Framework for Evaluating Electrochemical Characteristics of Vanadium Redox Flow Batteries

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Objectives

- Numerous studies focus on **the estimating cell performance** to evaluate the electrochemical characteristics and for **optimizing the geometric parameters and operating conditions**. In this work, we construct framework to estimate capacity data as well as the cell voltage to predict the electrochemical performance by measuring **the molar flux** of each vanadium ion flowing through the ion exchange membrane and **voltage-related parameters**.

Methods

- **Computational domain**
  - **Vanadium redox flow battery (VRFB)** consists of the cell and external tanks.
  - The electrochemical reactions occur in half-cell, and electrolytes are stored in tank, respectively.

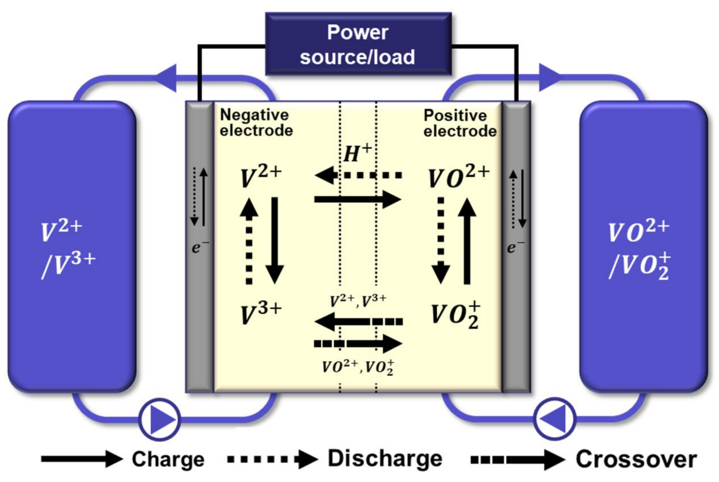

Fig.1 Schematics of VRFBs

- **Mathematical modeling**
  - **The zero-dimensional model (0-D)** model is constructed to describe the dynamics of VRFB.
  - The concentrations of existing vanadium ions in half-cell and tank are calculated using the mass balance equation as below:

$$V^{hc}\frac{dc_i^{hc}}{dt} = Q\left(c_i^{tk} - c_i^{hc}\right) - \sum N^m A^m + S_i \quad (1)$$

$$V^{tk}\frac{dc_i^{tk}}{dt} = Q\left(c_i^{hc} - c_i^{tk}\right) \quad (2)$$

  - The voltage is calculated explicitly using the estimated concentration.

$$E_{cell} = E_0 + \eta_{act} + \eta_{ohm} + \eta_{conc} \quad (3)$$

$$E_0 = E_0' + \frac{RT}{F}\ln\left(\frac{c_2^{hc}c_5^{hc}}{c_3^{hc}c_4^{hc}}\right) \quad (4)$$

$$\eta_{act} + \eta_{ohm} = R_{cell}I,\ \ \eta_{conc} = \frac{RT}{F}\ln\left(1 - \frac{I}{k_m c_{react} F A^{hc}}\right) \quad (5)$$

- **Parameter identification**
  - **Genetic algorithm (GA)** is an adaptive stochastic search algorithm appropriate to find solution in the multiple parameter optimization problem.
  - We consider the parameter vector consists of seven model parameters as follows:

$$\mathbb{x} = \left(N_2^m, N_3^m, N_4^m, N_5^m, k_m, E_0', R_{cell}\right) \quad (6)$$

  - The GA finds optimal solution $\mathbb{x}_{opt}$ to satisfy the fitness function such condition:

$$F\left(\mathbb{x}_{opt}\right) \le F(\mathbb{x});\ \forall \mathbb{x} \in \Omega \quad (7)$$

- **Global sensitivity analysis**
  - **Sobol' indices** are used to analyze sensitivity at non-linear system/model. Total Sobol' indices are applied to analyze the sensitivity of each parameter to the performance of RFB cell.
  - First- and second-order Sobol' index are calculated as below:

$$S_{1,i} = \frac{Var\{E(y|x_i)\}}{Var\{y\}} \quad (8)$$

$$S_{2,ij} = \frac{Var\{E(y|x_i x_j)\} - Var\{E(y|x_i)\} - Var\{E(y|x_j)\}}{Var\{y\}} \quad (9)$$

  - **Total Sobol index** is calculated by summing all order of Sobol' indices.

$$S_{T,i} = S_{1,i} + \sum_{j\neq i}^{n} S_{2,ij} + \sum_{j\neq i, k\neq i, j<k}^{n} S_{3,ij} + \cdots \quad (10)$$

Results

- We **validated** the 0-D model under two different applied current compared with the previous work [1]. After the validation, the parameters are identified with the reference voltage and capacity data [2].
- Firstly, the parameters are identified by using the reference **voltage data only**. The predicted voltage and capacity are shown in Fig. 2. The sensitivity of each parameter to voltage is analyzed using Sobol' index as shown in Fig. 3.

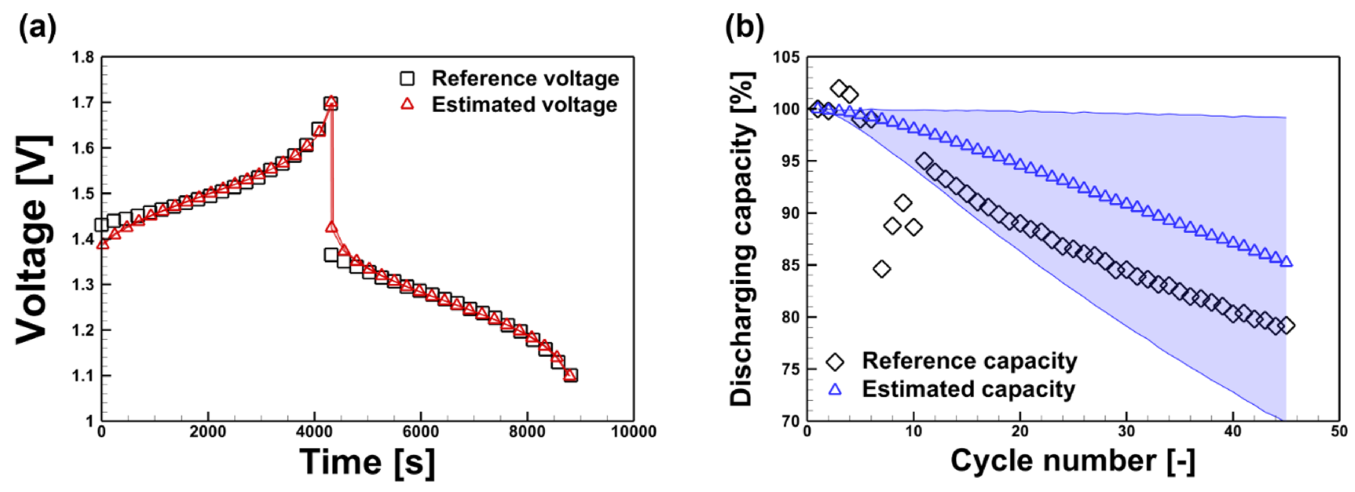

Fig.2 Comparison of reference and estimated data obtained from the parameters identified using only the voltage data.

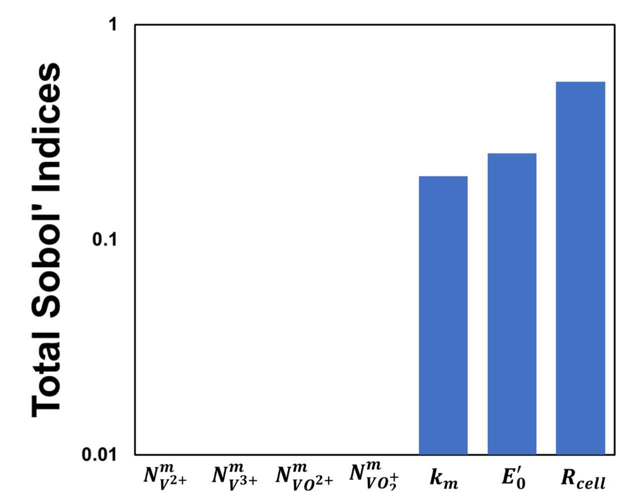

Fig.3 The sensitivity analysis of each parameter related to the voltage.

- Secondly, the parameters are identified by using **both the reference voltage and capacity data**. The predicted voltage and capacity and sensitivity analysis are shown in Fig. 4 and 5, respectively.

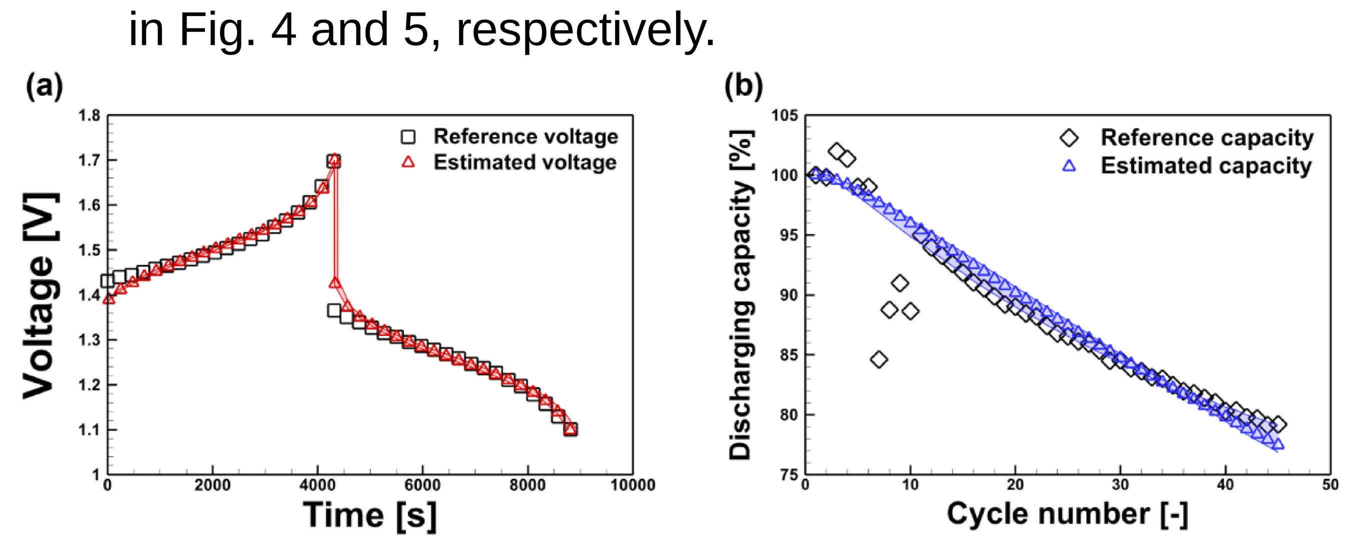

Fig.4 Comparison of reference and estimated data obtained from the parameters identified using both the voltage and capacity data.

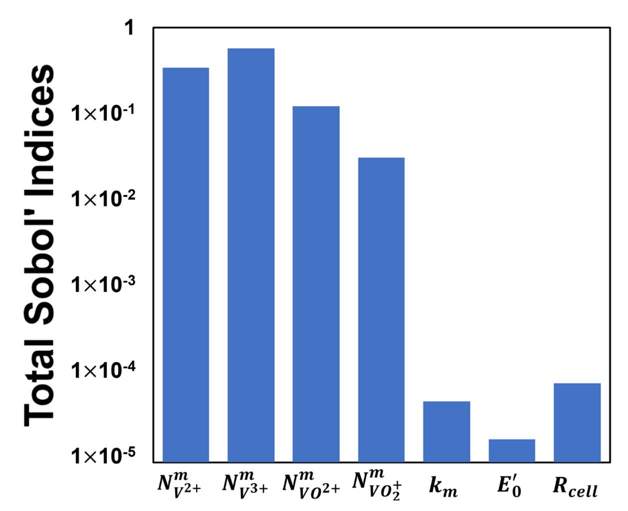

Fig.5 The sensitivity analysis of each parameter related to the capacity.

- Results show that the **voltage-related (k_m, E_0', R_{cell})** and **capacity-related ($N_2^m, N_3^m, N_4^m, N_5^m$)** parameters show high sensitivity to voltage and capacity, respectively. As a result, the reliable parameters should be estimated by considering both the voltage and capacity data.
- Furthermore, to confirm the **ability of 0-D model to predict discharging capacity**, we first identify the parameters to fit the discharging capacity data from 11 to 15-cycle data and predict the performance for the 16 to 45-cycle operation well, as shown in Fig. 6.
- In addition, the performances can be predicted under higher concentration and various operating conditions as shown in Fig. 7.

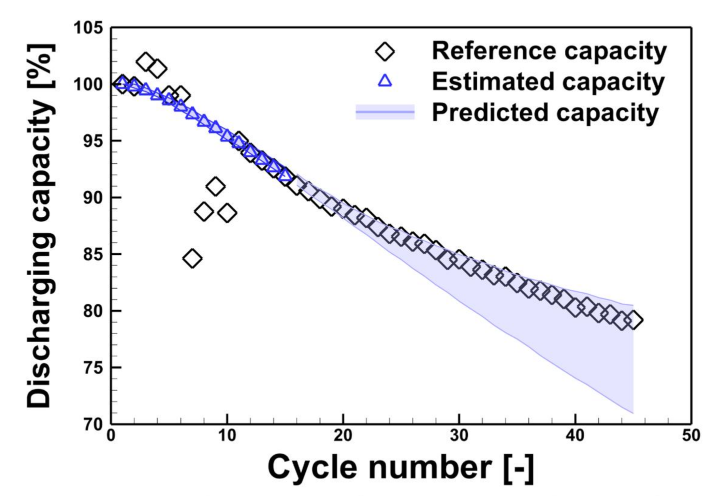

Fig.6 Prediction of capacity decay by using parameters identified with 15-cycle capacity data.

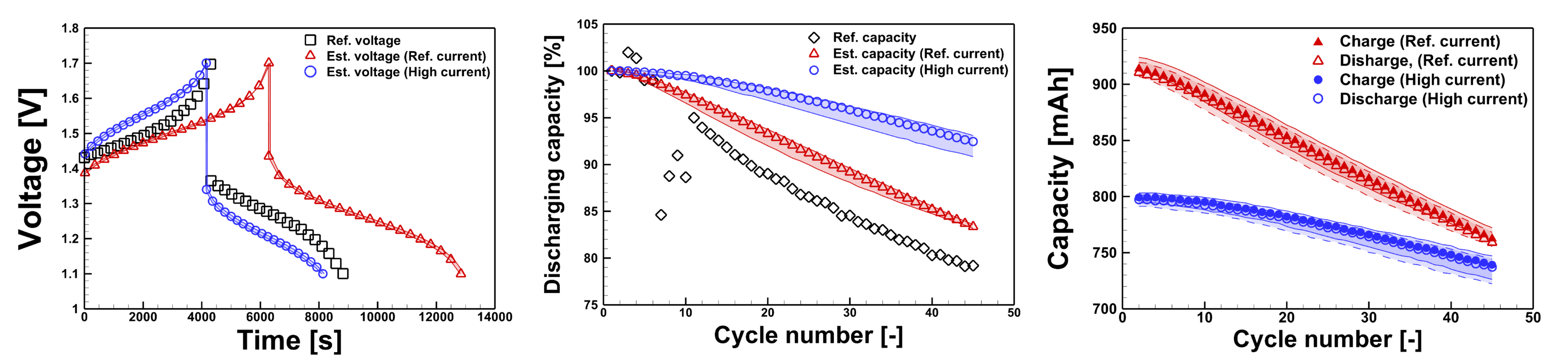

Fig.7 Prediction of performance under the reference and high current density at the increased vanadium concentration condition.

Conclusion

- **In this study, we constructed a framework for evaluating the electrochemical characteristics of VRFBs by identifying the parameters included in 0-D model.**
- **The parameters showed reliability to predict the electrochemical performances of VRFBs under various operating conditions by adopting 0-D model.**
- **This framework can be used to optimize the operation strategies and design parameters of VRFBs.**

References

1. M. Pugach et al., "Zero dimensional dynamic model of vanadium redox flow battery cell incorporating all modes of vanadium ions crossover", *Applied energy* 226 (2018) 560-569.
2. S. Kim et al., "Cycling performance and efficiency of sulfonated poly (sulfone) membranes in vanadium redox flow batteries", *Electrochemistry Communications* 12 (11) (2010) 1650-1653.