

## Self-Discharging and Corrosion Problems in a Vanadium Redox Flow Battery

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### Abstract

*Vanadium redox flow battery (VRFB) has a potential for large energy storage system due to its less dependency to energy capacity and power generation. However, VRFB is known to have challenges of high price, corrosion problem and lower energy efficiency. In this work, VRFB prototype was assembled from the existing parts available in the and its performance was tested. The estimated electrochemical reactions are discussed for initial charging process with Vanadium pentoxide powder as initial state to obtain fully charged battery state with  $V^{2+}$  ion in anolyte and  $VO_2^+$  ion in catholyte. Material corrosion tests were done by immersing the material in a Vanadium electrolyte and by using the material as a bipolar plate in the VRFB system. Immersion test showed that copper, steel, lead and zinc were corroded badly. In bipolar plate material test, stainless steel 316, aluminum and silver plates were corroded after some hours of electric charging process. Simple carbon plastic composites and 3-mm thickness graphite plates were tested in the bipolar plate material test and failed due to corrosion problem as well. In the VRFB prototype, corrosion problems occurred on brass nipples, polyurethane plastic pipes and porous silicone seals. Hence, stronger plastic components and better quality of silicone seals are needed for VRFB. Significant finding of this study is possible spontaneous chemical reaction within anolyte tank as a potential of self-discharging reaction which has never been identified previously. In addition, the good bipolar plate for VRFB is not easily available in the market.*

**Keywords:** Vanadium, flow battery, VRFB, corrosion, bipolar plate, electrode, electrolyte, anolyte, catholyte.

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### INTRODUCTION

The demand for large energy storage systems is increasing for various applications, such as renewable energy power system, load stabilizing of electric power, electric vehicle power system and electric power back-up applications. In addition to the low cost

load-stabilizing and power back-up applications, the longer energy storage life and higher volumetric energy densities are needed for electric vehicle power system.

The concept of redox flow batteries was proposed by the National Aeronautics and Space

Administration (NASA) in the 1970s (Thaller, 1974) and the first redox flow battery was using a ferric/ferrous ( $\text{Fe}^{2+}/\text{Fe}^{3+}$ ) electrolyte solution in the positive half-cells and a chromic/chromous ( $\text{Cr}^{2+}/\text{Cr}^{3+}$ ) electrolyte solution in the negative half-cells. Unfortunately, the cycle life of the system was seriously constrained by the cross-contamination of the two half-cell electrolytes due to diffusion of the active ions across the membrane and excessive hydrogen gas generation problem at the negative electrode during charging. To overcome these problems, all-vanadium redox flow battery (VRFB) was developed (Sum & Skyllas-Kazacos, 1985; Sum, et al., 1985; Rychcik & Skyllas-Kazacos, 1988). Through the use of vanadium salt solutions in both half-cells, the problem of cross-contamination has finally been solved.

The primary advantage to VRFB is independence of energy capacity and power generation. Capacity of the battery is related to the amount of stored electrolyte in the battery system and concentration of active species. The power generated is related to the voltage of each cell, the number of stacks in the battery, behavior of the active species and the electrode size. This leads to good flexibility and scalability of the technology. Unfortunately, the VRFB still suffers from its high price and lower energy efficiency due to problems in two main components of VRFB: electrode and bipolar plate. Electrode is usually made of carbon-based materials and within electrode, the electrochemical reactions take place. Bipolar plate (BPP) acts as a current collector and separator between two cells. Theoretically, the high electric resistance of electrode and BPP will lead to lower voltage efficiency of the VRFB. In general, BPP can be categorized into three types such as metallic, graphitic, and carbon plastic composite materials. The metallic BPP has disadvantage of highly corroded in highly acidic vanadium electrolyte solution. Similarly, the graphitic BPP also has some drawbacks, such as lack of mechanical strength and low processability. Compared with these aforementioned materials, the carbon plastic composite BPP is considered as a promising alternative in terms of good electrical conductivity, great mechanical strength and easy formability. Unfortunately, carbon plastic composite BPP for VRFB is not widely available in the market.

All components of VRFB must be able to withstand the high acidity of the vanadium electrolyte. In general, strong type of plastics are used to build components with no electric currents inside. However, some type of plastic is not strong enough to resist the acidity of vanadium electrolyte resulting in considerable cracks and deterioration.

Previously, several redox flow battery researches have been done in Indonesia (Silitonga et al., 2021; Kumara et al., 2022; Kusumah et al., 2019). In this work, metallic BPP will be evaluated based on the materials widely available in the market. Graphitic and simple carbon plastic composite BPP will be

evaluated as well. Evaluation will mainly focus on corrosion problem and energy efficiency. Different types of plastic will be evaluated for corrosion problem as material for the VRFB components. Possible electrochemical reactions are discussed in positive and negative electrodes and also more possible spontaneous chemical reactions within electrolyte are studied. Long term target is to develop large capacity battery VRFB as energy storage to support renewable energy electric generation (Hendrina et al., 2020). Therefore, the novelty of this study is mainly on the identification of possible spontaneous chemical reaction within anolyte tank as a potential of self-discharging reaction. Other researchers (Thaller, 1974; Sum & Skyllas-Kazacos, 1985; Sum et al., 1985; Rychcik & Skyllas-Kazacos, 1988; Silitonga et al., 2021; Kumara et al., 2022; Kusumah et al., 2019; Hendriana et al., 2020; Rahmana et al., 2009; Chen et al., 2017; Blanc et al., 2010; Wikipedia., 2022; Kim, 2019; Povar et al., 2019; Wagman et al., 1982; Jiang et al., 2016; Di Blasi et al., 2014; Kabtamu et al., 2017; Tang et al., 2014; Liu et al., 2011; Richards et al., 2012) have not identified this spontaneous reaction. Further investigation is needed to mitigate this possible self-discharging reaction in VRFB.

In this work, VRFB prototype with all components from existing parts sold in the market was assembled and tested. Another finding of study is that good bipolar plate for VRFB is not easily available in the market. All bipolar plates considered were corroded by the Vanadium electrolyte.

## VRFB THEORETICAL

One major difference between redox flow batteries and typical electrochemical batteries is the method of electrolyte storage: redox flow batteries store the electrolytes in the external tanks away from the battery electric generator. The main components of VRFB system include electrolyte, membrane, electrode, bipolar plate, compartment frame, gasket, storage tank and pump.

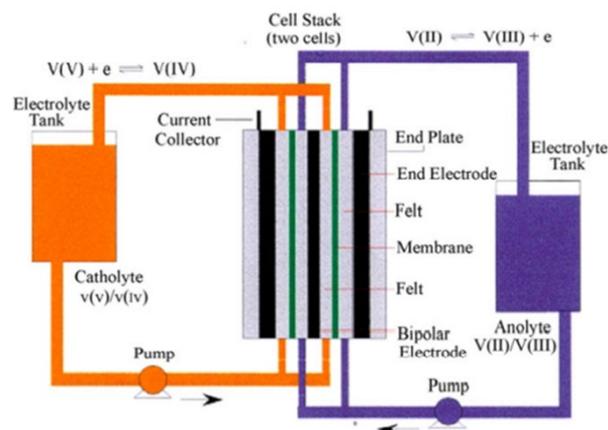


Figure 1. Schematic diagram of 2-Cell Vanadium redox flow battery (Rahmana et al., 2009).

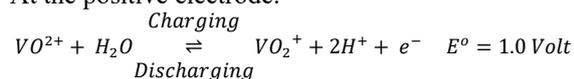
Figure 1 depicts the schematic diagram of VRFB for 2-cell configuration. Accordingly, the VRFB system with more than 2 cells will be an extension of this diagram.

Each cell consists of two compartments: positive half-cell and negative half-cell that are separated by a membrane to prevent cross mixing of the electrolytes in positive and negative sides but allows  $H^+$  ion to pass through. Each side of the cell contains an electrode made of a highly porous carbon felt. The electrolytes are stored in two external tanks. Pumps are used to deliver the electrolytes through the compartments. The electrolyte is prepared by dissolving vanadium oxide in sulfuric acid solution. The electrolyte is pumped through the electrode where the electrochemical reactions occur inside the compartment frame. During charging and discharging of the VRFB system, electrochemical reactions within the battery stack change the valence of the vanadium ions accordingly. Electrochemical reactions occur inside the electrodes and electric current will flow from the electrodes to BPP. All electrodes and BPPs need to have low electric resistance for efficient VRFB system. Current collectors at both ends are optional because the electric current can be drawn directly from the BPPs. Silicone seals are placed between the two components to prevent any possible electrolyte leakages.

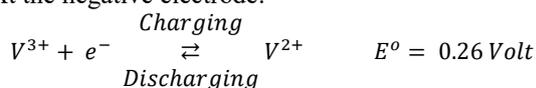
### ELECTROCHEMICAL REACTIONS

The VRFB system stores chemical energy and generate electricity as a results of redox reactions between vanadium ions dissolved in the electrolytes. The theoretical redox reactions occur as follows (Rahmana et al., 2009; Chen et al., 2017; Blanc et al., 2010)

At the positive electrode:



At the negative electrode:



While these redox reactions occur, proton ions ( $H^+$ ) diffuse across the membrane and electrons transfer through an external circuit as illustrated in Fig. 2. The theoretical cell voltage for the all-vanadium redox flow batteries is approximately 1.26 Volt.

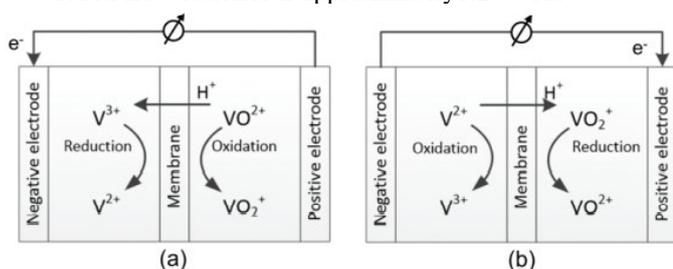


Figure 2. Schematic vanadium redox reactions in VRFB, (a) Charging, (b) Discharging (Chen et al., 2017).



Figure 3. From left:  $[V(H_2O)_6]^{2+}$  (Lilac),  $[V(H_2O)_6]^{3+}$  (Green),  $[VO(H_2O)_5]^{2+}$  (Blue) and  $[VO(H_2O)_5]^{3+}$  (Yellow). (Blanc et al., 2010).

As stated in the redox reactions, VRFB involves with 4 vanadium oxidation states which are  $V^{2+}$ ,  $V^{3+}$ ,  $VO_2^+$  and  $VO_2^+$  or commonly written as V(II), V(III), V(IV), and V(V). Interestingly, these 4 vanadium oxidation states exhibit different individual colors (Wikipedia., 2022) which are lilac, green, blue and yellow for V(II), V(III), V(IV), and V(V), respectively as shown in Fig. 3. When the battery is fully charged, the catholyte will mainly contain  $VO_2^+$  and its color is yellow and the anolyte will mainly contain  $V^{2+}$  and its color is lilac. On the other hand, when the battery is fully empty, the catholyte's color will be blue and the anolyte's color will be green. However, when the battery is half-charged, the catholyte's color will be a mixed of yellow and blue which can be seen as greenish and the anolyte's color will be a mixture of green and lilac, which can be obviously seen as dark green.

The battery performance is generally evaluated with three efficiencies: coulombic efficiency (CE), voltage efficiency (VE) and energy efficiency (EE), which are defined as following (Chen et al., 2017; Blanc et al., 2010; Kim, 2019)

$$CE = \frac{\text{discharge capacity}}{\text{charge capacity}} \times 100\% \quad (1)$$

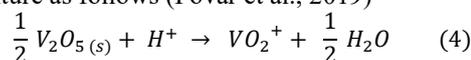
$$VE = \frac{\text{average discharge voltage}}{\text{average charge voltage}} \times 100\% \quad (2)$$

$$EE = CE \times VE \quad (3)$$

The CE value can reduce due to cross-over of vanadium ions during cell operation and side reactions or due to irreversible impurity (foreign metallic) reactions inside the electrolyte. The VE value is related to the operation current density, ionic conductivity of membrane, electric resistance in electrode and bipolar plate materials and flow rate and mass transport of electrolyte. As current density increases, the VE reduces due to the increase in polarization (Silitonga et al., 2021).

### INITIAL: VANADIUM PENTOXIDE

The initial form of the vanadium considered is Vanadium Pentoxide ( $V_2O_5$ ) in the solid powder state. The vanadium is then mixed with sulfuric acid liquid and pure water. Possible chemical reaction for this mixture as follows (Povar et al., 2019)



The change of Gibbs free energy for this chemical reaction is calculated from the total free

energies of the products minus the total free energies of the reactants. Similarly, the change of enthalpy can also be evaluated from the total enthalpy of the products minus the total enthalpy of the reactants.

$$\Delta G = \Delta G_{products} - \Delta G_{reactants} \quad (5)$$

$$\Delta H = \Delta H_{products} - \Delta H_{reactants} \quad (6)$$

If  $\Delta G$  is negative, then the reaction is spontaneous (occurs without external energy input), and if  $\Delta G$  is positive, then it is non-spontaneous (input of external energy is necessary for the reaction to occur). Table 1 shows the value of Gibbs free energy and Enthalpy of several ions involved in VRFB redox reactions. For endothermic or heat-absorbing processes, the change  $\Delta H$  is a positive value and for exothermic or heat-releasing processes, the change  $\Delta H$  is negative.

Utilizing data in Table 1,  $\Delta G$  and  $\Delta H$  of chemical reaction (4) are calculated: +4.15 kJ/mol and -17.4 kJ/mol. Since the change of Gibbs free energy for this chemical reaction is positive, the reaction will be a non-spontaneous reaction. In the experiment, stirring process was needed to help the reaction and the process took a shorter time. The change of enthalpy for this chemical reaction is negative indicating that the reaction is exothermic.

Table 1. Thermodynamics data for some chemicals at 1 atm, 298.15 K (Blanc et al., 2010; Povar et al., 2019; Wagman et al., 1982)

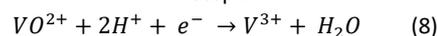
Formula	State	$\Delta H_f^\circ$ (kJ/mol)	$\Delta G_f^\circ$ (kJ/mol)
$V^{2+}$	aq	-226	-218
$V^{3+}$	aq	-259	-251.3
$VO^{2+}$	aq	-486.6	-446.4
$VO_2^+$	aq	-649.8	-587.0
$H_2O$	aq	-285.8	-237.2
$H^+$	aq	0	0
$V_2O_5$ (s)	solid	-1550.6	-1419.5
$SO_4^{2-}$	aq	-909.3	-744.5
$H_2$	gas	0	0
$O_2$	gas	0	0
$HSO_4^-$	aq	-887.3	-755.9
$H_2SO_4$	aq	-909.3	-744.5

In the mixture of  $V_2O_5$ ,  $H_2SO_4$  and pure water, after chemical reaction (4), exist some ions:  $VO_2^+$ ,  $H^+$ ,  $SO_4^{2-}$ ,  $H_2O$ . The same mixtures are used in the VRFB system as anolyte and catholyte. Initial charging is needed to reach ion  $V^{2+}$  in anolyte and  $VO_2^+$  in catholyte as the state of fully charged battery. To reach this state, possible initial electrochemical reactions in anolyte and catholyte are listed in Table 2.

Table 2. Initial Charging – Possible Electrochemical Reactions Process in Anolyte and Catholyte.

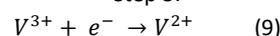
Anolyte	
Possible reactions:	
Step 1:	
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	(7)
$E^\circ = -1.00 \text{ Volt}$	

Step 2:



$$E^\circ = -0.44 \text{ Volt}$$

Step 3:

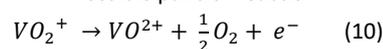


$$E^\circ = +0.35 \text{ Volt}$$

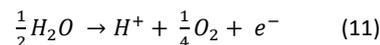
Final ion:  $V^{2+}$  (color: Lilac)

Catholyte

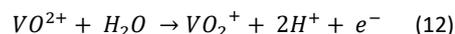
Possible pairs of reaction:



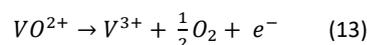
$$E^\circ = +1.46 \text{ Volt}$$



$$E^\circ = +1.23 \text{ Volt}$$



$$E^\circ = +1.00 \text{ Volt}$$



$$E^\circ = +2.02 \text{ Volt}$$

Final ion:  $VO_2^+$  (color: Yellow)

Possible electrochemical reactions in anolyte for step 1 and 2 in reactions (7) and (8) are giving negative voltage indicating that the processes are easy to occur as long as the electrons are available, while the step 3 in reaction (9) requires external voltage drive. On the other hand, all possible electrochemical reactions in catholyte require external voltage drive. Note that the reaction (11) is a pure water electrolysis reaction that can occur in positive electrode. However, due to required activation energy for water electrolysis and low water ion mobility (diffusion), this reaction does not occur widely. This is also indicated in the experiment that the electric current is very low when external voltage 2.0V (larger than required reaction voltage of 1.23V) is applied to do water electrolysis in the VRFB system with pure water as electrolyte in both sides. Reaction (10) becomes alternative of reaction (11) and its potential, +1.46 Volt, is slightly higher than reaction (11).

During the period of initial charging, the highest external voltage drive is required when anolyte reaction is in Step 3 and catholyte reaction is in reaction (10) and the total voltage is  $0.35 + 1.46 = 1.81$  Volt. So for initial charging, external voltage need to be higher than 1.81 Volt, such as using 2.0 Volt. When some amount of ion  $VO^{2+}$  exists, reaction (12) will start to occur due to its lowest potential and it converts back the  $VO^{2+}$  into  $VO_2^+$ . Reaction (10) is running alternatively with reaction (12) and actually, combination of reactions (10) and (12) is the same as reaction (11). However, in reactions (10) and (12) Vanadium ions are acting as conductive ions to facilitate the reactions and Vanadium ions have more mobility than water ions indicated by higher electric current in the experiment. Reaction (13) is less likely to occur because the reaction potential is higher. On the other hand, this reaction is also undesirable. To make sure that this reaction will not occur, do not

apply external voltage larger than its potential, +2.02 Volt.

### POSSIBLE REACTIONS IN ELECTROLYTE

Table 3. Possible Chemical Reactions within Electrolyte

Reactions	$\Delta G$ (kJ/mol)	No.
$VO_2^+ + H^+ \rightarrow VO^{2+} + \frac{1}{2}H_2O + \frac{1}{4}O_2$	+22.0	(14)
$VO^{2+} + H_2O \rightarrow VO_2^+ + H^+ + \frac{1}{2}H_2$	+96.6	(15)
$VO^{2+} + H^+ \rightarrow V^{3+} + \frac{1}{2}H_2O + \frac{1}{4}O_2$	+76.5	(16)
$V^{3+} + H_2O \rightarrow VO^{2+} + H^+ + \frac{1}{2}H_2$	+42.1	(17)
$V^{3+} + \frac{1}{2}H_2O \rightarrow V^{2+} + H^+ + \frac{1}{4}O_2$	+151.9	(18)
$V^{2+} + H^+ \rightarrow V^{3+} + \frac{1}{2}H_2$	-33.3	(19)

During the initial charging process, anolyte and catholyte can contain Vanadium ions V(II), V(III), V(IV), V(V), sulfuric acid ions and water. Investigation for spontaneous vanadium ion exchanges is needed to check the stability of the solution. Table 3 shows possible chemical (non-electrochemical) reactions within the electrolyte tank.

Chemical reactions (14) - (18) have positive  $\Delta G$  indicating that the reactions are not spontaneous to occur within the electrolyte. However, chemical reaction (19) has negative  $\Delta G$  indicating possible reaction to occur within the electrolyte. This reaction could become the self-discharging reaction in the anolyte and further investigation is needed to explain how this reaction will occur.

### VRFB PROTOTYPE

Total configuration of VRFB prototype is shown in Fig. 4 consisting main components of cell plates, two tanks of electrolyte and 2-channel peristaltic pump and with piping system.



Figure 4. Single cell  $10 \times 10 \text{ cm}^2$  size Vanadium redox flow battery prototype.

Vanadium Pentoxide ( $V_2O_5$ ) used for preparation of the electrolyte was purchased from China in the form of orange color powder with 99.9% purity (Fig. 5). Sulfuric acid of 98% purity was used in this work. The electrolyte is a mixture of Vanadium Pentoxide, sulfuric acid liquid and pure water.



Figure 5. Vanadium pentoxide powder.

Membrane is a component in the VRFB cell that keeps the positive and negative electrolyte solutions from mixing. In general, there are two types of membrane: the ion exchange membrane and the Nano filtration membrane. While preventing the cross mixing of the electrolyte solution, the membrane needs to allow hydrogen ions  $H^+$  to pass through, balancing and completing redox reactions in both sides. The membrane was purchased from China using Alibaba.com and its type is ion exchange membrane N115 with the brand name Prochema. Its conductivity is 0.1 S/cm and its thickness is 125  $\mu\text{m}$ . Reference (Jiang et al., 2016) showed that membrane N115 is the most optimum for VRFB.

Electrode is the component that facilitates the oxidation and reduction reactions within the flow battery. The surface of electrode acts as a catalyst for the reactions and its porous surface provides the reaction site for the electrolyte solution. The electrode used in the prototype is made of 4 layers of soft carbon graphite felt with its thickness of 5 mm and placed within the compartment frame similar to (Di Blasi et al., 2014). It is made by pre-oxidation and carbonization of a polyacrylonitrile-based flat felt as shown in Fig. 6. Its brand name is KWK steel and purchased through Tokopedia. Water-activation procedure as described in (Kabtamu et al., 2017) can be applied on the graphite felt to improve efficiency of the electrodes.



Figure 6. Soft carbon graphite felt.

Compartment frame could not be found in the market, therefore it was designed and built manually. Two different sizes of the frame were built,  $10 \times 10 \text{ cm}^2$  and  $25 \times 25 \text{ cm}^2$ . The frame material is acrylic with its thickness of 15 mm. Cut-out of  $6 \times 7 \text{ cm}^2$  and  $20 \times 21 \text{ cm}^2$  for the frame sizes of  $10 \times 10 \text{ cm}^2$  and  $25 \times 25 \text{ cm}^2$  are made for the electrode space and two passages are drilled on both ends of the frame for inlet and outlet of the electrolyte. Two different materials for nipple were tested, brass and plastic.

Different materials used for pipes were tested such as silicone, polyurethane and HDPE and with several different quality of silicone and different thickness of the pipes. Regular and medical quality of silicone and pipe thickness of 1, 1.5 and 2 mm were tested. All pipes were purchased from Tokopedia.

Silicone gasket with thickness of 3mm were used to seal between components in the VRFB prototype so the electrolyte would not leak out. Gaskets were placed between the bipolar plate, compartment frame and the membrane in both sides.

Peristaltic pump was used to circulate the electrolyte to the electrode inside the compartment frame and back to the tank. Working principle of a peristaltic pump is based on moving a liquid through a flexible hose by compressing and decompressing so there is no contact between any parts of the pump to the liquid. This type of pump is used to avoid contact with high acidity of the electrolyte. Double channel peristaltic pump with maximum flow rate of 1700 mL/min, maximum head of 8 m, maximum pressure of 3 bars, power 75W, brand name Signal from China, purchased using Alibaba.com was used as shown in Fig. 7. A mathematical and experimental study performed in Ref. (Tang et al., 2014) showed a higher flow rate would increase the cell voltage and allow the battery to remain operational at low states of charge.



Figure 7. Two-channel peristaltic pump.

#### EXPERIMENTAL BIPOLAR PLATE

Bipolar plate (BPP) connects adjacent cells electrically and separates them hydraulically. They need to have low electric resistance for better performance of the battery. Bipolar plate for the application of VRFB system was not found in the market. Possible bipolar plate materials which are widely available in the market are evaluated including several metals, such as aluminum, steel, stainless steel 316, zinc, silver, copper and carbon-based material

such as graphite plate and simple carbon plastic composite. The size of graphite plate used is  $10 \times 10 \text{ cm}$  with 2 mm thickness. Simple carbon plastic composites were built on a top of  $10 \times 10 \text{ cm}$  with 1 mm thickness aluminum metal plate and the mixture of carbon powder and simple plastic binders such as polyurethane and polystyrene, as shown in Fig. 8. Three different solvents were considered: thinner (methyl ethyl ketone), acetone, and methylene chloride.



Figure 8. Process of making simple carbon plastic composite on  $10 \times 10 \text{ cm}$  with 1 mm thickness aluminum metal plate.

#### PREPARATION OF THE ELECTROLYTE

Initial electrolyte was made from 36 gr Vanadium Pentoxide, 300 mL Sulfuric Acid and 500 mL pure water. Mixing process was assisted by stirring machine to help dissolving solid Vanadium Pentoxide and the process required around 30 minutes to do. During mixing process, the mixture was releasing heat and the temperature of liquid was hotter so extra precaution needed to slowly mix the pure water with the mixture. Good mixing process was indicated by no precipitation of the Vanadium powder on the bottom of the mixture. The mixture color was dark brown as shown in Fig. 9, but on a thin layer of the liquid, its color was yellow.



Figure 9. Initial electrolyte mixture during stirring process.

#### RESULTS AND DISCUSSIONS IMMERSION TEST

Some metallic plates, such as steel, stainless steel 316, zinc, copper, lead, aluminum, silver, were

dipped into Vanadium electrolyte for hours and days and the experiment showed that copper, steel, lead and zinc were corroded badly. The Aluminum plate were corroded slowly. Fig. 10 shows corrosion problem in copper, steel and aluminum plates while silver plate has no corrosion problem.

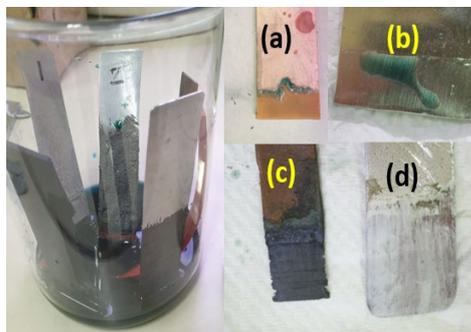


Figure 10. Immersion test: corrosion problems for (a) copper, (c) steel and (d) aluminum plates, but (b) silver plate survived in immersion test.

Stainless steel 316 and silver plates survived for two days in immersion test and then were tested as bipolar plate material in VRFB prototype. As comparison, other study (Richards et al., 2012) used stainless steel as bipolar plate but for polymer electrolyte membrane fuel cell (PEMFC).

### BIPOLAR PLATE CORROSION

Graphite plate with the size of 10x10 cm and 2 mm thickness was tested as a bipolar plate and quite bad corrosion occurred in the plate, especially at the positive side as shown in Fig. 11. The plate seemed to be completely broken while the plate on the negative side was still in good condition. This situation was also observed by researchers in Ref. (Liu et al., 2011). Further investigation is needed to check if lowering current density and thicker graphite plate can improve the condition.



Figure 11. Corrosion problem in the bipolar Graphite plate at the positive side.

Simple carbon plastic composite using polyurethane and polystyrene with solvents: thinner, acetone and Methylene Chloride were tested as bipolar plates. These composites were coating on 10x10 cm with 1 mm thickness metal plate. From the experiment, all composites were corroded after less

than 4 hours used in the VRFB system as shown in Fig. 12. Stronger plastic binder such as proposed by several researchers (Satola, 2021; Kim et al., 2014; Onyu et al., 2022) is needed to resist highly acid liquid, such as Vanadium electrolyte.



Figure 12. Corrosion problems for all simple carbon plastic composites.

### CORROSIONS IN VRFB PROTOTYPE

Corrosion problem also occurred on low quality or weak type of plastics and silicone. In the experiments, plastic pipe made of polyurethane became brittle, cracked, liquefied by the electrolyte after some time of service as shown in Fig. 13 (left image). Also, plastic nipple was getting brittle and broken after several days in service. Brass nipple corroded and become thinner and finally broken as shown in Fig. 13 (right image). Additionally, low quality silicone seals with high porosity also corroded after some time of service which was indicated by a lot of silicone particles trapped in the electrodes and the membrane.



Figure 13. Corrosion problem (left) on plastic polyurethane pipe where the plastic was liquefied, (right) on brass nipple.

### PERFORMANCE OF VRFB PROTOTYPE

Even with potential self-discharging reaction and with material corrosion problems, the VRFB prototype was successfully assembled and tested to evaluate its battery performance. Typical charging process of the VRFB system is shown in Fig. 14. The external voltage drive is set to around 2 Volt and charging current is decreasing as the battery charged

state growing higher from around 1 A to around 0.6A. In this experiment, the charging process was stopped based on the judgment that the electrolyte color starts to show yellow for the catholyte and lilac for the anolyte.

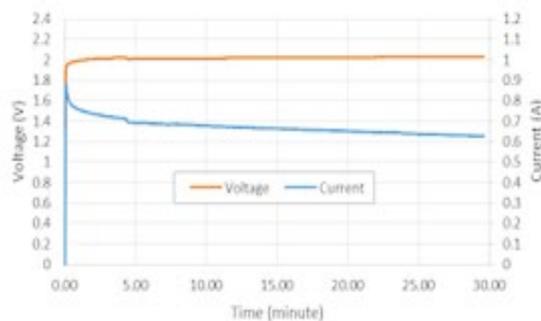


Figure 14. History of voltage and current of the cell during typical charging process.

Typical discharging process of the VRFB system is shown in Fig. 15. The current load is set to 0.7 A and the stop condition is set when the cell voltage is less than 0.8 V. During discharging process, the color of catholyte becomes more greenish due to the mix of yellow and blue ions and similarly, the color of anolyte becomes darker green due to the mix of lilac and green ions. After the discharging process, the electrolyte color starts to show bluer for the catholyte and greener for the anolyte. The working bipolar plate area for this prototype is  $6 \times 7 = 42 \text{ cm}^2$  so the current density for this case is  $700 \text{ mA}/42 \text{ cm}^2 = 16.7 \text{ mA}/\text{cm}^2$  which is low compared to other researches (Blanc et al., 2010; Kim, 2019).

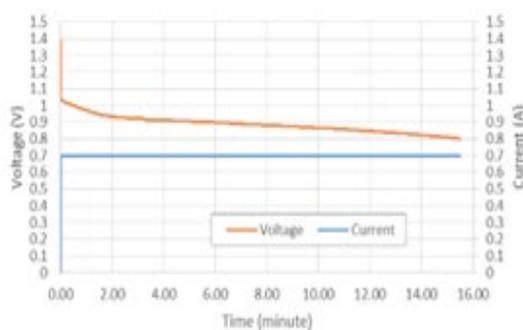


Figure 15. History of voltage and current of the cell during typical discharging process.

Charging-discharging cycle for  $25 \times 25 \text{ cm}^2$  prototype was run to evaluate the performance of the battery and the result is shown in Fig. 16. In this large prototype, the BPs were made of stainless steel 316 for both positive and negative sides. For this cycle test, the current is set to 3 A. However, only 5 cycles were done due to time limitation. Current density for this cycle is  $3000 \text{ mA}/420 \text{ cm}^2$  or around  $7 \text{ mA}/\text{cm}^2$ .

The data on the last cycle is used to evaluate coulombic efficiency (CE), voltage efficiency (VE) and energy efficiency (EE) from equations (1), (2) and (3) and they are CE = 76.9 %, VE = 57.8 %, EE = 44.4

%. Low coulombic efficiency is indicating the charging current loss due to impurity material in the electrolyte. The metallic BP might be corroded creating irreversible process of solid metal into metallic ions. Low voltage efficiency is indicating high electric resistance in the system, especially in electrodes, bipolar plates and membrane.

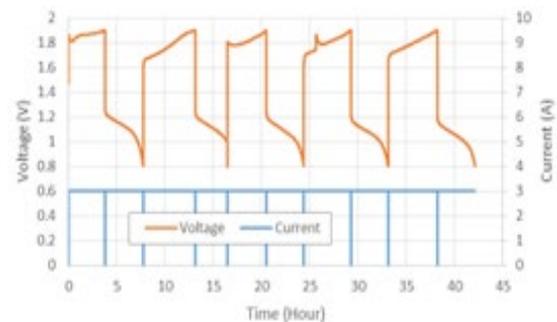


Figure 16. History of voltage and current of the  $25 \times 25 \text{ cm}^2$  cell during charging-discharging cycle process.

## CONCLUSIONS

The prototypes of a VRFB with all components from existing parts sold in the market have been assembled and tested and showed to have considerable battery capacity. Possible spontaneous chemical reaction within anolyte tank as a potential of self-discharging reaction in VRFB has been identified. Further study is needed to analyze and thoroughly mitigate this reaction. Materials for BP, such as graphite, simple carbon plastic composites and some metals have been tested, but none of them we capable to resist corrosion problem from the Vanadium electrolyte. Therefore, some stronger BP should be investigated in the future. Because weak plastics for pipes and nipples, such as polyurethane and polystyrene also cannot resist corrosion problem from the electrolyte, stronger plastic is required for the safe application of VRFB. Porous silicone seal was corroded by the electrolyte. In all cases, a solid and higher quality (medical or food grade quality) of silicone seal is needed for VRFB.

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## REFERENCES

Thaller, L.H., (1974), Electrically rechargeable redox flow cells. Proc. 9th Intersociety Energy Conversion Engineering Conference, San Francisco, CA, NASA TM X-71540, pp. 26–30.

Sum, E. and Skyllas-Kazacos, M., (1985), A Study of the V(II)/V(III) redox couple for redox flow cell applications, Journal of Power Sources, 15, pp. 179 – 190.

- Sum, E., M. Rychcik, Skyllas-Kazacos, M., (1985), Investigation of the V(V)/V(IV) system for use in the positive half-cell of a redox battery, *Journal of Power Sources*, 16, pp. 85 – 95.
- Rychci, M. k, Skyllas-Kazacos, M., (1988), Characteristics of a new all-vanadium redox flow battery, *Journal of Power Sources*, Vol. 22, pp. 59 – 61.
- Silitonga, S., Therisno, R., Napitupulu, R.A.M, Manurung, C.S.P., Siagian, P., Chen, Y.S., (2021), Redox Flow Battery Sebagai Perangkat Penyimpanan Energi, *Sprocket Journal of Mechanical Engineering*, Vol. 2 No. 2.
- Kumara, S.P.P., Hidayah, I.F., Hadila, S., Felindia, E., Syaharani, N., Pamungkas, M.A., Juwono, A.M., Pranata, K.B., Sulistyanto, M.P.T., Akbar, S., Irham, F.A., Ghufron, M., (2022), Simulasi Pengaruh Ketebalan Elektroda Terhadap Potensial Elektrolit dan Molaritas Spesies Vanadium Redox Flow Battery (VRFB), *Jurnal Fisika Flux: Jurnal Ilmiah Fisika FMIPA Universitas Lambung Mangkurat* Vol. 19, No. 1.
- Kusumah, F.M., Pridiana, D.B., Kusnadi, P., Ariyanti, D., (2019), Study on Organic Redox Flow Battery Mechanism Using TEMPO and FMN-Na Solutions, *Reaktor*, Vol. 19, No. 3, pp. 96-100.
- Hendriana, D., Budiarto, E., Djajadi, A., (2020), Simple Vertical Axis Wind Turbine for Low Wind Speed, *ICONETSI*, September 28-29, Tangerang.
- Rahmana, F., Skyllas-Kazacos, M., (2009), Vanadium redox battery: Positive half-cell electrolyte studies, *Journal of Power Sources*, Vol. 189, pp. 1212–1219.
- Chen, R., Kim, S. and Chang, Z., (2017), Redox Flow Batteries: Fundamentals and Applications, DOI: 10.5772/intechopen.68752
- Blanc, C., Rufer, A., (2010), Understanding the Vanadium Redox Flow Batteries, DOI: 10.5772/13338
- Wikipedia, Vanadium from Wikipedia, the free encyclopedia, <https://en.wikipedia.org/wiki/Vanadium>
- Sangwon Kim, (2019), Vanadium Redox Flow Batteries: Electrochemical Engineering, DOI: <http://dx.doi.org/10.5772/intechopen.85166>
- Povar, I., Spinu, O., Zinicovscaia, I., Pintilie, B., Ubaldini, S., (2019), Revised Pourbaix diagrams for the vanadium – water system, *Journal of Electrochemical Science and Engineering* 9 (2), pp. 75-84.
- Wagman, D.D., Evans, W.H., Parker, V.B., Schumm, R.H., Halow, I., Bailey, S.M., Churney, K.L., Nuttall, R.L., (1982), The NBS tables of chemical thermodynamic properties, *Journal of Physical and Chemical Reference Data* Vol. 11.
- Jiang, B., Wu, L., Yu, L., Qiu, X., Xi, J., (2016), A comparative study of Nafion series membranes for vanadium redox flow batteries, *Journal of Membrane Science*, Vol. 510, pp. 18-26.
- Di Blasi, A., Briguglio, N., Di Blasi, O., Antonucci, V., (2014), Charge–discharge performance of carbon fiber-based electrodes in single cell and short stack for vanadium redox flow battery, *Applied Energy*, Vol. 125, No. 15, pp. 114-122.
- Kabtamu, D.M., Chen, J.Y., Chang, Y.C., Wang, C.H., (2017), Water-activated graphite felt as a high-performance electrode for vanadium redox flow batteries, *Journal of Power Sources*, Vol. 341, pp. 270-279.
- Tang, A., Bao, J., and Skyllas-Kazacos, M., (2014), Studies on pressure losses and flow rate optimization in vanadium redox flow battery, *Journal of Power Sources*, vol. 248, pp. 154–162.
- Liu, H., Xu, Q., Yan, C., Qiao, Y., (2011), Corrosion behavior of a positive graphite electrode in vanadium redox flow battery, *Electrochimica Acta*, Vol. 56, No. 24, pp. 8783-8790.
- Richards, J., Cremers, C., Fischer, P., Schmidt, K., (2012), Corrosion studies on electro polished stainless steels for the use as metallic bipolar plates in PEMFC applications, *Energy Procedia*, Vol. 20, pp. 324 – 333.
- Barbara Satola, (2021), Review—Bipolar Plates for the Vanadium Redox Flow Battery, *Journal of The Electrochemical Society*, Vol. 168.
- Kim, K.H., Kim, B.G., Lee, D.G., (2014), Development of carbon composite bipolar plate (BP) for vanadium redox flow battery (VRFB), *Composite Structures*, Vol. 109, pp. 253-259.
- Onyu, K., Yeetsorn, R., Gostick, J., (2022), Fabrication of Bipolar Plates from Thermoplastic Elastomer Composites for Vanadium Redox Flow Battery, *Polymers*, Vol. 14 No. 11