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Short communication

Shunt current loss of the vanadium redox flow battery

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ABSTRACT

The shunt current loss is one of main factors to affect the performance of the vanadium redox flow battery, which will shorten the cycle life and decrease the energy transfer efficiency. In this paper, a stack-level model based on the circuit analog method is proposed to research the shunt current loss of the vanadium redox flow battery, in which the SOC (state of charge) of electrolyte is introduced. The distribution of shunt current is described in detail. The sensitive analysis of shunt current is reported. The shunt current loss in charge/discharge cycle is predicted with the given experimental data. The effect of charge/discharge pattern on the shunt current loss is studied. The result shows that the reduction of the number of single cells in series, the decrease of the resistances of manifold and channel and the increase of the power of single cell will be the further development for the VRFB stack.

1. Introduction

The vanadium redox flow battery (VRFB) is one of most promising large-scale storage technologies to meet the requirement of grid load-smoothing and smooth output of renewable energy sources, due to its characters like high performance, long cycle life and flexible design [1–3]. The cell stack is assembled by several single cells, which are connected in series by bipolar plates to meet the voltage requirement [4]. Each single cell shares the anode/cathode electrolyte with the anode/cathode manifold. The single cells are connected with the manifold and their channels. Because of the conductivity of electrolyte and non-zero electrical field potential gradient, the shunt current will be exited. Two problems are induced by the presence of shunt current, one is the corrosion of the key materials of cell stack, which will shorten the cycle life; the other is the capacity loss, which will decrease the energy transfer efficiency of the cell stack [4]. Thus, more efforts should be done to reduce and even eliminate the shunt current loss.

Up to now, most researches about VRFB were focused on the key materials like electrode, current collector and ion exchange membrane. Very few reports are related to the shunt current of the vanadium redox flow battery. White et al. proposed a method based on the circuit analog model for predicting shunt current in stack of divided plate cells [5]. Schaeffer et al. presented a stack-level model based on the electrical circuit to calculate the shunt current of fuel cells [6]. Henquín developed a simplified mathematical model to calculate the current distributions in bipolar electrochemical reactors [7]. In the available references, the sensitive analysis of shunt current and the shunt current loss are not considered. Moreover, the literatures are lack of the research on the shunt current of VRFB.

In this paper, a stack-level model based on the circuit analog method is proposed to investigate the shunt current of VRFB, in which the SOC (state of charge) of electrolyte is introduced. The model is validated by the given experimental data. The distribution of shunt current is described in detail. The sensitive parameters affecting shunt current such as voltage of the single cell, the number of single cells in series and the resistances of manifold and channel are considered. The shunt current loss in the charge/discharge cycle of cell stack is predicted with the given experimental data. The effect of charge/discharge pattern on the shunt current loss is studied. The further development for the VRFB is suggested.

2. Model description

Shunt current of the vanadium redox flow battery can be simplified as shown in Fig. 1 based on the circuit analog model, since the electrolyte inlet loop and outlet loop of the cell stack is symmetrical.

Where R_e is the resistance of single cell, R_A and R_C is the channel resistance for anodic and cathodic electrolyte, respectively; R_{MA} and R_{MC} is the manifold resistance for anodic and cathodic electrolyte, respectively; V_0 is the open-circuit voltage for each cell; V_n is the voltage for the nth single cell; k and K is the channel and manifold current for anodic electrolyte, respectively; l and L is the channel and manifold current for cathodic electrolyte, respectively; i_n is the current passed through the nth single cell; I_t is applied current.

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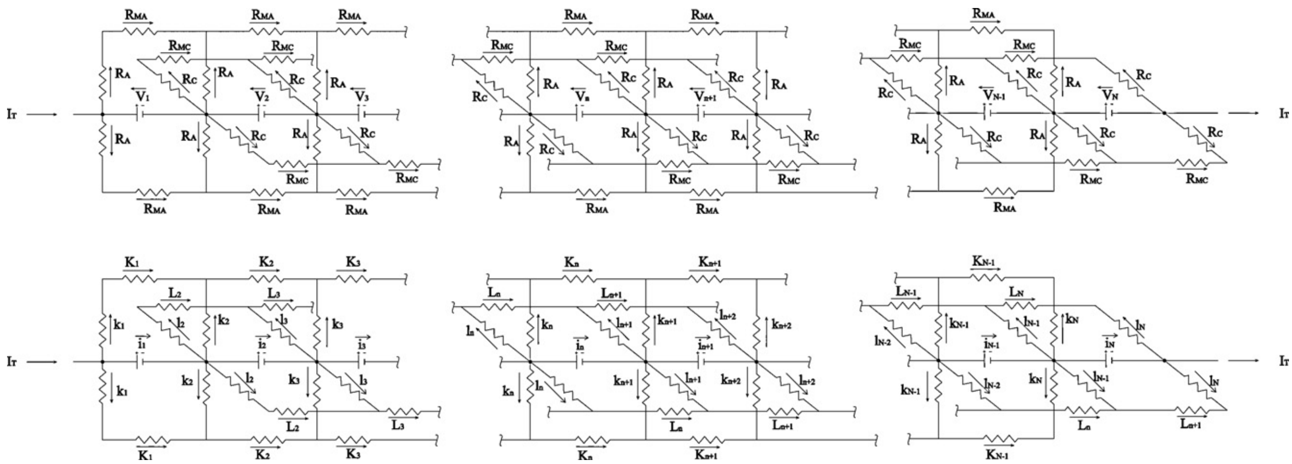

Fig. 1. The circuit analog model for a cell stack of *N* single cells.

Application of Kirchhoff's law to this symmetric network at the *n*th cell analog results in a set of five linear constant coefficient algebraic equations.

$$K_{n+1} - K_n - k_{n+1} = 0 \tag{1}$$

$$L_{n+1} - L_n - l_{n+1} = 0 \tag{2}$$

$$i_{n+1} - i_n + 2k_{n+1} + 2l_{n+1} = 0 \tag{3}$$

$$R_{MC}L_n + R_C(l_n - l_{n+1}) = V_n \tag{4}$$

$$R_{MA}K_n + R_A(k_n - k_{n+1}) = V_n \tag{5}$$

For the first cell and the *N*th cell in cell stack, there are special relationships as followed:

$$k_1 = K_1 \tag{6}$$

$$l_N = -L_N \tag{7}$$

$$i_1 = I_t - 2k_1 \tag{8}$$

Resistances of channel and manifold for anolyte and catholyte, respectively, can be calculated by [9]:

$$R_i = \rho \frac{l_i}{A_i} \tag{9}$$

ρ, denotes electrolyte resistivity. l_i, represents length of the *n*th electrolyte pipe, A_i is cross sectional area of the *n*th electrolyte pipe. In this paper, the voltage of the *n*th cell is related to SOC (charge of states) and over-potential. This means the model can simulate the variation of output terminal voltage in the whole charging and discharging process. It is important that the characteristic of shunt current changing with time can be well captured. The voltage of the *n*th cell is represented as [8]:

$$V_n = V_o + \eta_n \tag{10}$$

V_0, denotes the open-circuit voltage, which is a function of SOC:

$$V_0 = V_{cell}^0 + \frac{RT}{nF} \ln \frac{[\mathrm{SOC}]^2}{[1-\mathrm{SOC}]^2} \tag{11}$$

V_{cell}^0, denotes the standard cell potential at 50% SOC. The value of it is equal to 1.4 V (25 °C) which is derived from Haddadi's experimental result [9]. The relationship between charge (or discharge) time *t* and SOC is:

$$\mathrm{SOC} = S_0 + \frac{t}{t_0}(S_e - S_0) \tag{12}$$

where t_0 is the total charge (or discharge) time. S_0 and S_e represent the values of SOC at the beginning and the end of charge (or discharge). The over potential of each cell depends on the inner-resistance R_e, and current passed through the *n*th cell i_n:

$$\eta_n = i_n \cdot R_e \tag{13}$$

The output terminal voltage is a summation of voltage of each cell:

$$V_{stack} = \sum_{n=1}^{N} V_n \tag{14}$$

The shunt current loss during charge and discharge process can be calculated by:

$$Q_f = \int_0^{t_c} \sum_{n=1}^{N} I_n^c(t)\, dt + \int_0^{t_d} \sum_{n=1}^{N} I_n^d(t)\, dt \tag{15}$$

where I_n^c (*or* I_n^d) is the total shunt current in the process of charge (or discharge) for the *n*th cell, which is a summation of absolute values of shunt currents in manifold and channel, respectively. t_c (or t_d) is the charge (or discharge) time.

3. Results and discussion

3.1. Experiment and results

A kilowatt-class VRFB stack is employed to investigate the shunt current. The stack is manufactured by 10 VRFB single cells. The effective area of each electrode is 476 cm^2. The charge/discharge performance of the VRFB stack is conducted by using a charge–discharge controller (Arbin Instruments Corp., USA).

Table 1
The experimental results.

Applied current density/mA cm^{-2}	Charge capacity/Ah	Discharge capacity/Ah	S_0/%	S_e/%	Charge time/h	Discharge time/h
40	766	695	0.9	78.4	4.04	3.66
60	707	659	1.5	71.8	2.48	2.31
80	607	573	2.9	63.6	1.6	1.51

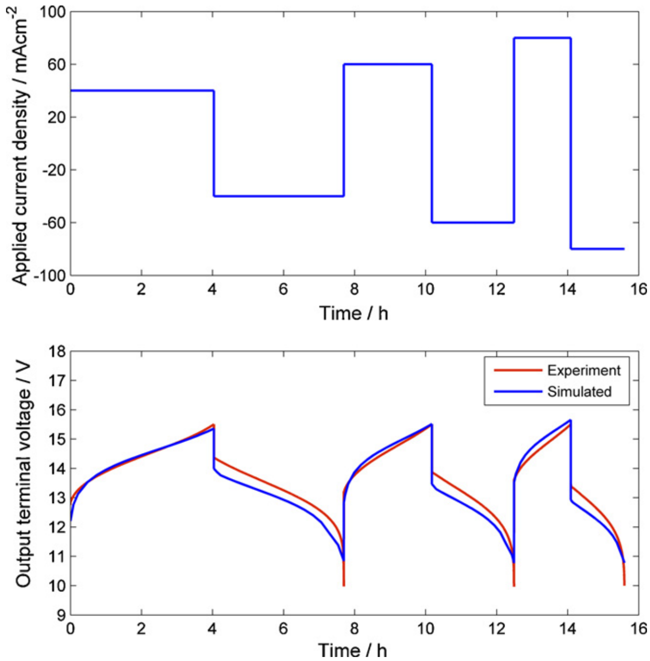

Fig. 2. Comparison of experimental and simulated charge/discharge curves for different applied current densities.

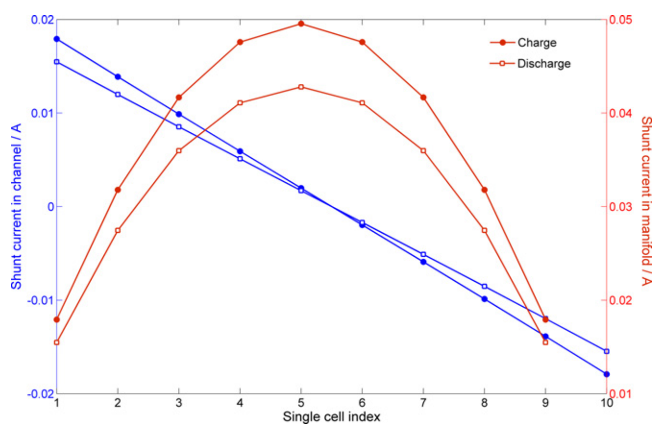

Fig. 3. Distributions of shunt current in manifold and channel during charge and discharge at 50% SOC for applied current density of 60 mA cm^{-2}.

The upper limit voltage of charge is 15.5 V. The lower limit voltage of discharge is 10 V. The experimental results are shown in Table 1.

3.2. Validation of the model

The resistances of manifold, channel and single cell of the kilowatt-class VRFB stack are 1.23, 365.89 and 0.0036 Ω, respectively. The charge/discharge curve is simulated, which is compared with the experimental curve. As shown in Fig. 2 the two curves are well-fitted with each other. The slight discrepancies between them are caused by inaccurate evaluation of the SOC at the beginning and the end of charge or discharge.

3.3. Distribution of shunt current

In Fig. 3, the maximum value of shunt current in manifold occurs in the middle of stack, and decreases towards two ends. The variation demonstrates a symmetrical profile. The maximum shunt current in channel occurs at two ends of cell stack. The minimum occurs in the middle, which is nearly equal to zero. The sum of shunt currents in channel is equal to zero.

Fig. 4 shows the distributions of single cell voltage and internal current during charge and discharge at 50% SOC for applied current density of 60 mA cm^{-2}. The distribution of single cell voltage shows the "U" profile during the charge and discharge process. The internal current passed through single cell shows the "U" profile during the charge process, however, shows the opposite profile during the discharge process.

3.4. Sensitive analysis of shunt current

The shunt current is dependent on the voltage of the single cell, the number of single cells in series and the resistances of manifold and channel. The shunt current during charge/discharge cycle for applied current density of 80 mA cm^{-2} is shown in Fig. 5. The variation is directly proportional to the variation of the single cell voltage.

With the increase of the number of single cells in series, the circuit loops generating shunt current increase. In order to analyze the influence of the number of single cells in series, the shunt current of the stack assembled by 20 single cells in series is calculated. Compared with the internal current of the stack assembled by 10 single cells in series as shown in Fig. 6, the internal current becomes more than thrice at the same SOC. So the reduction of the number of single cells in series is an effective method to reduce the shunt current.

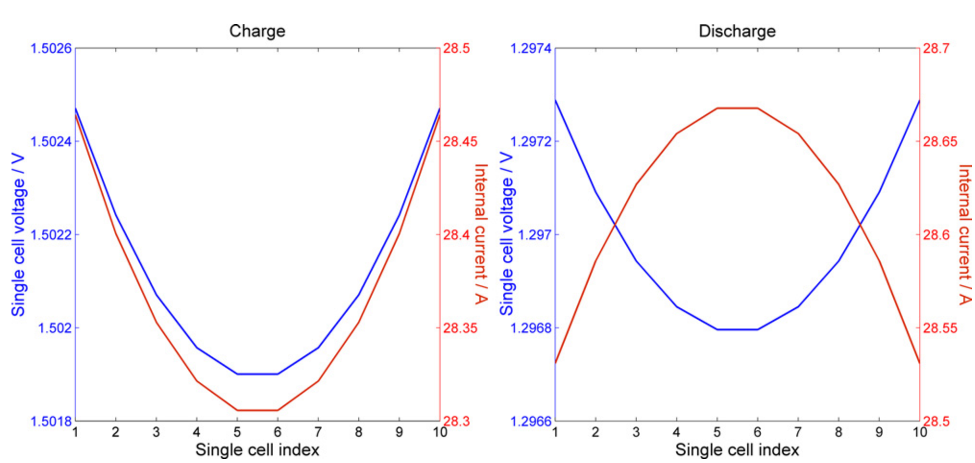

Fig. 4. Distributions of single cell voltage and internal current during charge and discharge at 50% SOC for applied current density of 60 mA cm^{-2}.

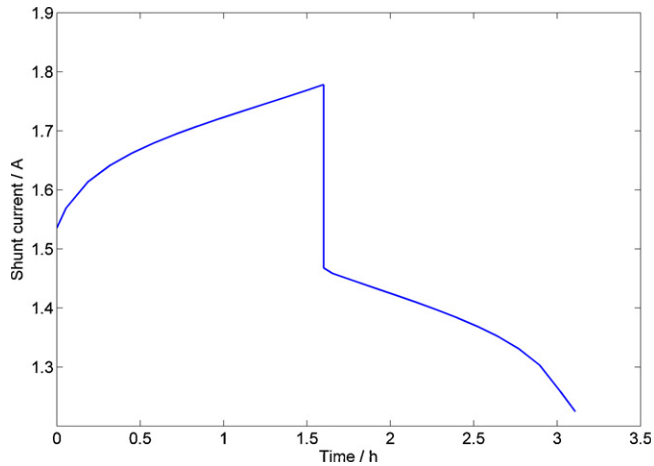

Fig. 5. Shunt current during charge/discharge cycle for applied current density of 80 mA cm^{-2}.

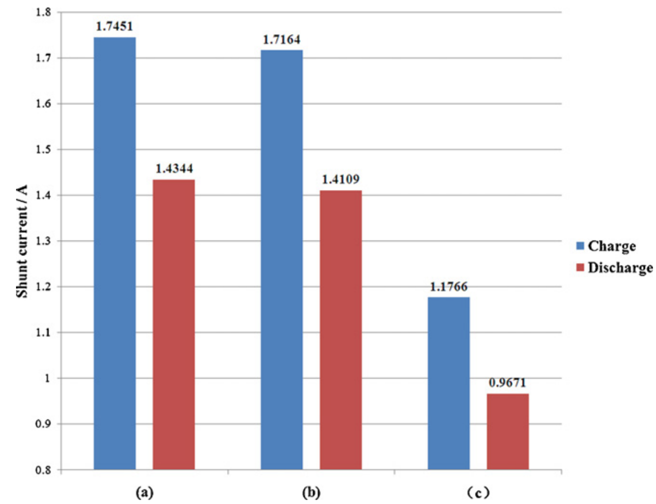

Fig. 7. Comparison of shunt current for different resistances at 50% SOC for applied current density of 80 mA cm^{-2}. For tick of *x*-axis: (a) original; (b) resistance of manifold increased by 50%; (c) resistance of channel increased by 50%.

The shunt current and the resistances of manifold and channel are in inverse variation. The effect of resistance on the shunt current is investigated via increasing the resistances of channel and manifold by 50%, respectively. As shown in Fig. 7 the former and the later shunt currents are decreased by 1.64% and 32.57%, respectively. It can be concluded that under the condition of increasing equal percentage of resistance, increasing resistance of channel is more effective to decrease the shunt current.

3.5. Shunt current loss

The shunt current loss for different applied current densities in the given experiment is calculated as shown in Fig. 8. With the increase of applied current density, the shunt current loss and the percentage of the shunt current loss in the total coulomb loss both decrease. The former is mainly because of the reduction of the charge/discharge time, and the later is due to the increase of the power of the stack. In the given experiment the percentage of the shunt current loss in the total coulomb loss is less than 17%. In case that the number of single cells and the area of the electrode are kept constant, increasing the applied current density is an effective method to decrease the shunt current loss.

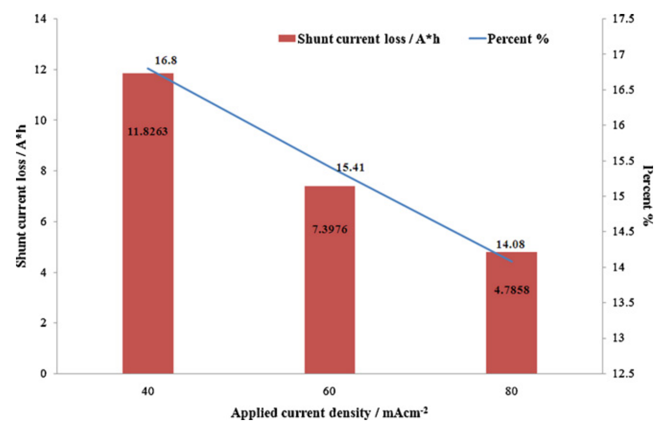

Fig. 8. Comparison of shunt current loss for different applied current densities.

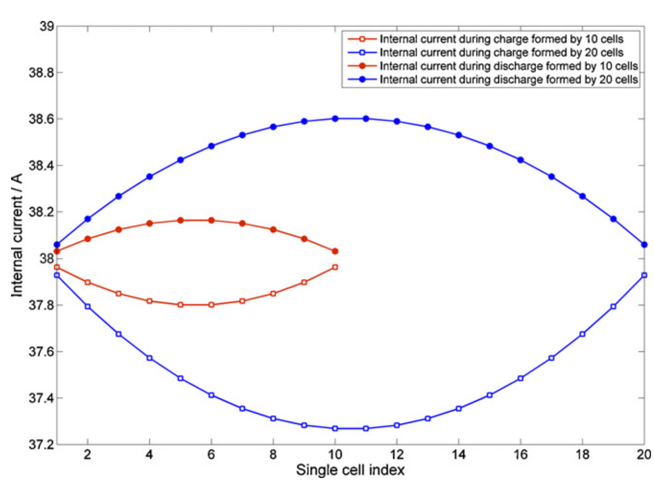

Fig. 6. Comparison of internal current for different number of cells in series at 50% SOC for applied current density of 80 mA cm^{-2}.

As described above, the shunt current is constant at the given SOC if the number of single cells in series and the resistances of manifold and channel are specified. The higher the power of the single cell, the lower the influence of the shunt current loss is. So the further efforts on VRFB stack should be focused on reducing the number of single cells in series, decreasing the resistances of manifold and channel and increasing the power of single cell.

4. Conclusion

A stack-level model based on the circuit analog method is proposed to investigate the shunt current loss of the vanadium redox flow battery, in which the SOC (state of charge) of electrolyte is introduced. The model is validated against the stack voltage of the given experiment, which is well-fitted with the simulated curve. The sensitive analysis of the voltage of the single cell, the number of single cells in series and the resistances of manifold and channel to the shunt current is reported. The shunt current loss of cell stack in the charge/discharge cycle is calculated with the given experimental data. The percentage of the shunt current loss in the total coulomb loss is less than 17%. The effect of charge/discharge pattern on the shunt current loss shows that the reduction of number of single cells in series, the decrease of the resistances of manifold and channel and the increase of the power of single cell are the further development for the VRFB stack.

The VRFB system is constructed by several stacks in parallel, in which the shunt current exits at the same time. The proposed model can be extended to calculate the shunt current of VRFB system. The results and validity of the model for the VRFB system will be discussed in a forthcoming paper.

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References

[1] Noëlle TASSIN, Storage Technology report: ST7-Redox Systems, 06/05/2003.
[2] M. Skyllas-Kazacos, M. Rychcik, R. Robin, A.G Fane, J. Electrochem. Soc. 133 (1986) 1057.
[3] E. Sum, M. Rychcik, M. Skylla-Kazacos, J. Power Sources 16 (1985) 85.
[4] E.A. Kaminski, R.F. Savinell, J. Electrochem. Soc. 130 (1983) 1103.
[5] R.E. White, C.W. Walton, H.S. Burney, R.N. Beaver, J. Electrochem. Soc. 133 (1986) 485.
[6] J.A. Schaeffer, Lea-Der. Chen, J.P. Seaba, J. Power Sources 182 (2008) 599.
[7] G. Codina, A. Aldaz, J. Appl. Electrochem. 22 (1992) 668.
[8] M.H. Li, et al., Power Conversion Conference-Nagoya, 2007, PCC 072-5 April 2007, pp. 221–225.
[9] T. Sukkar, M. Skyllas-Kazacos, J. Membr. Sci. 222 (2003) 234.