

Summer Scholar Report

Scalable, Versatile Synthesis of Bio-Inspired Vanadium Compounds for High Stability, High Solubility Flow Battery Active Materials

Rachael Howland and Patrick J. Cappillino
Department of Chemistry and Biochemistry, University of Massachusetts, 02747

Abstract:

Non-aqueous redox flow batteries (NRFBs) offer a viable solution to grid-scale energy storage. However, their implementation has been hindered by poor stability and low solubility of the active materials within the electrolyte solutions. To mitigate this issue, a bio-inspired approach was taken to find a vanadium complex that had been optimized for stability through natural selection.¹ Amavadin, produced by the *Amanita muscaria* mushroom, is a metal complex consisting of a vanadium ion bound by two tetradentate hydroxyiminodipropionic acid ligands that has the strongest binding for a vanadium compound ever reported.² An analogous, synthetic version of Amavadin, vanadium(IV)bis-hydroxyiminodiacetate (VBH^{2-}), retains this unique binding structure making it an auspicious candidate for an NRFB active material. Previous experiments with the calcium salt of this analogue, calcium(II)vanadium(IV)bis-hydroxyiminodiacetate (Ca^{2+}VBH), showed promising stability to deep cycling. However, it exhibited low solubility in all solvents tested other than dimethyl sulfoxide (DMSO) and water, neither of which are practical NRFB solvents. This investigation addressed the need for VBH^{2-} analogues that are soluble in battery-relevant solvents by changing the counter cation from calcium to alkylammoniums. High concentration NRFB electrolytes have been prepared in tetrahydrofuran (THF), and γ -butyrolactone (GBL) without compromising the inherent stability, as measured with UV-vis spectroscopy. These new compounds were characterized with X-ray crystallography and FTIR.

In addition, modifications to the synthesis of these compounds were made. Leveraging the remarkable stability of VBH^{2-} , a direct synthetic scheme was employed that obviates the need for costly ion-exchange resins that were used in the previously reported procedures. This scalable approach allowed for the Ca^{2+}VBH to become a reagent in the formation of new complexes by exploiting the low K_{sp} of calcium fluoride, facilitating cation metathesis between Ca^{2+} from the Ca^{2+}VBH and alkylammonium fluoride salts. These changes support the commercial feasibility of these electrolytes by removing limitations on scalability and providing a versatile synthesis pathway for VBH^{2-} active materials with arbitrary cations.

Introduction:

The adoption of renewable energy to the electrical grid system is hindered by the intermittent nature of the sources, such as wind and solar power.³ Developing grid-scale energy storage to mitigate the supply and demand discrepancy has been recognized as an integral component in transitioning energy dependence from fossil fuels to sustainable sources.⁴ With predictions from the U.S. Energy Information Administration (EIA) indicating an increase in renewable energy usage⁵, the need to develop and improve existing strategies is increasing.

Redox flow batteries (RFBs) have been a promising technology in energy storage for decades due to their design versatility, efficiency and unique scalability.⁶⁻⁸ A generic model of the RFB includes redox-active electrolytes stored independently and then pumped into a cell containing two half cells, positive and negative, that are separated by an ion selective membrane and connected to a power and a load source, respectively.³ This design accounts for their scalability given that power can be scaled by increasing the electrochemical apparatus and capacity is a function of the volume and concentration of the electrolyte solution.⁴

State-of-the-art RFBs consist of vanadium ions in aqueous, acidic solutions for both the anode and cathode active materials.⁹ However, non-aqueous systems (NRFBs) have begun to garner attention since they offer several key advantages with respect to the composition of their electrolyte solutions. These include wide electrochemical windows, low vapor pressures, high dielectric constants, potentially greater thermal stability and improvements in power and energy density.¹⁰⁻¹¹ Notwithstanding these clear advantages, development of NRFBs has been severely inhibited by the instability of the active materials within the electrolyte solutions during cycling, especially at high current densities.¹⁰ This degradation can result in as much as 80% capacity loss after only modest cycling¹²⁻¹⁵ crippling the batteries' lifespan. In addition, it is difficult to predict the behavior of active materials in advance, creating a general reliance on commonly known, commercially available compounds and discouraging more novel approaches.

Prior research had posited that a bio-inspired approach, that recognized nature had been optimizing for the stability of metal complexes through eons of evolution, led to the exploration of the biomolecule Amavadin. Amavadin binds a vanadium (iv) ion with two tetradentate ligands and has the strongest binding constant ($\log K = 23.4 \pm 5$), for that ion ever recorded.² A synthetic version of the molecule, vanadium (iv) hydroxyimino-diacetate (VBH²⁻), was used as a scaffold for active materials in NRFB electrolytes.¹ In initial experiments, conducted with a known Amavadin analogue, calcium(ii) vanadium(iv)bis-hydroxyiminodiacetate (Ca²⁺VBH), cyclic voltammetric (CV) analysis and exhaustive, deep redox cycling between vanadium(iv/v) in both static cell and flow

battery showed excellent chemical and stability and negligible capacity-fade.¹ In addition, Ca²⁺VBH was stable in both the reduced and oxidized states over time, as verified by UV-vis spectroscopy.¹

While the promising stability of Ca²⁺VBH has been demonstrated, it was only soluble in water and DMSO, neither of which are ideal solvents for NRFBs. This redirected the focus of the investigation from stability to solubility and the idea that different counter cations could have an impact on active material concentrations and in more relevant solvents. Initially, (bis)tetramethyl-ammonium vanadium(iv)(bis)hydroxy-iminodiacetate ([N1111]₂VBH), was synthesized and dissolved in propylene carbonate (5 mM). This was an improvement over Ca²⁺, allowing electrochemical evaluation and further suggested that changing the counter cation was a useful approach to increasing solubility.¹

Two challenges in terms of synthesis became apparent at this stage. First, the published synthesis for Ca²⁺VBH was not scalable due to the use of an ion exchange column.² To provide perspective, a recent trial at Case Western Reserve University used 45 gallons of electrolyte solution to produce a 1 KW scale prototype flow battery.¹⁶ To match this prototype scale, a 608 litre (160.0 U.S. gallon) ion-exchange column would be necessary! Second, a versatile synthesis, allowing either purification of VBH²⁻ with cations, or direct preparation of electrolytes was necessary. The commercial viability of VBH²⁻ as an NRFB active material scaffold would be improved if a scalable method could be found that also eliminated the need for an ion exchange column.

Methods:

General:

Bromoacetic acid, 98% (Alfa Aesar), hydroxylamine hydrochloride, 99% (Alfa Aesar), zinc acetate dihydrate (Acros Organics), calcium chloride (Fischer Technical), tetraethylammonium hydroxide, 35 wt% in water (Sigma Aldrich), tetraethylammonium fluoride \geq 98.0% (VWR), tetrabutylammonium fluoride 70-75% water (TCI), vanadium (iv) bis(acetylacetonato) oxide 98% (STREM), γ -butyrolactone (Sigma Aldrich) and tetramethylammonium hydroxide 25% in water (Acros Organics) were purchased and used without purification. Zinc hydroxyiminodiacetate (ZnHIDA) was prepared according to literature procedures.²

Physical Methods:

FTIR Analysis was conducted using a Nicolet iS5 spectrometer with iD7 ATR attachment (Thermo Scientific) UV-vis spectroscopy was performed with an Evolution 220 UV Visible spectrophotometer (Thermo Scientific) and XRD was collected with a Bruker D8

Venture X. UV-vis spectroscopy was carried out for both the initial synthesis concentrations of the analogues in their respective solvents and at a 1:10 volumetric dilution. The extinction coefficient $\epsilon_{825} = 24.8 \text{ M}^{-1}\text{cm}^{-1}$ had previously been determined for Ca^{2+}VBH and was used in this experiment.¹ Before determination of concentration any precipitate was removed using either centrifuging or vacuum filtration.

Preparation of (bis)tetraethylammonium vanadium(IV) (bis)hydroxyiminodiacetate [N2222]₂VBH – Method A: In 3 mL of solvent, 0.795 g (0.003 mol) Ca^{2+}VBH (265 g/mol), 1.11 g (0.006 mol) tetraethylammonium fluoride (185 g/mol) were combined and stirred overnight. Solvents used were either water, DMSO, GBL or PC. A bright blue solution formed with off-white solid. The precipitate was removed through centrifuging and then filtration.

Crystallization-

Crystals suitable for X-ray diffraction were obtained from samples of the compound that had been synthesized with Method B: In 40 mL of water, 3.4 g (0.008 mol) $[\text{N2222}]\cdot\text{OH}$ (35% wt H_2O ; 147.26 g/mol), 1.06 g (0.004 mol) $\text{VO}[\text{acac}]_2$ (265 g/mol), 1.2 g (0.008 mol) hydroxyiminodiacetic acid (H_3HIDA) (149 g/mol) were combined and stirred for 1 hour. A bright blue solution formed and was then roto-evaporated until a solid formed. This was filtered, dissolved in ethanol and slow diffused with diethylether; FTIR 3391(NH) 2991(CH) 1603(CO)1178(CC) 1005(CC)

Preparation of (bis)tetrabutylammonium vanadium(IV) (bis)hydroxyiminodiacetate [N4444]₂VBH – This compound was prepared by Method A above: In 5.0 mL of solvent, 1.3 g (0.005 mol) Ca^{2+}VBH (265 g/mol), 2.8 g (0.010 mol) tetrabutylammonium fluoride (280.5 g/mol) were combined and stirred overnight. The solvents used were either water, DMSO, GBL or THF. A bright blue solution formed with an off-white solid. The precipitate was removed through centrifuging and then filtration.

Crystallization-

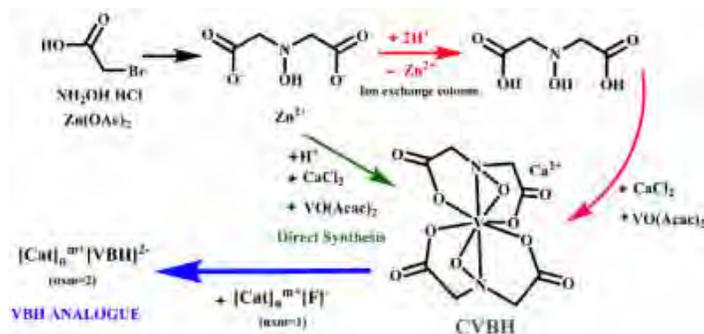
Crystals suitable for XRD were obtained from slow diffusion of diethylether into a high concentration THF solution prepared by method A; FTIR 3419(NH) 2957(CH) 1615(CO) 1127(CC)

Results and Discussion:

Modification of the Ca^{2+}VBH synthesis

The synthesis method for creating the VBH^{2-} analogues was modified in two ways; elimination of the ion exchange column and a cation metathesis approach utilizing the fluoride salt of the desired cation. One of the precursors to the Ca^{2+}VBH preparation from the literature is a zinc salt of the hydroxyiminodiacetate (HIDA).¹ In that procedure, an ion exchange column was used to remove the Zn^{2+} cation from the

zinc salt of the hydroxyiminodiacetate ligands HIDA, leaving a protonated version, hydroxyiminodiacetic acid (H_3HIDA) that could then be reacted with calcium chloride ($CaCl_2$) and vanadium (iv) bis(acetylacetonato) oxide ($VO(Acac)_2$) to produce $Ca^{2+}VBH$. (Scheme 1) The logarithm of the stability constant for Zn-Hida is 5.05(10) compared to that of 23.0(10) for VBH^{2-} , suggesting a strong preference of HIDA for the vanadium(iv) ion.¹ Initially, attempts were made to dissolve the ZnHIDA with phosphoric acid in the presence of vanadyl acetylacetonate $VO[acac]_{2(s)}$ since zinc phosphate has a K_{sp} of 5×10^{-36} ¹⁷ and should have precipitated, leaving VBH^{2-} in solution without further purification on the column. However, both the zinc phosphate and the $Ca^{2+}VBH$ precipitated and this pathway was abandoned after various efforts to isolate the product. The next attempt was to use 12 M hydrochloric acid in place of the phosphoric acid to dissolve the solid reagents, $VO[acac]_{2(s)}$, ZnHIDA and $CaCl_2$, once they were placed in water. (Scheme 1) The reagent mixture immediately turned a translucent blue color consistent with VBH^{2-} with the addition of the acid, at a pH of 0.24. The solution was then treated directly with isopropanol ($9^\circ C$) for precipitation and resulted in a purple powder consistent with $Ca^{2+}VBH$ through FTIR analysis and XRD after recrystallization in slow liquid diffusion with water and IprOH. Typical yield for this direct precipitation of $Ca^{2+}VBH$ is 17.75 g, 75.5% compared to 0.447 g, 91% $Ca^{2+}VBH$ for the literature procedures.¹⁹



Scheme 1. $Ca^{2+}VBH$ synthesis modification with the original pathway from literature in red and showing the use of the ion exchange column and the new method shown with the blue arrow and going directly from the Zn-HIDA to $Ca^{2+}VBH$.

The next challenge was developing a versatile, scalable synthesis method for VBH^{2-} compounds with varying cations. Appreciating the strength of the coordination between the vanadium(iv) and the HIDA ligands, calcium salts with low K_{sp} values were researched with the expectation that they would form as a solid and leave the desired product remaining in solution. Calcium fluoride has a K_{sp} of 3.9×10^{-11} ¹⁸ and when the $Ca^{2+}VBH$ was mixed in solution with the two fluoride salts of tetraethylammonium and tetrabutylammonium, products were obtained. This method was useful in obtaining pure compounds for analysis and was also reproducible in water,

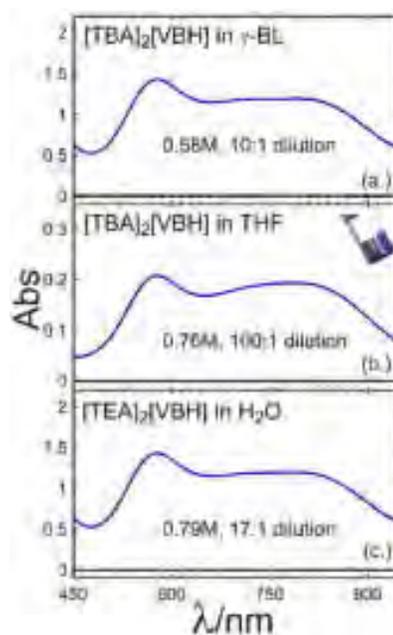
DMSO, PC, and GBL. This suggests the potential to directly prepare VBH²⁻ based electrolytes in various battery-relevant solvents by removing the CaF₂ solid, without isolation.

Synthesis of alkylammonium compounds in battery relevant solvents

The compound (bis)tetraethylammonium vanadium(iv)(bis)hydroxyiminodiacetate, [N2222]₂VBH was synthesized and electrolytes of 0.79 M in water, 0.2 M in PC, and 0.5 M in GBL were prepared. (Figure 1). The crystal structure was determined using XRD (Figure 2) and the compound was further characterized by FTIR. Similarly, (bis)tetrabutylammonium vanadium(iv)(bis)hydroxyiminodiacetate, [N4444]₂VBH was synthesized and electrolyte concentrations of 0.5 M in water, 0.76 M in THF, and 0.58 M in GBL. (Figure 1) The structure was characterized with both XRD (Figure 2) and FTIR. It should be noted that these concentrations are not necessarily the maximum concentrations achievable for the compounds in these solvents.

The exchange of the Ca²⁺ ion for the alkylammonium cations and the resulting trend from Ca²⁺VBH being insoluble in PC, THF and GBL to the range of concentrations seen between the three alkylammonium analogues strongly suggests that this would be a viable mechanism for addressing the need to increase active material concentrations in NRFB electrolytes. This is important because the concentration of activematerial in an electrolyte solution directly correlates with its energy density.

Figure 1. UV-vis spectra of solutions of [TBA]₂[VBH] in γ -BL (a.) and THF (b.) and [TEA]₂[VBH] in H₂O (c.), after dilution. Blank spectra are shown with black lines in (a.), (b.) and (c.). A photograph of 0.76 M [TBA]₂[VBH] in THF is shown in the inset of (b.). Concentrations are calculated using the absorbance and extinction coefficient of [VBH] at 825 nm of 24.8 M⁻¹cm⁻¹.



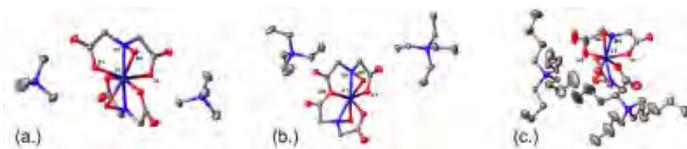


Figure 2. X-ray crystal structures of bis-TMA (a.), bis-TEA (b.) and bis-TBA (a.) [VBH] compounds. Thermal ellipsoids at 40% probability for (a.) and (b.) and 30% for (c.). Atoms labels show the position of the vanadium ion and the four donor atoms of one of the two ligands in all three structures.

Conclusions:

Utilizing the unique binding strength of VBH²⁻ and the low K_{sp} of calcium fluoride, two alkylammonium VBH compounds were produced at high concentration in battery-relevant solvents. The counter cation has a direct effect on solubility and will continue to be investigated both in terms of synthesis and electrochemical analysis. The fact that higher concentrations of alkylammonium salts of VBH²⁻ were obtainable in all solvents investigated, compared to Ca²⁺, suggests that factors affecting the lattice enthalpy, rather than solute-solvent interactions are more important in determining the solubility. The ability to directly synthesize active materials in NRFB solvents could provide advantages commercially in terms of ease of synthesis and scalability.

Acknowledgements:

The authors would like to thank Dr. James Golen for the X-ray crystallography.

Citations:

1. Huang, H., Howland, R., Agar, E., Nourani, M., Golen, J., Cappillino, P. Bioinspired, High Stability, Nonaqueous Redox Flow Battery Electrolytes. *J. Mater. Chem. A*, 2016.
2. G. Anderegg, E. Koch and E. Bayer, *Inorg. Chim. Acta*, 1987, 127, 183–188.
3. Weber, A.Z., Mench, M.M., Meyers, J.P. et al. *J Appl Electrochem* (2011) 41:1137. <https://doi.org/10.1007/s10800-011-0348-2>
4. G. L. Soloveichik, *Chem. Rev.*, 2015, 115, 11533–11558.
5. U.S. Energy Information administration, Short-Term Energy Outlook (STEO), September 2016, <https://www.eia.gov/forecasts/steo/archives/may16.pdf>, accessed September 29, 2016, 2016.

6. J. Winsberg, T. Hagemann, T. Janoschka, M. D. Hager and U. S. Schubert, *Angew. Chem., Int. Ed.*, 2016, 55, 2–28.
7. S. Ha and K. G. Gallagher, *J. Power Sources*, 2015, 296, 122–132.
8. V. Viswanathan, A. Crawford, D. Stephenson, S. Kim, W. Wang, B. Li, G. Coffey, E. Thomsen, G. Graff, P. Balducci, M. Kintner-Meyer and V. Sprenkle, *J. Power Sources*, 2014, 247, 1040–1051.
9. J. Winsberg, T. Hagemann, T. Janoschka, M. D. Hager and U. S. Schubert, *Angew. Chem., Int. Ed.*, 2017, 56, 686–711.
10. J. D. Milshtein, A. P. Kaur, M. D. Casselman, J. A. Kowalski, S. Modekrutti, P. L. Zhang, N. Harsha Attanayake, C. F. Elliott, S. R. Parkin, C. Risko, F. R. Brushett and S. A. Odom, *Energy Environ. Sci.*, 2016, 9, 3531–3543.
11. Gong, Q. Fang, S. Gu, S. F. Y. Li and Y. Yan, *Energy Environ. Sci.*, 2015, 8, 3515–3530.
12. W. T. Duan, R. S. Vemuri, J. D. Milshtein, S. Laramie, R. D. Dmello, J. H. Huang, L. Zhang, D. H. Hu, M. Vijayakumar, W. Wang, J. Liu, R. M. Darling, L. Thompson, K. Smith, J. S. Moore, F. R. Brushett and X. L. Wei, *J. Mater. Chem. A*, 2016, 4, 5448–5456.
13. E. V. Carino, J. Staszak-Jirkovsky, R. S. Assary, L. A. Curtiss, N. M. Markovic and F. R. Brushett, *Chem. Mater.*, 2016, 28, 2529–2539.
14. P. J. Cappillino, H. D. Pratt, N. S. Hudak, N. C. Tomson, T. M. Anderson and M. R. Anstey, *Adv. Energy Mater.*, 2014, 4, 1300566.
15. Shinkle, A. E. S. Sleightholme, L. D. Griffith, L. T. Thompson and C. W. Monroe, *J. Power Sources*, 2012, 206, 490–496.
16. “Researchers building flow battery prototype to augment grid.” *The Daily*, 28 June 2017, thedaily.case.edu/researchers-building-flow-battery-prototype-augment-grid/. (<http://thedaily.case.edu/researchersbuilding-flow-battery-prototype-augment-grid/>)
17. D. C. Harris, *Quantitative Chemical Analysis*. 8 ed.; W.H. Freeman and company New York, 2010; p 796.
18. Patnaik, P., *Handbook of Inorganic Chemicals*. 1 ed.; McGraw-Hill Professional: New York, 2002; p 1086.
19. P. D. Smith, R. E. Berry, S. M. Harben, R. L. Beddoes, M. Helliwell, D. Collison and C. David Garner, *J. Chem. Soc., Dalton Trans.*, 1997, 4509–4516, DOI: 10.1039/A703683C.