

VRFB paper

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VRFB Study: Metals, Plastics and Silicone Corrosion in Vanadium Electrolyte

Abstract

Vanadium redox flow battery has a potential to become large energy storage system due to its independence of energy capacity and power generation. Vanadium redox flow battery has challenges of high price, corrosion problem and lower energy efficiency. In this work, prototypes of Vanadium redox flow battery with all components from existing parts in the market have been verified and tested. 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^+ in catholyte. Possible spontaneous chemical reaction within anolyte tank as a potential of self-discharging reaction is identified. Bipolar plates from graphite, simple carbon plastic composites and metals considered have been tested and so far none of them can resist corrosion problem from the Vanadium electrolyte. Weak plastics for pipes and nipples such as polyurethane and polystyrene cannot resist corrosion problem from the Vanadium electrolyte.

1. Introduction

Demand for large energy storage systems is increasing for applications such as renewable energy power system, load stabilizing of electric power, electric vehicle power system and electric power back-up applications. Longer energy storage life and higher volumetric energy densities are needed for electric vehicle power system and lower cost are needed for load-stabilizing and power back-up applications.

The concept of redox flow batteries was proposed by the National Aeronautics and Space Administration in the 1970s [1] and the first redox flow battery was using a ferric/ferrous (Fe^{2+}/Fe^{3+}) electrolyte solution in the positive half-cells and a chromic/chromous (Cr^{2+}/Cr^{3+}) electrolyte solution in the negative half-cells. Unfortunately, the cycling life of the system was seriously limited 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 [2,3,4]. Through the use of vanadium salt solutions in both half-cells, the problem of cross-contamination has been solved.

A key 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.

VRFB still has challenges of higher prices 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) is acting as a current collector and separator between two cells. 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 very acid solution of vanadium electrolyte. Similarly, the graphitic BPP also has some drawbacks, such as lack of mechanical strength and low processability. Compared with these two types, 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 resist high acidity of the vanadium electrolyte. In general, strong type of plastics are used to build components with no electric currents in them. However, some type of plastic is not strong enough to resist the acidity of vanadium electrolyte resulting cracks and deterioration.

Several Redox Flow Battery researches have been done in Indonesia [23, 24, 25]. 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 [26].

2. Vanadium Redox Flow Battery 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 external tanks away from the battery electric generator.

2.1 Configuration

The main components of VRFB system include electrolyte, membrane, electrode, bipolar plate, compartment frame, gasket, storage tank and pump. Schematic diagram of VRFB for 2-cell configuration is shown in Fig. 1. The VRFB system with more than 2 cells will be an extension of this diagram accordingly.

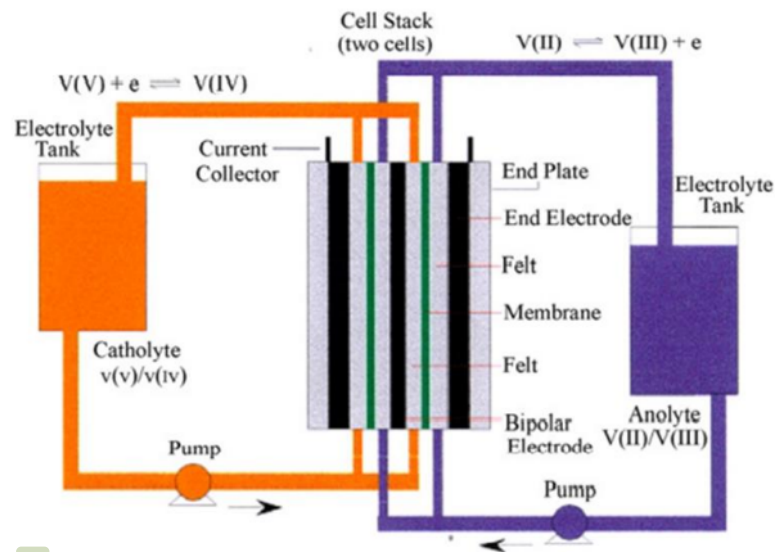


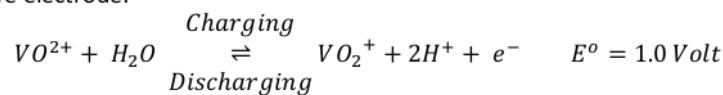
Figure 1: Schematic diagram of 2-Cell Vanadium Redox Flow Battery [5].

Each cell consists of two compartments: positive half-cell and negative half-cell and they are separated by a membrane which prevents 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 highly porous carbon felt. The electrolytes are stored in two external tanks. Pumps are used to push the electrolytes flowing 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 the bipolar plates (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 two components to prevent electrolyte leakage.

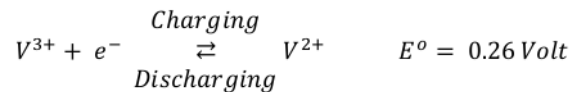
2.2 Electrochemical Reactions

VRFB system stores chemical energy and generate electricity by redox reactions between vanadium ions dissolved in the electrolytes. The theoretical redox reactions occur as follows [5, 7, 9]

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 1.26 Volt.

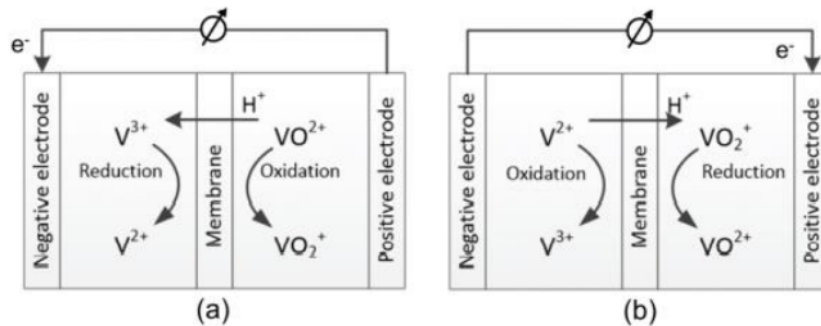


Figure 2: Schematic vanadium redox reactions in VRFB, (a) Charging, (b) Discharging [7].

As stated in the redox reactions, VRFB involves with 4 vanadium oxidation states which are V²⁺, V³⁺, VO²⁺ and VO₂⁺ or commonly written as V(II), V(III), V(IV), V(V). Interestingly, these 4 vanadium oxidation states have different individual colors [6] which are lilac, green, blue and yellow for V(II), V(III), V(IV), V(V), 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 mixed of green and lilac, which can be seen as dark green.



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). [6].

The battery performance is generally evaluated with three efficiencies: coulombic efficiency (CE), voltage efficiency (VE) and energy efficiency (EE), which are defined as following [7, 8, 9]

$$CE = \frac{\text{discharge capacity}}{\text{charge capacity}} \times 100\%$$

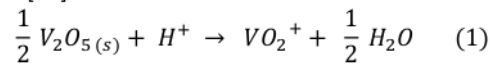
$$VE = \frac{\text{average discharge voltage}}{\text{average charge voltage}} \times 100\%$$

$$EE = CE \times VE$$

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 [23].

2.3 Initial: Vanadium Pentoxide

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 [10]



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 is calculated from the total enthalpy of the products minus the total enthalpy of the reactants.

$$\Delta G = \Delta G_{\text{products}} - \Delta G_{\text{reactants}}$$

$$\Delta H = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$$

If ΔG is negative, then the reaction is spontaneous (occurs without external energy input), and if ΔG 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 ΔH is a positive value and for exothermic or heat-releasing processes, the change ΔH is negative.

Table 1: Thermodynamical data for some compounds at 1 Atm, 298.15 K [9, 10, 11].

Formula	State	ΔH_f° (kJ/mol)	ΔG_f° (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

Utilizing data in Table 1, ΔG and ΔH of chemical reaction (1) 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 is non-spontaneous. In the experiment, stirring process was needed to help the reaction and the process took quite a bit of time. The change of enthalpy for this chemical reaction is negative indicating the process is exothermic or releasing heat.

In the mixture of Vanadium Pentoxide, Sulfuric acid and pure water, after chemical reaction (1), there are compounds: 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

Anolyte	Catholyte
Possible reactions:	Possible pairs of reaction:
Step 1: $VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$ $E^\circ = -1.00 \text{ Volt}$	$VO_2^+ \rightarrow VO^{2+} + \frac{1}{2}O_2 + e^-$ (C-1) $E^\circ = +1.46 \text{ Volt}$
Step 2: $VO^{2+} + 2H^+ + e^- \rightarrow V^{3+} + H_2O$ $E^\circ = -0.44 \text{ Volt}$	$\frac{1}{2}H_2O \rightarrow H^+ + \frac{1}{4}O_2 + e^-$ (C-2) $E^\circ = +1.23 \text{ Volt}$
Step 3: $V^{3+} + e^- \rightarrow V^{2+}$ $E^\circ = +0.35 \text{ Volt}$	$VO^{2+} + H_2O \rightarrow VO_2^+ + 2H^+ + e^-$ (C-3) $E^\circ = +1.00 \text{ Volt}$
	$VO^{2+} \rightarrow V^{3+} + \frac{1}{2}O_2 + e^-$ (C-4) $E^\circ = +2.02 \text{ Volt}$

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

Final ion: VO_2^+ (color: Yellow)

Possible electrochemical reactions in anolyte for step 1 and 2 are giving negative voltage indicating that the processes are easy to occur as long as the electrons are available, while the step 3 requires external voltage drive. All possible pairs of electrochemical reaction in catholyte require external voltage drive. Reaction C-2 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 1.23V is applied to do water electrolysis in the VRFB system with pure water as electrolyte in both sides. Reaction C-1 becomes alternative reaction of C-2 and its potential, +1.46 Volt, is slightly higher than C-2.

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 C-1 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 C-3 will start to occur due to its lowest potential and it converts back the VO^{2+} into VO_2^+ . Reaction C-1 is running alternatively with C-3 and actually, combination of reaction C-1 and C-3 is the same as reaction C-2. However, in reaction C-1 and C-3 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 C-4 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.

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.

Table 3: Possible Chemical Reactions within Electrolyte

No.	Reactions	ΔG (kJ/mol)
E-1	$VO_2^+ + H^+ \rightarrow VO^{2+} + \frac{1}{2}H_2O + \frac{1}{4}O_2$	+22.0
E-2	$VO^{2+} + H_2O \rightarrow VO_2^+ + H^+ + \frac{1}{2}H_2$	+96.6
E-3	$VO^{2+} + H^+ \rightarrow V^{3+} + \frac{1}{2}H_2O + \frac{1}{4}O_2$	+76.5
E-4	$V^{3+} + H_2O \rightarrow VO^{2+} + H^+ + \frac{1}{2}H_2$	+42.1
E-5	$V^{3+} + \frac{1}{2}H_2O \rightarrow V^{2+} + H^+ + \frac{1}{4}O_2$	+151.9
E-6	$V^{2+} + H^+ \rightarrow V^{3+} + \frac{1}{2}H_2$	-33.3

Chemical reactions E-1 until E-5 have positive ΔG indicating that the reactions are not spontaneous to occur within the electrolyte. However, chemical reaction E-6 has negative ΔG

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.

3. Experimental

3.1 VRFB configuration

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 10x10cm size Vanadium redox flow battery prototype.

Vanadium Pentoxide V_2O_5 is used for making electrolyte and it is purchased from China using Alibaba.com. Its color is orange in the shape of powdery substance and its purity is claimed to be 99.9% as shown in Fig. 5. The electrolyte is a mixture of Vanadium Pentoxide, sulfuric acid liquid and pure water. Sulfuric acid liquid used has purity of 98%.



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 μm . Reference [15] 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 [21]. 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 [22] 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, 10x10 cm and 25x25 cm. The frame material is acrylic with its thickness of 15 mm. Cut-out of 6x7 cm and 20x21 cm for the frame sizes of 10x10 cm and 25x25 cm 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. [12] 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.

3.2 Experimental BPP

The bipolar plate 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. Different 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. Metallic bipolar plates have low electrical resistance, however they tend to have corrosion problem. The size of graphite plate used is 10x10 cm with 2 mm thickness. Simple carbon plastic composites were built on a top of 10x10 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, Methylene Chloride.



Figure 8: Process of making simple carbon plastic composite on 10x10 cm with 1 mm thickness aluminum metal plate.

4. Results and Discussions

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.

Typical charging process of the VRFB system is shown in Fig. 10. 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.

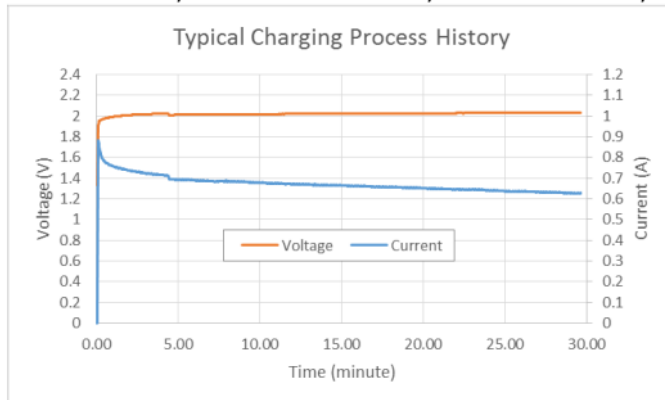


Figure 10: History of voltage and current of the cell during typical charging process.

Typical discharging process of the VRFB system is shown in Fig. 11. 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 [8, 9].

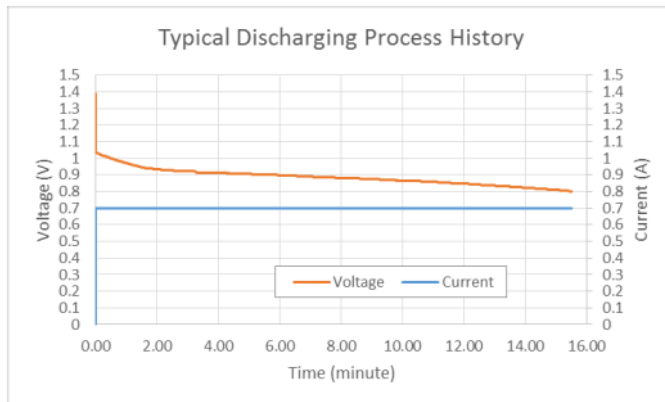


Figure 11: History of voltage and current of the cell during typical discharging process.

Charging-discharging cycle for 25x25 cm prototype was run to evaluate the performance of the battery and the result is shown in Fig. 12. In this large prototype, bipolar plates were made of stainless steel 316 for both positive and negative sides. For this cycle test, the current is set to 3 A. Due to time limitation, only 5 cycles were done. Current density for this cycle is $3000 \text{ mA}/420 \text{ cm}^2 = 7 \text{ mA}/\text{cm}^2$.

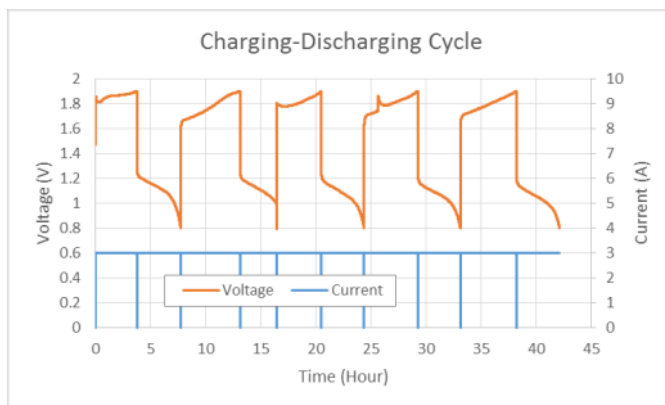


Figure 12: History of voltage and current of the 25x25 cm cell during charging-discharging cycle process.

The data on the last cycle is used to evaluate coulombic efficiency (CE), voltage efficiency (VE) and energy efficiency (EE) 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. Metallic bipolar plate 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.

4.1 Corrosion on bipolar plates

Graphite plate with the size of 10x10 cm and 2 mm thickness was tested as bipolar plate and quite bad corrosion occurred in the plate, especially at the positive side as shown in Fig. 13. The plate seemed to be completely broken while the plate on the negative side was still in good condition and this condition is similar to Ref. [19]. Further investigation is needed to check if lowering current density and thicker graphite plate can improve the condition.

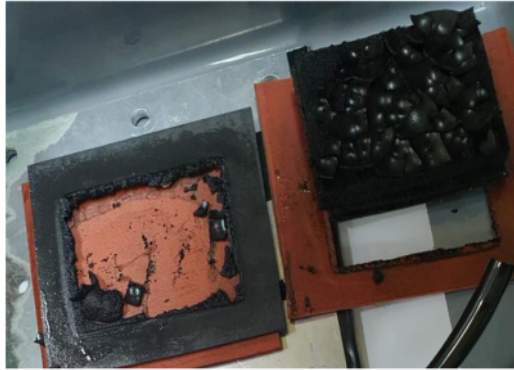


Figure 13: Corrosion problem in the bipolar Graphite plate at the positive side.

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. 14. Stronger plastic binder is needed to resist highly acid liquid, such as Vanadium electrolyte.



Figure 14: Corrosion problem for all simple carbon plastic composites.

Some metallic plates, such as steel, stainless steel 316, zinc, copper, lead, aluminum, silver, were dipped into Vanadium electrolyte for hours and the experiment showed that copper, steel, lead and zinc were corroded badly. Fig. 15 shows corrosion problem in steel and copper plates and in brass nipple. Stainless steel 316, aluminum and silver plates survived in two days electrolyte dipping test and then were tested for bipolar plates. Other study [20] used stainless steel as bipolar plate but for Polymer Electrolyte Membrane Fuel Cell (PEMFC). None of these metallic plates survived as bipolar plates and the corrosion problem for the silver bipolar plate is shown in Fig. 15.

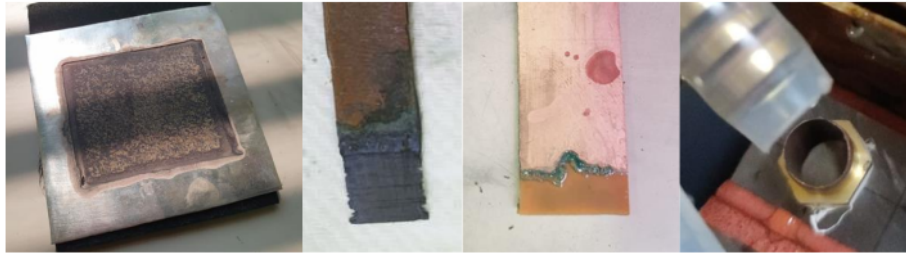


Figure 15: Corrosion problems for silver plate, steel, copper, brass nipple.

List of electromotive reactions for metals with its reaction potential is shown in Table 4. The higher the potential, the better it is for cathode material, such as gold (auras). Unfortunately, gold is quite expensive so economically not attractive material used for VRFB system. Silver has quite high potential value of 0.8 V, however, based on experiment, the silver plate had corrosion problem as shown in Fig. 15.

Table 4: Electromotive Series of Metals [13, 14]

Metal	Metal / Formed Ion	Potential* (V)
Lithium	Li / Li +	-2.96
Rubidium	Rb / Rb +	-2.93
Potassium	K / K +	-2.92
Strontium	Sr / Sr ++	-2.92
Barium	Ba / Ba ++	-2.90
Calcium	Ca / Ca ++	-2.87
Sodium	Na / Na +	-2.71
Aluminum	Al / Al +++	-1.70
Beryllium	Be / Be ++	-1.69
Manganese	Mn / Mn ++	-1.10
Zinc	Zn / Zn ++	-0.76
Chromium	Cr / Cr ++	-0.56
Iron (Ferrous)	Fe / Fe ++	-0.44
Cadmium	Cd / Cd ++	-0.40
Indium	In / In +++	-0.34
Thallium	Tl / Tl +	-0.33
Cobalt	Co / Co ++	-0.28
Nickel	Ni / Ni ++	-0.23
Tin	Sn / Sn ++	-0.14
Lead	Pb / Pb ++	-0.12
Iron (ferric)	Fe / Fe +++	-0.04
Hydrogen	H ₂ / H +	0.00
Antimony	Sb / Sb +++	+ 0.10
Bismuth	Bi / Bi +++	+ 0.23
Arsenic	As / As +++	+ 0.30
Copper (cupric)	Cu / Cu ++	+ 0.34
Copper (cuprous)	Cu / Cu +	+ 0.47
Tellurium	Te / Te ++++	+ 0.56
Silver	Ag / Ag +	+ 0.80
Mercury	Hg / Hg ++	+ 0.80
Platinum	Pt / Pt ++++	+ 0.82
Palladium	Pd / Pd ++++	+ 0.86
Gold (auric)	Au / Au +++	+ 1.36
Gold (auras)	Au / Au +	+ 1.50

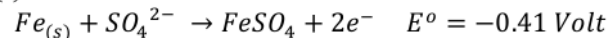
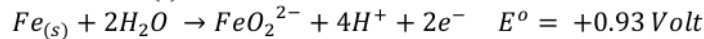
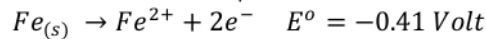
To study metal reactions, let's consider iron plate and its possible reactions. Table 5 is showing thermodynamical data for iron and its possible ions. From the table, Ion Fe^{2+} (Ferrous) is more stable than ion Fe^{3+} (Ferric) and more likely to exist.

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Table 5: Thermodynamical data for Iron at 298.15 K [11].

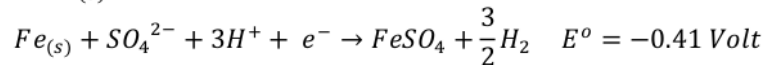
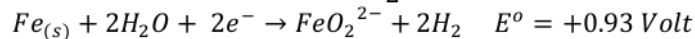
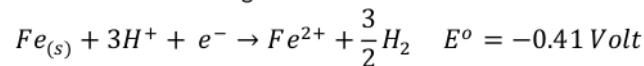
Formula	State	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)
Fe	solid	0	0
Fe^{2+}	aq	-89.1	-78.9
Fe^{3+}	aq	-48.5	-4.7
FeO_2^{2-}	aq		-295.3
$FeSO_4$	aq	-998.3	-823.4
$FeSO_4^+$	aq	-931.8	-772.7

For steel, possible electrochemical reactions in positive electrode are



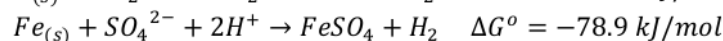
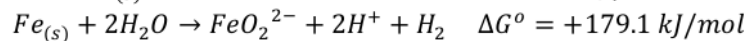
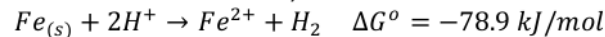
The first and third reactions are likely to occur because the reaction potentials are negative. Actually, the first and third reactions are the same for the iron, except with extra sulfuric ion in the third reaction.

Possible electrochemical reactions in negative electrode are



Similar reactions to the positive electrode reactions occur in the negative electrode. However, the reactions involve with hydrogen ion H^+ as one of the reactant and produces hydrogen gas H_2 . If the hydrogen ion is not available, these reactions will not occur.

Possible chemical reactions within the electrolyte are



The first and third reactions can occur spontaneously because their Gibbs free energy reaction change is negative and as long as all the reactants are available.

Other possible electrochemical reactions can be analyze similarly for different metals, such as Aluminum, Zinc, Copper, etc.

Corrosion problem also occurs on low quality or weak type of plastics and silicone. In the experiment, plastic pipe made of polyurethane became brittle, cracked, liquefied after some time of service as shown in Fig. 16. Plastic nipple was getting brittle and broken after some time of service. Low quality silicone seals with high porosity were corroded after some time of service which was indicated by a lot of silicone particles trapped in the electrodes and the membrane.

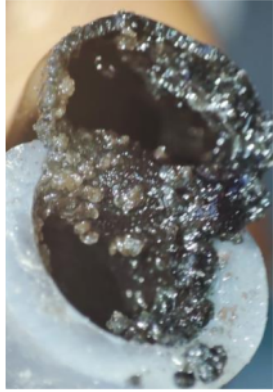


Figure 16: Corrosion problem on plastic pipe.

Conclusions

- Prototypes of Vanadium Redox Flow Battery with all components from existing parts in the market have been verified and tested and showing some battery capacity.
- Estimated electrochemical reactions have been 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^+ in catholyte. Initial charging process requires slightly higher external voltage (1.81 V) than regular charging process (1.26 V).
- Possible spontaneous chemical reaction within anolyte tank as a potential of self-discharging reaction has been identified. Further study is needed to analyze this reaction.
- Bipolar plates from graphite, simple carbon plastic composites and metals considered have been tested and so far, none of them can resist corrosion problem from the Vanadium electrolyte. Stronger bipolar plates proposed by several researchers [16, 17, 18] will be investigated in the future.
- Weak plastics for pipes and nipples such as polyurethane and polystyrene cannot resist corrosion problem from the Vanadium electrolyte. Stronger plastics such as polypropylene, polyethylene or acrylic seem to be able to resist the corrosion problem.

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