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Experimental analysis of discharge characteristics in vanadium redox flow battery

Jungmyung Kim, Heesung Park*

Department of Mechanical Engineering, Changwon National University, Republic of Korea

HIGHLIGHTS

- Electrical loss resolved to activation loss and ohmic loss.
- Electron transfer coefficient ranged from 0.31 to 0.51.
- Exchange current density expressed by Arrhenius-like equation.
- Overpotential extracted by using Tafel theory and internal resistance.

ARTICLE INFO

ABSTRACT

There has been growing interest in the performance of vanadium redox flow batteries (VRFBs) depending on the electrolyte temperature and flow rate. In this work, we have devised a single-cell test system with four reservoirs which can effectively control the temperature and flow rate of VRFB to investigate electrochemical properties during discharging in VRFB. The temperature has been set between 278 K and 318 K for the electrolytes composed of 1600 mol/m^3 V^{3+}/V^{4+} with 4000 mol/m^3 H$_2$SO$_4$, while the flow rate of the electrolytes is in the range of 10–100 mL/min. The exchange current density extracted by Tafel theory is expressed by Arrhenius-like equation and ranges between 38.83 and 49.07 A/m^2. Meanwhile, the electron transfer coefficient increases from 0.31 to 0.51 with increased temperature and flow rate. The area-specific resistance is found to decrease with increased temperature at the rate of 20.3 mΩ cm^2/K. With these, the proposed analytical method successfully predicts the obtained experimental data with excellent accuracy. Our study offers the fundamental understandings of electrochemical properties of VRFB as well as can be applied to evaluate the VRFB energy storage system at the early conceptual design even without prototypes.

1. Introduction

Sustainable and renewable energy sources have drawn worldwide attention to alleviate the excessive use of fossil fuels which induce global warming and environmental pollution [1–4]. The redox flow battery (RFB) has been intensively studied as a potential large-scale energy storage system due to various advantages, for example, unlimited electric power, long lifespan, minimal cross-over contamination, and high tolerance to over-charge/over-discharge [5–7]. Among the known redox couples employed in flow batteries (e.g., all-vanadium, poly-sulfide bromide, zinc bromine, and ferrum chromium), the vanadium redox couples proposed by Skyllas-Kazacos and co-workers have shown strong potential due to their unique features [8,9] and commercialization [10]. Since the performance of vanadium redox flow battery (VRFB) is highly independent on the properties of cell

components at the given operating condition, many studies have been conducted with the varied design of the electrodes [11–13], electrolytes [14], and separators [15,16]. Zhou et al. [13] has developed a high-performance carbon cloth electrode for VRFB which provides 80.1% energy efficiency at high current density (400 mA/cm^2). Recently, there have been attempts to modify electrode surface and attach functional groups to further increase electrochemical performance [17–21].

In parallel, the effects of critical operating conditions (e.g., temperature [22,23], electrolyte concentration [23–26], and flow rate [23,27]) on VRFB performance have been intensively investigated. Zhang et al. reported that the voltage efficiency was improved from 86.5% to 90.5% at 40 mA/cm^2 when the temperature was increased from 15 to 50 °C [22]. Indeed, the operating temperature has been always an important performance parameter in the VRFB based on aqueous electrolyte solutions. Mohamed et al. [23] showed that the
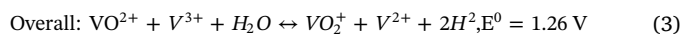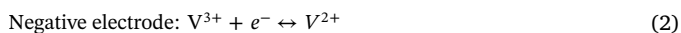
coulombic efficiency was improved with increased current density and temperature which enhanced charge acceptance and electrolyte conductivity, respectively. Meanwhile, it has been reported that secondary reaction can occur when the operation temperature is above 318 K. Zhou et al. [24] predicted the cell performance more realistically using the Stokes-Einstein relationship to account for the ion mobility. Watt-Smith et al. [27] analysed the effect of key manipulation variables on VRFB, such as electrode material, flow rate, operating current density, temperature. Chou et al. [28] investigated the effect of state of charge (SOC) on the performance of VRFB. SOC monitoring technique has been proposed by presenting online evaluation with fast convergence and high accuracy [25,26,29]. Xi et al. [30] studied performance variation and damage mechanism of VRFB cell under the temperature range from −20 °C to 50 °C. The exchange current density and Tafel constant for uranium in the LiCl/KCl eutectic mixture were investigated by Rose et al. [31]. They reported that the electron transfer coefficient is proportional to the operating temperature. The numerical modelling of the electrochemical reaction kinetics is carried out to simulate the effect of operating parameters in fuel cells [32,33].

In the application of a plant facility [34] by using VRFB, the stable operating conditions are significant even under extreme climate changes [30]. The electrical capacity and load managements in energy storage systems are critical to enhance their lifespan. The effects of the operating conditions on the VRFB performance can be assessed by examining the Tafel region. The overpotential according to the electric load in the Tafel region corresponds to the activation overpotential calculated by the Butler-Volmer equation [31,35,36]. In this study, we proposed a method to predict the voltage variations with respect to the temperature and flow rate of electrolytes. For this purpose, the exchange current density and electron transfer coefficient [37] were evaluated by conducting experiments under the different temperatures (278, 298, and 318 K) and flow rates (20, 60, and 100 mL/min). Futhermore, the extracted overpotentials by Tafel theory were compared with the experimental data to present the accuracy of the proposed experimental analysis. The outcomes of the study are to understand the electrochemical reaction characteristics and to evaluate the performance of VRFB energy storage system at the early conceptual design stage without prototypes.

2. Electrochemical reaction

2.1. Reaction at the electrode

The electrolyte of VRFB is stored in the external electrolyte reservoir as the anode electrolyte (V^{4+}, V^{5+}) and cathode electrolyte (V^{2+}, V^{3+}) according to the vanadium species, and supplied to the active area inside the cell by a pump. The electrolytic solution supplied to the cell is electrochemically reacted through the interfacial area of porous electrode in contact with the membrane. The charge/discharge process determines the direction of hydrogen ion movement and the number of electrons from the vanadium atom generated by the electrochemical reaction. The hydrogen ions generated in the redox process are transferred to the opposite porous electrode through the ion exchange membrane. Thus, the ion exchange membrane electrically and physically isolates the positive and negative regions of the cell [38–41]. The oxidation/reduction reaction to vanadium in the discharge process is shown in Fig. 1. The reaction of the vanadium species in the charge/discharge process is as follows:

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

Negative electrode: $V^{3+} + e^- \leftrightarrow V^{2+}$ (2)

Overall: $VO^{2+} + V^{3+} + H_2O \leftrightarrow VO_2^+ + V^{2+} + 2H^2, E^0 = 1.26 \text{ V}$ (3)

2.2. Overpotential

Regarding the electrolyte temperature, concentration, flow rate, and thermodynamics can theoretically determine the output voltage depending on the operating conditions; however, the measured output voltage is lower than the theoretical voltage due to irreversible losses in the system. This irreversible loss is proportional to the charge/discharge current, which results in a lower cell voltage at high currents. Herein, this irreversible loss is called overpotential. The system overpotential is classified as an activation overpotential due to electrochemical reactions at the porous electrode, and mass transfer overpotential due to ohmic overpotential and concentration variations due to internal resistance. Therefore, the VRFB cell voltage (E_{cell}) can be described by the following equation:

$$E_{cell} = E_{rev} - E_{act} - E_{ohm} - E_{con}$$ (4)

where E_{rev} is the thermodynamic open circuit voltage, E_{act} is the activation overpotential, which is the activation energy for the charge transfer reaction in the electric double layer. E_{ohm} is the ohmic overpotential due to ionic and electrical resistances, and E_{con} is overpotential due to mass transfer in the active area depending on the concentration of the electrolyte. The thermodynamic voltage or open circuit voltage (OCV), E_{rev}, is calculated using the Nernst equation (Eq. (5)), based on the vanadium concentration in the electrolyte [42].

$$E_{rev} = (E_2^0 - E_1^0) + \frac{RT}{F} \ln\left(\frac{C_{V(II)} C_{V(V)} (C_{H^+})^2}{C_{V(III)} C_{V(IV)}}\right)$$ (5)

where E_1^0 and E_2^0 are the standard reduction potentials, R is the molar gas constant, T is the electrolyte temperature, F is the Faraday constant, and $C_{V(i)}$ is the molar concentration of vanadium on both sides of the electrolyte reservoir. SOC is calculated from the measured open circuit voltage.

$$SOC = \frac{C_{V(V)}}{C_{V(IV)} + C_{V(V)}}$$ (6)

The electrochemical overpotential (activation overpotential) generated in the charge transfer reaction is defined by the theoretical Butler-Volmer equation. In addition, well-known Tafel analysis can derive two important physical parameters: Tafel slope (b) and exchange current density (a). The overpotential is calculated using the Butler-Volmer equation (Eq. (7)) or the Tafel equation (Eq. (8)). The activation overpotential generated by the charge transfer under low range discharge current conditions can be described by simplifying the Butler-Volmer equation to the Tafel equation [43,44].

$$E_{act} = \frac{RT}{\alpha F} \ln\left(\frac{i}{i_0}\right)$$ (7)

$$\eta = a + b\ln(i)$$ (8)

where α and i_0 in Eq. (7) are the electron transfer coefficient and exchange current density, respectively; these are experimentally obtained through polarization curves in the Tafel region of discharge current density through the Tafel equation. The Tafel equation consists of the overpotential η, Tafel intercept a, and Tafel slope b. In the discharge condition where the activation overpotential is dominant, it provides insight into the reaction mechanism by simplifying the Tafel equation and the Butler-Volmer equation. This method is used in Tafel analysis with the Butler-Volmer equation to analyse electrochemical performance in many studies [31,37,45]. Eq. (9) is derived from the above