



Highly accurate apparatus for electrochemical characterization of the felt electrodes used in redox flow batteries



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HIGHLIGHTS

- An electrochemical analysis cell was devised for the felt electrodes.
- The test with this analysis cell was easy and simple to screen the felt electrodes.
- The analysis cell showed excellent reproducibility in cyclic voltammetry analysis.
- The analysis cell was useful to distinguish the electrode performance finely.
- We could predict the actual battery performance precisely with this analysis cell.

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ABSTRACT

Because of the rise in renewable energy use, the redox flow battery (RFB) has attracted extensive attention as an energy storage system. Thus, many studies have focused on improving the performance of the felt electrodes used in RFBs. However, existing analysis cells are unsuitable for characterizing felt electrodes because of their complex 3-dimensional structure. Analysis is also greatly affected by the measurement conditions, viz. compression ratio, contact area, and contact strength between the felt and current collector. To address the growing need for practical analytical apparatus, we report a new analysis cell for accurate electrochemical characterization of felt electrodes under various conditions, and compare it with previous ones. In this cell, the measurement conditions can be exhaustively controlled with a compression supporter. The cell showed excellent reproducibility in cyclic voltammetry analysis and the results agreed well with actual RFB charge-discharge performance.

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1. Introduction

The dependence on the renewable energy sources is expected to rapidly increase worldwide because of dwindling fossil fuel reserves. According to the 2011 annual report of the European Commission, renewable energy will comprise 55–77% of total final energy consumption by 2050, compared to less than 10% in 2010 [1]. However, renewable energy is not a dispatchable energy system because of intermittence and fluctuations in electricity generation. As a solution

to such problems, large-capacity energy-storage systems, in conjunction with renewable energy, have been proposed. Such energy-storage devices have also been effectively used in smart grids in order to balance energy supply and demand. Among various energy-storage systems, the redox flow battery (RFB) is the most competitive in the 10 kW to 10 MW power range [2–4]. It affords rapid response, a long lifetime, low self-discharge, and the possibility of independently regulating the power and energy capacity.

A characteristic of RFBs is that redox-active species are present in the electrolyte, not on the electrode, which makes the decoupling of power and energy capacity possible. However, in RFBs, more steps are required to complete the reduction or oxidation of the redox-active species. Such species adsorb onto the electrode surface, where they accept or lose electrons, and are subsequently desorbed.

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This complicated process makes the reaction rate sluggish and increases the overpotential of the battery. For example, V^{2+}/V^{3+} and VO^{2+}/VO^{+} in all-vanadium RFBs, Br/Br^{-} in zinc–bromine RFBs, and Cr^{2+}/Cr^{3+} in Fe/Cr RFBs are all characterized by sluggish reaction rates [5–10]. In addition, many RFB systems use corrosive materials as the supporting electrolyte, such as sulfuric acid in all-vanadium RFBs, hydrochloric acid in Fe/Cr RFBs, and zinc bromide solution in zinc–bromine RFBs. Since these supporting electrolytes deactivate common metal electrodes, carbon-based electrodes are preferable for RFBs. However, carbon electrodes have inferior kinetics and reversibility compared to metal electrodes.

To overcome these limitations, graphite and carbon felts with large specific surface areas are commonly used as electrodes in RFBs, especially in all-vanadium RFBs. Such felt electrodes afford a large number of reaction sites where the electron-transfer reaction can take place. In addition, various approaches have been proposed to further enhance the electrochemical properties of felt electrodes by (1) attaching oxygen functional groups [11–15]; (2) including metal catalysts such as Ir, CuPt₃, Bi, Pt, Pd, Au, Mn, Te, and In [16–21]; (3) impregnating metal oxide particles such as WO_3 and Mn_3O_4 [22,23]; (4) doping nitrogen molecules [24,25]; and (5) introducing carbon materials in the form of nanotubes, nanofibers, and graphene [26–30].

To analyze the electrochemical properties of the felt electrodes in RFB systems, a charge–discharge experiment must be performed in a flow cell, which is time-consuming and labor-intensive. Moreover, the effects of electrolyte leakage, cross-over of active species through membranes, and electrolyte flow distribution must be taken into account along with the electrochemical characteristics of the felt electrodes. Hence, a simple analysis apparatus is needed for efficiently investigating the felt electrodes.

In actual RFBs, the electrochemical characteristics of the felt electrode are strongly affected by its compression ratio and the contact strength between the felt electrode and current collector. For example, the peak potential separation in cyclic voltammetry (CV) decreases and the reversibility of the electrode reaction increases as the contact strength increases. However, so far, no reported analytical method or apparatus for assessing the electrochemical properties of felt electrodes considers all these factors. Without considering these factors, the electrochemical analysis results cannot be closely correlated to battery performance. Previous studies have generally adopted three-electrode cells with the working electrode, wherein the felt is directly connected to the platinum wire. The contact strength and interfacial area between the felt and current collector cannot be controlled precisely in such cells, even though they are important variables that determine the electrochemical performance of the felt. To remedy these shortcomings, some studies have prepared the working electrode by sandwiching the felt electrode between two plastic sheets [13,16,29,31]. One sheet had a hole of fixed size, which served as the working area. The other sheet with the conductive metal, such as Ti plate [13], Pt wire [29], or Ag wire [16] functioned as the current collector. The inserted felt electrode can be divided into two regions: the central region, which is in direct contact with the electrolyte through the hole, and the rim region, which is interlocked by the two plastic sheets. The compressed rim region also takes part in the electrode reaction, as it is soaked in the electrolyte because of capillary action. In this case, the hole area cannot reflect the working electrode area. Therefore, there is growing need to develop a highly accurate and practical apparatus for analyzing the electrochemical properties of felt electrodes by controlling the main factors that strongly affect the performance of actual RFB systems.

In this work, we have devised a new type of electrochemical analysis cell for the felt electrode, which can control the vital

variables in RFBs, viz. compression ratio as well as contact strength and area. In order to evaluate the suitability of the cell as an analysis apparatus, the reproducibility of the cell was examined through CV analysis of felt electrodes and the results were compared with those of previous methods. In addition, electrochemical characterization of the felt electrodes was performed by varying different conditions, including material type, compression ratio, and thermal pretreatment durations. The characterization results were compared to the charge–discharge performance of a single flow cell under the same conditions to confirm that the results from the new analysis cell satisfactorily match actual RFB performance.

2. Experimental

2.1. Design of electrochemical analysis cells

Three types of cells were compared to investigate the electrochemical characteristics of the felt electrodes (Fig. 1). All the cells had a three-electrode system: a working electrode, a counter electrode, and an Ag/AgCl (3.0 M) reference electrode. The detailed design of cell #1 is shown in Fig. 1a. A felt with 5 mm diameter was chosen as the working electrode and was directly connected to the Pt wire. The felt electrode was hung on the Pt wire in an uncompressed state. Here, the Pt wire functioned as the current collector. The same felt electrode with an area of 3 cm² was used as the counter electrode. It was also directly connected to the Pt wire. To prevent kinetic limitation on the former, the area of the counter electrode was 15.3 times larger than that of the working electrode. The working electrode, counter electrode, and reference electrode were placed in a single 40-mm-diameter vessel. The distance between the working electrode and the tip of the reference electrode was 11.5 mm.

In cell #2 (Fig. 1b), the working electrode was prepared by sandwiching the felt electrode between two plastic sheets. One sheet had a 5-mm-diameter hole that served as the working area. The other sheet with the Pt wire functioned as the current collector. The counter electrode was the same as that in cell #1.

Cell #3 (Fig. 1c) was developed using our own design. A cylindrical felt electrode was placed on a graphite plate. The felt electrode was cut to a predetermined size by using a punch having a diameter of 5 mm. A 0.1-mm-thick coating of polytetrafluoroethylene (PTFE) was applied to the entire graphite plate, except for the central hole, through which the felt electrode was kept in contact with the graphite plate. The diameters of both the circle and working electrode felt were kept constant at 5 mm. A compression supporter was placed on the other side of felt electrode. The felt electrode was pressed between a graphite plate and compression supporter. The compression supporter had a center bar with a constant depth (d), which compressed the felt electrode to a constant thickness. The electrolyte was supplied through the open area of the compression supporter. The counter electrode with 3 cm² area was fixed onto the graphite plate using two felt holders constructed from PTFE plates. The counter electrode was inserted into one holder which had the pore of the same shape as the electrode and was covered by the other holder in the form of a mesh. A copper plate was assembled next to the graphite plate and used as the current collector. The reference electrode was inserted through the PTFE fitting on top of the electrolyte chamber. The distance between the working electrode and the tip of the reference electrode was kept constant at 22.5 mm.

2.2. CV analysis

The reduction/oxidation characteristics of VO^{2+}/VO_2^+ and V^{2+}/V^{3+} were investigated using CV. The positive (2.0 M $VOSO_4$) and

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