

An Effect of a Thermal Stability Agent for Vanadium Redox Flow Battery at Room Temperature

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Abstract. Vanadium redox flow battery (VRFB) is a rising technology for a wide range of applications such as large-scale renewable energy storage system (ESS) or electric vehicle (EV), but there are still thermal problems about that the concentration of vanadium species in the positive electrolyte is limited at high temperature. Thus, several studies have introduced to improve the thermal stability, such as a sodium formate. This paper describes the cyclic performance employing the positive electrolyte with the sodium formate at room temperature. The effect of the proposed electrolyte is demonstrated through the VRFB operation. Experimental results show that using the sodium formate leads to higher charge-discharge capacities and reduce of the capacity fading. Moreover, the coulombic (energy) efficiency employing the sodium formate one keeps stable above 81 % (96 %), and the average efficiencies of the miniature cell employing the sodium formate are higher than the pristine one. Therefore, this paper provides the effect of the sodium formate at room temperature and the additive can be considered for the VRFB.

Keywords: Energy storage system, Vanadium redox flow battery, Sodium formate.

1. Introduction

Vanadium redox flow battery (VRFB) is a promising technology as an energy storage system (ESS) for a wide range of applications such as large-scale renewable ESS or electric vehicle (EV) [1]-[6]. The power generation and capacity of VRFB are dependent on the stack design and concentration of vanadium electrolytes containing two redox couples of V²⁺ (II) / V³⁺ (III) and VO²⁺ (IV) / VO₂⁺ (V) in sulfuric acid solution as a catholyte and anolyte, respectively [7]-[8].

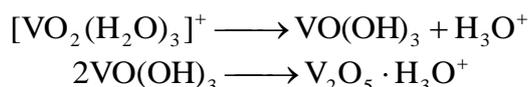
In anolyte,



In catholyte,



However, the concentration of vanadium species in the positive electrolyte is limited at high temperature [9]. Especially, the anolyte can suffer from precipitation reaction of VO₂⁺ ions to V₂O₅ above high temperature, such as the following reactions [10], which leads to degradation of electrochemical performance of VRFB.



Several studies have introduced to improve the thermal stability, such as organic additives which contain -OH, =O, -NH₂ or -SH functional groups [11]-[12] or using higher concentration of supporting electrolyte which prevent precipitation reaction by forming sulfate complexes [10]. These organic additives can

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encapsulate the hydrated penta coordinated vanadate ion and inhibit the precipitation formation [13]. Especially, using a sodium formate in the positive electrolyte can conduct as the precipitation preventing agent by the dispersion of the hydrated penta coordinated vanadate ion during cyclic operation [14]. Thus, the addition of sodium formate is focused on a battery performance at room temperature. In this paper, the sodium formate is used as additive to improve efficiencies and reduce capacity lose during cyclic operation. The electrolytes without or with added the additive are demonstrated through the charge-discharge test.

2. Experimental

2.1. Preparation of Vanadium Electrolytes

The positive electrolyte solution is prepared by dissolving 1.8 mol L^{-1} Vanadium (IV) oxide sulfate hydrate (Sigma Aldrich, USA) in 3.0 mol L^{-1} sulfuric acid as supporting electrolyte (Samchun Chemical, Korea). The negative electrolyte solution is prepared by electric charging the positive electrolyte in an electrolytic cell [9]. The sodium formate of 0.25 wt% (weight percentage of the additive to the solution) is also added into the positive electrolyte for electrochemical measurements [14].

2.2. Electrochemical Measurement

The VRFB charge & discharge tests are performed in a miniature flow cell, which consists of a Nafion 115 as separator, graphite foil (SGL, USA) and carbon felt (Toyobo, Japan) as electrodes with flow frame. The miniature flow cell (active area is about 6 cm^2) contains 10 ml as anolyte and catholyte, circulated into the flow cell from anodic and cathodic electrolyte reservoirs. The cyclic cell operation is carried out for 50 cycles by using WBCS3000 workstation (WonA tech Co., Korea) for a given galvanostatic charge and discharge between 1.7 V and 0.7 V under a current density of 80 mA cm^{-2} at room temperature. Fig. 1 shows the operation of the miniature flow cell used in this work.

3. Results and Discussion

3.1. Electrochemical Performance of VRFB

Fig. 2 shows charge and discharge capacities of the pristine electrolyte and with 0.25 wt% the sodium formate as a function of cycle number at room temperature. The anolyte with the additive indicates a higher initial charge and discharge capacity (304.88 mA h, 294.83 mA h) than the pristine one (267.36 mA h, 250.30 mA h). The cyclic performance employing the sodium formate one exhibits less capacity fading compared to the pristine one. It means that furthermore the sodium formate enhances performance of VRFB at room temperature as well as at high temperature [14].

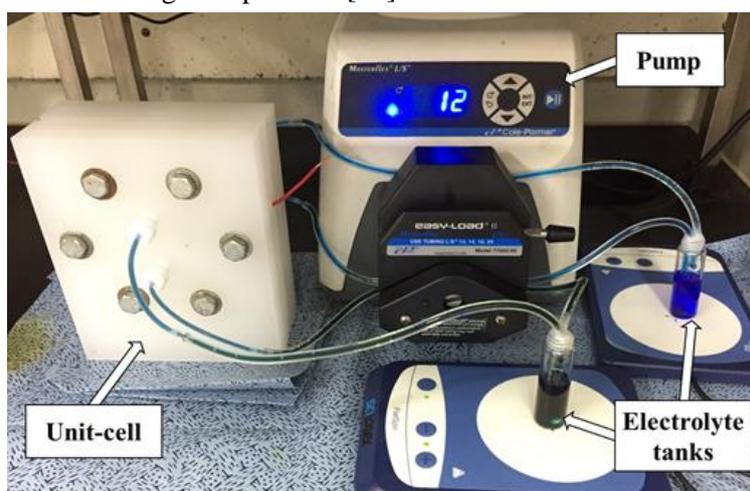


Fig. 1: The miniature flow cell (active area is about 6 cm^2) operating system.

Fig. 3 indicates the coulombic and energy efficiency of the miniature cell employing the pristine electrolyte and with 0.25 wt% the sodium formate. The result shows that the coulombic (energy) efficiency employing the sodium formate one keeps stable and remains above 81 % (96 %) at the current density of 80 mA cm^{-2} . Besides, it represents that the average coulombic (energy) efficiency of the miniature cell

employing the sodium formate is also 2.39 % (1.83 %) higher than the pristine one. It can be seen from these results that the additive leads to enhance the electrochemical performance in positive electrolyte (VO^{2+} (IV) / VO_2^+ (V)) of VRFB at room temperature as well as high temperature [14].

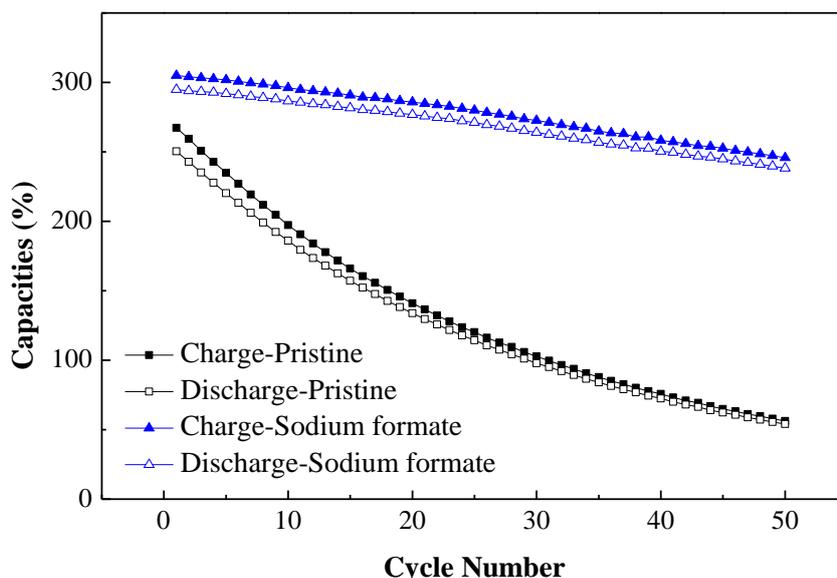


Fig. 2: Charge-discharge capacity of the miniature cell employing anolyte without additive (pristine) and with the sodium formate during cyclic operation at room temperature.

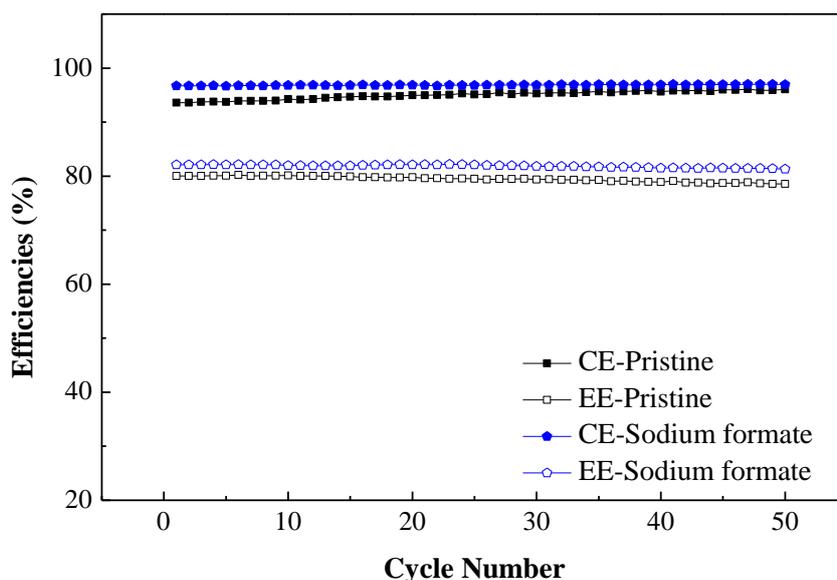


Fig. 3: Cyclic performance of the miniature cell employing anolyte without additive (pristine) and with the sodium formate during cyclic operation at room temperature.

4. Conclusion

This paper has focused on an effect of the sodium formate in the positive electrolyte on the performance of the VRFB at room temperature. The experimental results have demonstrated that the additive leads to higher charge-discharge capacities (304.88 mA h, 294.83 mA h) than the pristine one (267.36 mA h, 250.30 mA h) and reduce of the capacity fading. Moreover, the coulombic (energy) efficiency employing the sodium formate one keeps stable above 81 % (96 %), and the average coulombic (energy) efficiencies of the miniature cell employing the addition are 2.39 % (1.83 %) higher than the pristine one. Therefore, this paper provides the effect of the sodium formate at room temperature and the additive can be considered for the VRFB.

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6. References

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