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Modeling of ion transport through a porous separator in vanadium redox flow batteries

X.L. Zhou, T.S. Zhao*, L. An, Y.K. Zeng, L. Wei

Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

HIGHLIGHTS

- A 2-D, transient model is developed for VRFBs with a porous separator.
- Effects of design parameters and operation modes on ion crossover are examined.
- Convection is the main mechanism of ion crossover for available separators.
- Equalizing pressure on each half-cell reduces convection-driven ion crossover.

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ABSTRACT

In this work, we develop a two-dimensional, transient model to investigate the mechanisms of ion-transport through a porous separator in VRFBs and their effects on battery performance. Commercial-available separators with pore sizes of around 45 nm are particularly investigated and effects of key separator design parameters and operation modes are explored. We reveal that: i) the transport mechanism of vanadium-ion crossover through available separators is predominated by convection; ii) reducing the pore size below 15 nm effectively minimizes the convection-driven vanadium-ion crossover, while further reduction in migration- and diffusion-driven vanadium-ion crossover can be achieved only when the pore size is reduced to the level close to the sizes of vanadium ions; and iii) operation modes that can affect the pressure at the separator/electrode interface, such as the electrolyte flow rate, exert a significant influence on the vanadium-ion crossover rate through the available separators, indicating that it is critically important to equalize the pressure on each half-cell of a power pack in practical applications.

1. Introduction

The increasing concerns over fossil fuel depletion and the detrimental long-term environmental effects of greenhouse gas emissions compel an imminent transition from limited fossil fuels to renewable and environmentally sustainable energy sources, such as solar and wind. However, the intermittent and varied nature of these renewable resources make it challenging to utilize the valuable energies efficiently and cost-effectively [1–3]. One of the most effective solutions to address this issue is to employ large-scale electrical energy storages (EES) to decouple the electricity generation and load. Among large-scale energy storage technologies, vanadium redox flow batteries (VRFBs) stand out as one of the most promising and extensively developed systems thus far, as they offer high efficiency, long lifetime, excellent scalability, and are potentially developable at low cost [4–6].

A VRFB is typically composed of two porous carbon electrodes and two circulating electrolytes, which are separated by a membrane/separator. The membrane/separator is as a key component of a VRFB because it prevents crossover of the active species (vanadium ions) and provides charge transport pathways between the anolyte and catholyte during battery operation [7–10]. An ideal membrane should possess: i) high conductivity, ii) low vanadium permeability, iii) high chemical stability, and iv) low cost. To date, the most widely investigated and used membranes in VRFBs are Nafion membranes developed by Dupont, which possess high ionic conductivity and excellent chemical stability. However, there are two known issues associated with this type of membrane. First, it is highly permeable to vanadium ions, allowing for significant

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* Corresponding author.
E-mail address: metzhao@ust.hk (T.S. Zhao).

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vanadium-ion crossover, which leads to low coulombic efficiency and rapid capacity decay during prolonged cycling. Second, Nafion membranes are expensive, accounting for more than 20% of the total system cost and more than 40% of the cost of the power pack alone, significantly limiting the commercialization of VRFB systems [11–14]. Hence, much efforts have been devoted to the development of alternative membranes, including non-fluorinated polymer-based anion/cation exchange membranes, amphoteric membranes, and separators [15–30]. In particular, a number of separators such as microporous separators, nanofiltration membranes and polybenzimidazole membranes have been studied to evaluate their performance and suitability for use in flow batteries with different redox chemistry [24–30]. Zhang et al. [24] demonstrated the nanofiltration membrane made of hydrolyzed polyacronitrilein in VRFBs, showing promising results by achieving a coulombic efficiency of 95% and an energy efficiency of 76% at a current density of 80 mA cm^{-2}. Wang et al. [8] prepared a polytetrafluoroethylene/silica porous separator with an average pore size of 38 nm and a porosity of 48%, which delivered an energy efficiency of 80% at a current density of 50 mA cm^{-2}. Zhou and Zhao [25] reported a polybenzimidazole membrane, delivering a high coulombic efficiency of 99% at current densities ranging from 20 to 80 mA cm^{-2}.

While encouraging results have been reported in the past, the performance trade-off between the ohmic resistance and the active spices crossover in this class of membranes during battery operation was still not well-understood, limiting the degree of optimization of the ideal membrane design [23–30]. Particularly, ion-transport mechanisms that govern VRFB crossover through a porous separator are also not well-investigated [6]. Obtaining a more comprehensive understanding of the transport mechanisms and relationships between the critical parameters and battery performance will aid in developing an optimal porous separator. Li et al. [31] experimentally investigated the crossover mechanism of a VRFB installed with a microporous separator, showing that convection, caused by different hydraulic pressures at either sides of the separator, plays a primary role in active species crossover.

In line with the experimental investigations, developing sophisticated mathematic models to mimic the flow battery operation is also imperative to investigate the relationship between key properties of porous separators and cell performance as well as the associated mechanism of vanadium-ion crossover through a porous separator in VRFBs due to lengthy time, high cost requirements, and practical limitations of the experimental analysis [32–54]. In this work, we develop a two-dimensional, transient model to investigate the mechanisms of ion transport through a commercially-available porous separator in VRFBs and their effect on the battery performance. The commercially-available porous separator selected in the present study is the nanoporous polyvinyl chloride (PVC)/silica separator [29] with average pore sizes of 45 nm and porosity of 65%. The effects of key design parameters and operational modes are also examined.

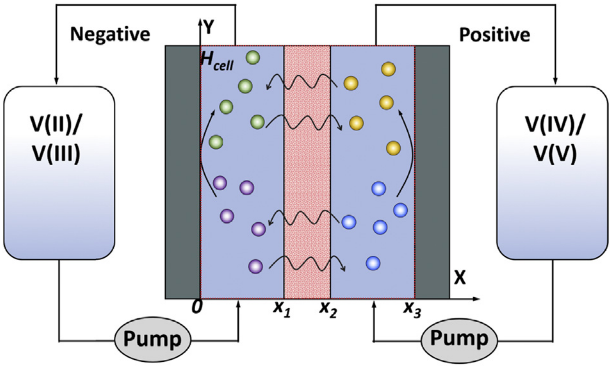

Fig. 1. Schematic of the computational domains.

Table 1
Geometric parameters and material properties.

Parameter	Value
Length of cell, H_{cell}	0.026 m
Width of cell, w_{cell}	0.026 m
Thickness of the electrode, L_e	0.0036 m
Thickness of the membrane, L_m	0.000125 m
Porosity of the electrode [37], ε	0.883
Porosity of the membrane, ε^m	0.65
Specific surface of electrode[a], a	1.75×10^5 m^2/m^3
Hydraulic permeability of electrode [37], κ	6.0×10^{-11}
Electronic conductivity of electrode [37], σ_s	220 S m^{-1}
Operating temperature, T	300 K
Touristy of membrane, τ[a]	4.6
Total contact resistance [37], R_{con}	74 mΩ cm^{-2}

[a] Fitted parameter.

2. Mathematical model

As shown in Fig. 1, the computational domain of the present model mainly includes two porous carbon electrodes and a porous separator. Table 1 summarizes the geometric parameters and physical/chemical properties of each component. To simulate physical/chemical processes occurring in the battery, several assumptions and simplifications are made in the present model:

(1) Variations in ion concentrations, potential, electrolyte velocity, and pressure in the direction perpendicular to the x-y plane are not considered.
(2) The electrolyte flow in the porous electrodes is treated as incompressible.
(3) All battery components are assumed to be isothermal.
(4) Parasitic reactions (hydrogen and oxygen evolution) are neglected.
(5) All the physical/chemical properties of the electrolyte, porous separator and porous electrode are isotropic.
(6) Both the first and second steps of the dissociation of sulfuric acid are fully complete.
(7) The vanadium ions with different valance will not react with each other when they meet in the separator since the reaction rate should be rather small in the separator, in which vanadium ion concentrations and activities are much lower than that in the electrode due to the confinement effects [55,56].
(8) The water crossover through separator is neglected.

2.1. Governing equations

2.1.1. In the positive/negative electrodes

In the positive/negative half-cells of the battery, the anolyte/catholyte containing solvent (water) and solutes (dissolved ions with positive or negative charges) are pumped to flow through the negative/positive electrodes. Hence, the bulk velocity of the anolyte or catholyte can be expressed by Darcy's law:

$$\mathbf{v} = -\frac{\kappa}{\mu}\nabla p \tag{1}$$

where κ denotes the hydraulic permeability of the positive/negative porous electrode, μ represents anolyte/catholyte viscosity, and p is