

Metal complexes with oxyiminodicarboxylate ligands - characterization and their potential applications in batteries

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Abstract

Preliminary studies on batteries that can optimize the use of renewable energy sources were carried out based on amavadin natural compound. After confirming the stability of the aqueous amavadin-analogous compound with a molybdenum metal centre, a new battery concept was developed, in which one electrolyte is a vanadium (V_{4+}) complex and the other the corresponding complex of molybdenum (Mo_{5+}). Single crystal X-ray characterization of two molybdenum compounds was achieved. It turned out that these molybdenum compounds are stable at a limited pH range, i.e. mildly acidic. In parallel, an analogous compound with the tungsten metal centre was characterized. Although not incorporated in the batteries, it has interest from coordination chemistry point of view, since this compound was not yet known.

Spectroscopic studies of the vanadium complex were carried out, concluding that radiation has an effect on the oxidation-reduction reaction, mainly in the range 500-560 nm, corresponding to green radiation.

In the design of the batteries, silica-based membranes were improvised. Several support electrolytes were tested, concluding that the most suitable for vanadium complex electrolyte solutions is $NaHSO_4$, as it maintains the pH of the solution ca. 2 and for molybdenum electrolyte solutions is the H_2PO_4K , as it maintains the pH of the solutions ca 5.

An innovative concept developed was membraneless batteries based on aqueous and water-immiscible solvents.

Keywords: Energy; Redox flow battery; Vanadium; Molybdenum; Tungsten; X-ray diffraction; visible spectroscopy;

One of the biggest concerns nowadays are climate changes. One of the actions that are being taken to mitigate this situation is the reduction of the CO_2 emissions (Paris Agreement)¹. In order to replace fossil energy by renewable energies it is necessary to store energy, since the energy generated from renewable sources is not constant (wind energy for example) over time. A simple way to solve this could be storing energy in batteries when renewable energy is produced in excess and it would be supplied when it is necessary.

The greatest purpose of this Project is the development of batteries for optimization the use of energy from renewable sources.

However, the batteries conceived are still in small-scale laboratorial tests. They were inspired in a natural system of amavadin, a vanadium complex with redox properties^{2,3}, alongside with redox flux batteries, since with vanadium are having the better performances^{4,5} and subsequently more application. In the studies carried out, priority was given to electrolytes in aqueous solution, as it is less harmful to the environment and have fewer costs.

Amavadin is formed by reaction of oxovanadium(IV) and the corresponding

proligands. In this project were used the related proligands *N*-oxyiminodiacetic acid (H_3HiDA) and *N*-oxyimino(2,2')-dipropionic acid (H_3HiDPA), figure 1.

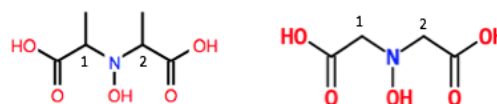
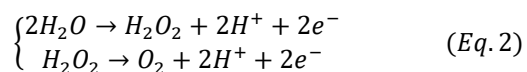
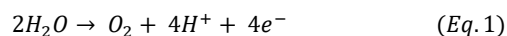


Figure 1-proligand H_3HiDPA (left) and H_3HiDA (right)

The ligands of the studied complexes are non-innocent because they participate in the reactions². They are already known with capacity to oxidize water (following eq. 1 and 2), being $VHiDPA$ more efficient.



This project was developed in three parts, in the first part verifies the stability of bis-(*N*-oxyimino-(2,2') dipropionic) molybdate complex ($MoHiDPA$) and bis-(*N*-oxyiminodiacetic) molybdate complex ($MoHiDA$) in aqueous medium at moderately acidic pH values, by obtaining crystals of two

complexes and their characterization by single crystal X-ray diffraction. Tungsten crystals analogues to amavadin complex were also obtained and their structure determined, which is novel.

In the second part the oxidation/reduction reaction of the vanadium complex (VHiDPA) was studied by visible absorption spectroscopy. The influence of visible radiation on the reaction was tested, as well as its behaviour in the presence of salts in order to serve as support electrolytes for the batteries.

Thirdly, it was based on the design and preliminary studies for assembling a battery, thereby creating a new concept of batteries containing vanadium.

Various solvents, however emphasizing water, have been used to make these batteries as non-polluting as possible.

Experimental Part

Materials and Analytical Methods

All reactants were purchased from Baker, Sigma-Aldrich, EKA Chemicals, Panreac, ReagentPlus and BioREagent and used with no further purification. Tungsten trioxide was synthesized according to the procedure described by⁷ and zinc complexes of HiDA and HiDPA were synthesized according to the procedures.

SCRXD data were collected with a Bruker AXS-KAPPA APEX II monocrystal diffractometer with *graphite-monochromated radiation* (Mo $K\alpha$, $\lambda = 0.71073 \text{ \AA}$) at 293 K. The programs SHELXT⁸ and SHELXL-97⁹ were used for data solution and refinement, respectively. All programs are included in the package WINGX-Version 2014.1^{10,11} Illustration of molecular structure done by the program ORTEP.

Visible absorption spectra were collected with a PerkinElmer Lambda 35 in a range of 450-800 nm. The programs PerkinElmer UV WinLab and UV WinLAB Data Processor & Viewer were used for data collection and viewer, respectively.

Multimeter from Velleman we used to check the ddp, R and i of batteries.

Complexes of molybdenum and tungsten with HiDA and HiDPA

Samples with 2,5:1 ratio of proligand:metal were prepared using the ligand HiDA and

HiDPA and a mixture of 1/3 of molybdenum trioxide and 2/3 of Na_2MoO_4 for the molybdenum solutions. 1/3 of WO_3 and 2/3 Na_2WO_4 for solutions of tungsten. In the crystallization tests counter ions (such as tetramethylammonium chloride [TMA], tetrafenylarsenium(V) chloride hydrate [TPA] and tetrafenylphosphonium bromide [TPh]) were added.

Complexes of vanadium with HiDPA for spectroscopy study

The spectroscopy studies had the objective of testing the stability of the complex which it will be used as an electrolyte for the batteries. Studies have been performed to verify the influence of light radiation on the complex in order to optimize future battery conditions.

For the spectroscopy assays of the complex VHiDPA, solutions contained a 2:1 ratio of proligand:metal using vanadium as VO_2^{+} . All samples were prepared in aqueous solution and at room temperature.

In the study of light radiation, several tests were performed, where a sample was irradiated without a direct source (VPA1), other with direct radiation (VPA1.1) and other with total absence of radiation (covered by an aluminium foil) (VPA1.2). Some other assays were also made for samples irradiated to certain wavelengths by covering with coloured filters protection (VPAG, for green filter; VPAR, for red filter; VPAR+B, for red + red bleu). In this study, potassium chlorate, KClO_3 was the oxidant.

Additional spectroscopy studies were also carried out with salts (sodium sulphate Na_2SO_4 in VPAS, and sodium bisulphate NaHSO_4 , in VPA2S) with the aim of their application as support electrolytes in batteries. These salts were used taking into account the verification, by theoretical calculations, that sulphate (and/or bisulphate) participates in the water oxidation mechanism by amavadin models¹². The oxidant used in this test was NaNO_2 , since this conclusion was taken with it.

Batteries

-Preparation of membranes

Silicate membranes were prepared by adding Na_2SiO_3 to a solution of NaHSO_4 . These solutions form a gel in a pH range of

6 to 9¹³. It was prepared a salt bridge with a pH ca. 6 and another ca. 9. The salt bridges were prepared with a 5 cm tube filled with these gel solutions and for membranes only 1 cm in the middle tube was filled with these gel solutions.

Silica membrane was prepared using a solution of concentrated sulphuric acid added to a solution of Na₂SiO₃ until pH ca. 3. Then the solution was heated at 60 °C, until viscosity of solution increased by moderate water evaporation. After that, it was left to dry at room temperature. The obtained solid was compressed inside the tube to form the membrane. Small balls of cotton soaked in the electrolytic solutions were added to the tip of the membrane.

Clay membranes were prepared by mixing a solution of NaHSO₄ with clay (green and white) left to dry and then inserted and compressed into the tube. In this case small balls of cottons were also added to the tip of the membrane.

-Preparations of electrolytic solutions

Molybdenum complex electrolytic solution were prepared in a 2,5:1 ratio of proligand:metal. All samples were prepared in aqueous solution and at room temperature. Na₂SO₄ and H₂PO₄K were added to the solutions to test them as support electrolytes. L-serine as added to other solution as a suppressor of the molecular hydrogen formation¹⁴.

Vanadium complex electrolytic solution were prepared in a 2:1 ratio of proligand:metal. Samples were prepared in water, DMSO, DMF, 2-pentanone, 3-pentanone and 2-octanone. Transfer agents were added to ketones to increase the solubility of the complex in these solvents.

NaHSO₄ were added to samples as support electrolyte and L-cysteine were added to other solutions as a suppressor of molecular oxygen formation.

Assembling of batteries

The batteries have been assembled with the elements prepared above, in which a salt bridge or membrane and two electrolytes solutions have been chosen. If both

solutions are aqueous, the metal centre of the complexes are different, if it is with an aqueous solution and another with an aprotic solvent, vanadium complexes are used in different oxidation states.

The batteries were grouped according to tested conditions.

Group 1: Salt bridge versus membrane;

Group 2: Addition of the support electrolytes to the electrolyte solutions;

Group 3: Membranes material;

Group 4: The effect of amino acids on electrolyte solutions performance;

Group 5: H₃HiDA proligand instead of H₃HiDPA, to test reaction rate;

Group 6: Complexes with the same metal centre (vanadium) in different solvents, aqueous solvent/water miscible aprotic solvent (DMSO; DMF);

Group 7: Complexes with the same metal centre (vanadium) in different solvents, aqueous solvent/water-immiscible aprotic solvent (ketones).

Results and Discussion

Complexes of molybdenum and tungsten with HiDA and HiDPA

MoHiDPA, MoHiDPA and WHiDA crystals were obtained using TPA, TPh and TPA as counterions, respectively, and were identified was Hi₃, PA₃, W₄i₃. The crystallographic data are presented in table 1 and the illustrations generated by ORTEP are shown in figure 2.

The application of molybdenum complexes in aqueous solution, in pH range of [5-7] values, as battery electrolytes appears as a possibility to be tested.

ORTEP¹⁵ illustration of MoHiDPA complex (PA₃) shows one of the ligands is in the form (R,S) and the other ligand was not possible to determinate its stereochemistry. This could be a consequence of the racemic mixture of proligand used in synthesis.

Regarding the novel tungsten complex obtained, it is proved that this metal also has the ability to coordinate without having a double oxygen bond, unlike the one previously obtained¹⁶ for the complex prepared from HiDPA proligand.

Table 1-Crystallographic data from Hi3, PA3 and W4i3

	Hi3	PA3	W4i3
Empirical formula	C ₃₂ H ₂₈ MoN ₂ O ₁₀ As	C ₃₀ H ₃₆ MoN ₂ O ₁₀ P	C ₃₂ H ₂₈ WN ₂ O ₁₀ As
Molecular mass	769.2	711.4	857.16
Temperature	Room temperature	150K	Room temperature
Crystalline system, space group	Orthorhombic, Pna2(1)	Orthorhombic, P212121	Orthorhombic, Pna2(1)
Unit cell dimensions	a=7.9908(20) α=90.044(30) b=15.9644(30) β=90.074(30) c=25.7164(50) γ=90.044(30)	a=9.051(11) α=90.000 b=13.5408(16) β=90.000 c=29.2010(37) γ=90.000	a=8.0170(14) α=90.000 b=16.006(28) β=90.000 c=25.7534(48) γ=90.000
Volume (Å ³)	3280.59	3578.45(8)	3300.97
F(000)	235.0	2096.0	1632.0
Crystal Dimensions (mm)	0.2 x 0.2 x 0.4	0.2 x 0.3 x 0.3	0.1 x 0.2 x 0.5
Limiting Indexes	-9<h<9 -18<k<18 -30<l<30	-12 < h < 7 -15 < k < 17 -36 < l < 38	-10 < h < 7 -20 < k < 20 -32 < l < 32
Collected Reflections / Unique Reflections	154622/5783 (R(int)=0.1417)	17669/8096 (R(int) = 0.0805)	32047/6704 (R(int)=0.2711)

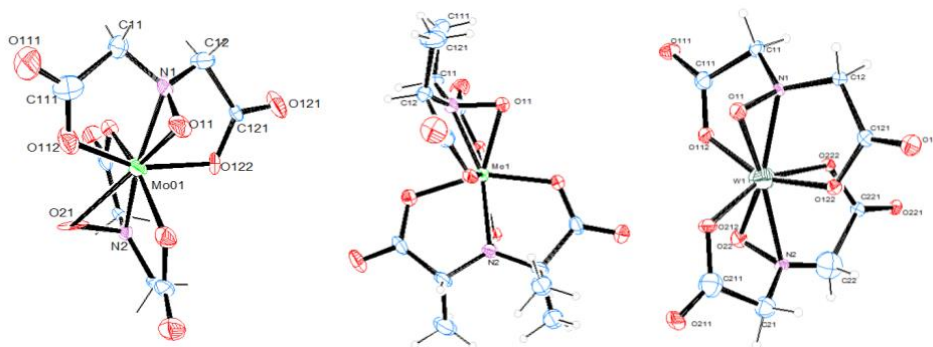


Figure 2-Illustration generated by ORTEP¹⁵ of Hi3 (left), PA3 (middle) and W4i3(right)

Complexes of vanadium with HiDPA

The complex VHiDPA in reduced form has a lilac colour and in the oxidized form has a red colour. It was decided to use absorption spectroscopy in the visible region to study the behaviour of the VHiDPA complex and stability in different ranges of visible radiation, influence of the addition of salts to study the possible reduction of the inhibitory effect of solvent in the oxidation reaction¹⁷ of water and their potential application as electrolytes support the solutions later used in batteries.

Although VPA1 showed an increased wavelength absorption of 763 nm, its higher absorption band remains at a wavelength of 563 nm, figure 3.

Sample VPA1.2 keeps the final spectrum after oxidation more similar to the initial one, therefore, in this case the complex has less level of degradation, figure 3.

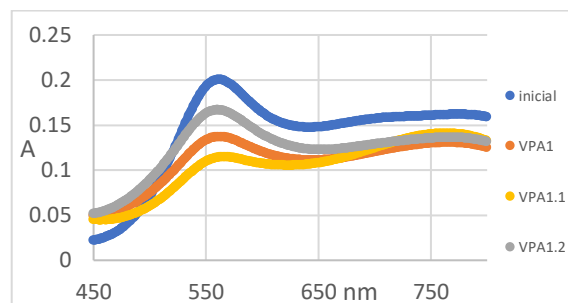


Figure 3-Absorption visible spectra of VPA1, VPA1.1, VPA1.2, optical length 1 cm

VPA1.1 has its highest absorption band at 763 nm, and it can be concluded that this sample contains the highest VO₂⁺ among those presented (the maximum wavelength related to this species is 762 nm).

It can be established that the irradiation with whole visible spectral range accelerates the redox reaction, both in the oxidation of the complex and its reduction, despite favouring a greater degradation of the complex.

After these conclusions, the VPA1 sample was placed outside, under direct solar radiation and instantly turned yellow,

indicating the degradation of the complex. This corroborates that every visible spectrum cycle increases the degradation of the complex. This solution was evaporated and an orange solid that must be a decavanadate salt¹⁸.

-Coloured filters:

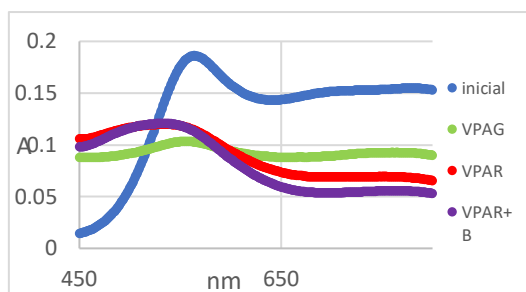


Figure 4-Absorption visible spectra of VPAG, VPAR, VPAR+B, optical length 1 cm

At the end of the third cycle of oxidation, it can be observed that the shapes of the spectra, figure 4, do not coincide with the shape of the initial spectrum, showing the degradation of the complex. The VPAG sample does not have the complex band at 563 nm, as well as the VPAR and VPAR+B samples. However, the latter two have a higher absorbance at 530 nm and may indicate a mixture of VHiPDA complex species as reduced, with species of the complex in oxidized form and side species formed by redox reaction.

Support electrolytes:

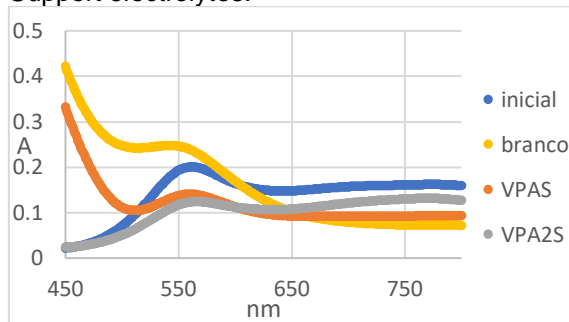


Figure 5-Absorption visible spectra of VPAb, VPAS, VPA2S, optical length 1 cm

As expected, the “blank” and VPAS spectra differ greatly from the initial one. They still have a band at 560 nm, figure 5, relative to the complex, but appear to have another in the UV region. A UV spectrum was performed on these samples, but no band was detected and the absorbance values at 400 nm were saturated.

The solutions were diluted in order to decrease saturation¹⁹, however it was not

possible to obtain a spectrum in the UV region.

The VPA2S sample in which the support electrolyte was sodium bisulphate, NaHSO_4 , presents a similar spectrum to the initial one suggesting that this electrolyte contributes to the stability of the complex after several oxidation cycles, figure 5, therefore, this is the most suitable for batteries

Since the complexes formation causes an acidification of the solution, and under these conditions NaHSO_4 in solution, as consequence of pKa_2 of sulphuric acid. In the oxidation reaction of water, H^+ is consumed, causing a rise in pH. In this way, the pH rises slowly and at the same time the complex begins to degrade and the concentration of free oxovanadium in the solution begins to increase. According to²⁰, when the pH approaches 4 and if the vanadium remains in oxidation state 4, oxovanadium hydroxide species precipitate. NaHSO_4 helps maintain acidic pH. It is a buffer at pH ca. 2. Based on these results it is possible to assume that NaHSO_4 can have two roles in the batteries, acting as a support electrolyte because it carries charge and also functions as a buffer, necessary to extend the vanadium complex stability over time.

Batteries

Group 1: Salt bridge versus membrane;

The ddp values obtained with the salt bridge with pH near to 6 were ten times higher than the values obtained with the salt bridge with pH near 9

Group 2: Addition of the support electrolytes to the electrolyte solutions;

The values of ddp cell without electrolyte support were very unstable unlike the cell with support electrolytes. Therefore, the addition of support is very important to maintain the stability of batteries.

Group 3: Membranes material;

The resistance value obtained with the acid membrane cell it was the lowest in this group.

This result indicates that a more acid membrane, leads to a lower resistance value.

Group 4: The effect of amino acids on the electrolyte solutions performance;

The addition of amino acids to the electrolyte solutions caused ddp and resistance values to remain constant longer (four times longer under our experimental conditions) than cells without amino acids.

It indicates that the instability caused in cells without amino acids could be from the agglomeration of gas bubbles in the electrode from reduction and oxidation of water.

L-cysteine prevents the formation of molecular oxygen by reacting with peroxide formed in the water oxidation reaction (Eq.2).

An assumption made, is that the product due to the addition of L-serine is serinol, due to a hydrogenation reaction according to¹⁴.

Group 5: HiDA proligand instead of HiDPA, to test reaction rate;

The results obtained with the HiDA proligand were not sufficient to state that the reaction rate is higher, as well the efficiency of the battery.

Group 6: Complexes with the same metal centre (vanadium) in different solvents, aqueous solvent/water miscible aprotic solvent (DMSO; DMF);

The ddp and R values after 48 h of assembly have fallen to the point where it is not promising to maintain them. The volume of solutions has drastically reduced (from 0.5 mL to 0.15 mL), which is unusual for solvents with boiling points above 100 °C²¹. Once again, we have the indication that the solvents are consumed in the reduction reaction of the complex.

Group 7: Complexes with the same metal centre (vanadium) in different solvents, aqueous solvent/water-immiscible aprotic solvent (ketones).

The transfer agent used in the ketone solutions was TPA, that it was available in the laboratory. TPA was tested on a smaller scale, which also worked, and it is cheap. TMA is not suitable for this purpose.

After 72 h stirring of the solution with the 2-octanone solvent a red precipitate formed, however the solution remained clear,

indicating that the VHiDPA complex formed but did not dissolve in the solvent, therefore this solution was not used.

The solutions with the solvents 2-pentanone and 3-pentanone turned red (indicating that the complex is at oxidation state five) after 48 h stirring indicating that the complex dissolved in the solvent.

The great advantage of this assembly is the absence of membrane. Since the water and ketones are immiscible, the interphase between the two electrolytes allows proton diffusion could lead to less resistance than the all membrane-mounted cells. Different contact areas between the solutions were tested to verify if the influence on the resistance. However, the expected low resistance was not verified²². Complementary studies are required.

Another interesting aspect of this cell is that the ketone volume decreases very quickly (0.2 mL in 30 min), 3-pentanone has a boiling point of 109 °C²¹ leading us to believe that the solvent is sacrificed in the reaction.

Final Remarks

Salt bridge or membrane should be acidic for the proposed concept. It has also been proved that the addition of support electrolyte to the solutions is also important. The membrane constituent material needs further study and a more reliable procedure, as reproduction is not easy as they may differ in composition, as well as pH value. Although clays are used in BFR membranes²³, the tested clays are not appropriate, since adding the NaHSO₄ solution to the green clay started a reaction that gave rise to a lot of foam and gave off a characteristic smell of hydrogen sulphide. This is from a significant ferrous oxide content of this clay, and the odour produced by the bisulphate ion was probably reduced by ferrous oxide, generating hydrogen sulphide.

NaHSO₄ is really the most appropriate support electrolyte to vanadium electrolyte solutions, and to molybdenum solutions the best was H₂PO₄K. pH values are a very important factor to consider in future studies. The volume of battery electrolyte solutions described above has decreased considerably, indicating a solvent consumption. We present an assumption for a reaction scheme in which the vanadium complex reduction leads to water oxidation and release molecular oxygen and the

molybdenum oxidation would mediate molecular hydrogen production from water reduction, see figure 6. For simplification of the figure, the complexes are not presented but only their metal centre and oxidation state.

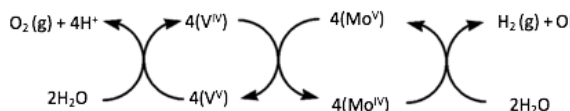


Figure 6- Reaction system hypothesis

Initially, it was intended to obtain molecular hydrogen and molecular oxygen. However, because small gas bubbles were observed around the electrodes (and also the very rapid reduction of the potential difference between the two solutions), it was found that they would prevent contact with the solution and consequently the energy flow and instability in the electrodes as observed in ddp and R values overtime.

The results of the cells with amino acids addition in order to eliminate the effect of gas formation led to a stabilization of ddp and R over time. L-serine was added on the molybdenum electrolyte side probably underwent a hydrogenation reaction, consuming molecular hydrogen could produce serinol¹⁴, further studies will be needed to confirm this hypothesis.

Resistance will need to be reduced and contact between electrolyte solutions will need to be reevaluated. On the other hand, to increase the value of current intensity, it would be convenient to accelerate the oxidation rate of water by the vanadium complex. In this case two hypotheses can be put:

1- Study the complex with the H₃HiDA proligand better, because the reaction is faster, but the complex degrades faster; can the effect of light radiation help? Studies in this regard must be done;

2- Accelerate the reaction with the studied complex by reducing the water content or taking into account the effect of light radiation.

The use of water miscible aprotic solvents (DMSO, DMF) makes the battery less green (environmentally friendly), perhaps not the best approach, but it may be inspiring new solutions, just as the use of water immiscible aprotic solvents is an interesting new concept as it removes one of the most costly elements of BFRs. Further studies are needed to pursue this.

The developed concept, besides its potential applicability to flow batteries, allowed to raise new hypotheses, such as:

Create conditions for the electrolysis of water, producing molecular oxygen and hydrogen without high energy expenditure;
2- Test hydrogenation reactions under ambient pressure and temperature;
Reactions hypotheses for systems have to be verified, as new synthesis methods may be discovered, which could have applications in synthesis of hydrogenated compounds with higher added value.

3. Since the reduction reaction of organic solvents should be radical, since vanadium varies only from one oxidation unit, these groups could be functionalized with appropriate reagents, which could pave the way for new synthetic procedures.

4- Different wavelengths of radiation on the cells to check reaction rate, as it has been shown that the reaction of the vanadium complex occurs faster rate with radiation in the green wavelength range;

5- Test other complexes that have high stability and electrochemical behaviour suitable for their use in batteries;

6- Regarding the membranes used in the batteries, improvements will be necessary, because as stated above, their reproducibility is not easy and the resistance values obtained were still very high; An interesting material to be tested would be based on, where the starting material is eggshell, which treatment it can be used as a membrane; The membrane-free battery is a point that should be given close attention as the cost of membranes in BFV is very high.

A new concept has been developed and further studies are needed.

References

1. E. Union, Conselho Europeu- Acordo de Paris sobre as alterações climáticas, 2019. [Online]. Available: <https://www.consilium.europa.eu/pt/policies/climate-change/timeline/>. [Accessed: 04-Oct-2019].
2. J. A. L. Da Silva, J. J. R. Fraústo da Silva, and A. J. L. Pombeiro, Amavadin, a vanadium natural complex: Its role and applications, *Coord. Chem. Rev.*, vol. 257, no.

- 15–16, pp. 2388–2400, 2013.
3. D. Rehder, *Bioinorganic Vanadium Chemistry*. 2008.
 4. A. Parasuraman, T. M. Lim, C. Menictas, and M. Skyllas-Kazacos, Review of material research and development for vanadium redox flow battery applications, *Electrochim. Acta*, vol. 101, pp. 27–40, 2013.
 5. T. Nguyen and R. F. Savinell, Flow batteries, *Electrochem. Soc. Interface*, vol. 19, no. 3, pp. 54–56, 2010.
 6. H. Kneifel, E. Bayer, and E. Koch, Synthesis of New Complexons: N-Hydroxy- α,α' -Iminodipropionic- and N-Hydroxyiminodiacetic Acid, *Zeitschrift fur Naturforsch. - Sect. B J. Chem. Sci.*, vol. 41, no. 3, pp. 359–362, 1986.
 7. S. K. Maiti, S. Banerjee, A. K. Mukherjee, K. M. A. Malik, R. Bhattacharyya, and P. Place, Oxoperoxo molybdenum(VI) and tungsten(VI) and oxodiperoxo molybdate(VI) and tungstate(VI) complexes with 8-quinolinol: synthesis, structure and catalytic activity, *New J. Chem.*, vol. 29, pp. 554–563, 2005.
 8. Sheldrick, G.M, SHELXT - Integrated Space space-group and crystal determination. *Acta Crystallographica a-Foundation and Advances* 2015, 71. pp. 3–8.
 9. Sheldrick, G. M., Crystal structure refinement with SHELXL. *Acta Crystallographica Section C- Structural Chemistry* 2015, 71. pp. 3–8.
 10. Farrugia, L., WinGX and ORTEP for windows: an update. *Journal of Applied Crystallography* 2012,45. .
 11. Farrugia, L. WinGX Suite for Single Crystal Small Molecule Crystallography. *Journal of Applied Crystallography* 1999,32, 837-838.
 12. L. Dias, N. Bekhti, M. L. Kuznetsov, J. A. B. Ferreira, M. C. Bacariza, and J. A. L. da Silva, Nitrite Reduction in Aqueous Solution Mediated by Amavadin Homologues: N₂O Formation and Water Oxidation, *Chem. - A Eur. J.*, vol. 24, no. 10, pp. 2474–2482, 2018.
 13. A. C. Franco Banha, Estudo de Meios Pré-biológicos Contendo Silicato e Borato, Instituto Superior Técnico, 2017.
 14. S. G. Bhandare and P. D. Vaidya, Kinetics of Hydrogenation of Serine and Glutamic Acid in Aqueous Solution over a Ru/C Catalyst, *Ind. Eng. Chem. Res.*, vol. 56, no. 14, pp. 3797–3803, 2017.
 15. L.J. Farrugia, ORTEP. *J. Appl. Crystallogr.* 30, 1997.
 16. M. T. Domarus, Studies with Amavadin and related complexes, Instituto Superior Tecnico, 2014.
 17. T. O. N. Hubregtse, amavadin-BASED VANADIUM COMPLEXES, Delft, 2007.
 18. G. K. J. and R. K. Murmann, Sodium and ammonium decavanadates(V), *Inorg. Synth.*, vol. XIX, no. V, pp. 140–145, 1979.
 19. H. Günzler and A. Williams,

- Handbook of Analytical Techniques*,
1st Editio., vol. 23, no. SUPPL. 34.
2001.
20. L. Vilas Boas and J. Costa Pessoa,
Vanadium, *Comprehensive
Coordinatin Chemistry- The
synthesis, Reactions, Properties and
Applications of Coordination
Compounds*. Pregamon Press, p.
500.
21. U.S. National Library of Medicine,
PubChem, 2019. [Online]. Available:
<https://pubchem.ncbi.nlm.nih.gov>.
[Accessed: 25-Oct-2019].
22. D. Halliday, R. Resnick, and J.
Walker, *Fundamentals of Physics*,
Volume 1, 10th editi. Jearl Walker
Cleaveland State University, 2007.
23. K. K. Jana, S. J. Lue, A. Huang, J.
F. Soesanto, and K.-L. Tung,
Separator Membranes for High
Energy-Density Batteries,
ChemBioEng Rev., vol. 5, no. 6, pp.
346–371, 2018.