

Modeling of an All-Vanadium Redox Flow Battery and Optimization of Flow Rates

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Abstract—Vanadium redox flow batteries (VRBs) are competitive for large energy storage systems due to low manufacture and maintenance costs and high design flexibility. Electrolyte flow rates have significant influence on the performance and efficiencies of the batteries. High electrolyte flow rates improve energy efficiency while degrade the battery efficiency due to high pump power losses. Thus, flow rates are necessary to be optimized for battery efficiency improvement. In this paper, an electrochemical model is firstly proposed to describe the charge-discharge characteristics based on the experimental data. Then, an empirical method is introduced to analyze the energy consumption of pumps under various flow rates. The optimal flow rates are obtained by applying new criteria. The results show that VRBs obtain peak battery efficiencies at the optimal flow rates around $90\text{cm}^3\text{s}^{-1}$ with respect to the proposed battery configuration. The optimal flow rates are provided as a reference for battery operations and control.

Index Terms— vanadium redox flow battery, model, optimal flow rate, battery efficiency.

I. INTRODUCTION

The all-vanadium redox flow batteries (VRB) initiated by Maria Skyllas-Kazacos and co-workers at the University of New South Wales (UNSW) are developed and successfully commercialized for large-scale energy storage systems, especially in the grids that utilize large amounts of the intermittent renewable energies. VRBs have been received much attention for the features such as the flexibility of power and energy capacity design, low manufacture cost, indefinite cycle lifespan and high energy efficiency[1-3].

The development of the VRB models has been analyzed in various approaches, which can be classified into two categories, electrochemical models, and electric-circuit models. The electrochemical models are based on the description of electrochemical reactions and conservation laws of mass, energy and momentum transport of electrolyte in stack and tanks, as in [4-7]. These models involve detailed considerations of the dynamic processes of vanadium species,

the structure of the stack, and large number of selected parameters. They are accurate in expense of large computational work. Electric-circuit models are equivalent circuits combined with capacitors, resistances, and voltage sources to represent the characteristics of the battery. The models are simple and straightforward without considering the inner structure of the battery, but require much experimental data to obtain parameters, and this method is used in [8-10]. For practical battery control, electric-circuit models are widely implemented due to simplicity.

The electrolyte flow rate is a unique and crucial factor for redox flow batteries compared with traditional lithium-ion batteries. The electrolytes are pumped into the stack where chemical reactions occur. The stack power increases with increased electrolyte flow rate, thus the capacity[11]. However, the energy consumption of pump power will deteriorate the overall battery efficiency. Thus, it is necessary to investigate optimal flow rates at certain operation conditions. In this paper, an empirical model is first developed. Then, an empirical method is proposed for pump power analysis. The overall battery efficiency is then evaluated under various flow rates.

II. MODEL DEVELOPMENT OF VRBS

An all-vanadium redox flow battery system consists of one stack, two electrolyte tanks, pumps, and hydraulic pipes as shown in Figure 1. The stack is assembled by a series of paralleled single cells that are constructed by electrodes, membranes, and current collectors. The chemical reactions in the stack are given by Eqn(1-2) [12-14],



The chemical reaction rate is dependent on factors such as flow rates, charging or discharging currents, and temperature. The tanks are filled with active vanadium species. The

concentration of electrolyte solutions in the tanks represents the state of charge (SOC) of the battery. The pumps are installed to sustain the circulation of the flow of electrolytes.

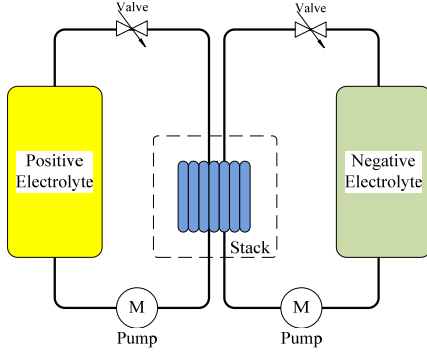


Figure 1 Configuration of vanadium redox flow battery.

A. Model Description

The model includes a battery voltage source, an equivalent internal loss resistance and pump power losses determined by the flow rates and battery structure. The battery voltage source represents the equilibrium electromotive force (EMF) of VRB stack under various SOC and flow rates. The behavior of EMF is described according to Nernst Equation in Eqn(3),

$$E = E_0 + N \frac{RT}{F} \ln \left(\frac{c_{v_{O_2^+},c} c_{v^{3+},c} c_{H^+}^2}{c_{v^{3+},c} c_{v_{O_2^+},c}} \right) \quad (3)$$

where E_0 denotes the standard potential for a redox reaction where the activity of vanadium species is unity. The term in bracket denotes the concentrations of vanadium species in cells, which are influenced by the flow rates. N denotes the number of cells in the stack. F denotes the Faraday constant.

The equivalent internal resistance represents ohmic losses due to the resistances of electrodes, membrane, electrolytes and the overpotentials due to activation and concentration. The stack terminal voltage, U_{stack} , has the following relationship in Eqn(4) with the voltage source and the internal resistance during charging and discharging.

$$U_{stack} = \begin{cases} E + R_c I & \text{during charge} \\ E - R_d I & \text{during discharge} \end{cases} \quad (4)$$

where R_c and R_d are equivalent charging and discharging resistance respectively. I denotes the applied current.

The state of charge of a battery reflects the energy stored in the battery and its value can be measured precisely by chemical method. SOC is related to vanadium species in tanks and defined in Eqn(5) [12],

$$SOC = \frac{c_{v^{2+},t} + c_{v^{3+},t}}{c_{v^{2+},t} + c_{v^{3+},t}} = \frac{c_{v_{O_2^+},t}}{c_{v_{O_2^+},t} + c_{v_{O_2^+},t}} \quad (5)$$

Assuming the concentration of vanadium species are the same in stack and tank, the stack voltage can be expressed as Eqn(6) by combining Eqn(3-5),

$$U_{stack} = E_0 + N \frac{mRT}{2F} \ln \left(\frac{c_{v_{O_2^+},c}}{1 - c_{v_{O_2^+},c}} \right) \pm R_{c,d} i \quad (6)$$

where $R_{c,d}$ denotes the resistance during charge or discharge. m denotes the correction factor for estimation.

B. Parameters Estimation

The predicted stack voltage during discharge can be determined as Eqn(7),

$$\hat{U}_{battery} = \hat{E}_0 + N \frac{mRT}{2F} \ln \left(\frac{SOC}{1 - SOC} \right) - \hat{R}_d i \quad (7)$$

To minimize the error between the estimated solution and the measured data, the least square method is applied for the curve fitting. The method is described as in [15],

$$\hat{Y} = \begin{bmatrix} \hat{U}_{stack,1} \\ \hat{U}_{stack,2} \\ \hat{U}_{stack,3} \\ \vdots \\ \hat{U}_{stack,N} \end{bmatrix} = Hx = H \begin{bmatrix} \hat{E}_0 \\ \hat{m} \\ \hat{R}_d \end{bmatrix} \quad (8)$$

where

$$H = \begin{bmatrix} 1 & \frac{RT}{F} \ln \left(\frac{SOC_1}{1 - SOC_1} \right) & -i_1 \\ 1 & \frac{RT}{F} \ln \left(\frac{SOC_2}{1 - SOC_2} \right) & -i_2 \\ 1 & \frac{RT}{F} \ln \left(\frac{SOC_3}{1 - SOC_3} \right) & -i_3 \\ \vdots & \vdots & \vdots \\ 1 & \frac{RT}{F} \ln \left(\frac{SOC_N}{1 - SOC_N} \right) & -i_N \end{bmatrix}$$

The parameters E_0 , m , R_c and R_d are estimated by using Eqn(9),

$$x = (H^T H)^{-1} H^T Y \quad (9)$$

A kilowatt class VRB stack is analyzed with charge-discharge characteristics for battery modeling. The constructed battery has the specifications in Table I of [16]. The estimated parameters are obtained from two charge-discharge curves at current density of 70 mAcm⁻² and 60 mAcm⁻². According to the active electrode area of 875 cm², the applied currents are 61.25A and 52.5A respectively. The validation of this model has been verified by applying a charge-discharge curve at current density of 50 mAcm⁻², or 43.75A.

TABLE I. SPECIFICATIONS FOR THE VRB STACK

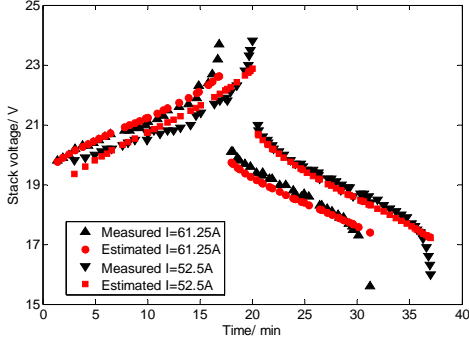
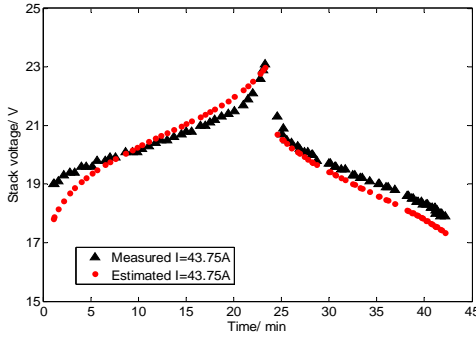
Configuration	Dimension
Area of active electrode	875 cm ²
Number of cells	14
Stack dimension	440mm×340mm×200mm
Concentration of vanadium species	1.5M
Electrolyte volume per cell	7.4L

C. Model Validation

By applying the charge-discharge curves based on the experimental test data of VRB stack, the estimated parameters are listed in Table II. For verification, the simulated charge-discharge curve and experimental curve are compared in Figure 2. The maximum error of the model is 3.2% during discharge while 6.2% during charge, which shows the model matches well with the data to describe the behavior of the battery.

TABLE II. ESTIMATED PARAMETERS FOR THE VRB MODEL

Parameters	Value
E0	20.15V
Rc	0.038 Ω
Rd	0.045 Ω
m	5.96


 Figure 2 Curve fitting for stack voltage at $I=61.25A$ and $I=52.5A$.

 Figure 3 Stack voltage estimation at $I=43.75A$.

D. Pump Power Analysis

The viscosity of electrolytes and hydraulic design in pipes and the stack attribute to the pressure drop. The pump power compensates the pressure drop and sustains a constant flow rate. Thus, the consumption of pump power, P_{pump} , is equal to the power loss, P_{loss} , in the stack and pipes according to energy conservation. Instead of a direct way to measure the energy consumption of pump power, the power loss in circulation is analyzed first. The pump power has a relation with the pressure drop and the flow rate Q and is given by [17],

$$P_{pump} = P_{loss} = \Delta p \times Q \quad (10)$$

The pressure drop can be divided into two parts, the friction pressure drop due to the fluid viscosity, $\Delta p_{friction}$ and a form loss, Δp_{form} due to an abrupt change in flow direction or geometry. Thus, the pressure drop can be expressed by,

$$\Delta p = \Delta p_{friction} + \Delta p_{form} \quad (11)$$

The pressure drop across a channel is given by [18, 19],

$$\Delta p_{friction} = f \frac{L}{D_h} \frac{\rho V_m^2}{2} \quad (12)$$

The form pressure drop is given by,

$$\Delta p_{form} = K \left(\frac{\rho V_m^2}{2} \right) \quad (13)$$

where f and K denotes friction loss factor and form loss factor respectively. V_m denotes the velocity of the flow rate in the channel. D_h denotes the hydraulic diameter.

Assuming the electrical efficiency and hydraulic efficiency of the pumps are 100%, the pump power has the characteristics shown in Figure 4. As the flow rates increase, the pump power increase quadratically and can reach as high

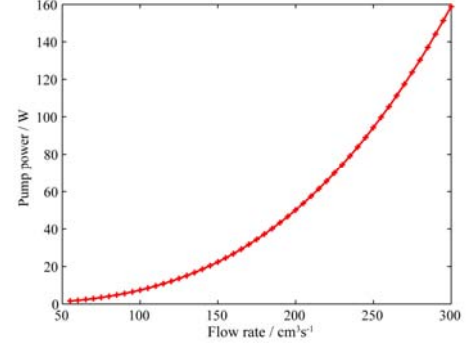


Figure 4 Pump power consumptions under various flow rates.

as 160W at flow rate of $300\text{cm}^3\text{s}^{-1}$.

III. FLOW RATES OPTIMIZATION

Electrolyte flow rate is a crucial variable that affect the battery performance. As stated in [11], an increase of flow rates leads to an increase of energy efficiency while a decrease of battery efficiency. Thus, it is necessary to obtain the optimal operational flow rates with high battery efficiency during the charging and discharging cycles.

A. Flow Rates Criteria for Battery Operation

The active vanadium species are delivered to the stack by pumps to sustain the electrochemical process of the battery. An increased flow rate increases the power of the stack as well as the energy consumption of pumps. The criteria for optimal flow rates are to maximize the battery energy during discharge while minimize the battery energy during charge. The relationship between battery energy, stack energy and pump energy is stated in Eqn(14).

$$E_{battery} = \begin{cases} E_{stack} - E_{pump} = \int P_{stack} dt - \int P_{pump} dt & \text{during discharge} \\ E_{stack} + E_{pump} = \int P_{stack} dt + \int P_{pump} dt & \text{during charge} \end{cases} \quad (14)$$

$$P_{stack} = U_{stack} \times I_{stack} \quad (15)$$

Another criterion for safe battery operation is the minimal flow rate. Flow rates are required beyond the limits to avoid side reactions in the stack when the active vanadium species deplete out in the cells. The output vanadium concentration of a cell is given in Eqn(16),

$$c_{out} = c_{in} \pm \frac{I}{zFQ} = \text{SOC} \cdot c_{in(0)} \pm \frac{I}{zFQ_{cell}} \quad (16)$$

The minimal flow rate of the stack is defined when $c_{out}=0$ in Eqn(17),

$$Q_{stack,min} = N \frac{I}{zF\text{SOC} c_{in(0)}} \quad (17)$$

B. Optimal Flow Rates and Minimal Flow Rates

The stack currents are selected as reference currents and remain constant in battery operations. Thus, the key factor for maximum power output of stack relies on stack voltage according to Eqn(15). The battery operates at SOCs within the limits of 10%-90%. The simulation was done under constant charge-discharge currents. Figure 5 shows the battery power under various flow rates during discharge when stack current is 60A. The figure indicates that battery power decreases during the discharge process. For each SOC, there is a maximum battery power point at the optimal flow rate.

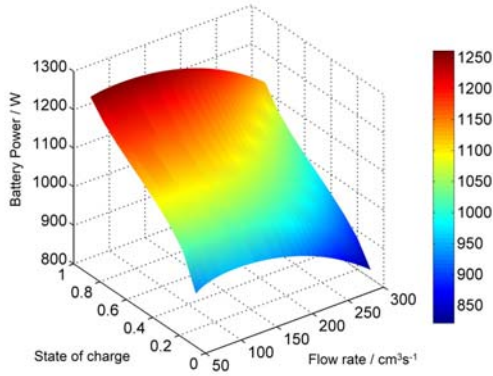


Figure 5 Battery power under flow rates and SOCs at I=60A.

Electrolyte flow rates affect the output stack power since the concentrations of vanadium species in the cells influence the stack voltage shown in Eqn(6). An increased flow rate leads to an increased stack voltage value during discharge while a decreased voltage value during charge. Figure 6 illustrates the optimal flow rates during discharge at each state when I=60A. The battery power drops as the battery operates at low SOCs. The optimal flow rate is around $90\text{cm}^3\text{s}^{-1}$ regarding to the battery configuration.

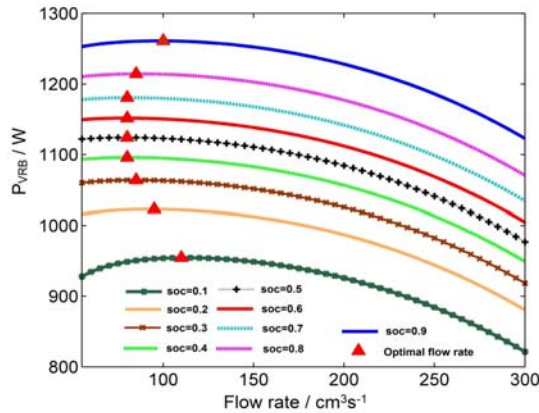


Figure 6 Optimal flow rates during discharge when I=60A.

Figure 7 shows optimal flow rates under various currents during charge. A relative high flow rates are required when batteries are fully charged. It can be explained by the fact that the stack voltage reaches to peak value when the concentration in cells is neither too high nor too low according to Eqn(6). The optimal flow rates increase as the stack currents increase due to fast consumption rates of active vanadium species. The

optimal flow rates data can be applied as a reference for battery control.

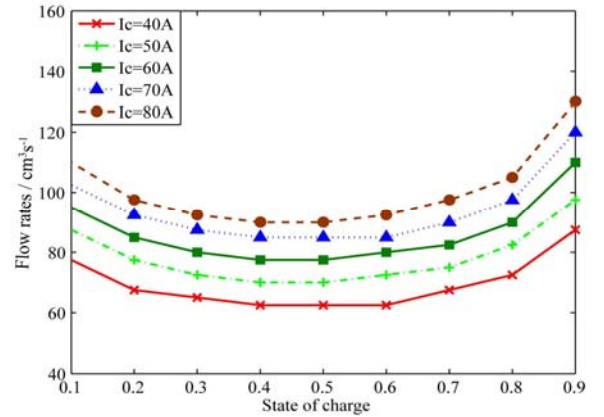


Figure 7 Optimal flow rates under various currents during charge.

Figure 8 shows the minimal flow rates that are required to sustain the assigned reference currents. The flow rate increases dramatically when the battery is fully discharged. Fast electrolyte flow rate is essential to replenish the scarce solution.

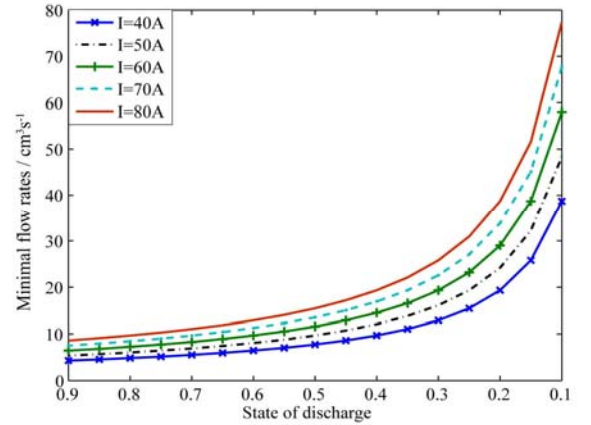


Figure 8 Minimal flow rates under various currents during discharge

C. Energy Efficiency and Battery Efficiency

Energy efficiency and battery efficiency are investigated in this section. The definitions of the efficiencies are described in Eqn(18) and Eqn(19). Table III shows the efficiency values under various flow rates when stack current is 60A. The energy efficiency improves as the flow rate increases since high stack output power will be obtained with fast flow rate. The battery efficiency reaches to the peak value at the flow rate of $110\text{cm}^3\text{s}^{-1}$ which is around the optimal flow rate. By minimizing the pump power in a full cycle, the battery efficiency is improved at such flow rate.

$$\eta_e = \frac{\text{Discharged Energy}}{\text{Charged Energy}} = \frac{\int P_{\text{stack,d}} dt}{\int P_{\text{stack,c}} dt} \quad (18)$$

$$\eta_{\text{battery}} = \frac{\text{Discharged Energy} - \text{Pump Energy}}{\text{Charged Energy} - \text{Pump Energy}} = \frac{\int (P_{\text{stack,d}} - P_{\text{pump,d}}) dt}{\int (P_{\text{stack,c}} + P_{\text{pump,c}}) dt} \quad (19)$$

TABLE III. ENERGY EFFICIENCY AND BATTERY EFFICIENCY UNDER VARIOUS FLOW RATES WHEN I=60A

$Q/\text{cm}^3\text{s}^{-1}$	55	82.5	110	137.5	165	192.5
$\eta_e/\%$	76.24	77.76	78.50	78.94	79.23	79.44
$\eta_{\text{battery}}/\%$	76.05	77.19	77.25	76.65	75.46	73.69

IV. CONCLUSION

An electrochemical model is set up based on charge-discharge characteristics of a kilowatt VRB stack. Flow rates determine the energy consumption of pumps and the output power of battery. The pump energy increases quadratically with the increase of flow rates. The criteria for optimal flow rates allow VRBs deliver maximal output battery energy during discharge while receive minimal battery energy for charge. At such flow rates, the battery energy is maximized by increasing the stack energy and reducing the pump energy during discharge while minimized by reducing the stack energy and pump energy during charge. The minimal flow rates are considered to prevent side reactions in the stack. The simulated results show that the optimal flow rates of VRBs are around $90\text{cm}^3\text{s}^{-1}$. At the optimal flow rates, VRBs reach to highest battery efficiencies. Data of optimal flow rates under various SOCs and currents can be applied for battery control.

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