Fast and Simplified Algorithms for SoC and SoH Estimation of Vanadium Redox Flow Batteries

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***Abstract*— Typically, the electrochemical model and Equivalent Circuit Model-based (ECM) algorithms of Vanadium Redox Flow Batteries (VRFB) are complex and require high computation-time, thus not suitable to be used in the Battery Management Systems (BMS). Therefore, two simplified fast ECM-based estimation algorithms are proposed for the VRFB's State of Charge (SoC) estimation. The methods are proposed based on two different parameter identification algorithms, namely discharge pulse response and the optimization-based parameter identification for the first-order ECM. The proposed approaches are further extended by an innovative, simplified mathematical model for the capacity fade of VRFBs based on the battery's electrochemical model. The simplified capacity loss model facilitates non-complex and fast estimation of VRFB's State of Health (SoH), useful for modeling in the BMS. This has been led to a more accurate SoC estimation in the long-term use of the battery when the VRFB's capacity fades due to electrolyte volume loss. Although the proposed joint estimation of VRFB's SoC and SoH estimations are simpler to be modeled in the BMS, the proposed estimations are still accurate since the models consider enough electrochemical details of VRFBs. The accuracy, less complexity, reduced computation-time, and lower BMS memory storage highlight the proposed algorithms.**

***Keywords*—Battery Management System; Battery Parameter Estimation; Energy Storage Systems; Capacity Fade; State of Charge; State of Health; Vanadium Redox Flow Batteries.**

I. INTRODUCTION

The Vanadium redox flow batteries (VRFB) are a suitable option for large-scale energy storage system applications where the output energy of the VRFBs can increase by adding more electrolyte to the battery system without modifying the VRFB's stack design [1-3]. To name some of VRFBs characteristics, the decoupled power and energy design (scalability), the long lifetime, the safe battery chemistry (non-toxic, non-flammable), and no cross-contamination risk are recognizable [1-7].

The efficient operation of batteries can only be achieved by accurately estimating their quiescent parameters like the State-of-Charge (SoC), State-of-Health (SoH), etc., during their operation. The SoC estimation is beneficial to know the remaining charge of the battery and prevents over-charge/discharging. The SoH estimation ensures the battery's efficient and safe operation, increases the battery's lifetime, and prevents the battery from over-charging/discharging. A Battery Management System (BMS) is required, which allows the real-time estimation of important properties such as the temperature, the electrolyte flow rate, the terminal voltage, and the battery's SoC and SoH. Contrary to the other types of batteries like the Li-ion batteries, in Redox Flow Batteries (RFBs), the presence of electrolyte's flow rate, pressure, and other chemical quantities in the battery models gives rise to higher complexity in the battery's electrochemical models for estimating the battery parameters.

Different models are proposed for batteries like electrochemical models [8-12], Equivalent Circuit Models (ECMs) [13-21], the adaptive filter-based models [22-24], etc. Each of these types of models has advantages and disadvantages. Usually, the required accuracy of ECMs, and the required electrochemical quantities to be estimated, determine the complexity of these models. If the models are more complex, the computation-time will be higher to estimate the battery's parameters. This issue is more evident in RFBs in which complex chemical models are necessary to estimate many of the battery's parameters [8-12]. For example, the electrochemical models are essential to model the capacity fade in VRFBs [8], and modeling capacity fading is required to estimate the battery's SoH [22]. Therefore, usually, ECMs, which usually lacks these chemical equations [16], cannot model all the battery parameters, like the available capacity and the SoH.

The electrochemical models of VRFBs [8-12] suffer from high complexity than ECMs, thus not appropriate for BMS design; however, they are necessary for modeling most of the battery's chemical parameters [8]. On the other hand, when non-complex circuit element identification algorithms accompany the ECMs, they can have less computation-time than electrochemical models [25,26]. The online identification of the circuit elements within every sample time [13-19] is highly time-consuming and results in higher memory usage and sometimes malfunction of the BMS. This drawback shows up more while usually storing considerable data of circuit elements for every sample time is not possible and can result in a processing delay of the BMS software. Therefore, there is a need to make simpler and faster estimation algorithms for VRFBs, which is the main concern of our study.

The two primary ECM parameter identification methods are the battery's discharge pulse response test [25] and the optimization-based techniques [26]. Suppose the pulse discharge response test is used for the circuit elements identification; a higher order of ECM (with a large number of parallel RC modules) guarantees more accuracy [13]. However, modeling more RC parallel modules in the ECM makes these estimation algorithms complex and more costly [14,15] to be used in the BMS.

Some research studies so far consider the ECM models for batteries, including the VRFBs [16-20]. However, most of the existing models are only for SoC estimation and are not extended to estimate other parameters like available battery capacity and the SoH. Further, these ECMs usually formulate and validate only for Constant Current (CC) charging [16], [20,21], and are not suitable for the Constant Current-Constant Voltage (CC-CV) charging. CC-CV charging is the predominant charging procedure implemented by the inverters and chargers. Moreover, the CC-CV charging protects the battery by not allowing the terminal voltage to exceed the limits; therefore, our proposed algorithms will be verified on a CC-CV charging.

The RC equivalent model of VRFB is proposed in [16], where the open circuit cell potential and SoC for charge/discharge cycles were measured by extended Kalman filter approach, and the model was proposed for terminal voltages at different SoC. But the models were not extended to estimate the SoH because the capacity loss model is ignored. This also results in inaccurate SoC estimation in the long-term use of the battery.

Most previous research studies on the joint estimation of SoC and SoH include highly complex algorithms, not suitable for implementation in BMS. Therefore, simplified algorithms need to be proposed capable of fast estimation of all parameters with reduced complexity to be suitable for the development of software-based BMS. In [18], a Lyapunov-based adaptive SoC and SoH procedure for Li-ion batteries is proposed. The adaptive strategy estimates the online parameters of the battery model using a Lyapunov-based adaptation law. In [19], a robust estimation for SoC and SoH of Li-ion batteries using integral-type terminal sliding-mode observers is proposed. The authors in [19] investigate the real-time estimation of SoC and SoH of Li-ion batteries by three Terminal Sliding-Mode Observers (TSMOs). Although the accuracy of the proposed approaches in [18,19] is promising, these kinds of estimation algorithms are highly complicated and time-consuming to model in the monitoring systems like in BMS software.

A basic equivalent circuit model of VRFB is proposed in [20,21] with a voltage source representing the stack voltage, a controlled current source, and a fixed loss resistance representing parasitic losses, reaction resistance, and electrode capacitors. However, it lacks validation of the proposed models. Additionally, in [20,21], the SoC is modeled based on the Coulomb counting method. This method is not an accurate algorithm for estimating the SoC in VRFBs, since it lacks chemical quantities considerations. The Coulomb counting method's accuracy also relies on the current sensor measurement accuracy and the accurate estimation of battery available capacity. However, in the long-term use of VRFBs, the available capacity decreases due to ion diffusions across the membrane and the depletion of active materials, a phenomenon known as capacity fading. Therefore, Coulumb counting-based algorithms should be extended to include capacity fade models for accurate SoC estimation in the battery's long-term use.

ECMs sometimes include adaptive filter methods to extend the algorithms for more parameter estimation of batteries. The battery's dynamic electrical behaviors and an appropriate filter can then be designed to observe the battery's internal states [22]. Adaptive filtering methods apply filtering algorithms and modern control theory to reduce the noise of SoC and other parameters' estimation, including battery terminal voltage [22-24]. Kalman Filters (KFs) are common algorithms used in systems parameters estimation. In [23-24], an improved EKF for SoC estimation of VRFBs is proposed, and the state-space model is based on the ECM of the battery. However, these types of models are also highly complex to code in BMS software. These methods' accuracy also relies on the model's complexity (usually ECMs) and measured data from the sensors.

The main contributions of our study are as follows:

- Many estimation algorithms are introduced in the literature using online parameter identification of VRFB's, for e.g. [17,18]; however, most of these methods are not suitable for the BMS due to their complexity and high computation-time. The current study aims to introduce faster and simpler parameter estimation algorithms.
- A simplified pulse discharge response method and a simplified optimization-based method are proposed by the 1st order ECM of VRFBs to achieve faster and simpler estimation algorithms suitable for the BMS.
- Contrary to previously proposed ECMs, which are mostly proposed only for the CC charging mode [16],[20-21], the two proposed methods are applicable for CC, CV, and CC-CV charging procedures.
- In addition to the fast and simple benefits of the proposed algorithms, the algorithms show low errors in SoC estimation compared to the electrochemical model, which verifies the accuracy of the estimation, as will be shown in the results.
- An innovative mathematical equation is proposed for capacity fade modeling of VRFBs, leading to a simpler SoH estimation method suitable to be used in BMS. This model dismisses the need to model highly complex electrochemical equations.

II. The Proposed Estimation Algorithms

In this section, the proposed estimation algorithms for VRFB's SoC and SoH are described. In subsection A, the dynamic model of VRFB is described briefly. In subsection B, the first order ECM for VRFBs is expressed. The circuit elements identification by pulse discharge response test is described in subsection C, and an optimization-based algorithm is introduced in subsection D. Subsection E explains the fast and simpler SoC estimation equation, which can be used in BMS design. Subsection F includes the initial cycle capacity estimation and explains the concepts of modeling capacity fade in the long-term use of VRFBs in this

study. Finally, subsection G shows how the SoH will be estimated in this study.

A. Dynamic Electrochemical Model of VRFBs:

The electrochemical model of VRFBs is expressed in this section. The chemical reactions in VRFBs are as follows [12]:

$$VO^{2+} + H_2O \rightarrow VO_2^+ + 2H^+ + e^-, \qquad E^0 = +1.0\,V$$
$$V^{3+} + e^- \rightarrow V^{2+} \qquad E^0 = -0.26\,V \quad (1)$$

In which *V* stands for Vanadium, *e* is the electron released from the reaction, and E^0 is the standard potential of each positive and negative reactions. The total reaction creates 1.26 Volts known as standard Open Circuit Voltage (OCV) [12]. The partial differential equations of VRFB can be reduced to the Ordinary Differential Equations (ODEs) by discretizing the VRFB cell. The vanadium ion concentration in the tank and each cell can be modeled as an ODE expressing as a vector function *f* in equation (2). The dynamic model considers the diffusion of Vanadium ions across the membrane. The ODEs consist of four differential equations for vanadium concentration in cells and four for vanadium concentration in the tanks. The cell's Vanadium ion concentrations derive from equation (2) [12]:

$$\frac{dc_i^{cell}}{dt} = f\big(c(t), Q(t), I(t)\big) \qquad i = (2,..,5) \quad (2)$$

The concentrations of Vanadium ions in tanks derive from:

$$\frac{dc_i^{tank}}{dt} = \frac{Q\left(c_i^{cell}(t) - c_i^{tank}(t)\right)}{U_{tank}} \qquad i = (2,..,5) \quad (3)$$

Where Q is the electrolyte flow rate, I is battery current, U_{tank} is the volume of electrolyte in the tanks. The Vanadium ion's concentrations (c_i^{cell}, c_i^{tank}) $i = (2,..,5)$ constitute all the eight state variables of the ODE-based state-space model of the VRFB. The details of the ODE electrochemical model of the VRFBs are described in the literature, e.g., [8-12]. The VRFB's SoC can be estimated by the electrochemical model considering SOC of both half-cells calculated based on the concentrations of Vanadium ions present in each electrolyte reservoir tank during the charge/discharge:

$$SoC^- = \frac{c_2^{tank}}{c_2^{tank} + c_3^{tank}} \quad (4)$$

$$SoC^+ = \frac{c_5^{tank}}{c_4^{tank} + c_5^{tank}} \quad (5)$$

Where the Vanadium ion concentrations are the solution of the VRFB's ODEs in equations (2) and (3). The overall SoC of the VRFB system is the average of $SOC^-$and SOC^+ as follows:

$$SoC = \frac{SOC^- + SOC^+}{2} \quad (6)$$

The terminal voltage (V_T=$M.V_{cell}$) where *M* is the number of cells can be estimated by equation (7) concerning the Open Circuit Voltage (OCV) as follows:

$$V_T = M(V_{oc} + j.r^{cell} + \eta^{cell}) \quad (7)$$

Where *j* is charging current density, r^{cell} is ohmic battery internal resistant, and η^{cell} is over-potential in VRFB cells. In electrochemical cells, the transport of chemical species to/from the electrodes is limited by the mass transfer resistance between the electrode surface and the bulk electrolyte. Thus, this mass transfer resistance contributes to voltage losses, referred to as mass transport losses or concentration overpotential, compared to the cell's reversible potential.

B. First-Order Equivalent Circuit Model (ECM) of VRFB:

The first-order Resistive-Capacitive (RC) ECM for VRFBs is expressed in this subsection. Fig. (1) shows the ECM. A higher order of ECMs by having more parallel RC modules increases the ECM complexity, resulting in the burden of algorithm implementation in the BMS software. Therefore, the first-order ECM is proposed leading to less computation-time by the BMS with sufficient accuracy, as will verify in the results section. Using the KCL, the first order ECM's differential equation can be written as:

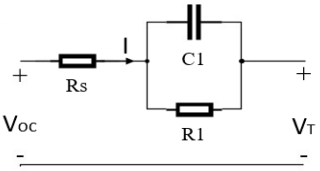

Fig. 1. First-order RC ECM for VRFBs.

$$\frac{dV_1}{dt} = -\frac{V_1}{R_1C_1} + \frac{I}{C_1} \quad (8)$$

In which V_1 is the voltage across the RC parallel impedances, and *I* is the charging current. The discrete form of the voltage of the parallel RC impedance is as follows:

$$V_1(k) = \exp\left(-\tfrac{\Delta t}{R_1C_1}\right)V_1(k-1) + [1 - \exp\left(-\tfrac{\Delta t}{R_1C_1}\right)]R_1I(k-1) \quad (9)$$

Where *k* is discrete-time instances, R_1 is the parallel resistor, C_1 is the parallel capacitor, and Δt is time intervals. In the first-order RC model, the battery terminal voltage can derive from:

$$V_T = M(V_{oc} \pm V_1 \pm R_sI) \quad (10)$$

Where *M* is the number of cells, R_s is the series resistor. The positive sign denotes charging mode, and the negative sign is for discharging mode.

C. Circuit Elements Identification Method 1: The Discharge pulse response test:

Some online methods estimate the ECM's elements in literature by identifying these elements per sample time. However, these methods need significant computation time. Therefore, for BMS design, there is a need to introduce simpler techniques that identify the circuit elements only once and use the optimal values for the rest of the charge/discharge processes instead of finding the circuit elements for every sample time. A simpler circuit parameter identification method that is suitable for BMS design is proposed here by the discharge pulse response test. Fig. 2 shows how the circuit elements can be found using this approach. To identify the first-order ECM parameters by this technique, the cell is subjected to a constant-current discharge pulse and then

allows the cell to rest while recording its voltage response (as shown in Fig. 2).

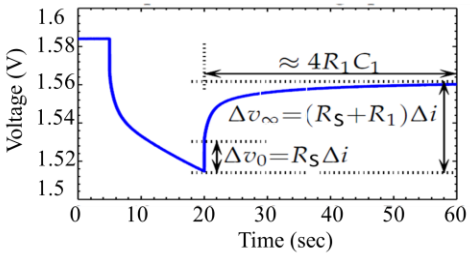

Fig. 2. A sample response to the discharge pulse technique.

At the instant when the discharge current pulse is removed, the instantaneous change in voltage must be equal to the instantaneous change in current multiplied by the series resistance *Rs*. This is because the capacitor voltage cannot change instantly, and the state of charge is not changing when the current is zero. This consideration implies $\Delta V_0 = R_s \Delta i$ (with signs computed such that R_s be positive), which leads to the estimation of R_s [25].

The steady-state change in voltage can be approximated. The overall steady-state voltage change can be found from $\Delta V_\infty = (R_s + R_1)\Delta i$, again with signs computed so that R_s and R_1 are both positive, knowing that the capacitor voltage will converge to zero in a steady state. This leads to the estimation of R_1. Finally, the pulse response converges to a value close to steady-state in about four-time constants of the RC circuit, where the time constant of the exponential decay is $\tau = R_1 C_1$. Therefore, C_1 can be estimated by knowing the settling time to the steady-state situation [25].

Therefore, having the R_s, R_1, C_1 elements computed, the terminal voltage, (V_T), and the battery current, (*I*) data by the sensors, the Open-Circuit Voltage (OCV) can be estimated by manipulating equation 10, as follows:

$$V_{oc} = (V_T \pm V_1 \pm R_s I) \tag{11}$$

D. *Circuit Elements Identification Method 2: Optimization-based approach*

Like the discharge pulse response method, the optimization-based method can also lead to identifying the ECM's elements only one-time, and the identification is not necessary for each sample time. However, the estimation of OCV by the second method uses the dynamic model of VRFBs only one-time to estimate ECM's parameters. V_{oc} can be estimated from the Vanadium ions concentrations dynamics from the electrochemical model equation (2) and (3) as follows:

$$V_{oc} = E_0 + \frac{2RT}{nF} Ln\left(\frac{C_2^{cell} C_5^{cell}}{C_3^{cell} C_4^{cell}}\right) \tag{12}$$

Where c_i^{cell} are Vanadium ions concentrations of cells, and. E_0 is standard cell potential equal to 1.4 Volts for SOC of 50% [12], *n* is number of electrons transferred in cell reaction, *R* is gas constant, *T* is temperature in Kelvin.

The values of circuit elements in the first-order RC ECM (R_s, R_1, and C_1), are estimated to fit experimental data of the VRFB prototype (here nine-cell VRFB unit). This method uses an optimization-based algorithm to estimate these circuit elements as follows. Thevenin impedance of the circuit is:

$$Z(j\omega) = R_s + \frac{R_1\left(\frac{1}{j\omega C_1}\right)}{R_1 + \left(\frac{1}{j\omega C_1}\right)} \tag{13}$$

On the other hand, the Thevenin equivalent impedances considering KVL is as follows:

$$Z_{th}(j\omega) = Avg((V_T - V_{oc})/I) \tag{14}$$

Where *Avg* is the average of the Thevenin impedances on the total samples. The circuit elements R_s, R_1, and C_1 can be estimated by minimizing the difference between the two proposed Thevenin impedances (equations (13) and (14)) for the first-order RC ECM as follows:

$$\begin{aligned} &Minimize\ Z_{th}(j\omega) - Z(j\omega) \\ &Subjected\ to\ R_s, R_1, \text{and } C_1 > 0 \end{aligned} \tag{15}$$

The constraints of the above optimization assume the series and parallel *RC* circuit elements are positive.

If an average function (Avg) were not considered in equation (14), the circuit elements will be computed per sample [$R_s(k), R_1(k)$, and $C_1(k)$]. Although computing these elements for each sample time results in more accurate estimations, but it is time-consuming and uses much more memory of the controller chip. Therefore, the Thevenin model's one-time average can result in less computation-time while having enough accuracy for estimations, as will be verified in the results section.

E. *SoC estimation by the proposed methods:*

For the discharge pulse response method, the OCV computes using equation (11) by having the battery current and terminal voltage from the sensors' measured data.

On the other hand, for the proposed optimization-based method, the OCV estimates from the result of the ODEs of the electrochemical model by equation (12). Assuming that all the vanadium species are fully balanced in the VRFB stack, the estimated open-circuit voltages ($\widehat{V_{oc}}$) can result in an accurate estimation for SoC of VRFBs by the Nernst equation-based model as follows:

$$SoC = \frac{\exp\left[\frac{nF}{2RT}(V_{oc} - 1.4)\right]}{1 + \exp\left[\frac{nF}{2RT}(V_{oc} - 1.4)\right]} \tag{16}$$

However, in the long-term use of VRFBs with performing several cycles of the charge/discharge, the Vanadium ions become unbalanced due to the depletion of active materials inside the battery stack and diffusion of the ions from the membrane. This results in VRFB's capacity fading and errors in the SoC estimation by equation (16). Therefore, the VRFB's capacity fading will be studied in the next section leading to an accurate estimation of the SoC in long-term VRFB's use.

F. *Capacity Estimation and Capacity Fading of VRFB:*

The battery capacity can be estimated as follows [27]:

$$Capacity = \frac{\eta_c \hat{I}_k}{\widehat{SoC}_{k+1} - \widehat{SoC}_k} \tag{17}$$

Where η_c is Coulombic efficiency of VRFBs as follows:

$$\eta_c = \frac{\int_0^{t_d} I_d \, dt}{\int_0^{t_c} I_c \, dt} \quad (18)$$

In which I_d is the discharging current and I_c is the charging current. Performing a cycle of charge/discharge, the Coulombic efficiency of our VRFB prototype under test is determined as about %85.

A simple solution for the capacity fading problem is reported in [8] as restoring the electrolyte volume by simply remixing the two half-cell solutions periodically. The cycle life of VRFB has been estimated at about 13000-15000 cycles of charge and discharge [28]. Suppose the electrolyte's remixing has not carried out periodically to balance the electrolyte volume in the two tanks. In that case, the capacity loss increases exponentially, and the available capacity will reach zero after about 520 cycles. These findings are shown in Fig. 9, by studying the capacity loss due to the electrolyte volume loss, with the following formulation to estimate the available capacity of VRFBs after several cycles of charge/discharging.

According to [8], the loss of volume in each cycle, also known as the bulk electrolyte osmosis, due to diffusion of Vanadium ions through the membrane is modeled as:

$$\Delta U_p = -\Delta U_n = \vec{v}^m S_M \, \Delta t \quad (19)$$

Where Δt is each cycle period time, S_M is the membrane surface area, and $\vec{v}^m$ is the velocity of electrolyte across the membrane, which can be derived from Schlogl's equation:

$$\vec{v}^m = -\frac{k_p}{\mu_w} |\Delta \Pi_{osmotic}| - \frac{k_p}{\mu_w} c_f . F (\varphi_m \frac{RT}{F} (c_{norm} + \frac{D_{H^+}^m \Delta C_{H^+}}{C_{H^+}}) \quad (20)$$

Where the pressure difference across the half-cells ($\Delta \Pi_{osmotic}$) can be approximated from the Van't Hoff equation. φ_m denotes the ionic potential of the membrane, C_{norm} denotes the normalized value of the contribution of each of the vanadium ions to the bulk transfer. The pressure difference ($\Delta \Pi_{osmotic}$) can be derived from the following equation [8]:

$$\Delta \Pi_{osmotic} = [((c_2 + c_3) - (c_4 + c_5) + (c_{H,neg} - c_{H,pos})] . RT \quad (21)$$

According to equations (19-21), the change of volume due to osmosis depends on membrane surface area (or cell size), the operation temperature, and Vanadium ion concentrations.

G. SoH estimation of VRFBs

SOH is defined as the ratio of current available capacity and initial capacity, as expressed in equation (22):

$$SoH = \frac{Current\ cycle\ available\ Capacity}{Initial\ Capacity} . 100\% \quad (22)$$

The initial capacity of VRFBs depends on the electrolytes' volume in the two tanks at the initial cycle. The available capacity reduces after each cycle of charge/discharge, as stated earlier. Therefore, the available capacity is always less than the initial capacity, resulting in the SoH of between 0 and 100 percent. In the next result section, a new method based on estimating the capacity fade model by equation (19-21) will be introduced to estimate the SoH of VRFBs.

III. Experimental Results:

In this section, the two proposed methods are verified by a sample CC-CV charging experiment on a nine-cell VRFB prototype, as shown in Fig.3. Table I shows the error associated with sensors used in VRFB experiments (extracted from sensors datasheet), which results in the most portion of error in parameter estimations. Table II shows the parameters used to simulate the proposed VRFB model.

In subsection A of this section, the result of the discharge pulse response technique is provided for the VRFB unit. In subsection B, the result of the optimization-based identification is described. Subsection C compares the estimated SoC by the two methods with the electrochemical and Coulomb counting methods. The initial cycle VRFB's capacity estimation and the result of capacity fade modeling of VRFBs are described in subsection D. According to the findings from subsection D, a new model for estimating the available capacity of VRFBs is proposed in subsection E. Finally, a new method for SoH estimation based on the proposed capacity fade model in subsection D is introduced in subsection F.

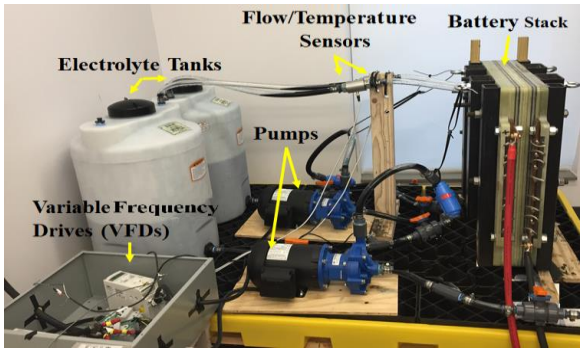

Fig. 3. The nine-cell VRFB prototype for experimental data.

TABLE I: Error of Sensors used in VRFB experiments

Sensor	error
Electrolyte Flow rate	±2% of the measured value
Electrolyte Temperature	2.5 (^oK)
DC Voltage	±1% of the measured value
DC Current	±2% of the measured value

A CC-CV charging procedure is used in this study, as shown in Fig. 4, to test and verify the proposed algorithm in section II and to estimate SoC, available capacity, and the SoH because a CC-CV charging has both CC and CV charging modes. At the first stage, in CC-CV charging, the battery charges with Constant Current (CC) until it reaches the pre-set value of voltage (1.6 Volts per cell in this study). In the second stage, the charging process will continue with Constant Voltage (CV) charging.

TABLE II: The parameters in the proposed VRFB model

Symbol	Quantity	Value
P	Rated power	2.25 (kW)
i_n	Nominal current density	58 (mA cm^{-2})
M	No. of cells in the stack	9
U_{tank}	The volume of tank electrolyte	25 (gallons)
L_{pe}	Length of the porous electrode	0.4 (m)
W_{pe}	Width of porous electrode	0.003 (m)
H_{pe}	Height of porous electrode	0.25 (m)
r^{cell}	Cell internal resistivity	2 (Ωcm^2)
F	Faraday constant	96485 ($Cmol^{-1}$)
R	Gas constant	8.314 ($J\,mol^{-1}K^{-1}$)
$(\frac{K_2}{D})$	Diffusion coefficient of V(II)	3.17e-6 (cms^{-1})
$(\frac{K_3}{D})$	Diffusion coefficient of V(III)	0.72e-6 (cms^{-1})
$(\frac{K_4}{D})$	Diffusion coefficient of V(IV)	2e-6 (cms^{-1})
$(\frac{K_5}{D})$	Diffusion coefficient of V(V)	1.25e-6 (cms^{-1})
ρ_{el}	Electrolyte density	1354 ($kg.m^{-3}$)
η	Electrolyte viscosity	4.928e-3 (Pa.s)
d_{fb}	Electrode fiber diameter	17.6e-4 (cm)
ϵ	Electrode porosity	0.93

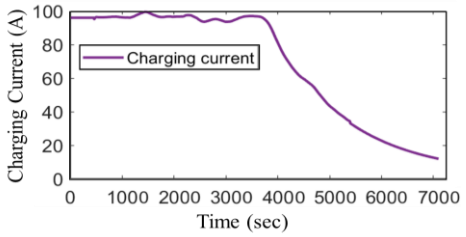

Fig. 4. The current sensors data for a CC-CV charging procedure.

A. The discharge pulse response technique results:

Fig. 5 shows the result of a sample discharge pulse response from the nine-cell VRFB prototype, where the discharging pulse current magnitude is 100A.

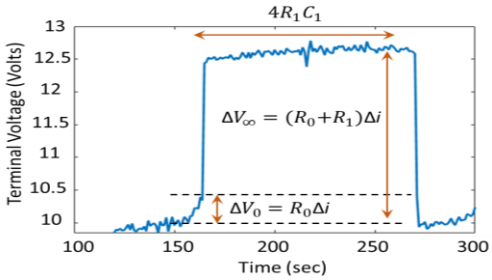

Fig.5. The pulse discharge response of the VRFB prototype

Fig. 5 shows the resting time of the battery after removing the load. According to the pulse response method discussed in section II-C, the circuit elements of the ECM can be estimated using Fig. 5 and measuring $\Delta i, \Delta V_0, \Delta V_\infty$, and τ. The parameters are extracted from Fig. 5 and are shown in Table III.

TABLE III: The discharge pulse technique parameters

Δi	ΔV_0	ΔV_∞	τ
100 A	0.45 V	2.5 V	100 sec

According to these values, the 1st order optimal ECM elements are derived and are shown in Table IV:

TABLE IV: The ECM elements by the discharge pulse technique

	Rs	R1	C1
Optimal Values	0.0045	0.02	1250

B. The optimization-based elements Identification result:

An identification approach is proposed for the ECM parameter estimation in subsection II-D. The optimal values of the 1st order ECM based on the optimization approach, which were the average of the circuit elements value in all samples, are shown in Table V:

TABLE V: The ECM's elements by the optimization approach

	Rs	R1	C1
Optimal Values	0.005	30	1e+5

C. Comparison of VRFB's SoC estimated results:

Based on the ECMs optimal elements shown in the last two subsections, the SoC in charging mode is estimated with equation (16), and the estimated curves of SoC with the different methods are compared in Fig. 6.

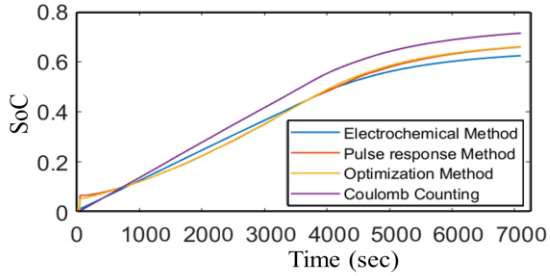

Fig. 6. Comparison of Estimated SoC by the proposed methods for the sample CC-CV charging.

The Root-Mean-Square Error (RMSE) is used to check the accuracy of estimations through measuring the difference of the electrochemical model-based SoC with the estimated SoC by the pulse response-based method, optimization-based method, and coulomb counting methods as follows:

$$RMSE = \sqrt{\sum_{i=1}^{k}[SoC_{Ech}(k) - \widehat{SoC}(k)]^2 / k} \qquad (23)$$

Where the SoC_{Ech} is the electrochemical-based SoC by equation (6), and $\widehat{SoC}$ is the estimated SoC by other method including the discharge pulse response, optimization-based, or Coulomb counting methods. The electrochemical method is proved to be the most accurate SoC estimation for VRFBs since it accounts Vanadium ion concentrations; therefore, other methods are compared with this method. The RMS errors of the SoC estimation methods are shown in Table VI.

TABLE VI: The RMS error of estimated SoC by different methods

Method:	Pulse Response	Optimization	Coulomb Count
RMS error:	0.1155	0.1119	0.1624

The relative error of SoC estimations is shown in Fig. 7. According to Fig.7, the Coulomb counting method has a bias error. As shown, the proposed methods based on the ECM are more accurate than the Coulomb counting method for SoC estimation of VRFBs.

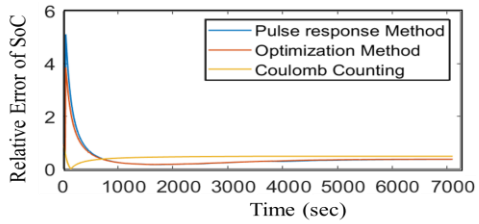

Fig. 7. Relative errors of the proposed estimated SoC methods

D. *Initial cycle's capacity estimation and the capacity fade modeling results for VRFBs*

Using equations (17-18), the nine-cell VRFB unit's capacity under test is estimated as 275Ah, considering 25 gallons of electrolyte in each tank, and Coulombic efficiency of ~%85. However, as mentioned, the VRFB capacity relies on the volume of the electrolytes in the tanks.

The capacity fading impacts on VRFB system parameter estimations are studied in this subsection by considering the electrolyte volume loss in each cycle described in equation (19). As shown in Fig. 8, the total volume loss after 200 cycles assuming an initial 25 gallons (94635 cm^3) of electrolyte is about ($\Delta V_p = -\Delta V_n$=17980 cm^3), which is about %19 of the initial electrolyte volume.

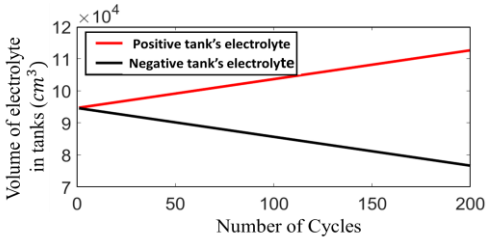

Fig. 8. Volume change in two tanks during 200 cycles.

Further, applying the volume change to the equation (3), the dynamic of VRFB studied for a sample of 200 cycles of charge and discharge. The results of available capacity estimation for 520 cycles are shown in Fig. 9. According to Fig. 9, the VRFB capacity decreases from ~275 Ah in the first cycle to zero after about 520 cycles. However, it reaches to ~210 Ah after 200 cycles, which is about 13.73% capacity fading after 200 cycles. The SoC estimated value after 200 cycles is compared with the SoC in the first cycle, and the result is shown in Fig. 10.

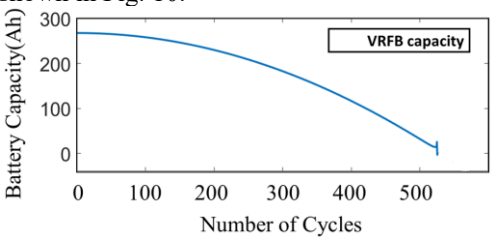

Fig. 9. Capacity Fading after 520 cycles of charge/discharge

According to Fig. 10, the SoC estimation has up to 7.1% error in the higher SoCs after the 200th cycle compares to the 1st charge/discharge cycle, which shows the importance of considering capacity fading in the accuracy of estimation of SoC in long-term use of VRFBs.

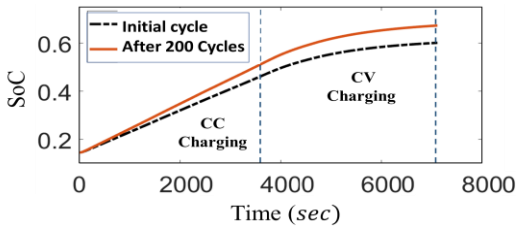

Fig. 10. The SoC estimation error if the capacity fading doesn't consider after 200 cycles of charge/discharge.

E. *A New Model for Capacity Fade in VRFBs*

According to Fig. 9, which shows the available capacity of VRFBs per cycle of charge/discharge based on the electrochemical model of VRFBs, an innovative mathematical equation is proposed to represent the available capacity of VRFBs in each cycle as follows. A second-order polynomial function fitted to Fig. 9 curve as follows:

$$\text{Available capacity} = f(x) = ax^2 + bx + c \quad (24)$$

Where x is the number of charge/discharge cycles, and the coefficients of the above polynomial function are found with 95% confidence bound, as shown in Table VII:

TABLE VII: The VRFB capacity's polynomial model coefficients

a	*b*	*c*
-9.67e-4	-1.2e-2	275

The coefficient c is the initial capacity of VRFB in the first charge/discharge cycle (equal to 275 Ah for our nine-cell VRFB unit), which depends on the electrolyte volume in the two tanks. The equation (24) introduces a new model for estimating the available capacity of VRFB, and it is simple enough to be used in BMS design to model capacity fade and available capacity after long-term use of VRFBs. This mathematical model can be generalized for all configurations of VRFBs since it is based on a general electrochemical model. However, there is no need to include the dynamic electrochemical differential equations in the BMS. It is enough to use the polynomial model results by equation (24) and the corresponding coefficients shown in Table VII in the BMS software, which is an accurate estimation while avoiding complexity.

F. *A new method for SoH estimation based on the proposed capacity fade model of VRFBs:*

According to the SOH definition, as the ratio of available capacity in the current cycle and initial capacity by equation (22), and the proposed available capacity model in the last subsections, a new model, can be proposed for SoH estimation of VRFB as follows:

$$SoH = \frac{Available\ Capacity}{Total\ Capacity}.100 = \frac{ax^2+bx+c}{c}.100 \quad (25)$$

The nominator in equation (25) is the available capacity of VRFB estimated by the polynomial function introduced in the last subsection, and the denominator (c) is the initial cycle (total) capacity of the VRFB, which is different for each battery unit (here 275 Ah). Fig. 11 shows the resulted SoH estimation by the newly proposed method.

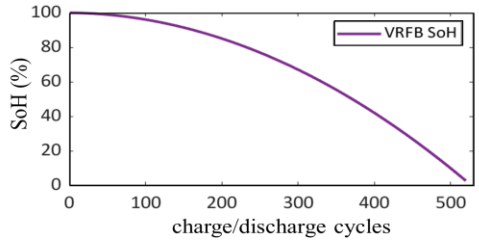

Fig. 11. SoH estimation of our VRFB prototype.

With the introduction of this new simplified approach for available capacity estimation by equation (24) and SoH estimation by equations (25), there is no need to include the electrochemical equation of (2-3,19-21) in the BMS design. This issue can significantly decrease the mathematical modeling burden in the software, leading to less computation-time and memory usage.

IV. CONCLUSION

Two simplified algorithms are proposed for parameter estimation of VRFBs. The non-complexity and accuracy of the proposed algorithms for SoC, SoH, and available capacity estimation of the VRFBs are promising for BMS design applications. The algorithms were based on introducing simplified ECM's parameter identification approaches for the first-order ECM of VRFBs, in which the circuit elements estimate only one-time in a cycle of charge/discharges and no need for identifying the ECM's parameter per sample time. This issue results in less computation-time and memory usage in the BMS. The two algorithms show accurate SoC estimations compared to the Coulomb counting method using the dynamic electrochemical model as a reference. Further, a new simplified mathematical model is introduced for available capacity and SoH estimation of VRFBs by modeling the capacity fade in the long-term use of the VRFB, resulting in a suitable polynomial model to be used in the BMS software of VRFBs. With this new simplified approach, there is no need to develop the complex chemical equations in the BMS design for capacity fading. This model significantly decreases the mathematical modeling burden in the software, leading to less computation-time and memory usage in the BMS.

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