Electrochimica Acta 164 (2015) 307–314

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

# Effects of phosphate additives on the stability of positive electrolytes for vanadium flow batteries

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ARTICLE INFO

*Article history:*
Received 16 October 2014
Received in revised form 17 December 2014
Accepted 22 February 2015
Available online 25 February 2015

*Keywords:*
Energy storage
Vanadium flow batteries
Precipitate
Phosphate additives
Capacity retention

ABSTRACT

A series of phosphates is investigated as additives to improve the stability of the electrolyte for vanadium flow battery (VFB). Two selected additives show positive effect on the stability of electrolytes under ex-situ stability tests and in situ flow cell experiments. The effects of additives on electrolyte are studied by Nuclear magnetic resonance (NMR), X-ray diffraction (XRD), Raman spectroscopy, Cyclic voltammetry (CV), Electrochemical impedance spectroscopy (EIS) and charge–discharge test. The results show that a VFB using the electrolyte with $NH_4H_2PO_4$additive demonstrates significantly improved redox reaction reversibility and activity, and higher energy efficiency. In addition, the cell employing the electrolyte with $NH_4H_2PO_4$ exhibits a charge capacity fading rate much slower than the cell without additives during the cycling at high temperature. These results indicate that the phosphate additives are highly beneficial to improving the stability and reliability of VFB.

## 1. Introduction

Large-scale energy storage has attracted increasing attention due to its urgent need in load leveling, uninterruptible power supply systems and renewable energy storage [1–3]. Vanadium flow batteries (VFBs) initiated by M. Skyllas-Kazacos from UNSW in 1980s [4], have been widely regarded as one of the most suitable options for large scale energy storage due to their significant advantages such as high energy efficiency (>75%), deep discharge ability, fast response, long cycle life and most importantly, independent power and energy ratings [5]. VFBs can realize a reversible conversion between electrical energy and chemical energy through the reactions of two redox couples of $V^{2+}/V^{3+}$in a negative half-cell and $VO^{2+}/VO_2^+$in a positive half-cell. By using the same element (vanadium) in both half-cell electrolytes, VFBs overcome the inherent issue of cross contamination caused by diffusion of different ions across the ion-exchange membrane [3].

In a VFB, the electrolyte serves not only as an ion conductor but also as an energy storage medium to store and release energy [6]. However, the poor stability of the electrolytes especially low solubility of vanadium based electrolytes has affected the final VFB performance [7]. The precipitate of the negative electrolytes at lower temperature and positive electrolytes at higher temperature, especially when the electrolytes' concentration exceeds 2 M, has limited the energy density of VFB ($\leq$25 Wh kg$^{-1}$), further increased the cost of the battery system [8,9]. Therefore the solubility and stability of electrolytes are of great significance in the development of VFB systems.

Specifically, the fully charged $V^{5+}$ electrolyte solution suffers from precipitation at elevated temperatures (>310 K). This poor stability is witnessed as the irreversible formation of hydrated $V_2O_5$ precipitates, which may cripple the pump circulation and lead to energy loss and the final failure of the battery [7,8,10].

In the past years, significant efforts have been devoted to improving the stability of the positive electrolyte, aiming at developing an electrolyte with high concentration and further improving the energy density for VFB systems [8,9,11]. The solubility of vanadium ions can be improved via the optimization of the supporting acid electrolyte. One of the effective methods was to enhance the solubility of the electrolyte. For example,

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http://dx.doi.org/10.1016/j.electacta.2015.02.187
0013-4686/

higher concentration of sulfuric acid in electrolytes can effectively stabilize V(V) ions [8]. However, increasing the $H_2SO_4$ concentration will accelerate the precipitation of V(II), V(III) and V(IV) ions due to the common ion effect [9,12]. Furthermore, a $H_2SO_4$ concentration of 3–4 M has been found to be more suitable, considering the cost and corrosive durability for materials. In addition, the employment of mixed acid as supporting electrolyte can considerably improve the thermal stability of V(V) ions [13,14]. The mixed acid-based vanadium flow battery has been recently reported and displayed enhanced energy efficiency and charge/discharge capacities due to a higher vanadium concentration with excellent thermal stability, however, it also requires a high concentration of the mixed acid, which may result in the increased risk of metal corrosion [15]. Another strategy to delay the precipitation of vanadium species is to add precipitation inhibitor [16], which is one of the most economic and effective methods to stabilize the vanadium electrolytes. Normally two types of additives, e.g., inorganic/organic can be used as stabilizer for VFB electrolytes [17–24].

Alcohols with ring or chain structures can increase the solubility of V(II)–V(V) ions in the solution, stabilize the electrolyte and reduce vanadium precipitates in the electrolyte [25]. However, these organic compounds suffer from low chemical stability in the strongly oxidative V(V) solution [19]. They could participate in the electrochemical reaction of the vanadium battery and subsequently result in capacity loss. Thus inorganic additives were widely investigated, e.g., phosphate based additive ($(NaPO_3)_6$, $Na_3PO_4$, $Na_4P_2O_7$) [16,17,19], sulfate based additives ($K_2SO_4$, $Na_2SO_4$, $Al_2(SO_4)_3$) [16,19,20], chloride based additives ($BiCl_3$, $CoCl_3$) [20] and metal ions ($Gr^{3+}$, $In^{3+}$) [26,27], et al.

Among the reported inorganic additives, phosphate based additives are a typical kind of efficient stabilizing agents due to the interaction between vanadate and pyrophosphate or phosphate, confirming the formation of the mixed anhydrides with vanadate analogous to pyrophosphate or triphosphate by vanadium NMR spectroscopy [28]. Skyllas-Kazacos proposed sodium hexametaphosphate ($(NaPO_3)_6$) containing six phosphate groups in a ring as precipitation inhibitors for supersaturated $VOSO_4$solutions, presumably by adsorbing on the surface of the nuclei and reducing the rate of crystal growth [16]. Zhang and co-workers also evaluated the influence of $Na_3PO_4$as stabilizing agents on both positive and negative electrolytes, indicating outstanding thermal stability but with deteriorated capacity retention through in situ flow cell test [19]. They deduced that phosphate and polyphosphate anions may have negative effects on the stability of vanadium solutions due to the formation of insoluble $VOPO_4$ with V(V) ions. Recently, Park employed sodium pyrophosphate tetrabasic ($Na_4P_2O_7$, SPT) in the positive electrolyte to improve long-term stability of a non-flow VFB single cell [17]. In spite of these reports, studies of stabilization mechanism are very limited and the systemically work on phosphate additives is not clear, leading to very few relevant strategies for improving the solubility and stability of electrolytes.

In this paper, we report our investigation of phosphate additives as an inorganic additive in positive electrolytes for VFBs and their effects on long-term stability and electrochemical performance in detail, including electrochemical properties and battery performance evaluation. We also provide an insight into the general and elementary stabilization mechanism of the phosphate additives.

## 2. Experimental

### 2.1. Electrolyte preparation and NMR study

The V(IV) electrolyte solutions were prepared by dissolving $VOSO_4 \cdot xH_2O$ in sulfuric acid solutions. The V(V) electrolyte solutions were prepared electrochemically by charging the V(IV) solutions in a flow cell. At the end of the electrolysis, the concentration of final solution was determined by using an Automatic Potentiometric Titration Instrument (Titrando 905, Metrohm, Switzerland). $^{51}V$ and $^{31}P$ NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer operating at 105.27 MHz and 162.01 MHz, respectively, equipped with a 5 mm broad band probe. The $^{51}V$ and $^{31}P$ chemical shifts were relative to $VOCl_3$ solutions and to 85% $H_3PO_4$, respectively. Spectral width of about 105.27 kHz and pulse width of 13 $\mu s$ have been used for $^{51}V$ NMR measurements. Spectral width of about 8.1 kHz and pulse width of 38 $\mu s$ have been used for $^{31}P$ NMR measurements. The free induction decay (FID) signals were exponentially line broadened (50 Hz for $^{51}V$ and 10 Hz for $^{31}P$) prior to Fourier transformation.

### 2.2. Thermal stability test

A certain amount of several phosphates with different structures (sodium or ammonium based normal salt, hydro phosphate, dihydric phosphate) were added into the electrolyte solutions before starting the stability tests. Each sample was sealed in a polypropylene tube and then immersed in a temperature-controlled liquid bath, using approximately 10 mL solution per sample. During the stability tests, the samples were kept static without any agitation and were monitored at regular intervals by naked eye for the formation of precipitation. After filtration and drying in air, the precipitation samples were completely dried in air at 520 °C for 24 h.

### 2.3. Crystal structures and morphology characterization of precipitation

In order to analyze the composition of the red precipitates extracted from the electrolytes, X-ray diffraction (XRD) was carried out to investigate the crystal structures of precipitates. The samples were analyzed and characterized by XRD using a X'Pert Prox (PANalytical) with Cu-K$\alpha$ radiation ($\lambda = 1.5406$ Å) in the 2$\theta$ range from 5° to 50°. A scanning electron microscope (SEM) (JEOL JCM-6000, Japan) was used to investigate the morphology of precipitates.

### 2.4. Raman spectroscopy

Raman spectroscopy experiments of vanadium species with and without additives were carried out on Renishaw inVia Raman Microscope. The samples were placed on a glass microscope slide, being both inert and weak Raman scatter, causing little or no interference to the Raman spectrum. One drop of sample can show reasonable Raman bands of the desired intensity. These vanadium samples were excited by using Renishawin Via Raman Microscope (514 nm, green) laser, which provides a strong monochromatic beam. Each experiment was repeated at least three times to ensure the reproducibility of the results.

### 2.5. Electrochemical measurements

#### 2.5.1. Cyclic voltammetry

Cyclic voltammetry (CV) measurements of V(V) solutions with and without the additive were carried out on CHI604E electrochemical workstation (Shanghai Chenhua Instrument, China) at a scan rate of 5 mV s$^{-1}$ in a potential range of 0.5~1.2 V at room temperature. The curves of current density versus potential were recorded in a three-electrode electrochemical cell with a graphite plate as a counter electrode, an aqueous saturated calomel electrode (SCE) as a reference electrode, and a freshly-polished graphite bar as a working electrode ($\Phi$8 mm).