Short communication

A high-temperature tolerance solution for positive electrolyte of vanadium redox flow batteries

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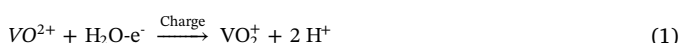
ABSTRACT

Vanadium redox flow battery (VRFB) is attractive for energy storage applications, but there still remains a problem of preventing V-precipitation reaction (i.e., V_2O_5) to provide the thermal stability of electrolyte employed in VRFB. The V_2O_5 precipitation is accelerated in the positive electrolyte under high temperature, resulting in decreasing the charge capacity and energy efficiency of VRFB. So far, previous supporting materials, which are used to solve such precipitation problem, provide a disadvantage of decreasing voltage efficiency of VRFBs by increasing electrolyte resistance. This paper describes an advanced vanadium-positive electrolyte with high-temperature tolerance for high-efficiency VRFBs, which uses a sodium formate as a supporting material. The sodium formate plays a role as an agent capable of preventing precipitation reaction in the positive electrolyte and it also provides an effect of decreasing a viscosity of the positive electrolyte. The effectiveness of the proposed electrolyte solution is demonstrated through the following experiments: UV–vis spectrometry, viscosity measurement, cyclic voltammetry (CV), VRFB operation and scanning electron microscopy (SEM) analysis. Then, for the performance comparison of high temperature stability, all experiments are carried out at 60 °C. Experimental results show that using the sodium formate leads to near 4.5 times increase of diffusion coefficient as compared to conventional electrolyte, and also provides 20.2% higher charge capacity (50th cycle) and 2.27% higher average energy efficiency (50 cycles) at the current density of 80 mA cm^{-2}. In addition, it appears that the precipitation of vanadium species is not observed in the electrolyte during VRFB operation. Therefore, this paper provides that new direction about effect of the additive in the positive electrolyte and the sodium formate can be considered as a promising additive for high-performance electrolyte of VRFBs.

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 [1–5]. "The power generation and capacity of VRFB are dependent on the stack design and concentration of electrolytes containing two redox couples of V (II)/(III) and V (IV)/(V) in sulfuric acid solution as a catholyte and anolyte, respectively [6]."

In anolyte,

$$VO^{2+} + H_2O\text{-}e^- \xrightarrow{\text{Charge}} VO_2^+ + 2\,H^+ \qquad (1)$$

and in catholyte,

$$V^{3+} + \ e^- \xrightarrow{\text{Charge}} V^{2+} \qquad (2)$$

However, the thermal stability of the vanadium species in the electrolyte solutions is limited [7]. Especially, the V (V) electrolyte suffers from precipitation reaction above high temperature, which leads to decrease the capacity and energy density of VRFB. Several studies have introduced to improve the solubility and stability of the electrolyte solutions, such as increasing the concentration of the aqueous sulfuric acid. Higher concentration of supporting electrolyte can prevent precipitation reaction of VO_2^+ ions to V_2O_5 by forming sulfate complexes, such as precipitation reaction through the following reactions [8],

$$[VO_2(H_2O)_3]^+ \rightarrow VO(OH)_3 + H_3O^+, \qquad (3)$$

$$2VO(OH)_3 \rightarrow V_2O_5 \cdot H_3O^+, \qquad (4)$$
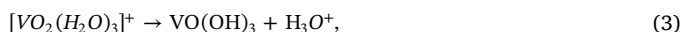
and achieve increased stability due to de-protonation or dimerization of VO_2^+ ions to $V_2O_4^{2+}$ and $V_2O_3^{4+}$ species [9]. However, it favors the precipitation of V (II, III and IV) and the solubility of V (IV) sulfate decreases with increasing sulfuric acid concentration due to the common ion effect [10,27]. Because of the reduced solubility of the V (IV) ions in the discharged positive half-cell electrolyte, it is not

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possible to increase the concentration of sulfuric acid above 6.0 M. Several organic additives, which contain –OH, =O, –NH$_2$ or –SH functional groups, can encapsulate the hydrated penta coordinated vanadate ion and inhibit the precipitation formation, are screened as potential additives [11,12]. Thus the addition of sodium formate is focused on the thermal stability of positive electrolyte. In this paper, sodium formate is used as additives to improve thermal stability and battery performance of positive electrolyte. This supporting material which is the sodium salt of formic acid with the formula NaCO$_2$H, acts as a preventing agent of precipitation reaction and can be added to the positive electrolyte for VRFB. The positive electrolyte without and with the additive are demonstrated through the thermal stability test, cyclic voltammetry (CV) measurement, charge–discharge test, and scanning electron microscopy (SEM) analysis.

2. Experimental

2.1. Preparation of vanadium electrolytes

V (IV) electrolyte solution is prepared by dissolving 1.8 M VOSO$_4$ (Sigma Aldrich, USA) + 3.0 M H$_2$SO$_4$ supporting electrolyte (Samchun Chemical, Korea). The V (III and V) electrolyte solutions are prepared by electric charging the V (IV) solutions in an electrolytic cell. The sodium formate of 0.25 wt% (weight percentage of the additive to the solution) is also added into the V (IV) electrolyte for electrochemical measurements [7].

2.2. UV–vis spectrometry

The absorbance of V (IV) electrolyte solutions are measured with a T60 UV–vis spectrophotometer in the range of 400–900 nm using 1.0 cm quartz cell [13]. The measured solutions are as follows: solution I: 0.036 M V (IV) electrolyte (pristine); solution II: 0.005 wt% sodium formate in solution I.

2.3. Viscosity measurement

The viscosity of V (IV) solutions (16 ml of 1.8 M VOSO$_4$ + 3.0 M H$_2$SO$_4$) is measured with a DV-E Viscometer (Brookfield, USA) using UL Adapter (Brookfield, USA) and all the viscosity measurements are carried out at 60 °C.

2.4. Thermal stability test

The thermal stability test of V (V) electrolyte solutions is carried out in an oil bath at different temperatures (50 and 60 °C). The electrolyte solutions are monitored and recorded the precipitation time when a slight precipitation appeared [14].

2.5. Electrochemical measurements

A pristine electrolyte consists of V (IV) solutions (1.8 M VOSO$_4$ + 3.0 M H$_2$SO$_4$) without and with 0.1, 0.25, 0.50 and 1.0 wt% the sodium formate as thermal stability agent is added into the pristine solution. Specific resistivity and cyclic voltammetry (CV) measurement of the V (IV) solutions are carried out on S470 SevenExcellence™ (Mettler Toledo, Switzerland) and ZIVE SP1 electrochemical workstation (WonA tech. Korea), respectively. The potential scanning range is from 0.4 V to 1.4 V with the scan rate as 10 mV s^{-1} at the room temperature, where a platinum wire is used as counter electrode, a saturated calomel electrode (SCE) as reference electrode and a graphite plate (surface area is 0.95 cm^2) as working electrode. 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) with flow frame. The Nafion 115 is treated in distilled water at room temperature for 1 h before charge and
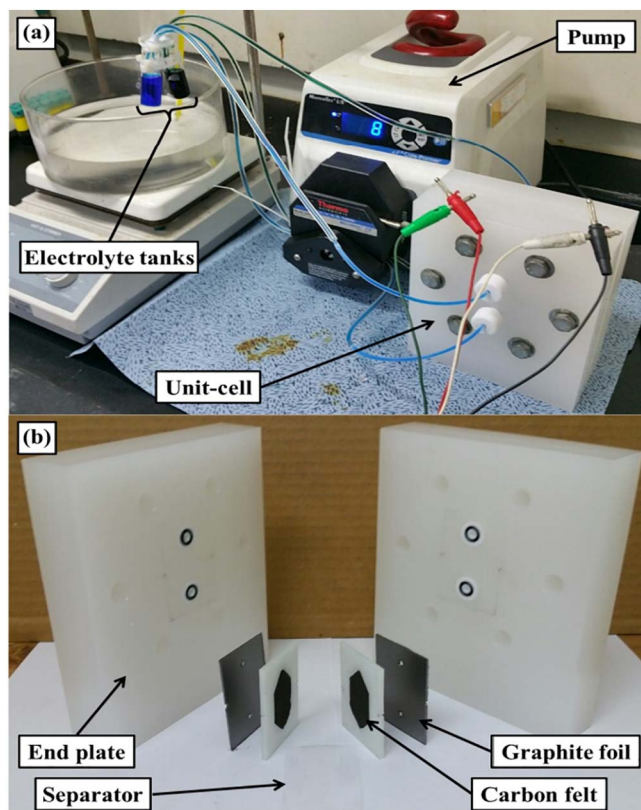

Fig. 1. The 6 cm^2 miniature flow cell: (a) operating system and (b) miniature cell components.

discharge cycle operation. The flow cell (active area is about 6 cm^2) contains 10 ml anolyte and 10 ml catholyte, electrolyte solution of 1.8 M V (III) and (IV) in 3.0 M H$_2$SO$_4$, respectively. A P/S 1400 pump (Thermo Co., USA) is used to circulate in the unit cell and controls 6 ml min^{-1}. Fig. 1 shows the operation of VRFB used in the work and the related specification is indicated in Table 1. 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 60 °C. To two electrolyte tanks are placed in the oil bath at high temperature and circulated into unit-cell for one hour before charge and discharge cycle operation-i.e., free-cyclic operation proceeds for one hour so that the electrolyte temperature is 60 °C. The coulombic efficiency (CE), voltage efficiency (VE) and energy efficiency (EE) of the cell are also calculated according to following equations: (5–7)

$$\text{The coulombic efficiency (CE)} = \left(\frac{\text{discharge capacity}}{\text{charge capacity}} \right) \times 100 \quad (5)$$

$$\text{The voltage efficiency (VE)} = \left(\frac{\text{average discharge voltage}}{\text{average charge voltage}} \right) \times 100 \quad (6)$$

Table 1
Data related to Fig. 1.

	Parts	Model/company	Value	Remarks
Cell composition	End plate	Poly propylene	14 × 17 cm^2	t$^{2)}$: 3 cm
	Flow frame	Poly propylene	24 (6)$^{1)}$ cm^2	t$^{2)}$: 0.3 cm
	Graphite foil	TF6/SGL Co.	24 (6)$^{1)}$ cm^2	t$^{2)}$: 0.06 cm
	Carbon felt	XF30A/Toyobo Co.	(6)$^{1)}$ cm^2	t$^{2)}$: 0.42 cm
	Separator	Nafion 115/ DuPont Co.	24 (6)$^{1)}$ cm^2	t$^{2)}$: 127 μm

()$^{1)}$: active area, t$^{2)}$: thickness.