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The quasi-steady state of all-vanadium redox flow batteries: A scale analysis

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ABSTRACT

In general, mathematical models for all-vanadium redox flow batteries (VRFB) that seek to capture the transport phenomena are transient in nature. In this paper, we carry out scale analysis of VRFB operation and derive the conditions when it can be assumed to be quasi-steady state in nature, i.e., time-dependence only through a boundary condition. We find that it is true for typical tank volume and flow rate employed for VRFBs. The proposed analysis is generic and can also be employed for other types of redox flow batteries.

1. Introduction

Recently, mathematical modeling and numerical simulations have come to play an important part in the research and development of all-vanadium redox flow batteries (VRFBs). A mathematical model can provide insight and detailed information about the various physical phenomena that take place in various functional layers of the flow battery, viz., current collectors, electrodes, and membrane. The models could be useful for various purposes, e.g., parametric studies to investigate the effect of the design, material and operating conditions, optimization, control, and troubleshooting malfunctioning; such studies would be time-consuming and expensive to carry out experimentally.

In many aspects, most of the VRFB models reported to date [1–15] solve the full set of transport equations numerically without analyzing them qualitatively first, in order to determine whether simplifications might be justified. Only Vynnycky [16] has analyzed the transport phenomena in a VRFB where scale analysis and asymptotic reductions were employed to reduce the complexity of the governing equations and, therefore, their computational cost. Two reductions were proposed in that paper: first, the plug flow in the electrodes at the leading order, and second, negligible species diffusion terms in the streamwise direction (x-direction in Fig. 1) as compared to the diffusion terms in the normal direction (y-direction in Fig. 1) due to the smaller aspect ratio (h_e/L) of the electrodes.

Since the concentration in the electrolyte tanks or the inlet concentration to the flow battery changes with time during charge/discharge, transient models [1,2,4,5,7,16,9–11,13,15] are required to capture the dynamic features of VRFB operation. A useful model reduction would be quasi-steady state operation to convert the transient model to one that is steady state in nature. Although this has previously been performed [3,8,12,14], the authors did not give any justification or any explanation on when this is applicable. In this regard, this paper adopts a similar approach to that of Vynnycky [16], i.e., scale analysis and asymptotic reduction, and derives a condition for when a transient model for VRFB operation can be reduced to quasi-steady state model, so that time-dependence enters the model equations only through a boundary condition. The derived condition for quasi-steadiness is then verified in context of a validated two-dimensional VRFB model.

2. Mathematical formulation and validation

We consider a transient two-dimensional model (see Fig. 1) accounting for conservation of species and charge in various

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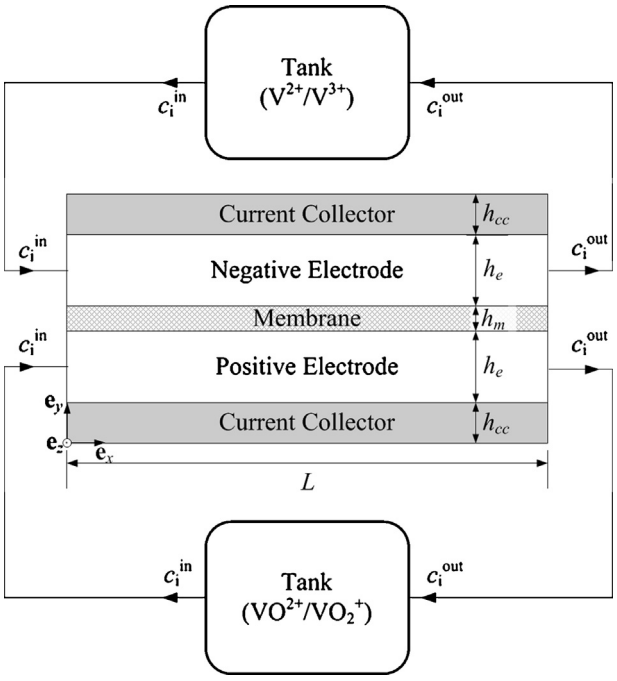

Fig. 1. A schematic of single cell vanadium redox flow battery.

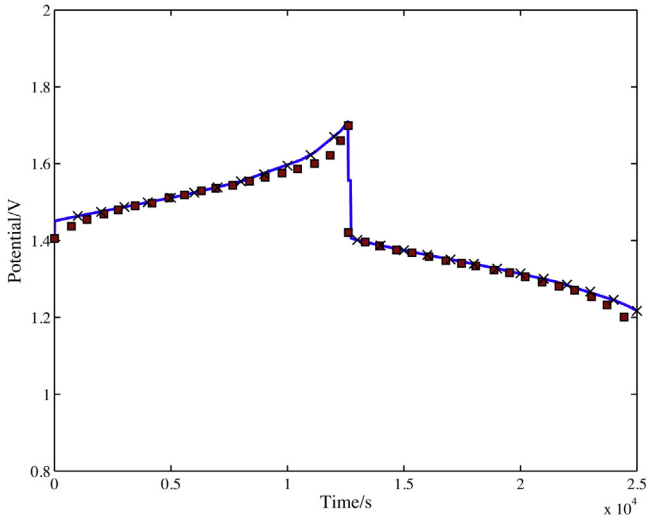

Fig. 2. A comparison of simulated and experimentally measured charge-discharge curves at a current density of 400 A m^{-2} using the data and results of Knehr et al. [9]: experimental measurements (■), and corresponding transient (—) and quasi-steady state (×) model predictions.

functional layers of the battery, viz. current collector, electrodes, and membrane; please refer to Appendix A for the governing equations, Appendix B for the boundary and initial conditions, and Appendix C for constitutive relations. The above model formulation is largely based on the work of Shah et al. and Knehr et al. [1,2,4,9]. The major model assumptions and characteristics are listed as follows:

1 The porous nature of the carbon felts and the membrane and the solid nature of the current collector allow for a reduction from three (x, y, z) to two dimensions (x, y) because changes in the dependent variables in the spanwise direction (z) are negligible.
2 The flow in the electrodes is plug flow at the leading order as proved by Vynnycky [16]. This obviates the need to solve equations for the conservation of mass and momentum in the battery.
3 The cell is isothermal.
4 The membrane is fully humidified.
5 H^+ can cross over the membrane, but all other ions cannot.
6 The dilute-solution approximation is valid (proven to incur a maximum of 9% error by Vynnycky [16]).
7 The electrolytes are incompressible.
8 There is no volume change due to transfer of water via electroosmosis.
9 The mass and charge transfer properties of the electrode, electrolyte and membrane are isotropic.
10 Hydrogen and oxygen evolution side reactions are negligible. The charging and discharging reactions can be summarized as

$$V^{3+} + e^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} V^{2+} \text{ at the negative electrode} \quad (1)$$

$$VO^{2+} + H_2O \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} VO_2^+ + e^- + 2H^+ \text{ at the positive electrode} \quad (2)$$

We carry out model validation to ensure that the model indeed predicts the performance of an actual system. For this purpose, we have chosen experimental results from Knehr et al. [9]. The simulated charge/discharge curves are compared against their experimental counterpart (see Fig. 2) for the parameters given in Table 1; a good agreement is obtained between model predictions and experiments. It should be noted that a total value of 72 mV is added to the simulated results in order to match to the experimental data [3,7].

Table 1
Base-case parameters [9]

Parameter	Value	Units
L	0.035	m
h_e	4×10^{-3}	m
h_m	2.03×10^{-4}	m
h_{cc}	6×10^{-3}	m
w_{cell}	0.0285	m
ω	5×10^{-7}	m^3 s^{-1}
V	6×10^{-5}	m^3
i_{app}	401	A m^{-2}
$D^0_{V_2}, D^0_{V_3}, D^0_{V_4}, D^0_{V_5}$	$(2.4, 2.4, 3.9, 3.9) \times 10^{-10}$	m^2 s^{-1}
$D^0_{H^+}, D^0_{SO_4^{2-}}, D^0_{HSO_4^-}$	$(9.312, 1.065, 1.33) \times 10^{-9}$	m^2 s^{-1}
T	300	K
$\sigma_m, \sigma_{el}, \sigma_{cc}$	$10, 66.7, 1 \times 10^6$	S m^{-1}
ϵ	0.93	-
a	3.5×10^4	m^{-1}
$E_{0,pos}, E_{0,neg}$	1.004, −0.255	V
k_{pos}, k_{neg}	$(2.5, 7) \times 10^{-8}$	m s^{-1}
$\alpha_{pos}, \alpha_{neg}$	0.5, 0.5	-
β	0.25	-
k_d	1×10^4	mol m^{-3} s^{-1}
R	8.314	J mol^{-1} K^{-1}
F	96487	A s mol^{-1}
$a^m_{H^+}$	1.99	-
$c^0_{V_2}, c^0_{V_3}, c^0_{V_4}, c^0_{V_5}$	156, 884, 884, 156	mol m^{-3}
$c^0_{H^+,neg}, c^0_{H^+,pos}$	5097.5	mol m^{-3}
$c^0_{HSO_4^-,neg}, c^0_{HSO_4^-,pos}$	2668.5, 3058.5	mol m^{-3}
$z_{H^+}, z_{HSO_4^-}, z_{SO_4^{2-}}$	1, −1, −2	-
$z_{V^{2+}}, z_{V^{3+}}, z_{VO^{2+}}, z_{VO_2^+}$	2, 3, 2, 1	-

3. Scale analysis

Let us employ scaling arguments to justify the model reduction from transient state to quasi-steady state. We exploit the inherent slenderness of a typical VRFB where length of the cell L is