

Characteristics of the all-vanadium redox flow battery using anion exchange membrane



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ABSTRACT

Three commercial anion exchange membranes were evaluated the chemical stability with an increase of soaking time in a pentavalent vanadium ion (VO_2^+) solution. The membrane resistances of anion exchange membranes in 1M (mol/L) H_2SO_4 aqueous solution were measured as an indicator of chemical stability. AFN membrane (ASTOM Co., Japan) was selected as a separator in an all-vanadium redox flow battery (V-RFB). The cell performance of V-RFB using AFN membrane was measured at a current density of 60 mA/cm². The cell resistance for the charge had almost the same value (in the range of 3.47–3.67 Ω cm²) with an increase in the state of charge (SOC). For the discharge, the cell resistance had almost the same value (in the range of 2.00–2.25 Ω cm²) with an increase in the state of discharge (SOD). The cell efficiency of the V-RFB using the AFN membrane was evaluated at each cycle. The average energy efficiency was 72.0%. Thus, the AFN anion exchange membrane is well suited for use in a V-RFB as a separator.

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1. Introduction

Power systems using renewable energy, such as solar and wind, are being actively investigated worldwide. A power system using renewable energy needs an energy storage system because of its low energy density and intermittent nature. The redox flow battery (RFB) is being investigated as an energy storage system for load leveling purposes and use in emergency uninterruptable power supplies. In particular, the all-vanadium redox flow battery (V-RFB) is being examined for this purpose, as proposed by Skyllas-Kazacos et al. [1].

In a V-RFB energy storage system, an ion exchange membrane (IEM) is the key component. The high membrane resistance causes a large internal iR drop, and the iR losses through the membrane lead to low voltage efficiency of the V-RFB. Therefore, the high permeabilities of the four types of vanadium ion (V^{2+} , V^{3+} , VO^{2+} , VO_2^+) through the membrane lead to low current efficiency. The low current efficiency is due to self-discharge of the vanadium ions permeating through the membrane [2,3]. An IEM should possess a low membrane resistance to minimize losses in voltage efficiency, and should exhibit low permeation rates of the active species to

minimize self-discharge. Finally, the IEM should also possess good chemical stability and be low in cost [2–7]. A V-RFB using an anion exchange membrane has a high current efficiency due to the low permeabilities of the four types of vanadium ion compared to a V-RFB using a cation exchange membrane [3,8–10].

An amphiphilic block copolymer using polyaryletherketone and sulfonated polyaryletherketone [11], crosslinkable sulfonated poly(diallyl-bisphenol ether ether ketone) [12], polyethylene-poly(4-vinylbenzyl chloride) [13], quaternary ammonium functionalized Diels–Alder poly(phenylene)s [14], disulfonated poly(arylene ether sulfone) [15], a blend of sulfonated poly(ether sulfone) and sulfonated poly(ether ether ketone) [16], and block copolymer using polysulfone and poly(phenylene sulfide sulfone) [17] have been used as a base polymer for ion exchange membrane preparation in V-RFB application due to satisfactory chemical and electrochemical properties and lower production costs. The prepared membranes using these base polymers have a good conductivity, low vanadium ion permeability, and high efficiency in V-RFB compared to Nafion 117 and Nafion 115. Porous membranes such as silica-modified nanofiltration membranes have been investigated for V-RFB application [18,19]. However, membranes exhibiting good electrochemical cell performance need more time for commercialization in the market.

In this research, membrane resistances of three commercial anion exchange membranes in 1M (mol/L) H_2SO_4 aqueous solution

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Nomenclature

R	membrane resistance in 1M H ₂ SO ₄ aqueous solution, $\Omega \text{ cm}^2$
R_1, R_2	electric resistance of the conductivity cell with membrane and without membrane, respectively, Ω
S	effective membrane area, cm^2
R_C, R_D	cell resistance for charge and discharge, respectively, Ω
E_C, E_D	cell voltage for charge and discharge, respectively, V
I_C, I_D	current during charge and discharge, respectively, A
E_M	open circuit voltage at each SOC, V
η_C	current efficiency, %
η_V	voltage efficiency, %
η_E	energy efficiency, %
Q_C, Q_D	quantity of the coulomb for charge and discharge, respectively, C
E_{AC}, E_{AD}	average cell voltage for charge and discharge, respectively, V

were evaluated as an indicator of chemical stability in pentavalent vanadium ion (VO_2^+) solution for various soaking times. The selected anion exchange membrane was used as a separator in a V-RFB, and its cell performance was measured at each cycle.

2. Experimental

2.1. Durability tests of commercial anion exchange membranes

Three commercial anion exchange membranes (APS from Asahi Glass Co., and AHA and AFN from ASTOM Co.) were measured for durability. Durability was determined from the change in membrane resistance in 1M (mol/L) H₂SO₄ aqueous solution and the change in the ion exchange capacity induced by the oxidative degradation during storage in the anolyte of 100% SOC (VO_2^+ , electrically charged solution of 1M VOSO₄ in 2M H₂SO₄).

The measurement method and experimental apparatus for membrane resistance in 1M H₂SO₄ aqueous solution are the same with the previous paper [20,21]. The membrane resistance of the conductivity cell shown in Fig. 1 with a membrane (R_1) and without a membrane (R_2) was measured at room temperature using an LCR meter (PM-6304, Furuka Co.). Each compartment of the cell was filled with 1M H₂SO₄ aqueous solution by circulation. The effective membrane area (S) of the cell was 0.79 cm². The membrane resistance (R , in $\Omega \text{ cm}^2$) was calculated as follows:

$$R = (R_1 - R_2) \times S \quad (1)$$

2.2. Performance of V-RFB using AFN membrane

The measurement method and experimental apparatus used to characterize the performance of the V-RFB using an ion exchange membrane are the same as reported in a previous paper [3,17].

2.2.1. Experimental apparatus

As shown in Fig. 2, the experimental apparatus is comprised of one measuring cell with an effective electrode area of 60 mm × 120 mm (having an effective area of 72 cm²); two

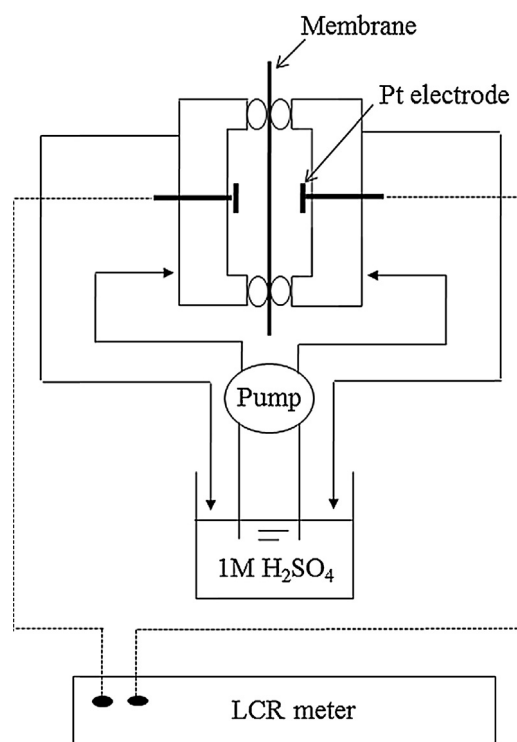


Fig. 1. Measuring equipment of electrical resistance in 1M (mol/L) H₂SO₄ aqueous solution.

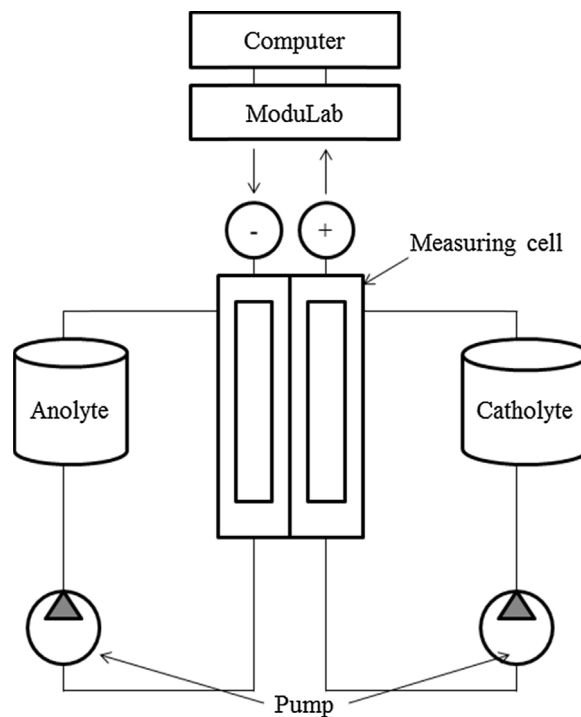


Fig. 2. Experimental set-up with measuring cell.

250 cm³ Erlenmeyer flasks (one was used as a reservoir for 1M VOSO₄ in 2M H₂SO₄ (VO_2^+) aqueous solution and the other for an electrically reduced solution of 1M VOSO₄ in 2M H₂SO₄ (V^{3+}) aqueous solution); and one micro tube pump. A Tygon tube was used to connect the components. The anolyte reservoir (220 cm³)

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