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Insights into the synergistic effect of ammonium and phosphate-containing additives for a thermally stable vanadium redox flow battery electrolyte

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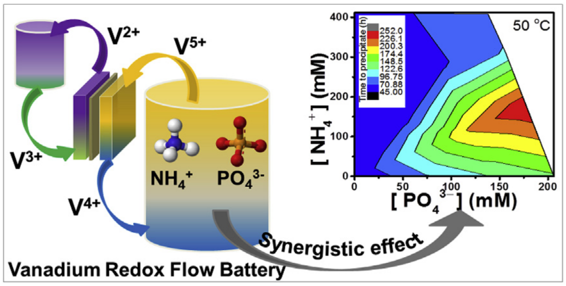
HIGHLIGHTS

- Phosphoric acid can give the formation of $VOPO_4$ in the positive vanadium electrolyte.
- $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$ have higher thermal stabilizing effectivity than H_3PO_4.
- Ammonium phosphates exhibit synergistic effect for V(V) electrolyte thermal stability.
- Ammonium ions can eliminate the formation of solid $VOPO_4$ as a bi-product.
- Adding a co-stabilizer can be a new approach in designing a new additive formula.

GRAPHICAL ABSTRACT



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ABSTRACT

In the field of large-scale electrochemical energy storage, the vanadium redox flow battery possesses many advantageous features. However, its performance is hampered by the low stability of the positive electrolyte at high temperatures, raising the necessity to use stabilizing agents. Phosphoric acid is commonly used to thermally stabilize the positive vanadium electrolyte, in place of effective hydrohalic acids additives, e.g. HCl, which have the risk of toxic halogen gas formation. However, the effectivity of phosphoric acid is restricted by its self-precipitation with V(V) ions in the sulfuric acid supported vanadium electrolyte to form $VOPO_4$. In this study, we explore the synergistic effect of ammonium and phosphate ions and show that ammonium ions can effectively prevent the formation of $VOPO_4$, hence leading to a significant improvement of the thermal stabilizing effectivity of ammonium phosphates over phosphoric acid. This study provides an insight into the thermal stabilizing effectivity of ammonium- and phosphate-containing additives for the positive vanadium electrolyte, which is useful for the understanding in the design of new additive formula.

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1. Introduction

The vanadium redox flow battery (VRFB) is an energy storage technology that possesses many advantages, especially at large scale, including the independence of power and energy capacity; simple structure of cell and stack design; quick response and long cycle life [1]. Such advantageous features make the VRFB well-suited to facilitate the continued integration of intermittent renewable energy sources.

The electroactive redox couples in the VRFB are V(II)/V(III) in the negative electrolyte and V(IV)/V(V) in the positive electrolyte. However, it is known that the positive vanadium species, particularly V (V), have a relatively low solubility in the H_2SO_4 supporting electrolyte [2,3]. With increasing state-of-charge (SOC) during the charging process, the ratio of V(V) to V(IV) in the positive electrolyte increases. The V(V) species in sulfuric acid exists prevailingly in the penta-coordinated hydrated form, as the $[VO_2(H_2O)_3]^+$ cation, at 25 °C. The precipitation reaction of V(V) ion occurs through a 2-step process, starting with the deprotonation of the penta-coordinated V(V) ion [3]:

Deprotonation: $2[VO_2(H_2O)_3]^+ - 2H^+ \leftrightarrow 2VO(OH)_3 + 2H_2O$

Condensation: $2VO(OH)_3 \leftrightarrow V_2O_5 + 3H_2O$

At this stage, the nano-sized V_2O_5 nuclei still can be re-dissolved, especially at lower SOC when the battery is discharged. However, if allowed to grow, these particles eventually form precipitates of V_2O_5, that do not readily re-dissolve. Currently, adding a thermally stability enhancing electrolyte additive is still the most effective method to allow a wider operating temperature window (e.g. $\geq$ 40 °C) for the VRFB. One method of action is that the additive forms a soluble complex with the penta-coordinated V(V) ion, inhibiting the deprotonation process and therefore restricting the precipitation at an early state. The most effective additive to date is hydrochloric acid, for which it has been suggested that soluble complexes such as $VO_2Cl(H_2O)_2$ are formed, hindering the deprotonation process [4–6]. However, chloride in the electrolyte gives rise to some safety issues: introducing the possibility of forming toxic chlorine gas under certain failure conditions (e.g. overcharging of cells); and 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. Alternatively, researchers have found that phosphate ions also can complex with V(V), resulting in the possibility to hinder the deprotonation process. The combination of V(V) and PO_4^{3-} ions has been intensively discussed by Gresser et al. in 1986 [7]. Recently, Roznyatovskaya et al. also have discussed about the role of phosphate ions in the stabilization of vanadium electrolyte as characterized by NMR, which also confirmed the formation of phosphate complexing V(V) species that postpones the precipitation process [8]. As of this result, phosphoric acid has been investigated as a thermal stabilizing agent as well as supporting electrolyte for the VRFB electrolyte [9–11]. However, the effectivity of phosphoric acid is restricted by the formation of $VOPO_4$ in the electrolyte solution [11,12]. This limits the maximum concentration of additive that can be practically employed. To overcome this obstacle, various alternatives of phosphoric acid have been investigated, including phosphate salts of alkali metals and ammonium [8,9,12–14], tripoly- and hexametaphosphates, pyrophosphate [15,16]. Among of them, ammonium phosphate compounds in general indicate the most effective thermal stabilizing capability for the positive vanadium electrolyte [8,9,13]. The separate addition of ammonium and phosphate-based compounds can obviously also provide the same function as ammonium phosphate as reported in the study of Kausar et al. [15]. The alkali phosphate salts can be used instead of phosphoric acid [15], but this will lead to the risk of $KVSO_4.3H_2O$ precipitate formation [12]. However, it should be noted that some other ammonium-based compounds, e.g. ammonium sulfate, also have been tested as a precipitate inhibitor for the vanadium electrolyte, but were found to have low effectivity [15,17]. Therefore, the high effectivity of ammonium phosphate compounds raises the question about its thermal stabilization mechanism. To date, except for phosphate ions, the role of ammonium ions for the thermal durability of the positive vanadium electrolyte is still unclear.

In this work, we examine the performance of different ammonium- and phosphate-based compounds to experimentally identify the role of NH_4^+ and PO_4^{3-} ions in the thermal stabilization of the positive vanadium electrolyte.

2. Experimental method

2.1. Positive electrolyte and additive preparation

The positive vanadium electrolyte was prepared by charging 1.6 M V(III/IV) in 4 M total SO_4^{2-} electrolyte (AMG Titanium Alloys & Coatings, Germany) using a 20 cm^2 single VRFB cell. The SOC was determined by measurement of the open circuit voltage (OCV) of the cell.

The additives were purchased and used as-received, including ammonium containing compounds: ammonium sulfate (ACS reagent, $\geq$ 99.0%), ammonium cerium sulfate dihydrate (Sigma-Aldrich); phosphoric acid ($\geq$85 wt.% in H_2O, $\geq$ 99.999% trace metals basis); and ammonium phosphate compounds: ammonium dihydrogen phosphate ($\geq$99.99% trace metals basis), ammonium hydrogen phosphate ($\geq$99.99% trace metals basis), ammonium phosphate (Reagent, Astral Scientific).

2.2. Thermal stability test

5 mL aliquots of positive vanadium electrolyte (90% SOC) were used for testing, with the addition of the given additives. All electrolyte samples were heated and kept at different constant temperatures (45, 50 °C). The samples were checked hourly to detect the precipitate by a physical method (see below the tested tube) when sufficiently large amounts had formed, and the time to onset of precipitation was noted. In order to gain accurate information regarding the onset time, the thermal stability test was repeated at least 3 times for each additive compound.

2.3. Precipitation analysis

A sample of 2 mL of the electrolyte solution (90% SOC) was heated at 50 °C, and the precipitate nuclei in the tested solution were analyzed by a transmission electron microscope (TEM JEOL 2010 HR) and a laser particle size analyzer (Fritsch, Analysette 22 Compact). To analyze the precipitation rate, the tested solution (2 mL, 90% SOC) was heated at 50 °C for 3, 5 and 7 days. The resulting V_2O_5 solid product after each heating period was collected by filtration and then dried in air at room temperature for 24 h.

To investigate the precipitate composition, the electrolyte samples (5 mL, 90% SOC) were also heated at 50 °C for 10 days and the precipitates collected by filtration and air-dried at 60 °C for over 24 h. X-ray diffraction (XRD) was conducted by a Shimadzu X-ray Diffractometer (Shimadzu XRD-6000, with the $\lambda_{Cu\text{-}K\alpha} = 0.15418$ nm). The morphology of the precipitate was observed by a field emission scanning electron microscopy (FESEM, JEOL 7600F). The elemental composition of the precipitates was characterized by microanalysis using an INCA EDS detector integrated with said FESEM equipment.

2.4. Oxidation state analysis

The effect of additives on the oxidation state of the positive vanadium electrolyte was investigated by the UV-Vis spectra, which were recorded by a Carry Series UV-Vis-NIR Spectrophotometer with a 10 mm path-length quartz cell using the protocol described in our previous study [18].