



# A dynamic plug flow reactor model for a vanadium redox flow battery cell



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## HIGHLIGHTS

- A plug flow reactor model for a VRB system is developed based on material balance.
- The effects of several key operation variables were studied by simulations.
- Results suggest the proper placement for cell voltage monitoring.
- Results highlight problems associated with setting cut-off limit based on inlet OCV.

## ARTICLE INFO

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## ABSTRACT

A dynamic plug flow reactor model for a single cell VRB system is developed based on material balance, and the Nernst equation is employed to calculate cell voltage with consideration of activation and concentration overpotentials. Simulation studies were conducted under various conditions to investigate the effects of several key operation variables including electrolyte flow rate, upper SOC limit and input current magnitude on the cell charging performance. The results show that all three variables have a great impact on performance, particularly on the possibility of gassing during charging at high SOC or inadequate flow rates. Simulations were also carried out to study the effects of electrolyte imbalance during long term charging and discharging cycling. The results show the minimum electrolyte flow rate needed for operation within a particular SOC range in order to avoid gassing side reactions during charging. The model also allows scheduling of partial electrolyte remixing operations to restore capacity and also avoid possible gassing side reactions during charging. Simulation results also suggest the proper placement for cell voltage monitoring and highlight potential problems associated with setting the upper charging cut-off limit based on the inlet SOC calculated from the open-circuit cell voltage measurement.

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## 1. Introduction

Energy generation based on renewable energy sources has grown rapidly in recent decades to reduce the consumption of fossil fuels and associated greenhouse gas emissions. Large scale energy storage systems can play a significant role in power and energy management to buffer the intermittent renewable power output and to achieve electricity peak shaving and load levelling. Among all energy storage technologies, the vanadium redox flow battery (VRB), pioneered by Skyllas-Kazacos and co-workers in the 1980s [1–6], is regarded as one of the most promising technologies for large scale energy storage systems because of the use of vanadium

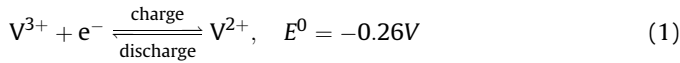
in both half-cell electrolytes that avoids the issue of cross contamination by ion diffusion across the membrane. With this unique property, the battery has a very long cycle life, its life being limited only by the calendar life of the cell components in the cell stack. The advantages of this technology have been demonstrated by several pilot scale and commercial systems [7].

The battery employs V(II)/V(III) and V(IV)/V(V) redox couples in sulphuric acid for the negative and positive half-cells respectively. Unlike conventional battery systems, energy in the VRB is stored in the electrolyte contained in two separate reservoirs. The capacity of the vanadium redox flow battery can therefore be scaled up by increasing the volume of electrolytes. The electrochemical reactions at the negative and positive electrodes can be described by the following equations:

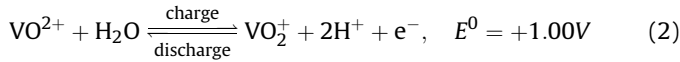
At the negative electrode:

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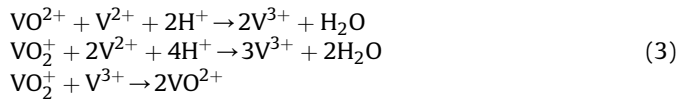


At the positive electrode:

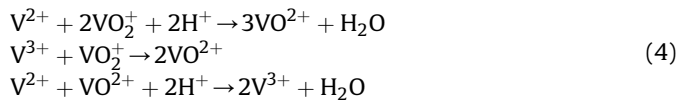


The negative and positive electrolytes are separated by an ion exchange membrane, which allows the movement of protons to balance the charge during cell operation. An ideal membrane should be impermeable to vanadium ions but highly permeable to protons. However, no membranes are 100% impermeable to vanadium ions so diffusion of vanadium ions from one half-cell to the other leads to self-discharge reactions that reduce coulombic efficiency and cell capacity.

The self-discharge reactions in the negative half-cell are caused by diffusion of  $\text{VO}_2^+$  and  $\text{VO}_2^+$  ions from the positive half-cell where they react with  $\text{V}^{2+}$  and  $\text{V}^{3+}$  as following according to [8].



The self-discharge reactions in the positive half-cell are caused by diffusion of  $\text{V}^{2+}$  and  $\text{V}^{3+}$  to the positive side where they react with  $\text{VO}_2^+$  and  $\text{VO}_2^+$  as following according to [8].



Current research on the VRB is aiming to improve the performance by investigating key components such as the electrolytes, electrodes and ion exchange membranes. During operation, the control system also plays a vital role in maximising its performance by optimising the overall efficiency and maintaining the health of the VRB system to ensure a long cycle life. In control system design, an accurate plant model is crucial to identify important dynamic characteristics to be used in controller synthesis. In recent years, several models have been developed for the VRB system. Shah et al. [9] proposed a two dimensional model which was based on conservation laws and combined with a global kinetic model of the reactions. This model was further extended by introducing temperature variations and considering gassing side reactions such as oxygen and hydrogen evolutions [10–12]. These models were used to study the effects of variations in concentration, electrolyte flow rate and electrode porosity on battery performance. More recently, Zheng et al. [13] extended the two dimensional model further into a three dimensional model. These models are useful in VRB stack design, yet they are not feasible to incorporate in the control system. Li and Hikiyama [14] presented a simple dynamic model based on chemical reaction, fluid flow and electrical circuit. Shah et al. [15] simplified the two dimensional model they proposed earlier to be used for control and monitoring purposes. Both studies have however neglected the effects of vanadium ion diffusions across the membrane that can lead to capacity loss during long-term cycling. On the other hand, Tang et al. [8] proposed a simple dynamic model to study the effect of ion diffusion through the ion exchange membrane so as to predict capacity loss during continuous charge-discharge cycling for different types of membranes. However, these models were developed on the assumption that the VRB cells act as continuous stir tank reactors (CSTR) in which concentrations of vanadium ions are uniformly distributed throughout each cell. This assumption does not hold in commercial systems which have

greater dimensions however, so potential problems such as gassing side reactions may be overlooked in the simulations. In this study, a dynamic model for a VRB cell has been developed by assuming the VRB cell acts as a plug flow reactor (PFR) in which concentration variations of vanadium ions between the inlet and outlet of the cell have been taken into account. This model can be easily extended to a multi-cell stack system and apply in control design and fault detection. Simulations have been conducted to investigate the effects of several critical operational inputs, including electrolyte flow rate, cut off state of charge (SOC) limit and input current.

## 2. Model development

A dynamic model for a single cell is developed with consideration of ion diffusion and self-discharge reactions. Similar to the CSTR model [16], this model contains two subsystems which include a VRB cell and two electrolyte tanks. In the VRB cell model, the concentration variation of vanadium ions on the vertical direction  $z$  is considered, while the variations on the horizontal directions  $x$  and  $y$  are neglected, where  $x$ ,  $y$  and  $z$  represent geometric directions of a battery cell as shown in Fig. 1. The model is derived under the following assumptions:

- (1) Diffusion of vanadium ions obey Fick's law;
- (2) Electrolytes in the tanks for each half-cell are perfectly mixed;
- (3) Volumes of both electrolytes remain constant;
- (4) With the implementation of porous electrodes, the effects of mixing in the  $z$  direction is believed to be small and neglected in this study;
- (5) Battery cell acts as a plug flow reactor (PFR);
- (6) Cell and electrolyte temperatures remain constant at room temperature;
- (7) Cell resistance remains constant;
- (8) Self-discharge reactions caused by diffusion of ions across the membrane are instantaneous;
- (9) The system is well designed and isolated properly from air, such that the effect of air oxidation of the V(II) ion on the negative side is neglected;
- (10) Oxygen and hydrogen evolution side reactions are negligible within the set SOC limits;

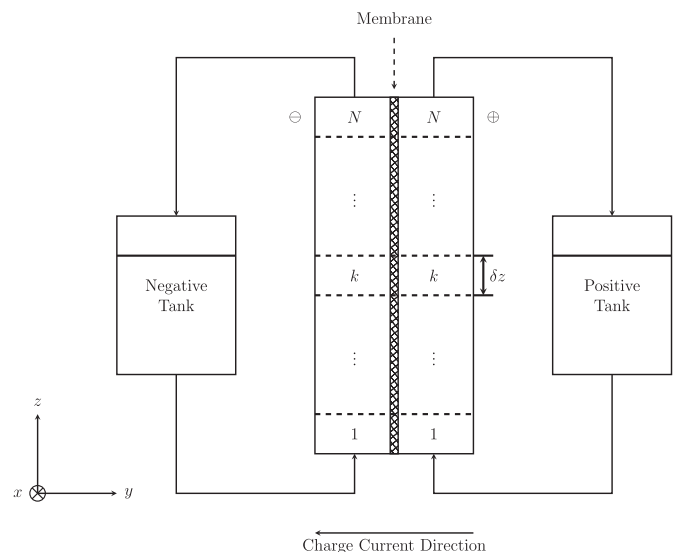


Fig. 1. Discretisation of a VRB cell.

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