Journal of Power Sources 399 (2018) 133–143

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Quantifying the impact of viscosity on mass-transfer coefficients in redox flow batteries

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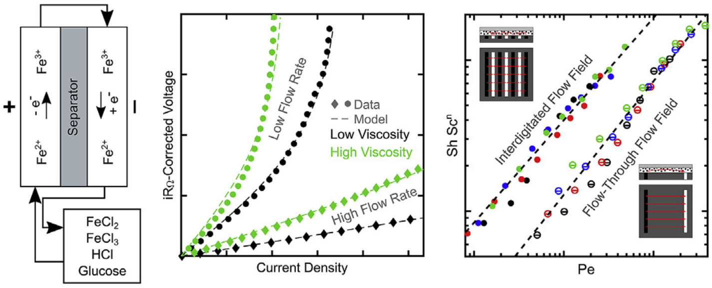
HIGHLIGHTS

- Electrolyte viscosity is experimentally modified using glucose.
- Half cells are studied with both interdigitated and flow-through flow fields.
- A model is used to determine the mass-transfer coefficients from polarization data.
- Sherwood, Péclet, and Schmidt numbers are correlated for both flow fields.
- Correlations explicitly describe dependence of mass transfer on viscosity.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Flow battery
Energy storage
Viscosity
Mass transfer
Electrochemical energy storage

ABSTRACT

Here, a model redox-active electrolyte (RAE) is fully characterized in terms of its transport properties, and subsequent flow cell polarization experiments enable extraction of mass-transfer coefficients. Specifically, experimental manipulation of flow rate and electrolyte viscosity are coupled with a 1-D polarization model in a flow cell to quantify the mass-transfer coefficients as a function of these material and operating parameters. Both flow-through and interdigitated flow fields are used to develop dimensionless correlations that describe mass-transfer rates as a function of RAE properties. Experimental results and fitted model parameters illustrate and quantify the changes in limiting current and mass-transfer coefficient as a function of electrolyte velocity and viscosity. The resulting power-law correlations for the Sherwood (*Sh*) number, in terms of the Péclet (*Pe*) and Schmidt (*Sc*) numbers, are $Sh = 0.0040Pe^{0.75}Sc^{-0.24}$ and $Sh = 0.018Pe^{0.68}Sc^{-0.18}$ for the flow-through and interdigitated flow fields, respectively. These correlations provide quantitative estimates of mass-transfer coefficients within high-performance flow cell architectures as a function of geometry and RAE properties, enabling front-end screening in future RAE development campaigns, as well as performance benchmarking for potential redox flow batteries (RFBs).

1. Introduction

Redox flow batteries (RFBs) are a rechargeable electrochemical technology whose independently-specified power and energy, long operational lifetimes, and simple manufacturing make them particularly appealing for energy-intensive grid storage applications [1–4]. In conventional RFBs, two redox-active species, operating at different potentials, are dissolved in liquid electrolytes which are stored in tanks

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https://doi.org/10.1016/j.jpowsour.2018.07.046
Received 22 June 2018; Accepted 11 July 2018

and pumped through an electrochemical stack where they are oxidized and reduced to alternately charge and discharge the battery. Within the reactor, the two redox-active electrolytes (RAEs), often referred to as the positive electrolyte and negative electrolyte based on their respective electrode potentials, are separated by a selective membrane and undergo electro-oxidation and electro-reduction reactions on the surfaces of porous carbon electrodes. Ions traverse the membrane to balance charge between the RAEs hence maintaining electroneutrality. While state-of-the-art RFB technologies, which are typically based on transition metal salts dissolved in acidic aqueous electrolytes (e.g., vanadium [5–9], iron-chromium [10–12]), have achieved success in niche applications, present embodiments are too expensive for universal adoption motivating research and development into new RAEs with an overarching goal of reducing system cost through the use of inexpensive active species or through improved power and energy densities.

This drive towards economically-competitive RFBs has expanded their design space beyond traditional redox chemistries, electrolyte formulations, and reactor configurations to new redox couples, RAEs, and cell formats. Many RFB system designs have failed to demonstrate cost-competitiveness due to some combination of cost-driving system properties, such as energy density, material cost, or power density, that falls short of economic targets [3,4]. Redox-active organic materials have emerged as fascinating alternatives to standard redox species as the molecular and associated RAE properties can be tuned through functionalization, enabling rational design of chemical (e.g., solubility) and electrochemical properties (e.g., redox potential [13,14]), hence dramatically increasing the material design space. The potential of this approach is exemplified by the diversity of RAEs reported in recent literature including charge-storage chemistries based on redox-active monomers, polymers, and colloids [13,15–17]. Novel electrolyte compositions have introduced the use of deep eutectics, suspension electrodes, and supporting-salt-free RAEs as methods for increasing active material loading, thus capacity, within the RAE [18–22]. These emergent approaches, however, lead to new challenges in RFB design including accounting for increased, and often state-of-charge-dependent, viscosity, which slows mass transport, increases pumping requirements, and, consequently, reduces power density and efficiency. The constant push towards higher energy density (i.e., higher active material concentration) systems inherently forces RAEs into higher viscosity regimes, where mass-transfer resistances play a significant role, thus motivating examination of the influence of viscosity on RFB performance.

Viscosity directly impacts three resistive losses within RFBs: hydraulic, ohmic, and active species mass transfer (i.e., concentration polarization). Hydraulic losses within flow batteries have been generally well described as functions of viscosity through an approximation of Darcy flow, and their contribution to cell losses is generally considered small for a high-performance system [23–25], thus, we do not consider hydraulic losses here. Ohmic and mass-transfer losses have been partially addressed in prior work, for example, varying RAE temperature to control viscosity [26–28] and linking RAE velocity to a mass-transfer coefficient [29–35]. To the best of our knowledge, recent literature lacks a complete study where viscosity is independently manipulated, as a system variable, to quantify its role in determining the relative magnitude of these resistances. Specifically, no reports have systematically varied both viscosity and flow rate to develop higher-order descriptions of transport coefficients, as have been extensively applied in other areas of heat and mass transfer [36–39]. We seek to develop such correlations using a generalized mass-transport model in combination with experiments that enable independent and systematic variation of viscosity and flow rate.

To develop general descriptions of mass-transfer behavior in RFBs, we require a physical model that captures this behavior in a dimensionless form. Within this work, we use a single-electrolyte flow cell with an iron (Fe)-based RAE to execute steady-state measurements of mass-transfer processes [23,30,40]. Our past work has utilized Fe^{2+}/Fe^{3+} as a model redox chemistry to study mass transfer as a function of flow field design [30], and we revisit this couple to study the effect of viscosity on RFB mass transfer due to its formal potential, 0.771 V vs. the standard hydrogen electrode (SHE) [41], which is well within the aqueous electrochemical stability window, its high solubility in relevant electrolytes (>1 M), and its moderately fast redox kinetics [42]. We employ glucose as a thickening agent to modify the viscosity of our model RAE without adversely impacting the stability or Fe redox reactions. Glucose has been demonstrated as a thickening agent in prior work [43], and, as its electro-oxidation occurs at a relatively high redox potential, greater than 1.0 V vs. SHE [44], we do not anticipate the compound will substantially alter the faradiac processes in our system. Thus, by varying the glucose concentration, solution viscosity can be independently tuned and its impact on solution-phase transport properties (i.e., diffusivity, conductivity) can be quantified. These properties are measured in isolation and then coupled with estimated mass-transfer coefficients, extracted from flow cell polarization curves using a one-dimensional polarization model [30,42], to develop traditional power-law relations between the Sherwood, Péclet, and Schmidt numbers. These correlations, and their generic form, will enable researchers to extend preliminary material characterization to cell-level performance through a polarization model. Additionally, this description of mass transfer may lend itself towards advancement of design rules for RAEs, guiding future material development activities.

2. Experimental

2.1. Electrolyte preparation

Iron(III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$, 97%), D-(+)-glucose (glucose, 99.5%), and hydrochloric acid (HCl, 37%, balance water) were purchased from Sigma-Aldrich and used as received. Iron(II) chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$, 98%) was purchased from Alfa Aesar and used as received. All RAE solutions were prepared in volumetric flasks at room temperature with deionized (DI) water (Milli-Q Millipore, 18.2 MΩ cm). Room temperature (T) was ca. 22.0 ± 0.5 °C for solution preparation and all subsequent measurements.

2.2. Density, conductivity, and viscosity measurements

Density (ρ) was measured by weighing 1.0 mL aliquots (VWR pipette) of electrolyte solution in triplicate. Solution conductivity (κ) was measured in a Swagelok® cell assembly as described previously [22,30,45]. In brief, a 0.5 mL aliquot of solution was enclosed between two 10.7 mm dia. graphite (McMaster-Carr) electrodes with an electrode-to-electrode distance of 5.6 mm. High frequency electrochemical impedance spectroscopy (EIS) was collected 10 times per sample on a Bio-Logic VMP-3 potentiostat, and each solution was sampled in triplicate. This conductivity cell was calibrated using 0.5, 1.0, 1.5, and 2.0 M HCl at 20 °C with reported conductivities of 168.2, 312.2, 431.3, and 528.8 mS cm^{-1}, respectively [46].

Solution viscosities (μ) were measured using a TA Instruments AR-G2 magnetic bearing controlled-stress rheometer. A parallel-plate configuration with a 60 mm dia. acrylic plate and a 1 mm gap was used. Eight shear rates per decade from 1 to 100 s^{-1} were sampled for 1 min each. The average dynamic viscosity used in subsequent analysis was calculated from shear rates of 10 s^{-1} and higher. The kinematic viscosity (ν_m) was calculated from the dynamic viscosity and density ($\nu_m = \mu/\rho$).

2.3. Voltammetric measurements

All voltammetric measurements were performed on a Bio-Logic VMP-3 potentiostat. Cyclic voltammetry (CV) measurements were collected at 20 mV s^{-1} using a glassy-carbon working electrode (3 mm