

Towards Understanding the Stabilities of Hydrated Vanadium (V) Complex Ions and the Pathway of V_2O_5 Precipitation in Catholyte Solution of Vanadium Redox Flow Battery

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Abstract – The renewable energy storage systems are being fascinated worldwide due to the rapid increase in global energy consumption rate and a wide-ranging scarcity of the nonrenewable natural resources. Being a vanadium redox flow battery (VRFB) a larger capacity electrochemical energy storage system, it is widely recognized as a promising technology more especially for compensating the fluctuated renewable energies in the electrical grids. Despite its unique uses of "all vanadium" species (V^{2+}/V^{3+} and V^{5+}/V^{4+} redox couples) as potential electrolytes for storing/delivering electric energy, it has been facing a major limitation related to poor thermal stability of the V^{5+} (catholyte) solution. This insight is mainly aimed at investigating the most stable hydrated V^{5+} complex ion exists in the VRFB catholyte solution among $[VO_2(H_2O)_4]^+$ and $[VO_2(H_2O)_3]^+ \cdot H_2O$, and understanding its most probable role to initiate the V_2O_5 precipitation process at high temperature ranges. By employing density functional theory (DFT) as a robust computational quantum mechanical model, the latter complex ion is revealed as an energetically low electronic structure with a stabilization energy $\Delta E = 25.73 \text{ kJ/mol}$. lower than that of the former complex ion, verifying theoretically the existence of $[VO_2(H_2O)_3]^+$ unit as a foremost V^{5+} species alike in experimental observations. The same DFT predictions are believed to be a root cause for making the VRFB catholyte solution less stable, as the $[VO_2(H_2O)_3]^+$ ions preferentially undergo thermal transition into $VO(OH)_3$ compound followed by the condensation and hydrolysis reactions, leading to the development of V–O–V structural unit that would ultimately results the V_2O_5 crystallization.

Keywords – Vanadium Redox Flow Battery (VRFB), V^{5+} hydrated complexes, VRFB hurdle, V_2O_5 precipitation.

I. INTRODUCTION

Over the last few decades, several research works with full of fascinating insights into human requirements such as energy and its resources have begun to take shape which would transpose our energy consumption to less polluting forms of energy. While the coal already served as the chief transportation energy source for over a century, other avenues of energy production such as 'clean coal'

technologies called carbon capture, use and storage (CCUS), and carbon-free technologies called nuclear energy and natural gas have already started losing their strength in terms of cost competitiveness. In the recent years, solar and wind energy generating technologies have been emerging with a significant market share around the world and becoming the most cost competitive in a great number of areas [1], [2]. However, the solar and wind energies would not be the best alternatives for the fossil fuels

as they are only the intermittent energy sources that must be supplemented by other nonrenewable type energy sources such as coal, and their ideal resources in nature are unavailable: the sun sets at night and the wind power drops off suddenly in many places, causing periodic disruption to the continuous energy production process. Therefore, to integrate them into the electrical power grids/stations, it is mandatory to use such type of energy storage systems that are very able to feed the grids whenever necessary so that the grids become stable for uninterrupted energy production/supply. Amid the essentiality of high energy storage systems, the very better technologies that can store more energy within the electrical grids are very crucial around the world, where huge demand of energy is increasing day to day. The vanadium redox flow battery (hereafter, VRFB) technology is one of them that works effectively not only for grid scale power storage but also for home storage systems [3], [4], [5] [6], [7]. Being the VRFB a low variable cost (\$/kWh) technology (especially for larger capacities) with a wider state of charge (SoC) range, it's home storage systems have also become a very competitive compared to the existing lithium ion batteries home storage systems [4], [5], [8]. Likewise, it has already exhibited remarkable performance in terms of charge-discharge cycles > 10,000 without significant aging (lead acid battery: $\leq 2,000$ cycles; Lithium ion battery: $\leq 5,000$ cycles) [8], and has been more popular day by day due to its deep discharge capabilities. Thus, the VRFB is one of the highly anticipated technologies that can offer benchmark capacity of the energy storage.

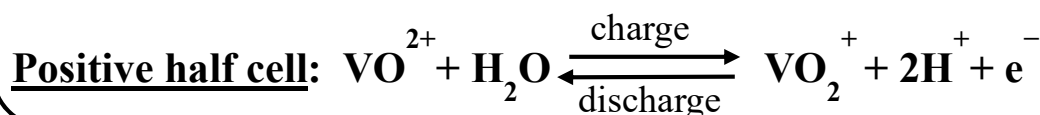
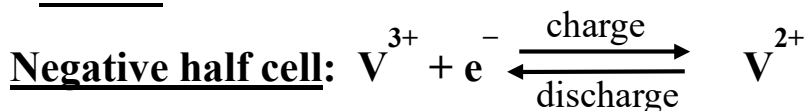
Since the VRFB is a low maintenance cost, rechargeable, and environment-friendly battery technology, several battery makers around the world have been putting in more efforts to implement it industrially. The increasing trend of its industrial installment globally is mainly due to the following specific features of the "all vanadium" solutions used as electrolytes: long lifespan cycles, durable and no performance degradation, no contamination of the active material, safe with no fire or smoke risk, reusable and recyclable upon decommissioning of the battery system etc. More specifically, the aqueous "all vanadium" solutions in the matrix of bench H₂SO₄ (2M to 5M) are used as the VRFB electrolytes. They are usually kept into two sides of the electrolyte chambers of the power cells as anolyte and catholyte solutions where they remain separated to each other by the proton exchange membrane. The bivalent and trivalent forms of the vanadium V²⁺/V³⁺ redox couple behaves as anolyte (kept into the negative half-cell) and the tetravalent and pentavalent forms V⁵⁺/V⁴⁺ (VO₂⁺/VO²⁺) redox couple behaves as catholyte (kept into the positive half-cell)

solutions. While charging/discharging such vanadium-based battery, redox type chemical reactions take place in each half-cell as summarized in **chart 1**, where redox species of the vanadium ions are simply represented by their unhydrated forms. Instead, all the four adjacent oxidation states of Vanadium (Vⁿ⁺; n = +2, +3, +4, +5) have very high tendencies for stabilizing themselves into their aqueous type electrolyte solutions by undergoing ionic hydration (co-ordinate covalent bond: H₂O → Vⁿ⁺) [9]. These variable oxidation states respectively form following hydrated complexes with distinguished color: lilac [V(H₂O)₆]²⁺, green [V(H₂O)₆]³⁺, blue [VO(H₂O)₅]²⁺, and yellow [VO₂(H₂O)₄]⁺ [9], [10]. Among them, the electronic stabilities and the ground state electronic structures of the hydrated pentavalent vanadium complex ions in the aqueous type solutions (yellow colored) are still debatable. Joanna *et al.* [10] reported VO₂⁺ as unhydrated and [VO₂(H₂O)₄]⁺ as the hydrated V⁵⁺ complex ions, Donald *et al.* [11] reported VO₃⁻ or [VO₃(H₂O)₃]⁻ as the predominating V⁵⁺ complex ions in the extracellular body fluids, and Vijayakumar *et al.* [12] reported the existence of [VO₂(H₂O)₃]⁺ as the hydrated V⁵⁺ complex (no any evidences of [VO₂(H₂O)₄]⁺ ions in the VRFB catholyte solution. Therefore, either [VO₂(H₂O)₄]⁺ or [VO₂(H₂O)₃]⁺.H₂O form of the hydrated V⁵⁺ ion may exist predominantly in the VRFB catholyte solution whose lower pH value infers their abundancy unlike in the extracellular body fluids. The main structural dissimilarity between these two complex ions [VO₂(H₂O)₄]⁺ and [VO₂(H₂O)₃]⁺.H₂O lies in the arrangement of the H₂O molecules: former has all the four H₂O molecules inside the first coordination sphere while the latter has only three whose remaining one H₂O lies outside of first coordination sphere. If the first one is a correct structural representation, all the four inner H₂O molecules must be bound with equal strength to the central V atom, and if second, an outer H₂O must be bound weakly unlike the three inner H₂O. Interestingly, either of these two representations possess two O atoms inside the first coordination sphere where they must be bound to the central V atom with an equal strength. Up to the knowledge of this author, there is no article addressing such structural consequences and explaining fully about the electronic stabilities of these two possible but unequally stable V⁵⁺ hydrated complexes in the aqueous type VRFB catholyte solution. By some computational/theoretical techniques (geometry optimizations and frequency calculations), it would be very easier to deal with them. As the former technique locates low energy electronic structure from the given trial structure, and the latter technique computes frequencies at a nuclear Cartesian coordinates of that specific structure (stationary point), their outcomes greatly ease us while analyzing the

three dimensional molecular structures/geometries and interpreting the experimentally observed evidences quantitatively. So, such computational skills would be definitely applicable to probe the structure that can exactly represent the energetically most stable hydrated V⁵⁺ complex

ion existing in the VRFB catholyte solution, and to generate specific structural parameters which in turn offers the quantitative aspects for predicting the accurate geometrical patterns.

Chart 1



It is not new for the VRFB technology favors that the poor stability of the V⁵⁺ solution has always become a hurdle in the fastest and finest development of the VRFB. Several experimental studies reported elsewhere [12], [13], [14], [15], [16], [17], [18], [19], [20] have concluded that the performance of the VRFB entirely depends on whether the V⁵⁺ solution is being utilized fully or not while operating the battery for quite long cycles. For improving its stability, some of them have varied the concentration of the supporting electrolytes (different acid solutions) [13], [14], [15], and some have mixed additives [16], [17] in the V⁵⁺ solution. Vijayakumar *et al.* [12] have observed a thermally induced structural transition of the vanadium species in the VRFB taken catholyte solution and hence, thought to initiate the V₂O₅ precipitation process causing to poor thermal stability of the V⁵⁺ solution. Kausar [18] has showed such V₂O₅ precipitation process is endothermic and is enhanced when the internal temperature of the VRFB rises. Likewise, Rahman *et al.* [19] have mentioned that such precipitation usually starts after 1000h at 50°C (working temperature range of the VRFB is between 10 and 50°C) and a redissolution of the V₂O₅ precipitate is almost impossible. To avoid such wastage of the V⁵⁺ active material, Peng *et al.* [16] and Cao *et al.* [17] have added Trishydroxymethyl aminomethane as a precipitation inhibitor and achieved better thermal stability of the V⁵⁺ ions at 40°C. All these experimental evidences inferred the poor thermal stability of the V⁵⁺ solution which when used as an electroactive material makes the VRFB incapable for utilizing all the quantity of V⁵⁺ ions. In this contribution, the pathway to precipitate V₂O₅ is qualitatively explained.

This study is attempted to investigate energetically low V⁵⁺ hydrated complex compound exists in the aqueous type VRFB catholyte solution quantitatively (out of [VO₂(H₂O)₄]⁺ and [VO₂(H₂O)₃].H₂O) and hence, to understand the structural relations of thus achieved V⁵⁺ complex to its thermally induced structural transition followed by the initiation of V₂O₅ precipitation process qualitatively. For this as a central research interest, a computationally robust density functional theory (hereafter, DFT) model is applied to each V⁵⁺ hydrated complex ion separately, and generated their low energy electronic structures and respective ground state frequencies. All the DFT derived electronic structures and the concerned structural data sets, and the experimentally analyzed results reported elsewhere [12], [13], [14], [15], [16], [17], [18], [19], [20] are interlinked here and attempted to seek the V₂O₅ precipitation pathway qualitatively. The structure of this paper is organized as: the theoretical approaches and computational methods are outlined in section 2, the results and discussions are presented in section 3, and the conclusions are given in section 4.

II. COMPUTATIONAL DETAILS

In order to explore the most stable electronic structure among the two possible pentavalent vanadium complexes in aqueous type catholyte solution: [VO₂(H₂O)₄]⁺ and [VO₂(H₂O)₃].H₂O, the starting (trial) structures for geometry optimization of them were built by using GaussView: the *Gaussian* graphical interface [21] and the concerned Cartesian coordinates of the atoms were extracted. Likewise, the new complex compound VO(OH)₃ that is produced after the deprotonation of water molecules of the [VO₂(H₂O)₃]⁺ was built and generated its atomic Cartesian coordinates for

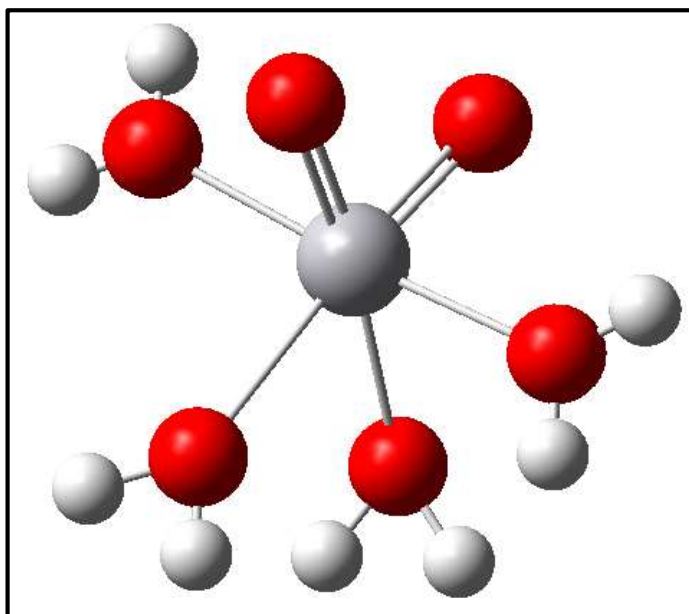
geometry optimization. Accordingly, the compound V₂O₅ that is precipitated after the condensation and hydrolysis reactions between the two VO(OH)₃ molecules was also constructed and confirmed its low energy structure under non-crystalline condition. All the trial structures are shown in **chart 2** where ash-brown, white, and red colored spheroids represent Vanadium (V), Hydrogen (H), and Oxygen (O) atoms respectively. For each optimization process, all the *Gaussian* keywords and methodologies were selected as instructed in *Gaussian* 09 manual [22]. The hybrid functional based DFT method known as B3LYP was used with the basis set of this type: 6-31G (d, p) i.e. the methodology used was DFT: B3LYP/6-31G (d, p). The better and more reliable computational results were assured by using the greater basis set of the type 6-31G (d, p) where the "6-31G" is the standard, split-valence double-zeta basis set: the functions that were used in *Gaussian* script computationally while describing the core and valence orbitals of the atoms; and the functions in parentheses "(d, p)" are polarization functions on heavy atoms and hydrogen that was used to properly describe chemical bonds. Again, to make *Gaussian* for running desirable computation, the molecular charge and spin multiplicity was specified as two integers accordingly. Here, (a) [VO₂(H₂O)₄]⁺ and (b) [VO₂(H₂O)₃].H₂O are cationic complexes; and (c) VO(OH)₃ and (d) V₂O₅ are neutral molecular specimens. So, the first two have charge = +1 and the last two have charge = 0; and they all are a spin-Singlet with *S* = 0 and the spin multiplicity (2*S* + 1) = 1. Thus, the set of integers used in the *Gaussian* input file to describe each cationic and neutral molecule was (1, 1) and (0, 1) respectively. Moreover, while solving the electronic Schrodinger equation iteratively, the self-consistent field (hereafter, SCF) with both default SCF procedure (*SCF=Tight*) and Berny algorithm for optimizations to a local minimum were selected in *Gaussian* 09 [22], [23]. To verify all the four theoretically converged geometries as the energetically minimum structures, the frequency calculation job (*Gaussian* keyword: *Freq*) for each structure was run computationally by using the atomic Cartesian coordinates of the concerned optimized geometry with the same methodology [22], [23], [24]. Every *Gaussian* output file produced from each computational job for each molecular specimen was read by using *GaussView* [21], and various chemical data displayed in three dimensions were extracted and visualized each optimized geometry in the three dimensional space.

III. RESULTS AND DISCUSSIONS

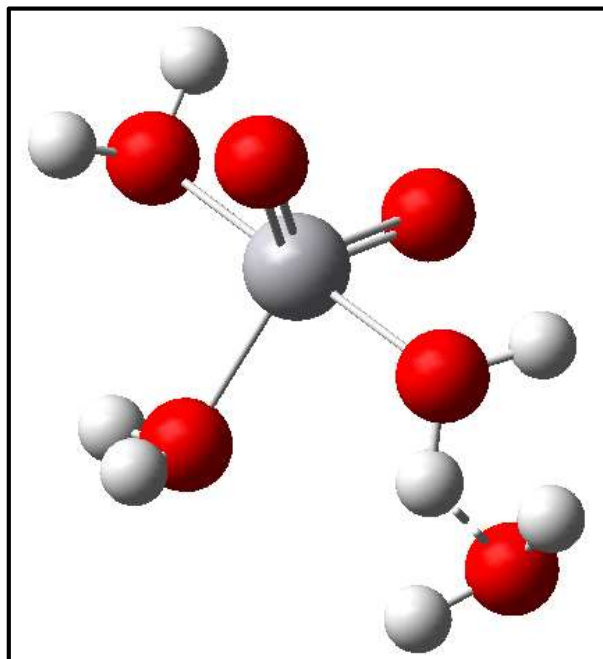
3.1 Electronic stabilities of the hydrated vanadium (V) complexes

In general, theoretical computations based on the first principles DFT method provide comparatively more reliable basis for quantum mechanical determination of the most stable ground state electronic structures of the multi-electron and/or many-body giant molecular systems [25], [26], [27], [28], [29], [30], [31], [32]. In this study, the trial structures of two possible hydrated V⁵⁺ complexes: [VO₂(H₂O)₄]⁺ and [VO₂(H₂O)₃].H₂O (**chart 2**) which are assumed to be existed in the VRFB catholyte solution are optimized separately using the B3LYP/6-31G (d, p) method and identified an energetically most stable equilibrium structure theoretically. The computationally converged equilibrium structures of them are shown in Figure 1 and Figure 2 respectively, where ash-brown, white, and red colored spheroids represent Vanadium (V), Hydrogen (H), and Oxygen (O) atoms respectively. Since the proper specification of the molecular geometries can only be drawn up if the structural parameters such as bond lengths, and bond angles are known, some sets of them that are involved to determine the molecular geometries more precisely in the three dimensional space are carefully chosen here. The theoretically computed values of them for the [VO₂(H₂O)₄]⁺ and [VO₂(H₂O)₃].H₂O complexes are listed in Table 1, where DFT derived bond lengths and bond angles are expressed in Angstrom (Å) and degree (°) respectively, and the symbols: V–OH₂(sb) and V–OH₂(wb) stands for strongly bound and weakly bound H₂O to central V atom respectively, and O₈–H₇(hb) stands for the hydrogen bond (hereafter, H–bond) exist in between O₈ and H₇ atoms. The detailed analyses of the different types of bonds and their lengths associated with the first complex ion [VO₂(H₂O)₄]⁺ listed in the first row and second column of Table 1 suggest that all the double bonded O atoms are strongly bound to the central V atom with equal strength while out of the four H₂O molecules, three are strongly bound with almost equal strength and the remaining one is weakly bound as can be seen in Figure 1, where question mark sign indicates such abnormality. This is reasonable as the bonding principle tells: a shorter bond length means a stronger bond and vice versa i.e. atoms that are closer to each other mostly form strong bond, and those that are far apart to each other form weak bonds, and the double bonds are much stronger than single bonds because they are quite shorter, allowing the atoms to be more closer together and overlapped strongly. Such strongly and weakly bound atoms/molecules to the central V atom can also be examined by the electron density map (mapped with the total density)

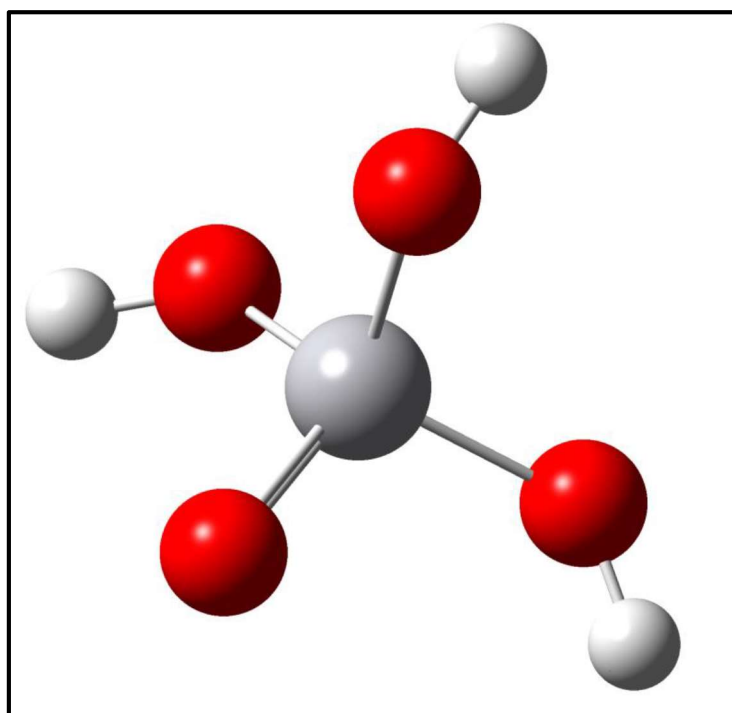
Chart 2: Trial structures



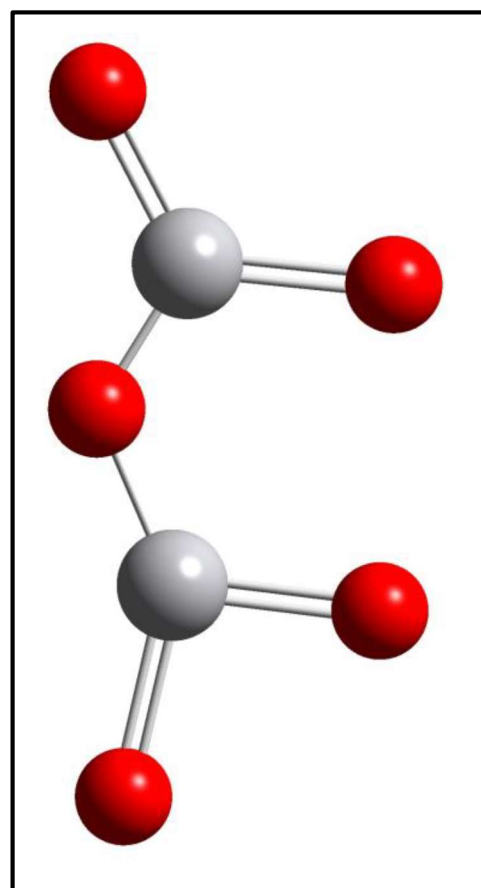
(a) $[\text{VO}_2(\text{H}_2\text{O})_4]^+$



(b) $[\text{VO}_2(\text{H}_2\text{O})_3]^+ \cdot \text{H}_2\text{O}$



(c) $[\text{VO}(\text{OH})_3]$



(d) V_2O_5

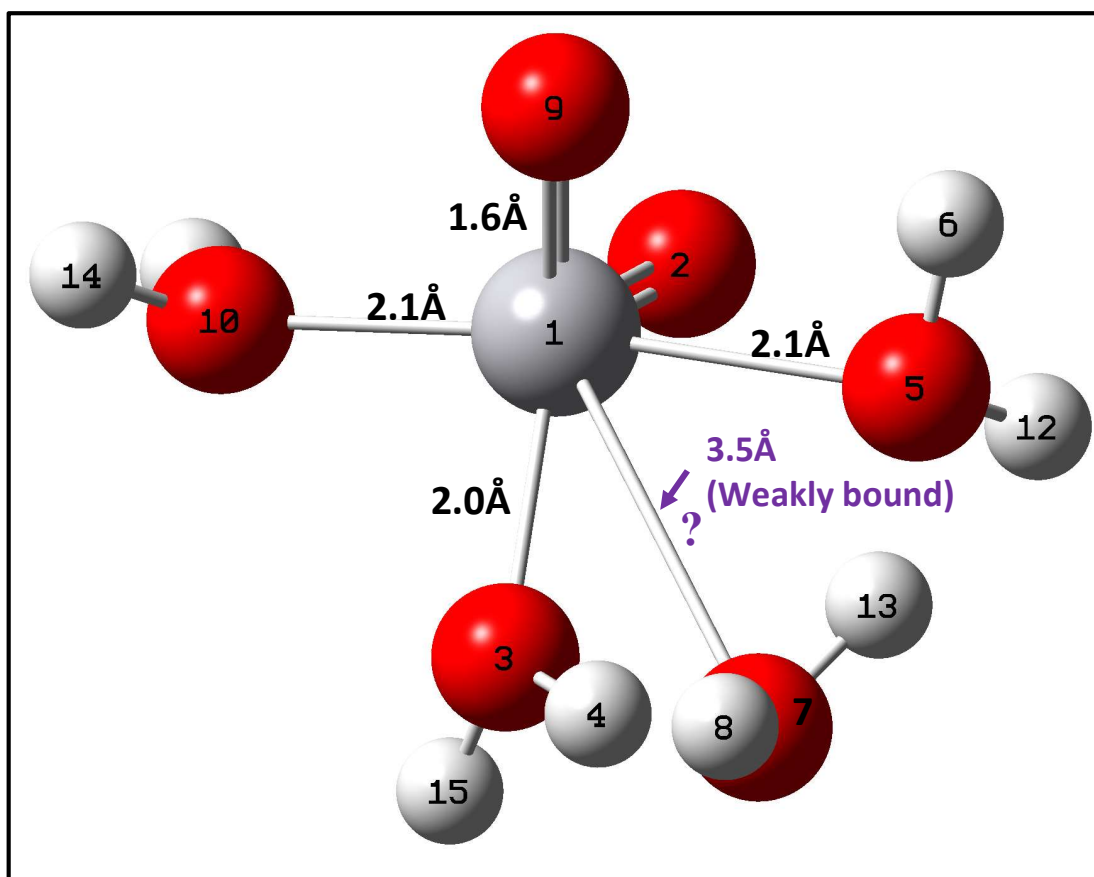


Figure 1. A DFT optimized geometry of $[\text{VO}_2(\text{H}_2\text{O})_4]^+$. The ash-brown, white, and red colored spheroids represent Vanadium (V), Hydrogen (H), and Oxygen (O) atoms respectively.

of the same hydrated complex of V⁵⁺ as displayed in Figure 3. Since the electron density map always illustrates the charge distributions of the molecules three dimensionally and it is an extremely useful mapping technique to visualize areas where electrons are present and where they are not leading to confirm the molecular geometry, it demonstrates well about the position of the weakly bound H₂O molecule whose electron density seems to be located far away (encircled by red color) from the central Vanadium, and the bonding sites of the remaining five atoms/molecules whose electron density are clearly distinguished in the immediate vicinity of the Vanadium center. The five protrusions in and around the central V atom appeared in the electron density map further speculates that the weakly bound H₂O molecule (outer edge protrusion) is being pushed/repelled away from the first coordination sphere, and the three H₂O molecules and two O atoms are being attached closely to the central V atom. Likewise, the tendency of forming an energetically more stable structure of the complex ion $[\text{VO}_2(\text{H}_2\text{O})_4]^+$ by rejecting an H₂O molecule from its first coordination sphere

can also be interpreted by the DFT derived bond angles associated with that weakly bound H₂O molecule. These angles made with the central V atom are $\angle\text{O}_5\text{V}\text{O}_7 = 48.6^\circ$ and $\angle\text{O}_7\text{V}\text{O}_3 = 40.2^\circ$ respectively, which are exceptionally small compare to others as can be seen in the third column-second row (marked by red color) of the Table 1. It again signifies that the atomic nuclear positions of that weakly bound H₂O molecule are dislocated from the center (first coordination sphere) and occupied an abnormal space (approaches to second coordination sphere) away from the central strongly bounded molecules/atoms as observed clearly in Figure 1. In contrast to such oddities on the DFT produced molecular structure, the computational process while optimizing the complex compound $[\text{VO}_2(\text{H}_2\text{O})_4]^+$ was terminated normally with the smooth change in the total electronic energy as can be seen in the GaussView sketched image of Figure 4. This normal Gaussian computations may make us to believe aforementioned converged structure as a real ground state structure in spite of possessing many anomalies.

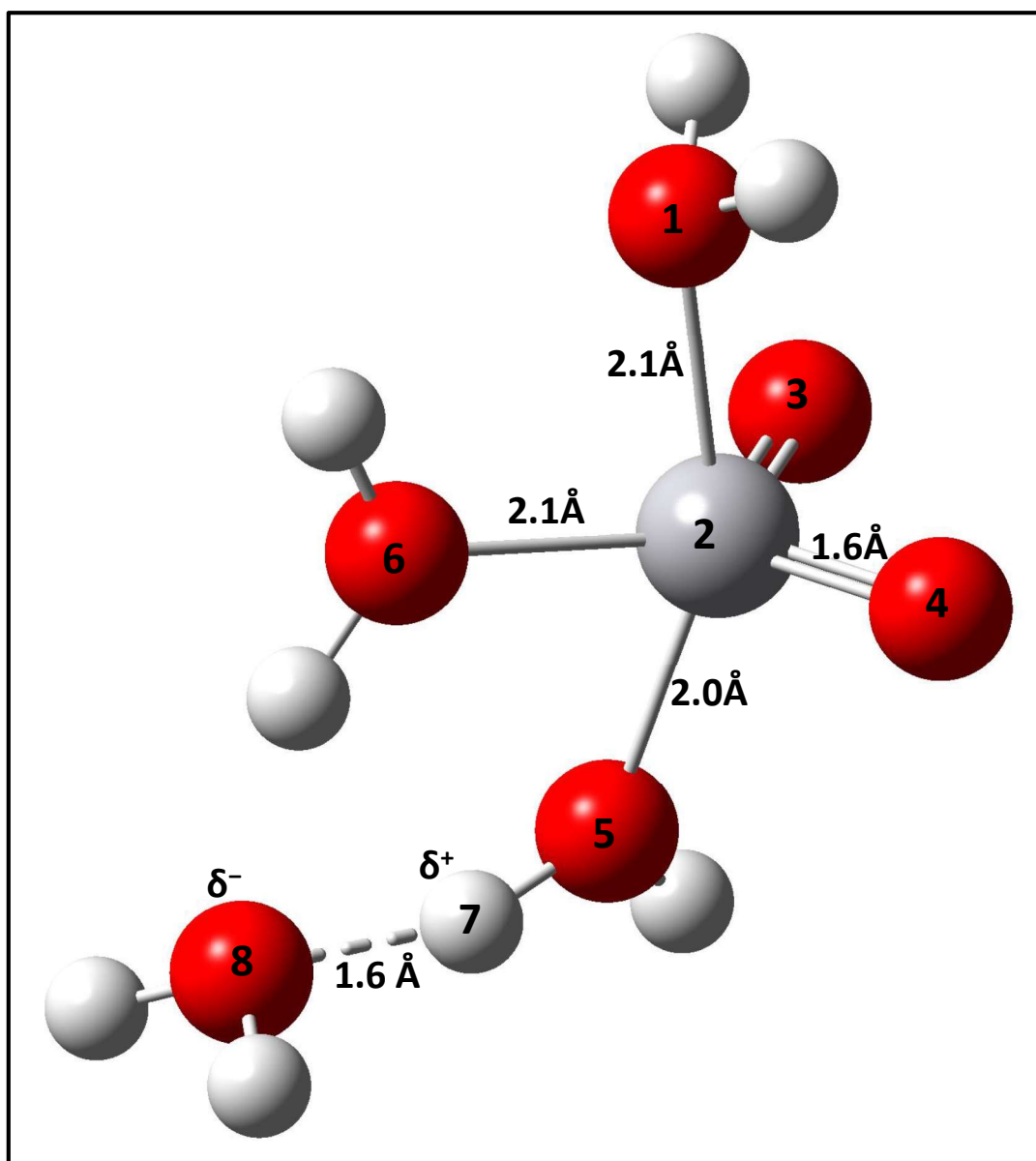


Figure 2. A DFT optimized geometry of $[\text{VO}_2(\text{H}_2\text{O})_3]^+ \cdot \text{H}_2\text{O}$. The ash-brown, white, and red colored spheroids represent Vanadium (V), Hydrogen (H), and Oxygen (O) atoms respectively.

To reconfirm this geometry produced from such normal convergence procedure and computational termination by obeying all the DFT endorsed criteria, the frequency-calculation job was run by explicitly mentioning the concerned atomic Cartesian coordinates of the optimized geometry with the same methodology: B3LYP/6–31G (d, p). Surprisingly, the result shows 10 imaginary frequencies

(negative frequencies) as can be seen in the screenshot image of the Gaussian output .log file shown in Figure 5. It assures that the DFT produced geometry displayed in Figure 1 is not a true minimum of the potential energy surface (hereafter, PES) or it never represents the most stable ground state electronic structure as expected from the earlier discussions,

Table 1. DFT derived structural parameters and number of imaginary frequencies for the Vanadium (V) hydrated complexes.

Vanadium (V) hydrated complexes	Bond length (Å) DFT <i>calc.</i>	Bond Angle (°) DFT <i>calc.</i> (Refer Figure 1 & 2)	Number of imaginary frequencies DFT <i>calc.</i>
1. $[\text{VO}_2(\text{H}_2\text{O})_4]^+$	V=O = 1.6 ^a V–OH ₂ (sb) = 2.0 ^b V–OH ₂ (wb) = 3.5	∠O9V1O2 = 110.5 ∠O2V1O5 = 88.8 ∠O5V1O7 = 48.6 ∠O7V1O3 = 40.2 ∠O3V1O10 = 90.1 ∠O10V1O9 = 100.9	10
2. $[\text{VO}_2(\text{H}_2\text{O})_3]^+ \cdot \text{H}_2\text{O}$	V=O = 1.6 ^a V–OH ₂ (sb) = 2.0 ^c O8–H7 (hb) = 1.6	∠O1V2O3 = 91.0 ∠O3V2O4 = 109.0 ∠O4V2O5 = 104.0 ∠O5V2O6 = 80.0 ∠O6V2O1 = 76.0 ∠O5H7O8 = 160.0	0

^a sb: strongly bound; ^b wb: weakly bound; and ^c hb: hydrogen bond.

instead it represents the structure that can be assigned to one of the saddle points of the PES. The appearance of the negative frequencies further means that the atomic Cartesian coordinates of the converged/optimized geometry was moved a little from the concerned local minimum structure while the frequency (keyword: Freq) calculation job was on the fly. Therefore, to resolve these contrasting results, the best two options are: either modifying the initial trial structure more closely to the expected ground state structure of V5+ hydrated complex or upgrading the convergence criteria and numerical accuracy of the DFT methodology. As the editing facility for the DFT convergence criteria is currently unavailable while implementing this model through the Gaussian program package, building up new trial structure by keeping aforementioned major structural abnormality in mind (one H₂O molecule is pushed away from the central V atom to outer coordination sphere) would be the best option for us. Accordingly, a new form of the trial structure was built up by taking that abnormal H₂O molecule out from the first

coordination sphere and placing it in the second coordination sphere whom are interlinked to each other through the H–bond. That is, the trial structure of the second attempt is for $[\text{VO}_2(\text{H}_2\text{O})_3]^+ \cdot \text{H}_2\text{O}$ representation as displayed in chart 2. This conclusion established from the aforementioned DFT results is very much consistent with the 51V NMR spectroscopy results [12]: $[\text{VO}_2(\text{H}_2\text{O})_3]^+$ ions would be the predominant hydrated pentavalent vanadium species exist in the VRFB catholyte solution.

In second attempt, the trial structure of $[\text{VO}_2(\text{H}_2\text{O})_3]^+ \cdot \text{H}_2\text{O}$ was optimized by the same computational methodology: DFT: B3LYP/6–31G (d, p). The optimized geometry is shown in Figure 2, where the ash-brown, white, and red colored spheroids represent Vanadium (V), Hydrogen (H), and Oxygen (O) atoms respectively. All the DFT derived structural data sets for this complex ion are shown in second row of the Table 1. Each V=O bond length is 1.6 Å and each V–OH₂ bond length is 2.0 Å in average. These values are as equal as the experimentally (X-ray

absorption fine structure (EXAFS) and large-angle X-ray scattering (LAXS) techniques) determined values [10]. While

analyzing these data sets carefully, one may find that all the double

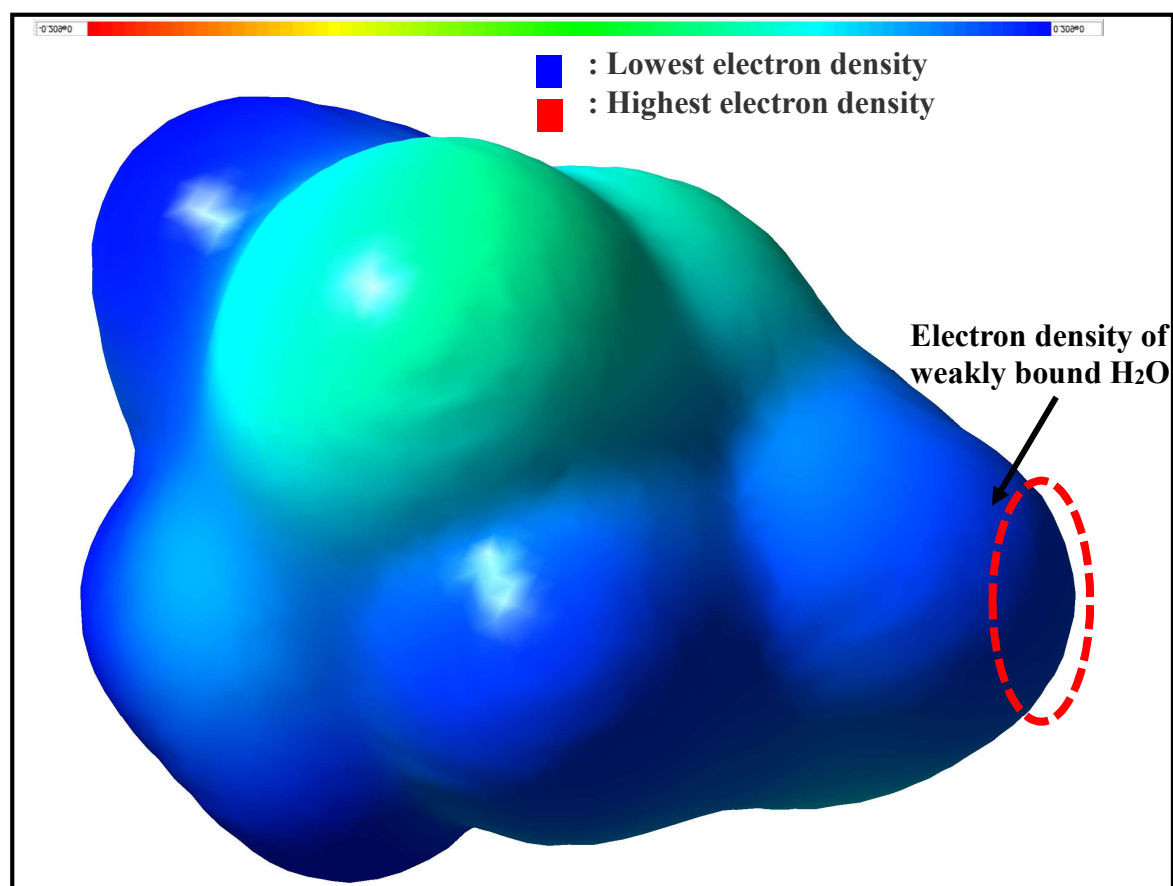


Figure 3. A DFT produced electron density map (mapped with total density) of the complex ion $[\text{VO}_2(\text{H}_2\text{O})_4]^+$. The protrusion encircled by red color approximates the location of weakly bound H_2O molecule.

bonded two O atoms (Oxo-groups) are bound to the central V atom with almost equal strength as in previously optimized $[\text{VO}_2(\text{H}_2\text{O})_4]^+$ complex ion and alike this, all the single bonded three H_2O molecules are also bound to the same V atom with equal strength. But, the intensity of the binding force is stronger in two $\text{V}=\text{O}$ groups than in the three $\text{V}-\text{OH}_2$. As can be seen clearly in the optimized geometry, the two Oxo-groups are in cis-configuration and affect the orientation of the three H_2O molecules directly making their plane slightly below the central vanadium atom. Unlike in $[\text{VO}_2(\text{H}_2\text{O})_4]^+$, present optimized structure has one H_2O molecule in the second coordination sphere which is connected directly to the nearby H_2O molecule of the first co-ordination sphere as can be seen in Figure 2. This sort of direct linkage is developed due to the intermolecular interaction exists in between the electronegative atom O (δ^-

atom) of the outer H_2O molecule and an H atom (δ^+ atom) bonded to the inner H_2O molecule (interacting atoms are labelled as 7H 8O). This special type of dipole-dipole attraction between the two nearby (inner and outer sphered) H_2O molecules is called H-bond whose length in $[\text{VO}_2(\text{H}_2\text{O})_3]^+.\text{H}_2\text{O}$ is estimated as $1.6\text{\AA}$. Interestingly, this length is found to be quite shorter than the intermolecular H-bond length ($1.8\text{\AA}$) exists in the liquid bulk water system. It reflects that the binding force between the first and the second co-ordination sphere in the $[\text{VO}_2(\text{H}_2\text{O})_3]^+.\text{H}_2\text{O}$ complex ion is stronger than the force created by the single H-bond (out of many) of the bulk water system. Similarly, while examining the bond angles of this complex ion listed in Table 1 closely, no any abnormal values can be seen unlike in previous $[\text{VO}_2(\text{H}_2\text{O})_4]^+$ complex ion. The outer H_2O molecule (H-bonded) is found to be aligned to the nearest

H₂O molecule of the first co-ordination sphere by almost 160° ($\angle 5O\ 7H\ 8O = 160^\circ$) as can be seen in Figure 2 as well..

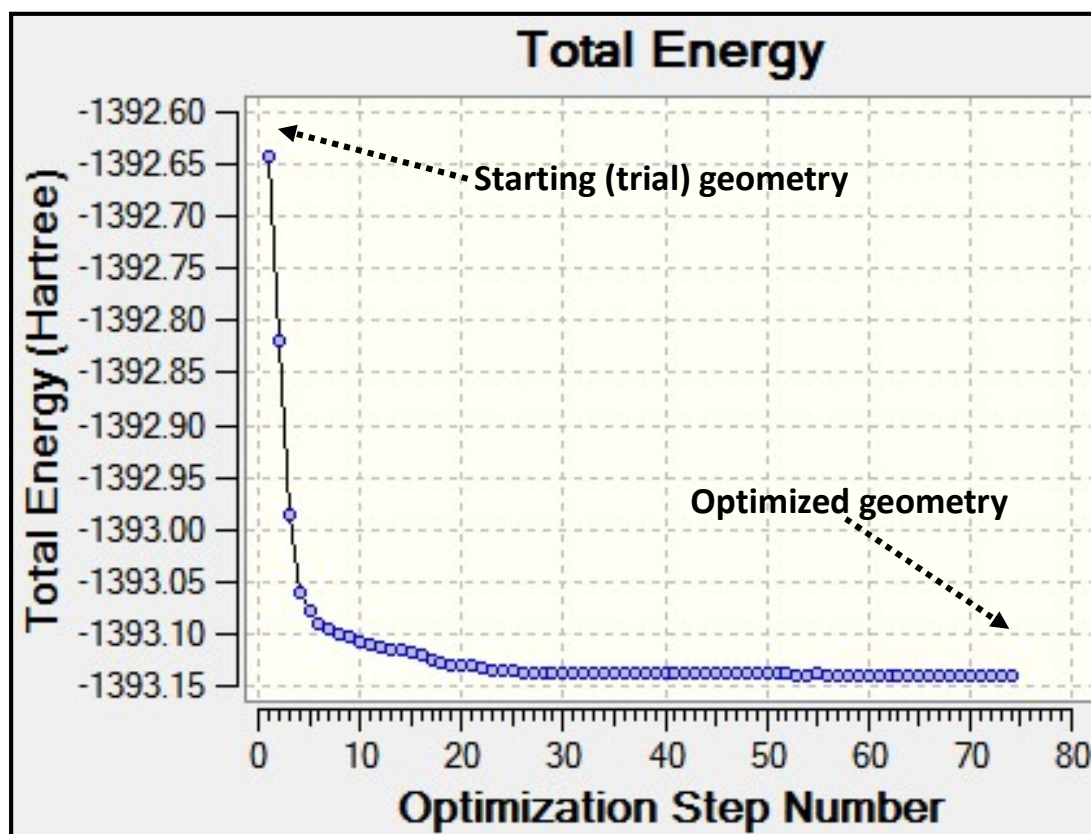


Figure 4. A DFT computed total electronic energy as a function of the optimization step number for the complex ion $[VO_2(H_2O)_4]^+$. The dotted arrows point out the starting (trial structure) and ending (optimized structure) positions of the optimization process.

Among the two type of bonds (coordinate-covalent and H-bond) present in the $[VO_2(H_2O)_3]^+ \cdot H_2O$ complex ion, the H-bond (7H----8O) is often considered as weak and quite vulnerable to stability. However, it is also ubiquitous and is increasingly recognized as an important control element in inter-/intra- molecular type interactions in coordination and hydration chemistry. That is why, the change in its length while the quantum mechanical optimization calculations were on the fly is closely monitored here (Figure 6(a)). This diagram shows that not much detachment or movement (H-bond relaxes to 1.9 Å from 1.3 Å, and finally set to 1.6 Å) of the outer H₂O molecule took place from the first coordination sphere while seeking an energetically low electronic structure computationally through the geometry optimization technique. It means, the outer H₂O molecule is being remained in the close vicinity of the first coordination sphere throughout the whole geometry relaxation procedure. Also, one may easily identify that the

H-bond length of the DFT produced structure (1.6 Å) is longer than that of the trial structure (1.3 Å), indicating a successful completion of the convergence criteria and generation of a decent value for the H-bond length. The same conclusion can be derived while tracing the change in bond angle associated with that H-bonded H₂O molecules (5O 7H 8O) with the optimization steps number (Figure 6(b)). As a whole, the overall accuracy of the DFT calculations can be evaluated by monitoring change in total electronic energy with respect to the increment of optimization step number. As can be seen in Figure 7, the DFT optimization process was terminated normally without any abrupt changes in the total electronic energy, further signifying a successful completion of the convergence criteria. Nevertheless, to reassure thus achieved electronic structure of $[VO_2(H_2O)_3]^+ \cdot H_2O$ as energetically low, the concerned frequencies on the final nuclear Cartesian coordinates were computed as in previous $[VO_2(H_2O)_4]^+$ case, and successively found no any

imaginary frequencies (zero negative frequencies) as listed in Table 1. This theoretical prediction guaranties that the DFT derived low energy electronic structure (Figure 2) for the [VO₂(H₂O)₃]⁺.H₂O trial structure represents a true minimum of the PES. Lastly, while comparing the DFT predicted total electronic energies (E) of the two dissimilar

hydrated complex ions of the V⁵⁺: [VO₂(H₂O)₄]⁺ and [VO₂(H₂O)₃]⁺.H₂O, the latter one (EII) is found to be energetically more stable than the former (EI) by 0.00980004 Hartrees i.e. EII < EI by the stabilization energy of ΔE = 25.73 kJ/mol.

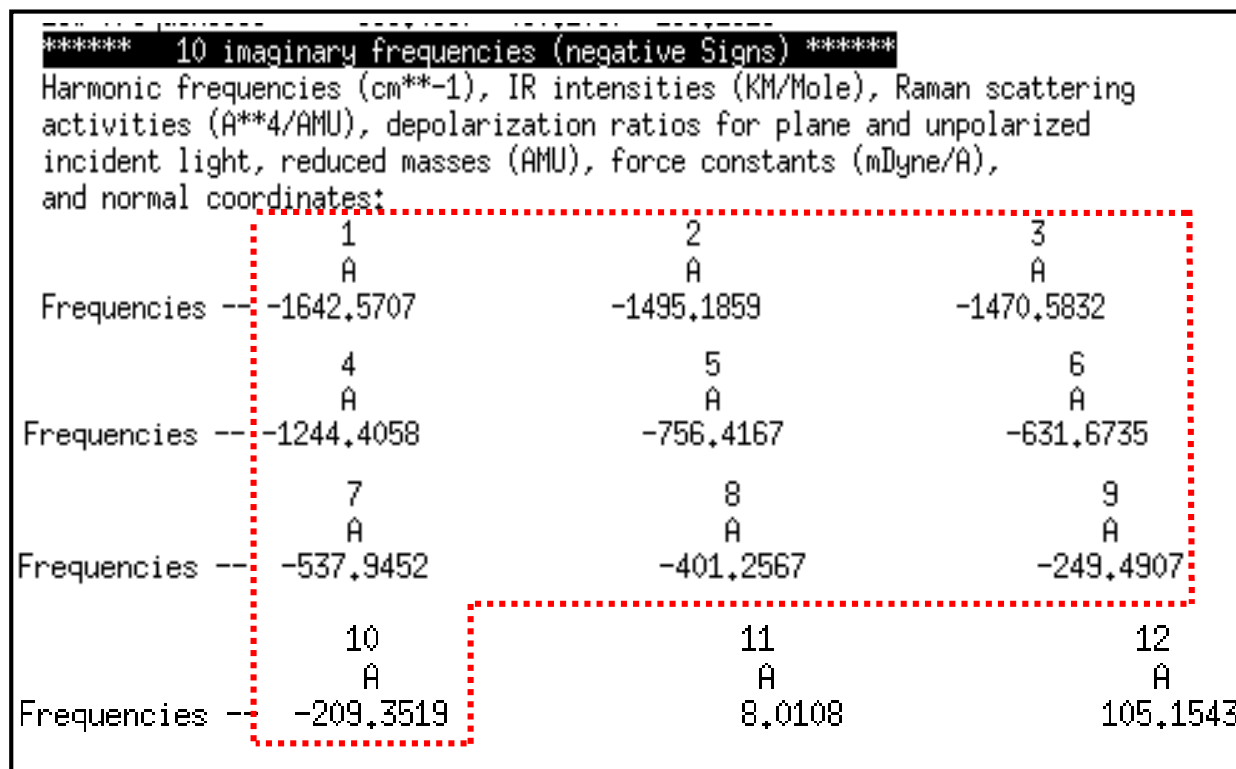


Figure 5. A DFT produced imaginary frequencies for the complex ion [VO₂(H₂O)₄]⁺. The ten negative frequencies (imaginary frequencies) are surrounded by the dotted shape.

3.2 The pathway of V₂O₅ precipitation

From the above results and discussions, it can be concluded that the [VO₂(H₂O)₃]⁺.H₂O complex ion must be the most stable hydrated pentavalent vanadium complex ion exists in the catholyte solution of the VRFB. The molecular formula of this complex ion (according to coordination chemistry rule) tells us that a weakly bound H₂O molecule is present in the second coordination sphere that remains attached to the first coordination sphere through the H-bond as explained earlier in subsection 3.1. Since the individual H-bonds are relatively weak interactions and easily broken from the first coordination sphere, the resulting predominant V⁵⁺ complex ion in the catholyte solution would be [VO₂(H₂O)₃]⁺. This qualitative but trustworthy explanation is analogous to the confirmation made by Vijayakumar *et al.* [12] after applying variable temperature ¹⁷O and ⁵¹V NMR

spectroscopy techniques to study the VRFB taken V⁵⁺ solution. In a reverse way, if the most stable V⁵⁺ hydrated complex ion was [VO₂(H₂O)₄]⁺ (just in case), there were no any chance of detecting [VO₂(H₂O)₃]⁺ ion (by NMR) as the predominant vanadium species in the VRFB catholyte solution. This is an obvious judgement because all the four H₂O molecules present in such [VO₂(H₂O)₄]⁺ form must be strongly bonded to the central vanadium atom through the coordinate-covalent type chemical bond and is relatively a strong bonding interaction that can keep the whole ion as a single entity. It would also be a strong evidence to validate the existence of [VO₂(H₂O)₃]⁺ complex ion as a premier vanadium species in the VRFB catholyte. Such theoretical and experimental confirmation of the prevalent vanadium species makes us easier to derive a route for V₂O₅ precipitation process in the VRFB catholyte. Generally, the

internal temperature and pH of the VRFB electrolyte solutions fluctuate while charging/discharging the battery (working temperatures range: < 20°C to > 40°C) [33], this

irregular variation in the internal conditions would be more particularly unsuitable for the $[\text{VO}_2(\text{H}_2\text{O})_3]^+$ ions to remain intact..

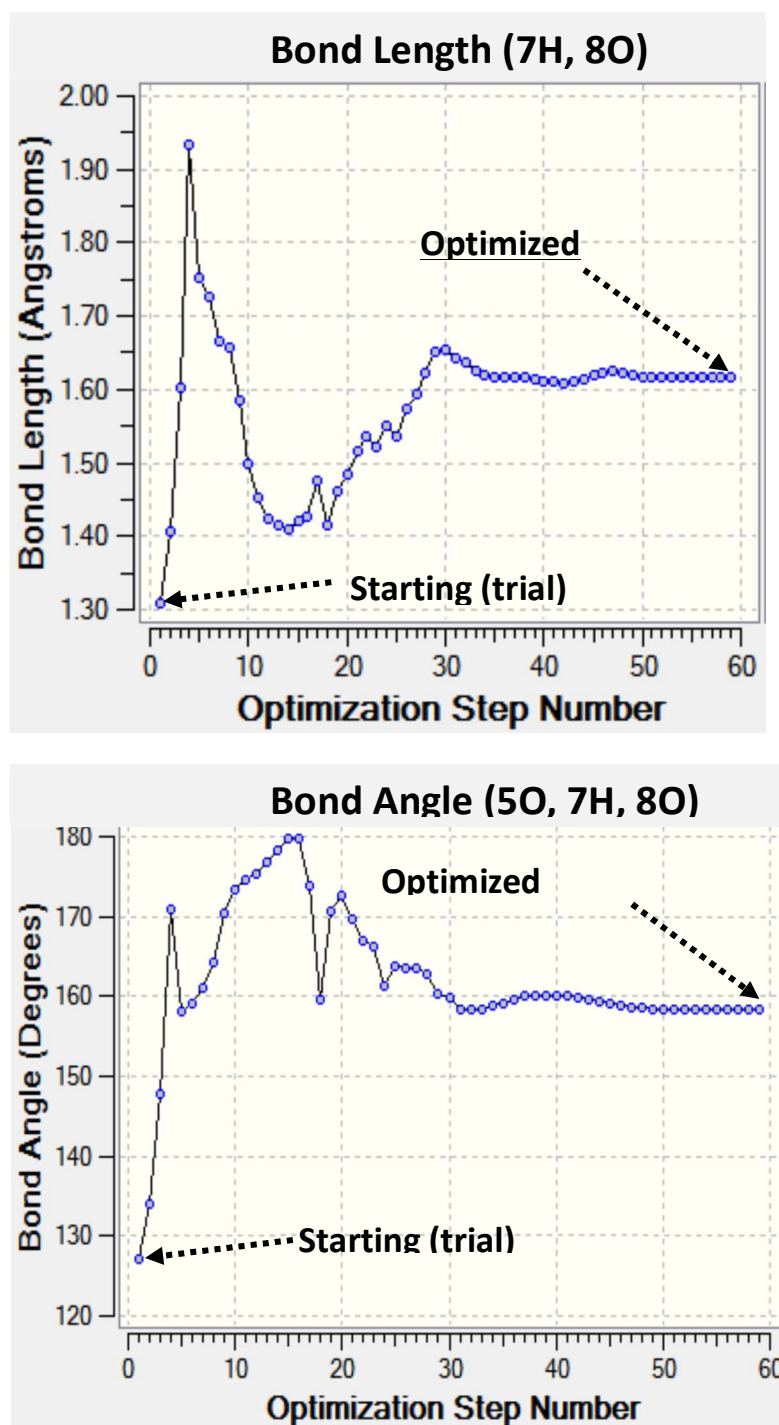


Figure 6. A DFT produced (a) H–bond length (7H, 8O), and (b) bond angle (5O, 7H, 8O) as a function of optimization step number for the $[\text{VO}_2(\text{H}_2\text{O})_3]^+ \cdot \text{H}_2\text{O}$ complex ion. The atom numbers are in accordance with the optimized geometry (Figure 2).

Thus, these complex ions prefer to undergo induced structural transition into another stable compounds

(endothermic reaction) at high temperature ranges ($\square 40^\circ\text{C}$). The effect of such internal thermal energy to destabilize the

V⁵⁺ electrolyte solution is already well established experimentally [12], [13], [14], [15], [16], [17], [18], [19], [20]. More specifically, the qualitative explanation presented just now is mostly supported by these studies reported elsewhere [10], [31], [32] which have stressed that such type of structural changes may occur most probably by deprotonation of the strongly bound H₂O molecules present in the first coordination sphere of the [VO₂(H₂O)₃]⁺ ions, leading to the formation of VO(OH)₃ compounds.

Even though, the appropriate theoretical computations are not performed here to verify such thermally induced structural transition of the vanadium species (it is beyond the current interest of the author), the electronic and structural stability of the resulting intermediate vanadium compound VO(OH)₃ is examined computationally. The DFT derived ground state electronic structure (no imaginary frequency) of this compound is shown in Figure 8 where ash-brown, white, and red colored spheroids represent Vanadium (V), Hydrogen (H), and Oxygen (O) atoms respectively. This optimized structure is visualized as a tetrahedral shaped geometry which is justified by the DFT derived structural data set: each

O–V–O and O–V=O bond angle is 110°, a typical tetrahedral bond angle. Similarly, each V–OH and V=O bond length of ~1.75 Å and ~1.6 Å respectively reflects that the Oxo group is bound strongly to the central vanadium (as in [VO₂(H₂O)₃]⁺.H₂O complex ion) and does affect the orientation of three –OH groups directly, resulting their arrangement into the regular tetrahedral geometry. Likewise, all the three –OH groups are bound to the central vanadium atom equally but weaker than that of the Oxo group, further signifies the existence of pronounced effect of latter group to align the former groups into a specific location of the three dimensional space. To confirm whether this DFT optimization process went smoothly or not, the change in total electronic energy with respect to optimization step number is monitored and found as expected (Figure 9), proclaiming a very trustworthy computational calculations. In this way, the stability of the proposed intermediate vanadium compound VO(OH)₃ is examined here theoretically prior to explain the initiation of V₂O₅ precipitation process.

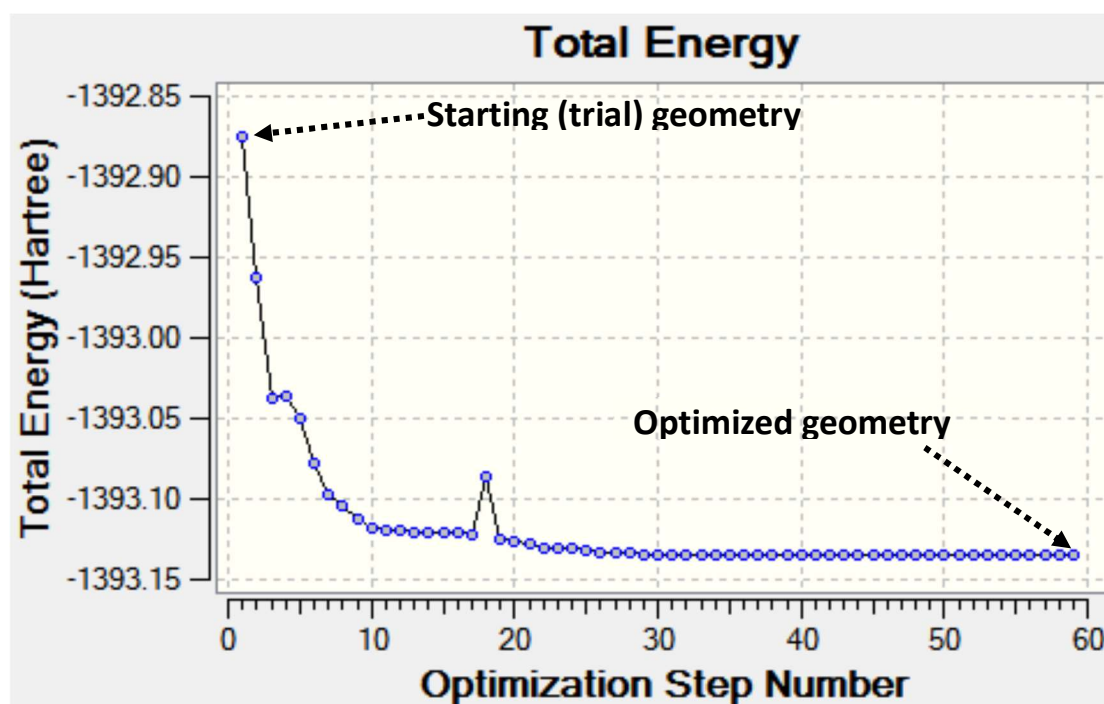


Figure 7. A DFT computed total electronic energy as a function of optimization step number for the complex ion [VO₂(H₂O)₃]⁺.H₂O. The dotted arrows point out the starting (trial structure) and ending (optimized structure) positions of the optimization process.

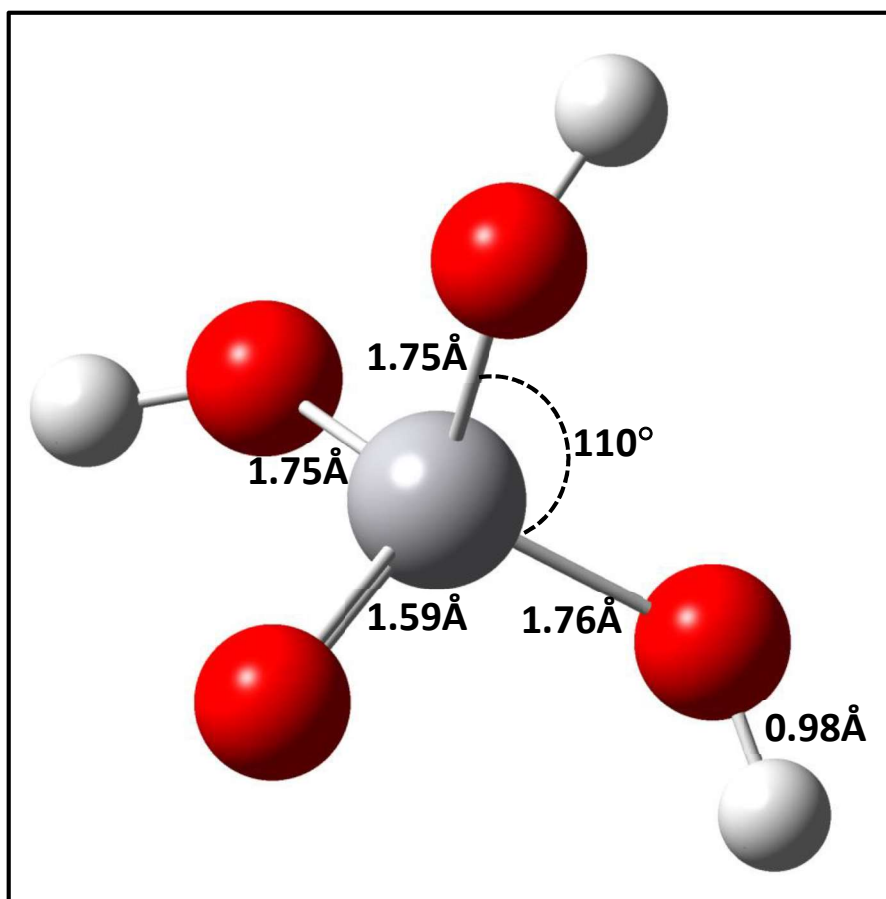


Figure 8. A DFT optimized geometry of $[\text{VO}(\text{OH})_3]$, an intermediate compound prior to precipitate V_2O_5 . The ash-brown, white, and red colored spheroids represent Vanadium (V), Hydrogen (H), and Oxygen (O) atoms respectively.

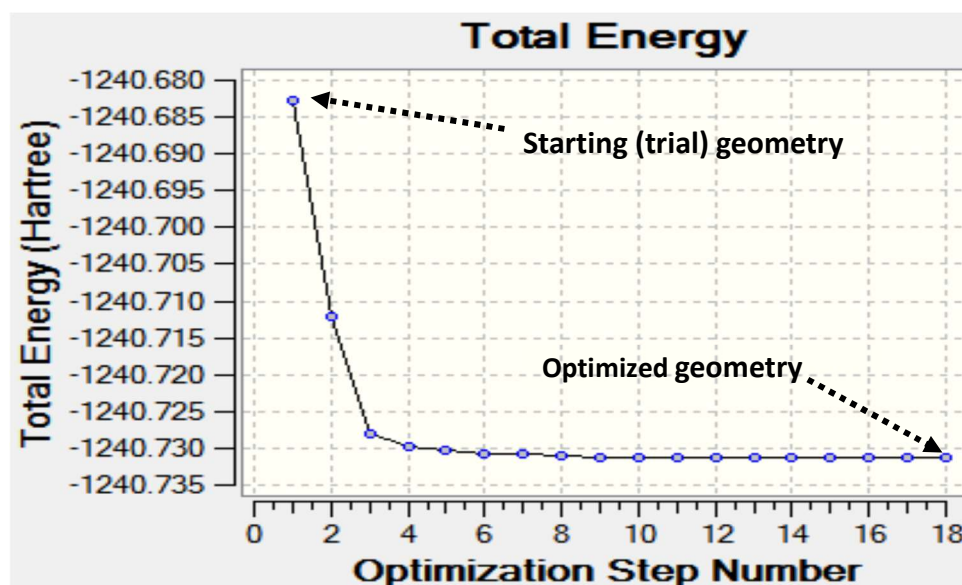


Figure 9. A DFT produced total electronic energy as a function of optimization step number for the $\text{VO}(\text{OH})_3$. The dotted arrows point out the starting (trial structure) and ending (optimized structure) positions of the optimization process.

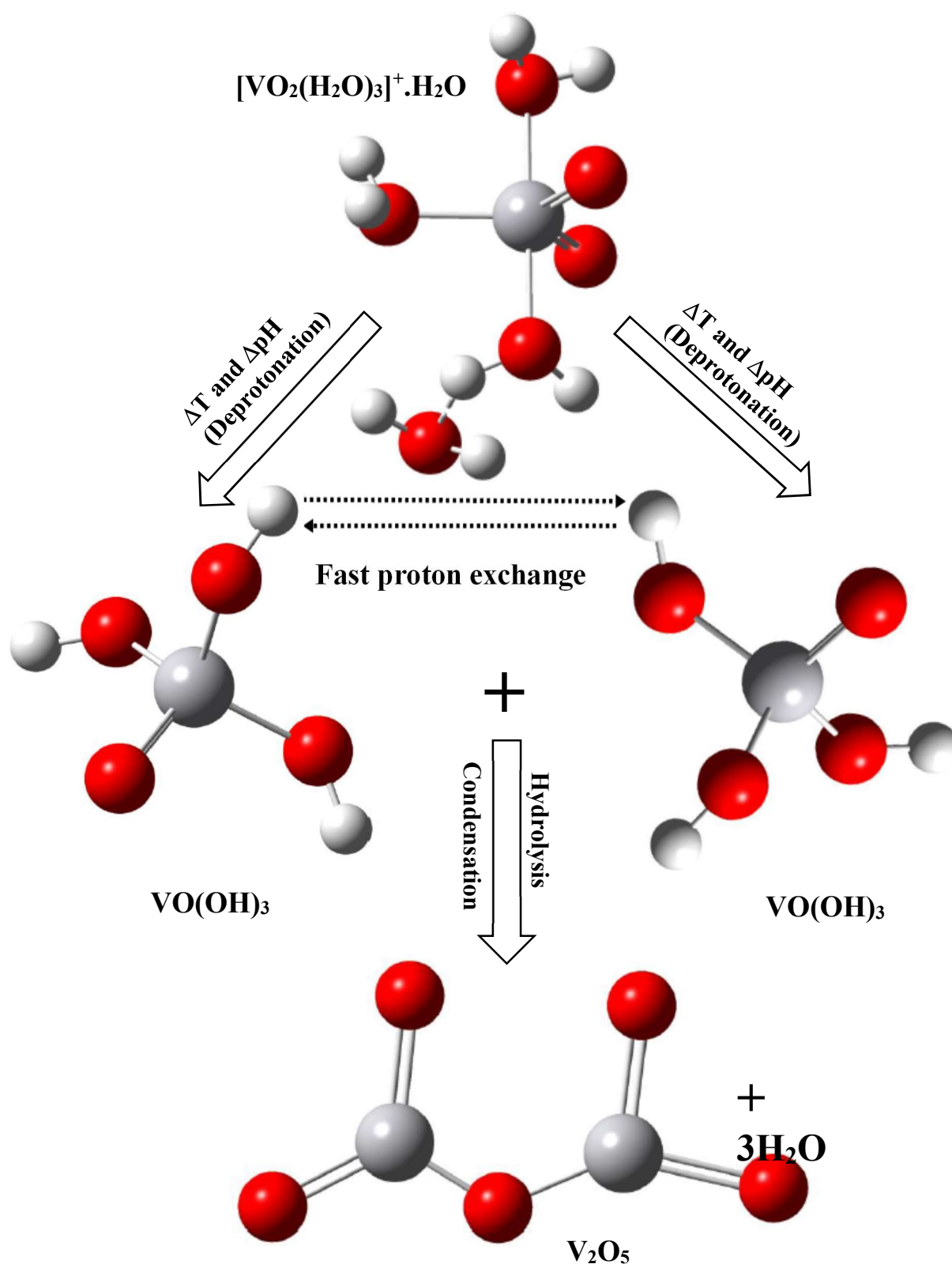


Figure 10. A proposed pathway of V₂O₅ precipitation in the cathodic solution (V⁵⁺ solution) of vanadium redox flow battery (VRFB). All the structures presented here are DFT derived structures.

Actually, the VO(OH)₃ is experimentally assumed to be a potential molecular compound for undergoing fast proton exchange between the two hydroxyl groups of two such molecules in the solution state [12], [33], [34], it is the main element to facilitate the condensation and hydrolysis reactions between themselves leading to the formation of V–O–V structural unit which would ultimately results the V₂O₅ crystallization [34], [35]. The pathway of this V₂O₅ precipitation process starting from the [VO₂(H₂O)₃]⁺.H₂O complex ion via VO(OH)₃ intermediate is outlined in Figure 10. This reaction pathway hypothesized here on the basis of the several experimental observations is possible if and only if [VO₂(H₂O)₃]⁺.H₂O is the most stable V⁵⁺ hydrated complex ion existing in the VRFB catholyte solution. And, this structure is already claimed here as the most stable V⁵⁺ hydrated complex ion (explanation: subsection 3.1), further implies that the V₂O₅ precipitation pathway presented in Figure 10 is quite agreeable at high temperature ranges of the VRFB. At last, the stability of this Vanadium (V) oxide (V₂O₅) is checked here by the same DFT model under non crystalline condition, and found no any structural abnormalities (Figure 10). The chemical structure presented in Figure 10 is the DFT derived low energy electronic structure of an isolated V₂O₅ molecule. The concerned structural data sets for the V₂O₅ molecule are not mentioned here as they are less significant because the DFT calculations were performed under non-crystalline condition and are usually not much reliable while considering the characteristic features of the crystalline V₂O₅ compound.

IV. CONCLUSION

Although, the Vanadium Redox Flow Battery (VRFB) technology has acquired a great significance due to its ability of converting and storing energy by utilizing four adjacent oxidation states of vanadium (V²⁺, V³⁺, V⁴⁺, V⁵⁺) as an electroactive material, several experimental studies on the VRFB have underscored its failure mainly due to poor thermal stability of the V⁵⁺ (VO₂⁺) solution (catholyte) that ultimately leads to V₂O₅ precipitation at high temperature ranges. However, the research works related to investigate the most stable hydrated V⁵⁺ complex ion exists in the VRFB catholyte solution (in the matrix of bench H₂SO₄), and its probable role to initiate such endothermic type V₂O₅ precipitation process are rarely available. As the redissolution of the V₂O₅ once precipitated in the catholyte solution is very difficult, understanding the phenomena at the molecular level that can mostly govern such precipitation process is very crucial. This research work was mainly aimed at identifying the most stable hydrated V⁵⁺ complex ion subsisting in the VRFB catholyte solution among these two questionable

complex ions: [VO₂(H₂O)₃]⁺.H₂O or [VO₂(H₂O)₄]⁺ quantitatively, and seeking its molecular connection to predict V₂O₅ precipitation pathway qualitatively. The density functional theory (DFT) model was employed for exploring the most stable hydrated form of the V⁵⁺ complex ion and computing the ground state frequencies at the particular nuclear Cartesian coordinates, and its general results show that [VO₂(H₂O)₃]⁺.H₂O complex ion is the most stable hydrated species of the V⁵⁺ with a stabilization energy $\Delta E = 25.73$ kJ/mol. lower than that of the [VO₂(H₂O)₄]⁺. While analyzing the calculated frequencies at the DFT optimized nuclear coordinates of each of these two complex ions, former one produced zero imaginary frequency and the latter produced ten, further reassuring the former ion as a ground state electronic structure of the hydrated V⁵⁺. The structural unity and the stability of such complex ion having first and second coordination spheres is guaranteed by the presence of an H-bond that is developed in between an outer-sphered and a nearby inner-sphered H₂O molecules. The presence of such a weak and delicate type intramolecular interaction speculates the most possible existence of [VO₂(H₂O)₃]⁺ ions as the primary vanadium species in the VRFB catholyte solution, as identified by the 17O and 51V NMR spectroscopy techniques. The same prevailing ionic units of the V⁵⁺ actually become a root cause for initiating V₂O₅ precipitation process as they preferably undergo thermal transition into VO(OH)₃ compounds at variable temperature/pH ranges being adapted while charging/discharging the VRFB, and a rapid proton exchange between the two hydroxyl groups of two VO(OH)₃ molecules facilitate themselves for undergoing condensation and hydrolysis reactions leading to the formation of V–O–V structural mosaic unit which would ultimately results V₂O₅ crystallization. While taking into account the results of the bibliography, the VRFB is mainly required to operate: in strong acidic conditions and mixed acid electrolytes, in the presence of chemical additives, in low temperature range (< 20°C) rather than in high temperature condition (> 40°C) for avoiding unwanted loss of the V⁵⁺ active material (through V₂O₅ precipitation) from its catholyte solution.

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