



# The oxidation of organic additives in the positive vanadium electrolyte and its effect on the performance of vanadium redox flow battery



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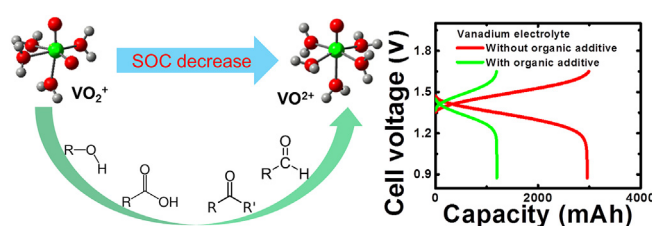
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## HIGHLIGHTS

- Organic additives containing polar functional groups could be oxidized by V(V).
- The SOC of vanadium electrolyte is reduced to different degrees by the additives.
- Some organic additives also affect the performance of a test cell.
- A standard screening method for thermally stable additives has been introduced.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Despite many desirable properties, the vanadium redox flow battery is limited, in the maximum operation temperature that can be continuously endured, before precipitation begins in the positive electrolyte. Many additives have been proposed to improve the thermal stability of the charged positive electrolyte. However, we have found that the apparent stability, revealed in laboratory testing, is often simply an artifact of the test method and arises from the oxidation of the additive, with corresponding partial reduction of V(V) to V(IV). This does not improve the stability of the electrolyte in an operating system. Here, we examined the oxidation of some typical organic additives with carboxyl, alcohol, and multi-functional groups, in sulfuric acid solutions containing V(V). The UV–vis measurements and titration results showed that many compounds reduced the state-of-charge (SOC) of vanadium electrolyte, for example, by 27.8, 88.5, and 81.9% with the addition of 1%wt of EDTA disodium salt, pyrogallol, and ascorbic acid, respectively. The cell cycling also indicated the effect of organic additives on the cell performance, with significant reduction in the usable charge capacity. In addition, a standard screening method for thermally stable additives was introduced, to quickly screen suitable additives for the positive vanadium electrolyte.

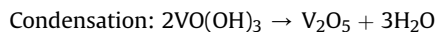
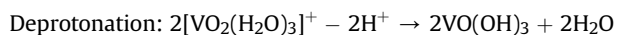
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## 1. Introduction

The large-scale implementation of renewable energy technologies, such as solar photovoltaic and wind energy, requires effective and stable electric energy storage systems, due to the intermittency of renewable energy. Among some potential candidates, the vanadium redox flow battery (VRFB) has become one of the most promising energy storage systems, thanks to several advantages: power and energy capacity can be independently designed; simple structure of cell and stack design; quick response and long cycle life [1]. Since the pioneering research of M. Skyllas-Kazacos's group in Australia [1], many efforts have been made to overcome the disadvantages of the VRFB. One of these drawbacks is that of the relatively low solubility of V(V) in sulfuric acid [2,3]. The positive electrolyte of the VRFB consists of a mixture of vanadium salts in oxidation states 4+ (IV) and 5+ (V), dissolved in sulfuric acid, with a total vanadium concentration of typically 1.5–2 mol dm<sup>-3</sup>. As the battery is charged, the ratio of V(V) to V(IV) increases. Therefore, the VRFB is generally operated with the positive electrolyte in a metastable state. Consequently, there exists the risk that V(V) ions may condense to form V<sub>2</sub>O<sub>5</sub> and subsequently precipitate, which is almost irreversible in charged electrolyte. In practice, the kinetics of precipitation are very strongly dependent on temperature and state-of-charge (SOC).

In sulfuric acid, at typical electrolyte concentrations, V(V) species exist predominantly in the form of the penta-coordinated [VO<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>]<sup>+</sup> cation, at 25 °C. At temperatures ≥40 °C precipitation occurs notably, e.g. via the deprotonation and condensation reactions, given below [3]:



By careful control of temperature and state-of-charge, VRFB manufacturers avoid precipitation. However, these measures add to the cost and can reduce performance. Therefore, much effort has been made to find electrolyte additives that would allow wider operational temperature windows.

Chemicals were proposed to be used as thermal stability additives for the positive vanadium electrolyte, based on two main criteria. Firstly, the ability to form soluble neutral species with penta-coordinated V(V) ion, which can prevent deprotonation [4]. Secondly, some organic additives can adsorb, via polar functional groups, such as OH, CHO, C=O, on the initial V<sub>2</sub>O<sub>5</sub> nuclei, hindering further growth and formation of particles large enough to precipitate [5,6]. In the past few years, many organic and inorganic additives have been investigated to improve the stability of the positive vanadium electrolyte at higher temperatures. Many of these organic additives contain one or more polar functional groups. It was reported that the addition of 0.5%wt of some acid compounds, such as methanesulfonic acid, trifluoroacetic acid, polyacrylic acid, oxalic acid, and methacrylic acid could improve the stability of 3 M V(V) in 5 M H<sub>2</sub>SO<sub>4</sub> electrolyte from -5 °C to 45 °C [7].

Research on 2 M V(V) in 3 M H<sub>2</sub>SO<sub>4</sub> electrolyte showed that the addition of 1%wt L-glutamate could delay the initiation of precipitation in the positive electrolyte for 12 h at 40 °C and for 5 h at 50 °C [5]. In another work, electrolyte stability tests at 45, 50, and 60 °C confirmed that the addition of 0.05–0.1%wt couler dispersant IIIA (mainly containing coconut oil amine adduct with 15 ethylene oxide groups) to the ~2 M V(V) in 5 M H<sub>2</sub>SO<sub>4</sub> electrolyte, could significantly delay the time of precipitate formation from 1.8–12.3 h–30.3 h–19.3 days [8]. Polyacrylic acid and its mixture with CH<sub>3</sub>SO<sub>3</sub>H were reported as promising stabilizing candidates

for vanadium positive electrolyte solution at temperatures higher than 40 °C [9]. The addition of 1–4%wt of trishydroxymethylaminomethane (Tris) was also demonstrated to improve the thermal stability of 2 M V(V) in 3 M H<sub>2</sub>SO<sub>4</sub> electrolyte at 40 °C [10]. Another study reported that fructose, mannitol, glucose, and D-sorbitol could be used as additives [11]. Inositol, phytic acid and sodium oxalate have been claimed to improve the thermal stability of 1.8 M V(V) in 3 M H<sub>2</sub>SO<sub>4</sub> electrolyte at up to 60 °C [6,12]. Several additives, although not tested for thermal stability, were proposed to improve the electrochemical properties of vanadium electrolyte [13]. Besides that, a wide range of organic compounds, proposed by M. Skyllas-Kazacos, have not been thoroughly investigated [1,14]. However, due to the strong oxidative property of V(V) ions, some organic chemicals, especially with the functional groups of OH, CHO, and C=O are known to be unstable in V(V) solutions [7,9]. Waters et al. published a comprehensive study on the oxidation of organic compounds by V(V) in a series of articles in the 1960's, which are especially relevant in light of the most recent VRFB developments [15–28].

It is known that V(V) ions can oxidize some organics in acidic solution and hence be reduced to V(IV), especially over the long testing times typically employed at 40–50 °C. However, the effect of organic additives on the positive vanadium electrolyte and especially on the performance of VRFB has not been widely reported. In practice, the rate of precipitation of V<sub>2</sub>O<sub>5</sub> is dependent on the SOC of the electrolyte (i.e. the relative concentration of V(V) to total vanadium). Therefore, it is clear that the apparent thermal stability improvement of an additive may be due to the reduction of V(V) to V(IV) in the test, rather than a genuine hindrance of the condensation and/or polymerization of V(V). To investigate this possibility, we examined the oxidation of some organic compounds in fully charged positive electrolyte. In this study, we classified the examined organic additives into three groups: carboxylic compounds (oxalic acid, sodium oxalate, potassium oxalate and EDTA disodium salt), alcohol compounds (pinacol, resorcinol, methyl resorcinol, xylose, glucose, poly-vinyl-alcohol (PVA) and pyrogallol), and multi-functional group compounds (containing more than 2 different functional groups) (lactic acid, citric acid, ammonium citrate, cysteine, tannic acid and ascorbic acid).

The change in the oxidation states of V(V), in the presence of organic additive, was quantified by UV–vis spectrometry and also by titration. The influence of organic additives on the performance of the VRFB, was studied by cycling a single cell with 20 cm<sup>2</sup> active area. In addition, due to the fact that there was no standard screening procedure for thermally stable additives for vanadium electrolyte, we also introduced a standard additive screening method which could be applied for any proposed additive compound.

## 2. Experimental method

### 2.1. Preparation of vanadium positive electrolyte and additives

The V(V) solution (100% SOC) was prepared by charging 1.6 M V(III/IV) in 4 M total SO<sub>4</sub><sup>2-</sup> electrolyte (AMG Titanium Alloys & Coatings, Germany) using a 20 cm<sup>2</sup> single VRFB cell. The SOC was determined by measurement of the open circuit voltage (OCV) of the cell.

Additives were purchased and divided into three groups: carboxyl compounds (containing only carboxylic group), alcohol compounds (containing only hydroxyl group) and multi-functional group compounds (containing more than 2 different functional groups). The list of the suppliers and grades of the additives are shown in following table:

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