



Short communication

## Towards understanding the poor thermal stability of $V^{5+}$ electrolyte solution in Vanadium Redox Flow Batteries

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## ABSTRACT

The  $V^{5+}$  electrolyte solution from Vanadium Redox Flow Batteries was studied by variable temperature  $^{17}\text{O}$  and  $^{51}\text{V}$  Nuclear Magnetic Resonance (NMR) spectroscopy and density functional theory (DFT) based computational modeling. It was found that the  $V^{5+}$  species exist as hydrated penta co-ordinated vanadate ion, i.e.  $[\text{VO}_2(\text{H}_2\text{O})_3]^{1+}$ . This hydrated structure is not stable at elevated temperature and change into neutral  $\text{H}_3\text{VO}_4$  molecule via a deprotonation process and subsequently leading to the observed  $\text{V}_2\text{O}_5$  precipitation in  $V^{5+}$  electrolyte solutions.

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### 1. Introduction

Recently, Vanadium Redox Flow Batteries (VRFB) have shown great promise as an efficient large scale energy storage system for a wide range of applications including uninterruptible power supply, stabilization of wind turbine output, and hybrid photo-voltaic cells [1–4]. Unlike other popular electrochemical energy storage systems (such as lithium ion batteries), VRFB store energy in electrolyte solutions rather than in electrodes. This setup could result in a considerable increase in life time due to low self discharge of the battery provided that the charged electrolyte solutions can be kept in stable conditions. In reality, the fully charged  $V^{5+}$  electrolyte solution displays poor stability at elevated temperatures (>310 K) and also at high vanadium concentrations (>2 M) [5–7]. This poor stability is witnessed as hydrated  $\text{V}_2\text{O}_5$  precipitation, which leads to energy loss and failure of the battery [8,9]. The incapacity to increase the vanadium concentration (>2 M) in the electrolyte solution without increasing the sulfuric acid concentration (>5 M) puts a limit on the maximum energy density of the VRFB ( $\leq 25 \text{ Wh kg}^{-1}$ ). Up to now, the chemistry behind the precipitation behavior of  $V^{5+}$  electrolyte solution is not

well understood. Understanding the chemistry behind this precipitation behavior is imperative for developing a stabilizer or even a new stable  $V^{5+}$  electrolyte solution, which can ultimately increase the life cycle, energy density and reduce the operating cost of the VRFB. In this work, a combination of Nuclear Magnetic Resonance (NMR) and density functional theoretical (DFT) studies was carried out to provide a clear view about structure of  $V^{5+}$  species and their precipitation behavior at elevated temperatures.

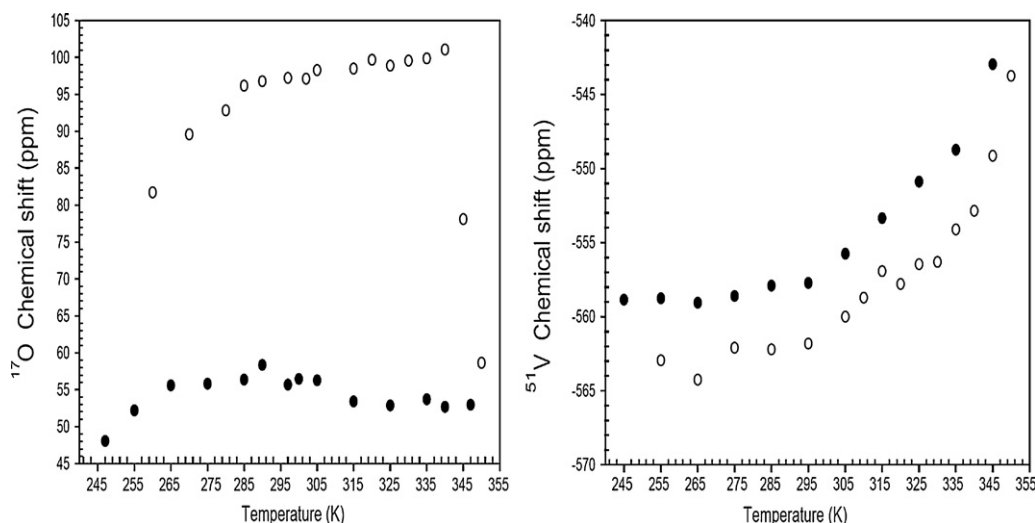
### 2. Experimental

The  $V^{5+}$  electrolyte solution is prepared by electrochemically charging the electrolyte stock solution (2 M  $\text{VOSO}_4 \cdot x\text{H}_2\text{O}$  dissolved in 5 M sulfuric acid) using a flow test cell with the current density of 1 A and voltage of 1.7 V. The 5 ml of  $V^{5+}$  electrolyte solutions is taken from the positive half cell after 12 cycles in which 10  $\mu\text{l}$  of commercial  $\text{H}_2^{17}\text{O}$  solution (20% enrichment) was added for  $^{17}\text{O}$  NMR measurements. The variable temperature  $^{17}\text{O}$  and  $^{51}\text{V}$  NMR measurements were performed using a Varian 500 Inova spectrometer ( $B_0 = 11.1 \text{ T}$  and  $^{17}\text{O}$  and  $^{51}\text{V}$  Larmor frequencies are 67.8 and 130.7 MHz, respectively) and their chemical shifts were externally referenced to a commercial  $\text{H}_2^{17}\text{O}$  and clear  $\text{VOCl}_3$  solutions, respectively. DFT calculations were carried out using the ADF 2009.01 program [10]. The hybrid B3LYP function with QZ4P (quad Z, 4 polarization functions, all electron) basis set with the zeroth order regular approximation (ZORA) is used for both geometry optimization and NMR calculation. All the DFT calculations reported

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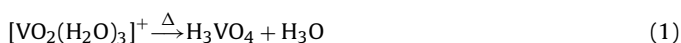
**Fig. 1.** Variable temperature chemical shift analysis of  $^{17}\text{O}$  NMR spectra (left) and  $^{51}\text{V}$  NMR spectra (right) of 2 M  $\text{V}^{5+}$  electrolyte solution measured at a magnetic field of 11.7 T. The open circles and the closed circles in the chemical shift analysis represent heating cycle and subsequent cooling cycle, respectively. The error in chemical shift measurements is  $\pm 0.5$  ppm.

here are carried out under *conductor-like screening model* (COSMO) with water as solvent [10].

### 3. Results and discussions

Fig. 1 shows the temperature dependent isotropic chemical shift of  $^{17}\text{O}$  and  $^{51}\text{V}$  NMR spectra measured on freshly prepared 2 M  $\text{V}^{5+}$  electrolyte solution. The chemical shift of both  $^{17}\text{O}$  and  $^{51}\text{V}$  NMR shows an irreversible change around 335 K, which indicates a thermally induced irreversible structural transition of the vanadium species in the  $\text{V}^{5+}$  electrolyte solution. This structural transition due to heat treatment is evidenced by visible yellowish red particles in the electrolyte solution few hours after the NMR measurements and the precipitated particles are known to be hydrated  $\text{V}_2\text{O}_5$  [11]. To understand the pathway of  $\text{V}_2\text{O}_5$  precipitation, the structures of the vanadium species before and after the structural transition must be identified. It is widely believed that oxovanadium ( $\text{VO}_2^+$ ) cation is the major species in highly acidic solutions ( $\text{pH} < 2$ ) such as our VRFB electrolytes [12,13]. This  $\text{VO}_2^+$  species reportedly exists in its hydrated form with a six-coordinated octahedral structure in which two oxygen atoms are coordinated in *cis*-configuration along with four complexed water molecules (i.e.  $[\text{VO}_2(\text{H}_2\text{O})_4]^+$ ) [14]. However, our DFT based geometry optimization revealed that this octahedral vanadate ion structure is not energetically favorable and a slightly more stable structure is formed by repelling a water molecule located at *trans* position to the vanadyl oxygen.

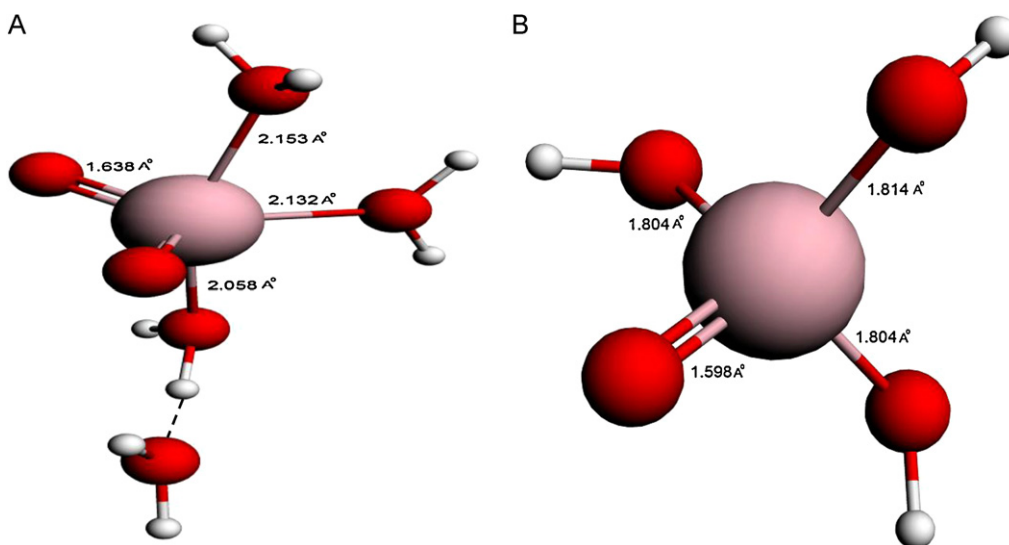
This turns the structure into a penta co-ordinated  $[\text{VO}_2(\text{H}_2\text{O})_3]^+$  molecule (hereafter called compound **A**) as shown in Fig. 2, which is in good agreement with results of Bühl and Parrinello [15]. Hence, compound **A** is the plausible initial structure in the  $\text{V}^{5+}$  electrolyte solution before the thermally induced structural transition. Since the structural transition is followed by  $\text{V}_2\text{O}_5$  precipitation, the most probable way this process can occur is by condensation of mononuclear vanadium species containing hydroxyl groups [16]. Therefore the new vanadium species formed at high temperature ( $>335$  K) most likely contain some hydroxyl groups in its structure. The possible scenario to form any such hydroxyl group is by deprotonation of water molecules complexed in the initial compound **A** which could lead to a neutral species  $\text{H}_3\text{VO}_4$  (hereafter called compound **B**) as shown below:



It is known that such deprotonation can happen if there is a change in pH and/or a change in the temperature of the vanadium solutions. This neutral molecule  $\text{H}_3\text{VO}_4$  (or more precisely  $\text{VO}(\text{OH})_3$ ) is well known to exist at room temperature and at low pH ( $\sim 3.5$ ) [14,17]. Recently, Sadoc et al. [18] reported that the hydrated  $\text{VO}_2^+$  molecule is prone to deprotonation at high temperatures (500 K), resulting in the formation of  $\text{VO}(\text{OH})_2(\text{H}_2\text{O})_2^+$  and subsequently the neutral  $\text{H}_3\text{VO}_4$ . The optimized structure of neutral compound **B** using ADF is shown in Fig. 2. We hypothesize that deprotonation in highly acidic medium ( $< 1$  pH), such as our  $\text{V}^{5+}$  electrolyte solution, is possible.

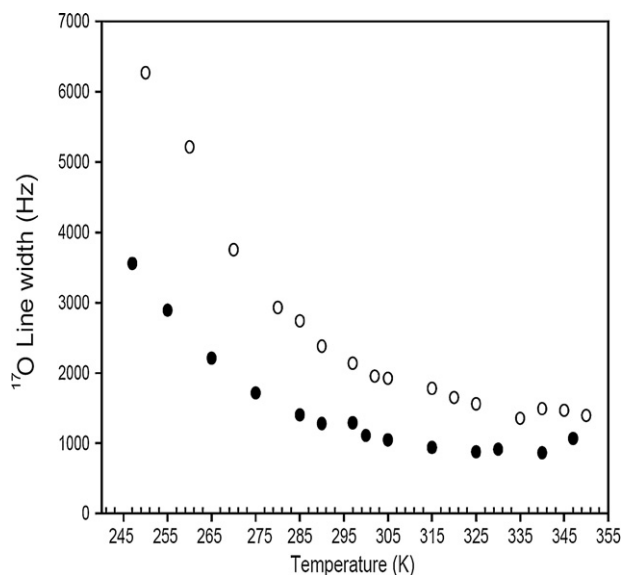
To confirm our hypothesis, we calculated the chemical reaction energy ( $\Delta E = E_{\text{A}} - E_{\text{B}} - E_{\text{H}_3\text{O}^+}$ ) of proposed deprotonation reaction (Eq. (1)) using total energy of DFT optimized compounds **A** ( $E_{\text{A}}$ ) and **B** ( $E_{\text{B}}$ ). The calculated  $\Delta E$  of Eq. (1) shows it as an endothermic reaction ( $\Delta E \sim 1.2$  eV). This means, the proposed structural transition and subsequent precipitation need thermal energy which agrees well with the reported poor stability of  $\text{V}^{5+}$  of electrolyte solution at high temperatures [5–7]. Since this deprotonation reaction is endothermic, it is more likely to be a reversible reaction such that the resultant compound **B** can be reversed to compound **A** by simple protonation at any given temperature. The isotropic chemical shift ( $\delta$ ) parameters for the isolated compounds **A** and **B** were calculated using ADF program and compared with experimental NMR chemical shifts. It should be noted that experimental NMR chemical shifts observed during cooling cycle represents the averaged state of both compounds **A** and **B**. Hence more attention should be paid to the trends in the DFT calculated  $\delta$  values between the compounds rather than to their actual values [15]. The DFT computed  $^{51}\text{V}$  chemical shifts for compound **A** ( $\delta \sim -623$  ppm) and compound **B** ( $\delta \sim -577$  ppm) show that any transition from compounds **A** to **B** should induce a shift towards higher frequency (i.e. nuclear deshielding) in the  $^{51}\text{V}$  NMR spectra, which is in good agreement with our experimental data (see Fig. 1). Similarly, the computed  $^{17}\text{O}$  chemical shift for water molecules in compound **A** ( $\delta = -23$  ppm) and hydroxyl groups in compound **B** ( $\delta = -410$  ppm) reveals that transition between compounds **A** and **B** would lead to significant  $^{17}\text{O}$  chemical shift towards lower frequency (i.e. increase in nuclear shielding), which also coincides with our experimental data.

The structural transition in Eq. (1) is mainly driven by proton migration between the water and hydroxyl molecules in compounds **A** and **B**. Such a proton migration in the solution is bound to directly influence the  $^{17}\text{O}$  NMR line width [19,20]. Fig. 3



**Fig. 2.** Geometry-optimized structures for  $[\text{VO}_2(\text{H}_2\text{O})_3]^+ \cdot \text{H}_2\text{O}$  (compound **A**) and the neutral  $\text{VO}(\text{OH})_3$  (compound **B**). The vanadium, oxygen and proton atoms are represented as pink, red and white spheres, respectively. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)

shows  $^{17}\text{O}$  line width during heating cycle (only compound **A**) and cooling cycle (representing both compounds **A** and **B**). The relatively smaller line width during cooling cycle indicates the possible faster proton exchange in solution and if this fast proton exchange happens directly between hydroxyl groups of two compound **B** molecules, it will facilitate the condensation followed by a hydrolysis reaction ( $2\text{H}_3\text{VO}_4 \rightarrow \text{V}_2\text{O}_5 + 3\text{H}_2\text{O}$ ) [16]. Such a hydrolysis reaction can lead to the formation of V–O–V bonding groups known as structural building mosaics of the solid  $\text{V}_2\text{O}_5$  which would ultimately lead to the crystallization of  $\text{V}_2\text{O}_5$  [16]. Further, it is interesting to note that the  $^{17}\text{O}$  NMR spectra shows relatively larger line width at low temperatures ( $<0^\circ\text{C}$ ) which indicates slower proton exchange rates in the solution at this low temperature region. This observed slow proton exchange proves that there is no significant protonation/deprotonation reaction at low temperatures and explains the relatively better stability of  $\text{V}^{5+}$  electrolyte solutions at low temperatures.



**Fig. 3.** Variable temperature  $^{17}\text{O}$  NMR line width analysis of 2 M  $\text{V}^{5+}$  electrolyte solution measured at 11.7 T. The open circle and the closed circle represent heating cycles and the subsequent cooling cycles, respectively. The error in line width measurements is  $\pm 100$  Hz.

Now the question arises, why the other vanadium species (i.e.  $\text{V}^{z+}$ ,  $z = 2-4$ ) despite their similar hydrated structures as compound **A** have more stability and show no structural transition associated with deprotonation [21]. In the electrolyte medium the vanadium cations are solvated by water molecules forming hydrated cations  $[\text{V}(\text{H}_2\text{O})_n]^{y+}$  where the electron density from molecular orbital of the water molecules is transferred to the empty orbitals of the metal cation [16]. This charge transfer weakens the O–H bond in the coordinated water molecules and makes it more acidic leading to deprotonation of the hydrated vanadium cations as follows [16]:



In this deprotonation reaction, the hydrolysis ratio ( $h$ ), i.e. the number of hydroxyl groups created, is directly proportional to the charge of the vanadium cation ( $z^+$ ) and inversely proportional to the pH of the solution, which is explained in the charge–pH diagram reported by Jørgensen [16,22]. In the case of compound **A**, the higher charge of the vanadium cation ( $\text{V}^{5+}$ ) in combination with the increase in temperature leads to a maximum hydrolysis ratio ( $h = 3$ ) leading to the neutral compound **B**. For other vanadium species ( $z^+ < 5$ ) the lower charge prevents the total hydrolysis of the vanadium cation and provides greater stability of the hydrated structure. It is reported that the increase in the sulfuric acid concentration in the electrolyte medium increases the stability of  $\text{V}^{5+}$  species [6]. This can be explained based on the above discussion, as the increase of sulfuric acid reduces the total pH of the solution and hence decreases the deprotonation, thereby stabilizing the  $\text{V}^{5+}$  species. This observation coincides with above discussion and provides additional proof for our hypothesis.

#### 4. Conclusions

The  $\text{V}^{5+}$  cation structure and its thermal stability in electrolyte solution are studied using  $^{17}\text{O}$  NMR,  $^{51}\text{V}$  NMR, and molecular modeling techniques. The  $\text{V}^{5+}$  species exist as hydrated penta coordinated vanadate ion, i.e.  $[\text{VO}_2(\text{H}_2\text{O})_3]^{1+}$  in electrolyte solution. This hydrated structure is found to be stable in the low temperatures ( $<330\text{K}$ ) but at elevated temperature it changes to neutral  $\text{H}_3\text{VO}_4$  molecule by deprotonation process. This neutral species undergoes a condensation reaction through its highly reactive hydroxyl groups and forms  $\text{V}_2\text{O}_5$  precipitate in the electrolyte solution. Hence, the precipitation can be avoided by preventing the

deprotonation process which is followed by the structural transition to neutral  $\text{H}_3\text{VO}_4$  molecule. A simple way to prevent the deprotonation process is to increase the solvent acid concentration and this explains the previously reported stabilization of  $\text{V}^{5+}$  electrolyte solution at high acid concentrations. Overall, it is necessary to stabilize the hydrated vanadium cation structure to achieve greater stability of the  $\text{V}^{5+}$  electrolyte solution.

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