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Zero dimensional dynamic model of vanadium redox flow battery cell incorporating all modes of vanadium ions crossover

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HIGHLIGHTS

- A control-oriented 0-D model of VRFB cell is proposed.
- Precise simulation of crossover is performed.
- Analytical solution for crossover flux with all three modes is elaborated.
- Contribution of different crossover components to the capacity decay is investigated.

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ABSTRACT

A 0-D dynamic mathematical model for a single Vanadium Redox Flow Battery (VRFB) cell is proposed. The model is based on the conservation principles of charge and mass transfer focusing on the precise simulation of crossover with diffusion, migration and convection. The influence of these phenomena on the capacity decay was systematically analyzed, revealing considerable impact of convection component, which dominates under diffusion and migration and mainly responsible for observed capacity loss. The model allows to simulate main characteristics of VRFB systems (such as battery voltage, state of charge, charge/discharge time and capacity decay due to crossover) with high accuracy. The model was validated with experimental data in the wide range of current densities (40–100 mA cm^{-2}), and the results demonstrated good agreement with experiments having an average error within 5% range. In addition, the model requires a modest computational time and power, and, therefore, it can be suitable for application in advanced control-monitoring tools, which are necessary for a long-service life and sustainable operation of VRFB systems.

1. Introduction

The share of renewable energy sources (e.g. solar and wind) in the world energy consumption is continuously increasing [1]. However, their intermittent nature makes them rather difficult to implement for stable power supply. Electrical Energy Storage (EES) systems are considered to be one of the key technologies that can tackle this issue [2,3]. Among various EES systems, Redox Flow Batteries (RFB) are considered as a promising solution for stationary energy storage on the grid-scale applications due to their strong features [4–6]: long life time (thousands of cycles), deep discharge without risk of damage, modularity and independence of energy and power ratings. Several types of RFB that use different redox couples have been proposed [7,8]. Most of them are under development, while Vanadium Redox Flow Batteries (VRB) have already found a number of applications ranging from hundreds kW to tens of MW of rated power. Vanadispower flow batteries have been tested in Germany (0.3 MW/1.3 MW h) [9] and in Italy (0.45 MW/1.44 MW h) [10]; UniEnergy Technologies storage systems was deployed at commercial scale in Washington, USA, for load leveling (2 MW/8 MW h) [11]; Hokkaido Electric Power Co Inc (HEPCO) commercial solutions are currently under construction in Japan for intermittent balancing and load levelling [12].

One of the challenges arising during operation of VRFB is the crossover (transfer of vanadium of ions across the membrane) [13], which implies an increase of vanadium ions concentration in one half-cell and the corresponding decrease in the other half. Such imbalance in electrolytes will consequently influence on the battery capacity, which will become limited by the half-cell with lowest vanadium concentration and

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Nomenclature

A_{ch}	half-cell channels cross-section area [m^2]
A_{ed}	electrode surface area [m^2]
A_m	electrode-membrane interface area [m^2]
c	molar concentration [$mol\,m^{-3}$]
c_f	fixed sites molar concentration [$mol\,m^{-3}$]
CE	columbic efficiency
D	diffusion coefficient [$m^2\,s^{-1}$]
d_m	membrane thickness [m]
E	energy [J]
EE	energy efficiency
F	Faraday constant [$C\,mol^{-1}$]
j	current density [$A\,s\,m^{-2}$]
I	current [A]
k_m	mass transfer coefficient electrode-electrolyte interface [$m\,s^{-1}$]
N	molar flux [$mol\,m^{-2}\,s^{-1}$]
P	permeability coefficient [$m^2\,s^{-1}$]
Q	electrolyte flow rate [$m^3\,s^{-1}$]
R_{ce}	cell equivalent electric resistance [Ω]
R	gas constant [$J\,K^{-1}\,mol^{-1}$]
SOC	state of charge
t	time [s]
T	ambient temperature [K]
u	electrolyte velocity [$m\,s^{-1}$]
U_{ce}	cell voltage [V]
U_{eq}	cell equilibrium potential [V]
U_0^*	formal potential [V]
V	volume [m^3]
VE	voltage efficiency
$VRFB$	vanadium redox flow battery
z_i	valance of i-th ion [–]

Greek symbols

α	first empirical constant in mass transfer coefficient
β	second empirical constant in mass transfer coefficient
η_{act}	activation overvoltage [V]
η_{con}	concentration overvoltage [V]
η_{ohm}	ohmic overvoltage [V]
ξ	water electro-osmotic coefficient [–]
λ	water content coefficient [–]
σ^m	membrane conductivity [$S\,m^{-1}$]
τ	process duration [s]

Acronyms, subscripts, superscripts

b	bulk
c	charge
$calc$	calculated value
ch	channel
ce	cell
d	discharge
eff	effective
ed	electrode
exp	experimental value
hc	half-cell
i	i-th vanadium ion
in	input
$init$	initial value
m	membrane
max	maximum
ne	negative electrode
pe	positive electrode
out	output
$react$	reactant
s	stored
tk	tank
th	theoretical
tot	total
van	vanadium
2	V^{2+} ion
3	V^{3+} ion
4	VO^{2+} ion
5	VO_2^+ ion

volume [14], and as a result, the battery capacity loss will spring up. Arisen capacity decay will in turn limit the usable capacity in long-time operation and therefore needs to be detected and periodically corrected by electrolyte remixing [15]. Accordingly, to ensure a long operation of VRFB it is compulsory to investigate capacity decay mechanism caused by crossover and to develop reliable capacity restoration methods [16]. Hence, modeling of crossover phenomenon is a very important issue in development of sustainable VRFB facilities.

During the last decade, there were a number of works devoted to the modelling of VRFB on the different levels. In general, they can be divided into two groups: equivalent circuit models and numerical models.

Equivalent circuit models simulate the cell by electrical circuit with capacitors and resistors [17,18]. Recently, such approach was adopted for real-time monitoring of capacity loss [19]. Modeling of VRFB with equivalent circuits has advantages and limitations. On the one hand, these models are able to capture dynamics of VRFB, while they are simple and do not require significant computations, and as a result, they can be applied for control-oriented purposes. On the other hand, equivalent circuit models do not reflect the details of internal processes taking place in the cell. Therefore, application of these models for simulation of real systems requires a lot of measured data and sophisticated optimization technics [19], which could allow to tune the model in accordance with specifications of the certain system and its' operating conditions. Contrarily, numerical models are more comprehensive tool as they are based on the modeling of physical processes and hence, can be adapted to any system by changing only the coefficients related to physical properties of cell components.

The first numerical dynamic 0-D model was developed by Li and Hikihara [20]. Then, Shah [21] proposed a 2-D transient model, which was based on computational fluid dynamics approach (CFD). Further, this model was reduced to 0-D unit cell model for control-oriented applications [22]. Vynnycky [23] simplified Shah's model with asymptotical methods suitable for large-scale VRFB stacks. Vynnycky's approach was transformed by Chen [24] into 1-D model that showed better results. You [25] simplified Shah's model transforming it into steady-state model that was further extended into 3-D model by Ma [26], Xu [27], Oh [28]. Recently, a non-uniform 3-D model was proposed by Wang [29] for study of optimal electrode compression. However, all of these works did not model the crossover phenomenon, considering the membrane as ideal separator conducting only the protons. The first model devoted to crossover modelling was developed by the group of Skyllas-Kazakos [13,30]. They proposed a 0-D dynamic model focusing on the diffusion-driven component for simulation of ions transport across the membrane. Further, they extended this approach into 1-D model [31]. Simulation of crossover, considering only diffusion driven transport of ions has advantages and limitations. On the one hand, it is rather simple, as diffusion component can be easily calculated once the diffusion coefficients are known. On the other hand, such model is not able to predict the real effect of crossover. as electric field in the cell also provokes migration and convection of vanadium ions. These phenomena could have a significant effect on the total transport of ions in