



A comparative study of species migration and diffusion mechanisms in all-vanadium redox flow batteries



Kyeongmin Oh, Seongyeon Won, Hyunchul Ju *

Department of Mechanical Engineering, Inha University, 100 Inha-ro, Nam-Gu, Incheon 402-751, Republic of Korea

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ABSTRACT

According to the Nernst–Planck equation, the transport of charged species in porous electrodes is mainly driven by diffusion and migration. Although a number of all-vanadium redox flow battery (VRFB) models have been developed by several VRFB modeling groups, a comparative study of these two ion transport mechanisms has not been clearly reported in the literature. In this study, we develop a three-dimensional (3-D), transient VRFB model that rigorously accounts for both diffusion and migration mechanisms of charged species, including V^{2+} , V^{3+} , VO^{2+} , VO_2^+ and H^+ . The VRFB model relies upon five principles of conservation: mass, momentum, species, electric charge, and thermal energy. Due to the general form of the conservation equations, both species migration effects on species transport and species diffusion effects on charge transport are considered in the source terms of the model equations. The model calculates species migration and diffusion fluxes through the membrane and compares their relative magnitudes under various charging and discharging stages. This paper clearly elucidates the role of species migration on vanadium crossover and the subsequent capacity losses, demonstrating that the present VRFB model is a valuable tool for optimizing the component design and operation of VRFBs.

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1. INTRODUCTION

All-vanadium redox flow batteries (VRFBs) have been recognized as a potential large-scale energy storage technology that can enable the effective storage of the fluctuating power produced by renewable energy systems such as photovoltaic solar panel and wind turbine systems. The long-term performance and cost effectiveness of VRFBs are decisive factors for their successful commercialization and the widespread use of renewable energy sources. To advance VRFB technologies in terms of their high performance, low cost, and excellent durability, a deeper understanding of the complicated electrochemical reactions and transport phenomena involved in VRFBs under various designs and operating conditions must be obtained. Numerical modeling and simulation of VRFBs dramatically mitigate the experimental efforts associated with expensive and time-consuming laboratory fabrication and testing procedures, and also allow for more effective design, optimization, and control of VRFB systems.

Over the past half-decade, considerable efforts involving VRFB modeling and simulations have been made by several research groups. These models have ranged from simplified, one-

dimensional (1-D) dynamic models [1] to detailed, electrochemical-transport coupled CFD-based models [2–18], and have been predominately used to investigate the impacts of the materials and properties of key VRFB components [5–7] and the operating conditions [8] on key species distributions, and the overall cell performance. In order to predict the capacity loss of a VRFB, some of these models also account for the crossover phenomena of vanadium ions and water through the membrane [9,10], resultant side reactions [11], self-discharge processes [12,13], and gas evolution [14,15]. However, the majority of the crossover models only consider diffusive transport mechanisms through the membrane and/or electrodes [7,16]. Recently, Knehr and Kumbur [17] carried out 2-D, transient, isothermal simulations and precisely examined the impact of electrolyte viscosity on the vanadium crossover flows driven by osmotic and electro-osmotic convection. Later, they improved their 2-D VRFB model by including all three crossover mechanisms (i.e., convection, diffusion, and migration) and then analyzed the relative magnitudes of the three crossover modes at various charging and discharging stages [9]. Their predictions demonstrate that the net species flux across the membrane is affected by all three crossover mechanisms.

Although VRFB performance and capacity loss are mainly determined by the crossover of vanadium ions through the membrane, the crossover phenomena must be closely related to

* Corresponding author. Tel. : +82 32 860 7312; fax: +82 32 868 1716.

E-mail address: hcju@inha.ac.kr (H. Ju).

Nomenclature

A	cross-sectional area, m^{-2}
a	specific surface area, 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, $A\ m^{-2}$
K	effective permeability, m^2
k	reaction rate/coefficient, $m\ s^{-1}$; or 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, $m^3\ s^{-1}$; or heat transfer rate, W
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, $m\ s^{-1}$
u_i	ionic mobility
V	volume, m^3
v	velocity, $m\ s^{-1}$
v_f	volume fraction of species i

Greek symbols

α	transfer coefficient
ε	porosity
η	overpotential, V
κ	proton conductivity, $S\ m^{-1}$
μ	dynamic viscosity, $kg\ m^{-1}\ s^{-1}$
ρ	density, $kg\ m^{-3}$
σ	electronic conductivity, $S\ m^{-1}$
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
e	electrolyte domain
i	species index
in	channel inlet
l	liquid electrolyte
mem	membrane domain
NE	negative electrode
out	channel outlet
PE	positive electrode
s	surface

Superscript

0	equilibrium or initial value
e	electrode or electrolyte domain
eff	effective value
s	solid electrode

species transport inside of the porous electrodes that is also driven by all three transport mechanisms (convection, diffusion, and migration). In particular, the role of migration in the transport of vanadium species in the membrane and electrodes has not been clearly analyzed in previous papers. In this study, we present a 3-D, transient, non-isothermal VRFB model wherein species transport in porous electrodes via convection, diffusion, and migration are taken into account and incorporated into our previous VRFB model [18]. Special emphasis is placed on the comparative study of diffusion and migration fluxes through the electrode and membrane regions under different charging and discharging stages. This study elucidates the ion transport characteristics inside VRFBs and the complex interplay between vanadium transport through the electrodes and the subsequent crossover and capacity losses during VRFB operations.

2. NUMERICAL MODEL

The model used in this work is based on our previous 3-D, non-isothermal, transient, electrochemical transport coupled VRFB model [18]. However, this current model has been further developed by considering vanadium ion crossover through the membrane as well as migration effects. The model considers the major components of a VRFB single cell geometry that includes a membrane, porous positive and negative electrodes, and current collectors. The schematic diagram of electrochemical reactions and resultant species transport in VRFB is shown in Fig. 1. The governing equations and relevant source terms are summarized in Table 1. In addition, the electrochemical equations are listed in Table 2.

2.1. Model assumptions

The main assumptions invoked by the model are as follows:

1. The electrolyte flow is incompressible and laminar because of the small pressure gradient and low flow velocities.
2. The evolution of hydrogen and oxygen and the accompanying gas bubble formation in the electrodes are ignored.
3. The dilute-solution approximation is used to describe species transport.
4. The properties of the electrode, electrolyte, and membrane are assumed to be isotropic.

2.2. Additional constitutive equations

The effective permeability of the carbon electrode can be determined using the Kozeny–Carman equation:

$$K = \frac{4r_p^2}{C_{KC}} \frac{\varepsilon^3}{(1-\varepsilon)^2} \quad (31)$$

In addition, \vec{N}_i in Eq. (3) accounts for the flux of each species via diffusion, migration, and convection. This can be described by the Nernst–Planck equation as follows:

$$\vec{N}_i = -D_i^{eff} \nabla C_i - \frac{z_i F}{RT} C_i D_i^{eff} \nabla \Phi_e + \vec{v} C_i \quad (32)$$

where \vec{v} is the velocity of the electrolyte and D_i^{eff} represents the effective diffusion coefficient of the ionic species i through various VRFB components. For the porous region of a VRFB, this should be modified from its intrinsic value using the Bruggeman correlation [19] to account for the effects of porosity and tortuosity in the porous region as follows:

$$D_i^{eff} = \varepsilon^{3/2} D_i \quad (33)$$

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