Temperature-sensitive Electrochemical Model of Vanadium Redox Flow Battery Cell

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ABSTRACT

Extreme cold and hot weather influence the performance of batteries significantly. Vanadium redox flow batteries (VRFB) work efficiently in the temperature range of 10⁰C to 40⁰C. In this work, a physics-based electrochemical model has been developed to calculate the overpotentials and cell voltage at different temperatures. Decrease in temperature hinders the performance of VRFB by increasing the overpotential. The model is validated with the experiment results of 426 cm^2 single cell VRFB at 25, 10 and -10⁰C.   .

Keywords: Electrochemical model, Vanadium redox flow batteries, Overpotential, Temperature

NONMENCLATURE

Symbols	Quantity
E_{cell}	Cell voltage (V)
η	*Overpotential (V)*
i	Current density (A m^{-2})
n	Charge
d_i	Thickness of material i (m)
σ_i	Conductivity if material i (S m^{-1})
D_i	Diffusivity of ion i (m^2 s^{-1})
C_i	Concentration of ion i (mol m^{-3})
D_f	Fibre diameter (m)
γ	Rate constant (m s^{-1})

1. INTRODUCTION

The rapidly upcoming commercialization of VRFB sets many new challenges to manufacturers of the technology, particularly, with regard to scale-up and optimization, enhancement in stability of the electrolyte, development of the electrodes resilient to oxidation and gas evolution. Most of these challenges are not typically viable for laboratory analysis due to high financial costs and long duration. In such cases, it is necessary to utilize validated modelling and simulation results taken in similar conditions to avoid extensive laboratory experimentation. In the literature, there are many models of the VRFB of sufficient complexity to simulate the performance at temperatures above 25⁰C. Yin et al. (2018) investigated the influence of temperature on the electrolyte properties and single cell performance for the range of temperature -10 to 50⁰C. Their results show that the temperature effect on the concentration polarization of reactive species and the ionic mobility of H⁺ in the membrane may be the main factors affecting the performance at low temperatures. Kim and Park (2016) used the Tafel kinetics to get the reaction parameters and expressed the exchange current density using Arrhenius equation. They validated their electrochemical kinetic model results with experimental results for the temperature range of 25 to 40⁰C.

In this work, an electrochemical model is used to determine the overpotential, voltage, and capacity of the cell based on the state of charge (SOC). Variation of the individual overpotentials are predicted at 25⁰C, 10⁰C and -10⁰C. The model is extended to low temperatures by using experimentally determined activation energies to evaluate the rate constants and conductivity of the electrode.

2. VANADIUM REDOX FLOW BATTERIES

Vanadium redox flow batteries (VRFB) is used to store chemical energy and generate electricity by redox

reaction between vanadium ions dissolved in electrolyte. In VRFB, during electrochemical processes, two pumps circulate two electrolytes consisting of V³⁺/ V²⁺ mixture and VO²⁺/VO₂⁺ mixture through the negative and positive electrodes, respectively, during charge and discharge. The reactions can be expressed as:

$$VO^{2+} + H_2O \leftrightarrow VO_2^+ + 2H^+ + e^- \qquad E^0 = 1.004V \qquad (1)$$

$$V^{3+} + e^- \leftrightarrow V^{2+} \qquad\qquad E^0 = -0.255V \qquad (2)$$
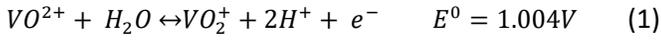
2.1. Electrochemical model

The electrochemical reactions of VRFB are shown in the Eq. 1 and 2. Uniformity in electrolyte flow is ensured by grooving the serpentine channel through the flow field. Additional assumptions considered for simplicity are: 1) Electrolyte flow is incompressible; 2) The electrolyte in the cell and tank is perfectly mixed; 3) Diffusion coefficient of ions and physical properties of electrode are constant at particular temperature; 4) Membrane is impermeable to vanadium ions; 5) Distribution of the vanadium ions are uniform throughout; 6) Electron transfer coefficient is 0.5 in anode and cathode; 7) Self discharge of the cell is negligible; 8) No hydrogen and oxygen evolution occur in the electrode.

Electrochemical models are used to describe the change in the battery voltage in terms of the open-circuit voltage (OCV) and overpotentials (namely, the ohmic, activation, and concentration overpotentials), which vary with vanadium and proton concentrations. The cell voltage is calculated by subtracting the over-potentials from the OCV as given in Eq. 3.

$$E_{cell} = OCV - \eta_{Ohmic} - \eta_{Act} - \eta_{Conc} \qquad (3)$$

2.1.1. Open circuit voltage

In the case of electrochemical equilibrium, the balance between chemical energies and electrical energies exists. The potential exists in the cell at electrochemical known as open circuit potential. It is the potential difference between the electrolyte and the electrode when there is no net reaction taking place in the cell. The OCV depends on the concentration of reactants and products and temperature. Nernst equation is used to obtain open circuit potential of any

electrochemical reaction. In case of VRFB, the Nernst equation is corrected with Donnan potential which exists across the membrane due to unequal proton concentration between negative and positive electrolytes. Difference in preparation methods of electrolyte can change the concentration of protons in the catholytes and anolytes (Knehr and Kumbur, 2011). Concentration of protons on either side of the membrane is included in the Nernst equation as shown in Eq. 4.

$$OCV = E_0 + \frac{RT}{nF}\ln(\frac{C_{VO^{2+}}.C_{V^{2+}}\,C_{H^+}^2 C_{H^+}}{C_{VO_2^+}.C_{V^{3+}}\,C_{H^-}}) \qquad (4)$$

Concentrations of vanadium ions and proton vary with SOC.

2.1.2. Ohmic overpotential

Ohmic overpotential arises from the electric current flowing through the cell. It is the summation of electrode, electrolyte, membrane and flow field resistances (Wang et al., 2017). The membrane and electrodes often make a significant contribution to the overall cell resistance, so it is therefore desirable to develop materials with a small resistivity and to utilize small anode-cathode distances in the cell and stack design.

Table1. Physicochemical parameters of the components of VRFB

Content	Quantity
Diffusivity of V^{3+} & V^{2+}	2.4×10^{-10} m² s⁻¹ [5]
Diffusivity of VO^{2+} & VO^{2+}	3.9×10^{-10} m² s⁻¹ [5]
H^+ diffusivity	9.3×10^{-9} m² s⁻¹ [5]
HSO_4^- diffusivity	1.33×10^{-9} m² s⁻¹ [5]
Porosity of electrode	0.94 [SGL datasheet]
Conductivity of electrode	130 S m⁻¹ [SGL datasheet]
Conductivity of membrane	10.4 S m⁻¹ [5]
Conductivity of flow field	71428 S m⁻¹ [SGL datasheet]
Rate constant for reaction 1	3×10^{-5} m s⁻¹
Rate constant for reaction 2	2.6×10^{-6} m s⁻¹

Ohmic overpotential is given by the Eq. 5.

$$\eta_{ohmic} = i(\frac{d_e}{\sigma_e} + \frac{d_m}{\sigma_m} + \frac{d_{gp}}{\sigma_{gp}} + \frac{d_{cc}}{\sigma_{cc}} + \frac{d_e}{k_{eff}}) \qquad (5)$$

Ionic conductivity of the electrolyte influence the overall conductivity in the cell. Ions involved in the process are $V^{2+}, V^{3+}, VO^{2+}, H^+, VO_2^+, HSO_4^-$. Effective conductivity of the electrolyte is given by

$$k^{eff} = \frac{F^2}{RT} \sum n_i^2 D_i^{eff} C_i \tag{6}$$

Highly porous electrode is used in the VRFB system so as to allow easy circulation of the electrolytes. The electrolyte is transported through the pores. So, diffusivity of the electrolyte needs to be calculated based on porosity.   Effective diffusivity of the electrolyte is obtained by using Bruggemann correction factor

$$D_i^{eff} = \varepsilon^{1.5} D_i \tag{7}$$

According to Stokes-Einstein equation, diffusivity of the ions is inversely proportional to the viscosity of the electrolyte.

$$D = \frac{RT}{6\pi r_i \mu} \tag{8}$$

where r_i ionic radius, T is absolute temperature, μ is the viscosity of electrolyte. Viscosity is related to the temperature according to the following correlation obtained by measured electrolyte viscosity given by Eq. 9.

$$\mu = 0.0074T^2 - 0.4112T + 9.9546 \tag{9}$$

Ohmic resistance of the cell was determined using the electrochemical impedance spectroscopy (EIS) at different temperatures. Ohmic resistance increased from 3.16 mΩ at 25°C to 6.2 mΩ at -10°C (Rao and Jayanti 2021).

$$\sigma_e = \frac{1}{R_{ohm}} = A e^{E_a/RT} \tag{10}$$

Where A is constant, E_a is the activation energy. The value of activation energy obtained from the experimental results of ohmic resistance is 12.23 kJ/kmol.

Membrane conductivity is calculated at different temperatures using the Eq. 11.

$$\sigma_m = 10.98 \exp(1268 \left[\frac{1}{303} - \frac{1}{T}\right]) \tag{11}$$

2.1.3. Activation overpotential

The electrochemical reactions occur on the surface of the electrode-electrolyte. Most of the reversible electrochemical reactions taking place on the porous electrode follow the Butler-Volmer equation. The activation over-potential in the negative and positive electrodes are given by Eq. 12 and 13 respectively.

$$\eta_{act}^{neg} = \frac{2RT}{nF} \left(\sinh^{-1}(\frac{i}{2F\gamma_- \sqrt{C_{V^{3+}} C_{V^{2+}}}}) \right) \tag{12}$$

$$\eta_{act}^{pos} = \frac{2RT}{nF} \left((\sinh^{-1}(\frac{i}{2F\gamma_+ \sqrt{C_{VO^{2+}} C_{VO_2^+}}})) \right) \tag{13}$$

Where γ_- and γ_+ are rate constant of negative and positive electrode respectively. The effect of temperature on rate constant is estimated using the experimentally determined charge transfer resistance by EIS. Charge transfer resistance increased from 2.05 mΩ at 25°C to 4.18 mΩ at -10°C with 4.6 mm electrode (Rao and Jayanti 2021).

$$\frac{1}{R_{ct}} = A exp(\frac{-E_a}{RT}) \tag{14}$$

The value of activation energy obtained experimental results of charge transfer resistance is 28.29 kJ/kmol.

2.1.4. Concentration over-potential

Concentration overpotential is the result of the concentration gradient between the bulk electrolyte and the surface of the electrode at high applied currents, and is predominantly prevailing at the end of charge or discharge in a flow battery when the concentrations of the active species are low. As a result, the reaction rate is limited by the concentration gradient in the diffusion layer so that the electron transfer process becomes mass-transfer controlled (Tang et al.   2014).

$$\eta_{conc} = -\frac{RT}{F} \ln(\frac{i}{k_m nF c_i^{bulk}}) \tag{15}$$

The local mass transfer coefficient k_m is obtained by considering flow rate and diffusion coefficient of the ions in the electrolyte. It is determined from the empirical formula given by Eq. 16 for laminar flow on the fibres of the porous carbon electrode (Schmal et al., 1986). Experimentally determined density and viscosity of the electrode are at desired temperatures are used in the model and can be calculated as follows:

$$k_{m,i} = \frac{D_i^{eff}}{D_f} 6.1 Re^{0.352} \tag{16}$$

2.2. Results

The cell voltage of single cell VRFB was predicted using material properties from the literature. The Input parameters for the model are current density, flow rate, compression ratio (CR), initial concentration electrolyte ions and proton.

2.2.1. Open circuit voltage

The variation of the OCV with SOC at different temperature is given in Figure 1. OCV increases with decrease in temperature. Reversible cell voltage increases with decrease in temperature, which contributes in increase in OCV with decrease in temperature.
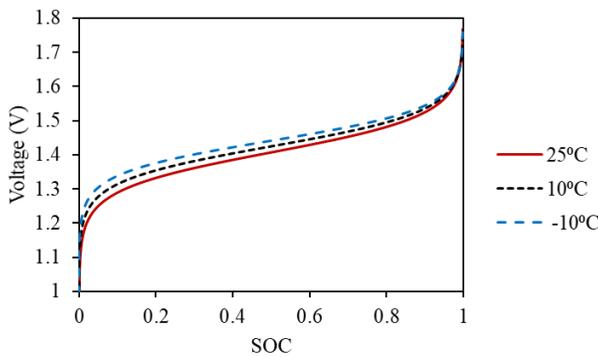
Fig. 1. Open circuit voltage at different temperatures

2.2.2. Effect of temperature

In this section, comparison of experimental results and the model predictions is presented at different temperatures 25, 10 and -10°C, at current density 60 mA cm^{-2}, flow rate 250 ml min^{-1}. The results are given in the Figure 2.
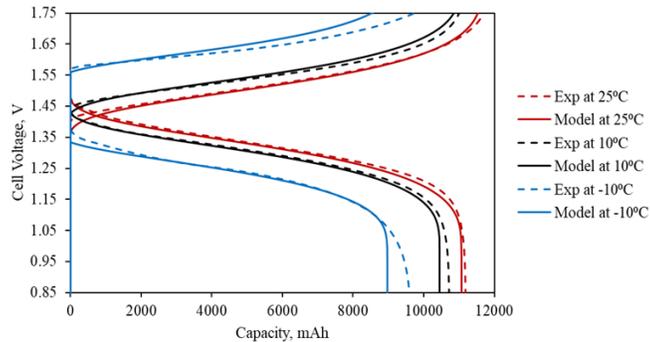
Fig. 2. Effect of temperature on charge-discharge studies of cell with area at 426 cm^2 with 4.6 mm thick electrode at 35% CR at current density of 60 mA cm^{-2} and flow rate of 250 ml min^{-1}.

We can clearly see the widening of voltage window with decrease in temperature at 10°C and -10°C. Mass transfer polarization reaches early in the model predictions at -10°C.

Ionic conductivity of the electrolyte depends on temperature, diffusivity of the ions and concentration of electrolyte. Ionic conductivity of the electrolyte is calculated from Eq. 6. The diffusivity of the ions change with temperature which leads to change in conductivity of the electrolyte solution. Figure 3 gives the changes in the ionic conductivity of the electrolyte with the temperature. Ionic conductivity of the electrolyte increases with increase in SOC and decreases with decrease in temperature. Proton contributes about 87% to the total ionic conductivity of the electrolyte.
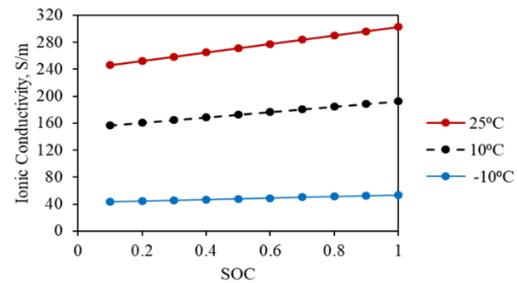
Fig. 3. Variation of ionic conductivity with SOC and temperature for the electrolyte concentration of 1.6 M vanadium and 3 M H_2SO_4

Ohmic, activation and concentration overpotential of 426 cm^2 single cell VRFB at current density of 60 mA cm^{-2} predicted at different temperature and 50% SOC is given in Table 2. We can observe that activation overpotential in the negative electrode is very high compared to the other overpotentials.

Table 2. Overpotentials at different temperatures and 50% SOC

Temperature	Over-potential (mV)			
(°C)	η_{ohmic}	η_{act}^{neg}	η_{act}^{pos}	η_{conc}
25	31.3	62.8	6.7	8.9
10	43.6	81.4	10.5	9.9
-10	85.5	100.3	16.9	16.0

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2.2.3. Effect of current density

Operating current density of the cell was changed from 40 to 80 mA cm^{-2}. The equilibrium potential, activation and ohmic overpotential increase with increase in current applied to the cell. The same trend can be observed in Figure 4. The reaction proceeds fast at higher current densities leading to attain concentration overpotential quickly. The charge-discharge cut off is reached early as the reactants are depleted in the active sites of the electrode. At low current density, the reaction proceeds slowly leading to increase in capacity.
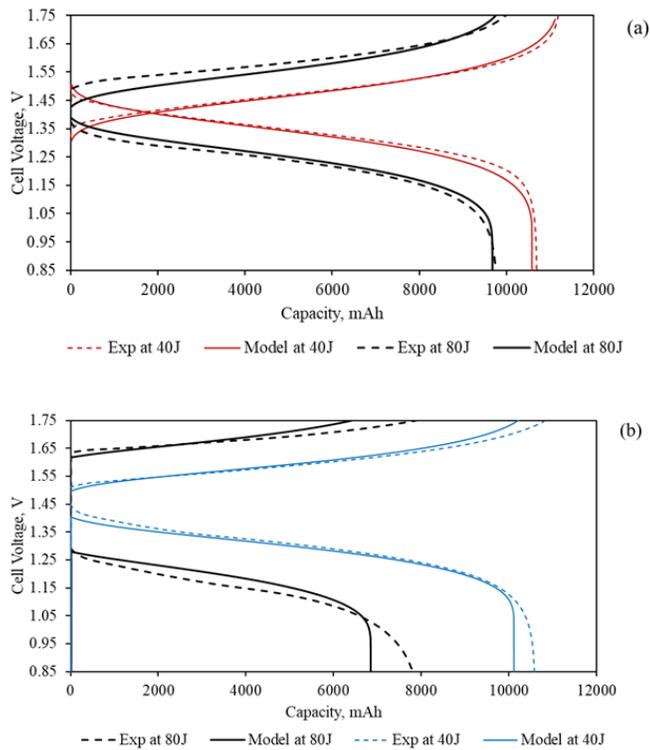
Fig. 4. Charge-discharge cycle of cell with active area of 426 cm^2 having electrode of 4.6 mm thickness, CR 35%, and corresponding model predictions for the current densities of 40 and 80 mA cm^{-2} a) at 25°C b) at -10°C

2.2.4. Effect of flow rate

The electrolyte flow rate plays a critical role in determining the change in the concentration of the vanadium ions, and the concentration overpotential. Electrolyte flow rate influences the mass transfer of ion in the cell. Insufficient flow rate may be destructive to the cell leading to overcharge of the cell. Comparison of experimental results and model predictions of discharge profiles of the cell with active area of 426 cm^2 having

electrode of 4.6 mm thickness, at current density 60 mA.cm^{-2} and -10°C is given in Figure 5.

It is observed that discharge capacity of the cell increases with increase in flow rate. Early onset of concentration polarization can be observed at low flow rate of 120 ml min^{-1} compared to the flow rates 240 ml min^{-1}. As the flow rate increased the discharge time was increased, which results in increase in discharge capacity of the cell.
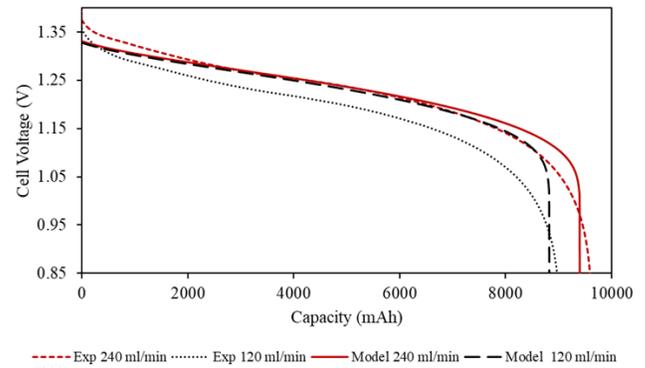
Fig. 5. Comparison of experimental results and model predictions of discharge profiles of the cell with active area of 426 cm^2 having electrode of 4.6 mm thickness and 35% CR at different flow rate, current density 60 mA.cm^2 and -10°C

2.2.5. Effect of electrode compression

The electrode compression improves the conductivity of the electrode. Porosity of the cell decreases with increase in compression. As the porosity increases bulk diffusion of the electrolyte increases, leading to increase in permeability of the electrolyte. This leads to the reaction to complete fast and capacity is reduced. One of the major disadvantages of increasing compression is increase in pressure drop in the cell. Electrode parameters considered for modelling the effect of compression is given in the Table 3. As the compression increases overpotential decreases improving the performance of VRFB. At 17% compression, activation and ohmic overpotential is more compared to 50% compression. The comparison of experimental and model results are given in Figure 6.

Table 3. Parameters of 6 mm thick SGL carbon felt electrode with different compression

Electrode properties	17%	35%	50%
Compressed thickness	5 mm	4 mm	3 mm
Porosity	0.9	0.88	0.84
Conductivity	28.3	58.2	83.1
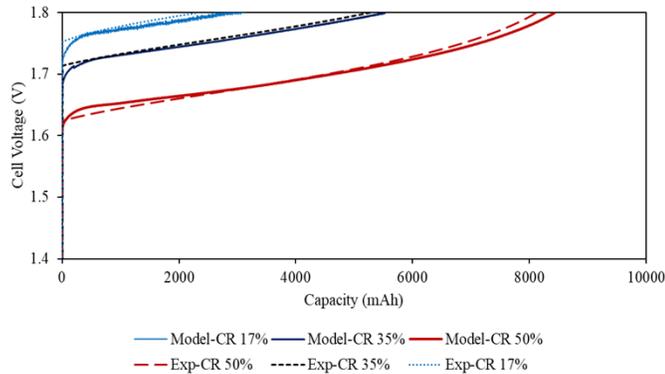
Fig. 6. Comparison of experimental results and model predictions of charge profiles of the cell with active area of 426 cm^2 having electrode of 6 mm thickness, at different compression, current density 60 mA cm^{-2} and -10°C

3. CONCLUSIONS

Extreme cold weather influence the performance of batteries significantly. Vanadium redox flow batteries (VRFB) work efficiently in the temperature range of 10°C to 40°C. In this work, a physics-based electrochemical model of the VRFB system is developed to predict the voltage as a function of the applied current, electrolyte flow rate, electrode compression and temperature. The model calculates the changes in ohmic, activation and concentration overpotential at low temperatures. Material properties, kinetic parameters and diffusivities are taken from literature. The measured data of cell impedance at different temperatures have been used to modify the electrochemical reaction rate to take account of temperature effect. The model is validated with the experiment results of 426 cm^2 single cell VRFB at 25, 10 and -10°C. This model shows good agreement with the experimental data over a range of circulation rates and operating temperatures and can be used to predict system performance under different climatic conditions and operating conditions.

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