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Effects of the electric field on ion crossover in vanadium redox flow batteries

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HIGHLIGHTS

- Effects of the electric field on ion crossover and capacity decay in VRFB are studied.
- The model enables the Donnan-potential jumps to be captured at electrode/membrane interfaces.
- Electric field arises and affects ion crossover even at the open-circuit condition.
- Enhancing electric-field-driven crossover can mitigate the capacity decay rate.

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ABSTRACT

A thorough understanding of the mechanisms of ion crossover through the membranes in vanadium redox flow batteries (VRFBs) is critically important in making improvements to the battery's efficiency and cycling performance. In this work, we develop a 2-D VRFB model to investigate the mechanisms of ion crossover and the associated impacts it has on the battery's performance. Unlike previously described models in the literature that simulated a single cell by dividing it into the positive electrode, membrane, and negative electrode regions, the present model incorporates all possible ion crossover mechanisms in the entire cell without a need to specify any interfacial boundary conditions at the membrane/electrode interfaces, and hence accurately captures the Donnan-potential jumps and steep gradient of species concentrations at the membrane/electrode interfaces. With our model, a particular emphasis is given to investigation of the effect of the electric field on vanadium ion crossover. One of the significant findings is that an electric field exists in the membrane even under the open-circuit condition, primarily due to the presence of the H^+ concentration gradient across the membrane. This finding suggests that vanadium ions can permeate through the membrane from H^+-diluted to H^+-concentrated sides via migration and convection. More importantly, it is found that the rate of vanadium ion crossover and capacity decay during charge and discharge vary with the magnitude of the electric field, which is influenced by the membrane properties and operating conditions. The simulations suggest that enhancing the electric-field-driven flow is a potential approach to minimizing the battery's capacity decay.

1. Introduction

Redox flow batteries (RFBs) have been considered as one of the most promising energy storage technologies that can be combined with intermittent renewable energy sources like wind and solar [1–5]. Unlike conventional rechargeable batteries, the RFBs store energy in electrolytes contained in external tanks, while energy conversion occurs in electrode compartments; thus the energy capacity of a RFB is decoupled from its power capacity, making it a unique candidate for large-scale electrical energy storage.Among the various RFB systems proposed in the literature, the all-vanadium redox flow battery (VRFB), invented and pioneered by Skyllas-Kazacos and her co-workers in 1980s [6], distinguishes itself by capitalizing on four different oxidation states of the same element, i.e. V^{2+}/V^{3+} in the negative half-cell and VO^{2+}/VO_2^+ in the positive half-cell. As such, conversion between electrical and chemical energy is achieved via the following reactions:

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Nomenclature

a	specific surface area, $m^2\ m^{-3}$
c	pore-phase molar concentration, $mol\ m^{-3}$
d	thickness, m
D	diffusion coefficient, $m^2\ s^{-1}$
F	Faraday constant, 96487 $C\ mol^{-1}$
I	operating current density, $A\ m^{-2}$
j	volumetric current density, $A\ m^{-3}$
$k_{+/-}$	reaction rate constant, $m\ s^{-1}$
k_d	dissociation reaction coefficient
k_m	mass transfer coefficient, s^{-1}
k_s	self-discharge reaction rate coefficient, s^{-1}
L	length of the electrode
$\vec{n}$	unit normal vector of boundary surfaces
N	superficial molar flux, $mol\ m^2\ s^{-1}$
p	pressure, Pa
R	universal gas constant, 8.3145 $J\ mol^{-1}\ K^{-1}$
$R_{i,+/-}$	reaction rate of self-discharge reaction, $mol\ m^{-3}$
S	source term
t	time, s
T	temperature, K
u	ion mobility, $mol\ s^{-1}\ kg^{-1}$
$\vec{v}$	superficial velocity, $m\ s^{-1}$
U_0	equilibrium potential, V
U_0'	standard equilibrium potential, V
V	electrolyte volume in half-cell tank, m^{-3}
w	width of the electrode
x	mole fraction
z	valence

Greek

ρ	density, $kg\ m^{-3}$
μ	viscosity, $kg\ m^{-1}\ s^{-1}$
ε	porosity
κ	permeability, m^2
σ	electronic or ionic conductivity, $S\ m^{-1}$
ϕ	potential, V
η	overpotential, V
α	charge transfer coefficient
β	degree of dissociation of HSO_4^-
ω	volumetric flow rate, $m^3\ s^{-1}$

Superscripts and subscripts

e	electrolyte
eff	effective
ele	electrode
f	fixed charge
i	species
in	inlet
l	liquid phase
m	membrane
mom	momentum
out	outlet
ox	oxidation
ref	reference
rd	reduction
s	solid
V2	V^{2+}
V3	V^{3+}
V4	VO^{2+}
V5	VO_2^+

$$V^{3+} + e^- \underset{discharge}{\overset{charge}{\rightleftharpoons}} V^{2+}\ \text{(Negative electrode)} \tag{1}$$

$$VO^{2+} + H_2O \underset{discharge}{\overset{charge}{\rightleftharpoons}} VO_2^+ + e^- + 2H^+\ \text{(Positive electrode)} \tag{2}$$

The cross contamination issue, inherent in most of other RFBs, is thus eliminated in VRFBs. Together with features like high efficiency, long cycle life, and tolerance to deep discharge without any risk of damage, the VRFB has attracted enormous attention from both academia and industry.

One essential component of a VRFB is the ion exchange membrane, typically proton exchange membrane (PEM), which prevents the mixing of the anolyte and catholyte while supporting proton transport to maintain electro-neutrality. Among PEMs, Nafion® from DuPont has been extensively studied and tested due to its high proton conductivity and excellent chemical stability. A critical issue associated with the use of Nafion®, however, is its low ion selectivity, leading to vanadium ions permeation from one half-cell to the other [7,8], and thus to reduced coulombic efficiency as well as capacity decay during cycling [9,10]. It is therefore vital to understand the mechanisms of vanadium ions transport across the membrane. A standard procedure in VRFB membrane research is to measure the diffusivity of vanadium ions in the membrane using the ex-situ static dialysis test, as have been done by many groups with respect to various types of membranes [11–14]. These ex-situ static dialysis tests, though very useful, are conducted without the presence of electric field (EF). Hence, only diffusional transport of vanadium ions along the concentration gradient is considered in these experiments. In real VRFB operation, electric field (EF) arises across the membrane, which induces two additional transport mechanisms. One is migration, representing movement of individual ions under EF with respect to the bulk flow; the other is electro-osmotic convection (EOC), representing flow of the bulk electrolyte under electrical force. These EF-driven migration and convection can affect significantly the ion concentration distributions and ion crossover rate across an ion-exchange membrane, as demonstrated by Schlogl [15] and by Verbrugge and Hill [16], but these studies are not related to VRFBs. Most Recently, Luo et al. [17] reported that the presence of EF affects not only the magnitude but also the direction of net vanadium crossover in a VRFB. Apart from their study, however, little work in the literature shed light on the EF effects over ion crossover.

Due to the high cost and lengthy time requirements of experimental study, mathematical modeling has become an indispensable tool in predicting and investigating the performance of VRFB systems. Li and Hikihara [18] proposed a 0-D transient model suitable for predicting the dynamic performance of a VRFB system. Shah et al. [19] developed a 2-D transient model of a single VRFB based on computational fluid dynamics (CFD) approach, and applied it to predict the distributions of current density, over-potential and reactant concentration during operation. They also extended this model in later publications to account for non-isothermal effect [20] and parasitic reactions like hydrogen and oxygen evolution [21,22]. Vynnycky [23] proposed an asymptotic method which can reduce the complexity of Shah's model and render it suitable for analyzing large-scale VRFB stacks. You et al. [24] simplified Shah's model by reducing it to a steady-state model, and emphasized the effect of applied current, electrode porosity and mass transfer coefficient on cell performance. This steady-state model was later extended to 3-D models by Ma et al. [25], Xu