

Estimating the State-of-Charge of all-Vanadium Redox Flow Battery using a Divided, Open-circuit Potentiometric Cell

M. R. Mohamed¹, H. Ahmad¹, M. N. Abu Seman²

¹*Sustainable Energy & Power Electronics Research (SuPER) Group, Faculty of Electrical & Electronics Engineering, Universiti Malaysia Pahang, 26600 Pekan, Pahang, Malaysia*

²*Faculty of Chemical Engineering & Natural Resources, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Kuantan, Pahang, Malaysia*
rusllim@ump.edu.my

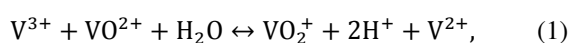
Abstract—In this paper, mathematical modelling of oxidation-reduction redox potential for estimating the state-of-charge of V-RFB is presented. The estimation is based on the Nernst equation, a mass balance, Faraday's law of electrolysis, and 1st order kinetic equation. The 25-100 cm² laboratories, unit cell V-RFB is chosen as a model reaction for electrolyte redox potential measurement. Preliminary experiment is carried out using a 100 cm² laboratory unit but the estimated value produced is inaccurate. An alternative design of 25 cm² laboratory, unit cell V-RFB using a divided, open-circuit potentiometric cell is used. The redox potential of V(III)/V(II) and V(IV)/V(V) is measured through combined Hg/Hg₂SO₄ reference electrode and carbon rod working electrode. The differences between the experimental and estimated values are highlighted.

Index Terms—Energy storage, modeling, redox flow batteries, state-of-charge

I. INTRODUCTION

Current economic developments demand stability in energy security for future accessibility [1]. Redox flow battery (RFB), developed in the 1970s [2] and shares similar principles as fuel cells, is a rechargeable battery that uses flowing redox species that flow through cell stack to convert chemical energy into electricity. RFB has the ability to decouple its power component from the energy components. Its modular nature presents it as a viable option for use in many applications, such as uninterrupted power supply, load levelling and stand-alone applications [3].

An all-vanadium redox flow battery (V-RFB) is one of the electrochemical energy storage systems that is suitable for many applications due to its high energy efficiency (>80%) [4], [5]. Fig. 1 depicts the principles of operation of a V-RFB. The overall cell reaction is as follows:



$$E^0 = 1.26V \text{ vs. SHE}. \quad (2)$$

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Theoretically, V-RFB does not suffer from capacity degradation as the same electrolyte species is used in both the positive and negative reservoirs. Also, V-RFB can be over-discharged without causing significant harm to the battery [6], [7]; the batteries could be cycled at lower state-of-charge (SOC) (20 % to 80 % SOC) [8].

However, overcharging the V-RFB should be avoided as it could have detrimental effects on the electrolyte and the cell components. Noack *et al.* [8] stated that overcharging beyond a certain voltage level would result in electrolysis of water into hydrogen on the negative electrode and oxygen at the positive electrode. Also, Mohammadi *et al.* stated that overcharging would increase the cell's resistance [9], which results in capacity loss of the battery [10].

Due to various cell reactions, as discussed in numerous literatures [9]–[13], estimation of SOC is best done at the reference cell instead of within the cell stack. The oxidation-reduction potential (ORP) method can be used, where the maximum point of redox could be related to the open-circuit voltage (OCV) of the V-RFB. Since OCV is a function of SOC [14], the accuracy of the battery's SOC is dependent on the accurate estimation of the OCV.

In this paper, potentiometric measurement is used for estimating kinetic parameters and current efficiency for electrolyte batches of V(IV) / V(V) and V(III) / V(II) to achieve its equilibrium state, and subsequently, V-RFB's SOC could be estimated. Also, continuous monitoring of the potential difference between two working electrodes and two half-cell potentials against Hg/Hg₂SO₄ reference electrodes is discussed.

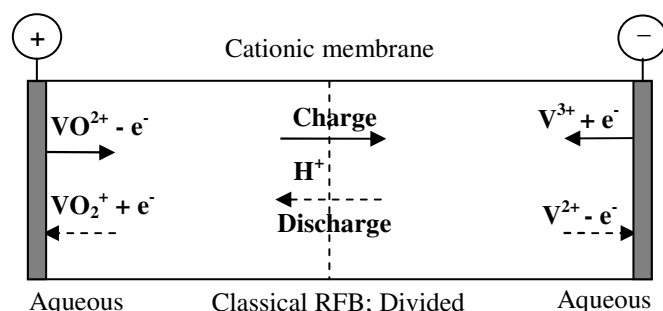


Fig. 1. Principles of operation of V-RFB.

TABLE I. NOMENCLATURE

$C_{V(II)}, C_{V(III)}, C_{V(IV)}, C_{V(V)}$	Concentration of vanadium species at different level of oxidation state, mol dm ⁻³	V(II), V(III) V(IV), V(V)	Vanadium species at different level of oxidation state
C_{oxd}	Concentration of oxidised species, mol dm ⁻³	F	Faraday constant, $F = 96485 \text{ C mol}^{-1}$
C_{red}	Concentration of reduced species, mol dm ⁻³	I	Constant current / A
E_{cell}	cell potential, measured across unit cell stack	R	Molar gas constant, $8.3145 \text{ JK}^{-1} \text{ mol}^{-1}$
$E_{cell(ORP)}$	open-circuit cell potential across two electrodes, otherwise abbreviated as $E_{cell(ORP)}$ for oxidation-reduction potential	z	Number of electrons transferred in the cell reaction
		T	Temperature / K
E_{cell}°	Standard cell potential	t	Time / s
E°	Standard electrode potential	V	Volume of electrolyte / dm ³
$E_{V(III)/V(II)}$	Positive half-cell potential for V-RFB	ϕ	Current efficiency
$E_{V(IV)/V(V)}$	Negative half-cell potential for V-RFB	SHE	Standard hydrogen electrode

II. METHODOLOGY ESTABLISHMENT

Sharkh *et al.* [15] noted that to establish the state-of-health (SOH) of a battery, correct estimation of SOC is essential. Besides, precise knowledge of SOC will facilitate optimal operation of a battery with minimal degradation effects, hence increasing the life cycle of the battery. Walsh [16] suggested that the details of the cell's equilibrium potential could be used to describe the thermodynamics of the electrochemical system.

The characteristics and parameters of well-known batteries are readily available from the manufactures; one is able to correctly estimate the SOC so as not to overcharge the battery. However, predicting the correct SOC for a newly developed battery, such as the V-RFB, could be difficult, especially for those who are trying to characterise the battery.

Numerous conventional methods, such as direct measurement, specific gravity measurement and current-based estimation (coulomb-counting), can be used to estimate and monitor SOC. However, open-circuit voltage (OCV) method results in very accurate estimation of the SOC but it needs a rest time and cannot be used in real-time [17]. Hence, in this study, OCV approach is adopted due to its suitability for current-controlled environment [18]. By definition, the open-circuit voltage is the voltage of the battery when no current is flowing in or out of the battery since the battery is in a state of equilibrium [14], and in this state the battery reaches 100 % SOC [19].

Oxidation – reduction potential (ORP), widely used in laboratory studies and industrial applications [20], can be used to monitor the concentration of redox species and is related to OCV as the points where oxidation and reduction are in a state of equilibrium. Using potentiometric measurement, the potential difference between the working electrodes and the reference electrodes is compared. The basis of which is the use of Nernst equation to describe the concentration of redox species in terms of the potential at the cell's electrode under equilibrium condition.

III. THEORETICAL EXPRESSION

Trinidad *et al.* [21] has applied the Nernst equation, mass balance equation of redox reaction and Faraday's law of electrolysis to establish the relationship between the half-cell redox concentration of Ce(IV)/Ce(III) and the ORP during electrolysis. In this study, the approach is extended to monitor both half-cells of redox couple, hence making

estimation of SOC possible.

For determining E_{cell}° , Blanc [22] suggested the use of thermodynamic characteristics of the elements involved in V-RFB reactions with E_{cell}° of 1.23 V, or the combination of two half-cell standard electrode potential with E_{cell}° of 1.255 V, where the latter value is also suggested by another researcher [8]. However, in this study, E_{cell}° of 1.26 V is chosen as the standard cell potential as this value is acknowledged by many researchers [7], [23]–[26].

Reaction (1) represents the kinetic reactions of vanadium species in the reversible cell reaction. Eq. (3) represents Nernst equation for determining $E_{cell(ORP)}$

$$E_{cell(ORP)} = 1.26 + 0.05916 \log_{10} \left[\frac{C_{V(IV)}C_{V(II)}}{C_{V(V)}C_{V(III)}} \right]. \quad (3)$$

The concentration parameters of the species, C_{red} and C_{oxd} , can be determined using Faraday's law of electrolysis. The law describes the amount of substance undergoing an electrochemical change in a constant volume reaction [21]. With constant current and duration for electrolysis, the concentration of a redox species could be determined using (4)[16], [21]. For simplicity, only the reduction process is considered, and the same principle applies to the oxidation process

$$(C_{red})_t = \frac{\phi I t}{z F V}. \quad (4)$$

In the case of mass transport control reaction, the current efficiency varies with time and since there is no co-exist species in the electrolyte during electrolysis, mass balance equation for oxidised species is given by (5)

$$(C_{oxd})_t = (C_{oxd})_o - (C_{red})_t. \quad (5)$$

Substituting (4) into (5), the expression of oxidised species at time t is given by (6)

$$(C_{oxd})_t = (C_{oxd})_o - \frac{\phi I t}{z F V}. \quad (6)$$

For example, if V(V) is the oxidised species, then

$$(C_{V(V)})_t = (C_{V(V)})_o - \frac{\phi I t}{z F V}. \quad (7)$$

Substituting (6) into (1) and (2), the Nernst equation for V-RFB becomes

$$E_{cell(ORP)} = 1.26 + 0.05916 \log_{10} \left[\frac{(C_{V(IV)})_o - \frac{\Phi I t}{z F V}}{(C_{V(V)})_o + \frac{\Phi I t}{z F V}} \right] - 0.05916 \log_{10} \left[\frac{(C_{V(III)})_o - \frac{\Phi I t}{z F V}}{(C_{V(II)})_o + \frac{\Phi I t}{z F V}} \right] \times \left[\frac{(C_{(II)})_o + \frac{\Phi I t}{z F V}}{(C_{(III)})_o - \frac{\Phi I t}{z F V}} \right]. \quad (9)$$

Rearranging the (8) in the form of (3), the open-circuit cell potential is as follows

$$E_{cell(ORP)} = 1.26 + 0.05916 \log_{10} \left[\frac{(C_{V(IV)})_o - \frac{\Phi I t}{z F V}}{(C_{V(V)})_o + \frac{\Phi I t}{z F V}} \right] \times \left[\frac{(C_{(II)})_o + \frac{\Phi I t}{z F V}}{(C_{(III)})_o - \frac{\Phi I t}{z F V}} \right].$$

IV. EXPERIMENTAL DETAILS

The experiments were carried out at the Electrochemical Engineering Laboratory, University of Southampton, UK. The redox couples in V-RFB are all soluble species [7] supplied by Re-Fuel Technology Ltd. with the initial concentration of 1.6 mol dm^{-3} of $V(III)/V(IV)$ in 4 mol dm^{-3} H_2SO_4 .

Fig. 2 illustrates the system in general of a 25 - 100 cm^2 unit cell laboratory unit V-RFB system with concentration flow-tubes, electrical connections, and nitrogen flow.

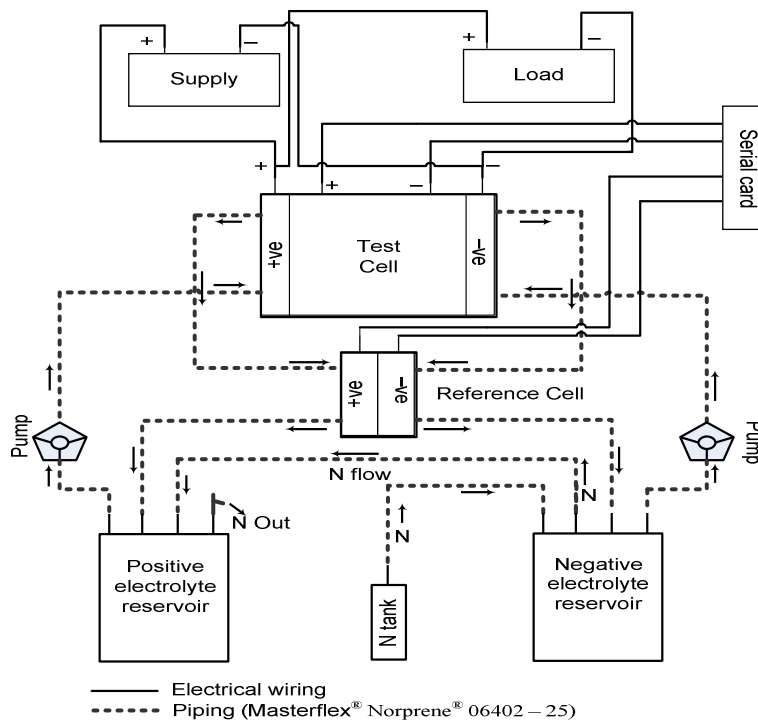


Fig. 2. Overview of electrical wiring and tubing system for un-optimised 25 - 100 cm^2 unit cell laboratory unit V-RFB system (adapted from [13]).

The experiment is carried out using two systems: the first is based on a 100 cm^2 unit cell laboratory V-RFB attached to a pair of reference electrodes, and the second is based on a 25 cm^2 unit cell laboratory unit V-RFB attached to a combination of reference and working electrodes as shown in Fig. 3. The 100 cm^2 unit cell - reference electrodes based system is used at the beginning of the study as it is capable of generalising the V-RFB system. Meanwhile, the 25 cm^2 unit cell laboratory units V-RFB is an extension of the initial cell with modification for potentiometric measurement of vanadium species at the reference cell. Details of both experimental setups has been detailed in paper [13].

The main frame compartments of each half of the reference cell consist of $5 \text{ cm} \times 5 \text{ cm} \times 2 \text{ cm}$ polyvinyl chloride polymer, separated by an ion exchange membrane. An opening of $1.5 \text{ cm} \times 1.5 \text{ cm}$ is made in the centre of the half-cell frame to allow the vanadium electrolyte flow-through and contact between the reference and working electrodes. The reference cell is connected to 25 cm^2 V-RFB unit as illustrated in Fig. 2. Temperature is maintained at $298 \pm 2 \text{ K}$ throughout the experiment and is monitored using

thermocouples.

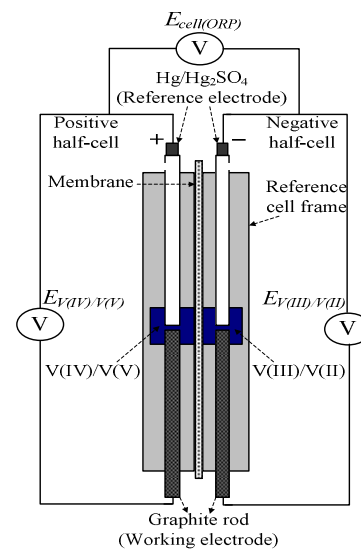


Fig. 3. Reference cell for potentiometric measurement for the new 25 cm^2 unit cell V-RFB.

V. RESULTS AND DISCUSSIONS

A. Estimation of electrolytes concentration

The redox potential of V-RFB unit cell has been estimated and plotted using the (10). Prior to the generation of the concentration of the redox species, the following assumptions were made:

Positive electrode

$$C_{V(IV)} = 0.01 C_{V(V)} \quad (10)$$

Negative electrode

$$C_{V(III)} = 0.01 C_{V(II)} \quad (11)$$

Both half-cell reservoirs of the V-RFB system use the same electrolyte, therefore both half-cells should contained a mixture of 50 % V(III) and 50 % V(IV) in H_2SO_4 . Consequently, since the supplied electrolyte is 1.6 mol dm^{-3} V(III)/V(IV) in 4 mol dm^{-3} H_2SO_4 , the electrolytes in both half-cells would undergo a formation charge process at the start of experiment. In the process, two mixtures of vanadium species is converted into a single electro-active species of V(III) at negative electrode and V(IV) at positive electrode. At the end of the formation charge process, the positive reservoir should contain 0.8 mol dm^{-3} V(IV) in 4 mol dm^{-3} H_2SO_4 , whereas negative reservoir should contain 0.8 mol dm^{-3} V(III) in 4 mol dm^{-3} H_2SO_4 .

In this approach, the concentration of reactants V(IV) and V(III) were assumed to start at very high value and decreases exponentially over time, but the concentration of products V(V) and V(II) increases inversely at the same rate as the reduction of the reactants. Fig. 4 illustrates the changes of concentration for reactant species against product over time.

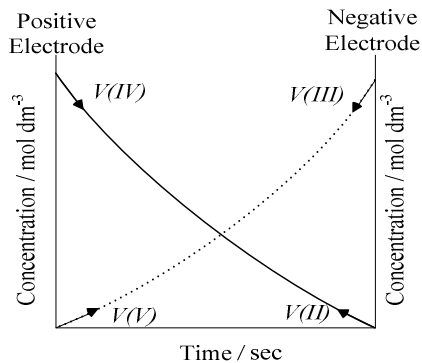


Fig. 4. Concentration of vanadium species changes exponentially over period of time during charge-discharge cycle.

Based on the assumptions made in (10) and (11), it was established that the estimated initial $E_{cell(ORP)}$ in (9) for 1.6 mol dm^{-3} V(III)/V(IV) in 4 mol dm^{-3} H_2SO_4 using the Nernst equation starts at 1.00 V. However, the experimental data for initial $E_{cell(ORP)}$ of 100 cm^2 unit cell V-RFB during the charging period was recorded at 1.263 V, which is higher than the estimated value. This is because the cycle of charge-discharge of V-RFB was delimited just before all the electrolytes species is completely consumed to prevent V-RFB operating under side reaction mode. This indicated that the experimental data does not represent the actual initial redox reactions of the species and the cell was not fully

discharged during the previous charge-discharge cycle. This implies that the cell is operating within the safe mode of its SOC, which is above 20 % of depth of discharge.

Therefore, to match with the experimental data, the starting concentrations of V(III) and V(IV) were manually calculated and the results is as shown in Fig. 5.

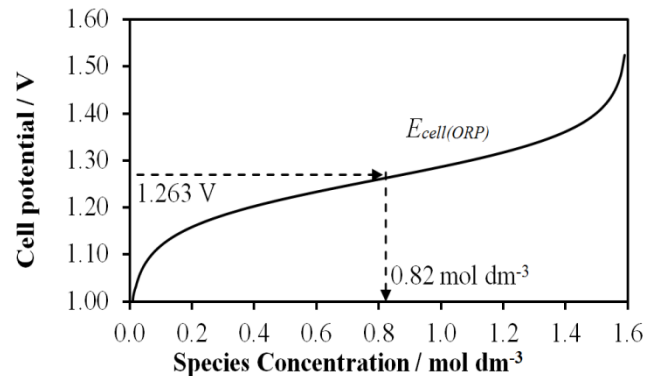


Fig. 5. Manual estimation of V(III) / V(IV) concentrations at the start of redox reaction based on $E_{cell(ORP)}$ recorded using experiment of 100 cm^2 unit cell V-RFB during charging cycle

Comparing the estimated data obtained from the calculation with the experimental data of 100 cm^2 unit cell V-RFB during the charging cycle, the concentration of V(III) and V(IV) in (9) should start at 0.82 mol dm^{-3} , a 2.4 % variance from the theoretical assumption of 0.80 mol dm^{-3} .

B. Effect of constant current efficiency

Fig. 6 illustrates the experimental $E_{cell(ORP)}$ compared to the estimated $E_{cell(ORP)}$ at different constant current efficiency in the range of $\phi = 0.5 - 1.0$. The result shows the effect of applying different current efficiency in predicting $E_{cell(ORP)}$ during the charging cycle. In the simulation, current efficiency is kept constant throughout the charging process. For 100 % current efficiency ($\phi = 1.0$), the model matched the experimental cell potential at equilibrium but the predicted curve swings 5 % off the experimental curve in the middle of charging the V-RFB; this is the effect of the logarithmic function (Log_{10}) in the Nernst equation. Note that the accuracy of the model decreases with decreasing current efficiency. For $\phi = 0.5$ and $\phi = 0.7$, the predicted model differs by 8 % and ~5 % from the experimental $E_{cell(ORP)}$, respectively.

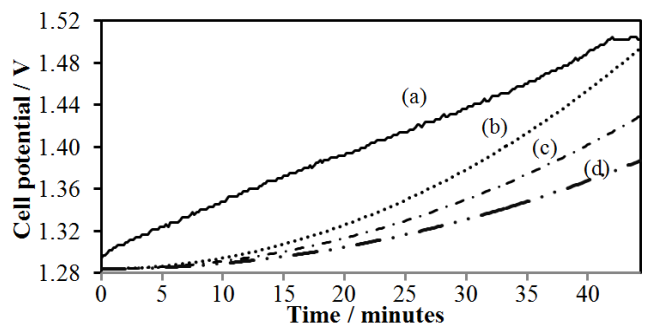


Fig. 6. Comparison of experimental $E_{cell(ORP)}$ and estimated $E_{cell(ORP)}$ at constant current efficiency vs. time (a) experimental curve obtained from potential different across two working electrodes of reference cell during charging of 100 cm^2 unit cell laboratory unit V-RFB of 1.6 mol dm^{-3} V(III)/V(IV) in 4 mol dm^{-3} H_2SO_4 at 10 A (100 mA cm^{-2}); (b) estimated $E_{cell(ORP)}$ at $\phi = 1.0$; (c) estimated $E_{cell(ORP)}$ at $\phi = 0.7$; (d) estimated $E_{cell(ORP)}$ at $\phi = 0.5$.

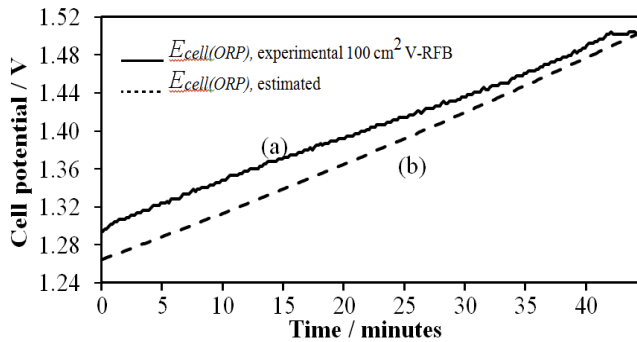


Fig. 7. Comparison of experimental $E_{cell(ORP)}$ and estimated $E_{cell(ORP)}$ (a) experimental curve obtained from potential different across two working electrodes of reference cell during charging cycle of 100 cm² unit cell laboratory unit V-RFB of 1.6 mol dm⁻³ V(III)/V(IV) in 4 mol dm⁻³ H₂SO₄ at constant current density of 100 mA cm⁻²; (b) estimated $E_{cell(ORP)}$ when the current efficiency is varied, $\phi=0.1-1.0$.

Walsh [27] suggested that current efficiency in (3) should be varied during the duration of the reaction. Thus, the current efficiency in (8) is varied during the charging process of 1.6 mol dm⁻³ V(III)/V(IV) in 4 mol dm⁻³ H₂SO₄ and the estimated result of $E_{cell(ORP)}$ is shown in Fig. 7. In the experiment, starting from 100 % current efficiency, it is reduced by 25 % for every 10 minutes of the reaction. The result shows that the error of the predicted $E_{cell(ORP)}$ is 2.3 % at the beginning of the reaction but the error reduces over time and on reaching equilibrium potential, it correctly predicts the E_{cell}^o of V-RFB.

C. Proposed potentiometric measurement of the 25 cm² unit cell V-RFB

Potentiometric measurement is a measure of kinetic reactions at working electrode compared to that at the reference electrode. Half-cell redox potentials and open-circuit cell potentials are monitored using a divided, open-circuit potentiometric cell via Hach Lange GmbH XR200 Hg/Hg₂SO₄ reference electrodes (Part No. B20B200) and Sigma-Aldrich 6 mm, 99.9999 % graphite rod working electrode (Batch No. 11903BB) separated by an ion exchange membrane (DuPont Nafion NF115/H⁺).

With this method, varying the current efficiency is not required when estimating the $E_{cell(ORP)}$ as both half-cell potentials are measured against the standard Hg/Hg₂SO₄ reference electrodes and the outcome of applying (9) is shown in Fig. 8.

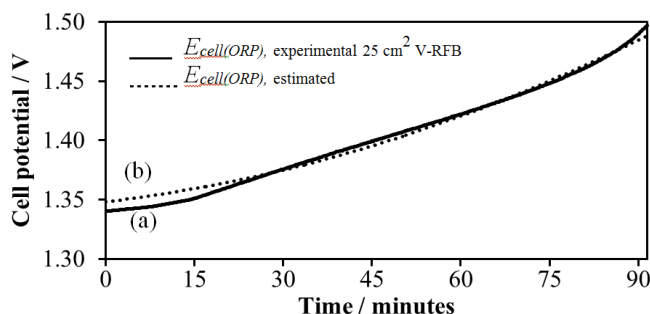


Fig. 8. Comparison of experimental $E_{cell(ORP)}$ and estimated $E_{cell(ORP)}$ (a) experimental curve obtained using a divided, open-circuit potentiometric cell, through Hg/Hg₂SO₄ reference electrodes and graphite rod working electrodes separated by ion exchange membrane (DuPont Nafion NF115/H⁺) during charging cycle of 25 cm² unit cell laboratory unit V-RFB of 1.6 mol dm⁻³ V(III)/V(IV) in 4 mol dm⁻³ H₂SO₄ at constant current density of at 100 mA cm⁻²; (b) estimated $E_{cell(ORP)}$ when current efficiency is varied, $\phi=0.1-1.0$.

Using this approach, the estimated $E_{cell(ORP)}$ of V-RFB system is more accurate compared to that obtained only from the working electrodes as the estimated curve fits the experimental $E_{cell(ORP)}$ of 25 cm² V-RFB unit cell laboratory unit. Since OCV is a function of SOC, the same approach is extended to discharge cycle, and the estimated SOC of V-RFB is as shown in Fig. 9.

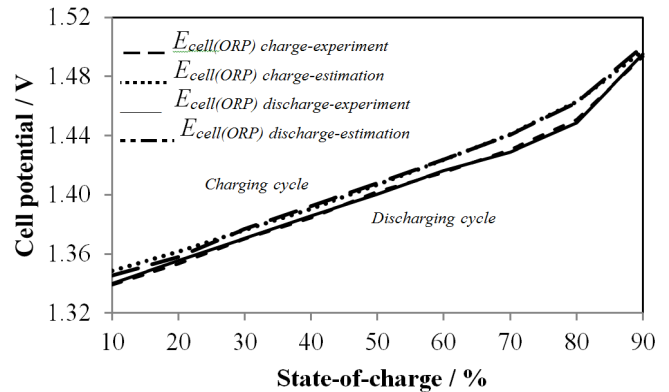


Fig. 9. Comparison of estimated SOC with respect to SOC obtained through experimental of 25 cm² unit cell laboratory unit V-RFB of 1.6 mol dm⁻³ V(III)/V(IV) in 4 mol dm⁻³ H₂SO₄ at constant current density of at 100 mA cm⁻².

VI. CONCLUSIONS

It should be noted that the use of Nernst equation and Faraday's law of electrolysis, with an appropriate manipulation of current efficiencies, $\phi=0.1-1.0$, able to predict the open-circuit potential of V-RFB, subsequently SOC of V-RFB. Two different approaches has been presented, direct estimation of $E_{cell(ORP)}$ compared to potential different between two working electrodes, which indicated by 2.3 % error. An improved estimated $E_{cell(ORP)}$ is observed with the proposed approach of a divided, open-circuit potentiometric cell, via Hg/Hg₂SO₄ reference electrodes and graphite rod working electrodes. The result shows the latter outperformed the former in estimating $E_{cell(ORP)}$, subsequently the SOC of the battery.

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