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Practical thermodynamic quantities for aqueous vanadium- and iron-based flow batteries

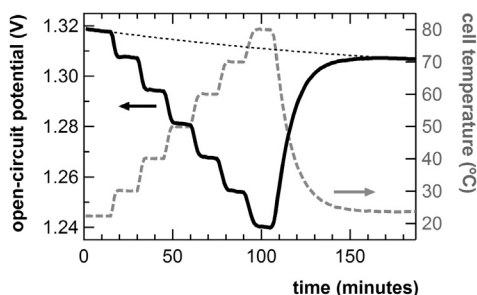
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HIGHLIGHTS

- Experimentally measured thermodynamic quantities for flow batteries are presented.
- Measured thermodynamic quantities differ from published standard values.
- Cell reaction entropy as a function of state-of-charge follows the Nernst Equation.
- Practical thermodynamic quantities can be used in flow battery modeling and design.
- Non-isothermal flow cell cycling exhibits improved voltage efficiency in some cases.

GRAPHICAL ABSTRACT



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ABSTRACT

A simple method for experimentally determining thermodynamic quantities for flow battery cell reactions is presented. Equilibrium cell potentials, temperature derivatives of cell potential (dE/dT), Gibbs free energies, and entropies are reported here for all-vanadium, iron–vanadium, and iron–chromium flow cells with state-of-the-art solution compositions. Proof is given that *formal potentials* and *formal temperature coefficients* can be used with modified forms of the Nernst Equation to quantify the thermodynamics of flow cell reactions as a function of state-of-charge. Such empirical quantities can be used in thermo-electrochemical models of flow batteries at the cell or system level. In most cases, the thermodynamic quantities measured here are significantly different from standard values reported and used previously in the literature. The data reported here are also useful in the selection of operating temperatures for flow battery systems. Because higher temperatures correspond to lower equilibrium cell potentials for the battery chemistries studied here, it can be beneficial to charge a cell at higher temperature and discharge at lower temperature. Proof-of-concept of improved voltage efficiency with the use of such non-isothermal cycling is given for the all-vanadium redox flow battery, and the effect is shown to be more pronounced at lower current densities.

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1. Introduction

As worldwide demand for electricity continues to rise, there is a need for increased utilization of energy storage in the electrical grid

[1]. The use of energy storage will improve grid reliability and efficiency, and it will enable further incorporation of renewable, intermittent energy sources such as wind and solar power [1,2]. The redox flow battery (RFB) is one of several energy storage technologies that are appropriate for the utility scale. Advantages of RFBs over other types of energy storage include the possibility for millisecond response times, the direct conversion from chemical to

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electrical energy, the ability to be sited anywhere, and the ability for energy content and power output to be scaled independently [3,4]. Accordingly, there has been a large amount of research in RFBs in recent years. The work has mainly been aimed at improving the cycling stability and energy efficiency of established cell chemistries and exploring new cell chemistries with potentially higher specific energies [5].

One approach to understanding and improving RFB performance is to develop cell-level models that incorporate electrochemistry, mass transport, reaction kinetics, and thermodynamics. Such models have been developed, with varying degrees of complexity, and compared to experimental results for all-vanadium [6–13], iron–vanadium [14], and iron–chromium [15] flow batteries. All such models of electrochemical systems must account for the thermodynamics of the cell reaction or individual electrode reactions in order to accurately predict the observed, measurable quantities of cell potential and heat output. The Gibbs free energy (ΔG) of the cell is present in even the simplest electrochemical models; it represents the maximum net amount of work obtainable from the cell and is proportional to cell potential (E) [16]. Thermo-electrochemical models of battery cells (those that incorporate heat output or consumption and do not assume constant temperature) must also account for the entropy (ΔS) of the cell [6,17,18]. This quantity represents the heat output or consumption of the cell under reversible conditions and is proportional to dE/dT , the partial derivative of cell potential with respect to temperature (also called the “temperature coefficient” [19]). (Note: Although temperature coefficients are partial derivatives, they are expressed here and in some previous references as dE/dT rather than $\partial E/\partial T$, for the sake of simplicity.)

In almost all cases, the thermodynamic quantities that were “plugged into” the models cited above were from unverified and varied sources. In many cases, the original sources for the reported values are difficult to identify, and various references reported conflicting values for the same species or electrode reactions. This is especially true for the entropy values, which have in some cases been estimated by “daisy-chaining” the experimental or calculated results from various studies conducted under different conditions [20]. Furthermore, the quantities used in the above-cited models were usually *standard* thermodynamic quantities, which assume standard conditions and unit activity for all dissolved species. The use of standard potentials (E^0), standard Gibbs free energies (ΔG^0), and standard entropies (ΔS^0) to model the electrode reactions or cell reactions of flow batteries is unlikely to produce accurate results. This is because the high concentrations of active redox species and supporting electrolytes that are typically used in flow batteries may result in species activities that are far from unity. Indeed, measured cell potentials of vanadium redox flow batteries (VRFB) have differed by as much as 140 mV from simulated values that were obtained by using the reported standard cell potential [7,9,12,13,21,22]. In one case, this discrepancy was accounted for by incorporating the solution’s proton activity and the membrane’s Donnan potential into the expression for cell potential [23]. However, the two effects could not be measured and verified separately, and the analysis was based on the assumption that previously published standard potential values were accurate. Several models arbitrarily applied a correction factor to the cell potential when the modeled potential curves did not match the experimental ones [9,12–14]. Thus, the equilibrium cell potential (along with its associated ΔG) has effectively become an additional fitted parameter rather than an independently determined value.

Presented here are the formal potential values (E^0), determined experimentally, for the cell reactions of aqueous all-vanadium, iron–vanadium, and iron–chromium flow batteries with typical concentrations of active materials and supporting electrolytes. Use

of the *formal potential* [16] for a specific cell composition rather than the standard potential of the cell reaction avoids the need for activity coefficients or arbitrary corrections and provides practical thermodynamic values that can be used in cell- or system-level models. Additionally, the concept of a *formal temperature coefficient* (dE^0/dT) is introduced here and measured for the three flow battery chemistries. As shown here and verified experimentally, the derivative of the Nernst Equation with respect to temperature can be used with the formal temperature coefficient to determine the temperature coefficient at any state-of-charge. The formal potential and temperature coefficient values for a given cell chemistry can be easily converted to the Gibbs free energy and entropy, respectively, for use in thermo-electrochemical models. While these values are specific to the flow battery chemistry and supporting electrolyte with which they are measured, the experimental method is simple and can be easily replicated to determine thermodynamic values for other flow battery compositions. Furthermore, the temperature coefficient values can be used for a more informed design of flow battery systems, specifically in the selection of operating temperature during cell charge and discharge. An example of such design, in which operation of charge and discharge at different temperatures results in improved efficiency relative to isothermal operation, is given with experimental verification.

2. Experimental methods

2.1. Materials

Vanadium(IV) oxide sulfate (VOSO_4) hydrate and chromium(III) chloride hexahydrate were used as received from Alfa Aesar. Iron(II) chloride tetrahydrate and vanadium(III) chloride were used as received from Sigma–Aldrich. An aqueous solution consisting of ~ 2 M VOSO_4 and 6 M HCl was prepared and used for the all-vanadium redox flow cells. This solution is referred to as a “sulfate–chloride mixed electrolyte” and is the state-of-the-art for VRFB [24]. This type of solution was chosen for the present study because it has an expanded temperature range and increased solubility compared to chloride-free VRFB solutions. An aqueous solution of 1.25 M FeCl_2 , 1.25 M VCl_3 , and 2.3 M HCl was prepared for the iron–vanadium (Fe–V) flow cells [25]. An aqueous solution of 1.25 M FeCl_2 , 1.25 M CrCl_3 , and 2.3 M HCl was prepared for the iron–chromium (Fe–Cr) flow cells [26]. The electrolyte solutions for Fe–V and Fe–Cr cells are called “mixed reactant solutions” because both metal ions are present in the same solution, which is used on both the positive and negative sides of the cell to prevent reactant crossover through the membrane.

Nafion 117 membranes (Ion Power) were used as received and stored in DI water at room temperature for at least 24 h prior to cell assembly [27]. Neosepta AMX anion-exchange membranes (ASTOM Corporation) were used as received and stored in 3 wt% NaCl, as directed by the manufacturer. Sigracell GFD2.5 carbon felt (SGL Carbon) was placed under O_2 plasma for 10 min using a Harrick plasma cleaner immediately prior to use in flow cells [28]. This “pre-treatment” process rendered the carbon felt hydrophilic.

2.2. Flow cell setup

Flow cell experiments were performed with an “acid cell” test fixture from Fuel Cell Technologies (Albuquerque, New Mexico, USA). The current collectors in this fixture were made of Poco graphite blocks with machined serpentine flow fields and 5-cm² active area. Pre-treated carbon felt was used as the electrode on each side of the cell, and Nafion 117 or Neosepta AMX was used as the electrolyte membrane. Polytetrafluoroethylene (PTFE) sheets and PTFE-coated fiberglass fabric were used as gaskets, and the

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