power plants is restricted because of environmental problems and the NIMBY attitude. In addition, because the power supply from renewable energy sources, such as solar and wind power, is unstable, the use of a power stabilization system is necessary. Therefore, the needs for energy storage systems (ESSs) are increasing, which enable the storage of excess electricity during non-peak time and release of it when the electricity demand increases [1,2].

In the past, lithium ion batteries were commonly used for ESSs; however, due to their explosiveness, such batteries have been replaced by vanadium redox flow batteries (VRFBs). The VRFB has no explosive character, as it uses a liquid electrolyte based on sulfuric acid, and the energy capacity of VRFBs is easily controlled by the amount of electrolyte. Basically, the charge and discharge of VRFBs occur through the reduction and oxidation of vanadium ions in the electrolytes based on sulfuric acid. The cathodic reaction is as follows:

$$VO_2^+ + 2H^+ + e^- \leftrightarrow VO^{2+} + H_2O$$
 (1)

In an anode, the reaction is as follows:

$$\mathsf{V}^{2+} \leftrightarrow \mathsf{V}^{3+} + e^{-} \tag{2}$$

These reactions occur simultaneously in the electrodes [3].

A VRFB system generally consists of a stack, two liquid electrolyte tanks, and two pumps, as shown in Fig. 1(a) [4]. A cell is composed of a proton exchange membrane, two electrodes, two flow frames, and two bipolar plates, as shown in Fig. 1(b). For the electrodes, carbon felt is used, which provides a large reactive surface and an electrolyte path. The flow frame is generally made of polymer, and it supports other components. The bipolar plate which separates each cell is generally made of graphite because it is highly conductive and resistant to sulfuric acid [5]. However, the graphite bipolar plate is very brittle and has low mechanical properties, which is not adequate for the VRFB as it has a large reactive area to compensate the low energy density less than 100 mA/cm² [6]. To overcome this issue, Kim et al. have developed a carbon/epoxy composite bipolar plate that has



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(b)

Fig. 1. Schematic diagrams of the VRFB: (a) a whole system; (b) a single cell.

an expanded flake-type graphite coating layer; this bipolar plate achieved both high electrical conductivity and good mechanical properties [7].

In VRFBs, all the components are exposed to the highly concentrated sulfuric acid which is a main ingredient of the electrolyte. In addition, the cell voltage can be higher than the necessary potential for water electrolysis, and water might be decomposed into oxygen and hydrogen during operation [8]. This phenomenon occurs mainly near the surface of bipolar plates, especially the graphite coating layer. If the water penetrated into the graphite is electrolyzed, then the generated gas may delaminate the graphite layer. Furthermore, oxygen molecules may combine with the graphite because the sulfuric acid in the electrolyte is a very strong oxidizing agent [9]. The oxidized graphite has weaker bonds between the graphene layer, which causes the intercalation and exfoliation of graphite eventually [10].

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