



A vanadium redox flow battery model incorporating the effect of ion concentrations on ion mobility



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HIGHLIGHTS

- An ion concentration-dependent mobility is proposed.
- A VRFB model incorporating the proposed mobility is developed.
- The model enables a more realistic simulation of cell performance.
- Numerical results show that thinning conventional electrodes improves performance.

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ABSTRACT

Previous vanadium redox flow battery models (VRFB) use the ion mobility deduced from the ion diffusivity measured at low ion concentrations, resulting in an overestimation of the ionic conductivity in VRFBs that virtually operate at much higher ion concentrations. To address this issue, we propose to use the Stokes–Einstein relationship to determine an ion concentration-dependent ion mobility. A two-dimensional, transient model that incorporates the effect of ion concentrations on ion mobility is developed for VRFBs. It is shown that the present model results in: (i) a more accurate estimation of ionic conductivity, (ii) a more accurate prediction of cell voltage particularly at high current densities, and (iii) a more realistic simulation of the concentration distributions and local current density distributions in the electrodes. Finally, the model is applied to the study of the effects of important electrode design parameters and operating conditions on cell performance. It is found that the local current density, being distributed across the electrode in a manner opposite to that predicted by previous models, is much lower at the current collector side than that at the membrane side. This fact suggests that the region away from the membrane is not well utilized in conventional electrodes, thus a thinner electrode is preferred.

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1. Introduction

Redox flow batteries are energy storage systems that are designed for use in large-scale applications such as peak load leveling and effective utilization of intermittent renewable energy sources [1–4]. In particular, the all-vanadium redox flow battery (VRFB) has been regarded as the most promising technology, primarily because it uses the same element in both half-cells, which avoids cross-contamination between the two half-cell electrolytes [5,6]. Although promising, issues with VRFBs, including a low power density on a system level, ion crossover through the polymer membrane, and corrosion of current collectors, must be addressed before the widespread commercialization of this type of technology. To address these issues, efforts have been devoted

to developing optimal materials for electrodes, ion exchange membranes and current collectors [7–11]. Moreover, electrode optimization was found to be critical in improving cell performance. Recently, Aaron et al. [12,13] experimentally demonstrated that the optimization of electrode thickness heavily relies on making a trade-off between the reaction surface area and charge transport resistances that result from the ion transport and electron transport processes.

In addition to experimental investigations, numerical modeling also plays an important role in improving and optimizing the performance of VRFBs. Previous numerical investigations on VRFBs mainly focused on developing robust formulations to describe the transport phenomena occurring in VRFBs [14–29], and little attention was focused on determining accurate transport properties. However, to ensure that numerical models provide meaningful insight into understanding these complex phenomena and optimizing engineering design and operation of a VRFB, accurate

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Nomenclature

a	specific surface area of porous electrode, m^{-1}	<i>Greek</i>	
c	concentration, mol m^{-3}	ρ	density, kg m^{-3}
d	thickness, m	μ	viscosity, $\text{kg m}^{-1} \text{s}^{-1}$
D	diffusivity, $\text{m}^2 \text{s}^{-1}$	ε	porosity
F	Faraday's constant, C mol^{-1}	κ	permeability, m^2
H_{cell}	length of the electrode	σ	conductivity, S m^{-1}
I	applied current density, A m^{-2}	ϕ	potential, V
j	local current density, A m^{-2}	η	overpotential, V
k_{\pm}	reaction rate constant, m s^{-1}	α	charge transfer coefficient
k_m	mass transfer coefficient, s^{-1}	ω	volumetric flow rate, $\text{m}^3 \text{s}^{-1}$
N	superficial molar flux, $\text{mol m}^2 \text{s}^{-1}$		
N_m	MacMullin number	<i>Superscripts and subscripts</i>	
p	pressure, Pa	e	electrolyte
R	universal gas constant, $\text{J mol}^{-1} \text{K}^{-1}$	eff	effective
S	source term	i	species
t	time, s	in	inlet
T	temperature, K	m	membrane
u	ion mobility, $\text{mol s}^{-1} \text{kg}^{-1}$	out	outlet
\bar{v}	superficial velocity, m s^{-1}	s	solid
U_0	equilibrium potential, V	V(II)	V^{2+}
U'_0	standard equilibrium potential, V	V(III)	V^{3+}
V	electrolyte volume in half-cell tank, m^{-3}	V(IV)	VO^{2+}
w_{cell}	width of the electrode	V(V)	VO_2^+
z	valence		

transport properties are needed, in addition to a robust formulation. One of the key transport properties is the mobility that is required to model the ion transport process in the framework of dilute solution theory. To date, most models for VRFBs simply adopt ion mobility deduced from ion diffusivity measured at low ion concentration solution and assume that ion mobility is independent of ion concentration. However, there is an intricate relationship between the ion mobility in the electrolyte of VRFBs and the ion concentration. With an increase in the ion concentrations, the ion mobility declines dramatically as a result of higher viscosity. A critical issue seen in previous models is the effects of this relationship are missing, resulting in an overestimation in the ionic conductivity of VRFBs that operate at much higher ion concentrations. Specifically, the ionic conductivity predicted by the previous model is around 200 S m^{-1} [23], while the actual value is closer to $10\text{--}40 \text{ S m}^{-1}$ [30]. The margin of errors in the estimation is over 500%. As a consequence, the error associated with the prediction of the ionic conductivity affects the accuracy of the predicted cell voltage and distribution of concentrations and local current density, especially at high current densities. Thus, to obtain more meaningful insight in the underlying physical processes and predicting cell performance, an accurate correlation between ion mobility and ion concentration is necessary. Since the electrolytes of VRFBs contain 4 or 5 charge ions, determining the link between these two properties by experimental measurements is a grueling task. A more straightforward method must be developed in securing more accurate and meaningful information on the relationship between ion concentration and ion mobility in the electrolyte of VRFBs.

The Stokes–Einstein relationship, which describes the relationship between ion diffusivity, dynamic viscosity and temperature, is typically used to characterize the temperature dependence of ion diffusivity and ion mobility in dilute solution theory [31]. It can also be adopted to estimate the concentration dependence of ion diffusivity and mobility and has been applied into models of electrochemical systems such as lithium ion batteries [32]. Based on the dilute solution assumption, we propose to use the

Stokes–Einstein relationship to determine the ion concentration-dependent ion mobility in electrolytes of VRFBs. A two-dimensional, transient model that incorporates the proposed ion motility is developed. In addition, the effects of applied current densities and electrode thickness on the cell performance are examined using the proposed model. The formulation of the model is detailed in Sections 2 and 3, followed by the results and discussion in Section 4 and the summary of main findings in Section 5.

2. The ion concentration dependence of ion mobility and diffusivity

Based on the framework of dilute solution theory, mobility, which is usually deduced from diffusivity measured by experiment, is a key transport property that describes the ion transport process. The ion mobility heavily depends on the electrolyte components and their respective concentrations. Namely, the mobility of a certain ion is the function of the concentrations of ions in the electrolyte. However, the composition of the electrolyte in VRFBs is very complex as it contains 4 or 5 charged ions. Thus, it is difficult to correlate the ion mobility directly with the concentrations of the charged ions. Thus, we propose to correlate the ion mobility indirectly with ion concentrations by using the Stokes–Einstein relationship, as depicted in Fig. 1a.

The Stokes–Einstein relationship can be expressed as [31]:

$$r_i = \frac{RT}{6\pi D_i \eta} \quad (1)$$

where r_i is the radius of the charged ion i , D_i is the diffusivity of ion i , η is the dynamic viscosity, R is the universal gas constant, and T is the operating temperature.

According to Nernst–Einstein equation, the ionic mobility of species i can be calculated by:

$$u_i = \frac{D_i}{RT} \quad (2)$$

where u_i is the ion mobility.

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