

Full Length Research Paper

# Design and development of unit cell and system for vanadium redox flow batteries (V-RFB)

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Vanadium redox flow battery (V-RFB) has been attracted by many researches; some are under field testing and demonstration stage, but information on construction, experimental characterization, electrolyte preparation, overall systems under study, etc. are still limited. This paper focus on the technical issues faced and the lessons learnt during the development of unit cell and system for V-RFB. Firstly, brief description on problem identification, development and implementation in cell design and system for V-RFB are discussed. Secondly, preliminary experiment on 25 cm<sup>2</sup> laboratory, unit cell V-RFB presents various difficulties such as its high tendency to fall under failure mode are presented. Finally, discussion on experimental result which shows significant improvement on V-RFB system efficiency up to 72% with reduction of contact resistance, recorded an average of 8.6 mΩ. In addition, the newly developed system provides a constructive base for future studies in temperature-controlled system and a divided, open-circuit potentiometric cell for half-cell redox analysis.

**Key words:** Redox flow battery, energy storage, cell design.

## INTRODUCTION

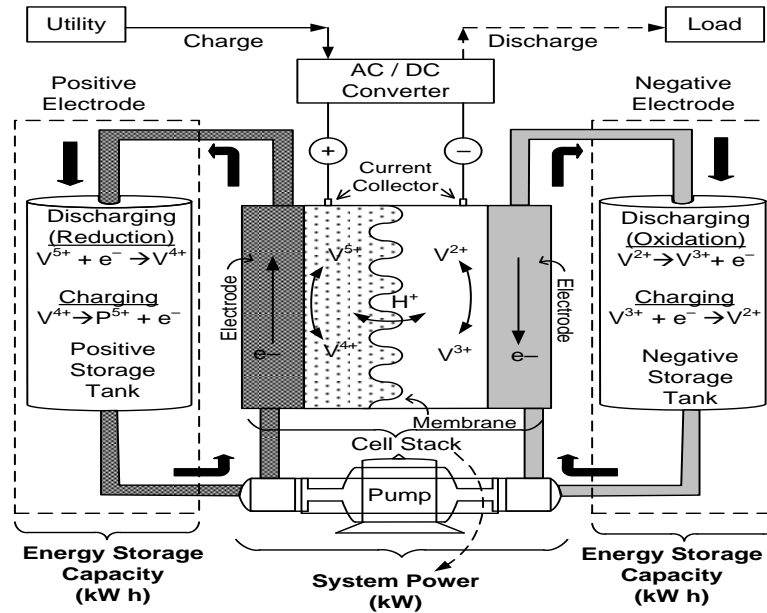
From last century, numerous forms of energy storage having different characteristics and application's suitability, has been developed. Redox flow batteries (RFBs) that emerge into energy storage technologies (Fedkiw and Watts, 1984) pose a promising prospect for both large scale and automotive applications. RFB is, an electrochemical energy storage device, whereby the electro-active species are stored externally and these reactants are circulated through cell-stack as required

(Mohamed et al., 2009). Founded in mid-1980s, vanadium redox flow batteries(V-RFB) uses vanadium reactants on both the anode and cathode half-cells, and consequently, cross-contamination of ions through the ion exchange membrane causes no harm on battery capacity, prolongs their cycle life and operates at high energy efficiencies (over 80%) (Skylas-Kazacos, 2003). The following features differentiate RFB from conventional batteries: flexible operation, modularity energy and power component ratings are independent to each other (for some RFBs), simple installation layout, moderate cost, long cycle life and transportability.

A lot of research has been carried out since pointed out by Skylas-Kazacos and Robins (1986), yet there are issues in the technology that still needs to be addressed. Shah et al. (2010) highlighted that several challenges remain in optimizing and improving current V-RFB designs, particularly with respect to scaling-up, minimizing gas evolution, improving electrolyte stability, resistance to carbon oxidation and membrane fouling. Perhaps, the most critical part in RFB system is the cell stack; hence, deserve the most attention in analysis and manufacturing. In general, the construction of the cell

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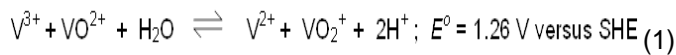
**Abbreviations:** V-RFB, Vanadium redox flow battery;  $E_{cell}$ , cell potential, measured across unit cell stack;  $E_{cell(ORP)}$ , open-circuit cell potential across two electrode, otherwise abbreviated as  $E_{cell(ORP)}$  for oxidation-reduction redox potential;  $E^0$ , open circuit cell potential,  $E_{V(III)/V(II)}$ , positive half-cell potential for V-RFB;  $E_{V(IV)/V(V)}$ , negative half-cell potential for V-RFB; HEV, hybrid electric vehicle; PTFE, polytetrafluoroethylene; PVC, polyvinyl chloride polymer; RFB, redox flow battery; SHE, standard hydrogen electrode; V(II), V(III), V(IV) and V(V), vanadium species at different level of oxidation state.



**Figure 1.** Single stack flow circuit to describe the principles of operation, main components of a V-RFB system and parts to establish the power and energy rating of the system [adapted from Mohamed et al. (2009)].

consists of cell frame, current collector, carbon plate, electrode and separator (except for lead-acid RFB that does not require any separator). The cell can be designed in unit cell stack; otherwise, a series of bipolar unit cell stack would form a cell stack. The former would provide unit cell potential and normally used for initial studies, while the latter increases the cell potential and used at a later stage of studies or demonstration mode design. Figure 1 shows the structure diagram and principles of operation of V-RFB (Mohamed et al., 2009).

The overall cell reaction is:

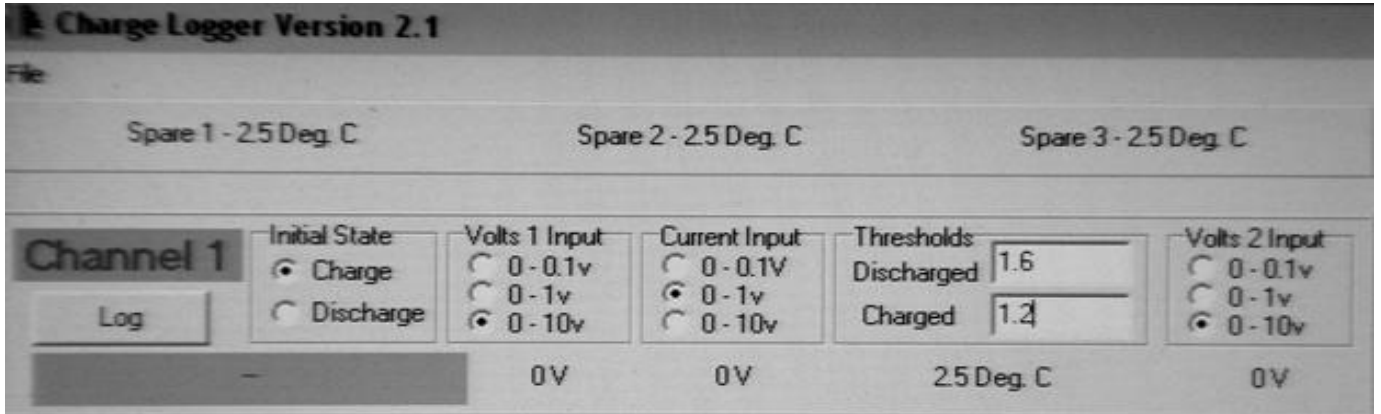


Ideally, the cell components should provide high chemical resistant, good electrical conductivity, good mechanical properties and reasonable cost. The optimal design of the cell should take into account the following principles (Lavelaine and Allanore, 2008): (a) configuration that eases the transfer of potential, which minimizes the resistance that oppose the transfer of electric charges and chemical species, (b) need to produce a uniform current distribution at both the anode and cathode electrodes, (c) mass and energy input and output are balanced to enable a steady state operation. Lavelaine and Allanore, (2008) stated that if the conditions of uniformity, steadiness and low transfer resistance are simultaneously checked then, the cell design is close to its foremost simplicity.

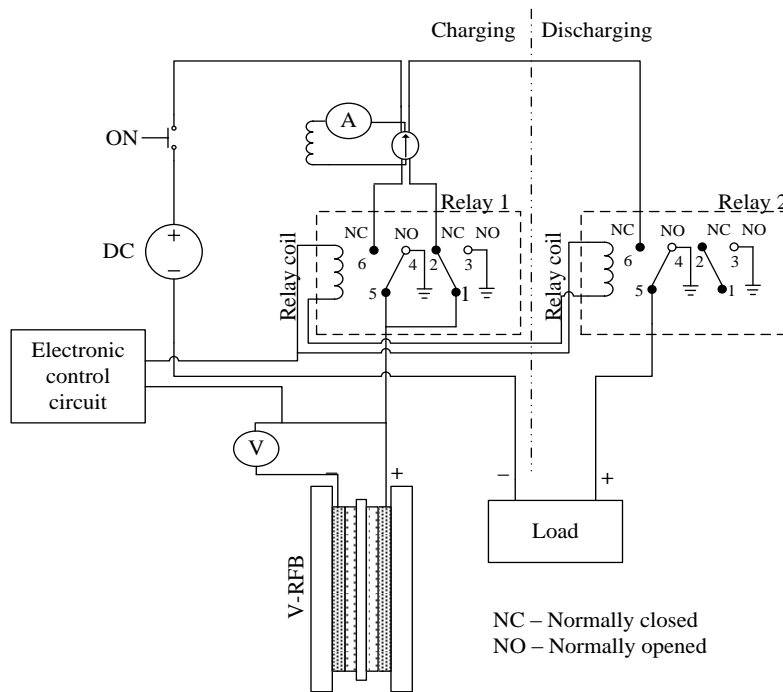
However, working with the already established battery

technology is different as long hours of experimental procedures required for the analysis or modeling of the battery could be eliminated by relying on its characteristics as supplied by the manufactures (Medora and Kusko, 2005). On the contrary, since the technology for the V-RFB system is yet to mature and still in field demonstration mode, the availability of in-depth information related to cell design, experimental procedures and system design for accurate characterizing of the system are limited. There are very limited discussions in literature, as far as the authors are aware of the system and cell design for V-RFB, presented in complete cases including systems in failure modes. Hence, in developing operational test rig, a new researcher needs to undergo the tedious and monotonous corrective actions or to make further adjustments to the systems.

In this paper, the discussion is focused on some technical issues in the design and development of the unit cell and system of V-RFB. Preliminary modification of the cell design and system has shown that the procedure does not impart any significant improvement on the characteristics of V-RFB and the problems related to the issue are discussed. Alternative cell design was proposed and the weaknesses of the proposed design are discussed. However, further modification of the cell design and system overcome the initial drawbacks, presenting significant improvement on cell performance and man-hour laboratory work hour. To further improve the performance of V-RFB system, other key parameters such as electrolytes stability, membrane and electrode development needs further research but are outside the scope of this study.



**Figure 2.** Charge logger v2.1 developed by Re-Fuel Technology Ltd capable of recording 3 V-RFB cell parameters that is, cell potential, reference cell potential and shunt current; including controls charge-discharge cycle according to preset on-load cell potential threshold.



**Figure 3.** Electrical schematic for charge-discharge mode of V-RFB system with details connection of relay control circuit.

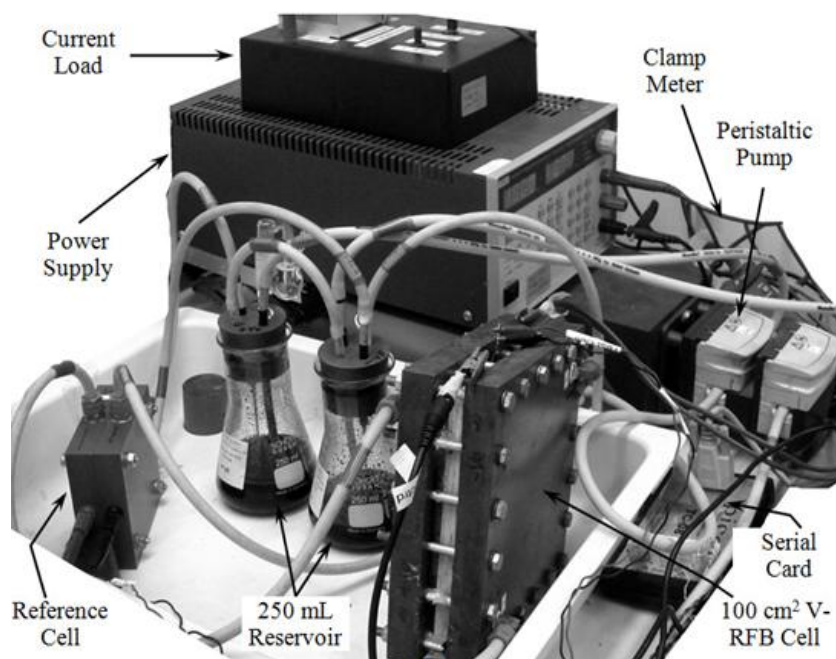
**EXPERIMENTAL SETUP**

This project focuses on experimental characterization, cell design, modeling and implementation of V-RFB for hybrid electric vehicle (HEV) applications. The preliminary experiments for 100 cm<sup>2</sup> unit cell laboratory unit V-RFB were carried out using in-house personal computer using a software program developed by Re-Fuel Technology Ltd (Mohamed et al., 2009); named as Charge logger v2.1 as shown in Figure 2. Charge logger v2.1 is used as a computer-controlled application for monitoring charge-discharge characterization of V-RFB system.

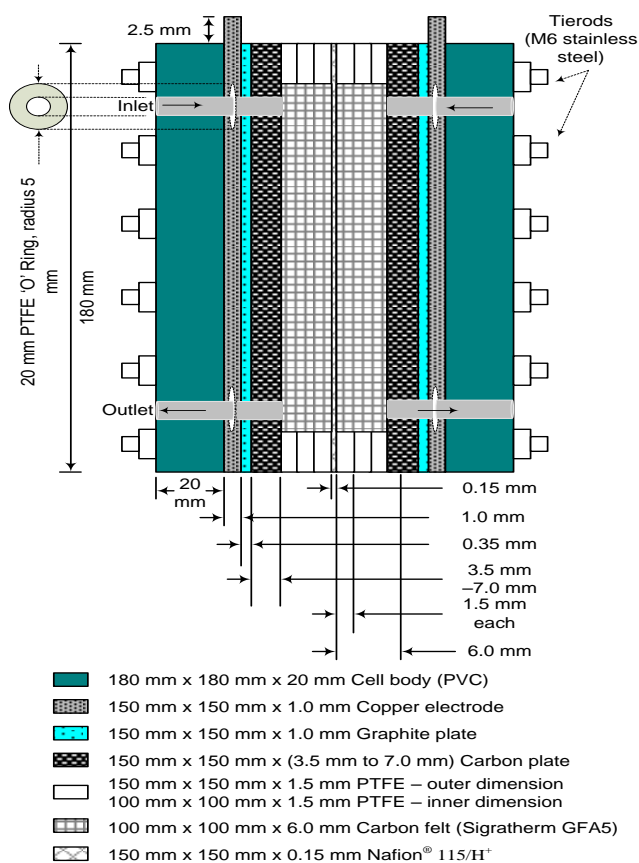
The system has shown the ability to capture the characterization and the results has been used for a transient, two-

dimensional model of V-RFB (Shah et al., 2008). Nonetheless, it requires further improvement for better packaging and reliability including an appropriate temperature-controlled system.

Charge logger v2.1 allows three V-RFB parameters to be recorded: on-load cell potential, shunt current and reference cell potential which corresponds to open-circuit potential. It is also capable of controlling charge-discharge cycle in accordance with the preset maximum and minimum on-load cell potential threshold as defined by users prior to the start of the experiment. The on-off circuit is controlled by an electronic control circuit and triggers single pole double-contact relay (IMO731 30A, 240V<sub>AC</sub> / 28 V<sub>DC</sub>) 12 V±25 ms. Figure 3 shows the electrical schematic for V-RFB charge logger that controls the charge or discharge cycle, and



**Figure 4.** A unit cell laboratory unit, un-optimized 100 cm<sup>2</sup> V-RFB. Modified from a laboratory system by Re-Fuel Technology Ltd (Mohamed et al., 2009).

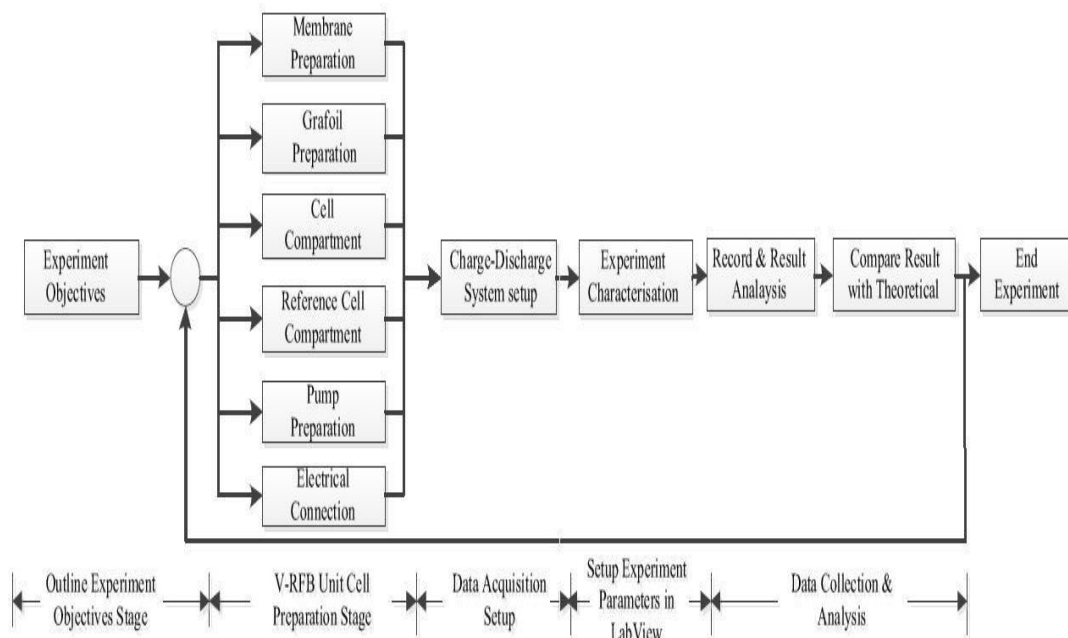


**Figure 5.** Specification of the cell stack of a laboratory, un-optimized 100 cm<sup>2</sup> unit cell laboratory V-RFB system.

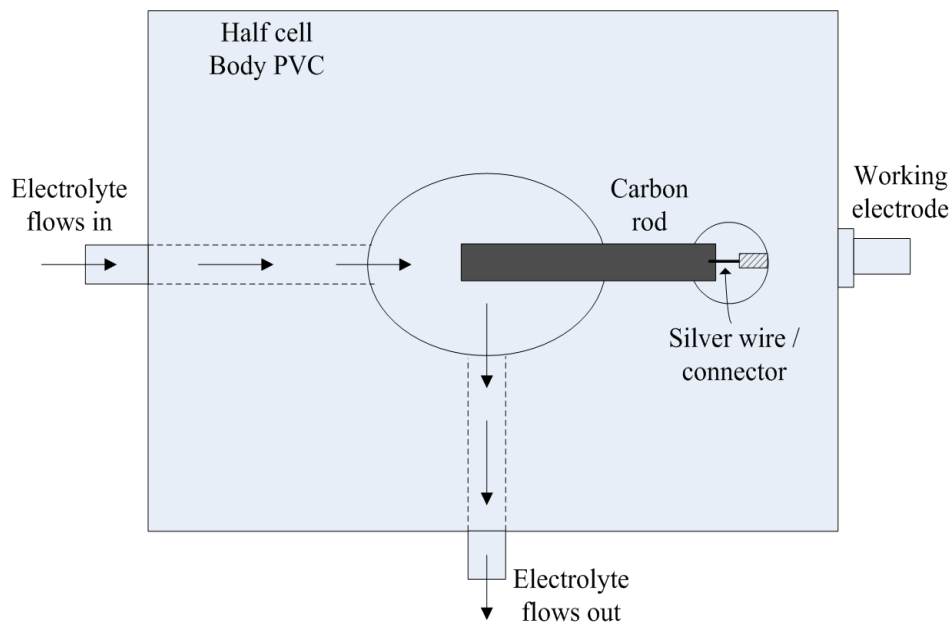
the operation mode is changed when the electronic circuit board and relay is triggered according to the pre-set threshold limit. Figure 4 shows main component of the V-RFB system, where the main frame compartment of the system is made from 18×18×2 cm polyvinylchloride polymer. Figure 5 details out the specifications for the cell stack including the position, material and dimensions.

A divided open-circuit cell was separated by a piece of Du Pont Nafion® 115/H<sup>+</sup> cationic exchange membrane, and is used as a reference cell for monitoring open-circuit cell potential through Sigma-Aldrich 6 mm, 99.9999% graphite rod working electrode (batch no. 11903BB). The cell adapts a flow-through configuration and has a projected electrode area of 10×10×0.4 cm Sigratherm GFA5; a porous and layered carbon felt electrodes (effective volumetric porosity of 0.68±0.07) on both positive and negative half-cell separated by Du Pont Nafion® 115/H<sup>+</sup> cationic exchange membrane. Vanadium electrolyte was prepared and supplied by Re-Fuel Technology Ltd; a mixture of V(III) / V(IV) at 1.6 mol dm<sup>-3</sup> in 4 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>. Different concentrations of the vanadium electrolyte in the range of 0.9 to 1.6 mol dm<sup>-3</sup> were prepared from the supplied electrolyte. Nonetheless, for the discussion of this paper, the concentration of vanadium species is at 1.6 mol dm<sup>-3</sup> in 4 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>.

The electrolyte was stored in 250 ml detached-glass reservoir for each half-cell. The electrolyte was circulated through the electrode compartment for each half-cell through Masterflex® Norprene® 06402-25 tube using peristaltic Watson-Marlow 505 s pump within nitrogen gas atmosphere, at volumetric flow rate in the range of 3 to 5 cm<sup>3</sup> s<sup>-1</sup>, corresponding to linear flow velocity of 1.11 to 1.85 cm s<sup>-1</sup>. The cell was charged using external direct current (dc) power supply (CPX200 Dual 35V 10A PSU Powerflex), and discharged using constant current load at 10 A which correspond to current density of 100 mA cm<sup>-2</sup>. The electrolyte flows out from each glass reservoirs through peristaltic pump, then flow through into 100 cm<sup>2</sup> electrode compartment and returns to reservoirs through divided open-circuit cell. Figure 6 simplifies the experimental details in preparing experimental characterization of V-RFB.



**Figure 6.** Experimental processes of 25 to 100 cm<sup>2</sup> unit cell laboratory unit V-RFB.

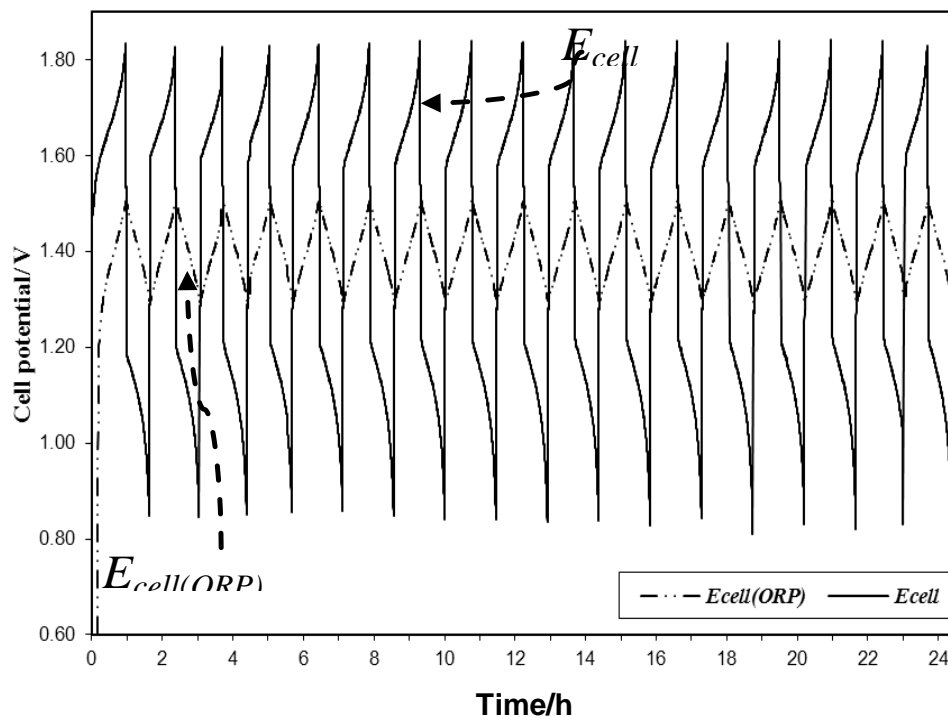


**Figure 7.** Overview of 10 × 10 × 2 cm half-cell of divided open-circuit cell (known as reference cell).

### Cell test and preparation

The significance of this section is that, it acts a basis next to be discussed. The test cell is prepared according to the arrangement as shown in Figure 5, whereas the reference cell is separated by cationic exchange membrane as shown in Figure 7. Proper sealant is required to prevent electrolyte leakage for each layer of materials shown in Figure 5, and UniBond super all-purpose interior and

exterior sealant is used for the sealing purposes. It is important to ensure that the sealant is dried and the surface of each cell's material is sealed before placing another layer of the cell materials. Normally, a weight is used to ensure proper sealing of the cell material, and at least 30 min of waiting time is required to complete the construction of the 6 layers of half-cells. Each half-cell are attached together and separated by ion exchange membrane and nuts and bolts are used to compress the cell.



**Figure 8.** A typical voltage charge-discharge characteristic of 100 cm<sup>2</sup> laboratory V-RFB at maximum charge and discharge currents of 10 A (100 mAcm<sup>-2</sup>) versus time (Mohamed et al., 2009).

### Electrolyte and supporting electrolyte -acid preparation

The redox couples in V-RFB are all soluble species (Menictas et al., 1994) and supplied by Re-Fuel Technology Ltd. with the initial concentration of 1.6 mol dm<sup>-3</sup> of V(III) / V(IV) in 4 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>. The concentration of electrolyte could be varied by adding the supporting electrolyte, that is, H<sub>2</sub>SO<sub>4</sub>, into the initial mixture. Nevertheless, the discussion in this paper is based on the assumption that the electrolyte is at its initial concentration of 1.6 mol dm<sup>-3</sup> V(III)/V(IV) in 4 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>.

## RESULTS AND DISCUSSION

This section is divided into 6 sub-sections, of which the discussion in the first three parts are based on previous 100 cm<sup>2</sup> unit cell laboratory unit V-RFB, while the latter parts are based on new proposed design of 25 cm<sup>2</sup> unit cell laboratory unit VRFB.

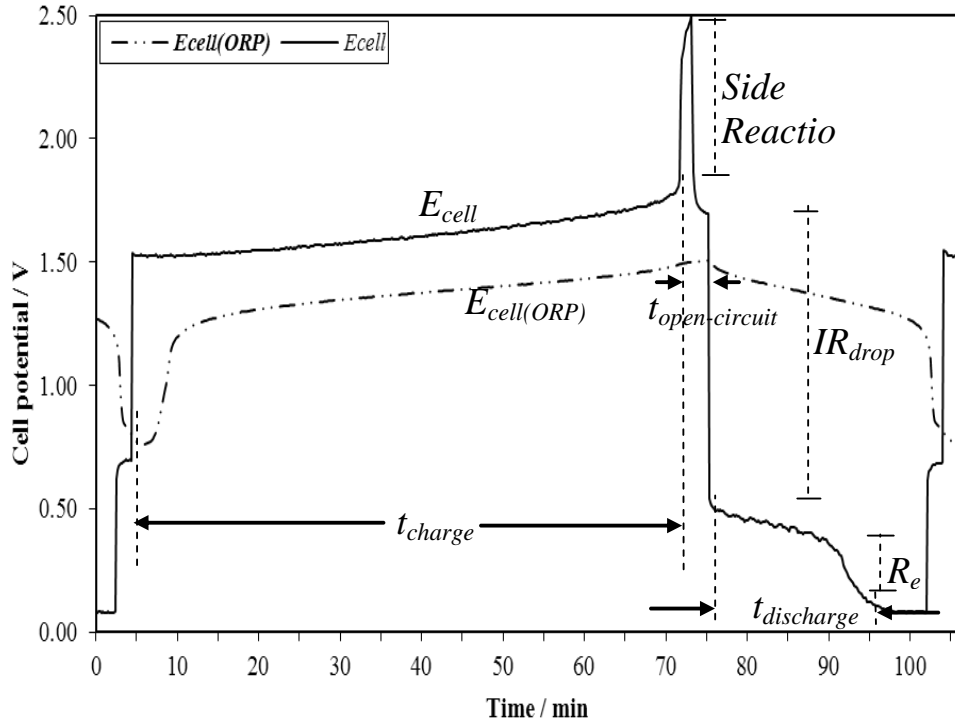
### Charge-discharge characteristic of V-RFB

Four oxidation states have been observed in the 100 cm<sup>2</sup> unit cell laboratory unit V-RFB, that is, V(II), V(III), V(IV) and V(V); distinguished by the different colours, which are violet, green, blue and aqueous, respectively. A typical charge-discharge characteristic of the battery at constant current of 10 A (100 mAcm<sup>-2</sup>) is shown in Figure 8 (Mohamed et al., 2009). It is observed that the

average power discharged is approximately 11.0 W and the discharged energy from 500 ml of reactants is 7.3 Wh. The coulombic and voltage efficiency are 91.5 and 70.5%, respectively. The overall energy efficiency is 65%, which is slightly inferior to most systems reported in the literature (Skylas-Kazacos and Grossmith, 1987; Skylas-Kazacos et al., 1991; Gonzalez et al., 2004).

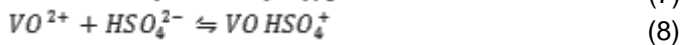
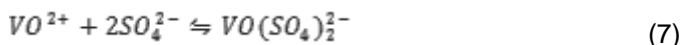
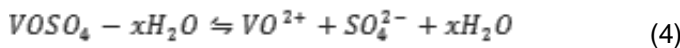
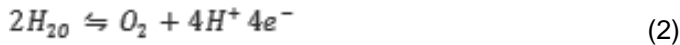
### V-RFB operating under a failure mode

From our observation throughout this preliminary experiment, a main reason which influences the operation of V-RFB unit working under a failure mode is due to the poor cell design, apparatus malfunction as well as system design. Figure 9 shows an example of charge-discharge characteristic of a V-RFB under a failure mode. Even though the curve indicated that the vanadium species are consumed and the V-RFB is charged for 65 min, but  $t_{discharge}$  of 15 min with the same constant current indicates that the battery failed to hold the charged properly. The coulombic and voltage efficiency are 37 and 18%, respectively, results in a poor energy efficiency of 7%. Also note that, just before the V-RFB switches into open-circuit mode and consequently discharging mode, there was steep rises on cell potential, recorded at 2.50 V. This indicated that the vanadium species has been completely consumed hence leading the system to run under side reactions period.



**Figure 9.** Single-cycle of voltage charge and discharge characteristic of 100 cm<sup>2</sup> laboratory V-RFB at maximum charge and discharge currents of 10 A operating under a failure mode versus time.

One possible explanation is that the problem is due to gas evolution or other side reactions as highlighted by Shah et al. (2010); Al-Fetlawi H et al., 2010, notably the evolution of O<sub>2</sub> at positive electrode and evolution of H<sub>2</sub> at negative electrode possible during charging cycle of V-RFB, indicated by Equations 2 to 3. On the other hand, other possible reactions outlined in V-RFB system are indicated by Equations 4 to 8 (Ivakin and Voronova, 1973; Rahman and Skyllas-Kazacos, 1998).



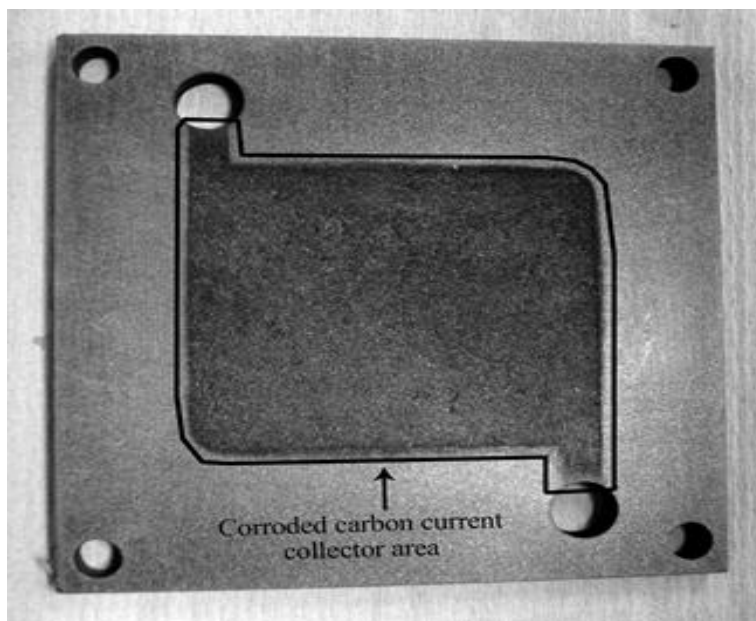
The same study that was conducted with lithium ion battery indicated that high amounts of evolution gas would cause severe leakage and safety problems (Goers

et al., 2004). Leakage and poor contact resistance between current collector and electrode could also be one of the factors, and so is a puncture in the membrane. On the discharging mode, there is also a large voltage drop as indicated by *IR<sub>drop</sub>* in Figure 9. Since the V-RFB unit was running at constant current, high *IR<sub>drop</sub>* suggested that there were changes on resistance within the cell during this period. Similarly with other types of battery, overcharging the V-RFB can have detrimental effects on the electrolyte and on the cell components, hence, should be avoided. Overcharging the battery beyond a certain voltage will result in electrolysis of water into hydrogen on the negative electrode and oxygen at the positive electrode (Eckroad, 2007). This could lead to corrosion of carbon current collector (Joerissen et al., 2004; Jia et al., 2010) as shown in Figure 10.

In addition, as the cell was half-way discharged, it seems that the cell experiences another side reaction or another change in reduction-oxidation state, as indicated a significant drop in *R<sub>e</sub>*. This could be the effect of overcharging during the charging mode.

**Technical issues on design of 100 cm<sup>2</sup> unit cell laboratory unit V-RFB**

Note that, charge-discharge characteristic of 100 cm<sup>2</sup>



**Figure 10.** Shaded area (~ 5×5 cm) illustrates the corroded 10×10×0.6 cm carbon current collector affected by side reaction within the V-RFB cell during charge-discharge cycles.

laboratory V-RFB in Figure 8 has been successfully recorded through extensive repetition and tedious laboratory work mainly due to poor cell design and system, a time-consuming and costly process.

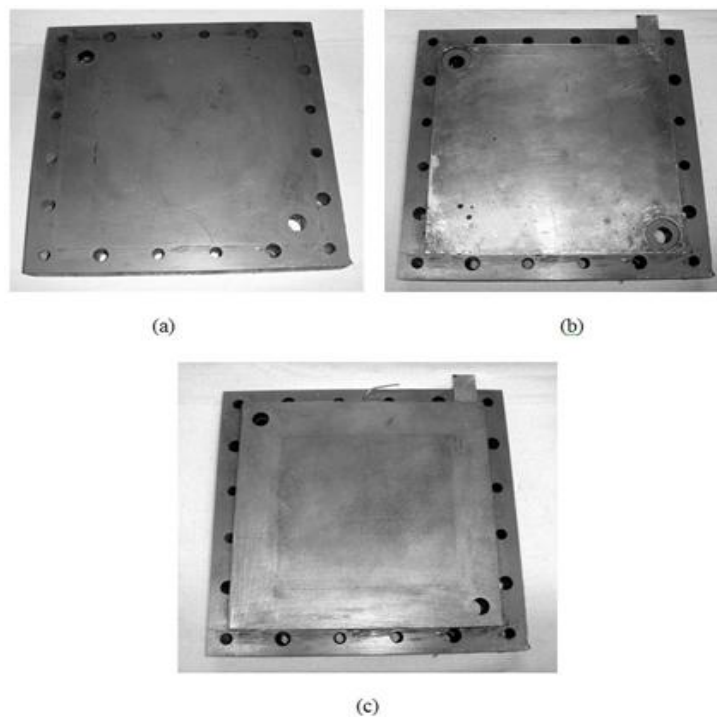
Figure 11 shows the initial assembly of 100 cm<sup>2</sup> unit cell according to the arrangement shown in Figure 5. The 18×18×2 cm main frame compartment of the cell is designed with a flat surface with two 0.5 cm – radius flow-through openings on the two corners of the cell frame, with 20 openings for M6 stainless steel on the outside as shown in Figure 11(a). Note that the absence of any rubber seals the design to prevent any leakage of the electrolyte. Figures 11(b) and (c) show the 15×15×0.1 cm copper plate and 15×15×0.6 cm carbon current collector were placed on top of the cell frame with 2 cm polytetrafluoroethylene (PTFE) 'O' ring with 0.5 cm radius, filling the gaps. The UniBond sealant was used to seal the gap between each cell compartment. Since the cell's gaps are dependent on the distribution of the sealant, it is essential to ensure the sealant is evenly layered throughout the cell compartment. When the sealant is uneven, the carbon current collector would crack when the cell is compressed by the M6 stainless steel nuts and bolts. It is also important to ensure that all the cells compartments remain intact as unparallelled cell compartment would lead to poor contact resistance, resulting in poor cell's performance. In the worst case scenario, cracks in the carbon current collector would cause the electrolytes to spill.

Another important compartment within the V-RFB unit cell is the 10×10 cm electrode compartment. The

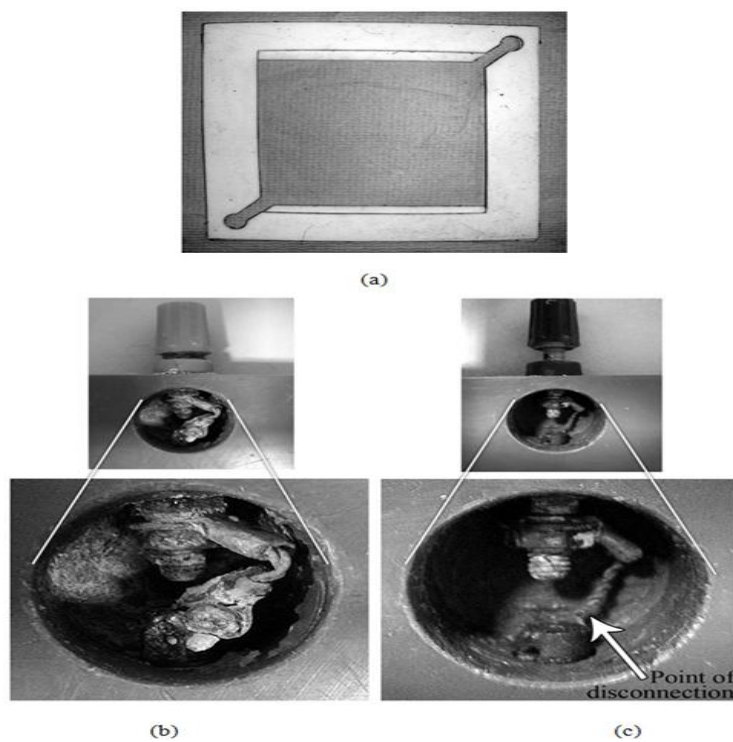
compartment is made of three 15×15×0.15 cm (outer), 10×10×0.15 cm (inner) PTFE layers to cover the 0.6 cm carbon felt. Proper sealant and good contact in between the PTFE layers is essential to prevent leakage. Nevertheless, due to a series of compression during cell assembly, the shape of PTFE is deformed (Davis and Pampillo, 1972; Rae and Brown, 2005) as shown in Figure 12(a) and this affects the contact distribution of the electrode and the current collector, resulting in very high resistance as well as causing electrolyte leakage.

Outside of the main compartment, the reference cell presents another important section in V-RFB system. Though the absence of this element will not affect the overall operation of V-RFB unit, but the reference cell presents an important part for monitoring the equilibrium state of the cell. As shown in Figure 7, the working electrode and graphite rod are connected by a silver wire and sealed by sealant. Since 1.6 moldm<sup>-3</sup> V(III) / V(IV) in 4 moldm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> is a highly corrosive species, any seep through of the species inside the silver cubicle will corrodes the silver, hence breaking the connection between the working electrode and the graphite rod resulting in a very high resistance and inaccurate measurement. Therefore, frequent maintenance and calibration is needed, thus adding extra laboratory work man-hour. Figures 12(b) and (c) show the phenomenon. Other important issues in the previous design of monitoring V-RFB system in our laboratory is the lack of temperature control and monitoring. The system was assumed to be operating at room temperature, corresponding to 298±2K. However, the literature stated

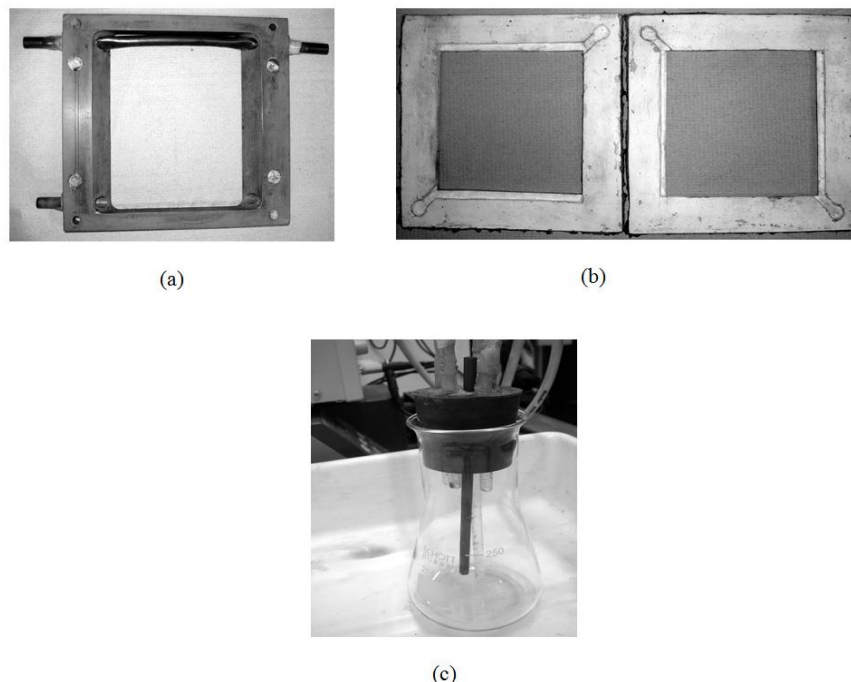




**Figure 11.** Assembly of cells compartments: (a), 18×18×2 cm cell's frame; (b), 15×15×0.1 cm copper plates placed on the cell's frame; (c), 15×15×0.6 cm carbon current collector on top of copper plate.



**Figure 12.** Affected V-RFB component: (a), Deteriorated 15×15×0.15 cm (outer), 10×10×0.15 cm (inner) PTFE layers due to compression during series of cell assembly; (b), corroded silver wire exposed to vanadium electrolyte; (c), disconnected silver wire.



**Figure 13.** Alternative of cell compartments: (a), 15×15×0.6 cm flow through electrode compartment made of PVC; (b), flow through electrode compartment made of rubber; (c), graphite electrode dipped-into vanadium electrolyte for measuring cell's equilibrium.

that the performance of the cell changes as the temperature changes (Rahman and Skyllas-Kazacos, 1998; Ponce-de-León et al., 2006). Since variable current load was used in this constant current operation of V-RFB, any change in temperature could affect the charge - discharge current. Therefore, the assumption that the cell is operating at constant room temperature could lead to wrong characterization of V-RFB system.

The V-RFB system uses a Fluke I30 alternating current (AC)/DC current clamp 30A, 100 mV/A±1% for monitoring shunt current that is required for a frequent calibration. As the range of output current of Fluke I30 is 0 to 30 A, proper calibration tools are required for accurate setting. Also, the charge logger v2.1 that is set for recording shunt current (measured in voltage) have a range of 0 to 1 V. In this case, if the shunt current goes beyond 0 V, the software would fail to record any reading. Therefore, the current clamp needs to be calibrated and shifted above the minimum 0 V, and the actual reading needs to be reversed by deducting the shifted value during the actual calculation and analysis.

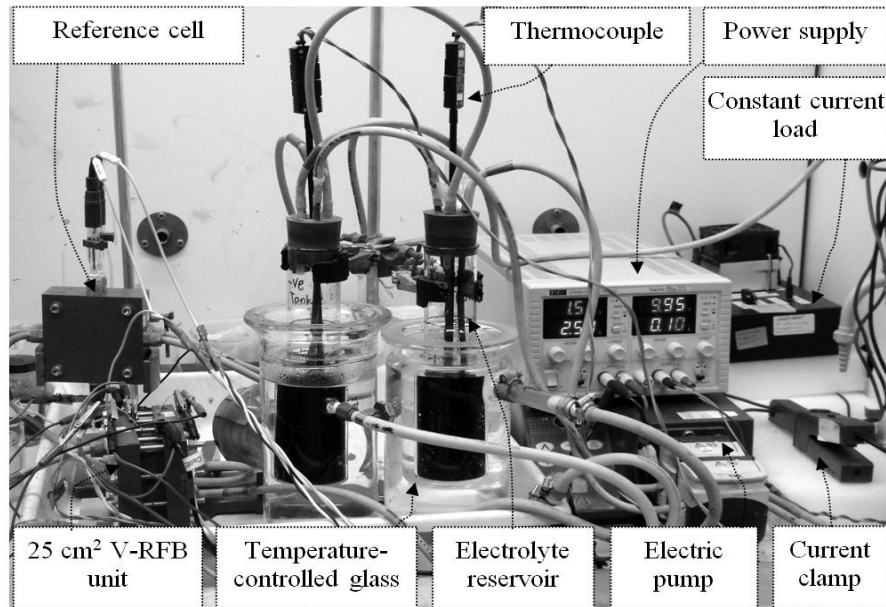
### Alternative cell design

Based on preliminary experiment and analysis on technical issues on previous cell, the performance of the

cell could be improved through better packaging, optimized cell design to reduce spacing between the plates, improve solubility of vanadium species using modified electrolytes and improve heat transfer within the cell (Mohamed et al., 2009).

Each cell assembly, based on 100 cm<sup>2</sup> V-RFB unit as described earlier would require at least 40 laboratory work man-hours, but with no assurance of achieving good cell performance; the biggest obstacle that can occur during cell assembly is electrolyte leakage. Therefore, in order to improve the cell performance for better contact as well as to reduce laboratory work man-hours, other alternatives of cell compartments have been proposed. Figure 13 shows a few examples of different cell compartments in V-RFB cell unit.

Figures 13(a) and (b) show other cell compartment designs alternative to the three layer PTFE electrode compartment. Both of the alternative design can reduce the laboratory work man-hours by half, yet new obstacles are encountered. In (a), since the 15×15×0.6 cm flow-through electrode compartment is made of polyvinyl chloride polymer (PVC), it eliminates the deterioration of the compartment and improves contact resistance between the electrode and the current collector. However, with no rubber seal used to surround the electrode compartment, the possibility of electrolyte leakage occurring is high. Meanwhile, in (b), leakage is no longer a problem as when the rubber is compressed it follows the shape of the cell. Nevertheless, the flow



**Figure 14.** New un-optimized V-RFB system of 25 cm<sup>2</sup> unit cell laboratory unit V-RFB.

channel shrunken due to the compression and electrolyte is partly blocked, and hence resulting in a poor flow distribution throughout the cell.

To eliminate the problem of corrosion in Figures 12(b) and (c) when measuring the equilibrium potential of the cell, a graphite rod is dipped directly into the electrolyte reservoir bypassing the reference cell as shown in Figure 13(c). Hence, the electrolytes from the cell flowed directly into the reservoir. It was first assumed that the graphite rod will provide the open-circuit cell potential similar to that when the reference cell is dipped directly into the electrolyte. On the contrary, it is observed that the graphite rod failed to emulate the function of reference cell as it provides the same reading as it was recorded on  $E_{cell}$ . This means that the electrolyte itself turns into a conductor. The absence of ion exchange membrane that separates both half-cells of the reference cell showed that the system failed to reach its equilibrium state. This shows that the transport of  $H^+$  across reference cell through ion exchange membrane is important in balancing the electrochemical reaction in the cell for the cell to reach its chemical equilibrium.

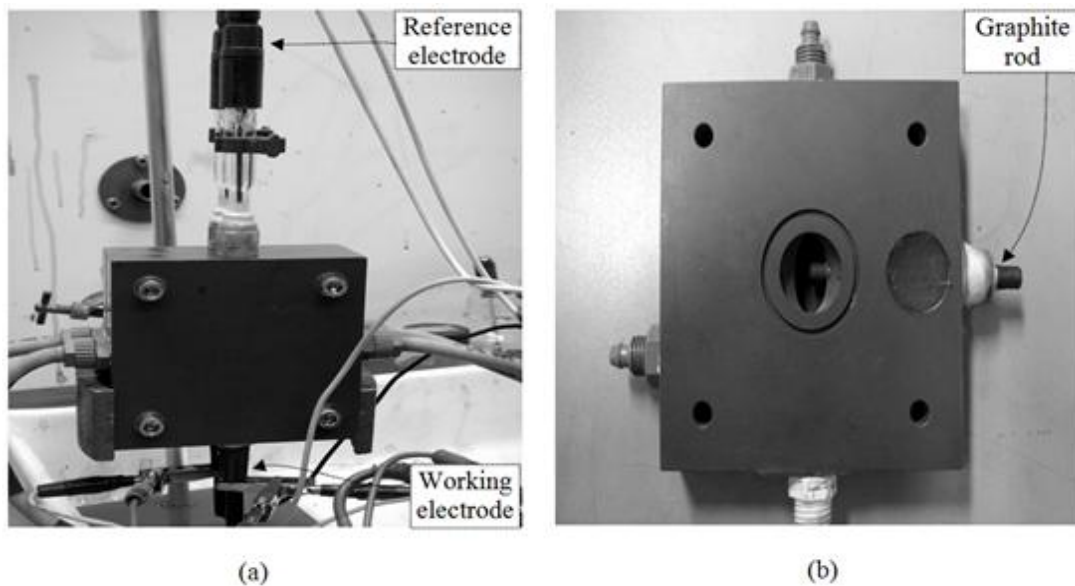
### Implementation

Based on the problem identified from preliminary experiments, a new experimental setup for the study of V-RFB system is shown in Figure 14. The main frame compartment of the V-RFB is made of 12.5 × 12.5 × 2 cm PVC, adapting flow through configuration and has projected electrode area of 5 × 5 × 0.4 cm. All readings are generated through a pre-written program in NI LabVIEW 2009 (Mohamed and Li, 2010) and recorded through a 16-

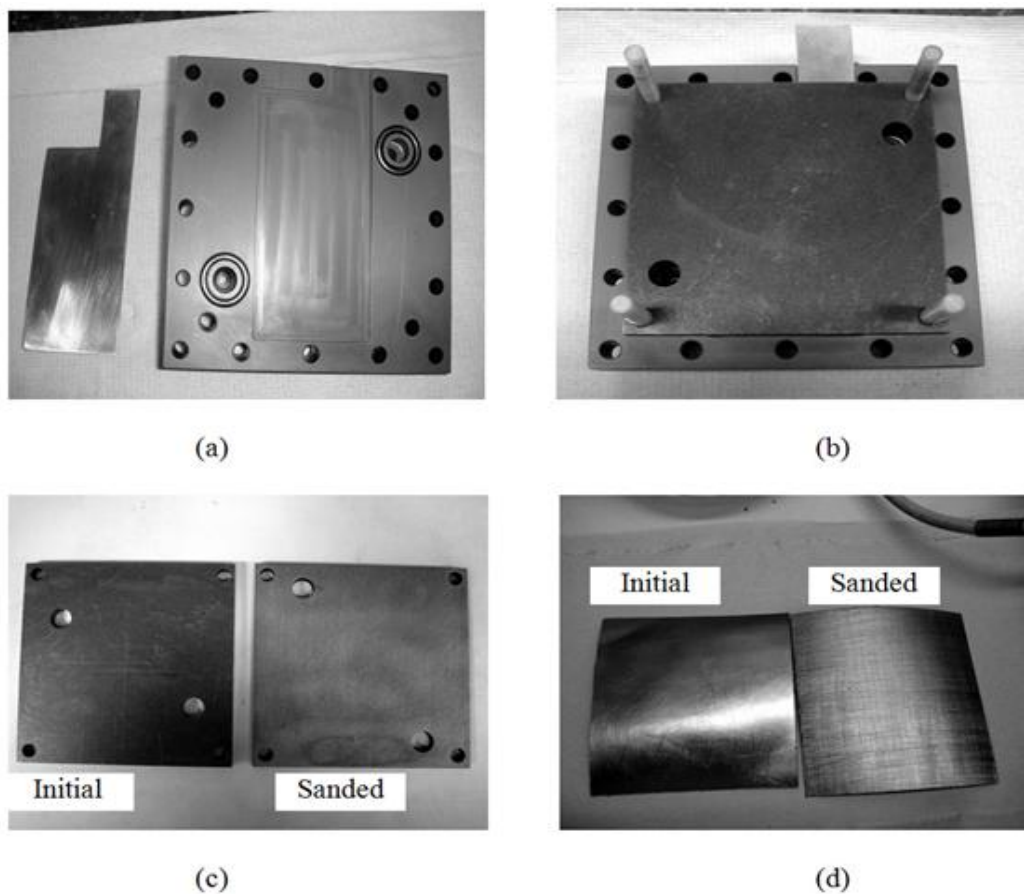
Bit, 250 kS/s isolated M series MIO, bus-powered NI USB-6215 DAQ card. Fluke 80i-110s AC/DC current probe with smaller output at 10 A ranges with output of 100 mV/A ± 3% is used instead of Fluke I30 AC/DC current clamp 30 A, 100 mV/A ± 1%. Temperature is measured using 205°C rated Iron-constantan J-type PFA coated thermocouple probe (part no. ICSS-14G-12-PFA). Characteristic of V-RFB at various temperatures is simulated using refrigerated circulators (Grant LTD6/20–LTD6G); this is achieved by circulating temperature-controlled water via flow-through temperature-controlled glasses which then heat up or cool the stored electrolyte in electrolyte reservoir accordingly to a desired temperature.

Open-circuit cell potential and half-cell redox potentials are monitored using a divided open-circuit potentiometric cell as shown in Figure 15, through a Hach Lange GmbH XR200 Hg/Hg<sub>2</sub>SO<sub>4</sub> reference electrode (part no. B20B200) and Sigma-Aldrich 0.6 cm, 99.9999% graphite rod working electrode (batch no. 11903BB) separated by ion exchange membrane (Du Pont Nafion NF115/H<sup>+</sup>). Eckroad (2007) stated that it is essential to predict state-of-charge (SOC) of the V-RFB through observing the open-circuit voltage in a reference cell outside the power generating stack. As shown in Figure 15(b), a graphite rod is used as the working electrode instead of a silver wire in order to eliminate a disconnected electrode.

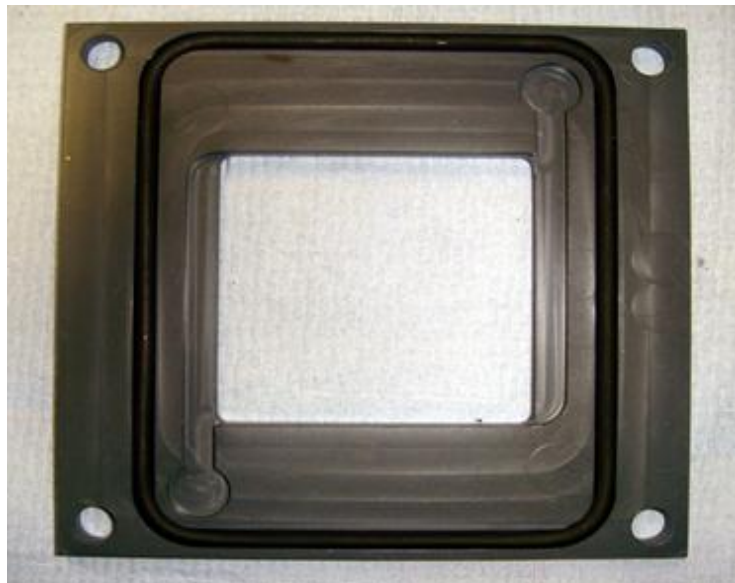
To improve the problem associated with electrolyte leakage and poor contact resistance, a new cell design is proposed as shown in Figure 16. Instead of having a flat frame as shown in Figure 11, a proper compartment is provided for copper plate current conductor in the new cell design, as shown in Figure 16(a). O-ring rubber seal is used instead of PTFE 'O' ring as the former provides better



**Figure 15.** A divided open-circuit potentiometric cell: (a), Reference and working electrode; (b), graphite rod as working electrode.



**Figure 16.** New 12.5x12.5x2 cm cell design: (a), New cell frame with copper plate slot and rubber seal; (b), 4 new holes at each corner with PTFE rod to hold carbon current collector and electrode compartments; (c), comparison of carbon current collector; (d), comparison of grafoil.



**Figure 17.** New PVC 5x5x0.4 cm electrode cell compartment enclosed by rubber seal.

protection during compression due to its flexibility. No extra UniBond sealant is required to fasten the rubber seals as a proper gap is provided in the compartment. Four extra holes were made at each corner of the cell to better hold the carbon current collector using PTFE rods as shown in Figure 16(b). The use of sanded carbon current collector and grafoil increase the contact resistance between the copper collector, the carbon current collector and the electrode area.

A new carbon electrode compartment is proposed, reproduced from the idea of alternative cell design as discussed earlier, using both PVC and rubber seal as shown in Figure 17, hence the associated leakage issues is reduced. This new cell's design significantly reduces the laboratory work man-hours as a minimum of 6 man-hour of laboratory works is needed to assemble the V-RFB cell, an improvement of 85% in the man-hour of laboratory work, before starting the charge-discharge cycle on V-RFB system.

## Experimental results

Figure 18 shows the comparison of the experimental characterization results of the previous design of 100 cm<sup>2</sup> to the new design of 25 cm<sup>2</sup> of V-RFB; both batteries are operated at 100 mA cm<sup>-2</sup> applied current density with 1.6 moldm<sup>-3</sup> V(III)/V(IV) in 4 moldm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> used at constant volumetric flow rate 3 cm<sup>3</sup>s<sup>-1</sup> and constant temperature of 298±2 K (note: old system are an assumed temperature).

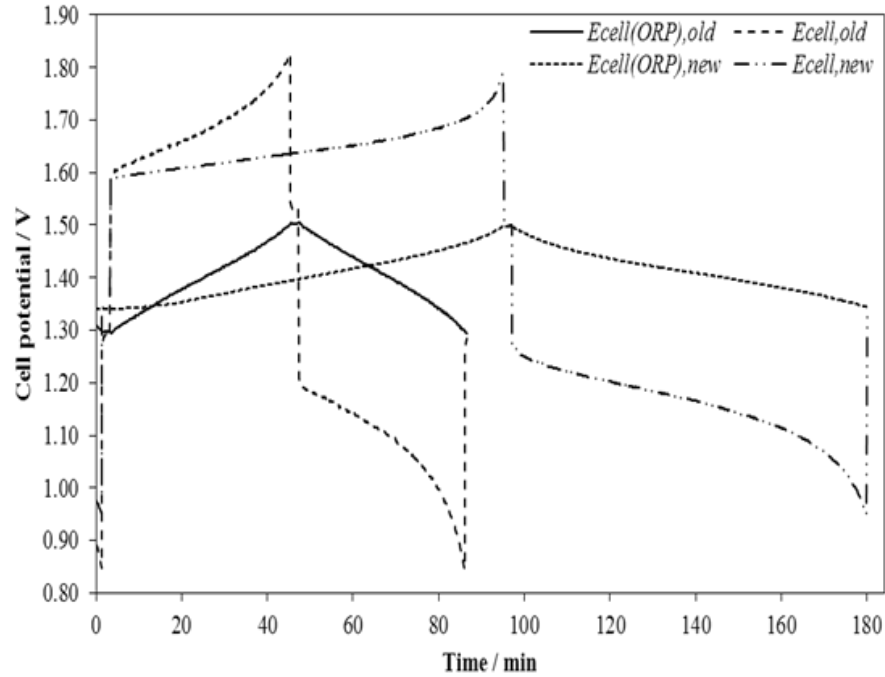
The coulombic and voltage efficiency for newly implemented design, 25 cm<sup>2</sup> of V-RFB are 93 and 77%,

respectively. Trivial improvement on energy efficiency of 72%, which is comparable with other system (Skylas-Kazacos et al., 1991) compared to 65% obtained from the previous cell design. It is observed that an improvement of 85% on contact resistance is recorded at an average of 8.6 mΩ from 11.2 mΩ recorded in previous system.

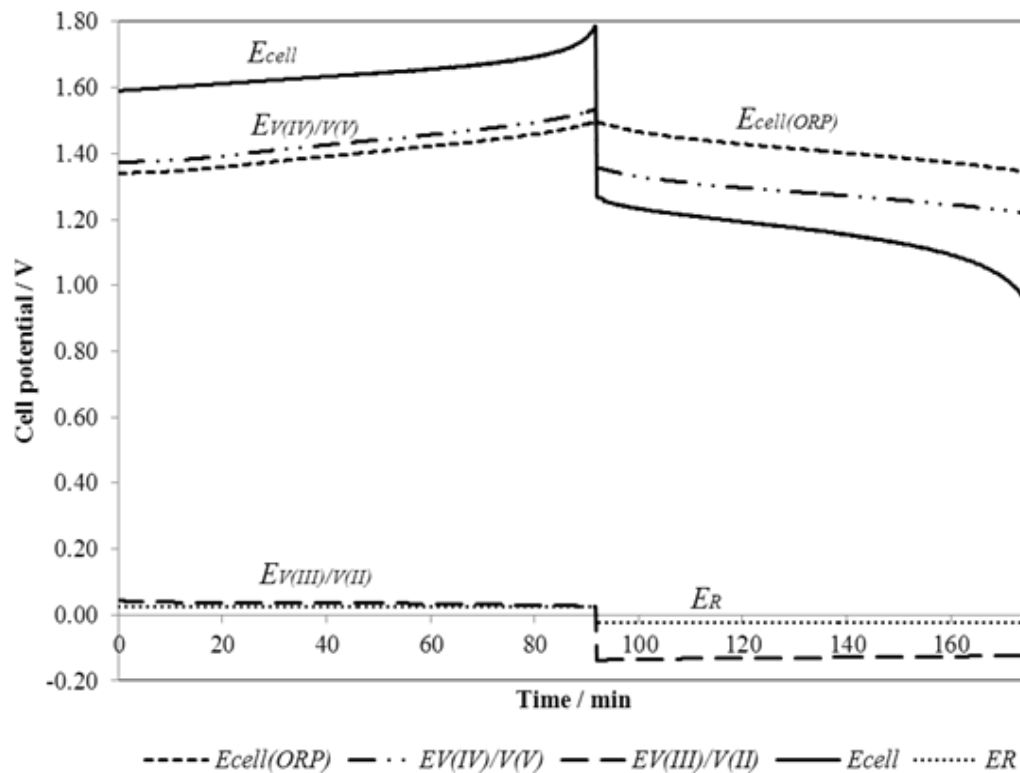
Alternatively, the newly implemented system has provided 50 times better resolution compared to the previous system; this has provided a substantial base for the future study in the dynamic characteristics of V-RFB. In addition, the system has provided a proper temperature-controlled system for experimental characterization of V-RFB.

Eventually, perhaps the most significant improvement built in the system is the ability to monitor half-cell charge-discharge characteristic of V-RFB for potentiometric monitoring of the SOC of a V-RFB as shown in Figure 19. Understanding this relation is of fundamental importance in electrochemistry because it regulates the behavior of most electrochemical systems. Walsh (1991) suggested that the measurement of a cell potential at an equilibrium state could be used to describe the thermodynamics of electrolyte solutions and cell reactions. This design could be extended to be used in an online prediction and monitoring SOC of a V-RFB, hence extending the lifespan of the battery when used within its design limits. Nonetheless, details of the experimental characterization of V-RFB will be presented in another paper.

Figure 19 shows the major differences between the characteristics of V(IV)/V(V) couples and that of V(II)/V(III) couples. The half-cell potential at positive



**Figure 18.** Experimental charge-discharge characteristic of previous design, 100 cm<sup>2</sup> and newly implemented design, 25 cm<sup>2</sup> of V-RFB at 100 mAcm<sup>-2</sup>, 1.6 moldm<sup>-3</sup> V(III)/V(IV) in 4 moldm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> used at constant volumetric flow rate 3 cm<sup>3</sup>s<sup>-1</sup> and constant temperature of 298±2K versus time.



**Figure 19.** Experimental charge-discharge characteristic of 25 cm<sup>2</sup> of V-RFB at 100 mAcm<sup>-2</sup>, with half-cell potentials and contact resistance potential versus time.

electrode,  $E_{V(IV)/V(V)}$  increases significantly by 90% from 1.37 V at initial value. In contrast, a trivial reduction in  $E_{V(V)/V(IV)}$  at negative electrode is observed. This is due the fact that V(IV)/V(V) couples are slower than V(II)/V(III) couples, hence larger over potential is needed to initiate charge transfer (Blanc, 2009). The same form can be observed during the discharge cycle as large voltage drop is recorded. Blanc (2009) indicated that reduction of V(V) are slower than reverse reaction of V(IV) oxidation; it means higher voltage losses should be observed during discharge state.

## CONCLUSION

Undoubtedly, the cell and system design still requires more attention in order to produce better packaging and optimized cell design. Nonetheless, to a lesser degree, the new cell design has significantly reduced the man-hour laboratory work, where a minimum of 6 man-hour laboratory works is needed to assemble V-RFB cell compared to at least 40 h needed for the previous cell. This is an improvement of 85% on man-hour laboratory work and the operation of V-RFB performed better within the controlled environment and parameters, and this will provide the basis for further enhancement of the system in the future. The performance of the cell could be improved through better packaging, optimized cell design to reduce spacing between the plates, improved solubility of vanadium species using modified electrolytes and improved heat transfer within the cell.

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