Development of a halide-free, stabilised vanadium redox flow battery electrolyte

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**NANYANG
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UNIVERSITY**

SINGAPORE

**DEVELOPMENT OF A HALIDE-FREE,
STABILISED VANADIUM REDOX FLOW
BATTERY ELECTROLYTE**

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ENERGY RESEARCH INSTITUTE @ NTU (ERI@N)**

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STABILISED VANADIUM REDOX FLOW
BATTERY ELECTROLYTE**

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A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for
the degree of
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Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

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Abstract

The large-scale implementation of renewable energy technologies, e.g. solar photovoltaic and wind turbine, requires effective and stable electric energy storage systems, due to the inconstancy of such renewable energies. Among some potential candidates, the vanadium redox flow battery (VRFB) is promising to play such a role, thanks to its advantages: power and energy capacity can be independently designed; the simple structure of cell and stack; quick response and long cycle life. One of the challenges in VRFB development is to improve the low solubility of V(V) species in sulfuric acid. The positive electrolyte of the VRFB consists of a mixture of vanadium salts in oxidation states 4+ (IV) and 5+ (V), dissolved in sulfuric acid, with a total vanadium concentration of typically $1.5 - 2 \text{ mol.dm}^{-3}$. As the battery is charged, the ratio of V(V) to V(IV) increases. Therefore, the VRFB is generally operating with the positive electrolyte in a metastable state. Consequently, there exists the risk that V(V) ions may condense to form V_2O_5 and then followed by the precipitation at high temperatures, which is almost irreversible in the charged electrolyte. In practice, the kinetics of precipitation is strongly dependent on temperature and state-of-charge (SOC).

By careful control of temperature and state-of-charge, VRFB manufacturers avoid precipitation. However, these measures add to the cost and can reduce performance. Therefore, much effort has been made to find electrolyte additives that would allow wider operational temperature windows. The most common stabilizers to date are H_3PO_4 , $(\text{NH}_4)_2\text{SO}_4$, and HCl . It has been suggested that halide ions can form complexes such as $[\text{V}_2\text{O}_3\text{Cl}_2.6\text{H}_2\text{O}]_2^+$ with the hydrate penta-coordinated $[\text{VO}_2(\text{H}_2\text{O})_3]^+$ cation, in which the chloride hinders the polymerization to V_2O_5 . However, halide in the electrolyte gives the risk of forming poisonous halogen vapors, while H_3PO_4 and $(\text{NH}_4)_2\text{SO}_4$ are rather

limited in their effectiveness. A large number of organic stabilizers have also been suggested, but little has been reported as to their long-term stability.

Therefore, in this thesis, a systematic development strategy (precipitation test, electrochemical test, material characteristics, and etc...) was conducted for finding out an electrolyte formulation (especially new additives) for a vanadium-based electrolyte, which is halide-free and stable to high temperatures. The electrolyte is also expected to demonstrate the longer-term stability and suitability for laboratory-scale VRFB and eventually for a 1 kW system.

In this Ph.D. thesis, we summarize the progress and achievement in the development of novel electrolyte formulation for the VRFB. It is demonstrated that the novel thermally stable additives have been successfully developed for the VRFB electrolyte, through the combination of one inorganic component and one organic component, which could provide the co-stabilizing effect to prevent the precipitation of positive vanadium electrolyte at high temperatures. The thermal stability of pristine vanadium electrolyte has been improved nearly 4 times by the addition of combined additives. In addition, as-developed combined inorganic-organic additives also could maintain the rate of V_2O_5 precipitate below the value of ~ 10 mol.% of V(V). By contrast, more than 60 mol.% of V(V) in the pristine electrolyte was precipitated within 7 days at 50 °C. Since the recipe is halide-free, the risk of toxic halogen vapor formation has been completely eliminated. Besides that, no other harmful contaminants were released under the operation of new electrolyte formula.

So-developed halogen-free thermally stable electrolytes also satisfied the longer-term stability and suitability in a practical VRFB cell at high temperatures. The electrolyte formulas with the presence of combined inorganic-organic additives could preserve the performance of a laboratory-

scale VRFB at 50 °C for over 100 cycling number. It also preserved the performance of a large-scale 3-stack VRFB system. Although there was a minimal drop in the efficiency of the cell, the drop could be diminished by varying the addition amount of additives or using suitable ion exchange membrane. Moreover, owing to its high thermal durability, the VRFB could be operated at relatively high temperatures without the necessity to install a cooling system, resulting in higher efficiency and lower cost.

The innovative vanadium electrolyte developed in this Ph.D. study is highly promising to be used in commercial VRFB system.

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Figure 5.21 The long-term voltage efficiency (a), cell resistivity (b), self-discharge current density (c), and capacity drop (d) of cell cycling with different electrolyte formulas at 25 °C. Cell: 20 cm² active area; electrolyte volume: 100 mL; flow-rate: 50 mL/min; current density: 100 mA/cm²; potential window: 0.9 – 1.65 V; oxidation prevention layer: Paraffin oil (10 mm); membrane: Nafion 117; temperature: 25 °C; number of cycle: 100.

Figure 5.22 The long-term voltage efficiency (a), cell resistivity (b), self-discharge current density (c), and capacity drop (d) of cell cycling with different electrolyte formulas at 50 °C. Cell: 20 cm² active area; electrolyte volume: 100 mL; flow-rate: 50 mL/min; current density: 100 mA/cm²; potential window: 0.9 – 1.65 V; oxidation prevention layer: Paraffin oil (10 mm); membrane: Nafion 117; temperature: 50 °C; number of cycle: 100.

Figure 5.23 The influence of combined inorganic-organic additive (formula 1) on the electrolyte temperature (a), flow-rate (b), and pressure (c) of 3-stack cell cycling. Cell: 625 cm² active area; electrolyte volume: 1.5 L; current density: 80 mA/cm²; membrane: Fumatech FAP 450; bipolar plate: PV15; end plate: PV15; number of cycle: 200.

Figure 5.24 The influence of combined inorganic-organic additive (formula 1) on the voltage efficiency (a), self-discharge current density (b), and resistivity (c) of 3-stack cell cycling. Cell: 625 cm² active area; electrolyte volume: 1.5 L; current density: 80 mA/cm²; membrane: Fumatech FAP 450; bipolar plate: PV15; end plate: PV15; number of cycle: 200.

Figure 5.25 The influence of combined inorganic-organic additive (formula 2) on the electrolyte temperature (a), flow-rate (b), and pressure (c) of 3-stack cell cycling. Cell: 625 cm² active area; electrolyte volume: 1.5 L; current density: 80 mA/cm²; membrane: Fumatech FAP 450; bipolar plate: PV15; end plate: F100 monolithic carbon plate; number of cycle: 200.

Figure 5.26 The influence of combined inorganic-organic additive (formula 1) on the electrolyte temperature (a), flow-rate (b), and pressure (c) of 3-stack cell cycling. Cell: 625 cm² active area; electrolyte volume: 1.5 L; current density: 80 mA/cm²; membrane: Fumatech FAP 450; bipolar plate: PV15; end plate: F100 monolithic carbon plate; number of cycle: 200.

Figure 5.27 The performance of 1 kW VRFB system cycling with pristine and novel vanadium electrolyte. Cell: 625 cm² active area; electrolyte volume: 10 L; current density: 80 mA/cm²; membrane: Fumatech FAP 450; bipolar plate: PV15; electrode: GFD 4.6 graphite felt; number of cycle: 150.

Figure 5.28 FESEM image of original graphite felt (a) and negative graphite felt electrodes (b-d) after cycling with different vanadium electrolytes at 50 °C for over 100 cycles.

Figure 5.29 FESEM image of original graphite felt (a) and positive graphite felt electrodes (b-d) after cycling with different vanadium electrolytes at 50 °C for over 100 cycles.

Figure 5.30 SEM image of original graphite felt (a) and negative graphite felt electrodes (b-d) after cycling with different vanadium electrolytes at 50 °C for over 100 cycles using the cell assembled with Nafion CEM.

Figure 5.31 SEM image of original graphite felt (a) and positive graphite felt

electrodes (b-d) after cycling with different vanadium electrolytes at 50 °C for over 100 cycles using the cell assembled with Nafion CEM.

Figure 5.32 The view of Fumatech FAP 450 membrane in original form and after cell cycling with different vanadium electrolyte formulas at 50 °C for over 100 cycles.

Figure 5.33 EIS measurement (a) and EDX analysis (b) for the Fumatech FAP 450 AEM after cell cycling with different vanadium electrolytes at 50 °C for over 100 cycles.

Figure 5.34 The view of Nafion 117 membrane in original form and after cell cycling with different vanadium electrolyte formulas at 50 °C for over 100 cycles.

Figure 5.35 EIS measurement (a) and EDX analysis (b) for the Nafion 117 CEM after cell cycling with different vanadium electrolytes at 50 °C for over 100 cycles.

Abbreviations

NTU	Nanyang Technological University
VRFB	Vanadium Redox Flow Battery
SOC	State-Of-Charge
OCV	Open Circuit Voltage
EDS(X)	Energy Dispersive X-ray Spectroscopy
CEM	Cation Exchange Membrane
AEM	Anion Exchange Membrane
IEM	Ion Exchange Membrane
PVP	Poly-Vinyl-Pyrrolidone
UV-vis	Ultraviolet–visible
XRD	X-ray Diffraction
FESEM	Field Emission Scanning Electron Microscopy
HRTEM	High-Resolution Transmission Electron Microscopy
CV	Cyclic Voltammetry
EIS	Electrochemical Impedance Spectroscopy
PHS	Pumped Hydro Storage
CAES	Compressed Air Energy Storage
SCMES	Super Conducting Magnetic Energy Storage
RFB	Redox Flow Battery
VBrRFB	Vanadium/Bromide Redox Flow Battery
VARFB	Vanadium/Air Redox Flow Battery
FTIR	Fourier Transform Infrared Spectroscopy
STEM	Scanning Transmission Electron Microscopy
CPE	Constant Phase Element
NMR	Nuclear Magnetic Resonance

Chapter 1

Introduction

This chapter aims to describe the scientific and technical issues related to the vanadium redox flow battery, resulting in the necessity to conduct this project. One significant problem encountered in the VRFB is the poor stability of the positive vanadium electrolyte at high temperatures, leading to a drop in usable capacity and eventually damage to the system. Subsequently, the aims of the project are also presented in this chapter, which is desired to develop a novel additive formula to maintain the thermal stability of vanadium electrolyte. Last but not least, this chapter also highlights the main outcomes of the project.

1.1 Problem Statement

Vanadium redox flow battery (VRFB) is one of the most promising candidates for future large-scale energy storage systems. They are particularly suitable for autonomous energy supply systems, e. g. remote farms or mobile radio antennas, as well as for the storage of energy generated by photovoltaic systems or wind power plants. The unique feature of flow batteries lies in the ability to independently scale the energy storage capacity and the power output of the system, thus rendering this technology very versatile with respect to the local circumstances of the energy source. Energy is stored and released chemically in the VRFB electrolyte, by means of simple redox processes involving the vanadium ions, dissolved in supporting electrolyte (typically sulfuric acid, with a total vanadium concentration of typically $1.5 - 2 \text{ mol.dm}^{-3}$). The electrolyte is pumped through an active cell to generate/store the energy, in which the V(II)/V(III) solution serves as the negative electrolyte (anolyte), while the V(IV)/V(V) solution is used as the positive electrolyte (catholyte).

However, it is known that V(V) has a relatively low solubility in sulfuric acid and intends to form a solid precipitate at high temperature. This process starts by the deprotonation of the hydrate penta-coordinated $[\text{VO}_2(\text{H}_2\text{O})_3]^+$ cation, which is the dominant species of V(V) in sulfuric acid and following by the condensation step to form V_2O_5 nuclei. The reaction of the whole process is given below [1]:

At this stage, the small-sized V_2O_5 nuclei still can be dissolved back into the electrolyte solution at lower state-of-charge (SOC) when the battery is

discharged. However, with the increasing temperatures, the precipitation of V_2O_5 develops faster, forming a bigger precipitate particle, which is unable to be re-dissolved, and damaging the operation system (blocking the electrolyte flow).

Based on this mechanism of solid V_2O_5 formation, many inorganic and organic additives have been studied to prevent the precipitation, and thus improving the thermal stability of vanadium electrolyte. The first priority is to restrict the precipitation at early state by inhibiting the deprotonation of the hydrate penta-coordinated $[VO_2(H_2O)_3]^+$ structure. This could be achieved by adding the additive that can form the soluble complex with hydrate penta-coordinated V(V) ion. The most effective additive to date is hydrochloric acid (HCl), which has been suggested that halide ions can form soluble complexes such as $[V_2O_3Cl_2.6H_2O]^{2+}$, in which the chloride hinders the deprotonation process to form hydrate penta-coordinated $[VO_2(H_2O)_3]^+$ structure [2, 3]. However, halide in the electrolyte gives the risk of some safety issues: introducing the possibility to form toxic chlorine gas under certain failure conditions (e.g. overcharging of cells); a very corrosive atmosphere of hydrogen chloride gas is formed in the tank and gas lines – this can also be a problem in the event of accidental spillage; the electrolyte is generally much more corrosive than the standard electrolyte, and therefore limiting the materials of construction.

Other common stabilizers to date are H_3PO_4 [4, 5] and $(NH_4)_2SO_4$ [6], which are rather limited in their effectivity. A wide range of additives also has been taught by Prof. Skyllas-Kazacos [7, 8]. However, the vast majority of these were not tested and they can, in fact, be shown to be completely ineffective in practice.

Besides, many other studies focus on the later state, prevention of the precipitation of V_2O_5 nuclei to become bigger particles. This idea is to allow

the formation but maintains the V_2O_5 nuclei size as small as possible that could not block the electrolyte flow. It has been claimed that some organic additives can adsorb via polarized functional groups, such as OH, CHO, C=O, on the initial V_2O_5 nuclei, hindering further growth and formation of particles large enough to precipitate. This will help to maintain the operation of the system, and the small nuclei of V_2O_5 can be dissolved back to the electrolyte solution during the discharging process. However, in some cases it is clear that the organic additives are oxidized by V(V) in the positive electrolyte, thereby reducing the state-of-charge [9]. At lower state-of-charge, the positive electrolyte is more thermally stable, but the usable capacity of the battery is reduced, and therefore this approach is not advantageous. It is also likely that many polymers would foul the ion exchange membranes or coat on the electrodes, causing the internal resistance of the battery to rise.

1.2 Objectives and Scope

As discussed above, the limitation on operating temperature due to the electrolyte precipitation is the major disadvantage of the VRFB. By careful control of temperature and state-of-charge, VRFB manufacturers can avoid precipitation. However, these measures add to the cost and can reduce performance. Therefore, much effort has been made to find new electrolyte formula that would allow wider operational temperature windows. Therefore, this Ph.D. project has been conducted which aims to:

- Develop a novel electrolyte formulation (especially new additives) for a vanadium-based electrolyte, which is halide-free and stable to higher temperatures than the conventional “Generation I” electrolyte.
- Demonstrate the longer-term stability and suitability of the new electrolyte in a practical laboratory-scale, and eventually in a 1 kW system.

By raising the thermal stability of the electrolyte, without the use of halides, it should be possible to reduce the cooling requirements in a VRFB, without compromising safety. This has the double advantages of reducing system cost and improving efficiency.

Along with two main objectives above, the new additives also have to demonstrate their stability and compatibility in strong oxidative (positive side) and reductive (negative side) condition of vanadium electrolyte. It is noted that the VRFB exploits two solutions of vanadium salt in sulfuric acid separated by an ion exchange membrane. During the operation, there is a chance for the electrolyte and additive species from this side to cross through the membrane to another side. Therefore, the novel additive should be added in both electrolyte tanks to warranty the homogeneity of the system.

The physical property of vanadium electrolyte, such as viscosity, is also required to be unchanged by using the new precipitation inhibitors. The VRFB manipulates two external pumps to flow the electrolyte through the active cell. The rising in the electrolyte viscosity will cause the higher energy expense to power the pump. Thus, this parameter should be noticed when developing the new additives, especially for the organic additives that have high molecular weight or low solubility.

The novel stabilizers are also recommended do not strongly influence the electrochemical property of pristine vanadium electrolyte, such as the redox reaction kinetics, reversibility or electrolyte resistance. Efficiency is an important factor for a battery system, and for the VRFB, it is partly governed by the redox reaction kinetics of vanadium ions at the carbon electrodes. The effective additives are desired to improve, or at least, do not remarkably restrict the kinetics of vanadium redox reaction.

Moreover, the new electrolyte formula is not permitted to seriously impact the other cell components, for instance, ion exchange membrane or electrode materials. This is an important thing to elongate the lifetime of a VRFB, which is proposed compulsorily to be by years. Ion exchange membrane and carbon electrodes are also quite chemically sensitive; hence, any serious degradation will necessitate costly replacement.

Last but not least, the new electrolyte is also desired to be easy and safe to install in any VRFB systems. A complete VRFB system is generally cumbersome, especially for large capacity systems. Therefore, to install a VRFB system in a remote region, the vanadium electrolyte will be transported separately. In this situation, the novel electrolyte should not contain any volatile species. The user-friendly property of the new electrolyte is also very helpful in the fast charging application of a VRFB by replacing the electrolyte.

1.3 Dissertation Overview

This Ph.D. thesis addresses the progress and achievement in the development of novel electrolyte formulation for the VRFB, which is halide-free and stable to a higher temperature. The new electrolyte formula, which contains the solution of vanadium electrolyte (1.6 M V in 4 M SO_4^{2-}) and the addition of 0.001 – 0.1 wt.% PVP and 0.01 – 0.5 wt.% ammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$ or $(\text{NH}_4)_2\text{HPO}_4$), have demonstrated the stability and suitability in different laboratory scales of the VRFB. The new advanced electrolyte formulation additionally satisfies all other requirements discussed in the aims of the project. The thesis includes 6 chapters:

Chapter 1 provides a rationale for the research and outlines the goals and scope.

Chapter 2 reviews the literature concerning the current development of renewable energy storage and conversion technology; the advantage and disadvantage of redox flow battery; and the progress on the vanadium-based electrolyte development.

Chapter 3 discusses the scope of work of this project, including the sequence of experiment will be conducted; the principles underlying the synthesis of vanadium-based electrolyte with high thermal stability; the characterization of thermal stability, electrochemical property, membrane resistivity; the cell cycling test with temperature control and the methods of data analysis, including errors.

Chapter 4 elaborates the effect of advanced halide-free additive formula on the properties of VRFB electrolyte. The studied evaluation includes the thermal stability improvement of positive vanadium electrolyte in the presence of thermally stable additives, the activity of advanced additives on the precipitation rate, the change in vanadium oxidation state in the presence of additives, the impact of additives on the electrochemical property of vanadium electrolyte.

Chapter 5 presents the practical performance of novel electrolyte formulas under cycling condition of vanadium redox flow battery; the improvement of long-term cell cycling performance at high temperatures with the presence of thermally stable stabilizers in the vanadium electrolyte; the effect of advanced precipitation inhibitors on the cell components during cell cycling process.

Chapter 6 presents our conclusions and summary for this study. The extent to which the hypothesis was proven/disproven, or the design target is met/not met is adequately addressed. The opportunities and strategies for future work are also highlighted to further enhance the application range of the VRFB.

1.4 Findings and Outcomes/Originality

Utilizing several previous studies on the thermally stable additives for vanadium redox flow battery electrolyte and combining with the current research strategy, this Ph.D. research has drawn out several novel outcomes and findings:

1.4.1 Standard Screening Method for Thermally Stable Additives for Vanadium Redox Flow Battery Electrolyte

It is reported that some organic additives containing polar functional group are often oxidized in the positive vanadium electrolyte.

Figure 1.1 Standard screening method for thermally stable additives for vanadium redox flow battery.

We have found that the apparent stability, revealed in laboratory testing, is often simply an artifact of the test method and arises from the oxidation of the organic additive with corresponding partial reduction of V(V) to V(IV). This actually does not improve the stability of the electrolyte in an operating system. In this study, we examined the oxidation of some typical carboxyl, alcohol, and multi-functional group organic additives in sulfuric acid solutions containing V(V). The UV-vis measurement and titration results showed that many organic compounds reduced the state-of-charge (SOC) of vanadium electrolyte, for example, by 27.8, 88.5, and 81.9% with the addition of 1 wt.% of EDTA disodium salt, pyrogallol, and ascorbic acid, correspondingly. The cell cycling also indicated the effect of the organic additive on the cell performance with a significant reduction in the usable charge capacity on the addition of the said additives.

It is known that the screening of thermally stable additive for vanadium electrolyte requires a long testing time due to the slow kinetics of V_2O_5 precipitation at the temperatures of 40 – 50 °C. This effort is obviously wasted if the additive is unstable. Therefore, a quick method to determine and eliminate unstable additives from lengthy test program is highly desired. In Figure 1.1, we proposed a standard screening method for vanadium thermal stability additives. The proposed chemicals have to undergo three consecutive experiments to demonstrate their chemical stability and thermal stability properties. Firstly, UV-vis spectra can quickly indicate the change in the oxidation state of V(V) ions in the presence of the additive. However, it could happen that the additives have absorption over the same range as the V(IV) solution. The second test, titration against Mn(VII), is optional, but strongly advised in instances where the additive is colored. It can provide similar information to the spectroscopy result, assuming that the reaction of the additive is not very rapid with Mn(VII). Finally, if a chemical appears stable to the oxidation by V(V) ions, it now can be used for the thermal stability test.

This is carried out with fully charged electrolyte, in glass test tubes, under thermostated conditions at 40 °C – 50 °C, and compared against an additive-free “blank” solution.

1.4.2 Physicochemical Interaction of Ion Exchange Membrane and Vanadium Ions in Acidic Medium

It is known that vanadium ions in different oxidation states have different existing structures in sulfuric acid. The communication of these vanadium ions and sulfate (or bisulfate) ions will determine how the ion exchange membrane does behave in vanadium redox flow cell. In this Ph.D. project, we examined the performance of two different typical ion exchange membranes: Nafion 117 cation exchange membrane (CEM) and Fumatech FAP 450 anion exchange membrane (AEM).

It is found that as-selected Nafion 117 CEM absorbs a little amount of all 4 vanadium ions due to the electrostatic attraction of sulfite group in its structure. No sulfate was observed in the adsorption behavior of Nafion 117 CEM. In contrast, as-studied Fumatech FAP 450 AEM absorbs a large amount of sulfate (or bisulfate), combining with the strong binding between sulfate (or bisulfate) ions and V(V) ions, a massive amount of V(V) was also found in the Fumatech FAP 450 AEM.

Vanadium entering the membrane, hindering proton transport and hence increases the cell resistivity. The increasing level depends on the number of vanadium species absorbed in the membrane. Therefore, the most significant resistivity increase was found for the Fumatech FAP 450 AEM soaked in V(V) solution because of the strong binding of V(V) and sulfate ions absorbed through the membrane. It is measured that the resistivity of FAP 450 AEM rises 10 times compared to the initial value after immersing in V(V) solution.

The interaction of ion exchange membrane and different ions existed in vanadium electrolyte directly governs the electrolyte crossover and self-discharge current. In general, the Fumatech FAP 450 AEM is more thermal-sensitive compared to the Nafion 117 CEM when being assembled in the vanadium redox flow cell. The detailed behavior will be discussed in following chapters.

1.4.3 An Advanced Thermally Stable Additives for Vanadium Redox Flow Battery

The most important outcome in this Ph.D. study is the finding of novel additive formula for thermally stable vanadium electrolyte. It is known that H_3PO_4 additive has poor thermal stabilizing effectivity for positive vanadium electrolyte due to the precipitation of V(V) and PO_4^{3-} ions. However, the presence of ammonium cation (NH_4^+) in different ammonium phosphate compounds ($\text{NH}_4\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$) can prevent such precipitation, hence improves the thermal stabilizing capability of PO_4^{3-} ions for vanadium electrolyte. In addition, surprisingly it has been found that polyvinylpyrrolidone (PVP) indicates advantageous thermal stabilizing for vanadium electrolyte, while is not oxidized to a significant degree by charged positive electrolyte, and that it does not cause a significant increase in the internal resistance of the battery. Furthermore, it has also been found that electrolyte containing small additions of PVP and ammonium phosphates ($\text{PVP} + \text{NH}_4\text{H}_2\text{PO}_4$, $\text{PVP} + (\text{NH}_4)_2\text{HPO}_4$) has a greater thermal stability than is found for either additive independently. This novel additive combination idea has not only demonstrated the superior thermally stable improvement for vanadium electrolyte but also will be a valuable reference for any future development of vanadium electrolyte formulation.

It is suggested that two mechanisms may operate to stabilize the electrolyte in

the case of using combined organic-inorganic additives:

- i) Ammonium phosphate hinders the initial condensation of V(V) by complexing with the VO_2^+ (V(V)) ions.
- ii) Polyvinylpyrrolidone (PVP), could block the surface of initial V_2O_5 nuclei, hindering further growth and formation of particles large enough to precipitate. This type of additive is not oxidized by V(V) and is therefore stable in the positive electrolyte.

Figure 1.2 Chemical structure of polyvinylpyrrolidone (PVP).

The ultraviolet-visible spectroscopy and titration test have indicated that the combined additives do not change the oxidation state of vanadium ions and the state-of-charge of vanadium electrolyte (i.e. the additives were not oxidized by the positive electrolyte).

Figure 1.3 Description of the thermal stabilizing mechanism of the combined inorganic-organic additives for vanadium electrolyte.

The combined additive had a relatively small influence on the redox reaction kinetics, electrolyte resistance in the static condition. Cyclic voltammetry (CV) curves show that there is a slight drop of the cathodic and anodic peak current of the positive electrolyte CV due to the addition of 0.5 – 1 wt.% ammonium phosphates, while the redox reaction kinetic is hardly changed. PVP, with high coverage property, has a more serious influence on the CV of vanadium electrolyte. However, the positive redox reaction still can be taken place with a glassy carbon working electrode. Therefore, the detriment of PVP could be eliminated when using high porosity electrode materials.

The combined additives have a relatively small influence on the cell performance, which does not significantly change the efficiency of VRFB cell. At room temperature (25 °C), a 1 W redox flow cell (20 cm² active area) can maintain the voltage efficiency of about 80% for over 100 cycles using pristine additive-free electrolyte. This value of electrolyte containing combined thermally stable additives is around 78%. At 50 °C, the voltage efficiency after over 100 cycles of such redox flow cell is about 83% for the pristine electrolyte, and about 78 and 80% new electrolyte formulas, respectively.

The combined additives do not increase the electrolyte viscosity and pressure drop of electrolyte flow in an operation VRFB system. The cycling with a 3-stack VRFB system (625 cm² active area) indicates that the electrolyte flow-rate and pressure when using combined additive are almost unchanged compared to the pristine additive-free electrolyte for over 200 cycles.

The combined additives are also friendly to the environment and safe for users. It is known that ammonium phosphates and PVP are non-toxic chemical agents. Therefore, there will be no safety issue needed to consider when using these additives.

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Chapter 2

Literature Review

This chapter will discuss the current situation of the increasing energy demand and its consequence, causing to the necessity to develop the renewable energy technology. Subsequently, the chapter also provides an intensive overview of renewable energy storage and conversion systems, including redox flow battery. In addition, the principle, structure and development of different redox flow batteries in general and vanadium redox flow battery, in particular, will be also presented. And most importantly, this chapter will also summarize up-to-date research progress on the additives for vanadium redox flow battery electrolyte.

2.1 Overview of Energy Storage Systems

With the increasing populations and standards of living, energy issues have become very important for almost every country in the world. The statistics from The Shift Project in 2014 indicate that the worldwide electricity production currently has reached more than 22000 terawatt hours (TWh). In which, in term of energy source, most of them come from conventional thermal methods, e.g. relates to the fossil fuel sources (coal, natural gas, oil...) and account for about 66% of total electricity production. The rest includes around 17% from hydroelectric source, 11% from nuclear power and the remaining 6% from renewable energy and others technologies. [1]

Figure 2.1 The worldwide electric production by energy sources in 2014.

Last year, a prediction is released by the International Energy Outlook 2016 (IEO2016) that the world energy use will increase by 69% from 2012 to 2040 to satisfy the energy demand of a strong economic growth in many countries, from 21600 terawatt-hours (TWh) in 2012 to 25800 TWh in 2020 and 36500 TWh in 2040. This prediction also suggests that the fastest-growing energy

sources are renewable energy and nuclear power, each increasing 2.9% per year. However, the main energy source continues to be fossil fuels, which provide about 59% of worldwide energy use in 2040 (29% from coal, 28% from natural gas, and 2% from petroleum and other liquid fuels). With the increase in the world energy demand and the consumption of fossil fuels, the global emissions of carbon dioxide (CO₂) are also predicted to increase by 46% from 2010, reaching the amount of 45 billion metric tons in 2040. [2]

The rise in CO₂ emissions is believed to drive global warming, via the greenhouse effect, the main reason causes many serious environmental problems, for instance, ice melting, prolonged drought or natural disasters. To curtail the dependence of energy production from fossil fuels, and thus reducing the amount of CO₂ emission, many researchers have been investigated and explored new energy sources and technologies to produce “clean” electrical energy. Solar, wind, tidal, waves and geothermal energy are some current popular energy technologies, in which solar and wind energy are two most common and effective technologies to produce “clean” electricity. However, solar and wind energy cannot supply the power consecutively and they also strongly depend on the weather condition. To prevent energy waste and to be used in case of higher demand or during fluctuation of the supply, the produced energy from renewable sources needs to be stored efficiently. Therefore, the development of a suitable energy storage system for renewable energy technology is highly desired.

In the last decades, a number of energy storage systems have been investigated and developed. They can be classified to different types such as mechanical energy storage systems (Pumped hydro storage (PHS), compressed air energy storage systems (CAES), flywheels), electrical energy storage systems (Superconducting magnetic energy storage (SCMES), capacitors and supercapacitors) and electrochemical energy storage systems (Fuel cells,

batteries and hybrid systems). The information about lifetime and efficiency of some different energy storage systems can be found in Table 2.1. It should be noted that efficiency and lifetime of following systems are very dependent on the practical use case. [3 - 7]

Table 2.1 The comparison of some different energy storage systems.

Energy Storage Systems	Roundtrip efficiency	Lifetime
Pumped Hydro Storage (PHS)	70-80%	>50 years
Compressed Air Energy Storage Systems (CAES)	70%	30 years
Flywheels	70-80% 25W/kWh standby losses	100,000 cycles
Super Conducting Magnetic Energy Storage (SCMES)	95%	20-30 years
Capacitors and Super Capacitors	95%	100,000 cycles
Vanadium Redox Flow Battery (VRFB)	70%	10-15 years

In practical use, some drawbacks have been realized with respect to each particular system. PHS and CAES need to be built on a special terrain which has suitable conditions for their requirements. The SCME has a small and short-lived energy contents, not capable for long duration applications. The flywheel has a low specific energy density opposed to chemical batteries. In this case, the electrochemical energy storage becomes the most promising technology, in which, battery and hybrid technologies are continuously investigated and developed.

2.1.1 Batteries

Batteries are electrochemical devices that can generate the electrical energy

from the chemical energy stored in electrode (or electrolyte) materials. A typical battery cell includes two electrodes, one negative and one positive, respectively. There is also an electrolyte that allows ions to move between two electrodes. Currently, people classify batteries into primary batteries and secondary batteries.

a. Primary Batteries

A primary battery, or disposable battery, is a portable voltaic cell that is not rechargeable. Here the electrochemical energy produced by the decomposition of electrode material and electrolyte will break down once the electrode or the electrolyte are degraded. Because of that, this procedure is irreversible and the battery needs to be replaced by a new battery. In a primary battery, the electrochemical reaction is not reversible. [8]

Table 2.2 Some commercial primary batteries.

Battery	Cell reaction	Potential
Zn/MnO ₂	$\text{Zn} + 2\text{MnO}_2 \rightarrow \text{ZnO} + \text{Mn}_2\text{O}_3$	1.43V
Zinc/Carbon (Leclanché)	$\text{Zn} + 2\text{MnO}_2 + 2\text{NH}_4\text{Cl} \rightarrow \text{Mn}_2\text{O}_3 + \text{Zn}(\text{NH}_3)_2\text{Cl}_2 + \text{H}_2\text{O}$	1.5V
Silver oxide/Zinc	$\text{Zn} + \text{Ag}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{Zn}(\text{OH})_2 + 2\text{Ag}$	1.6V
Lithium/Manganese dioxide	$\text{Li} + \text{Mn}^{4+}\text{O}_2 \rightarrow \text{LiMn}^{3+}\text{O}_2$	3.5V
Thionyl chloride	$4\text{Li} + 2\text{SOCl}_2 \rightarrow 4\text{LiCl} + \text{S} + \text{SO}_2$	3.9V

Primary batteries have some advantages such as high energy density, low initial cost and convenient to use. However, it is quite environmental unfriendly due to its disposable property.

b. Secondary Batteries

Different from the primary battery, the electrochemical reaction in the

secondary battery or rechargeable battery is reversible. Due to the reversible electrochemistry of the charge and discharge reaction of the system, they do not need to be replaced after every discharge cycle. Secondary batteries show many advantages compared to primary batteries: environmental friendly and inexpensive compared with a primary battery; best solution for high drain applications; for high utilization applications the cost of the charger is soon paid back. Some commercial secondary batteries and their properties are shown in Table 2.3 [8].

Table 2.3 Some commercial secondary batteries.

Battery	Cell reaction	Potential
Nickel/Iron	$2\text{NiOOH} + 2\text{H}_2\text{O} + \text{Fe} \leftrightarrow 2\text{Ni(OH)}_2 + \text{Fe(OH)}_2$	1.2V
Nickel/Cadmium	$\text{Cd} + 2\text{NiOOH} + 2\text{H}_2\text{O} \leftrightarrow 2\text{Ni(OH)}_2 + \text{Cd(OH)}_2$	1.3V
Nickel/Metal hydride	$\text{H}_2 + 2\text{NiOOH} \leftrightarrow 2\text{Ni(OH)}_2$	1.3V
Zinc/Bromine	$\text{Zn}_{(\text{s})} + \text{Br}_{2(\text{aq})} \leftrightarrow 2\text{Br}^-_{(\text{aq})} + \text{Zn}^{2+}_{(\text{aq})}$	1.8V
Zinc/AgO	$\text{Zn} + \text{Ag}_2\text{O} \leftrightarrow \text{ZnO} + 2\text{Ag}$	1.86V
Lead-acid	$\text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \leftrightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$	2V
Lithium-ion	$\text{Li}_x\text{C}_6 + \text{Li}_{1-x}\text{Mn}_2\text{O}_4 \leftrightarrow \text{C}_6 + \text{Li}_x\text{Mn}_2\text{O}$	3.6V

However, secondary batteries also have a specific lifetime and need to be replaced after certain charge-discharge cycles, depending on the charge-discharge conditions. Another disadvantage is that the currently applied secondary batteries show drawbacks in the field of large-scale energy storage, e.g. the trade-off between energy density and power density, the challenging in scale-up technology, safety issues, etc.”.

2.1.2 Hybrid Systems

Hybrid systems are energy conversion and storage systems which consist of two or more different systems, e.g. the combination of battery and fuel cell, flywheel and battery... However, there is not a clear definition of hybrid

systems. The development of such hybrid systems has been triggered by certain challenges in each component energy storage system. The advantage of the hybrid systems, however, is very individual and depends on the system configuration. Some interesting and common hybrid systems: fuel cell bioreactor, redox fuel cell, bi-functional redox flow battery, mixed reactant direct liquid redox flow battery. [8]

2.2 Development of Redox Flow Battery

2.2.1 General Overview of Redox Flow Battery

Redox flow battery (RFB) is one type of rechargeable batteries that can solve the limitation of secondary batteries in the large-scale application. Different from other secondary batteries storing the energy in electrode materials, RFB can convert the chemical energy of two aqueous redox couples stored in two external electrolyte tanks into electrical energy. The redox reactions to conduct the energy conversion occurs when these two electrolytes interact with electrodes after they are pumped from storage tanks to flow-through the cell. The electrolytes flowing through the cathode and anode are called the anolyte (negative electrolyte) and catholyte (positive electrolyte), respectively. There is a membrane that separates two electrodes and selectively allows non-active species to be transported through to maintain electrical neutrality and electrolyte balance.

The general redox reactions in a RFB can be written as [10]:

Anode reaction:

Cathode reaction:

Figure 2.2 General structure of redox flow battery.

The power of an RFB system is defined by the number of single cells composing in a stack and the size of electrodes, whereas the energy storage capacity is related to the volume and concentration of the electrolyte. Because it is easy to independently design both energy and power, RFB is very suitable for the renewable application. Another advantage of RFB is the simple structure of cell and stack design, which creates the convenience to set up a large system based on module design. In addition, the quick response of RFB system (sub-seconds) also makes it become ideally for utility applications. [11]

2.2.2 Overview of Electrolyte Used in Redox Flow Battery

Redox flow batteries can be classified by active species or solvent used in the electrolyte. Since the first demonstration, many different VRB electrolytes have been investigated and developed.

The name of corresponding VRB is also relevant to the redox couple used in its electrolyte. Table 2.4 shows some most common types of electrolyte used in

redox flow battery systems.

Table 2.4 Some common electrolytes used in redox flow battery systems.

Redox Flow Battery	Cell Reactions		Standard Cell Voltage (V)
	Charge	Discharge	
Iron/ Chromium	$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$ $\text{Cr}^{3+} + \text{e}^- \rightarrow \text{Cr}^{2+}$	$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$ $\text{Cr}^{2+} \rightarrow \text{Cr}^{3+} + \text{e}^-$	1.18
All- Vanadium	$\text{VO}^{2+} + \text{H}_2\text{O} \rightarrow \text{VO}_2^+ + 2\text{H}^+ + \text{e}^-$ $\text{V(III)} + 2\text{e}^- \rightarrow \text{V(II)}$	$\text{VO}_2^+ + 2\text{H}^+ + \text{e}^- \rightarrow \text{VO}^{2+} + \text{H}_2\text{O}$ $\text{V(II)} \rightarrow \text{V(III)} + 2\text{e}^-$	1.26
Vanadium/ Bromide	$2\text{VBr}_3 + 2\text{e}^- \rightarrow 2\text{VBr}_2 + 2\text{Br}^-$ $2\text{Br}^- + \text{Cl}^- \rightarrow \text{ClBr}_2^- + 2\text{e}^-$	$2\text{VBr}_2 + 2\text{Br}^- \rightarrow 2\text{VBr}_3 + 2\text{e}^-$ $\text{ClBr}_2^- + 2\text{e}^- \rightarrow 2\text{Br}^- + \text{Cl}^-$	1.3
Bromide/ Polysulphide	$3\text{Br}^- \rightarrow \text{Br}_3^- + 2\text{e}^-$ $\text{S}_4^{2-} + 2\text{e}^- \rightarrow 2\text{S}_2^{2-}$	$\text{Br}_3^- + 2\text{e}^- \rightarrow 3\text{Br}^-$ $2\text{S}_2^{2-} \rightarrow \text{S}_4^{2-} + 2\text{e}^-$	1.35
Vanadium/ Air	$2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$ $4\text{V(III)} + 4\text{e}^- \rightarrow 4\text{V(II)}$	$4\text{H}^+ + \text{O}_2 + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ $4\text{V(II)} \rightarrow 4\text{V(III)} + 4\text{e}^-$	1.49
Zinc/Bromide	$3\text{Br}^- \rightarrow \text{Br}_3^- + 2\text{e}^-$ $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	$\text{Br}_3^- + 2\text{e}^- \rightarrow 3\text{Br}^-$ $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$	1.85
Zinc/Cerium	$2\text{Ce}^{3+} \rightarrow 2\text{Ce}^{4+} + 2\text{e}^-$ $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	$2\text{Ce}^{4+} + 2\text{e}^- \rightarrow 2\text{Ce}^{3+}$ $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$	2.4

a. Iron/Chromium

The first pioneered and intensive study of iron/chromium RFB was conducted by NASA in the 1970s [12, 13]. The energy stored in an iron/chromium RFB system is by employing the aqueous solution of a ferric/ferrous ($\text{Fe}^{2+}/\text{Fe}^{3+}$) redox couple as catholyte and a chromic/chromous ($\text{Cr}^{2+}/\text{Cr}^{3+}$) redox couple as anolyte. The most common supporting electrolyte is hydrochloric acid. The redox reaction taken place in an iron/chromium RFB system can be written as [10]:

The iron/chromium RFB can be operated with carbon or graphite felt electrodes and an ion exchange membrane or separator to allow proton transfer. In practice, the kinetics of iron redox couple on carbon felt electrode is highly reversible; however, it is relatively low for the chromium redox couple. Therefore, the catalyst is generally required for the negative electrode of the iron/chromium RFB. The standard cell voltage of iron/chromium RFB is 1.18 V with the typical power density of 70-100 mW/cm².

One drawback of the iron/chromium RFB is that the standard potential of the Cr²⁺/Cr³⁺ couple is close to the potential of hydrogen evolution reaction (HER). This causes the side reactions and involves the capacity loss and electrolyte imbalance. To minimize the influence of parasitic side reactions, the optimum approach is required in the design of iron-chromium RFBs. There is currently some progress on the research to mitigate this side reaction and implement efficient re-balancing systems with minimal loss of system efficiency for iron-chromium RFB [10, 108].

b. Vanadium/Bromide (Halide)

In 2001, Skyllas-Kazacos and co-workers developed the Generation 2 of vanadium-based electrolyte to improve the low energy density of the first generation vanadium electrolyte (will be discussed later). The vanadium/bromide RFB (VBrRFB) uses the VBr₂ /VBr₃ (or VCl₂/VCl₃) couples as the negative electrolyte and the Cl⁻/BrCl₂⁻ (or Br⁻/ClBr₂⁻) couples in the positive electrolyte [10, 14-16]. The redox reaction in a VBrRFB can be written as:

The standard potential of a VBrRFB is 1.3 V. The vanadium species concentration in the vanadium/bromide electrolyte can achieve the value of 3-4 M which is equivalent to the energy density from 30-50 Wh/kg, twice that of the conventional VRFB system (25-35 Wh/L). The higher concentration of vanadium in the Generation 2 VBr electrolyte implies the capability to cut down the electrolyte volumes and redox cell system size. This makes the VBrRFB more effective for stationary applications of renewable energy storage. In addition, the VBrRFB is also reported that can be used in urban transportation applications. However, there is the risk of toxic bromine-vapor emissions during the operation of VBrRFB. Therefore, it is compulsory to minimize the amount of bromine vapor emission during operation by using bromine complexing agents [17].

c. Bromine/Polysulfide

The bromine/polysulfide RFB was patented by Remick in 1984 [18] and then extensively studied by Walsh [19] in 2001. In the bromine/polysulfide system, the sodium tribromide (NaBr_3) solution is used as the positive electrolyte, while the sodium polysulfide (Na_2S_2) serves as the negative electrolyte. The anode and cathode, and their corresponding salt solutions are separated by an ion exchange membrane. Activated carbon/polyolefin composite can be used as electrodes in this system with the standard potential of 1.35 V.

The redox reaction in bromine/polysulphide RFB is expressed as follows:

The main advantage of this system is that the redox species employing in two electrolytes are quite bountiful and thus inexpensive. Moreover, they possess

high solubility in aqueous electrolytes, which can improve the energy density. However, this system also shows the challenge in the electrolyte crossover, resulting in the sulfur precipitation and also the risk of poisonous H_2S and Br_2 emission. The other problem is due to oxidation of sulfide to sulfate as it crossed over the membrane. This leads to a permanent loss in capacity (requiring complex chemical rebalancing techniques).

d. Vanadium/Air

The concept of vanadium/air redox flow battery (VARFB) is firstly introduced by the researchers from the University of Twente [8, 20]. The active species of VARFB compose of a solution of 2 M V(II)/V(III) in 3 M H_2SO_4 in the negative side and the redox couple of $\text{H}_2\text{O}/\text{O}_2$ in the other side. The utilization of the air as the second redox couple can reduce the system weight and also increase the specific power density. The oxygen source is provided by ambient air.

The redox reaction in VARFB is expressed as follows:

The reports from the researchers from the University of Twente indicated that the VARFB can gain the value of 45.7 and 46% for the voltage efficiency and energy efficiency at 80 °C. This value is much lower than VRFB, for example, with the number of about 81 and 73% for voltage and energy efficiency, however, the specific weight storage capacity is almost twice compared to VRFB thanks to the fact that only one aqueous redox couple need to be stored.

e. Zinc/Bromine

In this hybrid redox flow battery system, the energy is also stored in external tanks of electrolyte, but the redox reaction of zinc species does not only take place in the aqueous phase. The positive side involves the redox reaction of bromide ions and bromine molecules. One thing to take note is the bromine molecules can combine with bromide ions in form of tribromide ions, which occurs primarily in liquid bromine [21]. In zinc-bromine hybrid RFB system, the catholyte (positive electrolyte) can exploit the solution of relatively high concentrations of Br^- and Br_2 to upgrade both reaction kinetics and energy density. A potential concern is the formation of toxic Br_2 , which can be eased by the addition of complexing agents [22]. However, the impact of complexing agents on the kinetics of bromine redox reactions has not been intensively quantified, particularly in strongly acidic supporting electrolyte. At the anode, zinc metal is dissolved and redeposited during operation.

The negative electrode is a compact metal electrode to increase the energy density. The cell separator is served by an ion exchange membrane or a microporous film [23]. The advantages of zinc/bromine hybrid RFB include good reversibility, high cell voltage (1.85 V) and low cost. However, this system also consists of several limitations, including the material corrosion, high self-discharging, dendrite formation, low energy efficiency and short cycle life. The first demonstration of zinc/bromine RFB was conducted by RedFlow Ltd. (Australia), with the capacity up to MW and energy efficiency of about 74% [24]. Zinc/chlorine RFB is one of the derivatives of the zinc/bromine system which typically has similar performance and obstacles [25].

f. Zinc/Cerium

Zinc–cerium RFB is firstly developed by Plurion Inc. (UK) during the years of 2000 [26, 27]. In this system, the solution of Ce(III)/Ce(IV) redox species is used as the positive electrolyte, while the solution of Zn(II)/Zn redox couple serves as the negative electrolyte. The cell reaction in zinc-cerium RFB can be expressed as follows:

Nafion (DuPont) is the typical ion exchange membrane used in zinc-cerium RFB. Similar to zinc–bromine, and zinc–chlorine RFB, this system is also classified as a hybrid flow battery because zinc is electroplated at the negative electrode during the charging process. The reagents used in the zinc-cerium RFB are considered to be cheaper than that of the vanadium flow battery.

The open-circuit cell voltage (OCV) of zinc-cerium RFB is relatively high, of about 2.43 V because of both zinc and cerium redox reactions in aqueous media have high standard electrode potentials [26]. The common supporting electrolyte used in zinc-cerium RFB is methanesulfonic acid, which can dissolve high concentrations of both zinc and cerium. It is reported that the solubility of methanesulfonates is about 2.1 M for Zn, [28] around 2.4 M for Ce(III) and up to 1.0 M for Ce(IV), respectively. [29]

The performance of zinc-cerium has not been intensively investigated. But one of the main drawbacks in this type of RFB is the self-discharge process at the cathode due to the Zn corrosion. Moreover, the use of expensive Pt-Ti electrodes is also another disadvantage compared to other RFB systems.

2.3 Vanadium Redox Flow Battery

One of the most typical matters observed in as-discussed RFB systems above is the incompatibility of two electrolyte species due to the contamination from the other. If the active species from two opposite sides transfer through the separator and interact with each other, it will not only scale down that corresponding charge/discharge cycle efficiency but also diminish the capacity and degrade the overall system performance. Subsequently, the costly electrolyte separation and reactant replacement are required to recover the initial operation parameter of the system. To solve this obstacle, employing an RFB system composed of more than two oxidation states of the same element is highly promising. In this case, the active species crossover only involves the efficiency loss due to the fact that no species are removed or irreversibly consumed by their reactive electrolytes. Overall, the all-vanadium system becomes the most promising candidate.

The vanadium redox flow battery (VRFB) uses the V(II)/V(III) redox couple as the negative electrolyte reagent and the V(IV)/V(V) redox couple as the positive electrolyte reagent. In this system, the vanadium electrolyte crossover only associates with the efficiency loss and capacity drop. The initial form of vanadium electrolyte can be regenerated electrochemically in case of any contamination.

The first investigation on the chemistry of vanadium redox couples was conducted by NASA researchers during the energy crisis of the 1970s. In the late 1980s, at the University of New South Wales, Maria Skyllas-Kazacos's research group invented and demonstrated the first operational VRFB. From that, there was an increase in the research activity of VRFB around the world. Because it is a promising technology for continuously renewable energy storage, many VRFB systems with higher capacity have been investigated and

developed. [10]

2.3.1 Electrochemistry of Vanadium Redox Flow Battery

Figure 2.3 illustrates two concurrent reactions happen on both sides of the membrane in a VRFB system. During the discharging process, electrons are released from the negative electrolyte during the oxidation of vanadium ions, moved through the external circuit and went to the positive electrolyte, where the reduction of vanadium ions happens. During the charging process, the electron flow direction is inverted, and the reduction of vanadium ions now occurs in the negative electrolyte and the oxidation happens on the positive side.

Figure 2.3 The vanadium redox reactions in VRFB cell during the charging and discharging process.

The VRFB chemical equations are as follows:

The presence of protons H^+ and water H_2O in the cathodic (positive side) reaction is to maintain the charge balance of the cell. [30]

a. Nernst Equation and Equilibrium Potential

In a stack composing a number of single cells, the stack voltage U_{stack} is driven by the internal losses U_{loss} and the equilibrium voltage U_{eq} . The equilibrium state is achieved in case of no current is flowing across the stack, that means $U_{stack} = U_{eq}$ and no internal loss. Thus, U_{stack} (with the time t) can be expressed by:

$$U_{stack}(t) = U_{eq}(t) - U_{loss}(t) [V] \quad (16)$$

The equilibrium voltage U_{eq} is equal to the total of different single cell equilibrium potentials E . By applying the Nernst equation on the concentration of vanadium species and protons, the equilibrium potential for a single cell can be written as:

$$E = E^{o*} + \frac{RT}{nF} \ln \left[\left(\frac{C_{VO_2^+} C_{H^+}^2}{C_{VO^{2+}}} \right) \left(\frac{C_{V^{2+}}}{C_{V^{3+}}} \right) \right] [V] \quad (17)$$

where R is the gas constant, T is the temperature, n is the number of electrons involved in the reaction, F is the Faraday constant, C is the concentration and E^{o*} is the formal potential. In practice, the standard potential E^o can be used to replace the formal potential E^{o*} . [30]

It should be noted that the applying of Nernst equation on concentration is only acceptable in the case of dilute concentration of vanadium species and proton. In practical high concentration of vanadium electrolyte, the Nernst equation should be with activities, not concentrations. Therefore, to describe all

important parameters in this part, we consider the redox reactions taken place in a standard condition: 1 M vanadium species concentration, the temperature at 25 °C and all activity coefficients γ_i equal to one.

b. Standard Potential

In the Nernst equation (17), the standard potential E° is a key parameter. There are two ways to determine the standard potential: by thermodynamic characteristics calculation of the components engaged in the VRFB reactions or by estimating from the standard reduction potentials of the two half-cell reactions.

• From the Thermodynamics:

To determine the standard potential by the thermodynamic method, we start with the Gibbs free energy ΔG :

$$\Delta G = \Delta H - T\Delta S \quad \left[\frac{J}{mol} \right] \quad (18)$$

where $\Delta H [J/mol]$ is the change in enthalpy and $\Delta S [J/K.mol]$ is the change in entropy.

The free energy change for vanadium redox reactions in standard condition can be expressed by the standard Gibbs free enthalpy of reaction ΔG° :

$$\Delta G^\circ = \Delta H_{reaction}^\circ - T\Delta S_{reaction}^\circ \left[\frac{kJ}{mol} \right] \quad (19)$$

where $\Delta H_{reaction}^\circ$ is the standard reaction enthalpy and depending on the molar formation enthalpy of products $\Delta H_{formation,product}^\circ$ and the molar

formation enthalpy of reagents $\Delta H_{\text{formation, reagent}}^{\circ}$:

$$\Delta H_r^{\circ} = \sum_{\text{products}} \Delta H_{\text{formation, product}}^{\circ} - \sum_{\text{reagents}} \Delta H_{\text{formation, reagent}}^{\circ} \left[\frac{\text{kJ}}{\text{mol}} \right] \quad (20)$$

And $\Delta S_{\text{reaction}}^{\circ}$ is the standard reaction entropy and depending on the molar formation entropy of products $S_{\text{formation, product}}^{\circ}$ and the molar formation entropy of reagents $S_{\text{formation, reagent}}^{\circ}$:

$$\Delta S_r^{\circ} = \sum_{\text{products}} S_{\text{formation, product}}^{\circ} - \sum_{\text{reagents}} S_{\text{formation, reagent}}^{\circ} \left[\frac{\text{J}}{\text{K} \cdot \text{mol}} \right] \quad (21)$$

Table 2.5 indicates the thermodynamic data for all components involved in vanadium redox reactions, which can be introduced into equations (20) and (21).

Table 2.5 Thermodynamic data for all components involved in vanadium redox reactions at 25 °C.

Compound	$\Delta H_{\text{formation}}^{\circ}$ [kJ/mol]	$\Delta G_{\text{formation}}^{\circ}$ [kJ/mol]	$S_{\text{formation}}^{\circ}$ [J/K.mol]	State
H+	0	0	0	aqueous
H ₂ O	-285.8	-237.2	69.9	aqueous
V(II)	(-266)	-218	(-130)	aqueous
V(III)	(-259)	-251.3	(-230)	aqueous
VO ²⁺	-486.6	-446.4	-133.9	aqueous
VO ₂ ⁺	-649.8	-587	-42.3	aqueous

Replacing the thermodynamic data into equation (20) and (21) for the standard reaction enthalpy $\Delta H_{\text{reaction}}^{\circ}$ and for the standard reaction entropy $\Delta S_{\text{reaction}}^{\circ}$

gives:

$$\Delta H_{reaction}^o = -155.6 \left[\frac{kJ}{mol} \right] \quad (22)$$

$$\Delta S_{reaction}^o = -121.7 \left[\frac{J}{K.mol} \right] \quad (23)$$

The relation of free energy change and the potential difference between the cell electrodes can be written as follows:

$$\Delta G = -nFE \quad [J/mol] \quad (24)$$

Thus, we can calculate the standard potential E^o when rewriting the equation (24) and combining with the equation ΔG^o (19):

$$E^o = -\frac{\Delta G^o}{nF} = -\frac{\Delta H_{reaction}^o - T\Delta S_{reaction}^o}{nF} [V] \quad (25)$$

Now the standard voltage E^o at 25 °C is 1.23 V.

• ***From the Standard Reduction Potential:***

From Figure 2.4, we can observe that the standard potentials of two VRFB electrodes are as follows:

The standard potential of a cell can be determined by subtracting cathode standard potential to the anode standard potential. Therefore, the standard potential of the VRFB can be calculated as:

$$E^o = E_{cathode}^o - E_{anode}^o = 1.255 \text{ V}$$

Figure 2.4 Potential diagrams for the vanadium species in the strong acidic solutions.

In comparison with the thermodynamic method, the standard potential calculation from standard reduction potential also gives a similar result. [31]

c. Concentration of Vanadium Ions

In the redox reactions, the ion concentrations are changed because of the vanadium ions transformation and the protons H^+ variation (produced or consumed). For example, during the discharging process, V(II) and V(V) are consumed and their concentrations should decrease; and V(III) and V(IV) are produced and therefore their concentrations should rise. During the charging process, this concentration change is reversed.

Table 2.6 The variation of different vanadium ions concentration during the charging and discharging process of the VRFB.

Ions	Salt	Concentration		Electrolyte
		Charge	Discharge	
V(II)	VSO ₄	↑	↓	Negative
V(III)	0.5 V ₂ (SO ₄) ₃	↓	↑	Negative
V(IV) or VO ²⁺	VOSO ₄	↓	↑	Positive
V(V) or VO ₂ ⁺	0.5 (VO ₂) ₂ SO ₄	↑	↓	Positive

• **Electron Exchange Rate:**

In general, the reaction rate is proportional to the concentration changes. For VRFB system, each vanadium redox reaction involved with an electron. Thus, the change in concentration is also corresponding to the electrical current. Therefore, the variation rate of the concentration can be estimated as follow:

$$Q_c = n_{e^-} \cdot e = \int i(t) dt \quad [C] \quad (26)$$

where Q_C is the charge, n_{e^-} is the number of electrons, e is the elementary charge, I is the current, and t is the time. From equation (26), we can calculate the number of electrons n_{e^-} involved for a specified current:

$$n_{e^-} = \frac{1}{eN_A} \int i(t) dt \quad [mol] \quad (27)$$

where N_A is the Avogadro number. From that, the definition of a molar flow-rate of electrons N_{e^-} can be expressed by:

$$N_{e^-}(t) = \frac{1}{eN_A} i(t) \left[\frac{mol}{s} \right] \quad (28)$$

In a single cell, an electron is produced from the oxidation reaction of a vanadium ion in this half-cell, traveling through the electrodes and after that being caught by the reduction reaction of another vanadium ion in the opposite side. In a practical system, with a stack contained N_{cell} cells, the electron will transfer across the bipolar plate to the neighboring cell (Figure 2.5). Therefore, if there is one electron flowing through the external circuit, there are N_{cell} vanadium redox reactions happen. Hence, the total molar flow-rate of electrons N_{e^-tot} for a stack is easy to calculate by multiplying (28) with the number of cells: [30]

$$N_{e_{tot}}(t) = \frac{N_{cell}}{eN_A} i(t) = \frac{N_{cell}}{F} i(t) \left[\frac{mol}{s} \right] \quad (29)$$

Figure 2.5 Illustration of the electron transference through a stack (containing 3 single cells) during the discharging process.

• **Average Concentration of Vanadium Ions:**

During the operation of a VRFB system, there are four electrolyte concentrations need to be considered: the tank concentration C_{tank} , the input concentration C_{in} , the cell concentration C_{cell} and the output concentration C_{out} . Normally the input concentration C_{in} is equal to the tank concentration C_{tank} due to the big size of the tank in comparison with the electrolyte flow-rate. The change of the tank concentration C_{tank} is corresponding to the amount of vanadium electrolyte has been changed the oxidation state in the stack and equal to the number of electrons involved in the vanadium redox reaction. Thus, the value of C_{tank} relies upon the initial ion concentrations $C_{tank_i}^{initial}$ and the size of the tank V_{tank} , which can be expressed as:

$$\begin{aligned}
 C_{in_i}(t) &= C_{tank_i}(t) = C_{tank_i}^{initial} + \frac{1}{V_{tank}} \int b N_{e_{tot}}(t) dt \\
 &= C_{tank_i}^{initial} + \frac{1}{V_{tank}} \int \frac{b}{F} i(t) dt \quad \left[\frac{mol}{l} \right]
 \end{aligned} \tag{30}$$

Where the sign factor b is equal to -1 for V(II) and V(V) ions and 1 for V(III) and V(IV) ions.

Assuming the system reacts immediately to the operating conditions, the output concentration C_{out} can be calculated based on the input concentration C_{in} , the electrolyte flow-rate Q and the electrons molar flow-rate N_{e-tot} :

$$C_{out}(t) = C_{in_i}(t) + b \frac{N_{e_{tot}}(t)}{Q(t)} = C_{in_i}(t) + \frac{b N_{cell}}{F} \frac{i(t)}{Q(t)} \left[\frac{mol}{l} \right] \tag{31}$$

d. Concentration of Protons

In the VRFB electrolytes, beside of the vanadium ions, protons H^+ and sulfate ions SO_4^{2-} also partially present in the redox reaction. These ions are very important to keep the charge balance and the preservation of mass. [32] The full ionic equations in Figure 2.6 can be used to explain all electrochemical mechanisms during VRFB operation.

Figure 2.6 The full ionic equations of the VRFB during the charging process.

In general, the proton concentration in the positive electrolyte is proportional to the amount of VO^{2+} oxidation during the charging process. During discharging process, the proton concentration can be identified by the quantity of sulfuric acid dissolved in the electrolyte, and therefore the proton concentration, in this case, can be determined, $C_{H^+,discharge}$. Now the concentration of protons in the positive electrolyte can be expressed as [30]:

$$C_{H^+} = C_{H^+,discharge} + C_{VO^{2+}}[M] \quad (32)$$

However, it should be noted that in practice, the concentration of “free” proton can only be calculated if we take into account the concentrations of HSO_4^- , H_2SO_4 , SO_4^{2-} , $\text{V}_x(\text{SO}_4)_y^{n+}$, etc. The concentration of bisulfate typically exceeds that of sulfate at these low pH values. Also, the vanadium species can form complexes with sulfate or bisulfate. Additionally, the V(IV) and V(V) species complex with each other (maybe with sulfate included) to form something like $\text{V}_2\text{O}_3^{3+}$.

e. The State of Charge

The state of charge represents the percentage of V(II) present in the negative electrolyte (which is equal to the percentage of V(V) in the positive electrolyte). Conventionally “0% state of charge” refers to the battery having in the negative electrolyte 100% V(III) and 0% V(II) and in the positive electrolyte 100% V(IV) and 0% V(V). And for “100% state of charge”, that means the battery has 0% V(III) and 100% V(II) in the negative electrolyte, and 0% V(IV) and 100% V(V) in the positive electrolyte. The state of charge SOC equation can be written as:

$$SOC = \frac{C_{V^{2+}}}{C_{V^{2+}} + C_{V^{3+}}} = \frac{C_{VO_2^+}}{C_{VO^{2+}} + C_{VO_2^+}} [\%] \quad (33)$$

f. Internal Losses

As discussed before, the equilibrium state is terminated if there is a current through the stack and the internal losses U_{loss} occur. These losses are regarded as the energy required to supply for the redox reaction to keep on at the given rate and often called as overpotentials:

$$U_{loss}(t) = \eta_{act}(t) - \eta_{conc}(t) - \eta_{ohm}(t) - \eta_{ion}(t)[V] \quad (34)$$

where η_{act} is the activation losses, corresponding to the initiation energy of charge transfer; η_{conc} is concentration losses, caused by the difference of concentration between the electrode surface and the bulk solution; η_{ohm} is the ohmic losses in the electrode components; and η_{ionic} is ionic losses in the electrolytes and the membranes. But these internal losses are often appropriate only to specific conditions and rarely found in the literature. Because of that, the internal losses can be replaced by an equivalent resistance:

$$U_{loss}(t) = R_{eq,charge/discharge}i(t)[V] \quad (35)$$

where $R_{eq,charge}$ is the charge resistance and $R_{eq,discharge}$ refers to the discharge resistance; these resistances depend on electrode materials, the electrolyte, the stack design and can be experimentally determined. [30]

g. Efficiency

Efficiency is one of the most important parameters to evaluate the performance of storage system. In this study, we consider three different efficiencies of VRFB: the energy efficiency, the coulombic efficiency, and the voltage efficiency.

The energy efficiency η_{energy} is identified as the ratio of the output energy during the discharging process to the supplied energy during the charging process:

$$\eta_{energy} = \frac{\int P_{VRFB,discharge}(t)dt}{\int |P_{VRFB,charge}|(t)dt} \quad (36)$$

The Coulombic efficiency $\eta_{coulombic}$ can be calculated by the ratio of $Q_{discharge}$ (the extracted charge from the system during the discharging process) to Q_{charge} (the supplied charge during the charging process):

$$\eta_{coulombic} = \frac{Q_{discharge}}{Q_{charge}} = \frac{\int i_{discharge}(t)dt}{\int |i_{charge}(t)|dt} \quad (37)$$

The voltage efficiency of VRFB, in the academic view, can be taken as the ratio of Coulombic to energy efficiency. Besides, the ratio of $U_{stack,discharge}$ (the total stack voltage during the discharging process) to $U_{stack,charge}$ (the total stack voltage during the charging process) can be also used to express the voltage efficiency:

$$\eta_{voltage} = \frac{\eta_{energy}}{\eta_{coulombic}} = \frac{\int U_{stack,discharge}(t)dt}{\int U_{stack,charge}(t)dt} \quad (38)$$

The voltage efficiency $\eta_{voltage}$ is calculated for a charge and discharge cycle at constant current. It is a measure of the ohmic and polarization losses during the cycling. However, when considering the voltage efficiency of a VRFB system with the mechanical losses P_{mech} (from the pump losses), $\eta_{voltage}$ is not equal to the ratio of η_{energy} to $\eta_{coulombic}$. [30]

h. Relationship between Open Circuit Voltage (OCV) and Stage of Charge (SOC)

The state of charge can be determined by measuring the open circuit voltage (OCV) or an electrolytic cell in which the positive and negative electrolyte is conveyed.

Table 2.7 The estimated value of SOC based on different OCV values.

Relation of Open Circuit Voltage and State of Charge									
SOC (%)	OCV (V)	SOC (%)	OCV (V)	SOC (%)	OCV (V)	SOC (%)	OCV (V)	SOC (%)	OCV (V)
1	1.16453	21	1.33719	41	1.3909	61	1.4365	81	1.4917
2	1.20089	22	1.34046	42	1.3932	62	1.4389	82	1.4952
3	1.22248	23	1.34363	43	1.3955	63	1.4412	83	1.499
4	1.23803	24	1.34671	44	1.3978	64	1.4436	84	1.5029
5	1.25027	25	1.34971	45	1.4001	65	1.4461	85	1.507
6	1.26042	26	1.35263	46	1.4023	66	1.4485	86	1.5113
7	1.26913	27	1.35549	47	1.4046	67	1.451	87	1.5159
8	1.27678	28	1.35828	48	1.4069	68	1.4536	88	1.5207
9	1.28363	29	1.36102	49	1.4091	69	1.4561	89	1.526
10	1.28985	30	1.36371	50	1.4114	70	1.4587	90	1.5316
11	1.29555	31	1.36635	51	1.4136	71	1.4614	91	1.5378
12	1.30084	32	1.36894	52	1.4159	72	1.4641	92	1.5445
13	1.30577	33	1.3715	53	1.4181	73	1.4668	93	1.5521
14	1.3104	34	1.37402	54	1.4204	74	1.4697	94	1.5608
15	1.31478	35	1.3765	55	1.4227	75	1.4725	95	1.5708
16	1.31893	36	1.37896	56	1.4249	76	1.4755	96	1.583
17	1.32289	37	1.3814	57	1.4272	77	1.4785	97	1.5985
18	1.32668	38	1.3838	58	1.4295	78	1.4817	98	1.62
19	1.33031	39	1.3862	59	1.4318	79	1.4849	99	1.6563
20	1.33381	40	1.3885	60	1.4342	80	1.4882		

Using the open circuit voltage, the SOC is calculated using the Nernst equation applied to the complete charging process.

$$OCV = E_{cell} = E_{cell}^o + \frac{RT}{nF} \ln \left(\frac{C_{VO_2^+} \cdot C_{V^{2+}} \cdot C_{H^+}^2}{C_{VO^{2+}} \cdot C_{V^{3+}}} \right) [V] \quad (39)$$

We have: $C_{VO_2^+} = C_{V^{2+}}$, $C_{VO^{2+}} = C_{V^{3+}}$ and also, $C_{VO_2^+} \propto SOC$, $C_{VO^{2+}} \propto (1 - SOC)$

Therefore, $C_{VO_2^+} = \frac{C_{VO_2^+}}{SOC^*}$ and $C_{VO^{2+}} = \frac{C_{VO^{2+}}}{1-SOC^*}$ (SOC^* is the state of charge expressed as a fraction).

Figure 2.7 The relation curve of Open Circuit Voltage (OCV) and State of Charge (SOC).

Replacing the concentration term with the SOC, we have:

$$OCV = E_{cell} = E_{cell}^o + \frac{RT}{nF} \ln C_{H^+}^2 + \frac{RT}{nF} \ln \left(\frac{SOC^{*2}}{(1 - SOC^*)^2} \right) [V] \quad (40)$$

The Nernst equation should always be used with activities rather than concentrations, and also for a cell, one should include a membrane junction

correction. Based on some experimental works (conducted by Gildemeister energy solution), we obtain the correction of the SOC estimation based on the OCV for the solution of 1.6M $V^{3.5+}$ in 4.5 M H_2SO_4 :

$$OCV = 1.38 - 0.00193(T - 273) + \frac{RT}{nF} \ln \left[\frac{(1.8 \times SOC' + 3)(1.8 \times SOC' + 4.8)SOC^2}{(1 - SOC')^2} \right] \quad (41)$$

where: 1 SOC' = 100% SOC. The relation of OCV and SOC, in this case, are showed in Figure 2.7 and Table 2.7.

2.3.2 Structure of Vanadium Redox Flow Battery

The main components of a VRFB system include two electrolyte tanks, two pumps and cell stack.

Figure 2.8 The schematics of the main components in a VRFB system.

A single cell stack includes two end plates, two current collectors, two bipolar plates, two carbon felts, two gaskets, two electrodes and one membrane. Figure 2.9 shows the detail of different components in a VRFB single cell:

- 1 - Bolt and nut: connect the cell components.
- 2 - End plates: made of thick stainless steel to uniformly distribute compressive stress on the cell.
- 3 - Insulating polypropylene plate: prevent shorting of the cell.
- 4 - Current collecting plates: copper plate acts as the current collecting plate and a connection to the external circuitry.

Figure 2.9 The detail of different components in a VRFB single cell.

- 5- Graphite bipolar plate: acts as the current collector for the electrode, as direct exposure of the copper to the porous graphite felt electrode will result in rapid corrosion of the copper plate as it will be exposed to the highly acidic electrolyte.
- 6 - Graphite felt electrode: acts as the main reaction site for the cell, through which the electrolyte is pumped.

7 - Polypropylene electrolyte pipe connects the flow frame to the electrolyte pipe.

8 - Gasket: an incompressible poly-tetrafluoroethylene gasket serves as a seal between the flow frame and the membrane.

9 - Membrane: commercial Nafion membrane is used as the ion-selective membrane for the cell, and must be large enough to fully separate the two half-cells.

10 - Flow frame is designed so as to allow an even distribution of the electrolyte flow to minimize dead regions.

a. Electrolytes

In a VRFB, a solution of V(III)/V(II) is used as the negative electrolyte (anolyte), and the solution of V(V)/V(IV) is used as the positive electrolyte (catholyte). H_2SO_4 is the most-common supporting electrolyte with the concentration is often less than 5 M. By optimizing the stability and the solubility of vanadium species in H_2SO_4 , the concentration of vanadium is also controlled at less than 2 M. It has been confirmed that the solubility of VOSO_4 (V(IV)) is decreased when the concentration of H_2SO_4 is rising, as shown in the Figure 2.10. [31, 33] Moreover, temperatures also can enhance the solubility of VOSO_4 in H_2SO_4 and the effect becomes stronger at a lower concentration of H_2SO_4 . [33]

In principle, the energy density of VRFB is controlled by the vanadium species concentration: higher concentration will bring out higher energy capacity. However, as mentioned before, the vanadium concentration is restricted due to the formation of solid vanadium oxide precipitates. For instance, when the

vanadium concentration increases beyond 2 M in H_2SO_4 solution, there is the formation of V_2O_5 precipitates in the positive electrolyte at temperatures higher than 40 °C, and the formation of VSO_4 (or VO) precipitates in the negative electrolyte under 10 °C [34, 35]. The vanadium precipitation rate depends on the temperature, the concentration of vanadium and H_2SO_4 , and the state of charge (SOC) of the vanadium electrolyte [34, 36, 37]. To inhibit the precipitation of both positive and negative electrolytes, several organic or inorganic agents have been added into the vanadium electrolyte as stabilizing agents, often called as the additives.

Figure 2.10 Relationship of V(IV) solubility and H_2SO_4 concentration at 25 °C.

The electrochemical properties of vanadium redox couples are strongly dependent on electrodes and operational conditions (electrode material, temperature, charge/discharge current, etc). Figure 2.11 shows an example of a cyclic voltammogram of 1 M VOSO_4 in 2 M H_2SO_4 solution with a glassy carbon as the working electrode and Ag/AgCl electrode as the reference electrode.[38] Four oxidation/reduction peaks are clearly showed in the CV curve, including the oxidation peak of V(IV) to V(V) (1.0 – 1.1 V), the reduction peak of V(V) to V(IV) (about 0.7 V), the oxidation peak of V(II) to V(III) (about –0.4 V), and the reduction peak from V(III) to V(II) (about –0.75

V). The large value of the peak potential separation within such potential window (the difference between anodic and cathodic peaks) indicates the slow kinetics of the electrochemical reactions for both V(V)/V(IV) and V(III)/V(II) redox couples. Therefore, the electrode modifications are required to optimize the electrochemical activity of redox couples in vanadium electrolytes. [10]

Figure 2.11 Cyclic voltammogram of 1 M VOSO₄ in 2 M H₂SO₄ solution at different scan rates: (1) 100, (2) 200, (3) 300, (4) 400, and (5) 500 mV.s⁻¹.

b. Electrode/Bipolar Plates

In a practical system, to reduce the electrical resistance, the VRFB porous electrodes are often combined with a bipolar plate as one component [10]. The bipolar plate plays a role as a current collector, isolating the positive electrolyte and negative electrolyte into two different sides. Moreover, to help to support the porous electrodes and to guide the flow of vanadium electrolytes through the cell, the bipolar plate is often designed with flow channels on both sides. To fulfill the operational requirements of VRFB, the bipolar plate must have many excellent properties: low bulk and contact resistance, high structural and mechanical stability, and chemically compatible with all chemicals present in

the electrolytes during operation. Because of that, the material choices are very limited. There are some materials currently often used in VRFB: conductive carbon-polymer composites, polymer-impregnated graphite plates, and polymer-impregnated flexible graphite. [39 - 48]

For the electrodes, to achieve a high performance, the electrodes also must demonstrate a low electrical resistance, high surface area, chemically compatible, appropriate porosity, and high electrochemical activity. Currently, graphite– or carbon-based materials are the most popularly used materials for VRFB electrodes, which often in forms of felt or porous structures. However, these types of electrode materials often show the poor electrochemical activity and reversibility with the redox reactions of vanadium species. To improve the electrochemical properties of such VRFB porous electrodes, there are several methods to modify the electrode property, including chemical treatment, heat treatment, electrochemical oxidation, and metal doping.

The heat treatment is a simple method to modify the property of porous electrodes of the VRFB. It has been reported that the presence of functional groups, such as C=O or C-O-H groups, on the electrode surface can catalyze the vanadium redox reactions. In this case, improvement of electrochemical activity of porous electrode after the heat treatment process can be attributed to the surface hydrophilicity enhancement as well as the formation of functional groups. [49, 50]

Chemical treatment is also can enhance the electrochemical properties of VRFB electrode materials. Some active agents (NaOCl , KMnO_4 , $(\text{NH}_4)_2\text{S}_2\text{O}_8$) and acids (H_2SO_4 , HNO_3) [51] have been used as the activation agents to modify the surface of porous carbon materials. The increase in concentrations of C=O and C-OOH surface functional groups will enhance the activity of the VRFB after chemical treatment. These functional groups not only act as the active sites

and catalyze for vanadium redox reactions but also increase the hydrophilicity of the graphite felt electrodes. Moreover, they also help to accelerate the electron and oxygen transfer processes during operation of VRFB. [52]

Electrochemical oxidation is a modification method was recently used to improve the electrochemical property of the VRFB porous electrodes. This method can create the C-OOH functional groups on the surface of porous electrodes, causing to the increase of surface area and the O/C ratio, and hence can accelerate the electron transfer process during the operation of VRFB. [53, 54]

Another method to modify the electrochemical properties of carbon electrodes in VRFB is metal-doping. By impregnating graphite fibers in the solution containing metal ions (Mn^{2+} , Pd^{2+} , Ir^{3+} , In^{3+} , Pt^{4+} , Au^{4+} , Te^{4+}), the electrochemical performance of carbon and graphite-based electrodes is improved. [55, 56] However, the metal-doping should be conducted with caution because in some cases, hydrogen evolution rates were enhanced more significantly than vanadium redox kinetics.

c. Membranes and Separators

The membrane is an important component in a VRFB that separates the anode and cathode compartments, and at the same time, keeping the electrical neutrality of the cell by allowing the transport of charge carriers. To be able to work in the strong acidic environment and also to reduce the resistance and power loss, membrane for VRFB has to fulfill some requirements: high and fast ionic conductivity, high selectivity of charge transport (maximize the charge carriers transport (H^+ , SO_4^{2-}) but minimize the vanadium cations transport), limited in the water transport across the membrane, high chemical stability, strong structural and mechanical stability and low cost.

There are two most common types of the membrane have been investigated for VRFB applications: cation and anion exchange membranes. In addition, there are also some studies on the traditional dense membrane, microporous membranes.

The Nafion membranes are probably the most common-used membrane in VRFB applications among widely researched materials. The Nafion membranes, in general, have a high proton conductivity, high chemical stability in strong acidic and oxidative environments. Even so, the vanadium ions still can react with each other by crossing through the Nafion membrane, causing the cell capacity loss and the reduction of energy efficiency in VRFB systems. Many factors can affect the transportation rate of the vanadium ions through the membrane: the vanadium ions H_2SO_4 concentrations, the electrolyte state of charge, the properties of membranes and the temperature. Sun *et al.* reported in a study that the diffusion coefficients of the vanadium ions through the Nafion 115 membrane can be arranged as follows: $\text{V(II)} > \text{V(V)} > \text{V(IV)} > \text{V(III)}$. [57] To improve the properties of Nafion membranes, some modification methods have been investigated. One of them is the synthesis of Nafion based hybrid membranes, such as Nafion/polyethylenimine (PEI) composite membrane, Nafion/sulfonated poly(ether ether ketone) (SPEEK) layered composite membrane, Nafion/pyrrole membrane. The hybrid structure of Nafion based membranes could help to reduce the vanadium ion permeability through the Nafion membrane and improve the energy efficiency of the VRFB systems. [10]

Discovery of alternative membranes is another solution to promote the performance of VRFB. In the past few years, some new types of IEM, including hydrocarbon-based proton exchange membrane (PEM) [58-60], anion exchange membrane (AEM) [61-63] and nanofiltration membranes (NFs) [64, 65], have been investigated for use in VRFB application. In which, it is reported that AEM has low vanadium permeability, which results from the

Donnan exclusion effect among the positively charged functional groups of the membrane and vanadium ions [66-68]. Therefore, it is received considerable attention for application in VRFBs. However, one concern related to AEM is the low chemical stability of functional groups in the strong acid medium. [69]

2.4 Thermal Stability of Vanadium Based Electrolyte

It is known that the vanadium concentration can determine the energy density of VRFB: higher vanadium concentration will bring out higher energy capacity. However, as mentioned in the part 2.3.2, the vanadium concentration is restricted by the formation of solid vanadium oxide precipitates, with the V_2O_5 formation in the positive electrolyte at temperatures more than 40 °C and $VOSO_4$ (or VO) formation in the negative electrolyte under 10 °C [34, 35]. The vanadium precipitation rate depends on the heating time, temperature, the concentration of vanadium and H_2SO_4 , and the state of charge (SOC) of the vanadium electrolyte [34, 36, 37]. In practical operation, the precipitation at the positive side is more important and appears more frequently due to the excess heat released from the working system and weather condition.

2.4.1 Effect of Temperature on the Positive Vanadium Electrolyte

It is known that the positive vanadium species, particularly is V(V), have relatively low solubility in H_2SO_4 supporting electrolyte [70, 71]. The positive electrolyte of the VRFB consists of a mixture of vanadium salts in oxidation states 4+ (IV) and 5+ (V), dissolved in sulfuric acid, with a total vanadium concentration of typically $1.5 - 2 \text{ mol.dm}^{-3}$. As the battery is charged, the ratio of V(V) to V(IV) increases. Therefore, the VRFB is generally operating with the positive electrolyte in a metastable state. Consequently, there exists the risk that V(V) ions may condense to form V_2O_5 nuclei via a two-step process. In sulfuric acid, at typical electrolyte concentrations, V(V) species exist

predominantly in the form of the hydrate penta-coordinated $[\text{VO}_2(\text{H}_2\text{O})_3]^+$ cation at 25 °C. At temperatures ≥ 40 °C precipitation occurs notably, e.g. via the deprotonation and condensation reactions, given below [71]:

At this stage, the small-sized V_2O_5 nuclei still can be dissolved back into the electrolyte solution at lower state-of-charge (SOC) when the battery is discharged. However, with the increased heating time or temperature, the precipitation of V_2O_5 develops faster, forming a bigger precipitate particle, which almost irreversible in the charged electrolyte, and damaging the operation system (blocking the electrolyte flow). In practice, the kinetics of precipitation is very strongly dependent on temperature and state-of-charge (SOC). The detailed description of the positive vanadium electrolyte precipitation at high temperatures is illustrated in Figure 2.12.

Figure 2.12 Precipitation process of the positive vanadium electrolyte at high temperatures and long heating time.

In the past few years, there are many studies on the thermal stability of the positive vanadium electrolyte have been conducted at various high temperatures.

Table 2.8 summarizes several reports on pristine positive vanadium electrolytes and their corresponding times to precipitate.

Table 2.8 Temperature dependence of the positive vanadium electrolyte stability.

Electrolyte formula	Temperature (°C)	Time to precipitate (h)
3 M V(V)/5 M H ₂ SO ₄ [72]	45	6
	60	1
2 M V(V)/3 M H ₂ SO ₄ [73]	40	18
	50	6
1.8 – 2.2 M V(V)/5 M H ₂ SO ₄ [74]	45	12.3
	50	5.2
	60	1.8
2 M V(V)/5 M H ₂ SO ₄ [75]	40	95
	50	18
1.8 M V(V)/5 M H ₂ SO ₄ [76]	50	4
1.6 M V(V)/3 M H ₂ SO ₄ [77]	50	2
2.8 M V(V)/5 M H ₂ SO ₄ [78]	45	18
	60	1
3 M V(V)/5 M total SO ₄ ²⁻ [79]	30	72

By careful control of temperature and state-of-charge, VRFB manufacturers avoid precipitation. However, these measures add to the cost and can reduce performance. Therefore, much effort has been made to find electrolyte additives that would allow wider operational temperature windows.

2.4.2 Thermally Stable Additives for the Positive Vanadium Electrolyte

To screen an effective additive, researchers usually rely on the thermal precipitation mechanism of the positive vanadium electrolyte. However, the explanation how the additive stabilizes the positive electrolyte solution at high temperatures is still complicated. Many research works have been done to explain the mechanism of the thermal stability improvement when adding some

stabilizing agents. Here are some most reliable mechanisms have been proposed after a number of investigations on vanadium additives:

The first thermal improvement explanation refers to the presence of more H^+ ions in the vanadium electrolyte when adding the stabilizing agents. These H^+ ions enhance the transformed reaction of solid vanadium into $V(V)$ ions. This can be achieved by using acid as an additive or co-supporting electrolyte. However, the increasing corrosion of electrolyte solution is also a serious issue that needs to pay attention [72, 80].

The second option is to inhibit the deprotonation of hydrate penta-coordinated $[VO_2(H_2O)_3]^+$ structure by adding the additive that can form the soluble complex with $V(V)$ ions. A typical example of this type of additive can be seen in the case of HCl , in which the chlorine (Cl^-) ion combines with $V(V)$ in form of soluble complex structure while giving no other negative effects [72, 81]:

Lastly, it is possible to use some organic additives can adsorb via polar functional groups, such as OH , CHO , $C=O$, on the initial V_2O_5 nuclei, hindering further growth and formation of particles large enough to precipitate. In this case, the V_2O_5 nuclei could be dissolved back to the electrolyte solution during the discharging process [73].

Since the first inventions of VRFB, there are many different organic and inorganic additives have been investigated to improve the thermal stability of vanadium electrolyte to a wider range of temperature.

a. Inorganic Additives

The addition of inorganic additives into vanadium electrolyte mainly aims to form the soluble neutral species with hydrate penta-coordinated V(V) ion or enhance the transformed reaction of solid vanadium into V(V) ions as discussed above.

The most commonly used and effective inorganic additive to date, as mentioned before, is HCl [82, 83]. Other common stabilizers to date are H_3PO_4 [75, 79, 84] and $(\text{NH}_4)_2\text{SO}_4$ [85], which are rather limited in their effectivity.

Gang Wang *et al.* have investigated the effect of some inorganic acids on the thermal stability of 3 M V(V) in 5 M H_2SO_4 electrolyte solution at different temperatures. The results show that 0.5 wt.% of HCl, $\text{CH}_3\text{SO}_3\text{H}$, $\text{CF}_3\text{SO}_3\text{H}$, PTA could enhance the thermal stability of such positive vanadium electrolyte from $-5\text{ }^\circ\text{C}$ to $45\text{ }^\circ\text{C}$. Besides, the electrochemical activities of vanadium redox reactions with these acid additives were also increased compared to the pristine electrolyte solution. [72]

The report by Jianlu Zhang *et al.* claimed that the combination of polyacrylic acid (PA) and with $\text{CH}_3\text{SO}_3\text{H}$ can stabilize the positive vanadium electrolyte at high temperatures. In which, the solution of 1.8 M V(V) in 5 M H_2SO_4 can be stable to the temperature up to $40\text{ }^\circ\text{C}$ by using PA. [75]

Kausar *et al.*, with a study on the electrolyte solution of 1.8 M V(V) in 5 M total SO_4^{2-} , have demonstrated the performance of several phosphate salt compounds (ammonium phosphate, potassium phosphate, sodium hexametaphosphate, phosphoric acid, ammonium phosphate) in the thermal stabilizing of V(V) ions at $50\text{ }^\circ\text{C}$. The thermal stability test shows that the time to precipitate for 1.8 M pristine 100% SOC V(V) solution is 3 days; while for

sodium hexametaphosphate, ammonium phosphate and ammonium sulfate is 5, 6 and 7 days for solutions, respectively. Especially, the combination of 1% phosphoric acid and 2% ammonium sulfate showed the best thermal stabilizing ability for positive vanadium electrolyte, which gave the value of > 150, 125, 32 and 15 days for 80, 90, 95 and 100% SOC solutions, correspondingly. [76]

A recent paper of Roe *et al.* introduced a high concentration vanadium electrolyte up to 3 M in 5 M total SO_4^{2-} . The thermal stability of this electrolyte formula was maintained by adding several stabilizing agents. In which, the solution containing 1 wt.% H_3PO_4 additive could improve the time for precipitation to over 47 days at 30 °C, compared to the value of 3 days for the blank solution. In addition, after 32 days, 3 M V(V) solutions with the presence of 1 wt.% sodium pentapolyphosphate, 1 wt.% K_3PO_4 and 2 wt.% $(\text{NH}_4)_2\text{SO}_4$ + 1 wt.% H_3PO_4 indicated the value of V(V) concentrations of about 2.7, 2.7 and 2.6 M, correspondingly, compared to 2.4 M V(V) in the pristine solution. [79]

The phosphates additives, recently, have been demonstrated that could effectively suspend the precipitate time of V(V) solution. The results show that the solution of 1.6 M V(V) in 3 M H_2SO_4 with the addition of 0.1 wt.% of Na_3PO_4 , Na_2HPO_4 , NaH_2PO_4 , and $\text{NH}_4\text{H}_2\text{PO}_4$ additive significantly improved the thermal stability up to 25, 17, 36 and 36 h, respectively, in comparison with the value of 2 h for the blank additive-free electrolyte. [77]

Another work on the electrolyte solution of 2 M V(V) solution in 4 M total SO_4^{2-} indicated that the addition of 0.05 M sodium pyrophosphate tetrabasic (SPT) could improve the long-term stability and also electrochemical performance. [86]

Moreover, a wide range of inorganic additives have been also taught by Prof. Skyllas-Kazacos, however, only a few of them were practically tested [87, 88].

b. Organic Additives

The organic stabilizing agent also attracts a huge attention thanks to its capability to hinder the growth of V_2O_5 nuclei to the larger precipitate particle. In the last decade, many organic compounds have been found to be effective thermally stable additives for the positive vanadium electrolyte.

The research of Gang Wang *et al.* (see above) also reported the improvement when adding some organic stabilizing agents. Organic additives such as polyacrylic acid (PAA), oxalic acid ($(COOH)_2$), methacrylic acid (MAA), 5-sulfosalicylic acid dehydrate (SHA) could also strongly improve the stability of V(V) solution from up to 45 °C compared with the original solution. For example, at 45 °C, the time to precipitate of the blank electrolyte is 6 h, while this value for PPA, oxalic acid, MAA, SHA is 25, 30, 18 and 34 h, respectively [72].

Zhang *et al.* reported the benefit of some organic stabilizing agents for ~2 M V(V) in 5 M H_2SO_4 solution. In detail, the stability of such positive vanadium solution at 40 °C was relatively improved from less than 95 h, up to ~ 150 h by the addition of polyacrylic acid (0.1–1 wt.%), ~236 h for CH_3SO_3H (2.1–7 wt.%), 120 h for Darvan®C (0.3 wt.%), no precipitation for isopropanol (10 wt.%), glucose (1.0 wt.%), polyethylene glycol (PEG, 0.3 wt.%), dimethyl sulfoxide (DMSO, 10 wt.%), and Tween 20 (0.01 mL).[75]

Research on 2 M V(V) in 3 M H_2SO_4 electrolyte showed that the addition of 1 wt.% L-glutamate could help to delay the initiation of precipitation in the positive vanadium electrolyte for 12 h at 40 °C and for 5 h at 50 °C [73].

In another work, electrolyte stability tests at 45, 50, and 60 °C confirmed that the presence of 0.05–0.1 wt.% coulter dispersant IIIA (containing mainly

coconut oil amine adduct with 15 ethylene oxide groups) to the ~2 M V(V) in 5 M H₂SO₄ electrolyte could strongly increase the time of precipitate formation from 1.8–12.3 h to 30.3 h–19.3 days [74].

In another work, polyacrylic acid and its mixture with CH₃SO₃H were reported as an effective stabilizing candidate for vanadium positive electrolyte solution at temperatures higher than 40 °C [75].

Another study of Wang *et al.* has employed several ionic organic agents as the thermally stable additives for positive vanadium electrolyte at the temperatures up to 60 °C. They claimed that the cationic organic additives could remarkably increase the thermal stability of the V(V) electrolyte at high temperatures. For instance, at 60 °C, the pristine solution of 2.8 M V(V) in 5 M H₂SO₄ showed the precipitation after 1h. By adding 0.5 wt.% of 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC), methylene blue (MB), cationic-type polyacrylamide (CPAM), this number increased up to 3, 4 and 3 h, correspondingly. [78]

Another work showed that the addition of 1-4 wt.% of trishydroxymethylaminomethane (Tris) can also improve the thermal stability of 2 M V(V) in 3 M H₂SO₄ electrolyte at 40 °C [89].

Another study reported that some organic compounds (fructose, mannitol, glucose, and D-sorbitol) could be used as thermally stable additives for the positive vanadium electrolyte [90].

Inositol, phytic acid, and sodium oxalate have been claimed to improve the thermal stability of 1.8 M V(V) in 3 M H₂SO₄ electrolyte at up to 60 °C [91, 92].

Some other additives, although not tested for thermal stability, but were proposed to improve the electrochemical properties of vanadium electrolyte [93].

2.5 Problems of Current Researches on Thermally Stable Additives for Vanadium Redox Flow Battery

Although a plenty of research has been done to improve the thermal stability of vanadium electrolyte, especially for the positive side, there are still many challenges need to be solved.

2.5.1 Safety Issues with Halogen and Acid Based Additives

The most effective additive to date is HCl and some other halogen agents, which have been suggested that halide ions can form soluble complexes such as $[V_2O_3X_{2.6}H_2O]^{2+}$, in which the halide ion hinders the deprotonation process to form V_2O_5 [82, 83]. However, halide in the electrolyte gives the risk of some safety issues: introduces the possibility to form toxic halogen gas under certain failure conditions (e.g. overcharging of cells); a very corrosive atmosphere of hydrogen chloride gas (for HCl additive) is formed in the tank and gas lines – this can also be a problem in the event of accidental spillage; the electrolyte is generally much more corrosive than the standard electrolyte, and therefore limits the materials of construction.

Other acid based additives (such as H_3PO_4 , HBO_3 ...) may not give the risk of toxic gas emission. However, the use of a large addition amount of acid additives will increase the corrosive level of final vanadium electrolyte.

2.5.2 Performance Demonstration of Tested Additive under Practical Conditions

Several additives have been tested demonstrated their performance under cell cycling conditions [73 - 79, 81, 86, 89], however, many others additives have only been tested in static conditions (cyclic voltammetry and/or electrochemical impedance spectroscopy). It is noted that an additive may be stable in a static condition, but not in dynamic flow condition of the cell due to the interaction with cell components (carbon electrode, ion exchange membrane...). In addition, even a flow cell test was employed to examine the effect of the additives, there are only a few studies applied the temperatures for the electrolyte, as showed similarly in static test [76, 77, 79]. Most of the cycling tests were conducted at the lab temperature (22 – 25 °C) to investigate the influence on cell efficiency but not the thermal stability. However, it is known that in practical condition, the electrolyte in a VRFB will be heated by the system operation itself and also probably by the impact of ambient temperature.

2.5.3 The Oxidation of Organic Additives in the Positive Vanadium Electrolyte

As discussed in the part 2.4.2, many organic additives have been investigated to improve the thermal stability of positive vanadium electrolyte at higher temperatures, which contain one or more polar functional groups. However, due to the strong oxidative behavior of V(V) ions, some organic chemicals, especially with the functional groups of OH, CHO, and C=O are known to be unstable in V(V) solutions [72, 75]. Waters *et al.* published a comprehensive study on the oxidation of organic compounds containing polar functional groups by V(V) in a series of articles in the 1960's, which are especially relevant in light of the most recent VRFB developments [94 - 107].

It is known that V(V) ions can oxidize some organics in acidic solution and hence be reduced to V(IV), especially over the long testing times typically employed at 40 – 50 °C. However, the effect of organic additives on the positive vanadium electrolyte and especially on the performance of VRFB has not been widely reported. In practice, the rate of precipitation of V₂O₅ is dependent on the SOC of the electrolyte (i.e. the relative concentration of V(V) to total vanadium). Therefore, it is clear that the apparent thermal stability improvement of an additive may be due to the reduction of V(V) to V(IV) in the test rather than a genuine hindrance of the condensation and/or polymerization of V(V).

At lower state-of-charge, the positive electrolyte is more thermally stable, but the usable capacity of the battery is reduced, and therefore this approach is not advantageous. It is also likely that many polymers would foul the ion exchange membranes or coat on the electrodes, causing the internal resistance of the battery to rise.

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Chapter 3

Experimental Methodology

This chapter describes the scope of work for this project, including the sequence of experiment and investigation will be conducted to find out a novel vanadium electrolyte formula. The material selection and preparation are also discussed in this chapter. In addition, all the characterization techniques employed in this Ph.D. study are also presented, including thermal stability test, electrochemical test, surface chemistry analysis, cell cycling test with temperature control. Moreover, the methods of data analysis, including errors are also pointed out.

3.1 Scope of Work

This 3.5 year Ph.D. study will look to develop a new vanadium-based electrolyte formulation through a series of development steps.

Figure 3.1 Scope of work for the study on thermally stable vanadium electrolyte additive.

The final outcome is introducing a novel advanced electrolyte formula with high thermal stability and safety to users.

3.1.1 Precipitation Test to Screen Effective Additives

Thermally stable additive screening is the first step to develop the novel electrolyte formula for the vanadium redox flow battery. Ideally, a large array of samples should be monitored to determine the average time to precipitation as a function of temperature and composition. Although precipitation times in 100% charged electrolyte (i.e. all vanadium in the +5 oxidation state) are easiest to prepare and monitor (due to their low optical absorption), solutions at lower charged states are more practically interesting (e.g. 80% - 90% SOC). Many techniques can be employed to detect the onset of precipitation (e.g. conductivity, viscosity, acoustic absorption [1], ICP of a solution sample, etc.). Colloid formation (the first stage of precipitation) has also been investigated by e.g. zeta-potential measurements (including in an acoustic field) and light

scattering techniques. However, due to the cost of many of the above techniques and also the complications associated with slow precipitation kinetics, many of the established techniques are not suitable for a large-scale additive screening.

Therefore, the common and simple static test, which includes a water-bath and a thermometer to control the temperature, is more suitable. One drawback is that the positive electrolyte solutions are strongly absorbing and it is hard to detect precipitate with the naked eye. In this case, the onset of precipitation should be extended to the further stage: the formation of large precipitate particles, which could be easy to observe at the bottom of the testing tube. In order to gain accurate information on a large library of compositions, the thermal stability test should be repeated several times with regularly checking.

The thermally stable additives, then, will be further investigated to examine the chemical stability in the strong oxidative medium of V(V) solution, especially for organic additives. Ultraviolet-visible spectroscopy and titration can be conducted to detect the oxidation of additives in the positive electrolyte. Moreover, the composition analysis should be also performed to clarify that there is no solid product formed between the positive vanadium solution and additive itself.

3.1.2 Electrochemical Testing of Thermally Stable Additives

It is essential that a stability additive is stable over the full range of chemical and electrochemical environments found in the vanadium redox flow battery, before testing in practical VRFB system. The electrochemical stability of the thermally stable additives will be investigated by cyclic voltammetry as well as electrochemical impedance spectroscopy.

3.1.3 Evaluation of Additive Influence on the Cell Performance

The stable additives are also required to demonstrate that they do not significantly reduce the efficiency of practical VRFB cell under cycling condition. More importantly, the novel thermally stable electrolyte is also demanded to maintain the long-term performance at high electrolyte temperatures (e.g. 40 – 50 °C), preventing the precipitation of the vanadium electrolyte.

3.1.4 Investigation the Effect of Additives on the Cell Components

It must also be demonstrated that the additive does not increase the cell resistance (e.g. by forming a film on the electrodes) or injure the membrane. Therefore, electrochemical testing of felts should be carried out with a short-list of suitable additives (provide after stage 3.1.1 – Thermally stable additive screening). The membrane may be studied by examining changes in the permeability to vanadium ions after a period of storage in the test electrolyte. Ex-situ FTIR of the membranes and felts may also be used to examine chemical changes.

3.1.5 Testing the Performance in 1 kW Stack

It is planned to design and build a 1 kW laboratory stack for testing in the other Ph.D. projects with SGL. This laboratory stack can also be used for studies of novel battery electrolytes and additives (interaction with this Ph.D. topic supervised by Gildemeister/Cellstrom). In particular cycle testing with a standard electrolyte and with the improved electrolyte would be required to demonstrate similar cycling stability and efficiencies at standard temperatures (< 40 °C). The improved electrolyte should also be tested at higher temperatures (e.g. 40 – 50 °C) to demonstrate stability in this region.

3.2 Materials Selection and Preparation

3.2.1 Proposed Additives for Positive Vanadium Electrolyte

The proposed additives for thermal stability screening were selected based on three thermal stabilizing mechanisms presented in the section 2.4.2. In this study, we classified all proposed compounds into inorganic additive and organic additive group. The list of the suppliers and grades of proposed inorganic additives are shown in Table 3.1:

Table 3.1 Proposed inorganic additives for vanadium electrolyte.

Type	Additive compound	Supplier
Inorganic acid	Hydrochloric acid (HCl) (reference additive)	Sigma-Aldrich, 36.5-38.0%, BioReagent
	Phosphoric acid (H ₃ PO ₄) (reference additive)	Sigma-Aldrich, 85 wt. % in H ₂ O, FCC, FG
	Boric acid (HBO ₃)	Sigma-Aldrich, ACS reagent, ≥99.5%
	Molybdic acid (H ₂ MoO ₄)	Sigma-Aldrich, ACS reagent, ≥85.0%
	Nitric acid (HNO ₃)	Sigma-Aldrich, ACS reagent, 70%
Inorganic salt	Ammonium dihydrogen phosphate (NH ₄ H ₂ PO ₄)	Sigma-Aldrich, 99.999% trace metals basis
	Diammonium hydrogen phosphate ((NH ₄) ₂ HPO ₄)	Sigma-Aldrich, ≥ 99.99% trace metals basis
	Ammonium phosphate ((NH ₄) ₃ PO ₄)	Sigma-Aldrich
	Ammonium nitrate (NH ₄ NO ₃)	
	Sodium pyrophosphate (Na ₄ P ₂ O ₇ • 10H ₂ O)	Sigma-Aldrich, 99.999% trace metals basis Sigma-Aldrich, ≥ 95%
	Ammonium metavanadate (NH ₄ VO ₃)	Sigma-Aldrich, 99.996% trace metals basis
	Ammonium persulfate ((NH ₄) ₂ S ₂ O ₈)	Sigma-Aldrich, ReagentPlus®, ≥99.99%
	Ammonium carbonate ((NH ₄) ₂ CO ₃)	Sigma-Aldrich, ACS reagent
	Ammonium sulfate ((NH ₄) ₂ SO ₄)	Sigma-Aldrich, ReagentPlus®, ≥99.0%
	Ammonium cerium sulfate	Sigma-Aldrich

$(\text{NH}_4)_2\text{CeSO}_4$	
Sodium molybdate (Na_2MoO_4)	Sigma-Aldrich, $\geq 99\%$
Sodium silicate nonahydrate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$)	Sigma-Aldrich, $\geq 98\%$
Ammonium hydrogen tungstate ($(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$)	Sigma-Aldrich, $\geq 99\%$

The proposed organic additives were divided into five groups: carboxyl compounds (containing only carboxylic group), alcohol compounds (containing only hydroxyl group), amide compounds (containing only amino group), alkyl sulfonic acid compounds (containing only sulfonic group) and multi-functional group compounds (containing 2 or more different functional groups). The list of the suppliers and grades of the additives are shown in the following table:

Table 3.2 Proposed organic additives for vanadium electrolyte.

Type	Additive compound	Supplier
Carboxyl	Oxalic acid (HOOCCOOH)	Sigma-Aldrich, purified grade, 99.999%
	Sodium oxalate ($(\text{COONa})_2 \cdot \text{H}_2\text{O}$)	Sigma-Aldrich, ACS reagent, $\geq 99.5\%$
	Potassium oxalate ($(\text{COOK})_2 \cdot \text{H}_2\text{O}$)	Sigma-Aldrich, ACS reagent, 99%
	EDTA disodium salts ($\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$)	Sigma-Aldrich, 98.5-101.5%
	Oleic acid ($\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$)	Sigma-Aldrich, $\geq 99\%$ (GC)
	Stearic acid ($\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$)	Sigma-Aldrich, technical grade, 90%
	Acetic acid (CH_3COOH)	Sigma-Aldrich, 99.8%, anhydrous
	Sodium acetate (CH_3COONa)	Sigma-Aldrich, anhydrous, for molecular biology, $\geq 99\%$
Alcohol	Resorcinol ($\text{C}_6\text{H}_6\text{O}_2$)	Sigma-Aldrich, ACS reagent, $\geq 99.0\%$
	Pinacol ($\text{C}_6\text{H}_{14}\text{O}_2$)	Sigma-Aldrich, 98%
	2-Methyl resorcinol ($\text{CH}_3\text{C}_6\text{H}_3(\text{OH})_2$)	Sigma-Aldrich, 98%
	Pyrogallol ($\text{C}_6\text{H}_6\text{O}_3$)	Sigma-Aldrich, $\geq 98\%$ (HPLC)
	Xylose ($\text{C}_5\text{H}_{10}\text{O}_5$)	Alfa-Aesar, 98+%
	Glucose ($\text{C}_6\text{H}_{12}\text{O}_6$)	Sigma-Aldrich, $\geq 99.5\%$

	PVA ((C ₂ H ₄ O) _n)	Sigma-Aldrich, Mw 9,000-10,000, 80% hydrolyzed
	myo-Inositol (C ₆ H ₁₂ O ₆)	Sigma-Aldrich, ≥ 99%
Amide	Melamine (C ₃ H ₆ N ₆)	Sigma-Aldrich, 99%
Alkylsulfo-nic acids	Methanesulfonic acid (CH ₃ SO ₃ H)	Sigma-Aldrich, ≥ 99.0%
Multi-functional group	Lactic acid (C ₃ H ₆ O ₃)	Sigma-Aldrich, ≥ 98%
	Cysteine (C ₃ H ₇ NO ₂ S)	Sigma-Aldrich, 97%
	Ascorbic acid (C ₆ H ₈ O ₆)	Sigma-Aldrich, 99%
	Citric acid (C ₆ H ₈ O ₇)	Sigma-Aldrich, ACS reagent, ≥ 99.5%
	Ammonium citrate (C ₆ H ₁₇ N ₃ O ₇)	Sigma-Aldrich, ~98% (capillary GC)
	Tannic acid (C ₇₆ H ₅₂ O ₄₆)	Sigma-Aldrich, ACS reagent
	Gelatin A	Sigma-Aldrich, gel strength 300, type A
	Gelatin B	Sigma-Aldrich, type B, powder, BioReagent
	Poly-Vinyl-Pyrrolidone (PVP10) (C ₆ H ₉ NO) _n	Sigma-Aldrich, average mol wt 10,000
	Poly-Vinyl-Pyrrolidone (PVP1300) (C ₆ H ₉ NO) _n	Sigma-Aldrich, average Mw ~1,300,000 by LS
	L-Glutamine (H ₂ NCOCH ₂ CH ₂ CH(NH ₂)CO ₂ H)	Sigma-Aldrich, ReagentPlus®, ≥ 99% (HPLC)
	Diisopropylamine ((CH ₃) ₂ CHNHCH(CH ₃) ₂)	Sigma-Aldrich, ≥ 99%
	L-Alanine (C ₃ H ₇ NO ₂)	Sigma-Aldrich, 99%
	Urea (CH ₄ N ₂ O)	Sigma-Aldrich, reagent grade, 98%
	Arginine (H ₂ NC(=NH)NH(CH ₂) ₃ CH(NH ₂)CO ₂ H)	Sigma-Aldrich, reagent grade, ≥ 98%
	Valine ((CH ₃) ₂ CHCH(NH ₂)CO ₂ H)	Sigma-Aldrich, reagent grade, ≥ 98% (HPLC)
	Lysine (H ₂ N(CH ₂) ₄ CH(NH ₂)CO ₂ H)	Sigma-Aldrich, ≥ 98% (TLC)

3.2.2 Electrolyte Preparation

The solution of 1.6 M V(III/IV) in 4 M total SO_4^{2-} (AMG Titanium alloys & Coatings, Germany) is used as the tested electrolyte for the entire project.

Figure 3.2 Cell setup for positive electrolyte preparation.

The positive electrolyte was prepared at room temperature (22 – 25 °C) by a single cell with 20 cm² active area. The main component of the cell includes PVC flow frame, expanded graphite bipolar plate (TF 6, SGL Carbon Group), graphite felt porous electrode (GFD 4.6 EA, SGL Carbon Group, heat treated at 600 °C for 5 h), and anion type exchange membrane (FAP 450, Fumatech). The constant applied current is of 40 mA.cm⁻² controlled by a NEWARE battery tester. The pristine vanadium electrolyte was pumped through the cell by a peristaltic pump with flow-rate of 10 mL/min. The state of charge (SOC) of the positive electrolyte was estimated based on the relation of the open circuit voltage (OCV) and SOC was calculated by Nernst equation (as described in Chapter 2). In this project, we employed the vanadium positive electrolyte with the 90% SOC for the thermal stability test. For UV-vis and titration experiment,

the 100% SOC electrolyte solution (V(V)) was prepared. Besides, the vanadium solution with different oxidation states was also prepared for the study on membrane-vanadium ions interaction.

3.2.3 Cell Component Selection and Preparation

The graphite felt (GFD 4.6 EA, SGL Carbon Group) was exploited as a porous electrode. To improve the cell efficiency, the felt was thermo-activated by heating at 600 °C for 5 h). The bipolar plate is mainly expanded graphite (TF 6/PV 15, 0.6 mm, SGL Carbon Group), and sometimes is monolithic carbon plate (F100, 2 mm, SGL USA).

The ion exchange membrane mainly used in this project is anion type (Fumatech FAP 450, 50 µm thickness) due to its low cost and convenience (could be directly used when receiving). In addition, cation exchange membrane (Nafion 117, 177.8 µm thickness) is also used for comparison purpose. In the study on the membrane-vanadium ions interaction, the selected ion exchange membrane was pretreated to remove the impurity. Nafion 117 cation exchange membrane (CEM) is dipped into a solution of deionized water and HNO₃ (65%) (1:1 vol) and heated at 90 °C for 1h. Fumatech FAP 450 anion exchange membrane (AEM) is dipped into 0.5 M NaCl solution and kept 25 °C for 72 h. Moreover, the cell also used PVC flow frame and a copper plate as a current collector.

3.3 Characterization of New Vanadium based Electrolyte Formulation in Static Condition

3.3.1 Thermal Stability Test for Additive Screening

The thermally stable additive screening was conducted by a common and

simple static test, which includes a water-bath and a thermometer to control the temperature. The electrolyte sample (containing pristine electrolyte with and without additive) was heated up and kept at different constant temperatures (45, 50 °C). All samples were checked hourly and the precipitate was observed by a physical method when it forms a large amount in the bottom of the tested tube. This setup is quite simple and can apply for a large number of samples at the same time to accelerate the screening. However, it is, sometimes, not so accurate. Therefore, in order to gain accurate information on a large library of compositions, the thermal stability test was repeated several times with regularly checking.

Figure 3.3 Static test for vanadium electrolyte precipitation.

In a typical experiment, 5 mL of positive vanadium electrolyte (90% SOC) was used as a tested sample. The additives were added into the pristine electrolyte with various amounts depending on their solubility, structure... All samples were kept in the same heating condition during the thermal stability experiment.

3.3.2 Precipitation Rate Testing

This test aims to precisely determine the amount of precipitate under high-temperature condition during a certain heating time. The tested sample contains 2 mL of positive vanadium electrolyte (90% SOC) with and without additives. All samples were heated at 50 °C for 3, 5 and 7 days. The precipitate was filtrated by Whatman filter paper (90 mm diameter), collected and dried at room temperature overnight to estimate the weight.

3.3.3 Laser Particle Analyzer

The laser particle analyzer uses a converging laser beam for determination of the particle size distribution of suspensions, emulsions, solids, and aerosols.

In this project, the laser particle analyzer is used to characterize the growth process of vanadium precipitate under a high-temperature condition. The solution of 2 mL of positive vanadium electrolyte with and without additive was heated at 50 °C for 5 days. The heated solution is then transferred to the laser particle analyzer to determine the size of the precipitate particle. The laser particle analyzer (Fritsch, Analysette 22 Compact) used in this work is available at Inorganic Materials Service Lab (N4.1-B3-03), School of Materials Science & Engineering, NTU (Measuring range 0.3 to 300 μm).

3.3.4 X-ray Diffraction

The X-ray diffraction (XRD) is a very common method to determine the structure of the crystal or the identification of a crystalline substance. The principle of XRD relies on the interference effect between the atoms of a crystal and X-ray when projecting an X-ray beam onto the crystal surface.

The X-ray diffraction measurement, in this case, will be used for phase identification to determine the solid chemical produced by the precipitation of vanadium electrolyte. The precipitates will be filtrated and dried in air before going to the X-ray analysis. The XRD patterns are compared with the standard value to identify the exact chemical compounds. The XRD facility used in this project is the Shimadzu X-ray Diffractometer (Shimadzu XRD-6000) available at the School of Materials Science and Engineering, with the $\lambda_{\text{Cu-K}\alpha} = 0.15418$ nm.

3.3.5 Scanning Electron Microscope

When scanning the surface of a sample with an electron beam, the interaction between the electron and sample's atoms can produce many signals that contain the information of that sample composition and surface topography. The electron microscope based on this principle is called a scanning electron microscope (SEM). SEM images will help to investigate the effect of additives on the structure of carbon components in VRFB after they contact with the electrolyte. Furthermore, it also can visually detect any precipitates present in the carbon felt and other components. The SEM equipment used in this work is the field emission scanning electron microscopy (FESEM, JEOL 7600F). The carbon felt was quickly washed after the cycling test and dried in air (60 °C) prior to the test.

3.3.6 Energy Dispersive X-ray Spectroscopy

Energy-dispersive X-ray spectroscopy (EDX or EDS) is a technique normally coupled with SEM to analyze the elemental and chemical composition of a sample. EDX uses the X-ray spectrum emitted by the bombarded interaction of a focused electron beam and a solid sample to identify the chemical and amount of element. In principle, all elements from atomic number 4 (Be) to 92 (U) can

be detected, though not all instruments are equipped with 'light' elements ($Z < 10$).

The XRD analysis cannot provide exactly the chemical compounds present in the vanadium precipitates because they only can determine the crystal structures. In this case, EDS can be used to further investigate the vanadium precipitates. In addition, the formation of precipitates in the cell components also can be determined by the EDS measurement. In this project, we use the INCA EDS equipment which is integrated with the SEM equipment (FESEM, JEOL 7600F) available in the MSE lab.

3.3.7 Transmission Electron Microscope

The transmission electron microscopy (TEM) uses a high energy electron beam to light up through a very thin sample. The interactions between the electrons and atoms reveal features regarding the crystal structure, dislocations and grain boundaries of the sample.

In this study, the TEM is used to investigate the formation of a V_2O_5 precipitate at early state (suspension solution). A JEOL 2010 TEM was employed in this work. The sample was sonicated in acetone solution and then dropped onto the amorphous carbon coated – copper grid for characterization. The particle size was evaluated from the TEM images by the ImageJ software.

3.3.8 Scanning Transmission Electron Microscope

A scanning transmission electron microscope (STEM) is one of transmission electron microscope (TEM) techniques. Different from the conventional TEM, the electron beam in the STEM is focused on a fine spot and then scanned over the sample in a raster. This feature of the STEM is suitable for several

analytical techniques such as Z-contrast annular dark-field imaging, spectroscopic mapping by energy dispersive X-ray (EDX) spectroscopy, or electron energy loss spectroscopy (EELS). These signals can be collected together, enabling the direct correlation of images and spectroscopic data.

In this project, the STEM coupled EDS mapping is used to intensively analyze the vanadium precipitation. It could demonstrate the thermal stabilizing mechanism of organic additive, by detecting the presence of organic additive on the surface of the precipitate particle to hinder the further growth of precipitate. The STEM JEOL 2100F instrument used in this work is available at FACTS Lab (N4.1-B4-03), School of Materials Science & Engineering, NTU.

3.3.9 Ultraviolet-Visible Spectroscopy

Ultraviolet-visible spectroscopy (UV-Vis) mentions to the absorption or reflectance spectroscopy of a substance in the ultraviolet-visible spectral region. The principle of this method based on the light energy absorption capability of molecules containing π -electrons or non-bonding electrons (n-electrons) in the range of ultraviolet or visible wavelength, to excite these electrons to higher anti-bonding molecular orbitals. The more easily excited the electrons, the longer the wavelength of light it can absorb.

UV-Vis spectra can provide the information about the change of valence state or concentration of vanadium species when they are added by the additives. Also, the vanadium adsorption behavior of ion exchange membrane can be analyzed by this technique. In this project, the UV-Vis spectra will be measured on either Carry Series UV-Vis-NIR Spectrophotometer or UV-Vis spectra were measured on a Shimadzu UV-2501 PC Spectrometer with a 10 mm path-length quartz cell at School of Materials Science and Engineering, NTU.

In the valence state change experiment, 1 mL solution of 1.6 M V(V) in 4 M total SO_4^{2-} solution (100% SOC) was prepared with 1.0 wt.% of tested additives. To achieve a complete dissolution, all samples were sonicated for 1 h and kept for 5 days at room temperature before performing UV-vis measurements. A solution of 4 M H_2SO_4 was used as the reference solution. In practice, an aliquot of 100 μL of sample was diluted in 3 mL with reference solution to practically eliminate interference from complexes of V(IV) and V(V) [2]. Spectra of 1 wt.% of selected additives in 4 M H_2SO_4 solution (without vanadium) were also recorded to examine the light absorbance behavior of organic additives in the region of interest.

For ion exchange membrane characterization, a 2 cm x 2 cm piece of membrane dipped into different vanadium solutions was used as a testing sample, while the membrane dipped into 4 M H_2SO_4 solution was used as reference sample.

3.3.10 Titration

The change in the oxidation state of the positive vanadium electrolyte in the presence of additive can be further investigated by titration technique. Additive compounds were added to 1 mL solution of 1.6 M V(V) in 4 M total SO_4^{2-} (100% SOC) to give a concentration of 1 wt.% and kept at room temperature for 5 days. A solution of 0.02 M KMnO_4 (volumetric, Sigma-Aldrich) was used as the oxidizing agent for the titration. All titrations in this work were done by Mettler Toledo titrator using DMi144-SC metal sensor (Plug & Play combined platinum ring redox electrode with a ceramic frit for redox titrations with a change of the pH value). The titration reaction for V(IV) to V(V) ions by KMnO_4 solution can be written as:

A titration for the sample containing 1 wt.% of selected additives in 4M H₂SO₄ solution (without vanadium) was also performed to determine the extent of direct reaction between the organic additives and Mn(VII) ions, over the time period of a typical titration measurement.

3.3.11 Fourier Transform Infrared Spectroscopy

Irradiating a sample with infra-red (IR) radiation results in absorption of the incident beam that is characteristic of the bonds present in the molecules (or lattice) of the sample. IR radiation of a specific energy (frequency) corresponds to the dipole moment of a molecule. This allows the identification of functional groups present in a sample. Relative intensities of the absorption spectra are qualitative indicators of the abundance of corresponding groups.

In this project, the FTIR spectroscopy is used to characterize the effect of additives on the bonds present in the molecules (or lattice) of carbon component of VRFB. It will allow investigating any change in the bonding and functional groups present in the carbon felt and carbon plate, after cycling with the new electrolyte containing additives. The equipment used in this project is PerkinElmer Spectrum GX FTIR system available at School of Materials Science and Engineering.

3.3.12 Cyclic Voltammetry

Cyclic voltammetry (CV) in this project is performed using a WaveDriver Potentiostat from PINE instrument, or BioLogic SP-150 potentiostat. A three-electrode electrochemical cell with a reference electrode, a working electrode, and a counter electrode are used for this CV test.

In this project, due to the use of sulfuric acid as the supporting electrolyte, the

Hg/Hg₂SO₄ reference electrode will be most suitable. Besides, a saturated calomel electrode (SCE) or an Ag/AgCl reference electrode also can be used. The counter electrode is platinum (Pt), while the working electrode could be carbon plate, graphite plate or glassy carbon electrode. In addition, a gas diffusion tube was also integrated into the CV setup.

Figure 3.4 Cyclic voltammetry setup for the positive vanadium electrolyte characterization.

CV measurement in this project will provide the information about the effect of additives on the electrochemical properties of the positive electrolyte.

3.3.13 Electrochemical Impedance Spectroscopy

The electrochemical impedance spectra (EIS) were used to investigate the mass transfer and charge transfer processes for vanadium redox couple and the kinetics of electrode reaction-diffusion of vanadium species by recording Nyquist plots of the electrolytes with and without additives.

In this project, the EIS measurement is conducted by a Solartron SI 1260 electrochemical workstation or BioLogic SP-150 potentiostat. The setup is similar to the CV setup for vanadium electrolyte characterization.

Moreover, EIS technique is also employed to examine the resistivity change of the ion exchange membrane. The measurement setup is showed in Figure 3.5, in which, a glassy carbon electrode was used as the working electrode, and a graphite plate served as the counter electrode. The tested membrane was placed in between the working and counter electrode. A thermometer was also positioned near the setup to record the ambient temperature.

Figure 3.5 EIS setup for the ion exchange membrane characterization.

In a typical measurement, a drop of corresponding vanadium solution was added onto the graphite electrode surface, between both electrodes to ensure the electrode contact area is not exposed to air. From the resultant data, the resistance value of R_1 (resistance between two electrodes) and R_2 (resistance between two electrodes through the membrane) can be obtained. Membrane resistivity of each sample is calculated using the equation:

$$R = S \times (R_2 - R_1)$$

where R = Resistivity, S = Electrode area.

3.4 Performance Evaluation of Vanadium Redox Flow Battery using New Vanadium based Electrolyte Formulation

3.4.1 Cycling Test with Temperature Variation

A single cell with 20 cm² active area was used to perform the cycling test with the variation of electrolyte temperature. The main component of the cell includes PVC flow frame, expanded graphite bipolar plate (TF 6, SGL Carbon Group), graphite felt porous electrode (GFD 4.6 EA, SGL Carbon Group, heat treated at 600 °C for 5 h), and anion type exchange membrane (FAP 450, Fumatech). The cell was charged and discharged with a current density of 40 mA.cm⁻² and within the potential window of 0.9 – 1.65 V. An amount of 100 mL vanadium electrolyte was pumped through the cell by a peristaltic pump with a flow rate 10 mL/min. The charged/discharged cycle was controlled by a NEWARE battery testing machine. The electrolyte temperature was controlled by two magnetic hotplates (Heidolph, 505-30080-00 MR Silver Package - Magnetic Stirrer MR Hei-Tec, Temp. Sensor PT 1000 (V4A), Clamp).

Figure 3.6 Cell cycling setup for the novel vanadium electrolyte characterization.

The additives were dissolved in the pristine vanadium electrolyte at room temperature prior to the cycling test.

3.4.2 Long-Term Cycling Test at Different Constant Temperatures

The practical thermal stabilizing ability of additives was demonstrated by the long-term cycling test at high constant temperatures. A 20 cm² single cell with the same assembling as shown in Figure 3.6 was also employed in this experiment. The cell was charged/discharged for over 100 cycles with the current density of 100 mA.cm⁻². The amount of electrolyte in each tank was 100 mL and was pumped with 50 mL/min flow-rate. The electrolyte tank was kept at constant temperatures 25 and 50 °C.

In this experiment, the cell was assembled with two types of ion exchange membrane: Fumatech AEM and Nafion CEM, in which, Nafion CEM was soaked into the pristine electrolyte 24 h prior to the cycling. This is to examine the interaction of thermally stable additives with different types of ion exchange membrane.

3.4.3 Long-Term Cycling Test with Stack Cell

To further investigate the long-term performance of new thermally stable vanadium electrolyte, a large scale VRFB with the 3-stacked cell was cycled using an electrolyte with and without combined additives.

The 3-stack VRFB was cycled for over 200 cycles with 1.5 L of vanadium electrolyte in each tank. The electrolyte was pumped through the VRFB system using the magnetic pump. The pressure sensor and thermometer were also integrated into the system to continuously measure the electrolyte flow-rate, pressure, and temperature. The charged/discharged current was controlled by a

NEWARE battery testing machine. The thermally stable additives were dissolved in the pristine electrolyte prior to the cycling test.

Two types of combined additive formula, which are selected after several screening tests and optimization for different proposed additives, were added to the electrolyte for this experiment:

- Formula 1: 0.025 wt.% PVP + 0.25 wt.% $\text{NH}_4\text{H}_2\text{PO}_4$: In the stack, the PV15 graphite plate (0.6 mm, SGL) was used as the bipolar plate in the stack and also in the end plate.

- Formula 2: 0.025 wt.% PVP + 0.25 wt.% $(\text{NH}_4)_2\text{HPO}_4$: In the stack, the PV15 graphite plate (0.6 mm, SGL) was used as the bipolar plate in the stack. While the F100 monolithic carbon plate (2 mm, SGL USA) was used as the bipolar plate at the end plate to prevent the corrosion of copper current collector.

Figure 3.7 A 3-stack VRFB system for the novel vanadium electrolyte characterization.

3.4.4 Long-Term Cycling Test with 1 kW Stack

A 1 kW stack of VRFB containing 20 single cells (625 cm^2 active area for each cell) developed by Arjun (a Ph.D. student supported by SGL Carbon Group) was used to test the performance of novel thermally stable vanadium electrolyte (Figure 3.8). Each cell was assembled with Sigracell GFD 4.6 EA electrode (600°C , 5 h, SGL Carbon), Sigracell PV 15 (SGL Carbon) bipolar plate, Fumatech FAP 450 AEM, and PVC flow frame. The tested amount of vanadium electrolyte in each tank is 10 L. The stack was charged/discharged at the current density of 80 mA.cm^2 . The novel thermally stable vanadium electrolyte contains 0.025 wt.% PVP + 0.25 wt.% $\text{NH}_4\text{H}_2\text{PO}_4$ dissolved into the pristine electrolyte prior to the cycling test.

Figure 3.8 A 1 kW VRFB system for the novel vanadium electrolyte characterization.

References:

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Chapter 4

Advanced Halide-free Additive Formula with High Thermal Stability for Vanadium Electrolyte

This chapter elaborates the effect of advanced halide-free additive formula on the properties of VRFB electrolyte. The studied evaluation includes the thermal stability improvement of positive vanadium electrolyte with the presence of thermally stable additives, the activity of advanced additives on the precipitation rate, the change in vanadium oxidation state in the presence of additives, the impact of additives on the electrochemical property of vanadium electrolyte.

4.1 Thermal Stability Improvement of Advanced Additive Formula

4.1.1 Thermally Stable Additive Screening

Table 4.1 below shows the summary of thermal stability test at 45 and 50 °C for the proposed thermal stabilizing agents (1 wt.% adding amount) with 90% SOC positive vanadium electrolyte (1.6 M V in 4 M total SO_4^{2-}). In comparison with blank additive-free electrolyte solution and HCl/H₃PO₄ (as reference additives), the tested additives are classified into three groups relied on their thermal stabilizing ability: *thermally stable* group represents the chemical compound that demonstrated the improvement for the thermal stability of the positive vanadium electrolyte; *not effective* group means the compound that did not effectively stabilize the positive vanadium electrolyte at high temperatures; and the last group, *stable with color change* indicates the group of chemical that can also stabilize the positive vanadium electrolyte at high temperature, but with the change in the solution color compared to the blank additive-free electrolyte (See Appendix: Fig. A.1).

Refer to Table 4.1, it is noted that along with as-known HCl and H₃PO₄ additives, some compounds of ammonium and phosphate/nitrate also can help to preserve the solubility of V(V) in sulfuric acid at high temperatures. In additions, several high molecular weight organic compounds such as PVP, gelatin, fatty acid are also able to improve the thermal stability of the positive vanadium electrolyte. On the other hands, a number of other ammonium based agents are not effective for vanadium electrolyte stabilizing, as well as some amino acids. Especially, methanesulfonic acid was reported as a good supporting electrolyte for vanadium species [1, 2]. However, it is relatively poor in term of the thermally stable additive with the small additional amount. Interestingly, all the additives denoted as “*stable with color change*” are organic compounds containing polar functional groups.

Table 4.1 Summary of thermally stable additive screening at 45 and 50 °C.

Compounds	Thermally stable	Not effective	Stable with color change
Inorganic	Hydrochloric acid	Sodium pyrophosphate	
	Phosphoric acid	Ammonium metavanadate	
	Ammonium dihydrogen phosphate	Ammonium persulfate	
		Ammonium carbonate	
	Diammonium hydrogen phosphate	Ammonium sulfate	
		Ammonium cerium sulfate	
	Ammonium phosphate	Ammonium hydrogen tungstate	
	Ammonium nitrate	Molybdic acid	
		Sodium molybdate	
		Sodium silicate	
		Boric acid	
Organic	Poly-vinyl-pyrrolidone (PVP)	Glutamine	Oxalic acid
		Alanine	Sodium oxalate
	Gelatin A	Arginine	Potassium oxalate
	Gelatin B	Lysine	Tannic acid
	Oleic acid	Valine	Ascorbic acid
	Stearic acid	Urea	Lactic acid
		Diisopropylamine	Citric acid
		Methanesulfonic acid	Ammonium citrate
		Acetic acid	Poly-vinyl-alcohol (PVA)
		Sodium acetate	Cysteine
		Melamine	EDTA disodium salt
			Glucose
			Xylose
			Resorcinol
			Pyrogallol
			myo-Inositol
			Methyl resorcinol
			Pinacol

The primary thermally stable additives were continued testing their suitability for the vanadium electrolyte. It was showed that ammonium nitrate is not stable in the negative side due to the strong oxidative behavior of NO_3^- ion, which could oxidize V(II), V(III) ions to V(IV) (see Appendix: Fig. A.2). This will cause to the problem in case of any contamination of ammonium nitrate in the negative electrolyte, e.g. in the cell capacity recovering process which often requires the electrolyte re-mixing, the additive in the positive side can enter the negative electrolyte. Gelatin compounds have no issue on the chemical incompatibility with vanadium electrolyte. However, it was destroyed under cyclic voltammetry condition within vanadium redox potential range, forming a large amount of gas bubble during CV test (see Appendix: Fig. A.3). Two fatty acids, oleic and stearic acid, even though reveal the ability to stabilize the positive vanadium electrolyte, but have quite a low solubility. This results in the risk of phase separation over longer time periods.

The rest of thermally stable additives, including ammonium phosphate agents and PVP (with two different molecular weights), have been successfully passed through all primary tests and been employed in further investigations.

4.1.2 Intensive Evaluation of Thermally Stable Additives

To estimate a proper amount of additives should be added into the vanadium electrolyte, we firstly examined the change in electrolyte viscosity with the presence of selected additives. Figure 4.1 shows the viscosity change of pristine vanadium electrolyte (1.6 M V(III/IV) in 4 M total SO_4^{2-}) by the addition of some thermally stable organic (a) and inorganic (b) additives. In Figure 4.1a, it can be observed that the viscosity of pristine vanadium electrolyte is not significantly changed when adding 0.5 and 1 wt.% of $\text{NH}_4\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_3\text{PO}_4$. Hence, for these inorganic additives, the material consumption and other performance factors should be more carefully considered rather than

the electrolyte viscosity failure. While, in Figure 4.1b, we noticed the increasing viscosity of vanadium electrolyte by the addition of soluble polymer, in which, the PVP compound with higher molecular weight (PVP 1300) raises more significantly the electrolyte viscosity compared to the smaller molecular weight PVP (PVP 10). In detail, with the presence of 0.1, 0.2 and 0.3 wt.% of PVP 10, the initial viscosity of pristine vanadium electrolyte rises up to 1.3, 3.1 and 8.8%, respectively. While with the same adding amount of PVP 1300, the increasing value is 18.6, 22.1, and 36.7%, correspondingly. Therefore, the volume of PVP addition has to be carefully controlled to minimize the detriment on electrolyte viscosity, along with the attention on the material consumption and performance.

Figure 4.1 Viscosity change of pristine vanadium electrolyte (1.6 M V(III/IV) in 4 M total SO_4^{2-}) by the addition of some thermally stable organic (a) and inorganic (b) additives.

After testing the viscosity change and identifying the optimum adding amount, we conducted the intensive inspection of the thermal stabilizing capability of as-selected additives. Figure 4.2 presents the dependence of vanadium electrolyte thermal stability on the change of additive amount at different temperatures. At 45 °C, the average time to precipitate of blank positive vanadium electrolyte is about 142.5 (± 47.5) h, and it is improved by the

addition of thermally stable additives. In detail, with the presence of 0.5, 1 and 1.5 wt.% of additive, the time to precipitate is extended to about 358.5 (± 23.5), 399 (± 36) and 540.5 (± 86.5) h for $\text{NH}_4\text{H}_2\text{PO}_4$, nearly 276 (± 82), 406.5 (± 24.5), and 504.5 (± 122.5) h for $(\text{NH}_4)_2\text{HPO}_4$, and around 242, 315 and 335 h for $(\text{NH}_4)_3\text{PO}_4$, respectively. It is also easy to see that the thermal stabilizing ability of those ammonium phosphate compounds can be arranged as follows: $\text{NH}_4\text{H}_2\text{PO}_4 > (\text{NH}_4)_2\text{HPO}_4 > (\text{NH}_4)_3\text{PO}_4$.

Figure 4.2 Dependence of vanadium electrolyte thermal stability on the variation of the additive amount at 45 (a-b) and 50 °C (c-d). Sample: 5 mL of 1.6 M V (90% SOC) in 4 M total SO_4^{2-} .

While for H_3PO_4 reference additive with the same adding amount, the time to precipitate rises to the value of 336.5 (± 21.5), 360.5 (± 2.5) h for 0.5 and 1 wt.% of H_3PO_4 , but slightly drops to 300 (± 154) h for 1.5 wt.%. The same trend is

also observed in the case of HCl, which increases the time to precipitate up to 204 (± 10), 216 (± 70) and 193.5 (± 68.5) h, correspondingly. For PVP at 45 °C (Fig. 4.2b), it is noted that the addition of 0.1 wt.% of PVP 10 can prolong the time to precipitate of the blank vanadium electrolyte up to 327 (± 85.5) h, but reduces to about 252 (± 82) h for both 0.2 and 0.3 wt.% addition. PVP 1300 also behaved similarly, which shows the number of 312 (± 70), 288 (± 94) and 303.5 (± 109.5) h for 0.1, 0.2 and 0.3 wt.% of addition, respectively. It is also noticed that the thermal stabilizing ability of PVP 1300 is better than PVP 10 at 45 °C.

At 50 °C, we recorded the same thermal stabilizing behavior of as-mentioned additives, in which can be arranged similarly as seen at 45 °C: $\text{NH}_4\text{H}_2\text{PO}_4 > (\text{NH}_4)_2\text{HPO}_4 > (\text{NH}_4)_3\text{PO}_4 > \text{PVP 1300} > \text{PVP 10}$. In detail, with the presence of 0.5, 1 and 1.5 wt.% of additive, the time to precipitate of positive vanadium electrolyte boosts from ~52 (± 6) h to about 118.5 (± 23.5), 204 (± 58) and 252 (± 82) h for $\text{NH}_4\text{H}_2\text{PO}_4$, around 90 (± 39), 132 (± 14), and 100 (± 5) h for $(\text{NH}_4)_2\text{HPO}_4$, and around 51, 70 and 77 h for $(\text{NH}_4)_3\text{PO}_4$. This value is about 82 (± 12), 75.5 (± 5.5), 75.5 (± 5.5) h for 0.1, 0.2 and 0.3 wt.% of PVP 10, and is all approximately to 100 (± 5) h for PVP 1300. In general, the results of above thermal stability test at 45 and 50 °C indicate the improvement of positive vanadium electrolyte thermal stability by the addition of as-selected additives. The stability is proportional to the increasing amount of inorganic agents (ammonium phosphate) but almost independent with the adding amount of organic additives (PVP).

The high thermal stabilizing effectivity of ammonium phosphate additives for the positive vanadium electrolyte is probably due to the combination of PO_4^{3-} ions with the hydrate penta-coordinated $[\text{VO}_2(\text{H}_2\text{O})_3]^+$ cation, resulting in the prevention of the deprotonation at high temperature. This combination has been intensively discussed by Gresser *et al.* in 1986, and the complexing reaction can be written as [3]:

Recently, phosphate-based compounds have been found to be a good additive for the positive vanadium electrolyte in some academic studies [4-6], as well as being employed in the industry [7]. However, the role of ammonium ions (NH_4^+) in this work is still very complicated. In our study, ammonium does not give a high impact on the thermal stability of positive vanadium electrolyte, as demonstrated by the poor activity of ammonium sulfate, urea and some other ammonium-based compounds in the thermal additive screening. But interestingly, the presence of ammonium in ammonium phosphate additives could improve the effectivity of phosphoric acid, as shown in Figure 4.2. In short, the thermal stabilizing activity of different phosphate additives can be arranged as $\text{NH}_4\text{H}_2\text{PO}_4 > (\text{NH}_4)_2\text{HPO}_4 > (\text{NH}_4)_3\text{PO}_4 > \text{H}_3\text{PO}_4$. Therefore, via the precipitate analysis, we suggested the key effect of NH_4^+ ions in this situation: to eliminate the formation of VOPO_4 precipitate in V(V) solution which is happening in the use of H_3PO_4 (will be proved in the following session).

The effectivity of PVP for the positive vanadium electrolyte stabilizing is also relatively impressive. PVP is known as a common surfactant to control the particle size in the synthesis of various metal nanoparticles by hydrothermal method. Here, in this study, we have found for the first time that PVP can serve as an effective additive for the positive vanadium electrolyte. The role of PVP is to block the surface of V_2O_5 nuclei and hinder the further growth of V_2O_5 particle, and hence maintaining the operation of the system.

4.1.3 Co-stabilizing Effect in the Combined Inorganic-Organic Additives for Positive Vanadium Electrolyte

The conventional concept of vanadium electrolyte additive prefers using one single stabilizing agent to reduce the complexity of the electrolyte formula. Even so, the vanadium precipitation is a slow process composed of several consecutive steps as we discussed in Figure 2.12. Therefore, we proposed a solution to completely eliminate the vanadium oxide precipitation by attacking both deprotonation and condensation strides. To achieve this purpose, we examined the thermal stabilizing ability of combined inorganic-organic additive for the positive vanadium electrolyte.

Figure 4.3 Thermal stabilizing ability for positive vanadium electrolyte of combined inorganic-organic additives at 45 and 50 °C. Sample: 5 mL of 1.6 M V (90% SOC) in 4 M total SO_4^{2-} . Inorganic concentration: 0.25 – 0.5 wt.%; organic concentration: 0.025 – 0.05 wt.%.

Relying on the result in the part 4.1.2, we chose $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$ as inorganic component, while PVP 1300 serves as an organic component for the combination. The result is showed in Figure 4.3. It is proved that the combined inorganic-organic additives demonstrated much better thermal stabilizing ability in comparison with corresponding mono additives at both 45 and 50 °C. In detail, at 45 °C, the time to precipitate of vanadium electrolyte when adding 0.025 wt.% PVP + 0.25 wt.% $\text{NH}_4\text{H}_2\text{PO}_4$ and 0.025 wt.% PVP + 0.25 wt.% $(\text{NH}_4)_2\text{HPO}_4$ is about 395.5 (± 10.5) and 371.5 (± 10.5) h, respectively,

compared to the number of 142.5 (± 0.5) h for blank additive-free solution. That value for the formula of 0.025 wt.% PVP + 0.25 wt.% $\text{NH}_4\text{H}_2\text{PO}_4$ is estimated to be increased up to 94.8 and 44.3% with respect to the performance of 0.25 wt.% $\text{NH}_4\text{H}_2\text{PO}_4$ (~203 h) and 0.025 wt.% PVP (~274.5 h) mono additive, correspondingly. For the addition of 0.025 wt.% PVP + 0.25 wt.% $(\text{NH}_4)_2\text{HPO}_4$, it can extend the time to precipitate of pristine vanadium electrolyte up to 123.1 and 35.3% compared to the value of 0.25 wt.% $(\text{NH}_4)_2\text{HPO}_4$ (~166.5 h) and 0.025 wt.% PVP (~274.5 h) mono additive, respectively. However, the increasing addition amount of each component in such combined additives does not give a significant change in the thermal stability of positive vanadium electrolyte at 45 °C. At 50 °C, we also observed the excellent performance of combined inorganic-organic additives against the mono additives. The time to precipitate of blank electrolyte can be prolonged from 47.5 (± 0.5) h up to about 172 (± 18) and 148 (± 6) h by adding 0.025 wt.% PVP + 0.25 wt.% $\text{NH}_4\text{H}_2\text{PO}_4$ and 0.025 wt.% PVP + 0.25 wt.% $(\text{NH}_4)_2\text{HPO}_4$, respectively. These values are much higher as compared to the number of 87, 63 and 107 h for the addition of 0.25 wt.% $\text{NH}_4\text{H}_2\text{PO}_4$, 0.25 wt.% $(\text{NH}_4)_2\text{HPO}_4$ and 0.025 wt.% PVP single agent, correspondingly. Similarly to the test at 45 °C, the increasing amount of each component in such combined additives also does not give remarkable impact on the thermal stability of vanadium electrolyte at 50 °C.

The strong improvement of thermal stabilizing ability obtained from the combined organic-inorganic additives could be attributed to its co-stabilizing effect for the positive vanadium electrolyte. This effect can be expressed in term of two mechanisms may co-operate to stabilize the electrolyte in one additive formula:

- i) Ammonium phosphates hinder the initial condensation of V(V) by complexing with the VO_2^+ ion as discussed above.

ii) Polyvinylpyrrolidone (PVP) could block the surface of initial V_2O_5 nuclei, hindering further growth and formation of particles large enough to precipitate.

These novel combined additive formulas do not only perfectly stabilize as-studied positive vanadium electrolyte, but also provide a benchmark for the future development of thermally stable VRFB electrolyte.

4.1.4 The Impact of Advanced Thermally Stable Additives on the Vanadium Precipitation Process

We continued examining the influence of novel additive formula on the precipitation process of solid V_2O_5 by heating beyond the thermal sustainability point. The tested electrolyte samples (with and without thermally stable additives) were kept at high temperature for a certain time that allows the formation of a precipitate. Although this test cannot reflect exactly the amount of precipitate production in each sample, the information on the precipitate particle size is still very valuable.

Figure 4.4 indicates the precipitate particle size distribution of different positive vanadium electrolyte solutions heated at 50 °C for 5 days. The results show that after continuously heating at 50 °C, in the blank additive-free vanadium electrolyte, the precipitate particle size is measured to be about 31.7 μm , with a wide range of particle size distribution, implying the non-uniform of the precipitate particle under static condition. For the electrolyte solution containing ammonium phosphate additives, the size of the precipitate particle is smaller, about 18.9 and 11.5 μm for $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$, respectively. However, with PVP additive, the particle size of precipitate is bigger, about 43.4 μm , which may due to the local condensation of precipitate nuclei under the high viscous matrix of PVP. The combined additives, similarly,

demonstrated better performance compared to mono additives, which produced much smaller precipitate, about 19.9 and 11.2 μm for the addition of 0.025 wt.% PVP + 0.25 wt.% $\text{NH}_4\text{H}_2\text{PO}_4$ and 0.025 wt.% PVP + 0.25 wt.% $(\text{NH}_4)_2\text{HPO}_4$, respectively. These results indicate the advantage of as-studied thermally stable additives to restrict the growth of precipitate particle at high temperature.

Figure 4.4 Precipitate particle size distribution of different vanadium electrolyte solutions (1.6 M V in 4 M total SO_4^{2-}): blank (a), mono (b-d) and combined additives (e-h). Sample: 2 mL, 90% SOC, heated at 50 °C for 5 days.

To precisely evaluate the performance of thermally stable additives, the rate of vanadium precipitation is also investigated and presented in Figure 4.5. We observed that the amount of vanadium precipitates proportionally increases with the heating time in 3, 5 and 7 days (see Appendix: Fig. A.4), but with varying degree of precipitation.

Figure 4.5 Precipitation rate of different positive vanadium electrolyte solutions in various heating times at 50 °C. Sample: 2 mL of 1.6 M V in 4 M total SO_4^{2-} (90% SOC). The precipitate was filtrated in 1 day after heating and dried in air at room temperature.

From the amount of collected precipitate and assuming that V_2O_5 is the sole product, the degree of precipitation is estimated with respect to the initial molar number of V(V). It is shown that the most rapid precipitation rate happens for the blank electrolyte solution, lower for the mono thermally stable additives and slowest for the presence of combined inorganic-organic additives. In detail,

after 3, 5 and 7 days heating at 50 °C, around 19.7, 44.3 and 62.6 mol.% of V(V), respectively, in the blank vanadium electrolyte solution has been precipitated. While with the use of 0.5 wt.% of $\text{NH}_4\text{H}_2\text{PO}_4$, this value is only about 6.4, 10.9 and 24.7 mol.%, for 0.5 wt.% of $(\text{NH}_4)_2\text{HPO}_4$ is 7.9, 15.2 and 26.2 mol.%, and for 0.05 wt.% of PVP is 5.5, 18.9 and 25.1 mol.%, correspondingly. For the combined inorganic-organic additives, the precipitation rate in 3, 5 and 7 days heating is only about 9.1, 11.7 and 16.1 mol.% for the addition of 0.025 wt.% PVP + 0.25 wt.% $\text{NH}_4\text{H}_2\text{PO}_4$, and roughly 7.2, 10.7 and 13.9 mol.% for the formula of 0.05 wt.% PVP + 0.5 wt.% $\text{NH}_4\text{H}_2\text{PO}_4$, subsequently. Also, in the case of 0.025 wt.% PVP + 0.25 wt.% $(\text{NH}_4)_2\text{HPO}_4$, this value is estimated to be around 7.8, 12.5 and 14.7 mol.%. Lastly, for the formula of 0.05 wt.% PVP + 0.5 wt.% $(\text{NH}_4)_2\text{HPO}_4$, the precipitation rate is 9.7, 13.7 and 14 mol.% of initial V(V) concentration.

All of the results presented in this section again confirm the excellent thermal stabilizing ability of as-studied inorganic and organic additives, and also prove the benefit of combined inorganic-organic additive formula. Herein, the advanced thermal stabilizing agents reduce the number of V_2O_5 nuclei formation and condensation rate, resulting in the less amount of V_2O_5 precipitate as compared to the blank electrolyte.

4.2 Effect of Additive on the Oxidation State of Positive Vanadium Electrolyte

As mentioned in Chapter 1, one of the criteria for the thermally stable additive is not to reduce the V(V) ion to V(IV). This section will present the study on the oxidation state change of positive vanadium electrolyte in the presence of the additive. This behavior was mainly characterized by UV-vis spectroscopy and titration technique. Firstly, we discuss the effect of organic additives

containing polar functional groups on the chemical stability of positive vanadium electrolyte.

4.2.1 The Oxidation of Organic Additive in the Positive Vanadium Electrolyte

In section 4.1.1, we have mentioned that some organic additives show high thermal stability but with the color change for the positive vanadium electrolyte. For further study, we classified these organic additives into three groups: carboxylic compounds (oxalic acid, sodium oxalate, potassium oxalate and EDTA disodium salt), alcohol compounds (pinacol, resorcinol, methyl resorcinol, xylose, glucose, poly-vinyl-alcohol (PVA) and pyrogallol), and multi-functional group compounds (containing more than 2 different functional groups) (lactic acid, citric acid, ammonium citrate, cysteine, tannic acid and ascorbic acid).

The UV-vis spectra of vanadium electrolyte solution in this study were compared with those reported by Xin [13]. In their research, a distinctive peak is observed for the 100% V(IV) solution at 760 nm, and there is also strong absorption at wavelengths below 340 nm. A 100% V(V) solution was essentially transparent above 500 nm but absorbed strongly at wavelengths below 500 nm. Figure 4.6 (a-c) shows the UV-vis spectra of 4 M H₂SO₄ solution after the 1 wt.% addition of carboxyl compounds (Fig. 4.6a), alcohol compounds (Fig. 4.6b), and multi-functional group organic compounds (Fig. 4.6c) over the wavelength range from 300 to 900 nm. By adding selected organic compounds, there was no absorption peak over the wavelength range of interest (500 – 900 nm). Therefore, they are suitable for evaluation by this spectroscopic technique. Figure 4.6 (d-f) shows the UV-vis spectra of 1.6 M V(V) in 4 M total SO₄²⁻ solution after addition of different organic additives over the wavelength range from 300 to 900 nm. An absorbance peak at 760 nm

and an onset of strong absorption below 340 nm is observed in the presence of 1 wt.% of carboxyl compounds (Fig. 4.6d), alcohol compounds (Fig. 4.6e), and multi-functional group organic compounds (Fig. 4.6f). By comparison with the reference spectra for V(IV) and V(V), it can be seen that V(V) was reduced to V(IV) by the additives listed above.

Figure 4.6 UV-vis spectra of 4 M H_2SO_4 solution (a-c) and 1.6 M V(V) in 4 M H_2SO_4 solution (e-f) with 1 wt.% of carboxyl compounds (a, d), alcohol compounds (b, e), and multi-functional group compounds (c, f). The UV-vis spectra of V(IV) and V(V) solutions are also displayed for comparison.

To again confirm the change in the valence state of V(V) from spectroscopic observations, we conducted the titration of V(V) solution containing 1 wt.% of those organic additives. Figure 4.7 a-c displays the titration curve of 4 M total SO_4^{2-} solution (without vanadium) with 1 wt.% of carboxyl compounds (a), alcohol compounds (b), and multi-functional group compounds (c).

Figure 4.7 Titration curve of 4 M H_2SO_4 solution (a-c) and 1.6 M V(V) in 4 M H_2SO_4 solution (e-f) with 1 wt.% of carboxyl compounds (a, d), alcohol compounds (b, e), and multi-functional group compounds (c, f).

Compared with blank 4 M H_2SO_4 solution curve, it can be seen that resorcinol, methyl resorcinol, pyrogallol, cysteine, tannic acid, and ascorbic acid have interaction with Mn(VII) over the timescale of the titration measurement. This could cause inaccuracy in the titration measurement if the six listed organic additives had not been fully oxidized in V(V) solution after 5 days. However, for the remaining additives, the titration method is considered valid. Figure 4.7 d-f show the titration curve of 1.6 M V(V) in 4 M total SO_4^{2-} solution (100% SOC) with 1 wt.% of those organic additives. Compared with the reference titration curves of V(IV) and V(V) solution, it was observed that in the presence of every additive, a certain amount of V(V) was reduced to V(IV) and thus the concentration of V(V) decreased.

Figure 4.8 The state-of-charge (SOC) reduction after 5 d at room temperature of 100% SOC vanadium electrolyte after the addition of 1 wt.% of carboxyl compounds (a), alcohol compounds (b), and multi-functional group compounds (c). The degree of additive oxidation in V(V) solution of carboxyl compounds (d), alcohol compounds (e), and multi-functional group compounds (f).

The SOC of V(V) solution before and after the addition of different organics additives was averaged calculated from the Beer-Lambert law, based on the

intensity of absorbance peak at 760 nm [13] and the titration results. Figure 4.8a-c shows the average SOC reduction of V(V) solution (100% SOC) after the addition of 1 wt.% of carboxyl compounds (a), alcohol compounds (b), and multi-functional group organic compounds (c). It can be noted that all of these organic additives could reduce the SOC of positive vanadium electrolyte under static conditions. In detail, for carboxyl additives, 1 wt.% of EDTA disodium salts could reduce up to 27.8% SOC of original V(V) solution, while the value for oxalic acid, potassium oxalate, and sodium oxalate are 12.5%, 8.9%, and 8.4%, respectively. For alcohol compounds, 1 wt.% of pyrogallol and glucose could diminish the SOC by about 88.5% and 77.4%, correspondingly. Xylose and resorcinol gave a similar effect, which could reduce about 68%, and pinacol indicated the lowest reduction of SOC, about 32.7%. For multi-functional group additives, ascorbic acid with 1 wt.% concentration could cut down 81.9% SOC of V(V) solution. Tannic acid and citric acid shortened about 70.3 and 63.7% SOC of original V(V) solution. The lowest reduction was observed when adding 1 wt.% of lactic acid, which scaled down about 38.2% of SOC.

To clarify the reactivity of each organic compound, we calculated the associated number of electrons involved in oxidizing the additive, which is indicated in Figure 4.8d-f. It is known that the vanadium reduction from V(V) to V(IV) goes through a one-electron reduction reaction:

Combined with the change in the SOC of V(V) solution, we can calculate the total number of electrons involved in the oxidation reaction of additives, and from that, we can get the average number of electron involved per molecule of additive (the number of additive molecule was calculated by conversion of adding amount from weight percentage to molar percentage). In general, from

the result displayed in Figure 4.8d-f, we observed that the degree of additive oxidation relatively increased with the increase of a number of functional group in additive molecule structure. In detail, for carboxyl additives, the strongest reductive additive was EDTA disodium salts, which underwent oxidation reactions involving $\sim 12\text{ e}^-/\text{molecule}$. EDTA possesses 4 carboxylic groups compared to two carboxylic groups for oxalic acid and its salts. However, the latter only underwent oxidation by about $1.3\text{ e}^-/\text{molecule}$ after 5 days at room temperature. For alcohol additives, the most extensively reductive additive was glucose, which released about $16.3\text{ e}^-/\text{molecule}$, while the weakest additive was pinacol, which produced about $4.5\text{ e}^-/\text{molecule}$ during oxidation. For multi-functional group compounds, we recorded the number of $16.8\text{ e}^-/\text{molecule}$ for ascorbic acid, which denotes as the strongest reductive agent, while lactic acid was the weakest reductive chemical, which showed the value of $4\text{ e}^-/\text{molecule}$ during oxidation. Two high molecular weight compounds not listed in Figure 4.8d-f, tannic and PVA, revealed a high value of oxidation degree, up to 139.5 and 808 $\text{e}^-/\text{molecule}$, respectively. Converted to their corresponding monomer (as-studied tannic acid contains 10 molecules of gallic acid, while PVA contains 216 monomers of vinyl alcohol), the recorded values are ~ 13.95 and $\sim 3.74\text{ e}^-/\text{molecule}$ for gallic acid and vinyl alcohol, correspondingly.

Relying on the degree of oxidation, we can describe the reaction mechanism of such organic additives in V(V) solution. Oxalic acid can theoretically undergo complete oxidation through a 2e^- process in aqueous acid solution [14, 15]:

Oxalic acid

In practice, we observed the number of $1.3 \text{ e}^-/\text{molecule}$ (Fig. 4.8d), which implies that the reaction goes about 65% through to completion, and about 35% amount of oxalic acid still remains.

One study reported that the oxidation of lactic acid by V(V) ions theoretically follows a 2e^- process to form acetaldehyde in the sulfuric acid medium at 30°C [16]:

Lactic acid

However, in practice we recorded the number of $\sim 4\text{e}^-/\text{molecule}$ (Fig. 4.8f), which is most likely to result from oxidation of acetic acid:

For aldose sugars such as glucose, a study in acid medium claimed that the oxidation of glucose by V(V) involved only 2e^- in $2 \text{ M H}_2\text{SO}_4$ (or HClO_4) solution at $40 - 50^\circ\text{C}$ [17]:

Glucose

In another paper using perchloric acid at 45 °C, the oxidation of glucose by V(V) was more intensive, at 12e⁻/molecule [18]:

However, in our case, the oxidation of glucose by V(V) in sulfuric acid proceeded through ~16 e⁻ process (Fig. 4.8e). To satisfy this number, the reaction has to form 4 equivalents of formic acid and 2 of CO₂, for example:

The oxidation process of other organic compounds is complicated. Analysis of the decomposition products between the organic molecules and V(V) in sulfuric acid would be required to support mechanistic arguments. However, what is obvious from these findings is that the charged positive vanadium electrolyte is a strongly oxidizing media, where all of the proposed additives were, to a greater or lesser extent, reacted. And not only in the static condition, the oxidation of organic additives also causes to the failure of cell cycling process, which is probably due to the formation of the CO₂ gas bubble during cycling of vanadium electrolyte (see Appendix: Fig. A.5, A.6).

4.2.2 Effect of Advance Thermally Stable Additives on the Oxidation State of Positive Vanadium Electrolyte

Previous observation on the organic additive oxidation in aqueous V(V) medium demands the essentiality to examine the influence of as-studied thermally stable additives on the oxidation state of V(V) ions. PVP, especially, is also an organic compound containing a ketone functional group in its structure. Ammonium phosphates are inorganic agents, therefore, having less chance to reduce V(V) ion, but the inspection is also compulsory.

Figure 4.9 UV-vis spectra of 1.6 M V(V) in 4 M H_2SO_4 solution with the addition of thermally stable inorganic (a) and organic (b) additives. The UV-vis spectra of V(IV) and V(V) solutions are also displayed for comparison.

Figure 4.9 indicates the UV-vis spectra of 1.6 M V(V) in 4 M total SO_4^{2-} solution with the addition of thermally stable inorganic and organic additives. Compared to the V(IV) and V(V) reference solutions, it can be seen that there is no strange absorption peak in the UV-vis spectra of initial V(V) solution with the presence of both ammonium phosphate compounds and PVP. Hence, we can confirm the chemical stability of as-studied inorganic and organic additives in the positive vanadium electrolyte.

Figure 4.10 UV-vis spectra of 1.6 M V(V) in 4 M H₂SO₄ solution with the addition of thermally stable combined inorganic-organic additives. The UV-vis spectra of V(IV) and V(V) solutions are also displayed for comparison.

The UV-vis measurement is also conducted for the combined inorganic-organic additives to surely affirm its substantiality under strong oxidative medium of V(V) electrolyte. The result showed in Figure 4.10 demonstrates that the combined additives also do not change the oxidation state of V(V), implying its stability in the positive vanadium electrolyte. Therefore, both as-studied mono and combined additives can be absolutely used for further investigations.

4.3 Analysis of Vanadium Precipitate

To further understand the precipitation and crystallization process of the precipitate in the positive vanadium electrolyte at high temperature, we analyzed the precipitate compound collected by heating the sample beyond the thermal sustainable point.

4.3.1 Crystal Structure of Vanadium Precipitate

Figure 4.11 shows the XRD patterns of different vanadium precipitates collected by heating different positive vanadium solutions containing some inorganic additives.

Figure 4.11 XRD patterns of different vanadium precipitates obtained by heating electrolyte solution with and without inorganic additives at 50 °C in 10 days. Sample: 5 mL. Precipitate: filtrated in 24 h, dried at 60 °C in the air for 24 h.

For the blank solution, the precipitate possesses the typical crystal structure of solid V₂O₅, with several major diffraction peaks at 22.5, 26.5, 32, 47, 52°, corresponding to the (001), (110), (301), (600) and (221) planes, respectively. For the precipitate obtained from the vanadium electrolyte solution containing an H₃PO₄ additive, along with the formation of the V₂O₅ product, there is a new peak at 2θ = 12° representing the presence of amorphous VOPO₄ solid product [19]. This concludes the self-precipitation when adding H₃PO₄ into the positive

vanadium electrolyte, explaining the poor effectivity of this acid in the thermal stabilization of V(V). Interestingly, with the addition of 0.5, 1 and 1.5 wt.% of $\text{NH}_4\text{H}_2\text{PO}_4$ and $(\text{NH}_4)_2\text{HPO}_4$, the crystal structures of precipitate compounds are similar to the one collected from the blank electrolyte solution, intimating that V_2O_5 is the sole product. This means the NH_4^+ group in the structure of ammonium phosphate additives can eliminate the production of a solid VOPO_4 compound as we predicted before. This observation also interprets the better thermal stabilizing ability of ammonium phosphate agents as compared to H_3PO_4 for the positive vanadium electrolyte at high temperatures. Moreover, there were no other by-products are found by XRD when adding ammonium phosphate additives into the positive vanadium electrolyte.

Figure 4.12 XRD patterns of different vanadium precipitate obtained by heating electrolyte solution with and without PVP at 50 °C in 10 days. Sample: 5 mL. Precipitate: filtrated in 24 h, dried at 60 °C in the air for 24 h.

We also investigated the influence of PVP on the crystallization process of the V_2O_5 precipitate. Figure 4.12 shows the XRD patterns of different vanadium precipitates collected by heating the positive vanadium solution with and without the addition of PVP. Similar to the blank solution, the precipitates collected from the sample containing PVP also have the crystal structure of solid V_2O_5 , with several major diffraction peaks at 22.5, 26.5, 32, 47, 52°, corresponding to the (001), (110), (301), (600) and (221) planes, respectively. One exciting information is that the diffraction peak intensity of V_2O_5 precipitate is gradually decreased with the increasing of PVP content, which means the precipitate is more amorphous. This can be attributed to the blocking of PVP on the V_2O_5 nuclei surface, which restricts the crystallization process of the V_2O_5 precipitate. However, PVP is not recommended to add into vanadium electrolyte with a large amount due to its high viscosity as discussed before. Additionally, as described in the thermal stability test, the increasing amount of PVP addition gives no benefit the thermal stability of the positive vanadium electrolyte. And similar to ammonium phosphates, no other bi-product compounds were detected by XRD when adding PVP into the tested positive vanadium electrolyte.

The novel combined inorganic-organic additives were also examined the possibility to form the solid by-product with the positive vanadium electrolyte. In Figure 4.13, it is also seen that there is no strange crystal phase forming in the positive vanadium solution with the presence of as-studied combined additives. The only precipitate compound is still V_2O_5 , with several major diffraction peaks at 22.5, 26.5, 32, 47, 52°, corresponding to the (001), (110), (301), (600) and (221) planes, respectively.

Those XRD results have proved the advantage of as-studied thermally stable mono and combined additives, which are “soluble” in the positive vanadium electrolyte solution. However, there is a chance that the additive could produce

an amorphous complexing compound which is unable to detect by XRD. Thus, we continued analyzing the precipitates to inspect that possibility.

Figure 4.13 XRD patterns of different vanadium precipitates obtained by heating electrolyte solution with and without combined inorganic-organic additives at 50 °C in 10 days. Sample: 5 mL. Precipitate: filtrated in 24 h, dried at 60 °C in the air for 24 h.

4.3.2 Elemental Composition Analysis of Vanadium Precipitate

We extended the analysis of vanadium precipitate to more deeply understand the interaction of thermally stable additive and V(V) ion during the precipitating process. Hence, we conducted the elemental composition analysis for different precipitate compounds. Firstly, in Figure 4.14, we showed the SEM image for different V_2O_5 precipitate samples. It can be observed that the surface morphology of all V_2O_5 precipitate samples is relatively similar to each other.

Figure 4.14 FESEM images of different vanadium precipitate obtained by heating electrolyte solution with and without additives at 50 °C in 10 days. Sample: 5 mL. Precipitate: filtrated in 24 h, dried at 60 °C in the air for 24 h.

Those precipitate samples were continued analyzing by EDS measurement. Figure 4.15 shows the elemental composition of different vanadium precipitate compounds. The elemental distribution also can be seen by EDS mapping (see Appendix: Figure A.7).

Similarly to XRD measurement, the main elements of all precipitate samples are vanadium (V) and oxygen (O), indicating the existence of V_2O_5 compound. However, we also recorded a large amount of sulfur (S), which could come from H_2SO_4 supporting electrolyte that was not clearly washed during the filtration of precipitate compounds. And same to the XRD data, a huge mass of phosphorous (P) is detected in the composition of the V_2O_5 precipitate obtained from the vanadium solution containing an H_3PO_4 additive, implying the formation of $VOPO_4$ by-product. Interestingly, for the sample filtrated from the solution with $NH_4H_2PO_4$, $(NH_4)_2HPO_4$ and PVP additives, the main elements are still V and O. That means no other impurities were produced by the addition of such thermally stable additives into the positive vanadium electrolyte.

Figure 4.15 Elemental compositions of different vanadium precipitate obtained by heating electrolyte solution with and without additives at 50 °C in 10 days. Sample: 5 mL. Precipitate: filtrated in 24 h, dried at 60 °C in the air for 24 h.

XRD and EDS results have demonstrated the solubility of as-studied thermally stable additive in the positive vanadium electrolyte, and also explained the higher effectivity of ammonium phosphate additives in comparison with phosphoric acid, in agreement with other experiments.

4.3.3 Precipitate Particle Analysis

It is important to investigate the V_2O_5 precipitation at the early stage, e.g. during the nuclei formation. At this time, the V_2O_5 nuclei are still on the nano-sized scale, therefore, it is difficult to identify by as-mentioned thermal stability test. And also these nuclei cannot block the electrolyte flow as it is still possible

to be pumped through porous electrodes. However, the early formation of V_2O_5 nuclei can reduce the cell efficiency and capacity during the cycling process.

Figure 4.16 TEM image of two positive vanadium solutions (90% SOC) heated at 50 °C for 2 days (blank) (a) and 3 days (with 0.05 wt.% of PVP addition) (b).

Figure 4.16 illustrates the TEM image and particle size distribution of V_2O_5 precipitate nanoparticle gained from different positive vanadium solutions. It is easy to see that after heating at 50 °C in 2 days, the V_2O_5 nanoparticles forming in the blank additive-free solution have the uniform average diameter of about 6.6 nm (Fig. 4.16a). By the addition of 0.05 wt.% of PVP, even the heating time was increased up to 3 days, the particle size of V_2O_5 nuclei is still smaller compared to the one in blank solution, about 5.2 nm and are also more uniform. The capping effect of PVP has been demonstrated in this case, which restricts the growth of V_2O_5 nuclei.

To deeply investigate the vanadium electrolyte thermal stabilizing ability of PVP, we continued conducting the STEM-EDS mapping for the V_2O_5 nanoparticles collected from the solution containing 0.5 wt.% of PVP. Figure 4.17 indicates the STEM-EDS mapping of V_2O_5 nuclei obtained after heating the solution sample at 50 °C for 3 days.

Figure 4.17 STEM-EDS mapping of the precipitate collect from the positive vanadium solution (90% SOC) containing PVP (0.05 wt.%) heated at 50 °C for 3 days.

We recorded the signal of both vanadium (V) (from V_2O_5) and nitrogen (N) (from PVP) through scanning of a V_2O_5 nuclei cluster. Interestingly, it seems that the signal of V is more condensed in the middle of the cluster, while the signal of N is broader. This may imply the fact that the V_2O_5 nuclei are blocked inside the matrix of PVP and unable to bind with the neighbor nuclei to form a bigger particle. This hypothesis also explains the affectivity mechanism of PVP in term of thermal stabilizing for the positive vanadium electrolyte as we discussed before. However, since PVP is a high viscous polymer, the increasing adding amount of PVP will result to the glutinous matrix of PVP inside the electrolyte solution, raising the electrolyte viscosity and giving the risk of V_2O_5 nuclei-PVP precipitation. This danger has been shown in the variation of PVP content, which gives no change in term of the thermal stability for the positive vanadium electrolyte. Therefore, the addition amount of PVP should be carefully considered.

4.4 Electrochemical Investigation of Advanced Thermally Stable Additives

In the electrochemical investigation of novel vanadium electrolyte formula, the influences of thermally stable additives on the kinetics of redox reaction, peak current reversibility, electrolyte resistance are some of the most important factors.

4.4.1 Electrochemistry of Vanadium Electrolyte with the Addition of Thermally Stable Mono Additive

We first characterize the electrochemical behavior of the pristine vanadium electrolyte at room temperature.

Figure 4.18 The full range CV scan of pristine vanadium electrolyte at 10 mV.s^{-1} sweep rate at room temperature. Working electrode: carbon plate (1 cm^2 active area); reference electrode: saturated calomel electrode; counter electrode: platinum.

Figure 4.18 shows the full range CV measurement for the pristine vanadium electrolyte with carbon plate as the working electrode at 10 mV.s^{-1} sweep rates at room temperature. The CV curves indicates four typical oxidation state transformations of vanadium species, including the oxidation peak of V(IV) to V(V) ($1.0 - 1.1 \text{ V}$), the reduction peak of V(V) to V(IV) (about 0.7 V), the oxidation peak of V(II) to V(III) (about -0.4 V), and the reduction peak from V(III) to V(II) (about -0.8 V). This result is similar to other studies on the electrochemistry of VRFB electrolyte [20].

Figure 4.19 The positive side CV scan of pristine vanadium electrolyte at different sweep rates at room temperature. Working electrode: carbon plate (1 cm^2 active area); reference electrode: saturated calomel electrode; counter electrode: platinum.

For the main interest in this study, we performed the CV test again at the positive side for the pristine vanadium electrolyte. Figure 4.19 presents the CV

curves of pristine vanadium electrolyte (1.6 M V(III/IV) in 4 M total SO_4^{2-} within the positive potential window at different scan rates.

The peak potential separation ΔE_p of every CV scan represents the kinetics of V(IV)/V(V) redox reaction at that corresponding sweep rate. In Figure 4.19, we noticed that the value of ΔE_p proportionally increases with the increase of scan rate, suggesting the lower redox reaction kinetics of V(IV)/V(V) couple at higher sweep rate that has been described in previous studies [20]. The detailed value is showed in the Table 4.2, with the scan rate of 5, 10, 15, 20, 30, 50, 80, 100 mV.s^{-1} , the value of ΔE_p is varied to 0.27, 0.33, 0.37, 0.40, 0.45, 0.52, 0.59 and 0.63 V, respectively. By contrast, the peak current ratio (the ratio between oxidation peak current and reduction peak current), I_{pa}/I_{pc} , is gradually dropped with the increase of scan rate. This reflects the worse redox reaction reversibility at higher sweep rates with carbon plate electrode. In detail, the number of I_{pa}/I_{pc} scales down from 0.7 to 0.61, 0.65, 0.65, 0.65, 0.62, 0.49 and 0.45 with the scan rate of 5, 10, 15, 20, 30, 50, 80, 100 mV.s^{-1} , correspondingly. These results suggest the necessity to optimize the scan rate in the cyclic voltammetry of positive vanadium electrolyte to obtain the most accurate information.

Table 4.2 Peak potential separation and peak current ratio of the CV profile for pristine vanadium electrolyte within positive potential range.

Scan rate	ΔE_p (V)	I_{pa}/I_{pc}
5 mV.s^{-1}	0.27	0.70
10 mV.s^{-1}	0.33	0.61
15 mV.s^{-1}	0.37	0.65
20 mV.s^{-1}	0.40	0.65
30 mV.s^{-1}	0.45	0.65
50 mV.s^{-1}	0.52	0.62
80 mV.s^{-1}	0.59	0.49
100 mV.s^{-1}	0.63	0.45

There is no other unusual anodic and cathodic peak in the CV profile of pristine vanadium electrolyte, which means that it is really pure and suitable to be investigated with the presence of thermally stable additives.

Figure 4.20 The CVs of the positive vanadium electrolyte with the addition of NH₄H₂PO₄ (a), (NH₄)₂HPO₄ (b) and PVP (c) at 10 mV.s⁻¹ sweep rate in Ar-saturated condition at room temperature. Working electrode: glassy carbon (0.196 cm² active area); reference electrode: Hg/Hg₂SO₄ electrode; counter electrode: platinum.

To precisely characterize the impact of thermally stable additives on the electrochemical property of the positive vanadium electrolyte, we employed the glassy carbon electrode instead of carbon plate as working electrode, which can provide a more uniform active surface. Figure 4.20 displays the CVs of positive vanadium electrolyte with the addition of the different thermally stable additive. It is showed that by adding 0.5 and 1 wt.% of NH₄H₂PO₄ to 90% SOC

vanadium solution, the kinetics of V(IV)/V(V) redox reaction is hardly changed, except for a small drop of cathodic peak current density, probably due to the slow mobility of PO_4^{3-} ions. There is no additional peak rising in the CV curve of this solution, implying the stability of $\text{NH}_4\text{H}_2\text{PO}_4$ under electrochemical condition within V(IV)/V(V) redox potential range.

The same phenomenon is observed in the case of $(\text{NH}_4)_2\text{HPO}_4$, which also shows a slight decrease of cathodic peak current density while no significant detriment on the kinetics. The most remarkable effect was seen by the addition of PVP, the initial CV curve was deformed seriously, reflecting the restriction of PVP on the kinetics of V(IV)/V(V) redox reaction. This influence is caused by the capping effect of PVP, which could block the active area of the working electrode. Moreover, there is no unusual peak appeared in the CV curve which means that PVP is also stable under such electrochemical condition of V(IV)/V(V) redox couple. In detail, for the adding amount of 0.5 and 1 wt.%, the ΔE_p value extracted from the CV curve of pristine vanadium electrolyte lightly increases from about 0.21 V to 0.25 and 0.3 V for $\text{NH}_4\text{H}_2\text{PO}_4$, and up to 0.31, 0.36 V for $(\text{NH}_4)_2\text{HPO}_4$, respectively. However, with the addition of PVP, there was a large rise, to about 0.71 V for both the addition of 0.05 and 0.1 wt.%. The peak current ratio of pristine vanadium electrolyte CVs is also worse due to the addition of such thermally stable additives, but with an acceptable value.

The Nyquist plot obtained from EIS measurement of the positive vanadium electrolyte containing different thermally stable additives is also shown in Figure 4.21a-c, together with the equivalent circuit (Fig. 4.21d). In general, the only PVP can create a large change in the Nyquist plot of pristine electrolyte, while two ammonium phosphates compounds give no meaningful effect. The detailed parameters are listed in Table 4.3, in which, the R_l composes of solution resistance, electrode resistance and contact resistance of the electrolyte;

CPE (constant phase element) refers to the double layer capacitance; and R_2 represents the charge transfer resistance of the active species and electrode.

Figure 4.21 The Nyquist plot (a-c) obtained from EIS measurement of positive vanadium electrolyte in the presence of different thermally stable additives at room temperature and the equivalent circuit (d). EIS setup: glassy carbon working electrode, $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference electrode, Pt counter electrode, saturated Ar condition.

As shown in Table 4.3, the addition of both as-studied inorganic and organic additives into the positive vanadium electrolyte does not strongly affect the value of R_1 . In detail, the value of R_1 is about 0.61 and 0.62 $\Omega\cdot\text{cm}^{-2}$ for the addition of 0.5 and 1 wt.% of $\text{NH}_4\text{H}_2\text{PO}_4$, compared to the value of 0.63 $\Omega\cdot\text{cm}^{-2}$ for the blank solution. Similarly, the addition of 0.5 and 1 wt.% of $(\text{NH}_4)_2\text{HPO}_4$ is resulting in the R_1 value of about 0.65 and 0.64 $\Omega\cdot\text{cm}^{-2}$, with respect to the number of 0.65 $\Omega\cdot\text{cm}^{-2}$ for original solution. Lastly, the value of 0.64 and 0.65

$\Omega\cdot\text{cm}^{-2}$ were obtained for the insertion of 0.05 and 0.1 wt.% of PVP, in comparison with the value of $0.65 \Omega\cdot\text{cm}^{-2}$ for the pristine solution.

Table 4.3 Electrochemical parameters of positive vanadium electrolyte in the presence of different thermally stable additives.

Sample $\text{NH}_4\text{H}_2\text{PO}_4$	CV		EIS		
	ΔE_p (V)	I_{pa}/I_{pc}	R1 ($\Omega\cdot\text{cm}^2$)	CPE ($\text{F}\cdot\text{cm}^{-2}$)	R2 ($\Omega\cdot\text{cm}^2$)
0 wt. %	0.21	0.86	0.63	2.0×10^{-5}	10.0
0.5 wt. %	0.25	0.73	0.61	2.3×10^{-5}	9.9
1 wt. %	0.30	0.60	0.62	2.6×10^{-5}	10.8
$(\text{NH}_4)_2\text{HPO}_4$					
0 wt. %	0.25	0.84	0.65	2.6×10^{-5}	10.7
0.5 wt. %	0.31	0.68	0.65	2.6×10^{-5}	9.8
1 wt. %	0.36	0.58	0.64	2.7×10^{-5}	10.6
PVP					
0 wt. %	0.27	0.78	0.65	3.1×10^{-5}	10.0
0.5 wt. %	0.71	1.17	0.64	3.3×10^{-5}	12.6
1 wt. %	0.71	1.17	0.65	3.6×10^{-5}	13.2

The remarkable change can be observed for the constant phase element, with the addition of 0.5 and 1 wt.% of $\text{NH}_4\text{H}_2\text{PO}_4$, the *CPE* rises from initially of about $2.0\times 10^{-5} \text{ F}\cdot\text{cm}^{-2}$ to 2.3×10^{-5} and $2.6\times 10^{-5} \text{ F}\cdot\text{cm}^{-2}$, respectively. For $(\text{NH}_4)_2\text{HPO}_4$, the *CPE* for the solution containing 0.5 and 1 wt.% adding amount is about 2.6×10^{-5} and $2.7\times 10^{-5} \text{ F}\cdot\text{cm}^{-2}$, subsequently, with respect to the number of $2.6\times 10^{-5} \text{ F}\cdot\text{cm}^{-2}$ for the pristine solution. For the insertion of 0.05 and 0.1 wt.% of PVP, the *CPE* value is about 3.3×10^{-5} and $3.6\times 10^{-5} \text{ F}\cdot\text{cm}^{-2}$, while is only $3.1\times 10^{-5} \text{ F}\cdot\text{cm}^{-2}$ for the blank sample.

The charge transfer resistance of the positive vanadium electrolyte is almost unchanged by the addition of two ammonium phosphate additives, which is

varied around $10 \Omega \cdot \text{cm}^{-2}$, but it boosts up to 12.6 and $13.2 \Omega \cdot \text{cm}^{-2}$ for the injection of 0.05 and 0.1 wt.% of PVP. This again confirms the detriment of PVP on the charge transfer process of vanadium species and the electrode surface. One additional reason for the poor activity of PVP is the limited active surface area of glassy carbon working electrode employed in the CV and EIS setup. In the practical VRFB operation with porous carbon electrode material, the disadvantage of PVP could be minimized.

Another point is the *CPE* value for the blank vanadium electrolyte solution is not the same for all EIS scans. This can be attributed to the slight shifting of electrodes in every EIS set up, or the small dissimilarity in the SOC of blank electrolyte solution in every scan.

4.4.2 Electrochemistry of Vanadium Electrolyte with the Addition of Advanced Combined Inorganic-Organic Additive

After analyzing the electrochemical property of the positive vanadium electrolyte with the presence of each thermally stable mono additive independently, we also conducted the CV and EIS experiment to examine the influence of combined inorganic-organic additives, which have been shown the co-stabilizing effect in thermal stability.

Figure 4.22 shows the CV scan at $10 \text{ mV} \cdot \text{s}^{-1}$ sweep rate (a-b) and Nyquist plot (c-d) of the positive vanadium electrolyte with the addition of combined inorganic-organic additives at room temperature. The deformation of pristine electrolyte solution CV curve (Fig. 4.22a-b) due to the addition of combined additives reflects the dominant impact of PVP on the electrochemistry of positive vanadium electrolyte compared to ammonium phosphates. This detriment includes the drop in V(IV)/V(V) redox reaction kinetics and the imbalance of peak current reversibility. As discussed before, this is mainly due

to the capping property of PVP which slightly blocks the surface of the glassy carbon electrode.

Figure 4.22 The CV scan at 10 mV.s⁻¹ sweep rate (a-b) and Nyquist plot (c-d) of the positive vanadium electrolyte with the addition of combined inorganic-organic additives at room temperature. CV and EIS setup: glassy carbon working electrode, Hg/Hg₂SO₄ reference electrode, Pt counter electrode, saturated Ar condition.

In detail, the value of ΔE_p is gained from 0.23 V for blank electrolyte to 0.54, 0.55 and 0.56 V for the addition of 0.025 wt.% PVP + 0.25 wt.% NH₄H₂PO₄, 0.025 wt.% PVP + 0.5 wt.% NH₄H₂PO₄, and 0.05 wt.% PVP + 0.5 wt.% NH₄H₂PO₄, respectively; while the peak current ratio I_{pa}/I_{pc} is scaled down from 0.79 for the pristine solution to 0.23, 0.17 and 0.17 with the addition of corresponding electrolyte formula. For the formula 2 of combined additives, it is showed that with the addition of 0.025 wt.% PVP + 0.25 wt.% (NH₄)₂HPO₄,

0.025 wt.% PVP + 0.5 wt.% $(\text{NH}_4)_2\text{HPO}_4$, and 0.05 wt.% PVP + 0.5 wt.% $(\text{NH}_4)_2\text{HPO}_4$, value of ΔE_p is boosted from 0.2 V for the blank solution to 0.42, 0.49 and 0.53 V, correspondingly. Similar to formula 1, the peak current ratio I_{pa}/I_{pc} is also reduced from 0.67 of the additive-free solution to 0.24, 0.14 and 0.22 with the presence of respective additive.

As seen in the investigation with mono additive, the parameters extracted from EIS measurement indicate the change in *CPE* and charge transfer resistance of the positive vanadium electrolyte with combined additives, while no fluctuation of electrolyte resistance. As shown in Table 4.4, for the formula 1 of combined additives, the value of R_l of blank solution is stable at about $0.67 \Omega\cdot\text{cm}^{-2}$, compared to the number of 0.67, 0.66 and $0.66 \Omega\cdot\text{cm}^{-2}$ for the addition of 0.025 wt.% PVP + 0.25 wt.% $\text{NH}_4\text{H}_2\text{PO}_4$, 0.025 wt.% PVP + 0.5 wt.% $\text{NH}_4\text{H}_2\text{PO}_4$, and 0.05 wt.% PVP + 0.5 wt.% $\text{NH}_4\text{H}_2\text{PO}_4$, respectively. The value of *CPE*, instead, slightly increase from $1.6\times 10^{-5} \text{ F}\cdot\text{cm}^{-2}$ for the original electrolyte up to 1.7×10^{-5} , 1.9×10^{-5} , and $2.0\times 10^{-5} \text{ F}\cdot\text{cm}^{-2}$ for the solution containing the corresponding additive. The charge transfer resistance R_2 , as mentioned, is also increased from the initial value of $11.2 \Omega\cdot\text{cm}^{-2}$ to 13.1, 13.7 and $13.7 \Omega\cdot\text{cm}^{-2}$ for as-listed adding the amount of combined additive.

Alike to the formula 1, with the addition of 0.025 wt.% PVP + 0.25 wt.% $(\text{NH}_4)_2\text{HPO}_4$, 0.025 wt.% PVP + 0.5 wt.% $(\text{NH}_4)_2\text{HPO}_4$, and 0.05 wt.% PVP + 0.5 wt.% $(\text{NH}_4)_2\text{HPO}_4$, the value of R_l of the positive solution is stable at about $0.61 \Omega\cdot\text{cm}^{-2}$. The value of *CPE* for the original electrolyte is about $1.8\times 10^{-5} \text{ F}\cdot\text{cm}^{-2}$, and it is fluctuated to be 1.8×10^{-5} , 1.8×10^{-5} , and $1.9\times 10^{-5} \text{ F}\cdot\text{cm}^{-2}$ for the solution containing the corresponding additive. The charge transfer resistance, as mentioned, is also increased from the initial value of $8.9 \Omega\cdot\text{cm}^{-2}$ to 12.3, 11.5 and $12.7 \Omega\cdot\text{cm}^{-2}$ for the as-listed adding amount of combined additive.

Table 4.4 Electrochemical parameters of positive vanadium electrolyte in the presence of combined inorganic-organic additives.

Sample	CV			EIS	
Formula 1	ΔE_p (V)	I_{pa}/I_{pc}	R_1 ($\Omega \cdot \text{cm}^2$)	CPE ($\text{F} \cdot \text{cm}^{-2}$)	R_2 ($\Omega \cdot \text{cm}^2$)
Blank	0.23	0.79	0.67	1.6×10^{-5}	11.2
0.025 wt.% PVP + 0.25 wt.% $\text{NH}_4\text{H}_2\text{PO}_4$	0.54	0.23	0.67	1.7×10^{-5}	13.1
0.025 wt.% PVP + 0.5 wt.% $\text{NH}_4\text{H}_2\text{PO}_4$	0.55	0.17	0.66	1.9×10^{-5}	13.7
0.05 wt.% PVP + 0.5 wt.% $\text{NH}_4\text{H}_2\text{PO}_4$	0.56	0.17	0.66	2.0×10^{-5}	13.7
Formula 2					
Blank	0.20	0.67	0.61	1.8×10^{-5}	8.9
0.025 wt.% PVP + 0.25 wt.% $(\text{NH}_4)_2\text{HPO}_4$	0.42	0.24	0.61	1.8×10^{-5}	12.3
0.025 wt.% PVP + 0.5 wt.% $(\text{NH}_4)_2\text{HPO}_4$	0.49	0.14	0.60	1.8×10^{-5}	11.5
0.05 wt.% PVP + 0.5 wt.% $(\text{NH}_4)_2\text{HPO}_4$	0.53	0.22	0.61	1.9×10^{-5}	12.7

It is noted that the small differences in all parameters of blank electrolyte solution are due to the position variation of all components in CV and EIS set up after every measurement. However, the set up was kept the same for each additive formula so the data for the solution containing with and without additive are reliable.

In conclusion, after a series of investigation, the thermally stable mono additives in general and combined additives, in particular, have demonstrated their excellent thermal stabilizing ability for the positive vanadium electrolyte at 45 and 50 °C. Moreover, as-studied advanced additives also indicate the chemical and electrochemical stability under inspection condition of pristine

vanadium electrolyte. Therefore, it is suitable to be tested in the practical cell cycling condition, which will be presented in the next chapter.

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Chapter 5

Long-term Cycling Performance of Advanced Halide-free Thermally Stable Vanadium Electrolyte

This chapter presents the practical performance of novel electrolyte formulas under cycling condition of vanadium redox flow battery; the improvement of long-term cell cycling performance at high temperatures with the presence of thermally stable stabilizers in the vanadium electrolyte; the effect of advanced precipitation inhibitors on the cell components during cell cycling process.

5.1 Effect of Ion Exchange Membrane on the Cycling Performance of Vanadium Redox Flow Battery

Ion exchange membrane (IEM) is an important component in VRFB, which separates two electrolyte reservoirs and allows the proton transfer to maintain the charge balance of the cell. IEM is also one of the key factors determines the cell resistance, efficiency and capacity drop. All of these parameters directly related to the nature of membrane and also its interaction with vanadium electrolyte. Therefore, before testing the influence of thermally stable additives on the cell performance, we characterized the behavior of IEM in the contact with vanadium electrolyte. As mentioned in chapter 3, two typical IEMs were selected for investigation: Fumatech FAP 450 anion exchange membrane (AEM) was used as the main type membrane in this Ph.D. study, while Nafion 117 cation exchange membrane (CEM) was chosen for comparison purpose.

5.1.1 The Interaction of Ion Exchange Membrane and Pristine Vanadium Electrolyte

There are several studies on the vanadium ion absorption have been published for CEM, but less for AEM [1-5]. It is reported that CEM, especially the perfluorinated based membrane containing the sulfonic group, could absorb a small amount of all vanadium ions in different oxidation states, resulting in the low ion selectivity for this type of membrane. While AEM was expected that can address this issue and therefore possesses higher ion selectivity compared to CEM in VRFB application. The only problem related to AEM is the concern about the low chemical stability of functional groups in the strong acid medium [5]. In this Ph.D. study, we first examined the vanadium adsorption behavior of IEM in a static condition.

Figure 5.1 indicates the UV-vis spectra of Nafion 117 CEM and Fumatech FAP 450 AEM dipped into different vanadium electrolyte solutions for over 24 h.

Compared to the UV-vis spectra of different vanadium electrolyte solutions (Fig. 5.1a) and as-tested membrane dipped into 4 M H_2SO_4 solution, it is confirmed that there is a small interpenetration of vanadium ions in different oxidation states in the Nafion 117 CEM, which due to the attraction by HSO_3^- ion-conducting groups in the membrane structure, as-reported previously. In detail, the Nafion 117 membrane dipped into V(II) solution showed the adsorption peak at 850, 580 and 370 nm, correspondingly. For V(III) solution, the tested membrane indicated the peak at 780, 600 and 400 nm, respectively. The membrane dipped into V(IV) solution displayed the absorption peak at 760 nm and a strong adsorption at the wavelength below 340 nm. And lastly, for V(V) solution, the as-studied membrane also showed a strong absorption peak at the wavelength below 500 nm.

Figure 5.1 The UV-vis spectra of different vanadium solutions (a), Nafion 117 CEM (b) and Fumatech FAP 450 AEM (c) dipped in those solutions for over 24 h. The membrane was pretreated prior to the experiment. Electrolyte: 1.6 M V in 4 M total SO_4^{2-} .

While for Fumatech FAP 450 AEM, there is also a weak permeation of V(IV) ions into the membrane, but no existence of V(II) and V(III) ions was recorded in the membrane. Interestingly, the V(V) solution demonstrated the strong absorption into the Fumatech FAP 450 AEM. All of these vanadium adsorption behaviors of Nafion 117 CEM and Fumatech FAP 450 AEM also can be visually seen in Figure A.8 (see Appendix).

Figure 5.2 The UV-vis spectra of Nafion 117 CEM and Fumatech FAP 450 AEM dipped in different concentration V(III), V(IV) and V(V) solutions at for over 24 h. The membrane was pretreated prior to the experiment. Supporting electrolyte: 4 M H_2SO_4 .

We continued investigating by varying the concentration of vanadium species in 4 M H_2SO_4 solution (except for V(II) species due to the low chemical stability in ambient condition). Figure 5.2 illustrates the adsorption behavior of different vanadium solutions in the CEM and AEM with the variation of vanadium species concentration. For Nafion 117 CEM (Fig. 5.2a-c), the result shows that even at low vanadium (III, IV, V) concentration (in 4 M H_2SO_4 solution), the Nafion 117 CEM still can absorb vanadium ions in different levels corresponding to the initial vanadium species concentration. For the Fumatech FAP 450 AEM, it mostly did not absorb V(III) ions at any concentration, while only the V(IV) species at high concentration (1.6 M) can enter to the membrane. However, for the V(V) solution, the AEM is able to absorb the V(V) ions even at very low concentration, and the absorbed amount of V(V) is proportional to the concentration of V(V) in 4 M H_2SO_4 solution.

These interesting results indicate that the interaction of vanadium species and IEM in VRFB system is not simple as reported.

5.1.2 Membrane Resistivity Change Due to the Vanadium Absorption and Mechanism

In Figure 5.3, we evaluated the change in resistivity of CEM/AEM after immersing in different vanadium solutions (1.6 M V in 4 M SO_4^{2-}).

Figure 5.3 The EIS measurement of Nafion 117 CEM and Fumatech FAP 450 AEM dipped in different vanadium solutions for over 24 h. The membrane was pretreated prior to the experiment. Electrolyte: 1.6 M V in 4 M total SO_4^{2-} .

For Nafion 117 CEM, the small absorbance of different vanadium ions into the membrane slightly increases its resistivity, compared to the membrane immersed in 4 M H_2SO_4 solution. In detail, the resistivity of Nafion CEM is about 0.68, 0.65, 0.54 and $0.41 \Omega \cdot \text{cm}^2$ when dipping in V(II), V(III), V(IV) and V(V) solutions, respectively, compared to the value of about $0.32 \Omega \cdot \text{cm}^2$ in 4 M H_2SO_4 . For Fumatech FAP 450 AEM, the membrane resistivity is also weakly increased up to 0.75, 0.63, and $0.73 \Omega \cdot \text{cm}^2$ when dipping in V(II), V(III) and V(IV) solutions, correspondingly, compared to the value of about 0.37 in 4 M H_2SO_4 . However, in particular, when immersing in V(V) solution, the

resistivity of Fumatech AEM rapidly rises to the value of about $8.2 \text{ } \Omega \cdot \text{cm}^2$. Figure A.9 (see Appendix) also indicates the variation of CEM/AEM resistivity when immersing in different concentrated V(III), V(IV) and V(V) solutions. In different concentrated V(III) and V(IV) solutions, the resistivity of CEM/EAM, interestingly, is slightly decreased at very low concentration ($< 0.4 \text{ M}$), and then increasing again ($> 0.8 \text{ M}$). While in different concentrated V(V) solutions, the increasing resistivity is only observed when dipping the Fumatech AEM, while the resistivity of Nafion CEM is hardly changing.

Table 5.1 The EDX analysis for Nafion 117 CEM and Fumatech FAP 450 AEM.

Nafion 117 CEM	Elemental weight%				
	C	F	S	O	K
As-received	24.9 ± 0.8	72.4 ± 0.8	0.8 ± 0.02	1.4 ± 0.1	0.4 ± 0.01
Pretreated	26.1 ± 0.1	71.9 ± 0.2	0.7 ± 0.05	1.4 ± 0.2	0
4 M H ₂ SO ₄	26.3 ± 0.5	71.4 ± 0.4	0.8 ± 0.03	1.5 ± 0.2	0
Fumatech FAP 450 AEM	Elemental weight%				
	C	F	S	O	N
As-received	51.6 ± 0.5	39.6 ± 2.4	0.4 ± 0.01	2.2 ± 0.8	5.9 ± 0.6
Pretreated	52.7 ± 1.1	32.9 ± 3.9	~ 0	6.9 ± 0.8	7.2 ± 4.2
4 M H ₂ SO ₄	49.5 ± 3.4	34.5 ± 1.1	3.8 ± 0.2	7.9 ± 1.2	4.3 ± 0.9

To understand the reason of vanadium permeability and thereof membrane resistivity change, we conducted the EDS analysis for different CEM/AEM samples after immersing into vanadium electrolyte solution. Table 5.1, firstly, shows in detailed the elemental composition of as-received, pre-treated and 4 M H₂SO₄ immersed Nafion 117 CEM and Fumatech FAP 450 AEM. The elemental composition of all Nafion 117 CEM samples is corresponding to its typical chemical structure, which mainly composes of carbon (C) and fluorine (F); and the presences of sulfur (S) and oxygen (O) represent the sulfonic ion exchange group (see Appendix: Fig. A.10a). As-received Nafion CEM contains a tiny amount of K impurity ($\sim 0.4 \text{ wt.}\%$), but it disappears after pre-treatment.

The amount of S is hardly changed for all three samples ($\sim 0.7 - 0.8$ wt.%), indicating that Nafion CEM does not absorb SO_4^{2-} ions in 4 M H_2SO_4 solution.

For Fumatech FAP 450 AEM, the major element composition also includes C and F. In addition, we detected a large amount of O (~ 2.2 wt.%) and nitrogen (N) (~ 5.9 wt.%) in the Fumatech membrane structure, which can come from the ion exchange group in the membrane structure, e.g. the diaza(bicyclo-octane) group (DABCO) (see Appendix: Fig. A.10b). Interestingly, the strong adsorption of SO_4^{2-} ions of Fumatech FAP 450 membrane is indicated by the large increasing amount of S (~ 3.8 wt.%) and O (~ 7.9 wt.%) in the membrane dipped in 4 M H_2SO_4 solution, compared to as-received and pre-treated membrane ($\sim 0\%$ for S).

The EDS analysis of the membrane dipped into different vanadium solution is presented in Figure 5.4 (the elemental weight percentage was normalized to C percentage for comparison purpose). For Nafion 117 CEM immersed in different pristine vanadium solutions (1.6 M V in 4 M total SO_4^{2-}) (Fig. 5.4a), it is showed that a few vanadium species absorbed into the membrane can be arranged as $\text{V(II)} > \text{V(III)} > \text{V(IV)} > \text{V(V)}$. Interestingly, the amount of S and O are also higher, corresponding to the amount of V. We also referred to the vanadium ion diffusion coefficient that has been reported in literature just for comparison. The study of Sun *et al.* claimed that the diffusion coefficients of the vanadium ions across Nafion 115 (Dupont) in a VRFB are measured and found to be in the order of $\text{V(II)} > \text{VO}^{2+} > \text{VO}_2^+ > \text{V(III)}$ [6]; and it is different to the work of Chieng on the same membrane, Nafion 117, which reported that the diffusivities of the V(IV) and V(V) species across the membranes were much higher than the V(II) and the V(III) species: $\text{V(IV)} > \text{V(V)} > \text{V(II)} > \text{V(III)}$ [1, 7]. Of course, in our study, the absorbed amount of vanadium ions in Nafion CEM do not directly reflect the ion transfer process through the membrane during cycling of VRFB.

For the Fumatech FAP 450 membrane, while only a little volume of V(II), V(III) and V(IV) ions are presented in the membrane, there is a huge amount of V(V) is detected. The percentage of O is also much higher for the membrane dipped into V(V) solution compared to others. With respect to this, the amount of S and O are also increased. This observation shows that the SO_4^{2-} ions are also absorbed together with V ions.

Figure 5.4 The EDX analysis of Nafion 117 CEM and Fumatech FAP 450 AEM dipped in different pristine vanadium solutions (1.6 M V in 4 M total SO_4^{2-}) (a-b) and various concentration V(V) solution (c-d) for over 24 h. The membrane was pretreated prior to the experiment.

We continued testing the permeability of only V(V) in as-studied IEMs by varying the concentration of V(V) solution. It is observed that for Nafion 117 CEM, the amount of V and O absorption are proportional to the increase of

V(V) concentration; while the increasing amount of S is unremarkable. From this, we can conclude that the absorbed V(V) compound in the Nafion membrane should be a structure containing mainly V and O, possibly in form of VO_2^+ ions. Differently, for Fumatech AEM, the increasing concentration of V(V) is also resulting in the increasing absorbed amount of V, S and O at the V(V) concentration from 0.1 to 0.4 M. Beyond 0.4 M of V(V) solution, only the amount of O and V absorbed in the membrane is increased, while the amount of S is steady (see Appendix: Fig. A.11).

Figure 5.5 The relationship of resistivity and elemental composition for the CEM/AEM immersed in different concentrated V(V) solutions for over 24 h.

Figure 5.5 illustrates the relationship of resistivity and elemental composition for the CEM/AEM immersed in different concentrated V(V) solutions. For Nafion CEM, in general, the variation of membrane resistivity is corresponding to the increase of V, S and O amount. For Fumatech AEM, with the concentration of V(V) below 0.8 M, the membrane resistivity is proportional to the amount of V, S, and O in the membrane. However, with the higher amount of V and O at the V(V) concentration of 1.6 M, the membrane resistivity significantly rises, while the amount of S is hardly changed.

While it is easy to explain the vanadium absorption behavior for Nafion 117 CEM, the vanadium permeability in Fumatech FAP 450 is relatively

complicated, in particular for V(V) species. Based on above data, the EDS analysis showed that when varying the concentration of V(V) in 4 M H_2SO_4 solution, the amount of V(V) presented in the membrane is also proportionally changed, while the SO_4^{2-} adsorption is unchanged. This indicates that the SO_4^{2-} ions are firstly absorbed into the membrane due to the binding with membrane's cation group. Additionally, the V(V) ions have a strong binding interaction with SO_4^{2-} ions, resulting in the high concentration of V(V) near or inside the membrane, and even following by the local V_2O_5 precipitation. This causes the significant rising of membrane resistivity as reported.

Figure 5.6 The mechanism of V(V) absorption in anion exchange membrane in positive vanadium electrolyte.

5.1.3 Cycling Performance with Different Ion Exchange Membranes

The absorption of vanadium electrolyte species into IEM in static condition has been discussed previously. The consequence of such interaction was continued investigating under cell cycling condition. We first noticed that the net electrolyte crossover of the cell using Nafion 117 CEM is from the negative

side to the positive, which may due to the higher permeability of negative vanadium species as observed in previous experiments (Fig. 5.7b). While in contrast, for the Fumatech AEM, the net electrolyte transfer is from the positive side to the negative side (Figure 5.7b). Moreover, with the same number of cycles, the degree of electrolyte imbalance when using Fumatech AEM is much larger than for Nafion CEM. This due to the strong adsorption of V(V) in the Fumatech AEM. In this case, the absorbed V(V) ion can slowly diffuse through the membrane and cross to the negative side.

Figure 5.7 Electrolyte imbalances after cell cycling with Nafion 117 CEM (b) and Fumatech FAP 450 AEM (c).

Figure 5.8 shows the cell cycling performance with anion/cation exchange membranes at different temperatures. The voltage efficiency for Nafion CEM is generally stable over the cycling process, while Fumatech AEM voltage efficiency falls after each cycle from 92% and 93% to 91.5% and 92.5% (at 25 °C and 40 °C respectively). The resistivity of the cell using Nafion CEM is relatively stable over 5 cycles at both temperatures, indicating the low electrolyte crossover behavior. Meanwhile, the resistivity of cell using Fumatech AEM increases significantly over 5 cycles, from $1.3\Omega\cdot\text{cm}^2$ and $1.4\Omega\cdot\text{cm}^2$ to $1.4\Omega\cdot\text{cm}^2$ and $1.6\Omega\cdot\text{cm}^2$ (at 25 °C and 40 °C respectively). The increase in resistivity is mainly due to electrolyte transfer, which is visible as shown in Figure 5.7 above. The cell capacity shows a decreasing trend across all experiments over cycle repetitions. This trend is more significant for

Fumatech AEM, at 120 mAh/cycle dropping rate for the temperature of 40 °C, which is likely to be caused by a large amount of electrolyte transfer across the membrane shown in Figure 5.7. For each parameter, it can be seen that temperature has a greater impact on the performance of cells using Fumatech AEM. The performance of Fumatech AEM is significantly poorer at 40 °C, making it unsuitable for operation at higher temperatures.

Figure 5.8 Voltage efficiency (a), cell resistivity (b), self-discharge current density (c), and capacity drop (d) of the cell cycling using different IEMs at 25 and 40 °C. Cell: 20 cm² active area; electrolyte volume: 100 mL; flow-rate: 50 mL/min; current density: 40 mA/cm²; potential window: 0.9 – 1.65 V; oxidation prevention layer: Paraffin oil (10 mm).

Cell cycling data was also collected for deviated charge and discharge currents as shown in Figure 5.9 (left half and right half of each graph), to observe any

effects. For the first 5 cycle, the cell was slowly charged with the current density of $10 \text{ mA}\cdot\text{cm}^{-2}$ and quickly discharged the current density of $100 \text{ mA}\cdot\text{cm}^{-2}$. For the next 5 cycles, the charged/discharged current density is reversed.

Figure 5.9 Voltage efficiency (a), cell resistivity (b), self-discharge current density (c), and capacity drop (d) of the cell cycling using different IEMs at 25 and 40 °C with deviated charge/discharge current. Cell: 20 cm^2 active area; electrolyte volume: 100 mL; flow-rate: 50 mL/min; current density: $40 \text{ mA}/\text{cm}^2$; potential window: 0.9 – 1.65 V; oxidation prevention layer: Paraffin oil (10 mm).

The result shows that the decrease in voltage efficiency is more significant at low-charge/high-discharge current, compared to high-charge/low-discharge current. When compared to the voltage efficiency of intermediate charge and discharge current in Figure 5.8, the decrease in voltage efficiency is larger for both high/low current combinations. As such, while the discharge process

appears to be more detrimental to cell performance than the charging process, it may be advantageous to subject the cell to a steady cycle rate. Aside from Fumatech AEM having the same highly positive trend of resistivity at 40 °C found in Figure 5.8, the impact of different charge and discharge currents is low as the resistivity changes are similar. The different charge/discharge current does not appear to affect the rate of decrease in capacity for both Nafion and Fumatech membranes (constant gradient). Fumatech AEM still has a steeper fall in capacity over the cycling process, making it less desirable for use in VRFB compared to Nafion.

Table 5.2 Cell performance comparison during 5 charge/discharge cycles.

Parameter	Nafion 117 CEM	Fumatech FAP 450 AEM
Interaction with vanadium ion	V(II), V(III), V(IV), V(V)	V(IV), V(V)
Thermal-sensitivity	Low	High
Electrolyte crossover	Low	High
Cell cycling voltage efficiency	At 25°C: 91.9% At 40°C: 92.2%	At 25°C: 91.8% At 40°C: 92.6%

The summary of cell cycling behavior using different IEMs is showed in Table 5.2. All of these results have proved that the interaction of different species presented in the vanadium electrolyte and IEM possess an important role in the overall performance of VRFB. Therefore, the interaction of IEM with thermally stable additives will be also an important factor that needs to clarify in the cell cycling test.

5.2 Impact of Temperature Variation on the Cycling Performance of Vanadium Redox Flow Battery

It is known that temperature does not affect only on the thermal stability of VRFB electrolyte, but also on the performance of an operating system [8].

Therefore, it is necessary to investigate the temperature dependence of the cell operation using the blank additive-free electrolyte and the additive contained the electrolyte. In this Ph.D. project, we employed a 20 cm² single cell to inspect the influence of temperature on the cycling performance. The setup has been described in detail in chapter 3. It is noted that in this test, only the temperature was varied, while the whole system (cell and electrolyte) was kept unchanged during the experiment. Therefore, the effect of electrolyte imbalance and degradation may become dominantly as compared to the influence of temperature at a higher number of charge/discharge cycles.

5.2.1 Temperature Dependence of Cell Cycling Performance Using Blank Additive-free Electrolyte

Firstly, we examined the temperature dependence of the cell operated with pristine vanadium electrolyte (1.6 M V in 4 M total SO₄²⁻). The result is showed in Figure 5.10.

It is observed that the voltage efficiency of the cell slightly increases with the increase of temperature due to the improvement of redox reaction kinetics and reduction of ohmic resistance [Fig. 5.10a). This is in agreement with the study of Zhang *et al.*, but with a Nafion 115 membrane [8]. However, by continuing to increase the temperature, the voltage efficiency is gradually dropped because of electrolyte crossover and decomposition. In detail, the average voltage efficiency of the cell at 25, 35, 40, 45 and 50 °C is recorded to be 88.1, 88.4, 88.3, 87.6 and 87.6%, respectively.

The cell resistivity, at the beginning, is reduced thanks to the lower ohmic resistance at high temperature. However, at a higher number of charge/discharge cycles and temperatures, the cell resistivity slowly rises, mainly due to the higher level of electrolyte imbalance as reported in section

5.1.3 for Fumatech FAP 450 AEM. For instance, the cell resistivity is measured to be 2.2, 2.1, 2.2, 2.3 and 2.3 $\Omega\cdot\text{cm}^2$ at the temperature of 25, 35, 40, 45 and 50 $^{\circ}\text{C}$, correspondingly. In addition, the growth of cell resistivity is also probably caused by the penetration of V(V) ion into the membrane during cycling process, as demonstrated above.

Figure 5.10 Voltage efficiency (a), cell resistivity (b), self-discharge current density (c), and capacity drop (d) of cell cycling at different temperature using blank electrolyte. Cell: 20 cm^2 active area; electrolyte volume: 100 mL; flow-rate: 10 mL/min; current density: 40 mA/cm^2 ; potential window: 0.9 – 1.65 V; oxidation prevention layer: Paraffin oil (10 mm); membrane: Fumatech FAP 450; temperature: 25 – 50 $^{\circ}\text{C}$; number of cycle: 10 cycles/temperature point.

The self-discharged current density is almost unchanged with the effect of temperature, which is shown the value of 0.48 – 0.65 $\text{mA}\cdot\text{cm}^{-2}$ at the

temperature ranging from 25 to 50 °C. Since the electrolyte flow was completely isolated from the air by tightly cell assembling and Paraffin oil electrolyte preventing layer, the self-discharge phenomena are mainly originated from the ion diffusion through the IEM. The capacity of the cell is sharply reduced over the change of temperature due to the electrolyte transfer through the membrane between two tanks as discussed before and is reflecting on as-mentioned cell resistivity increase. Moreover, the formation of inV_2O_5 precipitate also could be another reason for the cell capacity drop. We detected the presence of an orange solid compound in the positive electrolyte tank and flow frame after the test (Figure 5.11). By EDS analysis, that compound is identified to be a solid V_2O_5 product (see Appendix: Fig. A.12).

Figure 5.11 The view of positive electrolyte tank and flow-frame after cell cycling test at 25 – 50 °C with blank additive-free electrolyte.

5.2.2 Temperature Dependence of Cell Cycling Performance Using Electrolyte Containing Combined Thermally Stable Additives

To examine the behavior of combined inorganic-organic on the cell cycling performance under various temperatures, we added two different formulas of additive into the pristine vanadium electrolyte prior to the cycling test: Formula

1: 0.025 wt.% PVP + 0.25 wt.% $\text{NH}_4\text{H}_2\text{PO}_4$; formula 2: 0.025 wt.% PVP + 0.25 wt.% $(\text{NH}_4)_2\text{HPO}_4$.

The results for formula 1 are shown in Figure 5.12 and 5.13. In general, the cell cycling performance with two novel electrolyte formulas behaves similarly as the pristine vanadium electrolyte.

Figure 5.12 Voltage efficiency (a), cell resistivity (b), self-discharge current density (c), and capacity drop (d) of cell cycling at different temperature using electrolyte containing formula 1 of additive. Cell: 20 cm^2 active area; electrolyte volume: 100 mL; flow-rate: 10 mL/min; current density: 40 mA/cm^2 ; potential window: 0.9 – 1.65 V; oxidation prevention layer: Paraffin oil (10 mm); membrane: Fumatech FAP 450; temperature: 25 – 50 °C; number of cycle: 10 cycles/temperature point.

For the formula 1 (Fig. 5.12), it is akin to the blank electrolyte, the voltage efficiency of the cell with combined additives slightly rises with the increase of

temperature. However, the combined inorganic-organic could better maintain the voltage efficiency of the cell under the effect of temperature. In detail, the average voltage efficiency of the cell at 25, 35, 40, 45 and 50 °C is recorded to be 89.7, 90.3, 89.9, 89.4 and 89.2%, respectively.

The cell resistivity, at intermediate temperatures, is also dropped due to the lower ohmic resistance at high temperature. However, as seen with the blank electrolyte, the cell resistivity gently boosts, at a higher number of charge/discharge cycles and temperatures. For instance, the cell resistivity is measured to be 1.9, 1.8, 1.8, 1.9 and 2.0 $\Omega\cdot\text{cm}^{-2}$ at the temperature of 25, 35, 40, 45 and 50 °C, correspondingly.

Figure 5.13 The view of positive electrolyte tank and flow-frame after cell cycling test at 25 – 50 °C with the electrolyte containing 0.025 wt.% PVP + 0.25 wt.% NH₄H₂PO₄ (formula 1).

The self-discharged current density in the novel electrolyte formula is almost unchanged with the effect of temperature, which is shown the value of 0.06 – 0.30 mA.cm⁻² at the temperature ranging from 25 to 50 °C. However, the capacity of the cell using an electrolyte containing formula 1 of additive is still strongly dropped at higher temperatures and numbers of the cycle. By checking

the positive electrolyte tank and flow-frame, we observed that no formation of V_2O_5 was found after the test (Figure 5.13 and Appendix: Fig. A.12). Therefore, the cell resistivity increase and capacity drop principally subject to the electrolyte crossover through the Fumatech AEM.

Figure 5.14 Voltage efficiency (a), cell resistivity (b), self-discharge current density (c), and capacity drop (d) of cell cycling at different temperature using electrolyte containing formula 2 of additive. Cell: 20 cm² active area; electrolyte volume: 100 mL; flow-rate: 10 mL/min; current density: 40 mA/cm²; potential window: 0.9 – 1.65 V; oxidation prevention layer: Paraffin oil (10 mm); membrane: Fumatech FAP 450; temperature: 25 – 50 °C; number of cycle: 10 cycles/temperature point.

For the formula 2 (Fig. 5.14), as same as the blank electrolyte and formula 1, at higher temperatures, the voltage efficiency of the cell with formula 2 of additives is also elevated. Similar to the formula 1, the addition of 0.025 wt.% PVP + 0.25 wt.% $(NH_4)_2HPO_4$ into the pristine electrolyte also could retain the

voltage efficiency of the cell under the effect of temperature. In detail, the average voltage efficiency of the cell at 25, 35, 40, 45 and 50 °C is recorded to be 89.3, 90.6, 90.6, 90.3 and 89.6%, respectively.

The cell resistivity, in detail, is recorded to be 1.9, 1.7, 1.7, 1.8 and 1.9 $\Omega\cdot\text{cm}^{-2}$ at the temperature of 25, 35, 40, 45 and 50 °C, correspondingly. The self-discharged current density is varied with the effect of temperature, which is shown the value of 0.03 – 0.63 $\text{mA}\cdot\text{cm}^{-2}$ at the temperature ranging from 25 to 50 °C.

As discussed for the formula 1, we also did not see any formation of V_2O_5 precipitate after the cycling test with the formula 2 of additive in the vanadium electrolyte (Fig. 5.15 and Appendix: Fig. A.12). Therefore, we could conclude that the sharpened cell capacity drop and resistivity increase are caused by the higher amount of electrolyte transfer through the membrane.

Figure 5.15 The view of positive electrolyte tank and flow-frame after cell cycling test at 25 – 50 °C with the electrolyte containing 0.025 wt.% PVP + 0.25 wt.% $(\text{NH}_4)_2\text{HPO}_4$ (formula 2).

Table 5.3 Temperature dependence of cell cycling performance using vanadium electrolyte with and without thermally stable additives using Fumatech FAP 450 AEM.

Parameter	Temperature				
	25	35	40	45	50
Blank					
Voltage efficiency (%)	88.1	88.4	88.3	87.6	87.6
Cell resistivity ($\Omega\text{.cm}^{-2}$)	2.2	2.1	2.2	2.3	2.3
Cell resistivity increasing rate (%)	3.8	4.2	4.0	3.4	5.7
Self-discharge current density (mA.cm^{-2})	0.48	0.65	0.47	0.39	0.48
Formula 1: 0.025 wt.% PVP + 0.25 wt.% $\text{NH}_4\text{H}_2\text{PO}_4$					
Voltage efficiency (%)	89.7	90.3	89.9	89.4	89.2
Cell resistivity ($\Omega\text{.cm}^{-2}$)	1.9	1.8	1.8	1.9	2.0
Cell resistivity increasing rate (%)	-3.6	-1.9	5.6	1.5	4.1
Self-discharge current density (mA.cm^{-2})	0.06	0.30	0.04	0.08	0.07
Formula 2: 0.025 wt.% PVP + 0.25 wt.% $(\text{NH}_4)_2\text{HPO}_4$					
Voltage efficiency (%)	89.3	90.6	90.6	90.3	89.6
Cell resistivity ($\Omega\text{.cm}^{-2}$)	1.9	1.7	1.7	1.8	1.9
Cell resistivity increasing rate (%)	-5.3	1.4	7.7	7.1	7.0
Self-discharge current density (mA.cm^{-2})	0.03	0.56	0.59	0.63	0.61

All of the parameters reflecting the cell cycling performance using different electrolyte formulas under various temperatures are summarized in Table 5.3. In general, the fluctuation of temperature has a strong impact on the overall performance of vanadium redox flow battery. In which, the voltage efficiency is proportional to the temperature increasing, due to the faster electrochemical kinetics and lower resistance. However, the increment of temperature also gives the negative effect on the operation of the VRFB cell, which accelerates the electrolyte crossover through the Fumatech AEM. Moreover, with the temperature beyond 40 °C, the vanadium precipitation appears in the pristine electrolyte, causing the significant drop in capacity and voltage efficiency. With the addition of novel combined additives in the electrolyte, the VRFB cell behaves similarly to the blank electrolyte with the variation of temperature. Importantly, the combined organic-inorganic additives can prevent the

vanadium precipitation at the temperature more than 40 °C. Additionally, no other detriments were found for the novel vanadium electrolyte formula. Therefore, it is suitable for the long-term performance test of VRFB cell at different temperatures.

After this test, we selected two constant temperatures, 25 and 50 °C, to investigate the long-term cycling performance of the VRFB cell.

5.3 Long-term Cycling Performance of Advanced Thermally Stable Additives at Different Temperatures

5.3.1 Effect of Temperature on the Long-term Cycling Performance of Vanadium Redox Flow Battery

To investigate the effect of (electrolyte) temperature on the long-term performance of the VRFB, we cycled a 20 cm² single cell for over 100 cycles with the current density of 100 mA.cm⁻² at the constant temperatures of 25 and 50 °C. The results for the cell assembled with Fumatech FAP 450 AEM are presented in Figure 5.16. It was observed that the voltage efficiency at 50 °C is higher than that at 25 °C, about 83% compared to the value of 80%, respectively. This comes from the improvement of redox reaction kinetics and reduction of ohmic resistance at both sides at higher temperatures as discussed before.

However, it is also noted that the self-discharged current density of the cell is much higher at 50 °C, about 0.32 mA.cm⁻², compared to the value of 0.95 mA.cm⁻² at 25 °C. This increment is probably caused by the faster ion diffusion through the Fumatech membrane. Due to the lower ohmic resistance, the cell resistivity at 50 °C is lower than 25 °C, about 1.12 and 1.4 Ω.cm², subsequently. Nonetheless, the increasing rate of cell resistivity at 50 °C is higher than that of

25 °C, about 28.6% compared to the value of 15.7%, implying the greater electrolyte imbalance at 50 °C. In particular, the cell capacity at 50 °C rapidly drops during 100 cycles with the rate of 22.7 mAh/cycle, much faster than the speed of 10.5 mAh/cycle at 25 °C. This is partially attributed to the electrolyte crossover, but it is suggested that the capacity drop at 50 °C mainly due to the precipitation of positive vanadium electrolyte (will be proved in next session). While at 25 °C, the capacity drop is essentially the result of electrolyte crossover.

Figure 5.16 The long-term voltage efficiency (a), cell resistivity (b), self-discharge current density (c), and capacity drop (d) of cell cycling at different constant temperatures using blank electrolyte. Cell: 20 cm^2 active area; electrolyte volume: 100 mL; flow-rate: 50 mL/min; current density: 100 mA/cm^2 ; potential window: 0.9 – 1.65 V; oxidation prevention layer: Paraffin oil (10 mm); membrane: Fumatech FAP 450; temperature: 25, 50 °C; number of cycle: 100.

In the same testing condition, the long-term cell cycling performance with Nafion 117 CEM is relatively different from the Fumatech FAP 450 AEM, which is shown in Figure 5.17.

Figure 5.17 The long-term voltage efficiency (a), cell resistivity (b), self-discharge current density (c), and capacity drop (d) of cell cycling at different constant temperatures using blank electrolyte. Cell: 20 cm² active area; electrolyte volume: 100 mL; flow-rate: 50 mL/min; current density: 100 mA/cm²; potential window: 0.9 – 1.65 V; oxidation prevention layer: Paraffin oil (10 mm); membrane: Nafion 117; temperature: 25, 50 °C; number of cycle: 100.

For the voltage efficiency, as same as Fumatech AEM, the value at 50 °C is also better than that at 25 °C, about 80.1% compared to the number of 77%. The self-discharged current density of the cell assembled with Nafion CEM is much higher than that of Fumatech AEM, about 1.9 and 2.46 mA.cm⁻² at 25 and 50 °C,

respectively. This increment is probably due to the fact that Nafion CEM could absorb all vanadium ions in different oxidation state as mentioned before.

The cell resistivity possesses the same trend with Fumatech AEM, which shows the value of 1.8 and 1.5 $\Omega\cdot\text{cm}^2$ at 25 °C and 50 °C, subsequently. Interestingly, for the Nafion CEM, the increasing rate of cell resistivity is much lower in comparison with Fumatech AEM and stable for both temperatures. In detail, the cell resistivity increasing rate is estimated to be about 7.2 and 7.8% at 25 and 50 °C, correspondingly. This suggests that the electrolyte transfer process through the Nafion CEM is smaller than Fumatech AEM for over 100 cycles. Therefore, the capacity drops of the cell are also decreased, of only about 11.04 and 9.21 mAh/cycle at 25 and 50 °C, respectively.

The summary of long-term cell cycling performance at different temperatures with the cell assembled with Nafion 117 CEM and Fumatech FAP 450 AEM is listed in Table 5.4.

Table 5.4 Average cell cycling performance with different IEMs at 25 and 50 °C for over 100 cycles.

Parameter	Fumatech FAP 450 AEM		Nafion 117 CEM	
	25 °C	50 °C	25 °C	50 °C
Voltage efficiency (%)	80.0	83.0	77	80.1
Self-discharge current density($\text{mA}\cdot\text{cm}^{-2}$)	0.3	0.9	1.9	2.5
Resistivity ($\Omega\cdot\text{cm}^2$)	1.4	1.1	1.8	1.5
Resistivity increasing rate (%)	15.7	28.6	7.2	7.8
Capacity drop (mAh/cycle)	10.5	22.7	11.0	9.2

All of above results have demonstrated the detriment of high temperatures on the performance of VRFB, especially on the stability of the vanadium electrolyte.

5.3.2 The Improvement of Long-term Cell Cycling Performance at High Temperature with the Advanced Thermally Stable Electrolyte

The thermally stable additives in general and combined inorganic-organic additives, in particular, have demonstrated the thermal stabilizing capability for the positive vanadium electrolyte under static condition. We continued testing the performance of combined additives in the electrolyte of VRFB cycled at high temperature for over 100 cycles. Two novel additive formulas were used for this experiment:

Formula 1: 0.025 wt.% PVP + 0.25 wt.% $\text{NH}_4\text{H}_2\text{PO}_4$.

Formula 2: 0.025 wt.% PVP + 0.25 wt.% $(\text{NH}_4)_2\text{HPO}_4$.

Figure 5.18 presents the cell cycling performance with different electrolyte formulas at 25 °C using Fumatech FAP 450 AEM. It was seen that at room temperature, the presence of combined additives in the pristine vanadium electrolyte causes the slight decrease of coulombic, energy and voltage efficiency. In detail, the voltage efficiency of the cell drops from about 80.2% for the blank electrolyte to about 76.5 and 77.9% for the formula 1 and 2 of combined additive, respectively. This is mainly due to the high resistance of PVP, which had been confirmed by static CV and EIS measurements in chapter 4. The presence of PVP in the electrolyte may block the porous electrode surface. Therefore, it is necessary to minimize the amount of PVP in the additive formula to obtain higher cell cycling efficiency.

The self-discharge current density of the cell with the addition of combined additives is not so different from the blank electrolyte (Fig. 5.18c), in which, while the blank electrolyte shows the value of about $0.32 \text{ mA}\cdot\text{cm}^{-2}$, this is

recorded to be about 0.26 and 0.3 mA.cm⁻² for the electrolyte formula 1 and 2, correspondingly.

Figure 5.18 The long-term voltage efficiency (a), cell resistivity (b), self-discharge current density (c), and capacity drop (d) of cell cycling with different electrolyte formulas at 25 °C. Cell: 20 cm² active area; electrolyte volume: 100 mL; flow-rate: 50 mL/min; current density: 100 mA/cm²; potential window: 0.9 – 1.65 V; oxidation prevention layer: Paraffin oil (10 mm); membrane: Fumatech FAP 450; temperature: 25 °C; number of cycle: 100.

The same thing is also observed for the cell resistivity, for instance, the pristine electrolyte indicates the value of about 1.51 Ω.cm². And it rises to the number of around 1.84 and 1.71 Ω.cm² by using formula 1 and 2 for combined additive, subsequently. The cell resistivity increasing rate, implying the electrolyte crossover, is hardly changed because of the additive insertion. It is showed that the increasing rate is about 15.7, 14 and 13.1% for the blank, formula 1 and

formula 2 of vanadium electrolyte. Because of this, the cell capacity drop is also equivalent for all three electrolyte samples, about 10.5, 9.9 and 9.2 mAh/cycle for the pristine, formula 1 and formula 2 of vanadium electrolyte.

These results demonstrate that as-studied combined inorganic-organic additives can be used in the vanadium electrolyte a room temperature without causing any serious technical issue.

Figure 5.19 The long-term voltage efficiency (a), cell resistivity (b), self-discharge current density (c), and capacity drop (d) of cell cycling with different electrolyte formulas at 50 °C. Cell: 20 cm^2 active area; electrolyte volume: 100 mL; flow-rate: 50 mL/min; current density: 100 mA/cm^2 ; potential window: 0.9 – 1.65 V; oxidation prevention layer: Paraffin oil (10 mm); membrane: Fumatech FAP 450; temperature: 50 °C; number of cycle: 100.

At 50 °C, the long-term performance of the cell using different electrolyte formulas possesses several exciting results which are shown in Figure 5.19. The average voltage efficiency at 50 °C of the cell is still lower than the original value when using two formulas of combined additives, about 77.4 and 80% for the formula 1 and 2, respectively, compared to the efficiency of 83% for the pristine vanadium electrolyte.

The self-discharge current density of the cell now indicates the difference for each electrolyte formula (Fig. 5.19c), in which, while the blank electrolyte shows the value of about 0.95 mA.cm⁻², this is recorded to be about 1.51 and 0.88 mA.cm⁻² for the electrolyte formula 1 and 2, correspondingly. This suggests that the ion diffusion across the membrane in the electrolyte containing formula 1 of additive is faster than the pristine electrolyte and formula 2 at high temperatures.

At 50 °C, the cell resistivity of the pristine electrolyte indicates the value of about 1.29 Ω.cm². For the novel electrolyte, this value increases the number of around 1.76 and 1.54 Ω.cm² by using formula 1 and 2 of combined additive, respectively. The cell resistivity increasing rate, interestingly, is achieved the highest value for the formula 1 of new electrolyte, about 56.1%, while it is only about 28.6 and 31.6% for the blank electrolyte and formula 2. Corresponding to the variation of resistivity, the cell capacity drop for the formula 2 of electrolyte also gained the highest value of about 29.8 mAh/cycle, while the original electrolyte showed the number of about 22.7, and the formula 2 of vanadium electrolyte indicated the lowest value of 18 mAh/cycle.

These results demonstrate that as-studied combined inorganic-organic additives can be used in the vanadium electrolyte a room temperature without causing any serious technical issue. The sole problem is the acceleration of electrolyte

crossover process through Fumatech FAP 450 AEM by using the combined precipitation inhibitors.

Figure 5.20 The view of positive flow-frame coupled with EDS analysis for graphite felt for cell running at 50 °C using different electrolyte formulas for over 100 cycles.

The practical benefit of advanced thermally stable additives is shown in Figure 5.20, which indicates the view of the positive flow-frame after 100 charge/discharge cycles at 50 °C. We observed a massive formation of orange solid precipitate in the flow channel and porous electrode of the cell using blank additive-free electrolyte. While by adding the combined inorganic-organic additives, no precipitate was obviously seen. To confirm this, the EDX analysis was performed for the graphite felt at the positive side. The results indicate a large amount of V_2O_5 presented in the positive porous electrode of the cell using pristine electrolyte. While with the combined additives in the electrolyte, the amount of V_2O_5 precipitate on the positive porous electrode is unremarkable.

In a large-scale VRFB system, the formation of such V_2O_5 precipitate could block the electrolyte flow, resulting in many unpredicted accidents. Therefore, the excellent performance of new vanadium-based electrolyte formula in our study has provided a solution to eliminate this issue. Moreover, this result also confirms that the cell capacity loss when using combined additives is not contributed to the formation of the precipitate, but may due to the interaction of additive species and Fumatech AEM. The mechanism is probably similar to the interaction of Fumatech AEM and SO_4^{2-} as discussed before, the PO_4^{3-} ions released from ammonium phosphate additives could be also absorbed to the membrane and become the “channel” for V(V) diffusion, accelerating the electrolyte crossover.

The summary of long-term cell cycling performance of different electrolyte formulas at 25 and 50 °C with the cell assembled with Fumatech FAP 450 AEM could be found in Table 5.5. All the listed parameters were taken from the average value of cell cycling experiments for over 100 cycles.

Table 5.5 Long-term cell cycling performance of different vanadium electrolyte formulas at 25 and 50 °C using Fumatech FAP 450 AEM.

Temperature	25 °C			50 °C		
Electrolyte	Blank	Formula 1	Formula 2	Blank	Formula 1	Formula 2
Voltage efficiency (%)	80.2	76.5	77.9	83	77.4	80
Self-discharge current density (mA.cm ⁻²)	0.3	0.3	0.3	0.9	1.5	0.9
Resistivity (Ω.cm ²)	1.5	1.8	1.7	1.3	1.8	1.5
Resistivity increase (%)	15.7	14.0	13.1	28.6	56.1	31.6
Capacity drop (mAh/cycle)	10.5	9.9	9.2	22.7	29.8	18.0
Precipitation	No	No	No	Yes	No	No

To further understand the activity of combined thermally stable additives in VRFB, we continued performing the long-term cycling test with the cell assembled with Nafion 117 CEM. The cell cycling performance at room temperature for different electrolyte formulas is presented in Figure 5.21.

It was observed that two formulas of as-studied combined inorganic-organic additives behave differently in the cell assembled with Nafion 117 CEM compared to the cell separated by Fumatech FAP 450 AEM.

Figure 5.21 The long-term voltage efficiency (a), cell resistivity (b), self-discharge current density (c), and capacity drop (d) of cell cycling with different electrolyte formulas at 25 °C. Cell: 20 cm^2 active area; electrolyte volume: 100 mL; flow-rate: 50 mL/min; current density: 100 mA/cm^2 ; potential window: 0.9 – 1.65 V; oxidation prevention layer: Paraffin oil (10 mm); membrane: Nafion 117; temperature: 25 °C; number of cycle: 100.

Figure 5.21a indicates the improvement of the cell voltage efficiency by using novel electrolyte formulas, in which, the value of voltage efficiency over 100 cycles is about 77.4 and 81.2% for the formula 1 and 2, respectively, while the pristine electrolyte could only achieve the number of 77%. This is in contrast with the observation for the Fumatech FAP 450 AEM at the same temperature.

The self-discharge current density of the cell using pristine electrolyte is dramatically declined by the insertion of advanced thermally stable additives, from 1.9 mA.cm^{-2} down to 0.2 and 0.22 mA.cm^{-2} for the formula 1 and 2, respectively. This reduction suggests the lower ion diffusion through the membrane by using combined additives in the vanadium electrolyte.

The cell resistivity at 25°C is measured to be about $1.8 \text{ }\Omega.\text{cm}^2$ for the cell operated with pristine vanadium electrolyte and reduced to 1.76 and $1.43 \text{ }\Omega.\text{cm}^2$, correspondingly, by the addition of formula 1 and formula 2 of the combined inorganic-organic additive. In addition, the cell resistivity increasing rate is also slight dropped from 7.18% for the pristine electrolyte to 9.7 and 6.38% for the addition of two respective additive formulas. With respect to the cell resistivity increasing rate, the capacity drop of the cell is also reduced from the initial value of about 11.04 mAh/cycle to 5.97 and 6.06 mAh/cycle for the formula 1 and formula 2 of additives.

The improvement of the cell performance using novel electrolyte formulas in the cell assembled with Nafion 117 CEM is also achieved at 50°C (Figure 5.22).

The improvement of the cell cycling performance using novel electrolyte formula with the cell separated by Nafion 117 CEM may be originated from the interaction of membrane and additive species. PVP is a polymer which could restrict the kinetics of redox reaction as discussed in chapter 4, thus not relevant

for this improvement. The Nafion 117 CEM has been proved that does not absorb SO_4^{2-} ion, so as well as PO_3^- ion. Therefore, the only possible species that is responsible for this performance improvement is NH_4^+ ions, which could be absorbed into the Nafion 117 CEM, resulting in the lower membrane resistivity. This hypothesis is strengthened by the higher effectivity of formula 2 compared to the formula 1 of additive, since the formula containing $(\text{NH}_4)_2\text{HPO}_4$ agent, which could produce a larger concentration of NH_4^+ ion compared to the $\text{NH}_4\text{H}_2\text{PO}_4$ compound in the formula 1.

Figure 5.22 The long-term voltage efficiency (a), cell resistivity (b), self-discharge current density (c), and capacity drop (d) of cell cycling with different electrolyte formulas at 50 °C. Cell: 20 cm² active area; electrolyte volume: 100 mL; flow-rate: 50 mL/min; current density: 100 mA/cm²; potential window: 0.9 – 1.65 V; oxidation prevention layer: Paraffin oil (10 mm); membrane: Nafion 117; temperature: 50 °C; number of cycle: 100.

Table 5.6 Long-term cell cycling performance of different vanadium electrolyte formulas at 25 and 50 °C using Nafion 117 CEM.

Temperature	25 °C			50 °C		
Additive	Blank	Formula 1	Formula 2	Blank	Formula 1	Formula 2
Voltage efficiency (%)	77	77.4	81.2	80.1	79.7	83.0
Self-discharge current density (mA.cm ⁻²)	1.90	0.20	0.22	2.46	0.49	0.41
Resistivity (Ω.cm ²)	1.80	1.76	1.43	1.53	1.56	1.28
Resistivity increase (%)	7.2	9.7	6.4	7.8	14.3	11.1
Capacity drop (mAh/cycle)	11.04	5.97	6.06	9.21	7.78	10.26

The summary of long-term cycling performance of different vanadium electrolyte formulas at 25 and 50 °C using Nafion 117 CEM is listed in Table 5.6. In short, the long-term cycling testing at 25 and 50 °C has demonstrated the stability and suitability of advanced vanadium electrolyte formulas for the small scale of VRFB cell.

5.4 The Long-term Performance of Advanced Electrolyte in Large-Scale Vanadium Redox Flow Battery

Besides the electrochemical influence, it is also essential to investigate the effect of thermally stable additives on the physical and mechanical property of VRFB. Therefore, we employed a large scale VRFB system composed of the 3-stack cell with 625 cm² active area to examine the impact of novel electrolyte formula. The tested system was integrated with thermal sensor, pressure sensor, and flowmeter to record the change in several physical, mechanical parameters of the system when injecting the advanced thermally stable additives. The system was charged and discharged for over 200 cycles with 1.5 L of vanadium electrolyte in each tank. Two types of combined inorganic-organic additive formula were tested separately:

Formula 1: 0.025 wt.% PVP + 0.25 wt.% $\text{NH}_4\text{H}_2\text{PO}_4$: In the stack, the PV15 graphite plate (0.6 mm, SGL) was used as the bipolar plate in the stack and also in the end plate.

Formula 2: 0.025 wt.% PVP + 0.25 wt.% $(\text{NH}_4)_2\text{HPO}_4$: In the stack, the PV15 graphite plate (0.6 mm, SGL) was used as the bipolar plate in the stack. While the F100 monolithic carbon plate (2 mm, SGL USA) was used as the bipolar plate at the end plate to prevent the corrosion of copper current collector.

5.4.1 Long-term Performance of Formula 1 of Combined Inorganic-Organic Additive

The influence of formula 1 of combined inorganic-organic additives (0.025 wt.% + 0.25 wt.% $\text{NH}_4\text{H}_2\text{PO}_4$) on the physical and mechanical property of 3-stack cell performance is presented in Figure 5.23. The time point at which the tested additive was injected is marked on the figure.

It was observed that the electrolyte temperature is varied from 32.5 to 35.5 °C in the negative tank, and from 33.2 to 36.2 °C in the positive tank. By the injection of combined additive, no increment of electrolyte temperature was found after more than 16 h operating time (Figure 5.23a). The electrolyte flow-rate is measured to be about 892.7 – 1103.6 mL/min for the anolyte, and about 900.5 – 1070.3 mL/min for the catholyte, and was maintained stably after the addition of formula 1 of the combined additive. Similarly, the pressure in the electrolyte pipe is also almost unchanged by adding the combined additive, which is about 536.7 – 558.1 mbar at the negative side, and around 445.4 – 464.8 mbar at the positive side, respectively. These results indicate that there is no change of electrolyte physical property was found due to the addition of such additive. Therefore, the concern about the detriment of the combined

inorganic-organic additive, especially for PVP, on the physical property of vanadium electrolyte can be ignored.

Figure 5.23 The influence of combined inorganic-organic additive (formula 1) on the electrolyte temperature (a), flow-rate (b), and pressure (c) of 3-stack cell cycling. Cell: 625 cm² active area; electrolyte volume: 1.5 L; current density: 80 mA/cm²; membrane: Fumatech FAP 450; bipolar plate: PV15; end plate: PV15; number of cycle: 200.

The influence of formula 1 of combined inorganic-organic additives (0.025 wt. % PVP + 0.25 wt.% $\text{NH}_4\text{H}_2\text{PO}_4$) on the electrochemical property of 3-stack cell performance is showed in Figure 5.24. The result shows that the voltage efficiency of the 3-stack cell cycling is slightly reduced from about 81.8% for the pristine electrolyte to about 79.6% with the addition of combined additives (Fig. 5.25a). These results are similar to the performance of 20 cm² single cell

using the electrolyte containing the same formula of combined additive, which confirms the detriment of PVP.

Figure 5.24 The influence of combined inorganic-organic additive (formula 1) on the voltage efficiency (a), self-discharge current density (b), and resistivity (c) of 3-stack cell cycling. Cell: 625 cm^2 active area; electrolyte volume: 1.5 L; current density: $80\text{ mA}/\text{cm}^2$; membrane: Fumatech FAP 450; bipolar plate: PV15; end plate: PV15; number of cycle: 200.

The self-discharge current density is steady even with the addition of such combined additive, which is measured to be about 0.72 and $0.78\text{ mA}\cdot\text{cm}^{-2}$ for pristine electrolyte and novel electrolyte. However, the cell resistivity rises from about $1.73\text{ }\Omega\cdot\text{cm}^2$ for the blank electrolyte to around $1.96\text{ }\Omega\cdot\text{cm}^2$ for the novel electrolyte, due to the high resistance of PVP as discussed before.

5.4.2 Long-term Performance of Formula 2 of Combined Inorganic-Organic Additive

For comparison with the formula 1, the physical and mechanical change of pristine vanadium electrolyte due to the addition of formula 2 of combined inorganic-organic additive (0.025 wt.% PVP + 0.25 wt.% $(\text{NH}_4)_2\text{HPO}_4$) is illustrated in Figure 5.25. It should be noted that due to the small change in the stack component, some cell cycling parameters with the pristine vanadium electrolyte are not the same as when testing for the formula 1.

Figure 5.25 The influence of combined inorganic-organic additive (formula 2) on the electrolyte temperature (a), flow-rate (b), and pressure (c) of 3-stack cell cycling. Cell: 625 cm² active area; electrolyte volume: 1.5 L; current density: 80 mA/cm²; membrane: Fumatech FAP 450; bipolar plate: PV15; end plate: F100 monolithic carbon plate; number of cycle: 200.

Figure 5.26 The influence of combined inorganic-organic additive (formula 2) on the electrolyte temperature (a), flow-rate (b), and pressure (c) of 3-stack cell cycling. Cell: 625 cm² active area; electrolyte volume: 1.5 L; current density: 80 mA/cm²; membrane: Fumatech FAP 450; bipolar plate: PV15; end plate: F100 monolithic carbon plate; number of cycle: 200.

The electrochemical performance of 3-stack cell using different electrolyte formulas is also showed in Figure 5.26. With the addition of the combined additive (formula 2), the result shows that the voltage efficiency of the 3-stack cell cycling is slightly lower than when using blank electrolyte, about 73.2% compared to the value of around 76.6% (Fig. 5.26a). This result is also similar to the performance of 20 cm² single cell using the electrolyte containing the same formula of the combined additive. The self-discharge current density, instead, is almost unchanged with the addition of the combined additive, about 0.99 mA.cm⁻² for the blank electrolyte and 1.01 mA.cm⁻² for the new

electrolyte. The cell resistivity, as seen for the formula 1, also boosts from the initial value of about $2.29 \Omega\cdot\text{cm}^2$ up to $2.68 \Omega\cdot\text{cm}^2$ due to the insertion of formula 2 of the combined additive.

In short, the novel vanadium electrolyte formula, with the combination of ammonium phosphate and PVP, has demonstrated its stability and suitability in the practical VRFB system at very high temperatures (up to 50°C). The performance can be regulated by adjustment of additive volume, especially for PVP agent. No other toxic agents were found during the cycling with as-studied combined inorganic-organic additives.

5.5 The Long-term Performance of Novel Vanadium Electrolyte in 1 kW Vanadium Redox Flow Battery System

As mentioned in Chapter 3, a 1 kW VRFB system was developed and used to test the performance of so-developed novel vanadium electrolyte. The result is presented in Figure 5.27.

It is clearly observed that the novel thermally stable vanadium electrolyte demonstrates excellent performance as compared to the pristine electrolyte since it does not reduce the performance of original vanadium solution. In detail, there is only a small drop in the energy efficiency and voltage efficiency due to the addition of combined inorganic-organic additives into the pristine electrolyte, from about 80.2% to 78.9% for energy efficiency, and from about 83% to 82.3% for voltage efficiency (Fig. 5.27 a-b).

The stack resistivity is slightly increased with the use of novel vanadium electrolyte, from $1.57 \Omega\cdot\text{cm}^{-2}$ for the original electrolyte, up to $1.69 \Omega\cdot\text{cm}^{-2}$ for the new electrolyte. The self-discharge current density is also observed to be

higher for the new vanadium electrolyte formula compared to the pristine solution.

Figure 5.27 The performance of 1 kW VRFB system cycling with pristine and novel vanadium electrolyte. Cell: 625 cm^2 active area; electrolyte volume: 10 L; current density: $80 \text{ mA}/\text{cm}^2$; membrane: Fumatech FAP 450; bipolar plate: PV15; electrode: GFD 4.6 graphite felt; number of cycle: 150.

All of these results are extremely desired, since the novel vanadium electrolyte possesses an excellent thermal stability as proved, while it does not affect the performance of the pristine solution. By optimizing the additive amount and using suitable IEM, the performance of VRFB even can be improved by the use of advanced thermally stable additives in the electrolyte solution. As-developed vanadium electrolyte is now absolutely can be employed in current commercial VRFB technology.

5.6 Influence of Advanced Thermally Stable Additives on the Cell Components

All of above results have demonstrated the improvement of cell cycling stability at high temperatures by the addition of combined inorganic-organic additives. However, it is necessary to examine the influence of these additives on the cell component during the cycling process.

5.6.1 Effect on Electrode Materials

The graphite felts were collected and dried after cycling process to investigate.

Figure 5.28 SEM image of original graphite felt (a) and negative graphite felt electrodes (b-d) after cycling with different vanadium electrolytes at 50 °C for over 100 cycles.

Figure 5.28 shows the SEM image of original graphite felt and negative graphite felt electrodes after cycling with different vanadium electrolytes at 50 °C for over 100 cycles. Compared to the original felt, the cycling with blank electrolyte does not create any damage to the surface of carbon fiber at 50 °C. More importantly, for the felt cycled with novel thermally stable electrolyte, it was observed that the morphology of each carbon fiber is still unaffected. Therefore, we can conclude that the advance thermally stable vanadium electrolyte does not produce any detriment on the negative electrode material during cycling process at high temperatures. The more serious issues may be found in the positive porous graphite felt electrode, since we already detected the formation of vanadium precipitate in the positive side flow-frame.

Figure 5.29 SEM image of original graphite felt (a) and positive graphite felt electrodes (b-d) after cycling with different vanadium electrolytes at 50 °C for over 100 cycles.

Figure 5.29 indicates FESEM image of the original graphite felt (a) and positive graphite felt electrodes (b-d) after cycling with different vanadium electrolytes at 50 °C for over 100 cycles. For the cell operating with pristine vanadium electrolyte, we observed a massive formation of the precipitate on the surface of carbon fiber of graphite felt after 100 cell cycling cycles at 50 °C. The precipitate has been confirmed to be V_2O_5 in above EDX analysis. This V_2O_5 formation could block the flow-frame channel and porous positive electrode, causing many dangerous accidents, for example, electrolyte leakage. Moreover, it also sharply reduces the usable capacity of the cell. However, by using combined inorganic-organic additives in the electrolyte, there is no precipitate is detected on the positive side of porous graphite electrode, as shown in Figure 5.29c-d. This has again demonstrated the excellent thermal stabilizing ability of as-studied combined inorganic-organic additives for the vanadium electrolyte, not only in the static condition but also under practical VRFB operation.

For comparison, the graphite felt electrode cycling with the cell assembled with Nafion CEM is also investigated. Figure 5.30 shows the SEM images of the negative felt electrodes after cycling with different electrolyte formulas at 50 °C for over 100 cycles. Similarly, when running the cell assembled with Fumatech AEM, the advanced vanadium electrolyte also does not create any damage to the surface of carbon fiber.

At the positive side (Figure 5.31), interestingly, the amount of precipitate in the positive graphite electrode when cycling the cell assembled with Nafion CEM using blank vanadium electrolyte is much smaller than that of the cell assembled with Fumatech AEM. This result indicates the use of Nafion CEM in the VRFB application does not only give better cell cycling performance but also better thermal stability for the positive vanadium electrolyte as compared to the Fumatech FAP 450 AEM. Most importantly, when using novel vanadium electrolytes, no precipitate and other influences were detected on the surface of

graphite electrodes. This observation confirms that the advanced thermally stable electrolyte is safe to use, even with another type of ion exchange membrane.

Figure 5.30 SEM image of original graphite felt (a) and negative graphite felt electrodes (b-d) after cycling with different vanadium electrolytes at 50 °C for over 100 cycles using the cell assembled with Nafion CEM.

The results for both Fumatech AEM and Nafion CEM confirm the safety of as-studied advanced vanadium electrolytes for the porous electrode in the vanadium redox flow battery application. Even at very high temperature, the novel vanadium electrolyte also does not damage the electrode materials under cell cycling condition.

Figure 5.31 SEM image of original graphite felt (a) and positive graphite felt electrodes (b-d) after cycling with different vanadium electrolytes at 50 °C for over 100 cycles using the cell assembled with Nafion CEM.

5.6.2 Effect on Ion Exchange Membrane

After testing the performance of 20 cm² active area cell for over 100 cycles, we collected the Fumatech FAP 450 AEM (at fully discharged condition) for EIS and EDS analysis to investigate the change in the resistivity and elemental composition. Figure 5.32 shows the view of Fumatech FAP 450 membrane in original form and after cell cycling with different vanadium electrolyte formulas at 50 °C for over 100 cycles.

In general, compared to the original membrane, we can obviously see the swelling and color change of all membrane samples after 100 cell cycling

cycles at 50 °C. This membrane color is actually similar to the one in the static test above, implying the absorption of V(V) ions in the membrane under cell cycling condition for all types of the electrolyte.

Figure 5.32 The view of Fumatech FAP 450 membrane in original form and after cell cycling with different vanadium electrolyte formulas at 50 °C for over 100 cycles.

The EIS measurement (a) and EDX analysis (b) for the Fumatech FAP 450 AEM after cell cycling with different vanadium electrolytes at 50 °C for over 100 cycles are shown in Figure 5.33. It was observed that the resistivity of the membrane after cycling test increases in comparison with the original membrane, about $0.46 \Omega \cdot \text{cm}^2$ compared to the value of around $0.36 \Omega \cdot \text{cm}^2$ for the original membrane. This is caused by the diffusion of V(V) ions into the membrane during cell cycling process as discussed before. With the presence of the combined inorganic-organic additive in the electrolyte, the value of

membrane resistivity is higher compared to the blank solution, about 0.75 and $0.7 \Omega \cdot \text{cm}^2$ for formula 1 and formula 2 of additive, respectively.

Figure 5.33 EIS measurement (a) and EDX analysis (b) for the Fumatech FAP 450 AEM after cell cycling with different vanadium electrolytes at 50 °C for over 100 cycles.

The EDX analysis confirmed the presence of V in the Fumatech FAP 450 AEM after cell cycling at 50 °C. A large amount of S and O was also detected, suggesting the presence of V₂O₅ precipitate and SO₄²⁻ species. In addition, a tiny percentage of phosphorous (P) was also recorded for the membrane cycled with combined inorganic-organic additives, indicating that the PO₄³⁻ ions were also absorbed into the Fumatech FAP 450 AEM. This probably confirms the reason of strong capacity drop in the VRFB cell long-term cycling at high temperatures when using novel vanadium electrolyte formulas, which suggests that the PO₄³⁻ ions absorbed in the Fumatech AEM can be the “channel” for the diffusion of V(V) ions. The higher resistivity of Fumatech AEM with combined additives, despite the lower absorbed V concentrations, would also imply that PVP seems to foul the FAP membrane.

Figure 5.34 The view of Nafion 117 membrane in original form and after cell cycling with different vanadium electrolyte formulas at 50 °C for over 100 cycles.

For comparison, the Nafion 117 CEM after cycling at 50 °C for over 100 cycles with different vanadium electrolytes is also investigated. Figure 5.34 shows the original (a) and cycled (b-d) Nafion CEM with different vanadium electrolytes. It was observed that the cycled membranes look slightly more transparent as compared to the original form. The EDX analysis for such membrane samples was also conducted and showed in Figure 5.35. A small amount of V was seen in all membrane samples after cycling, in agreement with previous results. However, interestingly, we detected the presence of N in the Nafion membrane cycling with two novel vanadium electrolyte formulas. According to the performance improvement of for the VRFB cell assembled with Nafion CEM, this N absorption can confirm that the NH_4^+ ion can reduce the resistivity of CEM, and therefore improve the overall performance of VRFB cell.

Figure 5.35 EIS measurement (a) and EDX analysis (b) for the Nafion 117 CEM after cell cycling with different vanadium electrolytes at 50 °C for over 100 cycles.

In conclusion, the addition of novel additives into the vanadium electrolyte does not damage the ion exchange membrane under cell cycling condition at high temperatures. However, it was also observed that the functionality of membrane can be improved by using electrolyte additives.

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Chapter 6

Conclusion, Discussions and Outlooks

This last chapter presents our conclusions and summary for this study. The extent to which the hypothesis was proven/disproven, or the design target is met/not met is adequately addressed. The opportunities and strategies for future work are also highlighted to further enhance the application range of the VRFB.

6.1 Conclusion and Discussion

This Ph.D. study has been conducted through a series of scientific research and development. All of the contents presented in this thesis are firmly and logically organized. Here are several conclusions and discussions extracted from this study.

6.1.1 The Fulfillment of Objective and Scopes

The findings and outcomes presented in chapter 4 and 5 fully reflected the objectives and expectations that were highlighted in chapter 1.

Novel thermally stable additives have been successfully developed for the VRFB electrolyte, by the combination of ammonium phosphate agents (inorganic component) and PVP (organic component), which could provide the co-stabilizing effect to prevent the precipitation of positive vanadium electrolyte at high temperatures. The results presented in chapter 4 have demonstrated the thermal stability of pristine vanadium electrolyte has been improved nearly 4 times by the addition of 0.025 wt.% PVP +0.25 wt.% $\text{NH}_4\text{H}_2\text{PO}_4$, and more than 3 times when using 0.025 wt.% PVP +0.25 wt.% $(\text{NH}_4)_2\text{HPO}_4$. In addition, as-developed combined inorganic-organic additives also could maintain the rate of V_2O_5 precipitate below the value of about 10 mol.% of V(V), while more than 60 mol.% of V(V) in pristine electrolyte were already precipitated after 7 days at 50 °C.

Since it is halide-free, the novel combined additives could completely eliminate the risk of toxic halogen vapor when using halide based thermal stabilizing compounds in VRFB electrolyte. Besides that, no other harmful contaminants were released under the operation of new electrolyte formula. As ammonium phosphates are very stable under the electrochemical condition of VRFB

electrolyte, while PVP is a durable polymer with high molecular weight.

The novel advanced thermally stable electrolytes are also satisfied the longer-term stability and suitability for a practical VRFB cell at high temperatures. It has been showed that the new electrolyte formulas with the presence of combined inorganic-organic additives could preserve the performance of a laboratory-scale VRFB at 50 °C for over 100 cycling number, and eventually in a large-scale 3-stack VRFB system. Even though there was a minimal drop in the efficiency of the cell, however, it could be diminished by varying the addition amount of additives or using suitable ion exchange membrane. Moreover, thanks to its high thermal durability, the VRFB could be operated at relatively high temperatures without the necessity to install a cooling system, resulting in higher efficiency and lower investment cost.

The innovative vanadium electrolyte developed in this Ph.D. study could be absolutely used in commercial VRFB system.

6.1.2 Additional Findings of the Study in the Context of Current Research

Along with the objective achievement, this Ph.D. study also brings out some other valuable scientific discoveries, which are very useful for the future research and development of VRFB.

A comprehensive evaluation of the effect of organic additives on the positive vanadium electrolyte has been presented in this study. It is known that V(V) ions can oxidize some organics in acidic solution and hence be reduced to V(IV), especially over the long testing times typically employed at 40 – 50°C. However, the effect of organic additives on the positive vanadium electrolyte and especially on the performance of VRFB has not been widely reported. In

practice, the rate of precipitation of V_2O_5 is dependent on the SOC of the electrolyte (i.e. the relative concentration of V(V) to total vanadium). Therefore, it is clear that the apparent thermal stability improvement of an additive may be due to the reduction of V(V) to V(IV) in the test rather than a genuine hindrance of the condensation and/or polymerization of V(V). This Ph.D. study, by employing several experiments (UV-Vis, titration, cycling...), has evaluated intensively this issue. We have estimated the degree of oxidation based on the amount of additive and V(V) concentration and also provided the mechanism of several oxidation reactions. The failure in cell cycling process due to the presence of unstable organic additives is also reported.

From above organic additive study and relied on the fact of the time-consuming in thermally stable additive screening for vanadium electrolyte, we also introduced a standard additive screening method which could be applied for any proposed additive compounds (Fig. 1.1). This is an important contribution for future research on VRFB electrolyte additive, which could help to reduce the testing time.

In this Ph.D. thesis, we also have described meticulously the precipitation process of positive vanadium electrolyte based literature reports and our investigations. The whole process was illustrated in Figure 2.12, composed of two main steps: deprotonation and condensation. While the deprotonation of the hydrate penta-coordinated $[VO_2(H_2O)_3]^+$ cations at high temperatures was described by simulation in the literature [1], the condensation process expressed in this Ph.D. study was drawn out through particle size analysis and precipitate characterization. The specific description of vanadium precipitation in this study will help scientists to propose suitable thermal stabilizing additives for vanadium electrolyte.

Importantly, we also introduced the in-depth analysis and inspection of IEM

and vanadium species interaction in this Ph.D. study. By conducting both static characterizations and dynamic experiments, we explored that the vanadium species in different oxidation states and other ions presented in electrolyte medium could strongly interact with ion exchange group of IEM, and directly affecting on the cell performance and degradation.

Last but not least, with the help from other colleagues involved in this joint project, we have built up a reliable and systematic performance testing for vanadium electrolyte. The novel vanadium electrolyte was assessed by a small scale single VRFB cell with the applying of electrolyte tank temperature, and even by a large scale VRFB system integrated with multiple sensors and equipment to precisely evaluate the performance of new electrolyte. These strategies could be the reference for future studies on VRFB.

6.1.3 Disadvantages in the Current Study

During the time conducting this project, we also realized some disadvantages in this Ph.D. study that are caused by the limitation in facility and time frame.

The oxidation of organic additive in positive vanadium electrolyte has been intensively studied and explained, even so, some other organic compounds containing polar functional group were found to be stable in strong oxidative environment of V(V). These compounds could be seen in the “*not effective*” group in Table 4.1, for example, glutamine, alanine, arginine, lysine, valine, and even several thermally stable organic additives like oleic acid, stearic acid. Due to time constraints, we could not find out the reason for the chemical stability of these organic compounds in the positive vanadium electrolyte, when they also possess the same type of functional group as compared to other unstable agents.

One more limitation is that we could not experimentally prove the binding of PO_4^{3-} anion with the hydrate penta-coordinated $[\text{VO}_2(\text{H}_2\text{O})_3]^+$ cation because of no available instrument. With expectation, nuclear magnetic resonance (NMR) could be a potential technique for this purpose. But anyway, the hypothesis of thermal stabilizing ability for PO_4^{3-} anion is already investigated either simulated or experimentally [2-5]. However, the role of the NH_4^+ cation is still hidden and has not been fully clarified in this Ph.D. study.

In addition, even though we focused more on the effect of high temperatures on the positive electrolyte, which is more common in practice. However, it is also good if we could investigate the performance of as-studied novel vanadium electrolytes at low temperatures. Time constraints and the difficulty in the installation of a chiller to the testing system are the main reason for the lack of this experiment.

Last but not least, the advanced thermally stable electrolyte has passed through many tight testing conditions and been proved to be able to use in commercial VRFB. The time limitation did not allow us to assess the performance testing for failure condition, e.g. overcharging and over discharging of the cell.

6.2 Outlooks

Based on the outcomes and remaining challenges, there are some outstanding questions and issues that can extract the attention of researcher in the future that we pointed out.

We have observed the excellent thermal stabilizing ability of PVP in combination with ammonium phosphate for VRFB electrolyte. The question is any other promising soluble polymers can also do that? The answer is yes. A wide range of soluble surfactants can be investigated for vanadium electrolyte.

Some soluble fatty acids, with a long alkyl chain, are also potential.

The high thermal stability of as-studied electrolyte formula with the concentration of 1.6 M of vanadium species has created the opportunity to increase energy density for VRFB, by increasing the vanadium concentration. The average specific energy of vanadium electrolyte is calculated to be about 10 – 20 Wh/kg, if we increase the concentration of vanadium species from 1.6 M (density of about 1.3 – 1.4 kg/L) up to 2 M, then the corresponding energy density could be increased up to 17 – 34 Wh/L, compared to the current value of 15 – 25 Wh/L. The practical performance of as-proposed high energy density vanadium electrolyte using our novel precipitation inhibitors can be a promising research topic.

People usually spend many efforts to develop effective additive for vanadium electrolyte. For ion exchange membrane, also an important component of VRFB, the study mostly focuses on the discovery of membrane modification technique or a new type of membrane to improve its property and thereof overall VRFB performance. However, relied on the improvement of NH_4^+ ion on the property of Nafion 117 CEM that is presented in chapter 5. We proposed that development of an effective additive for ion exchange membrane should be an attractive research topic. In which, the new additive agent will be added into the liquid electrolyte, but to improve the performance of IEM assembled in the VRFB. This can be useful to reduce the complication and time-consuming in current research and development of electrolyte separator for VRFB application.

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APPENDIX

Figure A.1 An example of color change in pristine V(V) solution due to the addition of 1 wt.% tannic acid.

Figure A.2 The oxidation test of diluted V(II) solution by the addition of 1 wt.% $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, $(NH_4)_3PO_4$, and NH_4NO_3 . The oxidation from V(II) to V(IV) was detected by the change of initial color over the time. While the addition of different ammonium phosphate compounds only changed slowly the color of initial V(II) solution (due to the oxidation of V(II) in air), the presence of NH_4NO_3 quickly varied the V(II) solution color, indicating the effect of NO_3^- ion in the oxidation of V(II) to V(III) and V(IV).

Figure A.3 CVs of positive vanadium electrolyte with the addition of gelatin. CV setup: carbon plate working electrode, SCE reference electrode, Pt counter electrode, scan rate: 10 mV.s^{-1} , Ar saturated condition. The kinetics of V(IV)/V(V) redox reaction in the presence of gelatin seems to be stable. However, there was a large number bubble forming in the tested electrolyte solution during CV scanning.

Figure A.4 Precipitation weight forming in 2 mL of different vanadium electrolyte samples after 3, 5 and 7 heating days. The degree of precipitation has been estimated based on the amount of precipitate.

Figure A.5 Efficiency of VRFB with the addition of 1 wt.% EDTA disodium salts, glucose, and ascorbic acid. The erratic cycling is probably due to CO_2 gas bubbles in the cell, which are formed as a byproduct of the oxidation of those organic compounds.

Figure A.6 Capacity drop of VRFB during 11 charged/discharged cycles (a) and capacity drop vs. cell voltage after 10 cycles of VRFB (b) with the addition of 1 wt.% EDTA disodium salts, glucose, and ascorbic acid. It can be seen that by adding these three selected organic additives, the capacity of the cell strongly dropped, especially for the addition of glucose and ascorbic acid.

Figure A.7a EDS mapping of the vanadium precipitate collected from pristine vanadium electrolyte. Vanadium (V) and oxygen (O) are the main element components in the precipitate sample, implying the formation of the V_2O_5 product as observed by XRD analysis.

Figure A.7b EDS mapping the vanadium precipitate collected from vanadium electrolyte containing 1 wt.% PVP. Besides vanadium (V) and oxygen (O) as the main elements, there is a remarkable amount of sulfur (S) presented in the precipitate sample, which may come from the contamination of sulfuric acid. The amount of nitrogen (N) is very tiny, indicating that PVP does not condense in the precipitate compound.

Figure A.7c EDS mapping the vanadium precipitate collected from vanadium electrolyte containing 1 wt.% H_3PO_4 . A huge amount of phosphorous (P) was detected in the precipitate, suggesting the formation of the VOPO_4 compound.

Figure A.7d EDS mapping the vanadium precipitate collected from vanadium electrolyte containing 1 wt.% $\text{NH}_4\text{H}_2\text{PO}_4$. The amount of nitrogen (N) and phosphorous is very tiny, indicating that $\text{NH}_4\text{H}_2\text{PO}_4$ can prevent the formation of a solid VOPO_4 precipitate.

Figure A.8 The view of Nafion 117 CEM and Fumatech FAP 250 AEM dipped in different vanadium solutions for over 24 h. The membrane was pretreated prior to the experiment. Electrolyte: 1.6 M V in 4 M total SO_4^{2-} .

Figure A.9 The EIS measurement of Nafion 117 CEM and Fumatech FAP 450 AEM dipped in V(III), V(IV) and V(V) solutions at different concentrations for over 24 h.

Figure A.10 Typical chemical structure of Nafion CEM and Fumatech FAP AEM.

Figure A.11 The EDX analysis of Nafion 117 CEM and Fumatech FAP 450 AEM dipped in different V(V) solutions (in 4 M total SO_4^{2-}) for over 24 h. The membrane was pretreated prior to the experiment.

Figure A.12a EDS analysis for negative carbon felt electrode under cell cycling condition with different vanadium electrolytes at 50 °C for 10 cycles.

Figure A.12b EDS analysis for positive carbon felt electrode under cell cycling condition with different vanadium electrolytes at 50 °C for 10 cycles.

PUBLICATION

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