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# The effect of phosphate additive on the positive electrolyte stability of vanadium redox flow battery<sup>\*</sup>

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## ABSTRACT

The electrolyte is one of the most important components of vanadium redox flow battery (VRFB), and its stability and solubility determines the energy density of a VRFB. The performance of current positive electrolyte is limited by the low stability of  $\text{VO}_2^+$  at a higher temperature. Phosphate is proved to be a very effective additive to improve the stability of  $\text{VO}_2^+$ . Even though, the stabilizing mechanism is still not clear, which hinders the further development of VRFBs. In this paper, to clarify the effect of phosphate additive on the positive electrolyte stability, the hydration structures of  $\text{VO}_2^+$  cations and the reaction mechanisms of precipitation with or without phosphate in the supporting electrolyte of  $\text{H}_2\text{SO}_4$  solutions were investigated in detail based on calculations of electronic structure. The stable configurations of complexes were optimized at the B3LYP/6-311 + G(d,p) level of theory. The zero-point energies and Gibbs free energies for these complexes were further evaluated at the B3LYP/aug-cc-pVTZ level of theory. It shows that a structure of  $[\text{VO}_2(\text{H}_2\text{O})_2]^+$  surrounded by water molecules in  $\text{H}_2\text{SO}_4$  solution can be formed at the room temperature. With the temperature rises,  $[\text{VO}_2(\text{H}_2\text{O})_2]^+$  will lose a proton and form the intermediate of  $\text{VO}(\text{OH})_3$ , and the further dehydration among  $\text{VO}(\text{OH})_3$  molecules will create the precipitate of  $\text{V}_2\text{O}_5$ . When  $\text{H}_3\text{PO}_4$  was added into electrolytes, the V-O-P bond-containing neutral compound could be formed through interaction between  $\text{VO}(\text{OH})_3$  and  $\text{H}_3\text{PO}_4$ , and the activation energy of forming the V-O-P bond-containing neutral compound is about 7 kcal mol<sup>-1</sup> lower than that of the  $\text{VO}(\text{OH})_3$  dehydration, which could avoid the precipitation of  $\text{V}_2\text{O}_5$  and improve the electrolyte stability.

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## 1. Introduction

Renewable energy resources, such as solar energy and wind energy, become more and more important due to the critical issues of fossil fuel shortage and air pollution [1]. Meanwhile, the development of large-scale energy storage device is essential for the development and utilization of renewable energy resources due to their intermittent nature. Flow batteries, especially the Vanadium Redox Flow Battery (VRFB), are well suitable for large-scale energy storage, due to the high safety, high energy efficiency, long cycle life, and low environmental impact [2,3].

The electrolytes of VRFB act as the medium to store and release energy, whereas, the volume and the concentration of electrolyte determine the energy of a battery. Therefore, the stability and solubility of electrolytes exert significant influence on the cycle life and energy density of a battery. In a VRFB,  $\text{V}^{2+}/\text{V}^{3+}$  redox

couple in the supporting electrolyte serves as the negative electrolyte, while  $\text{VO}^{2+}/\text{VO}_2^+$  redox couple serves as the positive electrolyte. Currently, the stability of the electrolytes is poor because the  $\text{VO}_2^+$  in the positive electrolyte will precipitate at high temperature to form hydrated  $\text{V}_2\text{O}_5$ . The precipitates could attach to the carbon chain and reduce the charging and discharging efficiency of the battery, even destroy the cycle life of the battery [4–6]. Therefore, tremendous efforts for experimental investigation have been devoted to improve the stability of the positive electrolyte in the past years [6–12]. Park and his co-workers [10] proposed that sodium pyrophosphate tetrabasic (SPT) could be an effective additive for the positive electrolyte of VRFBs under limited laboratory short-term and small-scale conditions. A recent report of Ding [11] showed that a VRFB using the electrolyte with  $\text{NH}_4\text{H}_2\text{PO}_4$  additive can significantly improve the reversibility and activity of redox reactions.

At the same time, many vanadium complexes have been studied by theoretical investigations. Vijayakumar [13] and co-workers confirmed the hydration structure of  $[\text{VO}(\text{H}_2\text{O})_4]^{2+}$  by density functional theory and nuclear magnetic resonance spectroscopy. Sephehr [14] reported the hydration structures of all four vanadium cations

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**Table 1.** Bond lengths (Å), relative energies  $\Delta E$  (kcal mol<sup>-1</sup>), relative standard Gibbs free energies  $\Delta G^0$  (kcal mol<sup>-1</sup>), and estimated abundances of six hydration species of VO<sub>2</sub><sup>+</sup> obtained at the B3LYP/aug-cc-pVTZ level with the SMD model.

Species	V...O(H <sub>2</sub> O) <sup>a</sup>	V-O <sup>b</sup>	$\Delta E^c$	$\Delta E_{ZPE}^d$	$\Delta G^0_{298.15\text{ K}}$	$x^e, \%(298.15\text{ K})$
R <sub>1</sub>	2.02	1.60	0.00	0.00	0.00	78.99
R <sub>2</sub>	2.05	1.60	2.84	2.22	1.66	4.80
R <sub>3</sub>	2.04	1.60	1.42	1.11	0.94	16.21
R <sub>4</sub>	2.10	1.60	-2.94	1.88	13.20	0.00
R <sub>5</sub>	2.11	1.61	-10.69	-5.56	12.98	0.00
R <sub>6</sub>	2.22	1.61	-1.98	2.40	19.92	0.00

<sup>a</sup> Average bond length between oxygen atom of water and vanadium.

<sup>b</sup> Average V-O bond length.

<sup>c</sup> Binding energy based on uncorrected total electronic energies relative to R<sub>1</sub>.

<sup>d</sup> Binding energy based on ZPE corrected total electronic energies relative to R<sub>1</sub>.

<sup>e</sup> Calculated from  $\Delta G^0$  according to the Boltzmann law at 298.15 K.

at B3LYP/6-31+G(d,p) level of theory. However, all the studies are still in the structures of hydrated vanadium ions [15,16], and the investigations on the reaction mechanism and the stability of the electrolyte in the VRFB have been rarely reported.

In this paper, the hydration structures of VO<sub>2</sub><sup>+</sup>, the reaction mechanism of precipitation in positive electrolytes, the effect of phosphate additives on electrolyte stability were clarified by *ab initio* calculations.

## 2. Methodology

The calculations of electronic structures were carried out using the GAUSSIAN 09 suite of programs [17]. A universal solvation model - SMD model [18] was subsequently implemented in GAUSSIAN 09 to optimize all the structures in the solvent of water. Geometries were optimized using the density functional theory (DFT) with Becke's 3-parameter hybrid functional (B3LYP) [19] and the 6-311+G(d,p) split valence basis set [3]. To obtain more accurate results, Gibbs free energies and frequencies of these complexes were further calculated with correlation-consistent triple- $\zeta$  (cc-pVTZ) basis set [20]. Intrinsic Reaction Coordinate (IRC) was calculated with 6-311+G(d,p) split valence basis set to verify the correlation between corresponding transition states, reactants, and products [21].

## 3. Result and discussion

### 3.1. VO<sub>2</sub><sup>+</sup> in sulfate solution

It is known that VO<sub>2</sub><sup>+</sup> mainly exists as hydration structure in sulfate solution of the positive electrolyte [22]. Previous studies of Sepehr et al. [14] showed that the trigonal bipyramidal structure of VO<sub>2</sub><sup>+</sup> hydrated with three water molecules inside one hydration shell and one water molecule outside the shell was the most stable structure in solvation, because of the lowest energy. In this work, the hydrated molecules of VO<sub>2</sub><sup>+</sup> with octahedral, trigonal bipyramidal, tetrahedral structures at 298.15 K are reported. All the relevant structures are presented as Reactants (R) with numerical labels in Fig. 1. In Fig. 1, R<sub>1</sub> to R<sub>3</sub> indicate the cases that the VO<sub>2</sub><sup>+</sup> cations are hydrated with two water molecules, forming the tetrahedral structure. In the gas phase, the optimized structures show that R<sub>1</sub> and R<sub>2</sub> have C<sub>2v</sub> and C<sub>s</sub> point group symmetries. However, the liquid phase structures are slightly distorted and do not possess point group symmetries any more. Similarly, the trigonal bipyramidal structure R<sub>4</sub> has C<sub>s</sub> point group in the gas phase and distorted in the liquid phase. For the tetra-hydrated VO<sub>2</sub><sup>+</sup> complexes obtained by Sepehr [14], the two possible structures R<sub>5</sub> and R<sub>6</sub> are also shown in Fig. 1. R<sub>5</sub> has three water molecules inside one hydration shell and one water molecule outside the shell, which forms a trigonal bipyramidal structure. R<sub>6</sub> has four water

molecules inside the first hydration shell, which forms an octahedral structure.

In order to verify the main species of VO<sub>2</sub><sup>+</sup> hydration structure in sulfate solution, Table 1 summarizes the results of the binding energies relative to R<sub>1</sub>, which are computed in the liquid phase using the aug-cc-pVTZ basis set at 298.15 K. Taking into account the zero-point energy corrections, the binding energy of bipyramidal (R<sub>5</sub>) is the lowest, which is in consistent with the conclusion of Sepehr [14]. While the Gibbs free energy is usually affected by entropy, it is more reliable than binding energy for a chemical reaction. Although the free energy of R<sub>5</sub> is lower than that of the octahedral structure (R<sub>6</sub>) in the solvation at 298.15 K, it is much higher than that of the tetrahedral structure. It can be found from Table 1 that the Gibbs free energy of R<sub>1</sub> in the solvation at 298.15 K is the lowest, indicating that R<sub>1</sub> is the main species of VO<sub>2</sub><sup>+</sup> hydration structures. According to the Boltzmann law, the abundance of R<sub>1</sub> is estimated to be about 79%, much larger than that of R<sub>2</sub> and R<sub>3</sub>. While the percentages of the octahedral and trigonal bipyramidal structures in solvation are too small to be ignored.

### 3.2. Reaction mechanism

Since VO<sub>2</sub><sup>+</sup> mainly exists in sulfate solution as R<sub>1</sub> structure, we will focus on the performance of R<sub>1</sub> to study the features of VRFBs. As reported in Sadoc's work [23], two hydroxyl groups are formed from protonation of an oxo ligand and deprotonation of a water ligand, subsequently to [VO(OH)<sub>2</sub>(H<sub>2</sub>O)]<sup>+</sup>.

Fig. 2 illustrates the path of the proton transfer, includes the corresponding geometries of stationary points. Activation energy is one of the key evidences of deciding the real reaction path. It is shown that the barrier of transition state (TS2) is 19.48 kcal mol<sup>-1</sup> lower than that of TS1, which means that TS2 is the dominant path in this process. In other words, the water molecule possibly acts as the carrier of protons in proton transfer reaction, and the spontaneous process occurs to the direction of the Gibbs free energy releasing path. We could further confirm that the [VO<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup> will change to [VO(OH)<sub>2</sub>(H<sub>2</sub>O)]<sup>+</sup>, and a free energy of 3.16 kcal mol<sup>-1</sup> will be released in this process.

For convenience, in the following discussion, we use [VO(OH)<sub>2</sub>(H<sub>2</sub>O)]<sup>+</sup> as R for the reactant. Vijayakumar et al. [16] pointed out that VO(OH)<sub>3</sub> molecules could facilitate the precipitation via a dehydration reaction. In this paper, we will mainly discuss the process of R losing a proton to form VO(OH)<sub>3</sub> and further losing a water molecule to form the insoluble complex. We designed both concerted and stepwise reaction mechanisms but only the concerted reaction mechanism was located.

Fig. 3 summarizes the concerted reaction mechanism of the dehydrated process in the sulfuric acid electrolyte. Hydrogen proton in reactant R is firstly captured by water molecule and the intermediate of VO(OH)<sub>3</sub> (M) is formed immediately. Then, two VO(OH)<sub>3</sub> molecules form a V-O-V bond-containing product (P1)

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