



Broad temperature adaptability of vanadium redox flow battery-Part 3: The effects of total vanadium concentration and sulfuric acid concentration



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ABSTRACT

The broad temperature adaptability of vanadium redox flow battery (VFB) has been studied in our two previous works, including the study on the broad temperature adaptability of the vanadium electrolytes (Electrochim. Acta, 2016, 187, 525) and battery performance (Electrochim. Acta, 2016, 191, 695) with a fixed electrolyte composition of 1.5 M vanadium in 3.875 M total sulfate. As a follow-up study, the stability of the vanadium electrolytes with different valences, total vanadium concentrations and sulfuric acid concentrations is studied at a broad temperature range. In this work, the static stability of the vanadium electrolytes with four valences (V^{2+} , V^{3+} , VO^{2+} and VO_2^+), different total vanadium concentrations (0.4–2.2 M) and various sulfuric acid concentrations (1.5–3.0 M) is researched over a wide temperature range (–35 to 60 °C). Subsequently, the cell performance of VFBs with selected electrolyte compositions was evaluated at different temperatures and different current densities. This work systematically investigates the effects of the total vanadium concentration and sulfuric acid concentration on the temperature adaptability of VFBs for the first time as we know, which is an important reference for the battery's application.

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1. Introduction

With the excessive exploitation of natural resources and the continual deterioration of environment, redox flow batteries (RFB) are attracting much attention for both grid-connected and off-grid energy storage applications [1–4]. Among various RFBs under development, all-vanadium redox flow battery (VFB, also called VRFB or VRB) is considered as a promising candidate due to its many benefits including long cycle life, low environmental impact, and flexible operation [5–7]. VO_2^+/VO^{2+} and V^{3+}/V^{2+} redox couples are employed in the positive and negative electrolytes of a VFB, and sulfuric acid is chosen as the preferred supporting electrolyte [8–11].

The energy density of a VFB is limited by the vanadium concentration of the electrolyte [12–16] due to the finite solubility and poor stability of the vanadium species in the electrolyte [3,17–19]. Higher temperature increases the solubilities of V^{2+} , V^{3+} , VO^{2+}

species in sulfuric acid, but favors the precipitation of VO_2^+ species [3,20,21]. Higher sulfuric acid concentration stabilizes VO_2^+ species in the electrolyte, but leads to the instability of V^{2+} , V^{3+} , VO^{2+} species in the electrolyte [3,22]. Skyllas-Kazacos and co-workers have carried out considerable research to investigate the solubilities of V^{2+} , V^{3+} , VO^{2+} , VO_2^+ species in sulfuric acid at temperatures ranging from 10 °C to 60 °C and the stability of the positive electrolytes [3,15,16,20,21]. Our group have reported that the dissolution of V^{3+} species was an exothermic process, and the solubility of V^{3+} species in the electrolyte decreased with the increasing sulfuric acid concentration [23]. Characterization techniques and models have been applied to obtain a better understanding of the stability of vanadium electrolytes and VFBs [24–29]. Meanwhile, much attempt has been made to improve the stability of the vanadium electrolytes. Organic and inorganic additives were evaluated in stabilizing the vanadium species in the electrolyte [30–37]. Novel methods of employing the chloride supporting electrolyte or the sulfate-chloride mixed acid system were proposed by researchers from the Pacific Northwest National Laboratory (PNNL) [12,19,38,39].

Although a high vanadium concentration is required for a VFB, it

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can promote the precipitation of VO_2^+ species in the electrolyte, especially in high temperature environment [38]. The increasing sulfuric acid concentration can increase the stability of VO_2^+ species, but have an adverse effect on the solubilities of V^{2+} , V^{3+} , VO^{2+} species in the electrolyte [23]. Thus, the matching relationship between the total vanadium concentration and sulfuric acid concentration is very important for the concentration optimization and stability improvement of the electrolyte [21,22,40]. Therefore, the effects of the total vanadium concentration and sulfuric acid concentration on the broad temperature adaptability of electrolytes in VFBs with different valences need to be systematically studied. However, no such study has been reported, as far as we know.

Our group has focused on different approaches to improving the temperature stability of VFBs [41–43]. Recently, we studied the broad temperature adaptability of the vanadium electrolytes and battery performance with a fixed electrolyte composition of 1.5 M vanadium in 3.875 M total sulfate [13,44]. In this work, a systematic study on the stability of the vanadium electrolytes with different valences, total vanadium concentrations and sulfuric acid concentrations is carried out. The static stability of the vanadium electrolytes with four valences (V^{2+} , V^{3+} , VO^{2+} and VO_2^+), different total vanadium concentrations (0.4–2.2 M) and various sulfuric acid concentrations (1.5–3.0 M) was investigated over a wide temperature range (–35 to 60 °C). Subsequently, cell performance of VFB single cells with selected vanadium electrolytes was evaluated at a broad temperature range. The experimental data can serve as an important reference for the fundamental research and large-scale application of VFBs, as well as a standard database for evaluating the stabilizing methods of VFB electrolytes.

2. Experimental section

2.1. Electrolyte preparation

All chemicals used in the electrolyte preparation were analytically pure. The VO^{2+} electrolytes of the various vanadium concentrations (0.4 M, 0.8 M, 1.2 M, 1.6 M, 2.0 M) and different sulfuric acid concentrations (1.5 M, 2.0 M, 2.5 M, 3.0 M) were prepared by dissolving vanadyl sulfate ($\text{VOSO}_4 \cdot 3.5\text{H}_2\text{O}$, 99% purity, Shenyang Haizhongtian Fine Chemical Co., Ltd.) in concentrated sulfuric acid solutions. In this work, the V^{2+} , V^{3+} and VO^{2+} electrolytes were prepared by electrolytic oxidation or reduction of the VO^{2+} electrolyte with a homemade electrolytic cell. An APS anion exchange membrane (AGC Engineering Co., Ltd, Japan) with low vanadium permeability [42] was used in the electrolytic cell to ensure that the vanadium ion concentration remains constant during electrolysis. During the electrolysis, we found that the volumes of the electrolytes had little change at the both sides of the electrolytic cell. Similar to the analysis in our previous work [13], we could conclude that the V^{2+} , V^{3+} , VO^{2+} and VO_2^+ electrolytes from the same initial VO^{2+} electrolyte had equivalent vanadium concentrations but different sulfuric acid concentrations. In this work, electrolytes with four valences from the same initial VO^{2+} electrolytes were treated as one set, and the sulfuric acid concentrations of electrolytes in one set were labeled with the sulfuric acid concentration of the initial VO^{2+} electrolyte to avoid confusion. Subsequently, the four types of the vanadium electrolytes (V^{2+} , V^{3+} , VO^{2+} and VO_2^+) were sealed into sample bottles (5 mL capacity with an isobutylene isoprene rubber stopper), as shown in Fig. 1. As observed, the colors of the vanadium electrolytes deepen with the increasing of the vanadium concentration, but barely change with the increasing of the sulfuric acid concentration.

It should be noteworthy that during the electrolysis, the purities of the V^{2+} , V^{3+} , VO_2^+ electrolytes were confirmed by both spectroscopic examination and redox titration. Thus, each oxidation state

of the electrolytes was assured to be close to 100%.

2.2. Static temperature stability test

The static temperature stability test of the electrolyte samples was conducted in a thermostat (Guangdong HongZhan Technology Co. Ltd, PU-80), as shown in Fig. 2(a). The electrolyte samples with labels were contained in a transparent polymethylmethacrylate (PMMA) box (Fig. 2(b)–(c)). By reversing the PMMA box, it is convenient to observe whether there were precipitates at the bottom of each sample bottle (Fig. 2(d)–(e)). The static temperature stability test was conducted from –35 °C to 60 °C with 5 °C interval and carried out in two groups, including the low temperature stability test (–35 to 20 °C) and high temperature stability test (20–60 °C). At each temperature, the electrolyte samples were tested for 7 days. When the precipitate of each electrolyte was first observed, the temperature, time and amount of the precipitation as well as the label of the electrolyte were recorded. Although some dozens of days' stability tests have been reported [15,16,21,40], it is not necessary for fully charged electrolytes to be stored for such a long time in most VFB applications. Thus, the 7 days' stability data in this work are valuable references for the applications including storage of renewable energy, grid regulation, etc.

Fig. 3 shows the final states of the electrolyte samples after 7 days' low temperature stability test at –35 °C (Fig. 3(a)) and 7 days' high temperature test at 60 °C (Fig. 3(b)). In the static temperature stability test, we found that when the vanadium concentration is 1.2 M or 1.6 M, a relative broad temperature stable range and an acceptable energy density can be achieved. Such a conclusion led us to explore the vanadium concentrations between 1.2 M and 1.6 M. Furthermore, electrolytes with vanadium concentration higher than 2.0 M are also studied as an extreme situation. Thus, the static temperature stability test of the vanadium electrolytes with the vanadium concentrations including 1.3 M, 1.4 M, 1.5 M, 2.1 M and 2.2 M was conducted. The detailed data of the static temperature stability tests of the electrolytes with different vanadium concentrations (0.4–2.2 M) and sulfuric acid concentrations (1.5–3.0 M) were presented in the Supporting Information (See Tables S1–S4).

2.3. VFB single cell performance test

In our group's previous work, we have built a broad temperature research platform [44] to investigate the cell performance of VFBs with a fixed electrolyte composition of 1.5 M vanadium in 3.875 M total sulfate in the temperature range from –20 °C to 50 °C. In this work, we continually use this research platform to investigate the cell performance of VFBs with selected electrolyte compositions. The VFB single cell was assembled by sandwiching a Nafion 115 membrane (70 mm × 70 mm, Dupont) between two pieces of graphite felts (50 mm × 50 mm × 5 mm, Gansu Haoshi Carbon Fiber Co., Ltd.) clamped by two graphite polar plates (60 mm × 60 mm × 30 mm). The initial positive and negative electrolytes, whose volumes were both 50 mL, were circulated at a flow rate of about 60 ml/min by a two-channel peristaltic pump. During the cell performance test at different temperatures, the VFB single cell and electrolyte reservoirs were put into the thermostat, and the peristaltic pump was left outside because it cannot resist high and low temperatures. All the electrolyte pipelines outside the thermostat were covered with heat preservation cotton. Because the cooling power of the thermostat was much larger than the heating power of the cell, the heat produced by the VFB during the operation could be taken away immediately. Temperature sensors were attached to the exterior walls of the reservoirs to confirm that the temperatures of the electrolytes were in accordance with the setting temperatures of the thermostat (with a deviation of

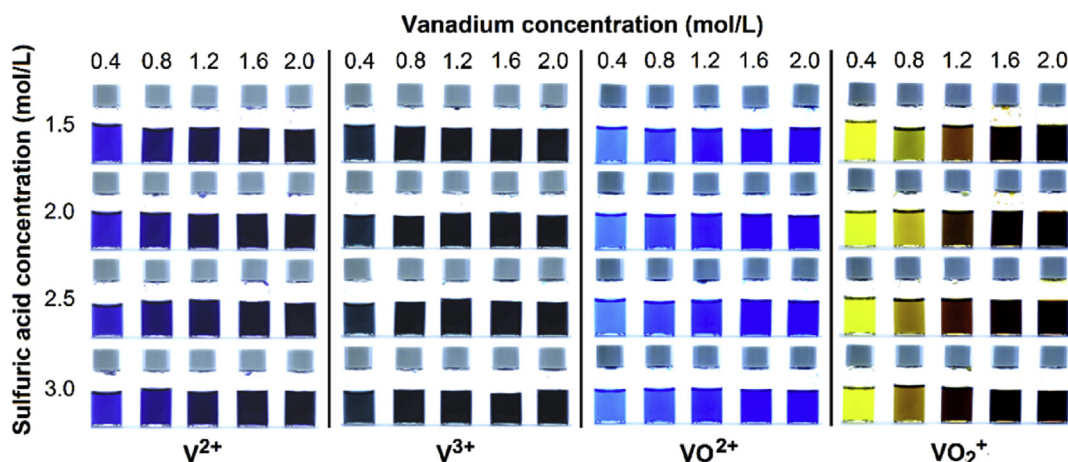


Fig. 1. Photograph of vanadium electrolytes (V^{2+} , V^{3+} , VO^{2+} , VO_2^+) with different vanadium concentrations (0.4 M, 0.8 M, 1.2 M, 1.6 M, 2.0 M) and sulfuric acid concentrations (initial VO^{2+} electrolyte, 1.5 M, 2.0 M, 2.5 M, 3.0 M).

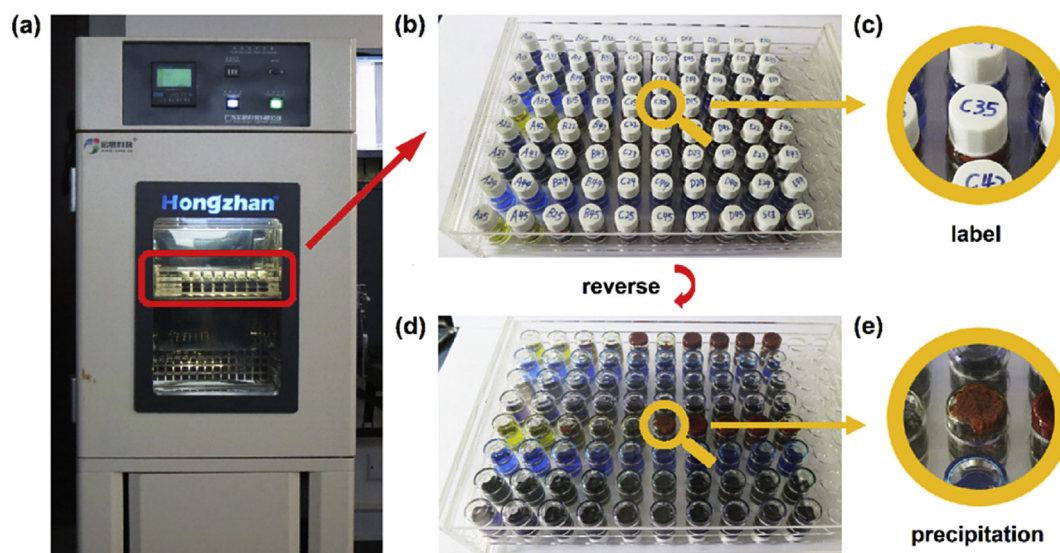


Fig. 2. (a) Photograph of the thermostat used to study the static temperature stability of the vanadium electrolytes; (b) Photograph of a transparent Polymethylmethacrylate (PMMA) box containing sample bottles with labels; (c) The enlarged marked area in (b); (d) Photograph of the reversed PMMA box in (b) to fast examine the precipitates of electrolytes; (e) The enlarged marked area in (d).

± 0.5 °C). Charge-discharge experiments under different current densities ($40\text{--}200\text{ mA cm}^{-2}$) were conducted at different temperatures. The cut-off voltages of 1.65 V and 0.8 V were set in order to avoid the corrosion of carbon felts and graphite polar plates. After the above test, the temperature range in which VFBs with the selected electrolyte can operate is obtained. Then cycling stability tests were carried out at the lowest and highest temperatures of the temperature range.

3. Results and discussion

3.1. Static temperature adaptability of electrolytes with single valence

Fig. 4 presents the low and high temperature stability of the four types of the vanadium electrolytes (V^{2+} , V^{3+} , VO^{2+} and VO_2^+) with different total vanadium concentrations (0.4–2.2 M) and sulfuric acid concentrations (initial VO^{2+} electrolyte, 1.5–3.0 M) over a wide temperature range from -35 °C to 60 °C. Different colors in

Fig. 4(a), (c), (e), (g) represent the lowest temperatures at which each electrolyte can stabilize, while different colors in Fig. 4(b), (d), (f), (h) represent the highest temperatures at which each electrolyte can stabilize. For example, the blue color represents the lowest temperature (-35 °C) and the black color represents the highest temperature (60 °C).

There are several reasons for the low temperature instability of the vanadium electrolytes. Higher vanadium concentration promotes the instability of the vanadium electrolytes because of the finite solubility. With the sulfuric acid concentration increasing, the solubilities of V^{2+} , V^{3+} , VO^{2+} species in the electrolyte decrease due to the common ion effect [3]. We define the above two factors as “solubility effect”. As we know, with the sulfuric acid concentration increasing from 1.5 M to 3.0 M, the freezing point of the sulfuric acid keeps dropping [46]. Here, we define the factor as “freezing point effect”. It can be seen from Fig. 4(a) that with the vanadium concentration increasing from 0.4 M to 2.2 M, the low temperature stability of the V^{2+} electrolytes becomes worse when the sulfuric acid concentration is fixed due to the solubility effect. While the

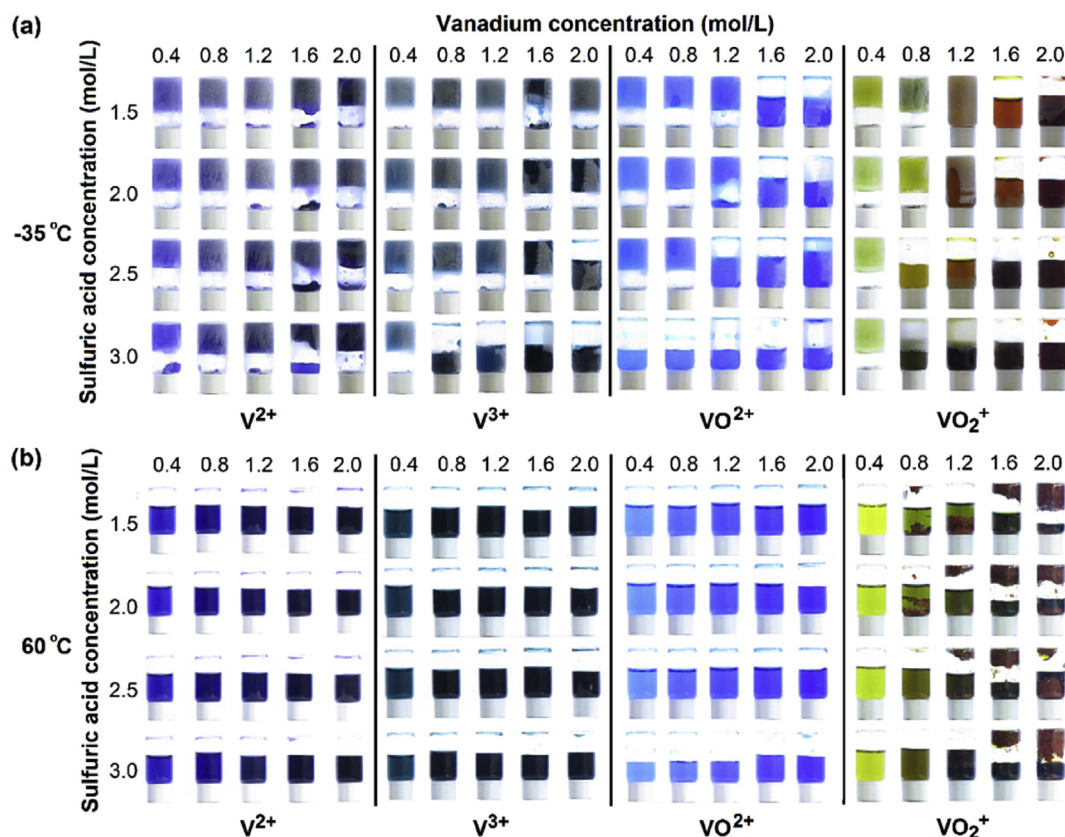


Fig. 3. Photograph of the final states of the vanadium electrolyte samples in Fig. 1 after 7 days' test at $-35\text{ }^{\circ}\text{C}$ (a) and $60\text{ }^{\circ}\text{C}$ (b).

changing tendency of the low temperature stability of the V^{2+} electrolytes with the increasing sulfuric acid concentration is complicated. Fig. 4(a) shows that when the vanadium concentration is no more than 0.8 M, the low temperature stability of the V^{2+} electrolytes gets better with the sulfuric acid concentration increasing from 1.5 M to 3.0 M. Maybe it is because the freezing point effect plays the major role in the low temperature stability of the V^{2+} electrolytes when the vanadium concentration is low ($<0.8\text{ M}$). When the vanadium concentration is between 0.8 M and 1.5 M, the low temperature stability of the V^{2+} electrolytes becomes better first then worse with the increasing of sulfuric acid concentration, which may be due to the alternative domination of the freezing point effect and solubility effect. When the vanadium concentration is more than 1.5 M, the low temperature stability of the V^{2+} electrolytes is worse with the increasing concentration of the sulfuric acid. It is because the solubility effect dominates the low temperature stability of the V^{2+} electrolytes when the vanadium concentration is high ($>1.5\text{ M}$).

In addition, it is obvious from Fig. 4(b) that the V^{2+} electrolytes possess the desirable stability at the temperature as high as $60\text{ }^{\circ}\text{C}$, because of the high solubility of V^{2+} species at elevated temperatures in the electrolyte.

Fig. 4(c) shows that with the vanadium concentration increasing from 0.4 M to 2.2 M and sulfuric acid concentration increasing from 1.5 M to 3.0 M, the low temperature stability of the V^{3+} electrolytes gets better. It indicates that the freezing point effect is more significant than the solubility effect on the low temperature stability of the V^{3+} electrolytes. The exception to this changing tendency is the low temperature stability of the V^{3+} electrolytes with compositions of 1.2–1.6 M vanadium concentration and 1.5–2.0 M sulfuric acid concentration. It may be due to some unknown effects, which

will be studied in our further works. Fig. 4(d) indicates that the V^{3+} electrolytes also maintain good high temperature stability at $60\text{ }^{\circ}\text{C}$.

It can be concluded from Fig. 4(e) that there are two unstable zones of the VO^{2+} electrolytes at low temperatures. One of the unstable zone is caused by the freezing point effect with both low vanadium concentrations and low sulfuric acid concentrations (bottom left of Fig. 4(e)). The other unstable zone results from the solubility effect with both high vanadium concentrations and high sulfuric acid concentrations (top right of Fig. 4(e)). Similar to the V^{2+} and V^{3+} electrolytes, the VO^{2+} electrolytes have good high temperature stability at $60\text{ }^{\circ}\text{C}$, as shown in Fig. 4(f).

It can be seen from Fig. 4(g) that VO_2^+ electrolytes have good low temperature stability at as low as $-35\text{ }^{\circ}\text{C}$, except for one unstable zone (bottom left of Fig. 4(g)) due to the freezing point effect with low vanadium concentrations and low sulfuric acid concentrations. Unlike the good high temperature stability of the V^{2+} , V^{3+} , VO^{2+} electrolytes, the VO_2^+ electrolytes have poorer high temperature stability attributing to the reaction precipitating V_2O_5 [15,16]. Fig. 4(h) shows that with the vanadium concentration increasing, the high temperature stability of the VO_2^+ electrolytes gets worse. While with the sulfuric acid concentration increasing, the high temperature stability of the VO_2^+ electrolytes becomes better, ascribed to the inhibition of sulfuric acid concentration on the reaction precipitating V_2O_5 .

Based on Fig. 4(a)–(h), we can conclude that, when the vanadium concentration is high, the sulfuric acid concentration is harmful to the low temperature stability of the V^{2+} electrolytes, but propitious to the high temperature stability of the VO_2^+ electrolytes. Therefore, in order to obtain a VFB with broad temperature adaptability, a proper sulfuric acid concentration should be selected.

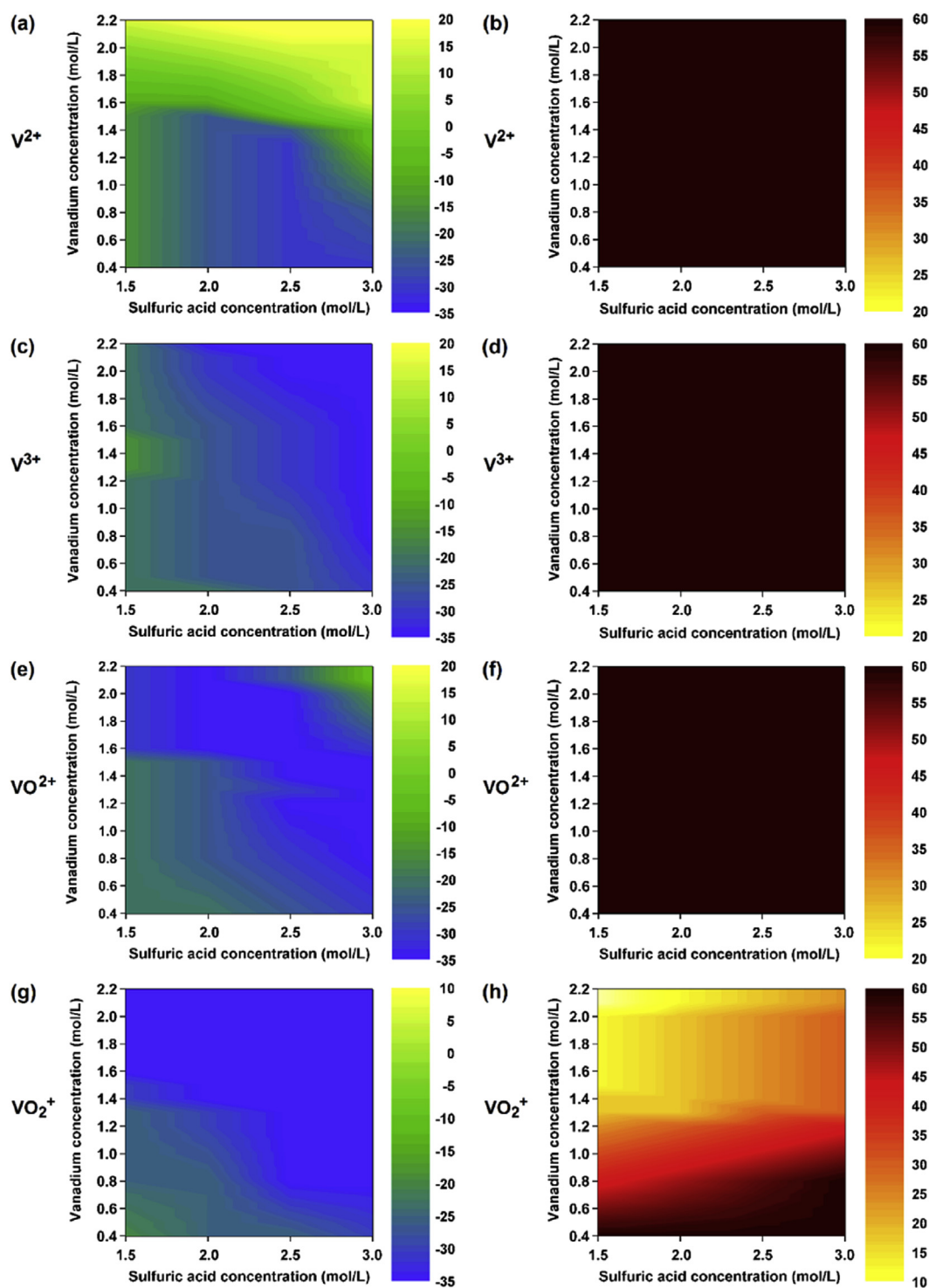


Fig. 4. Low and high temperature stability of the static V^{2+} (a–b), V^{3+} (c–d), VO^{2+} (e–f), VO_2^+ (g–h) electrolytes with different total vanadium concentrations (0.4–2.2 M) and sulfuric acid concentrations (initial VO^{2+} electrolyte, 1.5–3.0 M) over a wide temperature range from -35 °C to 60 °C.

3.2. Static temperature range of electrolytes with different compositions

Fig. 4 in Section 3.1 and Tables S1–S4 in the Supporting Information show the influences of vanadium concentration and sulfuric acid concentration on the temperature stability of single valence electrolytes. Because four types of vanadium electrolytes (V^{2+} , V^{3+} , VO^{2+} , VO_2^+) exist simultaneously in VFBs in practical operation, the

stable temperature range of electrolytes with one composition needs to be analyzed.

Fig. 5 presents the temperature range in which the V^{2+} , V^{3+} , VO^{2+} , VO_2^+ electrolytes can be simultaneously stable with different total vanadium concentrations (0.4–2.2 M) and sulfuric acid concentrations (initial VO^{2+} electrolyte, 1.5–3.0 M). The four types of the color bars (violet, green, blue, and yellow) represent the temperature ranges in which the V^{2+} , V^{3+} , VO^{2+} , VO_2^+ electrolytes can

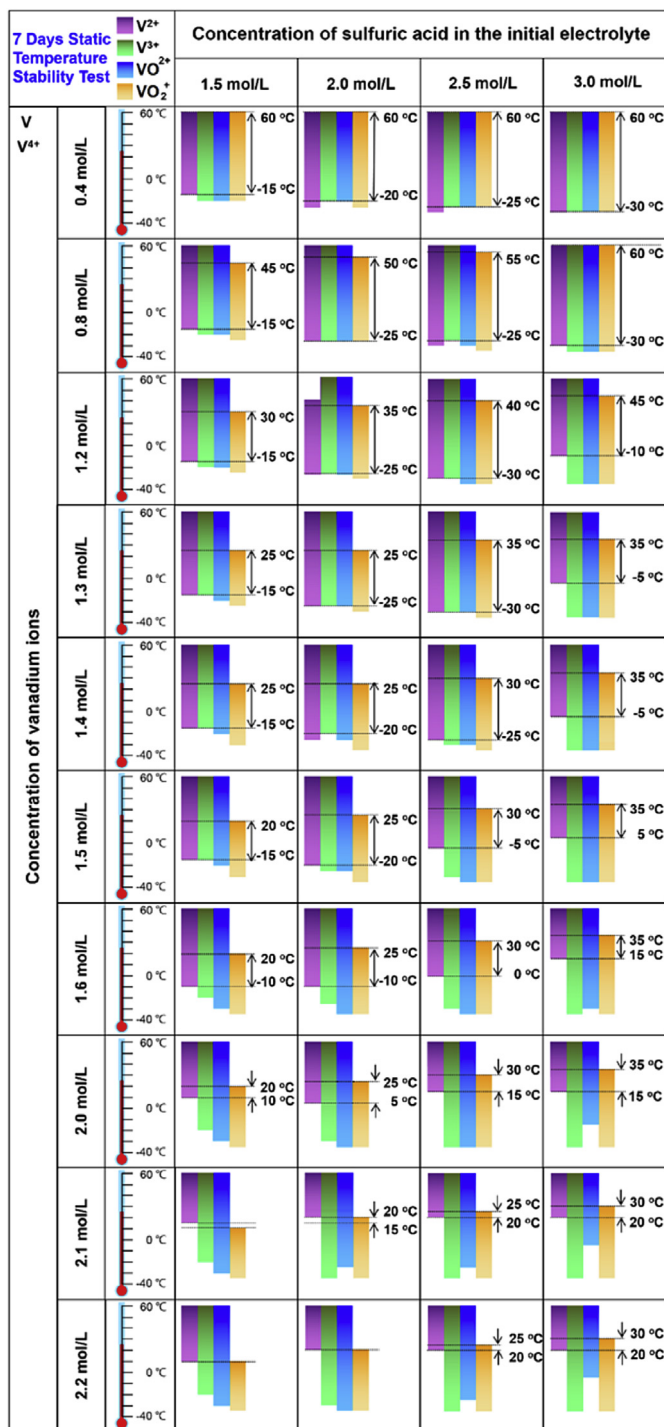


Fig. 5. Temperature ranges in which the V^{2+} , V^{3+} , VO^{2+} , VO_2^- electrolytes can be simultaneously stable with different total vanadium concentrations (0.4 M–2.2 M) and sulfuric acid concentrations (initial VO^{2+} electrolyte, 1.5 M–3.0 M).

be separately stable. Each black arrow represents the temperature range in which the V^{2+} , V^{3+} , VO^{2+} , VO_2^- electrolytes with the same composition can be stable at the same time. Fig. 5 indicates that when the vanadium concentration is low, the V^{2+} , V^{3+} , VO^{2+} , VO_2^- electrolytes can stably exist at a broad temperature range, but the energy density of VFBs may be not acceptable for application [15]. While with the vanadium concentration increasing, the temperature range in which the V^{2+} , V^{3+} , VO^{2+} , VO_2^- electrolytes can be

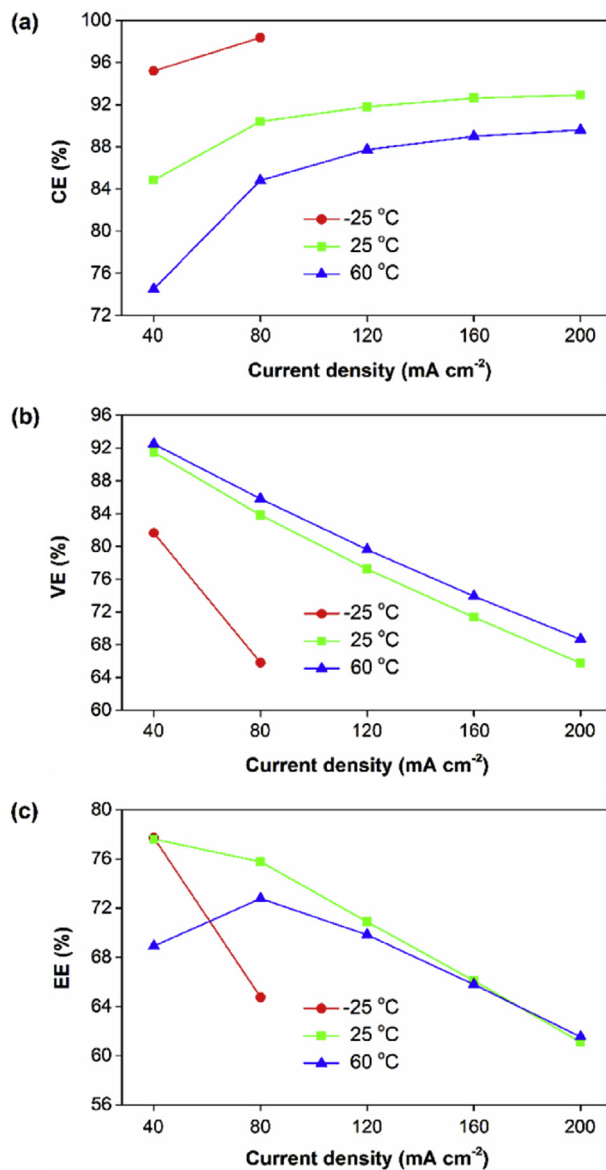


Fig. 6. Results of the cell performance tests. (a) CE, (b) VE, (c) EE of the VFB with selected electrolyte under various temperatures and current densities.

simultaneously stable is narrowed, but the energy density of VFBs can meet the requirement of application. We can also conclude from Fig. 5 that good high temperature stability can be achieved with high sulfuric acid concentration, while desirable low temperature stability requires low sulfuric acid concentration. Therefore, in order to obtain satisfied temperature range and energy density, the vanadium concentration and the sulfuric acid concentration should be deliberately combined [22]. According to practical situation, electrolytes with vanadium concentration of 1.4–1.6 M and sulfuric acid concentration of 2.0–2.5 M, is considered as the proper choices.

3.3. Cell performance of the VFB with selected electrolyte

Based on the conclusion at the end of Section 3.2, we select the vanadium electrolyte with the composition of 1.5 M vanadium and 2.0 M sulfuric acid for single cell evaluation. During the charge and discharge processes of VFBs, the acid concentrations of the positive

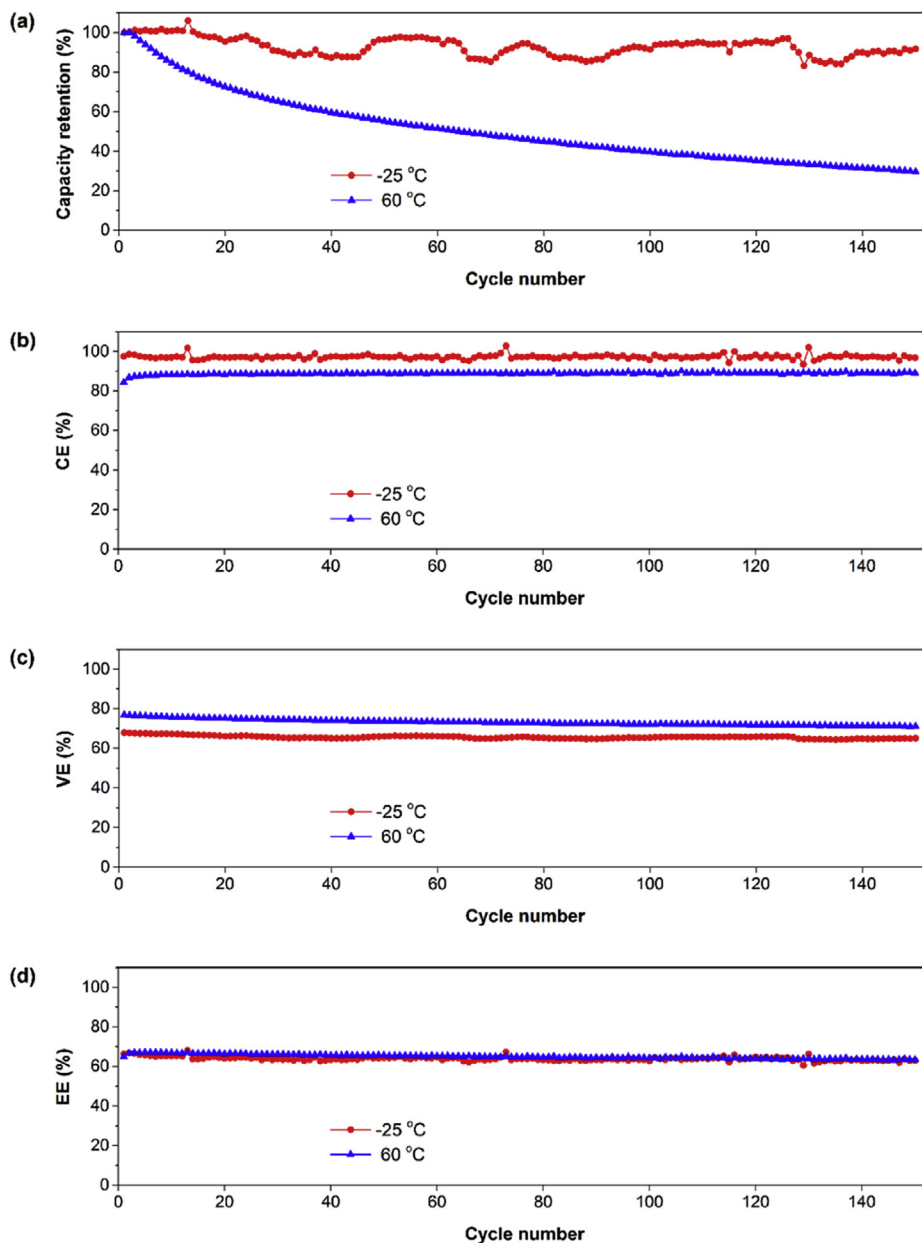


Fig. 7. Results of the cycling stability tests. (a) Capacity retention, (b) CE, (c) VE and (d) EE of the VFB with selected electrolyte at $-25\text{ }^{\circ}\text{C}$ under current density of 80 mA cm^{-2} and at $60\text{ }^{\circ}\text{C}$ under current density of 160 mA cm^{-2} .

and negative electrolytes change continually, which is shown in Fig. S1 in the Supporting Information. This is in accordance with the phenomenon in Section 2.1 that proton concentration of the electrolyte varies with vanadium valence during the electrolysis.

The static temperature range of the selected electrolyte is $-20\text{ }^{\circ}\text{C}$ to $25\text{ }^{\circ}\text{C}$ (in Fig. 5), and the temperature range in which VFBs with the selected electrolyte can operate was evaluated. At low temperatures, VFBs could operate normally at $-25\text{ }^{\circ}\text{C}$, but they could not carry out the charge-discharge cycles at $-30\text{ }^{\circ}\text{C}$. At high temperatures, VFBs could operate normally at $30\text{ }^{\circ}\text{C}$, $35\text{ }^{\circ}\text{C}$... $55\text{ }^{\circ}\text{C}$, $60\text{ }^{\circ}\text{C}$. Because the material of the electrolyte reservoirs (PMMA) is not stable at higher temperatures, the charge-discharge experiments at temperatures above $60\text{ }^{\circ}\text{C}$ were not carried out.

Therefore, cell efficiency tests of the VFB with the selected electrolyte (1.5 M vanadium and 2.0 M sulfuric acid) were conducted at $-25\text{ }^{\circ}\text{C}$, $25\text{ }^{\circ}\text{C}$ and $60\text{ }^{\circ}\text{C}$ under the current densities of

40 mA cm^{-2} , 80 mA cm^{-2} , 120 mA cm^{-2} , 160 mA cm^{-2} , 200 mA cm^{-2} . The results of the coulombic efficiency (CE), voltage efficiency (VE) and energy efficiency (EE) of the VFB are shown in Fig. 6. It is noteworthy that the VRB single cell can only operate under the current density of $40\text{--}80\text{ mA cm}^{-2}$ at the temperature as low as $-25\text{ }^{\circ}\text{C}$, which results from the large polarization resistance of VFBs at low temperatures. Fig. 6(a) shows that the CE decreases with the increasing of temperature at a fixed current density, which is due to the high permeability of vanadium ions across the membrane at high temperatures [47]. With the current density increasing from 40 mA cm^{-2} to 200 mA cm^{-2} , the CE keeps increasing because of a lower crossover of vanadium ions and capacity loss resulting from the decreasing charge-discharge time [44]. It can be seen from Fig. 6(b) that the VE increases with the increasing of temperature at a fixed current density, owing to the improvement in the conductivity of the electrolyte and reduction in

the ohmic resistance [44,48]. Fig. 6(c) indicates that the EE, which is the product of the CE and the VE, decreases with the increasing current density at $-25\text{ }^{\circ}\text{C}$ and $25\text{ }^{\circ}\text{C}$. However, the EE increases first and then decreases with the increasing current density at $60\text{ }^{\circ}\text{C}$.

In order to verify that the VFB with the selected electrolyte can operate steadily at high and low temperatures, cycling test were conducted at $-25\text{ }^{\circ}\text{C}$ under the current density of 80 mA cm^{-2} and at $60\text{ }^{\circ}\text{C}$ under the current density of 160 mA cm^{-2} . The results of the discharge capacity retention, CE, VE and EE of the VFB are shown in Fig. 7. Fig. 7(a) illustrates that the discharge capacity retention of the VFB at $-25\text{ }^{\circ}\text{C}$ under 80 mA cm^{-2} remain almost stable during 150 charge-discharge cycles, due to the low permeability of vanadium ions across the membrane at such a low temperature. The discharge capacity retention of the VFB at $60\text{ }^{\circ}\text{C}$ under 160 mA cm^{-2} decreases gradually during the cycling stability test, as a result of the high permeability of vanadium ions across the membrane at such a high temperature. Fig. 7(b)–(d) present the efficiencies of the VFB are almost changeless at both $-25\text{ }^{\circ}\text{C}$ and $60\text{ }^{\circ}\text{C}$.

In the static temperature stability test, the selected electrolyte (1.5 M vanadium and 2.0 M sulfuric acid) can be stable at the temperature range from $-20\text{ }^{\circ}\text{C}$ to $25\text{ }^{\circ}\text{C}$. While in an operating VFB, both the positive and the negative electrolytes cannot be fully charged to 100% SOC (pure VO_2^+ and pure V^{2+}). Especially as a result of the electrolyte imbalance (net transfer of vanadium ions from the negative to the positive electrolyte), the maximum SOC of the positive electrolyte keeps dropping during the cycling. Moreover, in the charge-discharge cycles of VFBs, the existence time of the electrolytes with high SOC are shorter than test time (seven days) in the static temperature stability test. Hence, the VFB single cells with the selected electrolyte can operate at a wider temperature range from $-25\text{ }^{\circ}\text{C}$ to $60\text{ }^{\circ}\text{C}$.

Much attempt has been made to study the performance of VFBs at different temperatures, such as M.R. Mohamed et al. ($15\text{--}35\text{ }^{\circ}\text{C}$) [45] and Zhao et al. ($15\text{--}55\text{ }^{\circ}\text{C}$) [48]. However, only a few researches on low temperature performance of VFBs were reported, including Skyllas-Kazacos et al. ($5\text{ }^{\circ}\text{C}$, 2 wt% ammonium phosphate additives) [32] and researchers from PNNL ($0\text{--}50\text{ }^{\circ}\text{C}$, sulfate-chloride mixed system; $5\text{--}50\text{ }^{\circ}\text{C}$, chloride supporting electrolyte) [12,19]. In this work, the VFBs without additives in the electrolytes can operate at such a wide temperature range (-25 to $60\text{ }^{\circ}\text{C}$), which has not been reported as far as we know. It is worthwhile to note that the discharge capacity retention of VFBs decreases rapidly at high temperatures. This capacity decay can be reduced by decreasing the electrolyte imbalance, with the methods such as electrolyte reflow [49], electrolyte mixing [50] and online electrolysis [51–54], etc.

4. Conclusions

In this work, the static temperature stability of the vanadium electrolytes with four valences (V^{2+} , V^{3+} , VO^{2+} and VO_2^+), different total vanadium concentrations ($0.4\text{--}2.2\text{ M}$) and various sulfuric acid concentrations ($1.5\text{--}3.0\text{ M}$) is studied over a wide temperature range (-35 to $60\text{ }^{\circ}\text{C}$) for seven days. The temperature ranges in which the V^{2+} , V^{3+} , VO^{2+} , VO_2^+ electrolytes can be stable independently and simultaneously with different total vanadium concentrations and sulfuric acid concentrations are obtained. The complex influences of total vanadium concentration and sulfuric acid concentration on the low and high temperature stability of the vanadium electrolytes are studied and analyzed. Moreover, the cell performance of the VFB with one selected electrolyte composition (1.5 M vanadium and 2.0 M sulfuric acid) was evaluated at different temperatures and different current densities. The results show that the VFB with the selected electrolyte can steadily operate for more than 150 cycles at $-25\text{ }^{\circ}\text{C}$ and $60\text{ }^{\circ}\text{C}$. This work systematically

investigates the effects of the total vanadium concentration and sulfuric acid concentration on the temperature adaptability of VFBs, and the resulting temperature ranges of electrolytes with different compositions and valences are important references for the VFB studies and applications. Also, the demonstrated wide operating temperature range (-25 to $60\text{ }^{\circ}\text{C}$) of VFBs without additives in the electrolytes has not been reported as far as we know. This wide operating temperature range makes VFBs suitable for application in most areas of the world.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.electacta.2017.10.148>.

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