In electrochemical cells, transport of chemical species to/from the electrodes is limited by the mass transfer resistance between the electrode surface and the bulk electrolyte. This mass transfer resistance thus contributes to voltage losses, referred to as mass transport losses or concentration overpotential, compared to the reversible potential of cell. In this paper, we derived analytical expressions for estimating the mass transport losses in all-vanadium redox flow batteries. A step-by-step analysis allows us to relate the surface and bulk concentrations and then, identify the voltage losses due to mass transport from the Nernst equation and the Butler-Volmer kinetics. A zero-dimensional (0D) model with the derived expressions for the concentration overpotential is calibrated and validated with experimental data; good agreement is obtained. The mass transport losses from the Butler-Volmer kinetics are found to be approximately twice of that from the Nernst equation.

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and scaling arguments. The 0D model for a single cell of VRFB is as follows:

$$E_{\text{cell}} = E^{\text{OCV}}(c) - \eta_{\text{neg}}(c, I) + \eta_{\text{pos}}(c, I) + I R_{\text{cell}},$$  \[3\]

$$E^{\text{OCV}} = E_{\text{pos}} - E_{\text{neg}},$$  \[4\]

$$E_{\text{pos}} = E_{\text{pos}}^0 + \frac{RT}{F} \ln \left( \frac{c_{\text{V}_3^{2+}}}{c_{\text{V}_2^{2+}}} \right),$$  \[5\]

$$E_{\text{neg}} = E_{\text{neg}}^0 + \frac{RT}{F} \ln \left( \frac{c_{\text{V}_2^{2+}}}{c_{\text{V}_3^{2+}}} \right),$$  \[6\]

where $I$ is the applied current ($I > 0$ during charge and $I < 0$ during discharge), $R_{\text{cell}}$ is the total electronic resistance for ion and electronic conduction in the cell, $E$ is the reversible potential, $E^0$ is the standard reduction potential, $R$ is the molar gas constant, $F$ is the Faraday constant, $c$ is the average concentration of the vanadium ions, $\eta$ is the overpotential, $T$ is the cell temperature; subscripts, pos and neg, denote the positive and the negative electrode respectively. The bulk concentration of the species, $c^{(b)}$, are given by,

$$c^{(b)}_{\text{V}_2^{2+}} = c^{(b)}_{\text{V}_3^{2+}} = c^0_{\text{V}_2^{2+}} + \frac{n I t}{V_{\text{tank}} F},$$  \[7\]

$$c^{(b)}_{\text{V}_3^{2+}} = c^{(b)}_{\text{V}_2^{2+}} = c^0_{\text{V}_3^{2+}} - \frac{n I t}{V_{\text{tank}} F},$$  \[8\]

where $c^0_{\text{V}_2^{2+}}$ and $c^0_{\text{V}_3^{2+}}$ are initial concentration of $V^{2+}$ and $V^{3+}$ ions at the start of each charge and discharge cycle, and $V_{\text{tank}}$ is the volume of the electrolyte tanks. Assuming that all the cells in the stack are identical in terms of both design and operating conditions, only a single cell is simulated and voltage of a single cell ($E_{\text{cell}}$) is multiplied by the number of cells ($n_c$) to obtain the stack voltage ($E_{\text{stack}}$):

$$E_{\text{stack}} = n_c E_{\text{cell}}$$  \[9\]

The assumption of extrapolating a single cell to describe the behavior of the whole stack has drawbacks as identified in Refs.30,31. Hence, $\Delta c$ can be approximated by the following functional form:

$$E^{\text{OCV}} = E_{\text{pos}} - E_{\text{neg}} + \epsilon,$$  \[18\]

where $\epsilon$ is the superficial velocity of the electrolyte flowing through the electrodes, $a$ and $b$ are fitted parameters. We determine $a$ and $b$ by fitting with the experiments.

**Formal potentials.—** While evaluating the reversible potential with the Nernst equation of the form in Eqs. 5–6, activity coefficients of the species are ignored, i.e., considered to be equal to unity. This is a common assumption employed in VRFB modeling. However, the assumption has limitations that were indeed confirmed in Refs. 38,39. In the above works, the open circuit voltages predicted by the Nernst equations with standard reduction potentials were observed to deviate from the experimentally measured OCVs. Pavelka et al.38 further analyzed this deviation and revealed the limitations of ignoring the activity coefficients (equal to unity) in the Nernst equation. Thus, incorporating the activity coefficients in the Nernst equations is suggested.38 An easy way to account for activity coefficients of the species in Nernst equation is to use the formal potential instead of the standard reduction potential.40,41 In this work, we group the deviation between the formal and the standard reduction potential for the two electrodes in a single parameter, $\epsilon$ and thus, write

$$E^{\text{OCV}} = E_{\text{pos}} - E_{\text{neg}} + \epsilon,$$  \[20\]

**Analysis**

**Nernst potential.—** Having correlated the bulk and surface concentration of the species, we analyze the Nernst equation to deduce the concentration overpotential component arising from it. When the mass transport of the species from the bulk to the surface or vice-versa is a limiting step in the overall electrochemical process, the equilibrium potential of the electrode is given by the Nernst equation of the form

$$E_{\text{neg}} = E_{\text{neg}}^0 + \frac{RT}{F} \ln \left( \frac{c^{(s)}_{\text{V}_3^{2+}}}{c^{(s)}_{\text{V}_2^{2+}}} \right),$$  \[19\]

$$E_{\text{pos}} = E_{\text{pos}}^0 + \frac{RT}{F} \ln \left( \frac{c^{(s)}_{\text{V}_2^{2+}}}{c^{(s)}_{\text{V}_3^{2+}}} \right).$$  \[20\]

Based on the reactions taking place during charge and discharge, we can write after substituting surface concentrations,

$$E_{\text{neg}} = E_{\text{neg}}^0 + \frac{RT}{F} \ln \left( \frac{c^{(b)}_{\text{V}_2^{2+}} - \Delta c}{c^{(b)}_{\text{V}_3^{2+}} + \Delta c} \right),$$  \[21\]
\[
E_{\text{pos}} = E_{\text{pos}}^0 + \frac{RT}{F} \ln \left( \frac{c_{\text{VO}_2}^{(b)} + \Delta c}{c_{\text{VO}_2}^{(b)} - \Delta c} \right) \tag{22}
\]

In order to distinguish bulk and surface concentrations, Eqs. 21 and 22 can be rearranged to give
\[
E_{\text{neg}} = E_{\text{neg}}^0 + \frac{RT}{F} \ln \left( \frac{c_{\text{V_3}^{(b)}}^{(b)} + \Delta c/c_{\text{V_3}^{(b)}}^{(b)}}{c_{\text{V_3}^{(b)}}^{(b)} - \Delta c/c_{\text{V_3}^{(b)}}^{(b)}} \right), \tag{23}
\]
\[
E_{\text{pos}} = E_{\text{pos}}^0 + \frac{RT}{F} \ln \left( \frac{1 + \Delta c/c_{\text{VO}_2}^{(b)}}{1 - \Delta c/c_{\text{VO}_2}^{(b)}} \right). \tag{24}
\]

The first two terms in the expression for \(E_{\text{neg}}\) and \(E_{\text{pos}}\) respectively constitute the Nernst equation with bulk concentrations for the negative and positive electrode (Eqs. 5–6). They are applicable as it is in the case of negligible mass transfer resistance (\(k_m \rightarrow \infty\) or \(\Delta c \approx 0\)), i.e., when the rate of transfer of species is fast enough compared to the rate of consumption or production of the ions. The remaining two terms in Eqs. 23 and 24 are correction terms for a significant mass transfer resistance, i.e., on employing the surface concentrations instead of bulk concentrations and therefore, represent the voltage losses due to mass transport resistance at the surface of the electrodes. We can write expressions for such voltage losses, i.e., concentration overpotential from the Nernst equation for the two electrodes as follows
\[
\eta_{\text{neg,Nernst}} = \frac{RT}{F} \ln \left( \frac{1 - \Delta c/c_{\text{V_3}^{(b)}}^{(b)}}{1 + \Delta c/c_{\text{V_3}^{(b)}}^{(b)}} \right), \tag{25}
\]
\[
\eta_{\text{pos,Nernst}} = \frac{RT}{F} \ln \left( \frac{1 + \Delta c/c_{\text{VO}_2}^{(b)}}{1 - \Delta c/c_{\text{VO}_2}^{(b)}} \right). \tag{26}
\]

**Reaction kinetics.**—In this subsection, we aim to deduce the concentration overpotential component arising from the BV equation and also show that the overpotential is the sum of the activation and concentration overpotentials. To do so, we consider the generalized BV equation which incorporates the mass transport resistance of the species while accounting for the reaction kinetics at the electrodes in the VRFB.\(^{3,4,6,8}\)

\[
J_{\text{neg}} = a_{\text{neg}}^0 \frac{c_{\text{V_5}^{(b)}}^{(a)}}{c_{\text{V_3}^{(b)}}^{(b)}} \exp \left\{ \frac{1 - a_{\text{neg}} F \eta_{\text{neg}}}{RT} \right\} - \frac{c_{\text{V_3}^{(b)}}^{(a)}}{c_{\text{V_5}^{(b)}}^{(b)}} \exp \left\{ - a_{\text{neg}} F \eta_{\text{neg}} \frac{RT}{F} \right\}, \tag{27}
\]
\[
J_{\text{pos}} = a_{\text{pos}}^0 \frac{c_{\text{VO}_2}^{(b)}}{c_{\text{V_3}^{(b)}}^{(b)}} \exp \left\{ \frac{1 - a_{\text{pos}} F \eta_{\text{neg}}}{RT} \right\} - \frac{c_{\text{V_3}^{(b)}}^{(a)}}{c_{\text{VO}_2}^{(b)}} \exp \left\{ - a_{\text{pos}} F \eta_{\text{neg}} \frac{RT}{F} \right\}, \tag{28}
\]

where \(\eta\) represents the total voltage losses for an electrochemical reaction taking place, i.e., it incorporates the voltage losses to overcome the activation barrier (activation overpotential) as well as the mass transport resistance (concentration overpotential), and
\[
Fk_{\text{neg}} \left( \frac{c_{\text{V_3}^{(b)}}^{(b)}}{c_{\text{V_3}^{(b)}}^{(b)}} \right)^{1-a_{\text{neg}}} \left( \frac{c_{\text{V_3}^{(b)}}^{(b)}}{c_{\text{V_3}^{(b)}}^{(b)}} \right)^{a_{\text{neg}}}, \tag{29}
\]
\[
Fk_{\text{pos}} \left( \frac{c_{\text{V_3}^{(b)}}^{(b)}}{c_{\text{V_3}^{(b)}}^{(b)}} \right)^{1-a_{\text{pos}}} \left( \frac{c_{\text{V_3}^{(b)}}^{(b)}}{c_{\text{V_3}^{(b)}}^{(b)}} \right)^{a_{\text{pos}}}, \tag{30}
\]

where \(a_{\text{neg}}\) and \(a_{\text{pos}}\) are the charge transfer coefficients for negative and positive electrode respectively, and \(k_{\text{neg}}\) and \(k_{\text{pos}}\) are the reaction rate constants for negative and positive electrode respectively.

When there is negligible mass transfer resistance, i.e. \(c_{\text{V_3}^{(b)}}^{(b)} \approx c_{\text{V_3}^{(b)}}^{(a)}\), the voltage losses at the electrodes are purely due to charge transfer resistance. For such a case, Eqs. 27 and 28 reduce to
\[
J_{\text{neg}} = a_{\text{neg}}^0 \frac{c_{\text{V_5}^{(b)}}^{(a)}}{c_{\text{V_3}^{(b)}}^{(b)}} \exp \left\{ - \frac{F \eta_{\text{neg}}}{2RT} \right\}, \tag{31}
\]
\[
J_{\text{pos}} = a_{\text{pos}}^0 \frac{c_{\text{V_3}^{(b)}}^{(a)}}{c_{\text{V_5}^{(b)}}^{(b)}} \exp \left\{ - \frac{F \eta_{\text{neg}}}{2RT} \right\}. \tag{32}
\]

Substituting \(J_{\text{pos}} = \frac{J_{\text{neg}}}{\alpha_{\text{pos}}}\), \(J_{\text{neg}} = -J_{\text{pos}}\), and symmetric charge transfer \((\alpha = 0.5)\), the expression for \(\eta_{\text{act}}\) in Eqs. 31 and 32 becomes,
\[
\eta_{\text{act}}^{\text{neg}} = -2RT \sinh \left( \frac{I}{2a_FV_c k_{\text{neg}} \sqrt{c_{\text{V_3}^{(b)}}^{(b)}}} \right), \tag{33}
\]
\[
\eta_{\text{act}}^{\text{pos}} = 2RT \sinh \left( \frac{I}{2a_FV_c k_{\text{pos}} \sqrt{c_{\text{V_3}^{(b)}}^{(b)}}} \right). \tag{34}
\]

The above two terms represent the voltage losses to overcome the activation barrier and therefore, are referred to as the activation overpotentials.

Next, we proceed to pull out the concentration overpotential terms inherent in the Butler-Volmer equations (Eqs. 27–28). The concentration losses are most pronounced at higher current densities where one term in the BV equation is typically much larger than the other. The relative magnitude of the two terms depends on the electrode and charge/discharge. For example, the second term dominates for the negative electrode (Eq. 27) during charging and thus, the BV equation is simplified to
\[
J_{\text{neg}} = -a_{\text{neg}}^0 \frac{c_{\text{V_5}^{(b)}}^{(a)}}{c_{\text{V_3}^{(b)}}^{(b)}} \exp \left\{ \frac{F \eta_{\text{neg}}}{2RT} \right\}, \tag{35}
\]

After substituting surface concentration in terms of bulk concentration, Eq. 35 becomes
\[
\eta_{\text{neg}} = -2RT \frac{a_{\text{neg}}^0}{F} \ln \left( -\frac{J_{\text{neg}}}{a_{\text{neg}}^0} \right) = 2RT \frac{a_{\text{neg}}^0}{F} \ln \left( \frac{c_{\text{V_5}^{(b)}}^{(a)}}{c_{\text{V_3}^{(b)}}^{(b)}} \right) - \Delta c. \tag{36}
\]

The first term is a simplified expression of the activation overpotential at higher current densities. This is identified by substituting \(\Delta c \approx 0\) in Eq. 36 which corresponds to a negligible mass transfer resistance \((k_m \rightarrow \infty)\). Note that we shall continue to use expressions in Eqs. 33, 34 for estimation of the activation overpotentials. The second term in Eq. 37 accounts for the losses associated with the mass transport resistance between the bulk and surface of the electrodes:
\[
\eta_{\text{neg,bV}}^{\text{conc}} = -2RT \frac{a_{\text{neg}}^0}{F} \ln \left( \frac{c_{\text{V_5}^{(b)}}^{(a)}}{c_{\text{V_3}^{(b)}}^{(b)}} \right) + \Delta c. \tag{38}
\]

During discharging, the first term dominates for the negative electrode (Eq. 27) whence the BV equation is simplified to
\[
J_{\text{neg}} = a_{\text{neg}}^0 \frac{c_{\text{V_5}^{(b)}}^{(a)}}{c_{\text{V_3}^{(b)}}^{(b)}} \exp \left\{ \frac{F \eta_{\text{neg}}}{2RT} \right\}. \tag{39}
\]

Again, substituting surface concentration in terms of bulk concentration, the term describing the mass transport losses can be identified as
follows:

$$\eta_{\text{neg,BV}}^{\text{conc}} = \frac{2RT}{F} \ln \left[ \frac{c_i^{(b)}}{c_i^{(b)} + \Delta c} \right].$$ \[40\]

Similarly, the mass transport losses contained in the kinetics expression for the positive electrode during charge are written as follows

$$\eta_{\text{pos,BV}}^{\text{conc}} = \frac{2RT}{F} \ln \left[ \frac{c_i^{(b)}}{c_i^{(b)} + \Delta c} \right].$$ \[41\]

and during discharge, they become

$$\eta_{\text{pos,BV}}^{\text{conc}} = \frac{2RT}{F} \ln \left[ \frac{c_i^{(b)}}{c_i^{(b)} - \Delta c} \right].$$ \[42\]

The generalized expression for the BV component of the concentration overpotential at the negative electrode can be written as,

$$\eta_{\text{neg,BV}}^{\text{conc}} = \frac{2RT}{F} \ln \left[ \frac{c_i^{(b)}}{c_i^{(b)} - |\Delta c|} \right],$$ \[43\]

During charging, the negative sign holds and species $i$ represents $\text{V}^{3+}$ whereas the positive sign holds and species $i$ represents $\text{V}^{2+}$ during discharging.

Similarly, the generalized expression for the BV component of the concentration overpotential at the positive electrode can be written as,

$$\eta_{\text{pos,BV}}^{\text{conc}} = \frac{2RT}{F} \ln \left[ \frac{c_i^{(b)}}{c_i^{(b)} - |\Delta c|} \right].$$ \[44\]

During charging, the negative sign holds and species $i$ represents $\text{VO}^{2+}$ whereas the positive sign holds and species $i$ represents $\text{VO}^{3+}$ during discharging.

### Results

**Cell voltage.**—In the preceding section, we have deduced the concentration overpotential components from both the Nernst and BV equation. Thus, the equation for cell voltage prediction (Eq. 3) becomes (N.B.: we refer to earlier sections for nomenclature of symbols):

$$E_{\text{cell}} = E^{\text{OCV}}(c^{(b)}) - \eta_{\text{neg}}^{\text{act}}(c^{(b)}, I) - \eta_{\text{pos}}^{\text{conc}}(c^{(b)}, I) + \eta_{\text{pos}}^{\text{act}}(c^{(b)}, I) + \eta_{\text{IR}}^{\text{cell}}.$$

$$E^{\text{OCV}} = E_{\text{pos}} - E_{\text{neg}} + \epsilon,$$

$$E_{\text{pos}} = E_{0}^{\text{pos}} + \frac{RT}{F} \ln \left( \frac{c_i^{(b)}}{c_i^{(b)} + \Delta c} \right),$$ \[47\]

$$E_{\text{neg}} = E_{0}^{\text{neg}} + \frac{RT}{F} \ln \left( \frac{c_i^{(b)}}{c_i^{(b)} - \Delta c} \right).$$ \[48\]

$$\eta_{\text{act}}^{\text{neg}} = -\frac{2RT}{F} \sinh^{-1} \left( \frac{I}{2aFV_k \Delta n_{\text{neg}}^{(b)} \sqrt{c_{\text{V}^{2+}}^{(b)} c_{\text{V}^{3+}}^{(b)}}} \right).$$ \[49\]

$$\eta_{\text{act}}^{\text{pos}} = \frac{2RT}{F} \sinh^{-1} \left( \frac{I}{2aFV_k \Delta n_{\text{pos}}^{(b)} \sqrt{c_{\text{V}^{2+}}^{(b)} c_{\text{V}^{3+}}^{(b)}}} \right).$$ \[50\]

| Parameter | Value | Units |
|-----------|-------|-------|
| $L$       | 0.35  | m     |
| $w_{\text{cell}}$ | 0.25  | m     |
| $h_z$     | 4     | mm    |
| $a$       | $2 \times 10^5$ | m$^{-1}$ |
| $N$       | 15    | -     |
| $T$       | 300   | K     |
| $V_{\text{tank}}$ | 20    | L     |
| $c_{\text{V}^{3+}}^{(b)}$ | 1499  | mol m$^{-3}$ |
| $c_{\text{V}^{2+}}^{(b)}$ | 1499  | mol m$^{-3}$ |
| $c_{\text{O}^{2-}}^{(b)}$ | 1     | mol m$^{-3}$ |
| $V$       | 0.2, 0.71 | m$^3$ h$^{-1}$ |
| $l_{\text{app}}$ | 45, 75 | mA cm$^{-2}$ |
| $E_{\text{act, pos}}$ | 1.004 | V     |
| $E_{\text{act, neg}}$ | -0.255 | V    |
| $R$       | 8.314 | J mol$^{-1}$ K$^{-1}$ |
| $F$       | 96500 | A s mol$^{-1}$ |
| $R_{\text{cell}}$ | 2.2   | mΩ    |

$$\eta_{\text{neg}} = \eta_{\text{neg, Nernst}} + \eta_{\text{neg, BV}},$$ \[51\]

$$\eta_{\text{pos}} = \eta_{\text{pos, Nernst}} + \eta_{\text{pos, BV}},$$ \[52\]

$$\eta_{\text{neg,BV}}^{\text{conc}} = \frac{2RT}{F} \ln \left[ \frac{c_i^{(b)}}{c_i^{(b)} - |\Delta c|} \right],$$ \[53\]

$$\eta_{\text{pos,BV}}^{\text{conc}} = \frac{2RT}{F} \ln \left[ \frac{c_i^{(b)}}{c_i^{(b)} - |\Delta c|} \right],$$ \[54\]

$$\eta_{\text{neg,Nernst}} = RT \ln \left( \frac{1 - \Delta c/c_i^{(b)}}{1 + \Delta c/c_i^{(b)}} \right),$$ \[55\]

$$\eta_{\text{pos,Nernst}} = RT \ln \left( \frac{1 + \Delta c/c_i^{(b)}}{1 - \Delta c/c_i^{(b)}} \right).$$ \[56\]

When there is no mass transport resistance, i.e., $\Delta c = 0$, the concentration overpotential at both the electrodes (given by Eqs. 51 and 52) is zero and we have the following equation for cell voltage:

$$E_{\text{cell}} = E^{\text{OCV}}(c^{(b)}) - \eta_{\text{neg}}^{\text{act}}(c^{(b)}, I) + \eta_{\text{pos}}^{\text{act}}(c^{(b)}, I) + IR_{\text{cell}}.$$

This equation is widely used to predict cell voltage of a VRFB cell; however, this does not account for the concentration overpotential at both the electrodes and thus could lead to erroneous model predictions as discussed in the next section.

**Calibration and validation.**—We have thus far derived analytical expression for estimating the concentration overpotential in VRFBs and incorporated it in a 0D model. For numerical computation, this model is implemented on MATLAB R2015a.

In order to determine the unknown model parameters ($k_{\text{neg}}, k_{\text{pos}}, a, b,$ and $\epsilon$) and verify the fidelity of the derived expression, we calibrate and validate the resulting 0D model with experimental data from Ma et al.\(^b\) Table 1 summarizes the operating and physical parameters set in their experiments; the derived model is simulated for these values here. The above work reported a wide range of experimental measurements for varying current densities and flow rates. The latter

---

Table 1. Operating and physical parameters.\(^{43}\)

| Parameter | Value | Units |
|-----------|-------|-------|
| $L$       | 0.35  | m     |
| $w_{\text{cell}}$ | 0.25  | m     |
| $h_z$     | 4     | mm    |
| $a$       | $2 \times 10^5$ | m$^{-1}$ |
| $N$       | 15    | -     |
| $T$       | 300   | K     |
| $V_{\text{tank}}$ | 20    | L     |
| $c_{\text{V}^{3+}}^{(b)}$ | 1499  | mol m$^{-3}$ |
| $c_{\text{V}^{2+}}^{(b)}$ | 1499  | mol m$^{-3}$ |
| $c_{\text{O}^{2-}}^{(b)}$ | 1     | mol m$^{-3}$ |
| $V$       | 0.2, 0.71 | m$^3$ h$^{-1}$ |
| $l_{\text{app}}$ | 45, 75 | mA cm$^{-2}$ |
| $E_{\text{act, pos}}$ | 1.004 | V     |
| $E_{\text{act, neg}}$ | -0.255 | V    |
| $R$       | 8.314 | J mol$^{-1}$ K$^{-1}$ |
| $F$       | 96500 | A s mol$^{-1}$ |
| $R_{\text{cell}}$ | 2.2   | mΩ    |

---

\(^{b}\) The data are from a different facility and not those from Ma et al.
is of particular interest as the mass transfer coefficient $(k_m)$ varies with the flow rates mainly.38,39 The model is then calibrated for the unknown parameters with the help of charge-discharge measurements. Two different sets of data are generally used for model calibration and validation, referred to as the training and test sets. Here, we classify the charge-discharge measurements at 45 mA cm$^{-2}$ for a flow rate of 0.2 m$^3$ h$^{-1}$ as the training set and the remaining measurements at 45 and 75 mA cm$^{-2}$ as the test set. Comparing model predictions and experimental voltages for the training set using the nonlinear least-squares method, the model is calibrated to determine the unknown model parameters:

\[
k_{\text{neg}} = 7.9 \times 10^{-8} \text{ m s}^{-1}, \quad [58]
\]

\[
k_{\text{pos}} = 6.4 \times 10^{-8} \text{ m s}^{-1}, \quad [59]
\]

\[
a = 10^{-4}(\text{m s}^{-1})^{0.1}, \quad [60]
\]

\[
b = 0.9, \quad [61]
\]

\[
e = 155 \text{ mV}, \quad [62]
\]

Note that the reaction rate constants for both the electrodes $(k_{\text{neg}}$ and $k_{\text{pos}}$) are reported to be of the same order of magnitude in the earlier modeling studies.2–17 Similarly, the prefactor $(a)$ and the exponent $(b)$ in the empirical correlation for mass transfer coefficient are also found to be in the range reported earlier for carbon felt electrodes.36,37 Further, the deviation between the formal and standard reduction potential for a VRFB cell has also been found to be comparable with earlier reports.38,39,41 Subsequently, to confirm the reliability of the calibrated model, the voltage profiles predicted by the model are compared with the test set for another flow rate of 0.71 m$^3$ h$^{-1}$ at 45 mA cm$^{-2}$ and another current density of 75 mA cm$^{-2}$ at 0.2 and 0.71 m$^3$ h$^{-1}$. Good agreement is obtained as shown in Figs. 2–3 with an average relative error of $\sim 5\%$ for all charge-discharge cycles.

The open circuit voltage of a VRFB cell is a function of vanadium species concentrations (Eqs. 46–48). Thus, it changes continuously during both charge and discharge of the cell (see Fig. 4). Initially, there is only one ionic species at each of the electrodes – $\text{V}^{3+}$ at the negative and $\text{VO}_2^{2+}$ at the positive electrode – whence there is a relatively large change in OCV against a small change in concentrations. This results into a non-linear increase in the stack voltage at the beginning of charge as observed in Figs. 2–3. Here, charging is terminated after reaching a certain voltage. In this voltage range, both the vanadium species at each electrode are found to be in moderate concentrations (see Fig. 4) whence the stack voltage changes almost linearly at the end of charge and at the beginning of discharge. At the end of discharge, the reactant species at both the electrodes tends to their lower concentrations (see Fig. 4). This in conjunction with the mass transport effects results in sharp fall in stack voltage at the end of discharge (see Figs. 2–3).

To highlight the mass transport effects on voltage predictions, we proceed to compare the simulated voltage profiles with and without inclusion of different mass transport effects. For this purpose, let us consider the discharge operation of the flow battery at an applied current density of 75 mA cm$^{-2}$ and an electrolyte flow rate of 0.2 m$^3$ h$^{-1}$. When no mass transport effects are accounted for, all terms of the concentration overpotential can be dropped from the voltage equation (Eq. 45). With such a model, the fall in stack voltage toward the end of discharge is less steep as compared to the case when all these terms (mass transfer effects) are considered as shown in Fig. 5. Quantitatively, there is a relative difference of $\sim 10\%$ in voltage predictions toward the end of discharge. Similarly, there are relative differences of $\sim 6\%$ and $\sim 3\%$ in predictions respectively when the mass transport effects on only the reversible potential (with the Nerst equation) and only on the reaction kinetics (with the BV equation) are accounted for. Thus, we can infer that the contribution of the BV equation
Figure 5. Discharge stack voltage predictions at current density of 75 mA cm$^{-2}$ and and electrolyte flow rate of 0.2 m$^3$ h$^{-1}$. Model without any mass transport effects or concentration overpotential (dotted line), mass transport effects only on the reversible potential included (dashed-dotted line), mass transport effects only on the kinetics included (dashed line), mass transport effects on both the reversible potential and kinetics included (solid line).

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