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Numerical analysis of vanadium crossover effects in all-vanadium redox flow batteries

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ABSTRACT

In this work, a crossover model is newly developed to account rigorously for the crossover of vanadium ions through the membrane and resultant side reactions occurring in both positive and negative electrodes. The crossover model is then numerically coupled with previously developed three-dimensional (3-D), transient, thermal VRFB model in which key physicochemical phenomena including the electrochemical reactions, waste heat generation, resultant species and heat transport are all included. Using the comprehensive VRFB model, we investigate the effects of vanadium crossover between the negative and positive electrodes during a single charge/discharge cycle. Numerical simulations successfully capture capacity loss related to vanadium crossover, clearly showing the difference in species distributions due to side reactions. The results show that due to effect of vanadium ion crossover, more charging time and less discharging time have been achieved.

1. INTRODUCTION

All-vanadium redox flow batteries (VRFBs) utilize the V^{2+}/V^{3+} and VO_2^+/VO^{2+} redox couples in sulfuric acid as the anolyte and catholyte, respectively. Using the same vanadium species with the different oxidation states in both electrodes significantly mitigates the major critical issues in RFB technologies such as electrolyte cross-contamination, irreversible capacity loss, and undesirable side reactions. As a result, VRFBs exhibit relatively higher energy efficiency (up to 80%) and longer life-cycle among the redox flow batteries developed to date, showing the greatest commercial prospects for large-scale energy storage applications.

However, considerable crossover of vanadium ions and resultant capacity loss during charging and discharging processes have been continuously reported in the literature [1–3]. The fact implies that periodical electrolyte rebalancing and system maintenance are inevitably required for long-term VRFB operations, which in turn significantly raises operational cost of VRFB systems. Therefore, suppressing vanadium ions crossover must be one of key factors to achieve success in VRFBs and their widespread use.

The amount of vanadium crossover is mainly determined by ion-exchange membranes. So far, the commercial perfluorinated Nafion® membranes have been commonly used for VRFBs due to their high proton conductivity and excellent mechanical and chemical stability [4–7]. However, these membranes suffer from high cost and more importantly, high vanadium ions permeability. Therefore, considerable efforts have been made in the development of alternative ion-exchange membranes to meet the majority of aforementioned membrane characteristics for VRFBs [8–10].

Besides the development of new VRFB membranes, many groups have studied transport phenomena of vanadium ions through the membranes with a primary goal to obtain vanadium ions crossover data and analyze detailed crossover processes under different types of membranes and operating conditions [11–13]. Wiedemann et al. [14] measured the crossover diffusivity of vanadium ions through three different kinds of cation exchange membranes, i.e. CMX, CMS, and CMV membranes. They concluded that the CMS membrane is most suitable for VRFB applications due to its relatively lower crossover diffusivity values of vanadium ions ranging between 10^{-13} and 10^{-14} m^2/s. Sun et al. [15] experimentally analyzed vanadium ions crossover through Nafion 115 membrane, emphasizing that a major driving force for vanadium ions crossover is the concentration difference of vanadium ions between the positive and negative electrodes. In addition, their crossover data qualitatively showed the close interactions between vanadium ions, water, and proton transfer under various self-discharge and charge-discharge processes. Most recently, Lawton et al. [16] experimentally illustrated decreasing behavior of the permeation rate of VO^{2+} through Nafion 117 with increasing sulfuric acid concentration in the electrolyte solutions. They suspected the trend to be mainly caused by increasing level of

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membrane dehydration and resultant stronger partitioning/clustering effects with more sulfuric acid.

The issues of vanadium ions crossover have been also investigated by theoretical modeling and simulations. Skyllas-Kazacos and co-workers [17,18] presented simplified mathematical models wherein the mass and energy balance equations were coupled to describe the diffusion of vanadium ions through the membrane and predict resultant side reactions and capacity loss. However, electrochemical kinetics and the transport of charges were neglected in their models. Recently, Knehr et al. [19] accounted for all three crossover mechanisms of vanadium ions (i.e. diffusion, convection, and migration) in their two-dimensional (2-D), isothermal VRFB model. They numerically compared the relative magnitudes of diffusive, convective, and migrated fluxes and evaluated their contributions to total crossover flux during charging and discharging processes.

Although the aforementioned complex crossover phenomena entail a detailed account of electrolyte potential redistribution, various side reactions, and capacity loss, the crossover influences and related mechanisms were not precisely analyzed in the previous model development and theoretical analysis. In this paper, the above-mentioned crossover phenomena in VRFBs are newly modeled and incorporated into a 3-D electrochemical-transport-thermal coupled model for VRFBs. In this model, we consider four different oxidation states of vanadium ions, bisulfate, proton, and water as crossover species and account for relevant side reactions due to these crossover species in the negative and positive electrodes of VRFBs. In addition, the three crossover mechanisms including diffusion, convection, and migration are taken into account in order to more accurately capture the effects of crossover phenomena during VRFB operations. The 3-D simulation results presented in this study clearly address detailed crossover impacts on multi-dimensional species distributions as well as on overall thermal-electrochemical behaviors of VRFBs and capacity loss during charging/discharging cycles.

2. Model development

The model considers essential parts of the VRFBs including membrane, porous carbon electrodes and current collectors for a single cell. The schematic diagram and computational domain used for the simulation is well displayed on Figs. 1 and 2.

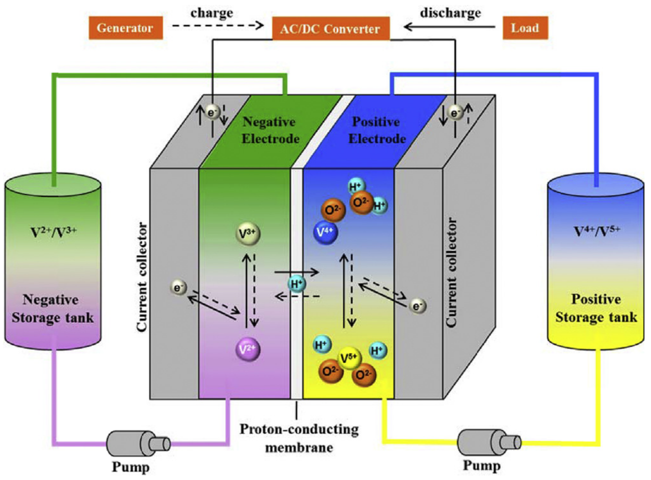

Fig. 1. Schematic diagram of VRFB illustrating the redox reactions and transport processes.

Nomenclature

A	cross-sectional area, m^{-2}
a	effective catalyst area per unit electrode volume, m^{-1}
C	molar concentration, $mol\,m^{-3}$
C_{KC}	Kozeny-Carman constant
D	diffusion coefficient, $m^2\,s^{-1}$
E_0	thermodynamic equilibrium potential, V
F	Faraday's constant, 96,487 $C\,mol^{-1}$
h	heat transfer coefficient, $W\,K^{-1}$
I	current, A
j	transfer current density, $A\,m^{-3}$
K	effective permeability, m^2
k	reaction rate/coefficient, $m\,s^{-1}$, and thermal conductivity, $W\,m^{-1}\,K^{-1}$
M	molecular weight, $kg\,mol^{-1}$
$\vec{N}$	species flux, $mol\,m^{-3}\,s^{-1}$
P	pressure, Pa
Q	volumetric flow rate, $m^3\,s^{-1}$
R	universal gas constant, 8.314 $J\,mol^{-1}\,K^{-1}$
r_p	pore radius, m
S	source/sink term
s	entropy, $J\,K^{-1}\,mol^{-1}$
T	temperature, K
$\vec{u}$	fluid velocity, $m\,s^{-1}$
V	volume, m^3
v	velocity, $m\,s^{-1}$
vf_i	volume fraction of species i

Greek symbols

α	transfer coefficient
ε	porosity
η	overpotential, V
κ	ionic conductivity, $S\,cm^{-1}$
μ	dynamic viscosity, $kg\,m^{-1}\,s^{-1}$
ρ	density, $kg\,m^{-3}$
σ	electronic conductivity, $S\,cm^{-1}$
τ	viscous shear stress, $N\,m^{-2}$
Φ	potential, V

Subscript

0	equilibrium or initial value
amb	ambient
cc	current collector domain
ch	charged species
dis	discharged species
elec	electrode
i	species index
in	channel inlet
l	liquid electrolyte domain
mem	membrane domain
NE	negative electrode
out	channel outlet
PE	positive electrode
s	solid electrode domain

Superscript

0	equilibrium or initial value
e	bulk electrolyte
eff	effective value
s	electrode surface
xover	crossover