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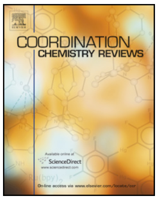

Review

A journey into the electrochemistry of vanadium compounds

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Contents

Abbreviations: Ac, acetyl CH_3CO; DCM, dichloromethane; DMSO, dimethylsulfoxide; EGH_2, 1,2-ethanediol (ethylene glycol); FcH, ferrocene; imz, imidazole; MeCN, acetonitrile; $MeNO_2$, nitromethane; PC, 1,2-propanediol carbonate or propylene carbonate; pic, methylpyridine (picoline); Tf, trifluoromethanesulfonate (triflate); THF, tetrahydrofuran; CPE, carbon paste electrode; FTO, fluorine doped tin oxide; NHE, normal hydrogen electrode; SCE, saturated calomel electrode; DPV, differential pulse voltammetry; FESEM, field-emission scanning electron microscope; NPV, normal pulse voltammetry; SEM, scanning electron microscope; TEM, transmission electron microscope; XAS, X-ray absorption spectroscopy.

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ABSTRACT

Vanadium is an element with a fascinating history, a widespread diffusion in bacteria and eukaryan organisms, and rich coordination chemistry. The properties of vanadium compounds attracted the interest of researchers in different fields, such as biochemistry, medicinal chemistry, and catalysis, leading to several reviews. However, although the rich and varied chemistry of vanadium was acknowledged to be due to the variety of easily accessible oxidation states, no review was devoted – to the best of our knowledge – to electrochemical properties of vanadium compounds. The present review aims at filling this lacuna, presenting a survey of electrochemical data related to vanadium compounds, starting from the eighties of the last century until mid 2014. The data are organized in tables, with experimental information necessary for comparisons, according to oxidation states of vanadium, beginning with the largest set, that is that of vanadium(IV) compounds and, within this set, on the basis of ligand coordinating atoms. The original ligands abbreviations were kept, when possible, or adapted, according to recent IUPAC recommendations. We hope to offer the reader a comprehensive – if not complete – overview of electrochemistry of vanadium compounds and to make relatively easy to retrieve the desired information. What is evident is the variety and versatility of vanadium compounds also in redox processes.

1. Introduction

Vanadium is an element with a fascinating history [1], a widespread diffusion in bacteria and eukaryan organisms [1], and a rich coordination chemistry, as it can be inferred even from old reviews [2]. The properties of vanadium compounds attracted the interest of researchers in different fields, such as biochemistry, medicinal chemistry, and catalysis, leading to several reviews. To cite a few of them, even limiting the period to the years from 2010 to 2014, reviews appeared on the natural occurring vanadium complex amavadin [3], on enzymatic and biochemical properties [4–7], on medicinal chemistry [8–11], and of course, on chemical aspects, i.e., synthesis and reactivity [12,13], catalysis and mechanisms [14–20].

Strangely enough, although the rich and varied chemistry of vanadium was acknowledged to be due to the variety of easily accessible oxidation states, no review was devoted – to the best of our knowledge – to electrochemical properties of vanadium compounds. For example, in 1992 a review dealing with soluble metal oxides of molybdenum and vanadium had a section discussing electrochemistry [21], but only molybdenum species were considered. The present review aims at filling this lacuna, presenting a survey of electrochemical data related to vanadium compounds, starting from the eighties of the last century. Although we cannot be sure that all the published data (and we apologize if some is missing) are reported, also because very often the electrochemical information is embedded in papers discussing other aspects, we believe we are presenting a panorama as complete as possible of electrochemical properties of vanadium compounds. The data are organized according to oxidation states of vanadium, beginning with the largest set, that is that of vanadium(IV) compounds.[1]

The original ligands abbreviations were kept, when possible, or adapted, according to recent IUPAC recommendations. However, they are too many to be listed as a footnote. Therefore, a list of abbreviations is presented at the end of the review. The same abbreviations appear under the ligands formulae. Literature is covered from 1980 until mid 2014.

2. Electrochemistry of vanadium(IV) compounds

Electrochemical studies on vanadium compounds date back to early seventies of the last century, when data were collected to understand the structure in solution of new compounds. For more than a decade, Riechel and Sawyer – separately or together – published a number of papers, where electrochemistry was performed on vanadium derivatives with ligands that could provide model complexes, in order to mimic the chemistry of biologically relevant transition metals containing species [22–24].

In some cases the complexes were not isolated, but investigated in solution, such as in the case of oxido-vanadium(IV) gluconate [24], that showed an one-electron oxidation at 0.118 V (vs SCE) at pH 6 and at −0.280 V in 0.5 M NaOH, respectively. In earlier papers, Riechel investigated complexes of V(III), oxido-V(IV), and oxido-V(V), comparing the results obtained with different ligands for each oxidation state. Later, the attention was focused on oxido-V(V) species with tetradentate ligands (vide infra, Section 3.1).

2.1. Oxido-vanadium (IV) species

2.1.1. Complexes with bidentate ligands

The electrochemistry of VOL_2 complexes, with L = bidentate monoanionic ligand, appeared to be strongly influenced by the nature of bonding atoms and the ring size (metal to bidentate ligand), as inferred by comparing potentials of $VO(quinol)_2$, $VO(etdtc)_2$, $VO(acac)_2$, and $VO(sesa)_2$ in Table 1 ([22,23,25,26], entries 1–4, structures and abbreviations in Chart 1, in alphabetical order of abbreviations).

After Riechel's pioneering work, numerous bidentate ligands were used to prepare oxido-vanadium(IV) compounds. *O-O* bidentate ligands as catecholate and the corresponding 3,5-di-*tert*-butyl derivative were used. Complexes of the type VOL_2^{2-} were prepared with 3,5-di-*tert*-butylcatecholate [27] and used in a detailed electrochemical investigation in solution. Results are collected in Table 1 (entry 5). The cyclic voltammograms for $[VO(^tBucat)_2]^{2-}$ were performed in DCM and MeCN, with the same general appearance, even though substantially different potentials for the various electrochemical processes were found. Controlled-potential electrolysis at the peak potential removed one electron per complex to yield a product with the same UV-visible spectrum in both solvents, that was identified as the oxido-V(V) species, $[VO(^tBucat)_2]^{-}$. Oxido-V(V), non-oxido V(IV), and V(III) species were also prepared with the same ligand (see Tables 3 and 5).

Following the studies of catecholato complexes and in view of testing possible anti-proliferative effect against cancer cells,

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[1] The reader, not to get lost among the different reference electrodes, may keep in mind that potentials vs NHE are, roughly, 0.2 for AgCl/Ag, 0.24 for SCE, and 0.4-0.7 V for FcH^+/FcH. However, different solvents, supporting electrolytes and even their concentration can affect potential values significantly, especially as far as ferrocene is concerned (N.G. Connelly, W.E. Geiger, Chem. Rev. 96 (1996) 877).