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Effect of Operating Condition on Electrical Resistance and Voltage Efficiency of an Electrochemical Cell in a Vanadium Redox Flow Battery

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Effect of electrical resistance in the electrochemical cell of a vanadium redox flow battery system on system efficiency is important. Suitable operating conditions can be determined to improve the efficiency of the system without additional cost. In this study, the effect of key parameters, such as, percent compression of fibre electrode, flow rate of electrolyte solution, current density and state of charge (SOC), on the cell electrical resistance and voltage efficiency is analyzed. The results show that the percent compression of fibre electrode and flow rate of electrolyte solution cannot be independently considered due to their coupling effect. Higher percent compression (50 %) and flow rate contribute to the lowest electrical resistance and highest voltage efficiency of the cell. The current density slightly affects the electrical resistance but significantly affects the voltage efficiency of the cell. It shows that high voltage efficiency of the cell is obtained at low current density operation. It is also found that the cell resistance is minimized when the voltage efficiency shows the highest value at 50 %SOC.

1. Introduction

Vanadium redox flow battery (VRB) is an attractive energy storage technology owing to its flexibility to a system design. In addition, the energy and power of the VRB system can be distinctly designed (Tang et al., 2012). The system energy is determined by electro-active species in an electrolyte solution while the system power is dependent on the effective area and the number of cell (Al-Fetlawi et al., 2009). In the VRB cell, an electrochemical principle can be applied and thus, a conversion between electrical energy and chemical energy is occurred during the system operation through redox reactions of vanadium in the electrochemical cell.

The VRB is constructed by two half-cells of positive and negative. Each half cell consists of a current collector, fibre electrode and electrolyte solution. An ion exchange membrane is used to separate the two half-cells (Xi et al., 2007). Because both the half-cells use the same electrolyte solution (vanadium), the problem of electrolyte contamination between the two half-cells by ions transfer across the exchange membrane is neglected (Skyllas-Kazocos, 2003).

Many researches on the VRB have presently reported in literatures. Chen et al. (2014) investigated the limiting current density of VRBs. The results revealed that the cell limiting current density increases as the state of charge and stoichiometric ratios increase. Because the electrochemical cell constitutes various components, determining the cell design and operating parameters is important to achieve high cell efficiency. In addition, the comprehensive understanding of internally electrical resistance of the VRB cell is significant for improvement of the cell performance.

In this study, the electrical resistance and voltage efficiency of an electrochemical cell in a VRB is analyzed. Experimental of the VRB is set up and the effect of key operating parameters, such as, percent compression of fiber electrode, flow rate of electrolyte solution, current density and state of charge, on cell performance is discussed.

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2. Experimental

A single cell of VRB system was utilized and set up as shown in Figure 1. The system composes of 1) an electrochemical cell with effective area of 140 cm^2; thicknesses of the three layers of fibre electrode are 2.5 mm, 1 mm and 1 mm, 2) two peristaltic pumps (positive and negative) used to pass the electrolyte to the cell, 3) power supply, 4) DC load tester, 5) open circuit voltage (OCV) cell utilized to measure the state of charge (%SOC) of electrolyte solution, 6) electrolyte solution tanks, 7) data logger used to collect data (i.e., OCV and cell voltage), 8) electrolyte solution with vanadium concentration of 1.6 mol L^{-1}, sulfuric concentration of 3.2 mol L^{-1} and the volume of 280 mL (each side). In each experiment, the charge-discharge cycle was operated at a constant current mode. The data was recorded for every 3 second.

In order to investigate the effect of percent compression (%compression) of fibre electrode and flow rate of electrolyte solution, the 5.0 mm thickness of graphite felt from SGL carbon company was utilized. The gap between the current collector and the membrane was varied by using different frames of fibre electrode. The gaps of 4.5 mm, 3.5mm and 2.5 mm corresponding to 10, 30 and 50 %compression, respectively, were considered. A constant current density of 80 mA cm^{-2} and the operating temperature of 28-30 ^{o}C were employed. At the constant %compression, flow rates of the electrolyte solution were varied as 150 mL min^{-1}, 300 mL min^{-1} and 450 mL min^{-1}, which corresponds to the average electrolyte velocity of 1.07 cm min^{-1}, 2.14 cm min^{-1} and 3.21 cm min^{-1}, respectively. The coupling effect of %compression and flow rate of electrolyte solution was also analyzed.

To study the effect of current density, the current of 5.6 A, 8.4A and 11.2A were employed which corresponds to the current density of 40 mA cm^{-2}, 60 mA cm^{-2} and 80 mA cm^{-2}. The %compression of fibre electrode (10%) and flow rate of electrolyte solution (300 mL min^{-1}) were kept constant. Regarding the effect of %SOC, the OCV in a range of 1.277V and 1.503V which corresponds to 10 % to 90 %SOC was set for experiment.

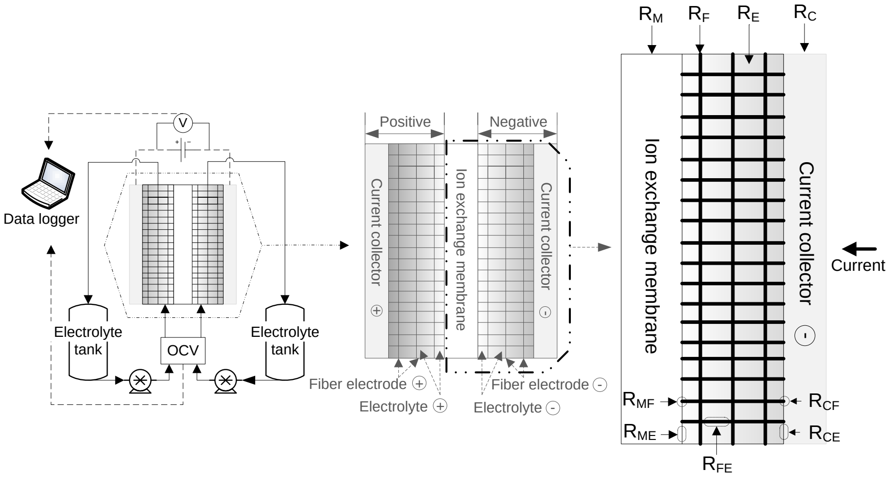

Figure 1: Schematic diagram of a VRB system and the electrical resistances in negative half-cell.

3. Results and Discussion

An electrochemical cell in the VRB system includes different components as shown in Figure 1. A single cell is considered and found that it consists of 17 electrical resistances as follows: 1) current collector resistance at the positive ($R_{C(+)}$), 2) current collector-fibre electrode interface resistance at the positive ($R_{CF(+)}$), 3) current collector-electrolyte interface resistance at the positive ($R_{CE(+)}$), 4) fibre electrode resistance at the positive ($R_{F(+)}$), 5) fibre electrode-electrolyte interface resistance at the positive ($R_{FE(+)}$), 6) positive electrolyte resistance ($R_{E(+)}$), 7) positive electrolyte-ion exchange membrane interface resistance ($R_{ME(+)}$), 8) positive fibre electrode-ion exchange membrane interface resistance ($R_{MF(+)}$), 9) ion exchange membrane resistance (R_M), 10) negative fibre electrode-ion exchange membrane interface resistance ($R_{MF(-)}$), 11) negative electrolyte-ion exchange membrane interface resistance ($R_{ME(-)}$), 12) negative electrolyte resistance ($R_{E(-)}$) 13) fibre electrode-negative electrolyte interface resistance ($R_{FE(-)}$), 14) fibre electrode resistance at the negative ($R_{F(-)}$) 15) current collector-electrolyte interface resistance at the negative ($R_{CE(-)}$), 16) current collector-fibre electrode interface resistance at the negative ($R_{CF(-)}$) 17) current collector resistance at the negative ($R_{C(-)}$). The electrical resistances in the negative and positive half-cells are shown in Figure 1. Changes in operating conditions or parameters influence the electrical resistances. In this study, the total resistances in charging and discharging process are reported. These resistances can be calculated by Eq(1) for charging process (R_{ch}) and Eq(2) for discharging process (R_{dch}). The voltage efficiency of charging (η_{v_ch}) and discharging (η_{v_dch}) processes can be calculated from Eq(3) and Eq(4), respectively.

$$R_{ch} = (V_{cell} - V_{ocv}) / I_{ch} \tag{1}$$

$$R_{dch} = (V_{ocv} - V_{cell}) / I_{dch} \tag{2}$$

$$\eta_{v\_ch} = V_{ocv} / V_{cell} \tag{3}$$

$$\eta_{v\_dch} = V_{cell} / V_{ocv} \tag{4}$$

3.1 Effect of %compression and flow rate of electrolyte solution

Three %compressions of fibre electrode of 10, 30 and 50 with three flow rates of 150 mL min^{-1}, 300 mL min^{-1} and 450 mL min^{-1} are investigated. The correlations of %SOC and electrical resistance at different %compressions and flow rates during the charging and discharging processes are illustrated in Figure 2. Besides, the correlations of %SOC and voltage efficiency at different %compressions and flow rates during charging and discharging processes are illustrated in Figure 3.

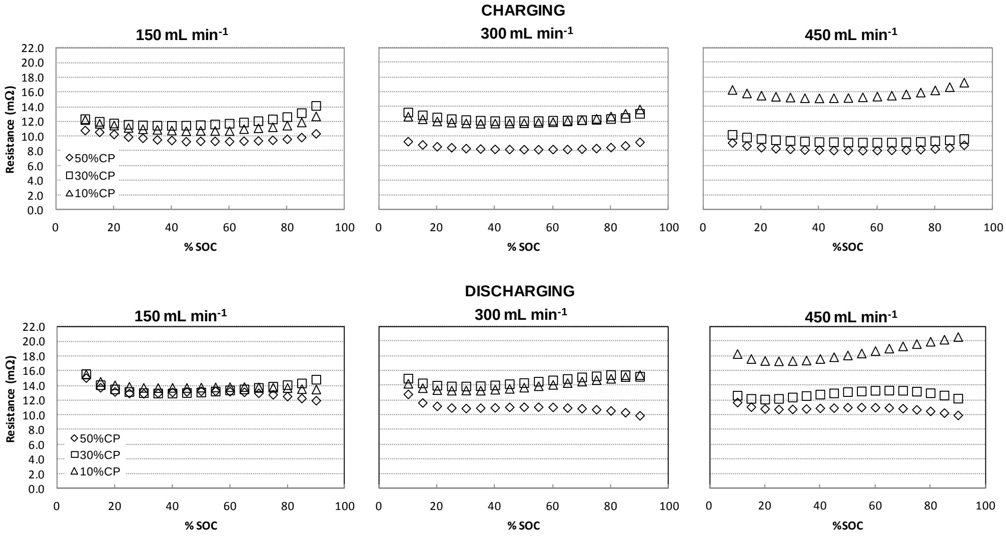

Figure 2: Correlation of %SOC and electrical resistance at different %compression and flow rate of electrolyte solution during charging and discharging processes (current density of 80 mA cm^{-2}).

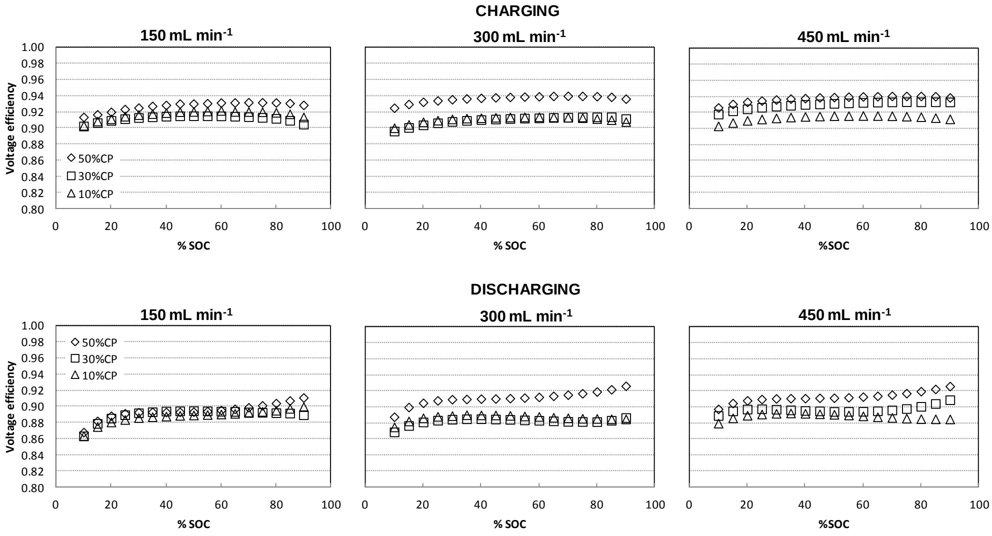

Figure 3 Correlation of %SOC and voltage efficiency at different %compressions and flow rates of electrolyte solution during charging and discharging processes (current density of 80 mA cm^{-2}).

In Figure 2, at the flow rate of 150 mL min^{-1}, the lowest resistance is obtained in the charging process when the fibre electrode with 50 % compression is used. However, in the discharging process, the fibre electrode with different %compressions has approximate resistance. It indicates that the %compression of fibre electrode insignificantly affect the resistance at flow rate of 150 mL min^{-1}. When the flow rate is increased to 300 mL min^{-1}, the resistance of the electrode with 50 %compression decreases and differs from that with 30 % and 10 %compression. At the flow rate of 450 mL min^{-1}, the resistance of the electrode with 30 %compression decreases and is closed to that with 50 %compression, whereas the resistance of the electrode with 10 %compression increases in both the charging and discharging processes. Consequently, it implies that the suitable % compression of the electrode needs to be considered along with the flow rate of electrolyte solution. This finding was also reported by Bromberger, et al. (2014) in which a two-dimensional model was proposed to explain VRBs. The lowest resistance and the highest voltage efficiency will be obtained from selecting the optimal %compression of fiber electrode and flow rate of electrolyte solution.

In Figure 3, at flow rate of 150 mL min^{-1}, the voltage efficiencies of the electrode with different %compressions are closed, especially in the discharging process. When the flow rate is increased to 300 mL min^{-1}, the voltage efficiency of 50 %compression electrode increases while that with 30 % and 10 % compression electrode is unchanged. At the electrolyte flow rate of 450 mL min^{-1}, the voltage efficiency of the 30 %compression electrode increases and is closed to the 50 % compression electrode. This result implies that the 10 %compression fiber electrode can be used with low electrolyte flow rate (electrolyte velocity of 1.07 cm min^{-1}). Furthermore, the use of the 50 % compression electrode results in the highest voltage efficiency in both charging and discharging processes; the output power of the cell using 50 % compression electrode is higher than the others. The result is similar to that given by Chang et al. (2014).

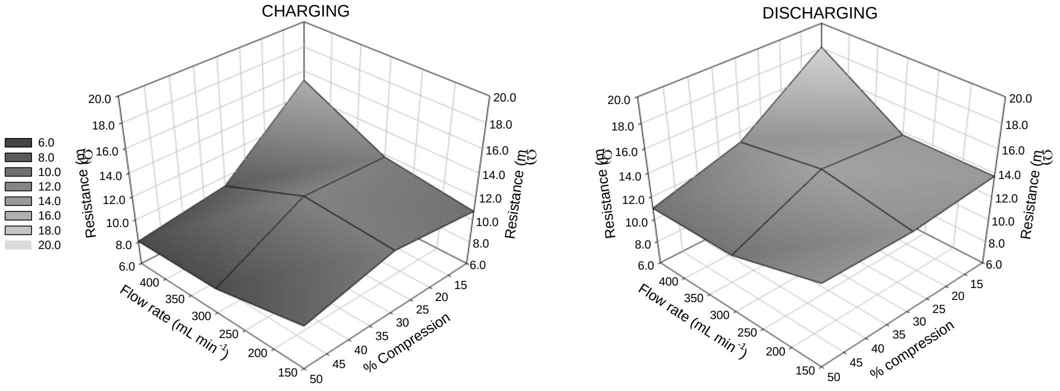

Figure 4: Coupling effect of % compression and flow rate of electrolyte solution on the electrical resistance of VRB cell in charging and discharging process at 80 mA cm^2 and 50 %SOC.

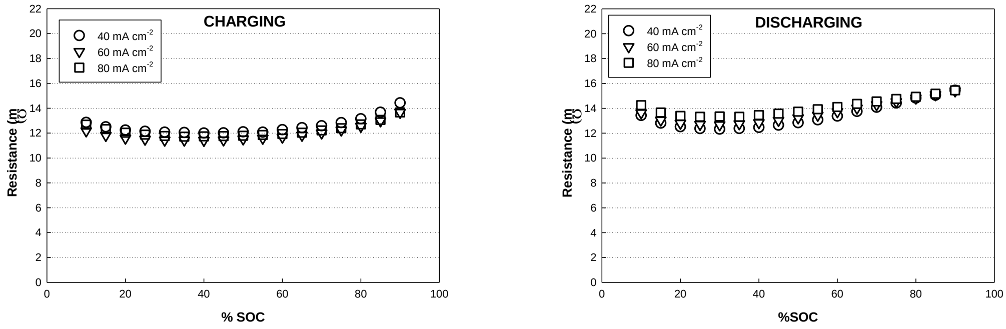

Figure 5: Correlation of % SOC and electrical resistance during charging and discharging processes by using the cell with 10 % compression and 300 mL min^{-1} of flow rate.

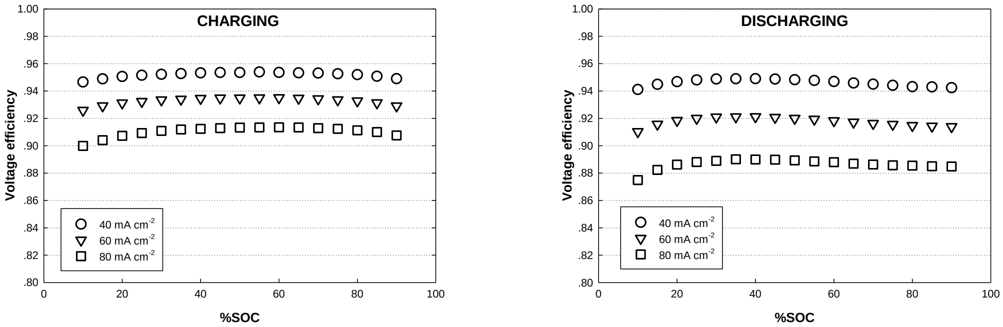

Figure 6: Correlation of % SOC and voltage efficiency during charging and discharging processes by using the cell with 10 % compression and 300 mL min^{-1} of flow rate.

Figure 4 shows the correlation of electrical resistance at different %compressions and flow rates during charging and discharging processes. The results indicate that the highest resistance is obtained when using electrode with low % compression (10 %) and high electrolyte flow rate (average electrolyte velocity of 3.21 cm min^{-1}). Nevertheless, the use of high %compression (50 %) electrode and high electrolyte flow rate results in the lowest resistance. Additionally, the resistance of discharging process is higher than charging process. It implies that the rates of redox reaction during charging and discharging processes are different.

Therefore, the % compression of fibre electrode is considered a key design parameter because the redox reactions are occurred at the fibre electrode. The suitable selection of % compression lowers the resistance, but increases the voltage efficiency. However, the %compression of electrode relates to the flow rate of electrolyte solution as a change in the flow rate also affects the cell performance. In addition, from Figure 1, there are the resistances which are influenced by the variation of %compression of fiber electrode, i.e., R_F, R_{CF}, R_{CE}, R_{FE}, R_{ME} and R_{MF}. A change in the electrolyte flow rate impacts five resistances including R_{CF}, R_{CE}, R_{FE}, R_{ME} and R_{MF}. The changes in both the parameters result in different resistances in the VRB cell.

3.2 Effect of current density and SOC

Current density is an important parameter affecting the VRB performance in terms of electrical resistance and voltage efficiency. Here, the % compression of fibre electrode and flow rate of electrolyte solution are fixed as 10% and 300 mL min^{-1}. The results show that the resistances of the VRB cell run at different current densities are slightly different in both charging and discharging process as shown in Figure 5. These resistances are the slope of correlation of current and voltage (polarization curve) in an ohmic loss region which is quite a linear relation. The results show that the cell operated at high current density results in low voltage efficiency. On the other hand, the high voltage efficiency is obtained at low current density as shown in Figure 6.

The % SOC is another key parameter that affects the electrical resistance and voltage efficiency. Figures 2 and 4 show that the high % SOC results in high resistance during the charging process and the lowest resistance is obtained at the % SOC of 50. This is caused by the effect of electrolyte resistance (R_E). In discharging process, the resistances vary depending on operating condition when the % SOC is higher than 50 %. It can be explained by different kinetics of vanadium redox reaction in discharging process. The voltage efficiency is low at low and high % SOCs. The highest voltage efficiency is obtained at 50 % SOC. Therefore, the utilization of the VRB system around 50 % SOC leads to the best efficiency of the system.

4. Conclusions

In this study, the performance of a VRB in terms of electrical resistance and voltage efficiency is studied. Four key parameters including % compression of fiber electrode, flow rate of electrolyte solution, current density and % SOC are considered. The results show that the VRB cell using the electrode with high % compression (50 %) and high electrolyte flow rate (velocity of 3.21 cm min^{-1}) shows the lowest electrical resistance and the highest voltage efficiency. In addition, the operating current density insignificantly affects the electrical resistance; however, it significantly influences the cell voltage efficiency. Effect of % SOC in the cell in the charging process is different from the discharging process. It is found that the best efficiency is obtained when the system is operated around 50 % SOC.

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