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Thermodynamic derivation of open circuit voltage in vanadium redox flow batteries

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HIGHLIGHTS

- Nernst relation for VRFB is derived using equilibrium thermodynamics.
- Revealing new terms in the Nernst relation.
- There are different Nernst relations for anex and catex membranes.
- The derived theory is compared with experiments.

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ABSTRACT

Open circuit voltage of vanadium redox flow batteries is carefully calculated using equilibrium thermodynamics. This analysis reveals some terms in the Nernst relation which are usually omitted in literature. Due to the careful thermodynamic treatment, all uncertainties about the form of Nernst relation are removed except for uncertainties in activity coefficients of particular species. Moreover, it is shown (based again on equilibrium thermodynamics) that batteries with anion-exchange membranes follow different Nernst relation than batteries with cation-exchange membranes. The difference is calculated, and it is verified experimentally that the formula for anion-exchange membranes describes experiments with anion-exchange membranes better than the corresponding formula for cation-exchange membranes. In summary, careful thermodynamic calculation of open circuit voltage of vanadium redox flow batteries is presented, and the difference between voltage for anion-exchange and cation-exchange membranes is revealed.

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1. Introduction

Vanadium redox flow batteries [1,2] (VRFB) represent a promising way for storing electrical energy. In many aspects they are similar to fuel cells, where electric energy can also be stored into or produced from fuel (e.g. hydrogen). In VRFB, however, the energy is stored in the electrolytes. A VRFB single-cell consists of a positive half-cell, where V^{IV} ions are oxidized to V^{V} when charging, and of a negative half-cell, where V^{III} is reduced to V^{II} when charging. The two half-cells are separated by a membrane through which either cations or anions are transported. The former kind of membrane is referred to as cation-exchange (catex) membrane while the latter as anion-exchange (anex) membrane. The half-cells are also connected through an external circuit, which enables the flow of electrons (i.e., electric current). The battery voltage, i.e. difference of the electrochemical potentials of electrons in the positive and the negative half-cell, is measured on the terminals of the cell. How does the voltage depend on the state of charge (SOC) of the battery in a steady state when no current is passing through the circuit? In other words, how does the open circuit voltage (OCV) depend on SOC? Although this fundamental question has been addressed many times due to its high importance, it seems that the precise quantitative description for the dependence of OCV on SOC has not been found so far, and this is the goal of this article.

Usually, the dependence of OCV on SOC is derived from the Nernst relation [3,4]. Probably the most frequently used dependence in literature is

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$$E_{usual} = E^{\circ} + \frac{RT}{F} \ln \frac{c^P_{VO_2^+} c^N_{V^{2+}} \left(c^P_{H^+}\right)^2}{c^P_{VO^{2+}} c^N_{V^{3+}}} \tag{1}$$

where c^P_α stands for concentration of species α in the positive electrolyte (N stands for negative). However, several possible dependencies have been suggested in the literature. For example, Al-Fetlawi et al. suggest a simple form where only concentrations of vanadium ions are present. Heintz and Illenberger [5] and Hudak [6] include also concentration of protons in the positive half-cell (as in formula (1)) as well as Knehr and Kumbur [4], who moreover suggest the inclusion of Donnan potential due to different proton concentrations in both electrolytes. In all these works it was assumed that activity coefficients of all species taken into account can be neglected (i.e. be equal to unity). Corcuera and Skyllas-Kazacos [7] introduce formal potentials for each half-cell, which could possibly lead to evaluation of the activity coeffients when formulated within thermodynamics properly. Is it possible to derive any even more accurate formula describing the OCV as a function of SOC?

This question is answered by equilibrium thermodynamics. Indeed, the Nernst relation itself [3,8] is derived from thermodynamics. So what if we do not start with any form of Nernst relation but rather with thermodynamic equality of electrochemical potentials? This is the way followed in this manuscript. At first, conditions for the steady state where OCV is measured are carefully stated and complete electrochemical potentials of all species participating in the electrochemical reactions are written down. Consequently, the Nernst relation for VRFB is derived. In the derivation careful attention is paid to the definition of standard states so that thermodynamic data are used consistently. The here derived Nernst relation is different from the Nernst relations mentioned above, and it is free of any possible inconsistencies (at least in the form with activities), since it is derived directly from thermodynamics. In summary, thermodynamics yields the final form of Nernst relation.

The thermodynamic Nernst relation is then compared to our own experimental data and good agreement is demonstrated. It is shown that VRFB with an anex membrane follows a different Nernst relation than a battery with a catex membrane since bisulphates are equilibrated in the former case while protons are equilibrated in the latter case. To the best of our knowledge this behavior has not been yet presented.

Note, however, that anex membranes are, in fact, not completely impermeable for protons, see Ref. [9]. This brings uncertainty to our analysis, with which one could deal by taking into account non-equilibrium transport of protons through the anex membranes. Since non-equilibrium treatment of the membranes is out of scope of this paper, we neglect that phenomenon in our calculations while mentioning it when comparing theoretical predictions with experimental results.

In summary, this article provides careful thermodynamic derivation of Nernst relation for VRFB with both anex and catex membranes. Interestingly, these two Nernst relations are different, since different species are equilibrated in both cases. The forms of the Nernst relations in terms of activities are free of any possible inconsistencies and there is no way how to enhance them (at least in the steady state) because otherwise they would not agree with thermodynamics. Uncertainties are introduced when rewriting activities in terms of concentrations (or molalities) and activity coefficients because activity coefficients for the considered electrolytes are not available in general. The here derived Nernst relations show good agreement with experimental data.

2. Electric potential

Before calculating the OCV, let us recall how electrochemical potential is introduced within thermodynamics. Electrochemical potential of species α in a solution can be generally expressed as

$$\tilde{\mu}_\alpha = \mu^{\circ}_\alpha + RT \ln \underbrace{\left(\gamma_\alpha \frac{b_\alpha}{b^{\circ}}\right)}_{a_\alpha} + z_\alpha F \phi \tag{2}$$

where $\tilde{\mu}^{\circ}_\alpha$ is the standard chemical potential of the species (here in aqueous solution), b_α is its molality, γ_α is activity coefficient[1], a_α is activity, z_α is charge number and ϕ is the Maxwell potential, see Ref. [10].

Which potential is measured by a voltmeter? The value a voltmeter measures is, in fact, proportional to the electric current passing through the voltmeter and, since the electric current is proportional to gradient of electrochemical potential across the voltmeter, the voltmeter measures differences in electrochemical potentials of electrons. Therefore, we identify the electric potential measured by a voltmeter with electrochemical potential of electrons, i.e.

$$\tilde{\mu}_{e^-} = -F\Phi, \tag{3}$$

which should be regarded as the definition of electric potential Φ, see Refs. [11,10] for more details.

3. OCV for catex membranes

This section provides a thermodynamic calculation of OCV in all-vanadium VRFB with cation exchange membrane at standard temperature and pressure. The OCV is calculated in two ways differing in definition of the reference voltage. Both ways, however, are equivalent as they give the same dependence of OCV on SOC.

3.1. General Nernst relation

During discharging the following electrochemical reactions take place in the battery, see e.g. Ref. [4],

- Positive half-cell:

$$VO_2^+ + e^- + 2H^+ \rightarrow VO^{2+} + H_2O \tag{4}$$

- Negative half-cell:

$$V^{2+} \rightarrow V^{3+} + e^- \tag{5}$$

It is known from non-equilibrium thermodynamics, see for example [12] [13], or [11], that electrochemical reactions are driven by their electrochemical affinities, which are negatives of the corresponding reaction Gibbs energies. An electrochemical reaction then proceeds in the direction from left to right if and only if its electrochemical affinity is positive, and in the opposite direction if the affinity is negative. In particular, it does not proceed in any

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[1] Activity coefficients of particular ionic species are experimentally unavailable because one can only measure activity coefficient of the neutral species composed of an ion and its counter-ion, $\gamma_\pm$. However, this activity coefficient can be split into contribution γ_+ and γ_- geometric mean of which is equal to $\gamma_\pm$, see Ref. [3]. Formulas for OCV (30) and (32) are invariant to such splitting as they can be rewritten in such a way that they contain only activity coefficients of neutral species.

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