A parametric analysis of the output voltage of all-vanadium redox-flow battery system

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Abstract. Vanadium redox flow battery (VRFB) becomes a global technology used in stationary applications like grid storage. The characteristics of output voltage during the charge-discharge cycles and the resulted power of VRFB are strongly based on solving a multidisciplinary problem. In this paper, a 2D steady state numerical model for the operation of a single VRFB has been formulated, validated with good agreement, and tested. The output voltage response of VRFB at different state of charges (SOCs) has been investigated under range of volumetric flow rates and current densities. Next, a comprehensive parametric analysis, sensitivity study, for the major electrode and electrolyte material properties is conducted which can improve confidence in model predictions. The results showed that increasing flow rate can help to minimize concentration polarization, however, pumping power would be dominated. A low flow rate can cause some poor covered regions, but would reduce pumping power. Based on the sensitivity results, only cathode reaction rate, specific surface area, conductivity of porous electrode and electrolyte, and carbon felt porosity are input parameters that dominate the simulation results. It is expected that this proposed model would be applicable to most flow batteries architectures and can be extended to stack flow batteries.

1. Introduction
Redox flow battery (RFB) is a type of rechargeable electrochemical cell that has recently attracted a huge attention as a stationary energy storage technology. VRFB is considered as a preferable choice among many (RFBs) where it has two different features compared to conventional batteries: 1) reactions take place between the solution species in both sides instead of being between the liquid solution and porous electrode, so no losing in electrolyte solution during the charge-discharge cycles. 2) two external reservoirs are normally utilized to store vanadium solutions and pumped to the cell by two pumps. Vanadium redox flow battery (VRFB) is considered as a new representative efficient chemical energy storage battery where an electricity is produced from the stored chemical energy in electrolyte solutions by changing the valence of species through an electron transfer process [1-3].

VRFB is one of the promising electricity energy storage system (ESS) technologies for storage of renewable energy and maintain stable power output due to its desirable characteristics of high efficiency, thousands of cycles, deep discharge, active thermal management and independence of energy, design flexibility, and elimination of electrolyte cross contamination due to using same vanadium species for both halves of the cell [4-11]. Despite the aforementioned advantages associated with VRFB, issues such as low electrolyte density, cell/stack geometry structure, and high capital cost due to expensive materials of vanadium and membrane, can stand against its wide-spread adoption by the global sector[12-17]. However,
relatively high cost, mechanical degradation, long charging time etc. issues of lithium-ion, Nas, and lead-acid batteries, have brought more attention to the VRFB as a suitable technology for energy storage[18-20].

Up to now, a lot of efforts (numerical and experimental work) have been conducted by focusing on different hydrodynamic and electrochemical parameters and cell designs that lead to improve the performance of VRFB, and subsequently, facilitate the commercialization and industrialization of VRFB. Different pattern of flow field channels such as parallel, serpentine, and interdigitated, has been achieved experimentally to study the overall VRFB performance, and it was shown that a serpentine cell pattern has better battery efficiency among them, which can be attributed to the dual impact of better voltage efficiency and lower pumping power losses [21]. A novel cell structure has been introduced in [22], which includes a non-porous and non-brittle case and it was shown that the new design not only improves battery performance, but also lowers assembly costs and facilitates assembly. In Ref. [23], three different flow field channel heights have been selected to investigate their impact on VRFB cell performance in a 3D numerical model under various operating conditions, and highest battery efficiency was obtained at low channel design. The distribution of vanadium solution species was investigated for a parallel flow field design through an experimental and numerical study [24], and the simulated results were in a good agreement with the obtained ones from experiment work. Temperature impact on the capacity degradation and columbic efficiency of a single cell VRFB setup has been conducted under different operating conditions [25], and it was found that increasing the temperature from 15 to 55 °C can increase both voltage efficiency and peak discharge power density while a slight decrease in current efficiency occurs. A polarization study to investigate the performance of two VRFB cells with a serpentine flow channel and without a flow field was performed, and it was concluded that the ohmic losses were dominating other losses for a serpentine cell configuration [26]. Numerically, a 3D model of VRFB with an interdigitated flow channel was investigated by examining the impact of one/multi inlet structures on current density, species concentration, and pressure losses distributions [27].

So far, most the previous work focused on studying different open issues that affect VRFB efficiency and a little or no attention has been paid to the material property inputs impact on cell performance[28-30]. The current work aims to better understand the behavior of VRFB output voltage under different operating conditions through a general 2D numerical model that can provide a guidance for future VRFB designs. A comprehensive analysis of many input material parameters of the full flow battery model is conducted in order to study their sensitivity and find the one(s) might affect the cell performance in hopes of improving system efficiency. The origin operating parameters were already taken from literature [31] in this work, and they were changed within (± 15 %) to see if they affect the performance or not. Details of the studies and the obtained results were discussed below.

2. Development of Model

Basically, the electrochemical reactions in a VRFB involve various transport phenomena including the dissociation and association of molecules, ions and electrons, which required a formulation of a multidisciplinary problem.

2.1. Flow battery model

As the geometric size of a regular VRFB cell is too large for computational modeling, a simplified 2D geometric model was built in this paper as depicted in figure 1a. The whole schematic flow VRFB cell components is shown in figure 1b, which includes two porous electrodes, anode and cathode, membrane positioned between the electrodes, two current collectors outside the electrodes, two species solutions, catholyte and anolyte, stored in external tanks where they can be circulated to the porous electrodes through a pump for each electrode, and load/ power supply source for charge-discharge processes.
2.2. Simplifications and assumptions
Some assumptions to develop the VRFB model are made to describe the transfer of vanadium species, and ionic/electronic currents, as follows:
1. Constant electrolyte density is assumed for the electrolyte as no significant change occurs in volume.
2. The electrolyte is considered as a dilute solution since the ionic concentrations are sufficiently low. In electrolytes, the water molecules dominate other species. For a crude evaluation, the water concentration in pure liquid water is \( \sim 55,000 \text{ mol/m}^3 \); while other ions are usually around 1,000 mole/m^3 in electrolyte, thus the molar fraction of all the other species in the electrolyte can be estimated [32]:

\[
\frac{\sum k \neq \text{H}_2\text{O} C_k}{C_{\text{H}_2\text{O}}} < 10\%
\]  

(1)

where \( C_k \) is the concentration of each vanadium species and \( C_{\text{H}_2\text{O}} \) is the water concentration.
3. A steady-state model is considered for a large tank size assumption.
4. The effect of gravity is neglected.
5. Based on the Reynolds number calculation (86-2280), the flow in the cell is a laminar flow, hence, all the transport equations are formulated as a laminar flow behavior.
6. Protons are only assumed to cross the membrane.
7. Side reactions and crossover are not taken into account.
8. Porous electrodes are isotropic and homogeneous.

2.3. Transport through the porous electrodes
In porous electrodes, Brinkman equation is utilized to formulate the mechanism of species transport for a non-compressible fluid [27]:

\[
\frac{\rho}{\varepsilon} \left( \bar{u} \cdot \nabla \right) \bar{u} = -\nabla p + \nabla \cdot \left( \frac{\mu}{\varepsilon} \left( \nabla \bar{u} + (\nabla \bar{u})^T \right) \right) - \frac{2}{3} \varepsilon \mu \left( \nabla \cdot \bar{u} \right) - \left( \frac{\mu}{K} + Q \right) \bar{u} + \bar{f}
\]  

(2)

\[
\rho \left( \nabla \cdot \bar{u} \right) = 0
\]

(3)

where \( \rho, u, p, f, \mu, \varepsilon, Q, K \) are density of electrolyte, velocity of flow, pressure in electrodes, volume force vector, electrolyte viscosity, porosity of electrode, source of mass, and hydraulic permeability of the electrode, respectively. The Carman–Kozeny equation is utilized to calculate the hydraulic permeability, as follows [33]:
\[ K = \frac{d_{fib}^2 e^2}{16 C_k (1-\varepsilon)^2} \]  

where \( d_{fib} \) and \( C_k \) are mean fiber diameter and Carman–Kozeny constant for a fibrous media, respectively.

2.3. Electrochemical kinetics

Battery electrodes are porous media with interconnected pore networks, enabling electrolyte flows. The primary half-reaction in the negative electrode is [23]:

\[ V^{3+} + e^{-} \xrightarrow{\text{disch–char}} V^{2+} \quad (E^0_{0,ne} = -0.255 \text{ V vs. SHE}) \]  

(5)

In the positive electrode, the primary reaction is:

\[ V^{4+} + H_2O \xrightarrow{\text{disch–char}} V^{5+} + 2H^+ + e^{-} \quad (E^0_{0,po} = 1.004 \text{ V vs. SHE}) \]  

(6)

In each half-cell, water, components of a dissociated liquid electrolyte in the case of sulfuric acid (for example \( H^+, HSO_4^- \), and \( SO_4^{2-} \)); in addition to the four vanadium species (for example \( V^{2+}, V^{3+}, V^{5+}, \) and \( V^{4+} \)) can exist and flow through the anode and cathode electrodes. The species conservation equation (Nernst–Planck equation) in both electrodes is applied [32]:

\[ \nabla \cdot \bar{N}_{i,e} = R_i \]  

(7)

where \( i \) is the different utilized species in electrolyte solution (represented by subscript \( e \)), \( \bar{N} \) is the superficial flux of species, and \( R_i \) denotes the source term for the species. Equation (7) applies to all charged species except \( SO_4^{2-} \) which is calculated from the condition of electroneutrality in the electrolyte as shown below [32]:

\[ \sum_i Z_i C_{i,e} = 0 \]  

(8)

where \( Z_i \) and \( C_{i,e} \) are the valence and concentration species, respectively. The source term \( R_i \), listed in table 1, represents the reaction rate of species \( i \) due to the electrochemical reactions or the dissociation of \( H_2SO_4 \) [37]. In general, the dissociation of \( H_2SO_4 \) occurs in the following steps [32]:

\[ H_2SO_4 \rightarrow H^+ + HSO_4^- \]  

(9)

\[ HSO_4^- \rightarrow H^+ + SO_4^{2-} \]  

(10)

Since the electrolytes contain less than the experimentally observed limit of \( H_2SO_4 \) (\( \sim 40 \text{ mole/kg} \)), it is reasonable to assume that the first step of dissociation, equations (9 and 10), is fully complete [32]. The dissociation rate in the second step is calculated as follows:

\[ R_d = K_{dis} \left( \frac{C_{H^+,e} - C_{HSO_4^{2-},e}}{C_{H^+,e} + C_{HSO_4^{2-},e} - \beta} \right) \]  

(11)

where \( K_{dis} \), \( C_{H^+,e} \), and \( \beta \) are the coefficient of dissociation reaction, concentration of proton, and the dissociation degree of \( H_2SO_4 \). The species movement due to diffusion, migration, and convection in flux equation (7) are described by the Nernst-Planck equation [31]:

\[ \bar{N}_{i,e} = -D_i^{eff} \nabla C_{i,e} - Z_i M_{i,e} F \nabla \phi_{i,e} + \bar{u}_i C_{i,e} \]  

(12)

where \( M_{i,e} \), \( F, \phi_{i,e} \), and \( \bar{u}_i \) are the liquid mobility, potential of moving ions, Faraday constant, and superficial velocity of electrolyte, respectively. The term \( D_i^{eff} \) represents effective diffusion coefficient which is evaluated by the Bruggeman relation [34]:

\[ D_i^{eff} = D_i \varepsilon^{1.5} \]  

(13)

The ionic mobility, \( M_{i,e} \), is determined by using the Nernst- Einstein equation [35]:

\[ M_{i,e} = \frac{D_i^{eff}}{RT} \]  

(14)

where \( R \) is the universal gas constant and \( T \) is temperature.
Table 1. Source and sink terms [31].

| Parameter | Definition                                                                 | Cathode          | Anode          |
|-----------|-----------------------------------------------------------------------------|------------------|----------------|
| $R_2$     | $V^{2+}$ concentration equation $(mol \cdot m^{-3})$                        | $- I/F$          |                |
| $R_3$     | $V^{3+}$ concentration equation $(mol \cdot m^{-3})$                        | $- I/F$          |                |
| $R_4$     | $V^{4+}$ concentration equation $(mol \cdot m^{-3})$                        | $I/F$            |                |
| $R_5$     | $V^{5+}$ concentration equation $(mol \cdot m^{-3})$                        | $- I/F$          | $- I/F$        |
| $R_{H^+}$ | Proton concentration equation $(mol \cdot m^{-3})$                          | $- R_d$          | $- 2 \left(\frac{I}{F}\right) - R_d$ |
| $R_{HSO_4^-}$ | Bisulfate concentration equation $(mol \cdot m^{-3})$                  | $R_d$            | $R_d$          |

Constant value of solution viscosity $\mu_j$ is considered due to the lack of data regarding the electrolyte of a VRFB, which represents the viscosity of the electrolyte at (SOC=50%) [31]. The values of $\mu_j$ and the other electrolyte properties are listed in Table 2.

Table 2. Properties of electrolyte [31].

| Symbol | Definition                                              | Value    |
|--------|---------------------------------------------------------|----------|
| $K_{dls}$ | $HSO_4^-$ dissociation reaction rate constant $(S^{-1})$                             | $10^4$   |
| $\beta$ | $HSO_4^-$ degree of dissociation                                                   | 0.25     |
| $\mu_{ne}$ | Average anolyte viscosity $(Pa \cdot s)$                      | 0.0025   |
| $\mu_{po}$ | Average cathlyte viscosity $(Pa \cdot s)$                        | 0.005    |
| $\rho_{ne}$ | Average density of anode $(kg \cdot m^{-3})$                     | 1300     |
| $\rho_{po}$ | Average density of cathode $(kg \cdot m^{-3})$                    | 1350     |
| $\rho_w$ | Density of water $(kg \cdot m^{-3})$                                          | 999      |
| $D_2$ | $V^{2+}$ diffusion coefficient $(m^2 \cdot s^{-1})$               | $2.4 \times 10^{-10}$ |
| $D_3$ | $V^{2+}$ diffusion coefficient $(m^2 \cdot s^{-1})$               | $2.4 \times 10^{-10}$ |
| $D_4$ | $V^{2+}$ diffusion coefficient $(m^2 \cdot s^{-1})$               | $3.9 \times 10^{-10}$ |
| $D_5$ | $V^{2+}$ diffusion coefficient $(m^2 \cdot s^{-1})$               | $3.9 \times 10^{-10}$ |
| $D_{H^+}$ | Proton diffusion coefficient $(m^2 \cdot s^{-1})$            | $9.312 \times 10^{-9}$ |
| $D_{HSO_4^-}$ | $HSO_4^-$ diffusion coefficient $(m^2 \cdot s^{-1})$           | $1.33 \times 10^{-9}$ |
| $D_{SO_4^{2-}}$ | $SO_4^{2-}$ diffusion coefficient $(m^2 \cdot s^{-1})$ | $1.065 \times 10^{-9}$ |

The charge conservation equation in the electrode includes electrochemical reactions, transport of species, and ionic/electronic current as follows [34]:

$$\nabla \cdot \vec{j}_i = - \nabla \cdot \vec{j}_{ie} = I \tag{15}$$

where $I$ is the reaction current density. $\vec{j}_i$ and $\vec{j}_{ie}$ refer to the ionic and electronic current densities in the electrode domain, respectively, and are given as follows [34]:

$$\vec{j}_i = F \sum_i Z_i \vec{N}_{ie} \tag{16}$$

The total current density in the electrolyte then satisfies (invoking electro neutrality):
\[ \vec{j}_i = -K^{\text{eff}} \nabla \Phi_{\text{le}} - F \sum_i Z_i D_i^{\text{eff}} \nabla C_{i,e} \]  

(17)

where the effective conductivity, \( K^{\text{eff}} \) is given by:

\[ K^{\text{eff}} = \frac{F^2}{RT} \sum_i Z_i^2 D_i^{\text{eff}} \nabla C_{i,e} \]  

(18)

\[ \vec{j}_s = \sigma_{\text{ca}}^{\text{eff}} \nabla \Phi_s \]  

(19)

where \( \sigma_{\text{ca}}^{\text{eff}} \) is the effective electrical conductivity of porous electrode that can be calculated from the value of the solid material, \( \sigma_s \), via using Bruggemann correction as follows [34]:

\[ \sigma_{\text{ca}}^{\text{eff}} = (1 - \varepsilon)^\frac{3}{2} \sigma_s \]  

(20)

Also, \( \sigma_s \) is the bulk conductivity of the electrode, and its value is given in table 3 along with the other properties of the electrodes.

The local reaction current density \( i_{a,c} \) is expressed by the Butler-Volmer equations, which are given in Eq. (23-24) for both the negative (‘a’) and positive (‘c’) electrodes [34].

\[ i_a = \alpha F K_{\text{ne}} \left( \frac{C_{2,e}}{C_{3,e}} \right)^{(1-\alpha_{ne})} \left( \frac{C_{3,e}}{C_{4,e}} \right)^{\alpha_{ne}} \exp \left( \frac{1 - \alpha_{ne}}{R_{\text{con}} T} F \eta_{\text{ne}} \right) \exp \left( \frac{-\alpha_{ne}}{R_{\text{con}} T} F \eta_{\text{ne}} \right) \]  

(21)

\[ i_c = \alpha F K_{\text{po}} \left( \frac{C_{4,e}}{C_{5,e}} \right)^{(1-\alpha_{po})} \left( \frac{C_{5,e}}{C_{6,e}} \right)^{\alpha_{po}} \exp \left( \frac{1 - \alpha_{po}}{R_{\text{con}} T} F \eta_{\text{po}} \right) \exp \left( \frac{-\alpha_{po}}{R_{\text{con}} T} F \eta_{\text{po}} \right) \]  

(22)

where \( C_{i,e} \) refers to the surface concentration of species \( i \) at the interface between liquid and solid of the electrode. For the negative half-cell, these concentrations are determined by solving for \( C_{2,e}^s \) and \( C_{3,e}^s \) in the following equations [31]:

\[ FD_2 \left( \frac{C_{2,e}^s - C_{2,e}}{R_p} \right) = FK_{\text{ne}} \left( \frac{C_{2,e}}{C_{3,e}} \right)^{(1-\alpha_{ne})} \left( \frac{C_{3,e}}{C_{4,e}} \right)^{\alpha_{ne}} \exp \left( \frac{1 - \alpha_{ne}}{R_{\text{con}} T} F \eta_{\text{ne}} \right) \exp \left( \frac{-\alpha_{ne}}{R_{\text{con}} T} F \eta_{\text{ne}} \right) \]  

(23)

\[ FD_3 \left( \frac{C_{3,e}^s - C_{3,e}}{R_p} \right) = FK_{\text{ne}} \left( \frac{C_{2,e}}{C_{3,e}} \right)^{(1-\alpha_{ne})} \left( \frac{C_{3,e}}{C_{4,e}} \right)^{\alpha_{ne}} \exp \left( \frac{1 - \alpha_{ne}}{R_{\text{con}} T} F \eta_{\text{ne}} \right) \exp \left( \frac{-\alpha_{ne}}{R_{\text{con}} T} F \eta_{\text{ne}} \right) \]  

(24)

where \( R_p = d_{f,ib} / 2 \) (the mean pore radius of the electrode) is the average path-length of diffusion. In the positive half-cell, these concentrations can be determined by developing a similar system of equations using equation (24). Also, in equations (23-24), \( K \) is the standard rate of reaction constant, and \( \alpha_{ne} \) and \( \alpha_{po} \) are the transfer coefficients in anode and cathode, respectively. The surface-to-volume ratio \( \alpha \) is the specific surface area of carbon electrode, whereas \( \eta \) is the overpotential determined as follows:

\[ \eta_f = \Phi_{\text{le}} - \Phi_{3,e} - E_{0,i} \]  

(25)

where \( E_{0,i} \) represents the open circuit voltage (OCV) of each half-cell calculated using the Nernst equations given as follows:
\[ E_{0,ne} = E_{0,e}^g + \frac{RT}{F} \ln \left( \frac{C_{3,e}}{C_{2,e}} \right) \]  
\[ E_{0,po} = E_{0,p,o}^g + \frac{RT}{F} \ln \left( \frac{C_{5,e} \cdot (C_{H,po})^2}{C_{4,e}} \right) \]

\( E_{0,ne}^g \) and \( E_{0,po}^g \) represent the equilibrium potentials in anode and cathode electrodes, respectively. In equation (27), \( C_{H,po} \), concentration of proton, is considered because the protons are involved in the redox reaction at the electrode equation (6). Also, the membrane potential at the interface in both sides with electrolyte is taken into account through applying Donnan potential equation as follows [36]:

\[ E_m^k = \frac{RT}{F} \ln \left( \frac{C_{i,m}^k}{C_{i,m}^{k+}} \right) \]

Where \( m \) is the membrane and \( k \) is the positive or negative electrode side depending on the electrolyte. The electrodes properties and reaction kinetics input parameters are presented in tables 3 and 4, while membrane properties are shown in table 5.

**Table 3.** Properties of electrode [31].

| Symbol | Definition                  | Value  |
|--------|-----------------------------|--------|
| \( \varepsilon \) | Electrode porosity | 0.93 |
| \( d_{fib} \) | Fiber diameter (µm) | 50.3 |
| \( a \) | Specific surface area (m\(^{-1}\)) | \( 3.5 \times 10^4 \) |
| \( C_k \) | Kozeny-carmen coefficient | 180 |
| \( H_{cell} \) | Electrode height (m) | 0.04 |
| \( l_e \) | Electrode thickness (m) | 0.00834 |
| \( \sigma_{ca} \) | Electronic conductivity of electrode (S \( \cdot \) m\(^{-1}\)) | 66.7 |

**Table 4.** Kinetic parameters [31].

| Symbol | Definition                                      | Value  |
|--------|------------------------------------------------|--------|
| \( K_{ne} \) | Reaction rate constant in anode (m \( \cdot \) s\(^{-1}\)) | \( 7 \times 10^{-8} \) |
| \( K_{po} \) | Reaction rate constant in cathode (m \( \cdot \) s\(^{-1}\)) | \( 2.5 \times 10^{-8} \) |
| \( \alpha_{ne} \) | Negative charge transfer coefficient | 0.45 |
| \( \alpha_{po} \) | Positive charge transfer coefficient | 0.55 |
| \( E_{0,ne}^g \) | Equilibrium potentials in anode (V) | -0.255 |
| \( E_{0,po}^g \) | Equilibrium potentials in cathode (V) | 1.004 |

**Table 5.** Properties of membrane [31].

| Symbol | Definition                                      | Value  |
|--------|------------------------------------------------|--------|
| \( l_m \) | Membrane thickness (µm) | 203 |
| \( Z_f \) | Fixed acid concentration | -1 |
| \( C_f \) | Fixed acid charge (mol \( \cdot \) m\(^{-3}\)) | 1990 |
| \( \sigma_{mem} \) | Electronic conductivity of membrane (S \( \cdot \) m\(^{-1}\)) | 24.88 |
2.4. Boundary conditions
The boundary conditions of the formulated model can be specified as follows:

\[
\begin{align*}
V &= V^0 / A \quad \text{(inlet)} \\
\rho &= P_0 \quad \text{(outlet)}
\end{align*}
\] (29)

where \(V, V^0, A, P_0\) are electrolyte inlet velocity for both electrodes, volumetric flow rate of electrolyte, anode and cathode cross-section area, outlet gauge pressure which was set to zero. The outlet gauge pressure is usually set to zero. For the walls of electrodes, slip boundary condition was considered while a Neumann boundary condition was satisfied pressure satisfies at electrode boundaries:

\[\nabla p \cdot \vec{n} = 0\] (30)

All input species concentrations are placed as a function of SOC, and they can be expressed as follow:

\[
\begin{align*}
C_{l,e}^{in} &= C^0 \cdot SOC, \quad i = 2,5 \\
C_{l,e}^{in} &= C^0 \cdot (1 - SOC), \quad i = 3,4
\end{align*}
\] (31)

where \(C^0\) is the total vanadium concentration in anode/cathode. As no species are allowed to cross the electrode/membrane interface, no-penetration boundary conditions are applied:

\[\nabla C_{l,e} \cdot \vec{n} = 0\] (32)

Other electrode boundaries are set to wall condition:

\[(−D_{l}^{eff} \nabla C_{l,e} + \bar{w}_{l} C_{l,e}) \cdot \vec{n} = 0\] (33)

Boundary condition of electrode potential distribution is needed, and it is written along electrode/current collector interface as follows:

\[−σ_{ca}^{eff} \nabla \Phi_{e} \cdot \vec{n} = −I\] (34)

where \(I\) represents the total applied current density, also, electrolyte potential distribution at the electrode/membrane boundary is set as follows:

\[−K^{eff} \nabla \Phi_{l,e} \cdot \vec{n} = I\] (35)

For discharge the situations are reversed. Also, there are insulated conditions for the rest of the electrode surfaces.

\[
\begin{align*}
−\vec{n} \cdot \vec{j}_{l} &= 0 \\
−\vec{n} \cdot \vec{j}_{s} &= 0
\end{align*}
\] (36)

The electronic potential at the anode boundary is set to zero:

\[\Phi_{ca} = 0\] (37)

No flux of vanadium species is allowed at the cathode/current collector boundary, in addition to, the top and bottom interfaces of membrane:

\[
\begin{align*}
−\vec{n} \cdot \vec{N}_{l,e} \quad \text{(for electrodes)} &= 0 \\
−\vec{n} \cdot \vec{N}_{l,m} \quad \text{(for membrane)} &= 0
\end{align*}
\] (38)

The remaining boundaries of the cell (top and bottom of the electrode and membrane domains) are considered electrically insulated:

\[−\vec{n} \nabla \cdot \vec{j}_{l,e} = −\vec{n} \nabla \cdot \vec{j}_{s,e} = −\vec{n} \nabla \cdot \vec{j}_{l,m} = 0\] (39)

Finally, in the current simulation, the vanadium species are initially considered at 15% SOC. All the operating conditions and initial concentrations are listed in table 6, where SOC is formulated as follows:

\[
\text{For Anode} : \quad \text{SOC} = \frac{C_{2,e}}{C_{2,e} + C_{3,e}}
\] (40)

\[
\text{For Cathode} : \quad \text{SOC} = \frac{C_{4,e}}{C_{4,e} + C_{5,e}}
\] (41)
3. Results and discussion

A finite-element method in COMSOL Multiphysics® package was used to solve the governing equations in the presented model. A quadratic basis was used in all of the simulations with setting $1 \times 10^{-5}$ as a relative error tolerance. This 2D model was already validated in previous 3D model study [23] in which same electrochemical and fluid mechanic physics equations were used for the utilized cell size configuration, but without considering the flow field impact. However, sensitivity analysis of different input parameters that are hard to be predicted experimentally were conducted here, besides verifying the current model through the obtained variations in output voltage due to the ($\pm 15\%$) changes in input material parameters. The charging curves was performed at an initial state of charge (SOC) of 15% to (SOC) of 95% or when the cell reached to 1.7 V. All the presented figures were made by Matlab 2013a software.

### 3.1. Effects of volumetric flow rates and current densities

It is important to control the electrolyte volumetric flow rate to avoid poor electrode covered regions at low supplied rates, and leakage issues and high pressure drops at high pumped flow rates. Simulation results at low, medium, and high values of flow rates (3, 8, 20, 50, 100 ml/min) are presented to determine their impact on output voltage during charge process under various current densities (15, 30, 55, 85 mA/cm$^2$) as a function of SOCs. The responses of cell on charge voltage at various conditions are shown in figure 2 and figure 3. It is obvious that increasing flow rates becomes more dominant when the current density increases as shown in figure 2d (d: 85 mA/cm$^2$). For instance, in figure 2a, there is a slight difference in charging
voltage among different ranges of flow rates along SOCs, while this difference becomes more significant in figure 2d (Voltage ~1.7 V at SOC = 0.75 at flow rate 3 ml/min, and Voltage ~1.7 V at SOC = 0.89 at flow rate 100 ml/min). This caused due to the competition between diffusion and surface reaction. The diffusion rate becomes more dominant than the rate of the surface reaction at a low flow rate where a quick raise in cell voltage occurs (high concentration polarization) because of the insufficient supplied amount of electrolyte to the electrode surface. This is not the case at high flow rate whereas the cell voltage was affected by the surface reaction rate more than the diffusion rated. Also, an ohmic drop becomes larger at higher current density and constant volumetric flow rate which in turn leads to a quick raising in cell voltage through charging as shown in figure 3, for instance at flow rate 3 ml/min and SOC = 0.15 in figure 3a, the voltage =1.31 V at current density 15 mA/cm², while voltage =1.5091 V at current density 85 mA/cm².

Figure 2. The response of cell voltage in a charge process at different volumetric flow rates: (a) at current density 15 mA/cm², (b) at current density 30 mA/cm², (c) at current density 55 mA/cm², (d) at current density 85 mA/cm².
Figure 3. The response of cell voltage in a charge process at different current densities: (a) at flow rate 3 ml/min, (b) at flow rate 8 ml/min, (c) at flow rate 20 ml/min, (d) at flow rate 100 ml/min, (e) Cell voltage against range of flow rates at different current densities at SOC = 0.55.
3.2. Effects of electrode and electrolyte material properties

In this section, parameters that related to the electrode and electrolyte material properties such as $K_{ne}$, $K_{po}$, $a$, $\sigma_{ea}$, $\sigma_{el}$, $D_2$, $D_3$, $D_4$, $D_5$, $d_{fib}$, $\varepsilon$ have been studied where some of these parameters were picked either from experiment tests or frequently used as a fitting parameters in an approximate way[30, 37]. Each parameter changed with ($\pm$ 15%) of its origin value in [31] in the aim of detecting which one(s) might have more influence on cell performance during the charge process, which can also, improve the confidence in model predictions.

Two different voltage responses are performed for each parameter, one at constant flow rate 20 ml/min for SOC = 0.15 and SOC = 0.85 at current densities 30 mA/cm$^2$ and 85 mA/cm$^2$ for each SOC as shown in figures 4 (a, c); and the other response at constant current density 30 mA/cm$^2$ for SOC = 0.15 and SOC = 0.85 at flow rates 8 ml/min and 50 ml/min for each SOC as shown in figures 4 (b, d). For the parameter (a), specific surface area (m$^{-1}$) in figures 4 (a, b), all the plots have same trend with an improvement of cell voltage as the parameter increases with 15% due to the increased surface area –to- volume which leads to more reaction surface area. For instance, ~0.8% V voltage improvement in figure 4a for the case of SOC= 0.85 and current density 85 mA/cm$^2$, whereas ~0.4 V in figure 4b for the case of SOC= 0.85 and flow rate 50 ml/min. Since higher porosity, $\varepsilon$, leads to enlarge the surface area of reaction, almost same improvements in cell voltage of parameter (a) were found in figures 4 (c, d).
The impact of $K_{p_0}$, cathode reaction rate ($m \cdot s^{-1}$), is shown in figure 5a. An improvement of $\sim 0.5\%$ V in the case of SOC= 0.85 and current density 85 mA/cm$^2$ as its value increases 15%, whereas $\sim 0.4\%$ V in figure 5b for the case of SOC= 0.85 and flow rate 50 ml/min. Since the transformation from V4 to V5 during a reaction in anode is slower than from V2 to V3 reaction in cathode, $K_{p_0}$ dominates the reaction overpotential with an enhancement in voltage, while $K_{ne}$, anode reaction rate ($m \cdot s^{-1}$), has almost no change in this analysis as shown in table 7. The parameters $\sigma_{oa}$ and $\sigma_{el}$ (electronic and ionic conductivities ($S \cdot m^{-1}$ )) have initial values 66.7 and 80 ($S \cdot m^{-1}$) which are responsible of electron movement in the carbon felt skeleton and ion travelling through the membrane, respectively. The improvements in these parameters are $\sim 0.6\%$ V and $\sim 0.55\%$ V in the case of SOC= 0.85 and current density 85 mA/cm$^2$, whereas $\sim 0.3\%$ V and $\sim 0.2\%$ V for the case of SOC= 0.85 and flow rate 50 ml/min, respectively, as shown in figures 5 (c, d, e, f). Although electronic conductivity has lower initial value, but it has more sensitivity than ionic conductivity which comes from the fact that electrochemical reactions tend to occur preferentially near the separator interface and the current in both the anode and cathode is carried through the carbon felt, which gives a higher response voltage. The remaining parameters $\sigma_{mem}, D_2, D_3, D_4, D_5, d_{fib}$, have almost no change in their response voltages in both cases as shown in table 7. For $\sigma_{mem}$, crossovering of species is not considered in the assumptions of this model which cancel its effect, but we would expect it if considered. For the diffusivities and $d_{fib}$, their very small initial values are not enough to get response within ($\pm 15\%$) changes, also, species diffusivity in each electrode is the same which gives identical response voltages.


**Table 7.** Voltage responses of material properties at different operating conditions.

| Parameters values | Volumetric flow rate 20 ml/min | Current density 30 mA/cm² |
|-------------------|---------------------------------|---------------------------|
|                   | SOC=0.15 30 mA/cm² | SOC=0.85 30 mA/cm² | SOC=0.15 85 mA/cm² | SOC=0.85 85 mA/cm² | SOC=0.15 8 m/minute | SOC=0.85 8 m/minute | SOC=0.15 50 ml/min | SOC=0.85 50 ml/min |
|                   | σₘₑₘ (S·m⁻¹) | | | | | | | |
|                   | 21.148 | 1.3481 | 1.5367 | 1.4927 | 1.6891 | 1.3503 | 1.5411 | 1.3473 | 1.5351 |
|                   | 24.881 | 1.3479 | 1.5365 | 1.4921 | 1.6885 | 1.3501 | 1.5408 | 1.3471 | 1.5349 |
|                   | 28.613 | 1.3477 | 1.5363 | 1.4917 | 1.688 | 1.3499 | 1.5407 | 1.3469 | 1.5347 |
|                   | Kₙₑ (m·s⁻¹) | | | | | | | | |
|                   | 5.95E-08 | 1.3498 | 1.5384 | 1.4966 | 1.6932 | 1.3519 | 1.5428 | 1.349 | 1.5368 |
|                   | 7E-08 | 1.3479 | 1.5365 | 1.4921 | 1.6885 | 1.3501 | 1.5408 | 1.3471 | 1.5349 |
|                   | 8.05E-08 | 1.3465 | 1.5351 | 1.4887 | 1.6848 | 1.3488 | 1.5394 | 1.3457 | 1.5335 |
|                   | D₂ and D₃ (m²/s⁻¹) | | | | | | | | |
|                   | 2.04E-10 | 1.348 | 1.5365 | 1.4921 | 1.6885 | 1.3502 | 1.5408 | 1.3471 | 1.5349 |
|                   | 2.4E-10 | 1.3479 | 1.5365 | 1.4921 | 1.6885 | 1.3501 | 1.5408 | 1.3471 | 1.5349 |
|                   | 2.76E-10 | 1.3479 | 1.5365 | 1.4922 | 1.6885 | 1.3501 | 1.5409 | 1.3471 | 1.5349 |
|                   | dₕₑ (mm) | | | | | | | | |
|                   | 0.04276 | 1.35 | 1.5407 | 1.347 | 1.5348 | 1.3478 | 1.5364 | 1.4919 | 1.688 |
|                   | 0.0503 | 1.3501 | 1.5408 | 1.3471 | 1.5349 | 1.3479 | 1.5365 | 1.4921 | 1.6885 |
|                   | 0.05785 | 1.3502 | 1.541 | 1.3472 | 1.535 | 1.348 | 1.5366 | 1.4923 | 1.689 |
Figure 5. Charge voltage response of material properties (cathode reaction rate, electrolyte and electrode conductivity) with (± 15%) changes: (a, c, e) at flow rate 20 ml/min for the SOC= 0.15 and 0.85 at current densities 30 mA/cm² and 85 mA/cm² for each SOC, (b, d, f) at current density 30 mA/cm² for the SOC= 0.15 and 0.85 at flow rates 8 ml/min and 50 ml/min for each SOC.

3.3. Effects of flow rate on pressure drop and pumping power

Assessment of battery performance is based on two competitive objectives: concentration overpotential and pumping power. When the flow rate is too high, mass transfer rate can be improved, but there is a problem of leakage and low cell performance due to the excessive pumping power. Also, at too flow rate, pumping power can be reduced with the possibility of high concentration overpotential due to the lack of provided electrolytes. Pumps are mainly meant to provide the cell with electrolyte during the charge-discharge cycles, and the obtained pumping power was calculated according to [38]:

\[ P_{\text{Pump-power}} = \frac{N_{\text{Pum}} \cdot V^o \cdot \Delta p}{\eta_{\text{Pum}}} \]  

(43)

where \( N_{\text{Pum}} \) is the number of pumps in battery system, \( V^o \) is the actual provided amount of flow rate, \( \eta_{\text{Pum}} \) is the pump efficiency, which is around 0.85, and \( \Delta p \) refers to the pressure losses in the whole components.
of battery. In this part, only pressure drop along cathode electrode was considered. Based on the adopted cell configuration, laminar flow was obtained and fluid pressure distribution at two flow rates 3 ml/min and 100 ml/min is shown in figure 6a (left and right), respectively. Also, the total pressure losses as a function of various flow rates and the corresponding pumping power were depicted in figures 6b, and 6c, respectively. Linear behavior was obtained to pressure variation with flow rate, whereas a non-linear relation for pumping power [39].

![Figure 6](image)

**Figure 6.** (a) Distribution of electrolyte pressure at 3 ml/min (on left) and at 100 ml/min (on right), (b) Pressure drop at different volumetric flow rates, (c) Corresponding pumping power.

4. Summary and future development

In the current paper, a 2D isothermal model was formulated and performed to simulate a single cell of VRFB. The model was validated experimentally in previous work [23]. The presented work focused on investigating the impact of different ranges of flow rates and current densities with respect to range of SOCs on the output cell voltage during charge cycle. As the flow rate increases, the cell voltage response becomes better, however, the pressure losses and corresponding power increases too in a bigger ratio compared to the voltage enhancement which required finding an optimal flow rate for better performance. In addition, the battery has larger charge-discharge depths at high flow rates and state of charges. Also, a sensitivity
analysis of many input electrode and electrolyte material properties were conducted with change of (± 15%) of the initial values. Based on the sensitivity results, only $K_{pa}$, $a$, $\sigma_{ca}$, $\sigma_{el}$, $\varepsilon$ input parameters dominate the simulation results, which are cathode reaction rate, specific surface area, conductivity of porous electrode and electrolyte, and carbon felt porosity. Accordingly, further investigation and modeling are required for simulation fidelity of these parameters. This model is capable to predict other characteristics of VRFB such limiting current density, species distribution on electrode surface, overpotentials in both sides, and battery efficiency, so it can be employed to optimize both VRB design and system operating conditions. Also, it can be extended to include another physical phenomenon (heat losses), which is related to temperature gradients that could affect the cell performance if there are quick changes between the cell and surrounding.

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