



Open circuit voltage of vanadium redox flow batteries: Discrepancy between models and experiments

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ABSTRACT

A major issue with the existing vanadium redox flow battery (VRFB) models is the inaccurate prediction of the open circuit voltage (OCV), which results in a discrepancy of 131 to 140 mV in predicted cell voltages when compared to experimental data. This deviation is shown to be caused by the incomplete description of the electrochemical double layers within the cell when calculating the OCV using the Nernst equation adopted from fuel cell literature. Here, we propose a more complete description of the Nernst equation, which accounts for two additional electrochemical mechanisms that exist in a VRFB, namely: i) the proton activity at the positive electrode due to the involvement of the protons in the redox reaction, and ii) the Donnan potential due to the proton concentration differences across the membrane. The complete form of the Nernst equation proposed herein accurately predicts the reported experimental data with an average error of 1.2%, showing a significant improvement over the incomplete Nernst equation (8.1% average error) currently used in VRFB models.

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1. Introduction

Vanadium redox flow batteries (VRFBs) are electrochemical energy storage systems designed for use in large scale applications such as peak load leveling and effective utilization of intermittent renewable energy sources. The energy conversion process of a VRFB occurs in an electrochemical cell, and is dictated by three main components: i) liquid electrolytes that consist of vanadium compounds dissolved in sulfuric acid (H_2SO_4), ii) inert graphite felt electrodes that provide sites for the reactions, and iii) an ion exchange membrane that separates the two electrolytes and allows for mobile ion transport.

Recently, a few modeling efforts have emerged to understand the system behavior and performance of the VRFB [1–3]. One major issue with the current models is the inaccuracy of the predicted cell voltage. A constant fitting voltage of 131 to 140 mV (~10% of the total voltage) is typically added to the predicted voltage outputs in order to account for unknown discrepancies with the experimental data. The observed voltage discrepancy between models and experiments is primarily caused by the incomplete representation of the open circuit voltage (OCV) in the current VRFB models.

To predict the OCV, current VRFB models adopt the form of the Nernst equation used in fuel cell studies due to the similarity of these

systems. However, when directly applied to VRFBs, the form of the Nernst equation used in fuel cell models underestimates the measured OCV by almost 140 mV [4]. Consequently, the error associated with the prediction of the OCV affects the accuracy of the overall predicted charge/discharge voltages of the VRFB system. Therefore, to provide a better means of predicting the cell potential, we propose a more complete description of the Nernst equation, which accounts for additional electrochemical mechanisms that exist in VRFBs and accurately represents the cell potential of the VRFB electrodes.

2. Theory

2.1. Incomplete Nernst equation used in VRFB models

For electrochemical systems, such as VRFBs, the equilibrium potential at a single redox electrode is predicted using the Nernst equation, which describes the potential difference between the electrolyte and the electrode when there is no net reaction inside the cell, and is defined as follows [5]:

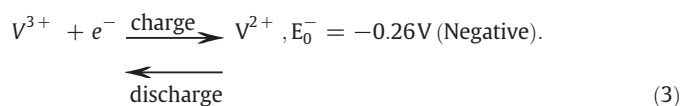
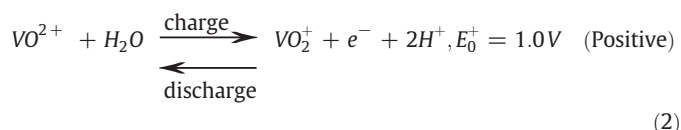
$$E = E_0 + \frac{RT}{nF} \ln \left(\frac{c_{\text{ox}}}{c_{\text{red}}} \cdot \frac{\gamma_{\text{ox}}}{\gamma_{\text{red}}} \right) \quad (1)$$

where E is the potential difference, and E_0 is the standard reduction potential, calculated using the thermodynamic properties of the global reactions at the given electrode. R is the universal gas constant,

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T is the absolute temperature, n is the number of equivalents transferred per mole of species reduced or oxidized ($n=1$ for a VRFB), and F is Faraday's constant. The subscripts *ox* and *red* represent the oxidized and reduced species, respectively. The term, c , represents the ionic concentration, and γ is defined as the activity coefficient of the species, which represents the deviation of an ion from ideal reactivity due to interionic interactions within the solution. However, in a VRFB, the liquid electrolytes are typically well-circulated, yielding negligible interactions among the ions. Therefore, it is reasonable to assume that the activity coefficient (γ) for all species is equivalent to one [6].

Similarly, the OCV of a VRFB cell is described as the difference between the equilibrium potentials at each electrode, where the positive and negative electrode potentials depend on the global reactions given as follows:



In existing VRFB models, Eq. (1) is used to define the potentials at each electrode, where the vanadium ions from the reactions are employed as the oxidized and reduced species, yielding the following form of the Nernst equation [1–7]:

$$E = E^+ - E^- = E_0 + \frac{RT}{nF} \ln \left[\left(\frac{c_{\text{VO}_2^+} \cdot c_{\text{V}^{2+}}}{c_{\text{VO}^{2+}} \cdot c_{\text{V}^{3+}}} \right) \right] \quad (4)$$

where the superscripts '+' and '-' represent the positive and negative half-cells, and the total standard reduction potential (E_0) is the difference between the positive (E_0^+) and negative (E_0^-) standard reduction potentials. While Eq. (4) represents a useful starting point for predicting the OCV, it does not account for the complex electrochemistry, ignoring two important mechanisms that exist in VRFB systems, namely: i) the proton concentration at the positive electrode, which is assumed to have a negligible effect on OCV in current VRFB studies, and ii) the Donnan potential across the membrane, which does not exist in fuel cells, therefore is not included

in the Nernst equation adopted from fuel cell literature. These two additional mechanisms are discussed in the following sections.

2.2. Inclusion of protons at the positive electrode

One major deficiency of the standard form of the Nernst equation (Eq. (4)) currently used in VRFB models is the incomplete representation of the positive electrode potential. According to Eq. (4), the equilibrium potential at the positive electrode is defined as follows:

$$E^+ = E_0^+ + \frac{RT}{F} \ln \left(\frac{c_{\text{VO}_2^+}}{c_{\text{VO}^{2+}}} \right) \quad (\text{Positive}). \quad (5)$$

The activity of the protons is not included in Eq. (5), since the contribution of the protons towards the equilibrium potential is assumed negligible. However, the proton concentration should be included because the protons are involved in the redox reaction at the electrode (Eq. (2)), and the chemical potential associated with these protons will have an effect on the equilibrium potential (~100 mV in a VRFB). Therefore, by incorporating the proton concentration, a complete description of the equilibrium potential at the positive electrode can be given as follows:

$$E^+ = E_0^+ + \frac{RT}{nF} \ln \left(\frac{c_{\text{VO}_2^+} \cdot c_{\text{H}^+}^2}{c_{\text{VO}^{2+}}} \right) \quad (\text{Positive Electrode}). \quad (6)$$

The importance of Eq. (6) has been addressed in previous studies [8]; however, it has not been incorporated into any VRFB models. If included, Eq. (6) would eliminate 75% of the 131–140 mV discrepancy observed between model predictions and experimental data, yielding a more accurate representation of VRFB performance.

2.3. Addition of the Donnan potential

Another important factor ignored by the standard form of the Nernst equation used in VRFB models is the Donnan potential, which exists across the membrane due to unequal proton concentrations between the two electrolytes (Fig. 1a). The difference in proton concentration is attributed to the methods employed for electrolyte preparation, and can be clearly explained through the analysis of two common methods: i) the suspended powder electrolysis of vanadium pentoxide [4] and ii) the charging of vanadyl sulfate to produce the negative vanadium electrolyte (–ve) [9].

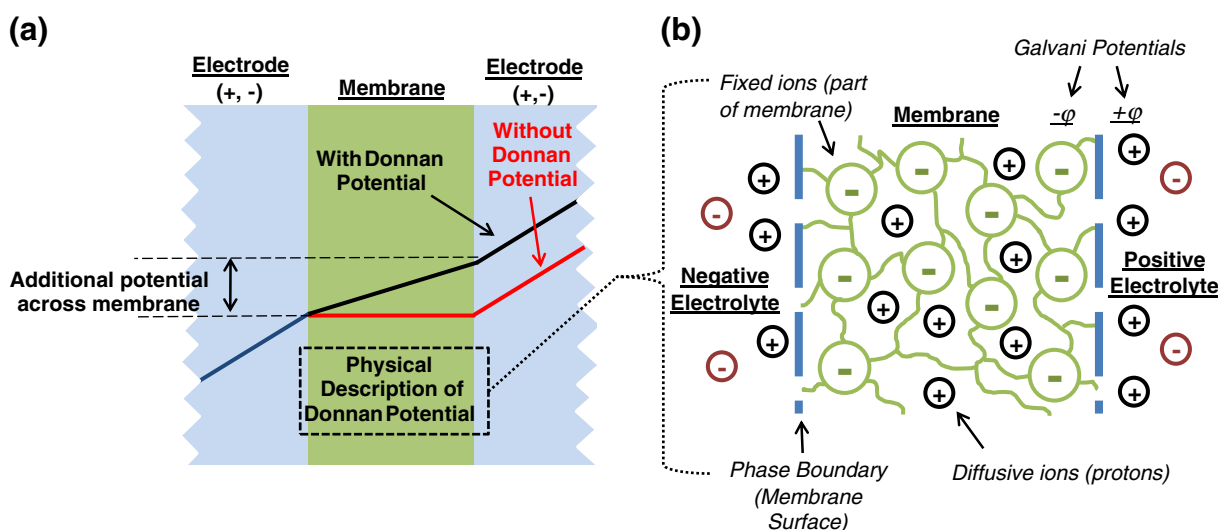


Fig. 1. a) OCV with and without the membrane potential, b) Physical representation of the electrolytic double layers on both sides of the ion exchange membrane.

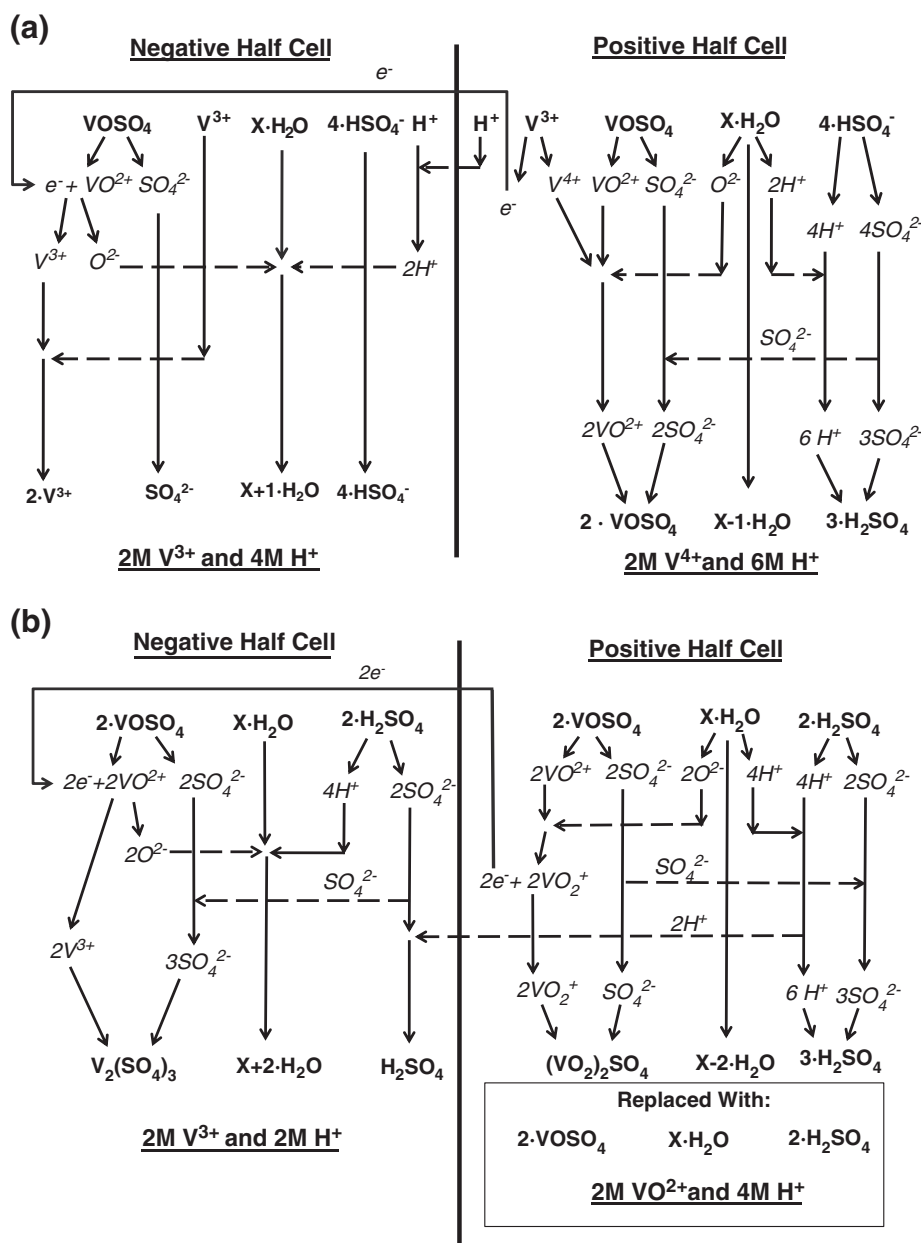


Fig. 2. a) Second step of the suspended powder electrolysis of vanadium pentoxide, b) Preparation of the electrolytes involving vanadyl sulfate.

In the first method, suspended powder electrolysis, a solution consisting of $1\text{ M V}_2\text{O}_5 + 5\text{ M H}_2\text{SO}_4$ is reduced into a new solution composed of $1\text{ M VOSO}_4(\text{V}^{4+}) + 1\text{ M V}^{3+} + 4\text{ M HSO}_4^- + 1\text{ M H}^+ + x\text{ M H}_2\text{O}$. Then, an equal amount of the new $\text{V}^{4+}/\text{V}^{3+}$ solution is placed into both the positive and negative half-cells of a VRFB, and the cell is charged to produce two unique electrolytes, one containing only V^{3+} and the other only V^{4+} (Fig. 2a). In the second electrolyte preparation method, a solution of vanadyl sulfate (2 M VOSO_4) dissolved in sulfuric acid ($2\text{ M H}_2\text{SO}_4$) is placed into both the positive and negative half-cells of a VRFB. When the cell is charged, the vanadium in the positive half-cell oxidizes to V^{5+} , while the vanadium in the negative half-cell reduces to V^{3+} (Fig. 2b). The solution in the positive half-cell is then replaced with the original vanadyl sulfate solution, resulting in a VRFB at 0% state-of-charge (SOC) with a $-ve$ containing 2 M fewer protons than $+ve$. In both preparation methods, the imbalance of H^+ arises due to the formation and dissociation of H_2O , which is directly related to the existence of V^{4+} and V^{5+} as oxides.

To calculate the Donnan potential within the VRFB, the same theoretical framework used for deriving the Nernst equation can be utilized. When a VRFB is in equilibrium, a membrane potential occurs at each electrolyte/membrane phase boundary, and can be defined as follows:

$$E_m^k = \frac{RT}{F} \ln \left(\frac{c_{H^+}^k}{c_{H^+}^m} \right) \quad (7)$$

where k is '+' or '-' depending on the electrolyte and the term, m , represents the membrane. These membrane potentials result from positively and negatively charged layers that exist at the electrolyte/membrane interfaces, and are formed by the positions of the protons in the electrolytes and membrane (Fig. 1b). If the concentrations of the protons in the positive and negative electrolytes differ, the potentials at each electrolyte/membrane phase boundary will be unequal, and a

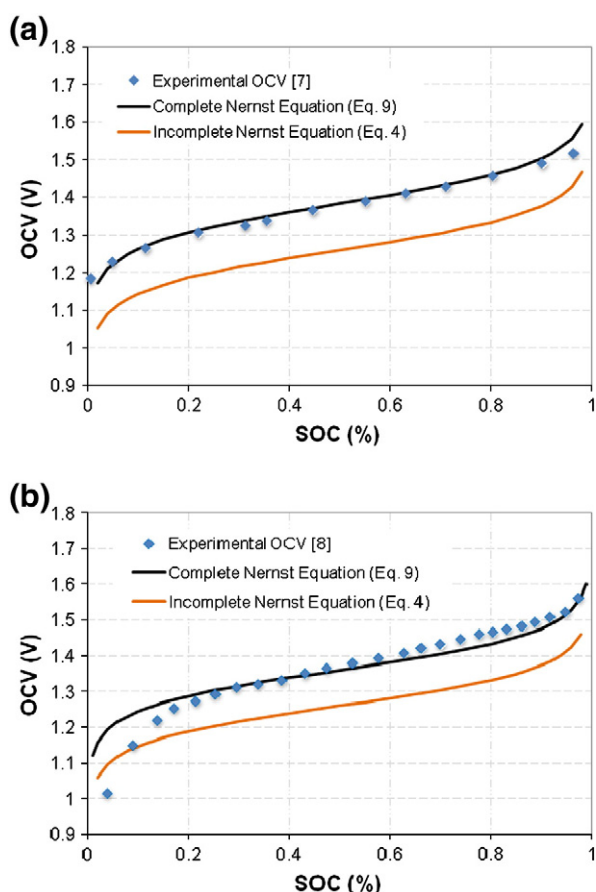


Fig. 3. Comparison of experimental OCV [7,8] and predicted OCV using the standard Nernst equation (Eq. (4)) and the proposed correlation (Eq. (9)). Experimental conditions: a) $T=303$ K, initial $-ve$ and $+ve$ concentrations of $2\text{ M V}^{3+} + 6\text{ M H}^+$ and $2\text{ M VO}^{2+} + 8\text{ M H}^+$, respectively ($c_v=2\text{M}$, $c_{H^+}^{0,+}=8\text{M}$, $c_{H^+}^{0,-}=6\text{M}$) [7], b) $T=298$ K and initial $-ve$ and $+ve$ concentrations of $1\text{ M V}^{3+} + 5\text{ M H}^+$ and $1\text{ M VO}^{2+} + 6\text{ M H}^+$, respectively ($c_v=1\text{M}$, $c_{H^+}^{0,+}=5\text{M}$, $c_{H^+}^{0,-}=5\text{M}$) [8].

net potential (Donnan potential) will exist across the membrane. If Eq. (7) is applied to both half-cells, the Donnan potential within the VRFB can be expressed as follows [5]:

$$E_m = E_m^+ - E_m^- = \frac{RT}{F} \ln \left(\frac{c_{H^+}^+}{c_{H^+}^-} \right) \quad (8)$$

3. Complete Nernst equation for VRFBs

By incorporating the proton concentration at the positive electrode and adding the Donnan potential, the complete form of the Nernst equation for a VRFB can be defined as follows:

$$E = E_0 + \frac{RT}{F} \ln \left(\frac{c_{VO_2^+} \cdot c_{V^{2+}} + (c_{H^+}^+)^2 \cdot c_{H^+}^+}{c_{VO^{2+}} \cdot c_{V^{3+}} \cdot c_{H^+}^-} \right) \quad (9)$$

A comparison of the complete form of the Nernst equation (Eq. (9)) with two sets of experimental data [7,8] has been performed to evaluate the accuracy of the approach. For both sets of experimental data, the electrolytes were prepared using the method illustrated in Fig. 2b with the only difference being the initial species concentrations.

During operation, the reactions at the electrodes cause the vanadium and proton concentrations to vary as follows [10]:

$$c_{VO_2^+} = c_{V^{2+}} = c_v \cdot \text{SOC} \quad (10)$$

$$c_{VO^{2+}} = c_{V^{3+}} = c_v \cdot (1 - \text{SOC}) \quad (11)$$

$$c_{H^+}^k = c_{H^+}^{0,k} + c_v \cdot \text{SOC} \quad (12)$$

where c_v is the total vanadium concentration, and $c_{H^+}^{0,k}$ represents the initial proton concentrations in the $+ve$ or $-ve$. In the presence of an electric field, like the Galvani potentials of a VRFB, ionic bonds become stretched and weakened, leading to an increase in the dissociation of the ions [5]. Therefore, when determining $c_{H^+}^k$, all protons initially bonded to SO_4^{2-} are assumed to be fully dissociated, existing as free protons.

As Fig. 3 clearly demonstrates, the complete form of the Nernst equation (Eq. (9)) shows very good agreement with the experimental data ($\pm 1.2\%$ average error) within the normal operating conditions ranging from 5% to 95% SOC, whereas the standard form of the Nernst equation (Eq. (4)) used in current VRFB models yields $\pm 8.1\%$ average error within the same SOC range. Any discrepancy between the complete form of the Nernst equation and experimental data at the extreme conditions (i.e. SOC < 5% or > 95%) can be attributed to the assumption of unity activity coefficients.

4. Conclusion

In this study, a more complete form of the Nernst equation for a VRFB was proposed, which provides a better means for predicting the OCV and alleviates the discrepancy between the current model predictions and measured cell potentials. One important extension to the current Nernst equation was the incorporation of the protons at the positive electrode. The accuracy of the equation was further improved by adding the Donnan potential which exists across the membrane in VRFBs. When compared to experimental data, the complete form of the Nernst equation proposed herein shows a much better agreement ($\pm 1.2\%$ average error) than the standard form of the Nernst equation ($\pm 8.1\%$ average error) currently used in VRFB models. The proposed form of the Nernst equation provides a better representation of the complex electrochemistry in VRFBs, enabling high fidelity modeling of these systems.

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