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Effect of phosphoric acid additive on the electrolyte of all-vanadium flow batteries†

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A phosphoric acid additive with an optimal concentration of 0.1 M can vastly promote the diffusion kinetics of the redox reaction between V(IV) and V(V) without a significant decline in energy efficiency for 300 cycles, and maintain the high-temperature stability (55 °C) of an electrolyte at a high state of charge (SOC) of 70% over the course of 30 days.

For energy storage applications, the electrolyte is one of the most important components in vanadium flow batteries (VFBs).^{1–6} The concentration of vanadium and the amount of electrolyte determine the capacity of the battery, and the performance of the vanadium electrolyte has a direct impact on battery performance. The electrolyte currently used in vanadium battery systems is typically 1.5 to 2 M vanadium ions dissolved in a 4 to 5 M sulfuric acid solution. Elevating the concentration of vanadium ions can increase the energy density of VFBs, but the concentration is limited by the solubility of vanadium ions in a certain temperature range.^{7–9} Some studies have indicated that when the concentration of vanadium ions is higher than 2 M, the V(II), V(III), and V(IV) in the electrolyte will crystallize and precipitate below 10 °C, and the V(V) in the cathode electrolyte will turn into a thermal precipitate of V₂O₅ above 40 °C, which greatly limits the operating temperature of VFBs.^{10–12} In addition, the solubility of the V(II), V(III), and V(IV) in the electrolytes increases with increasing temperature, while the increase in sulfate ions accelerates their precipitation as sulfates at low temperatures. Conversely, the solubility of V(V) decreases with increasing

temperature and increases with increasing sulfate ions.^{13,14} With the commercialization of VFBs, the study of the stability of vanadium ions at different concentrations and temperatures is truly important and essential to achieve the efficient and stable operation of VFBs.

For the study of additives, they can be divided into two main categories, namely organic and inorganic additives. Organic additives, such as trihydroxymethyl aminomethane, sorbitol, phytic acid, *etc.*, are rich in –OH, =O, –NH₂, or –SH functional groups, which can be used as vanadium-ion stabilizers.^{9,15–17} However, most organic compounds can be slowly oxidized in strongly oxidizing pentavalent vanadium solutions. Inorganic additives mainly include amino compounds, phosphoric acid and its salts, polyphosphates, *etc.*^{7,18,19} Some researchers have also found that phosphate ions can form complexes with V(V) ions, thus limiting precipitation in the early state. In 1986, Gresser *et al.* provided insights into the binding reactions of V(V) and PO₄^{3–} ions.²⁰ More recently, Roznyatovskaya *et al.* also discussed the role of phosphate ions in stabilizing vanadium electrolytes,²¹ confirming using NMR that the formation of phosphate-complexed vanadium V(V) species delays the precipitation process. Therefore, phosphoric acid has been investigated for use as a thermal stabilizer and supporting electrolyte in VRB electrolytes.^{22,23} Inorganic substances have antioxidant properties towards pentavalent vanadium ions,^{24–26} so phosphoric acid is preferred for investigation.

Owing to a strong coordination ability, phosphate ions can generate soluble complexes with many metal ions. For example, Fe³⁺ and PO₄^{3–} can generate colorless soluble coordination compounds [Fe(PO₄)₂]^{3–} and [Fe(HPO₄)₂][–].^{27,28} Based on this property, PO₄^{3–} is commonly used in analytical chemistry to mask Fe³⁺ ions. Concentrated phosphoric acid can dissolve tungsten, zirconium, silicon, ferrosiliconized iron, *etc.*,^{29–32} and form stable coordination compounds. In this work, phosphoric acid was used as a vanadium electrolyte additive. The effects of ion concentrations, vanadium valence state, phosphate additive content, and temperature on the stability of the electrolyte were investigated. To improve the high-temperature stability of

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the cathode electrolyte at a high state of charge (SOC), the preferred concentration of phosphoric acid was 0.1 M, and the sulfate ion concentration was increased to 4.3–4.5 M. Moreover, the addition of 0.1 M H_3PO_4 could enhance the diffusion coefficients of V(IV) oxidation and V(V) reduction, and maintained an excellent cycle stability of VFBs over the course of 300 cycles.

Table S1 (ESI[†]) shows the effect of phosphoric acid concentration on the high-temperature stability performance of the cathode electrolyte, in which the vanadium ion concentration was 1.6 M, the sulfate ion concentration was 4.0 M, the charge state was 85%, and the temperature for the investigation was 50 °C. It can be seen that with a gradual increase in phosphoric acid concentration to 0.1 M, the time for the precipitation of pentavalent vanadium ions in the cathode electrolyte at 50 °C was prolonged from 1 day to 3 days (0.05 M phosphoric acid) and to 6 days (0.1 M phosphoric acid), indicating that the addition of phosphoric acid enhances the stability of pentavalent vanadium ions in high-temperature environments. The effect of phosphoric acid on the enhancement of the high-temperature stability of pentavalent vanadium ions is attributed to the coordination between VO_2^+ and the phosphate group, which was adsorbed on the surface of the precipitation nucleus and hindered the growth of the nucleus. With an increase in the concentration of phosphoric acid from 0.1 to 0.15 M, the stability of the electrolyte deteriorated, and the excess phosphoric acid generated VOPO_4 with pentavalent vanadium. Moreover, this has a low solubility under acidic conditions, and accelerated the precipitation of pentavalent vanadium ions. Therefore, the preferred concentration of phosphoric acid in the electrolyte is 0.1 M. Table S2 (ESI[†]) shows the effect of different vanadium ion concentrations on the high-temperature stability performance of the cathode electrolyte, in which the sulfate concentration was 4 M, the phosphoric acid concentration was 0.1 M, the charge state was 85%, and the examination temperature was 50 °C. It can be seen that the stability of the electrolyte gradually decreased as the vanadium ion concentration rose. Besides, the electrolyte was stable for >30 days at a total vanadium ion concentration of 1.2 M. As the vanadium ion concentration increased to 1.4, 1.6, and 1.7 M, the time for precipitation to occur in the electrolyte decreased to 17, 6, and 2 days, respectively.

Table S3 (ESI[†]) shows the effect of sulfate concentration, charge state, and temperature on the high-temperature stability performance of the positive-to-positive electrolyte, where the phosphoric acid concentration is 0.1 M and the vanadium ion concentration is 1.6 M. As shown in Table S3 (ESI[†]), the 1.6 M electrolyte has good stability at and below the temperature of 40 °C, where the electrolyte has been stored for more than 30 days. However, as the temperature increased, the stability of the electrolyte gradually deteriorates. When the battery is operated at 50–55 °C, it is extremely easy to produce a precipitate and clog the vanadium battery stack, piping system, etc., leading to the permanent failure of the battery. By increasing the concentration of sulfate ions, the high-temperature stability of the electrolyte can be effectively improved. With a gradual increase in the concentration of sulfate ions in the electrolyte, the stability of the electrolyte at 50 °C increases

from 6 days to 10 days and 15 days. Nevertheless, the effect of sulfate on the stability enhancement gradually diminishes at higher temperatures, and the appearance of precipitate in the electrolyte is only delayed from 2 days to 3 and 5 days at 55 °C. In order to avoid damage to the battery due to precipitation of the cathode electrolyte, the operating temperature of the battery must be strictly controlled. From the above high-temperature data, the operating temperature of the battery should be kept below 40 °C under the condition of 4.0 M sulfate. When the battery operates at higher ambient temperatures, or to reduce the energy loss due to heat exchange, it is necessary to appropriately increase the concentration of sulfate ions in the electrolyte to 4.25 or 4.5 M.

Since Al^{3+} is a common impurity in the electrolytes of VFBs, the effect of the phosphoric acid additive on the impurity Al^{3+} was further investigated. From the comparison of 0.1 M $\text{VOSO}_4 + 3 \text{ M H}_2\text{SO}_4$ and 0.1 M $\text{VOSO}_4 + 3 \text{ M H}_2\text{SO}_4 + 50 \text{ ppm Al}^{3+}$, it can be seen that the reversibility of the redox reaction of the anode is enhanced when increasing the content of Al^{3+} to 50 ppm, whereas the addition of 0.1 M H_3PO_4 leads to an increase in the redox peak current of the anode (Fig. 1a). From the comparison of 0.05 M $\text{V}_2(\text{SO}_4)_3 + 3 \text{ M H}_2\text{SO}_4$ and 0.05 M $\text{V}_2(\text{SO}_4)_3 + 3 \text{ M H}_2\text{SO}_4 + 50 \text{ ppm Al}^{3+}$, it can be seen that the increased Al^{3+} content of 50 ppm weakens the reversibility of the redox reaction at the anode electrode and decreases the peak current, while adding 0.1 M H_3PO_4 further causes the reversibility of the redox reaction at the cathode electrode to be weakened, and the peak current decreases (Fig. 1b). In addition, multi-sweep tests were used to characterize the ion diffusion kinetics of the redox reaction (Fig. S1 and S2, ESI[†]). As shown in Fig. 2, in the positive reaction, the addition of 50 ppm Al^{3+} increased both the oxidation slope of V(IV) and the reduction slope of V(V) without phosphoric acid, indicating that the vanadium ion mass transfer rate was increased. In the phosphoric-acid-containing electrolyte, for the positive electrode reaction, the addition of 50 ppm Al^{3+} decreases the oxidation slope of V(IV) and the reduction slope of V(V) , which indicates that the vanadium ion mass transfer rate is reduced, but the degree of reduction is not the same. For the anode electrolyte, the addition of 50 ppm Al^{3+} and 0.1 M phosphoric acid decreases the oxidation slope of V(II) and the reduction slope of V(III) , indicating that the vanadium ion mass transfer rate is reduced.

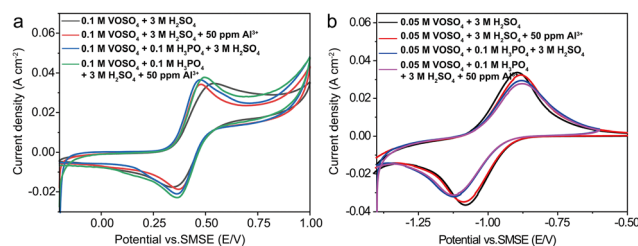


Fig. 1 Cyclic voltammetry (at a scan rate of 1 mV s^{-1}) for (a) $\text{VO}_2^+/\text{VO}_2^+$ with 0.1 M VOSO_4 and for (b) $\text{V}^{2+}/\text{V}^{3+}$ with 0.05 M $\text{V}_2(\text{SO}_4)_3$, in 3 M H_2SO_4 or 0.1 M H_3PO_4 and 3 M H_2SO_4 solutions with blank or addition of 50 ppm Al^{3+} .

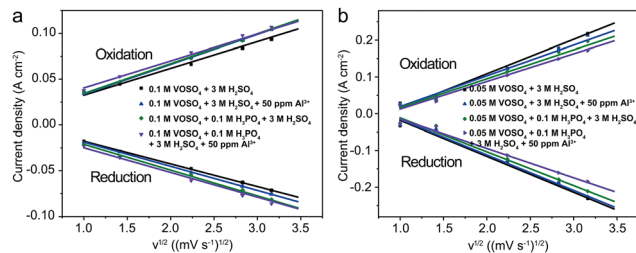


Fig. 2 Plots of the redox peak current density versus the square root of scan rate for (a) $\text{VO}_2^+/\text{VO}_2^+$ and (b) $\text{V}^{2+}/\text{V}^{3+}$.

To further analyse the effect of the phosphoric acid additive on the vanadium electrolyte, full batteries of VFBs were assembled to assess their electrochemical performance. As shown in Fig. 3, the efficiency of the VFBs remains stable as the cycles progress. Among these, the VFBs without phosphoric acid (1198) possess an average current efficiency, voltage efficiency, and energy efficiency of 99.1, 80.2, and 79.5%, respectively, with standard deviations of 0.58, 0.89, and 0.72, respectively. By contrast, the VFBs with phosphoric acid added (1199) exhibit an average current efficiency, voltage efficiency, and energy efficiency of 98.3, 79.8, and 78.4%, respectively, with standard deviations of 0.55, 0.82, and 0.65, respectively. The addition of phosphoric acid made the efficiency of the VFBs decrease slightly; the current efficiency, voltage efficiency and energy efficiency decreased by 0.8%, 0.49%, and 1.3%, respectively. Both blank and experimental stacks have efficiency standard deviations of less than 1, and the smaller fluctuation of the efficiency value indicated that the performance of the battery remained stable during the charging and discharging process. Furthermore, the discharge capacity of the stack with phosphoric acid added was lower than that of the blank stack (Fig. 4). Comparing the average discharge capacity of the first ten cycles, the discharge capacity of the blank stack is 16.07 A h, and that of the stack with phosphoric acid added is 15.11 A h, which suggests a lesser discrepancy. Thus, judging from the trend in the decay of the capacity and the number of cycles, the capacity when phosphoric acid is added has no effect on the cycling performance of the battery.

In order to examine the ion migration in the electrolyte in the stack with phosphoric acid added, the electrolyte was taken at the 20th, 50th, 100th, 150th, and 200th cycles for testing. As shown in Table 1, during long cycling, the concentration of

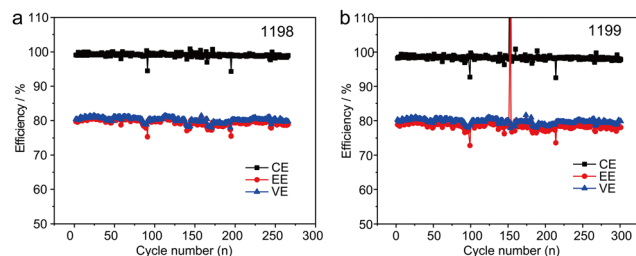


Fig. 3 Relationship between the efficiency and charge-discharge cycles of (a) the 1198 stack without 0.1 M phosphate and (b) the 1199 stack with 0.1 M phosphate and vanadium electrolyte.

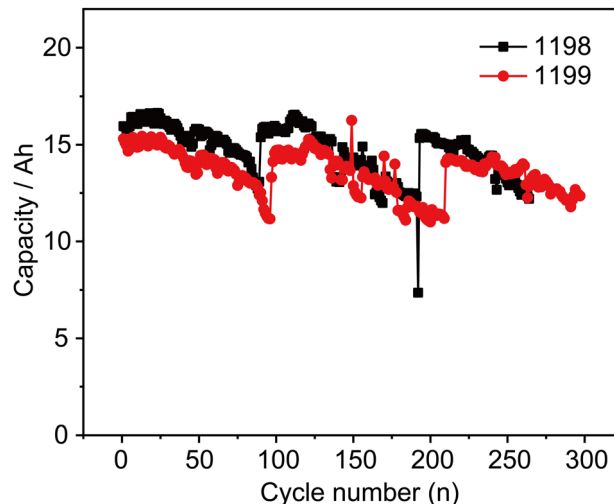


Fig. 4 Relationship between discharge capacity and number of cycles of the 1198 and 1199 stacks.

vanadium ions in the cathode electrolyte increased from the initial 1.6 M to 1.65 ± 0.02 M, and the concentration of vanadium ions in the positive electrolyte dropped to 1.55 ± 0.02 M. The anions in the electrolyte, such as sulfate and phosphoric acid, showed an opposite trend to vanadium ions. During long cycling, the sulfate ions in the positive electrolyte gradually decreased to 3.7 M, and those in the negative electrolyte increased to 4.3 M and then basically remained stable. After 150 cycles, phosphoric acid decreased to 0.065 M at the positive electrode and rose to 0.14 M at the negative electrode, reaching an equilibrium state. From the viewpoint of ion migration, the effect of ion migration on the stability of the electrolyte needs to be taken into account in the actual operation process. Although the addition of 0.1 M phosphoric acid will improve the stability of the electrolyte, with cycling, the concentration of phosphoric acid and sulfate will decrease, and the role of phosphoric acid in improving the stability of the electrolyte will be weakened. Finally, the concentration of vanadium ions in the positive electrode will gradually rise to a certain degree, which will also reduce the stability performance of the electrolyte.

In this paper, we have studied phosphoric acid as an additive of vanadium electrolyte. The phosphoric acid additive for vanadium electrolyte has broadened the range of high-temperature applications of vanadium electrolyte, with a preferred concentration for

Table 1 Effect of ion migration of the vanadium electrolyte on the high-temperature stability of the positive electrolyte

| Electrolyte | Precipitation time/Days | Electrolyte (phosphoric acid) | Precipitation time/Days |
|--------------|-------------------------|-------------------------------|-------------------------|
| 1.6-3.5-85% | 3 | 1.6-3.5-85%-0.1 | 5 |
| 1.6-3.5-80% | 3 | 1.6-3.5-80%-0.1 | 6 |
| 1.6-3.5-70% | 6 | 1.6-3.5-70%-0.1 | — |
| 1.6-3.5-60% | — | 1.6-3.5-60%-0.1 | — |
| 1.6-3.75-85% | 3 | 1.6-3.75-85%-0.1 | 5 |
| 1.6-3.75-80% | 3 | 1.6-3.75-80%-0.1 | 6 |
| 1.6-3.75-70% | 6 | 1.6-3.75-70%-0.1 | — |
| 1.6-3.75-60% | — | 1.6-3.75-60%-0.1 | — |

phosphoric acid of 0.1 M and for sulfate ions of 4.3–4.5 M. In addition, the addition of 0.1 M H₃PO₄ increases the diffusion kinetics of the redox reaction between V(IV) and V(V), and decreases the diffusion kinetics of the anodic reaction of V(II) oxidation and V(III) reduction, which causes a small decrease in energy efficiency and discharge capacity of vanadium batteries, but does not affect the cycling performance of VFBs.

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Conflicts of interest

The authors declare no conflict of interest.

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