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Electrochemical behaviour of Vanadium(V) on electrochemically synthesized magnetite film electrodes

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ABSTRACT

In this work, the electrochemical response of Vanadium(V) species on magnetite film electrodes is investigated. Magnetite is deposited electrochemically on glassy carbon electrodes, with an intermediate layer of poly(thiophene) to avoid water infiltration. These electrodes show good reproducibility and stability up to pH = 2.0. Mononuclear V(V) species show low electroactivity on this surface. Cyclic voltammetry at low V(V) concentration shows that it is electroactive only at pH < 3. i.e. as VO_2^+. A single reduction peak is observed at ~ − 0.7 V vs SCE (at 50 mV s^{-1}), and an oxidation one at ~0.5 V vs SCE, indicating high irreversibility of the V(V)/V(IV) couple; these peaks are found to be solution phase reactions. These features are interpreted in terms of mononuclear V species. At higher V concentrations, where polymeric V(V) species are dominant, a somewhat higher electroactivity is observed, with two reduction peaks and two/three oxidation peaks.

1. Introduction

Magnetite is unique among the iron oxides because of its conducting and magnetic properties [1]; its magnetism is the basis of a number of simple methods for removal of arsenic, a well-known toxic element, from natural waters. These methods are generally based on the adsorption of As anionic species onto the oxide following extraction of the Fe_3O_4 particles via a magnetic field [2–5]. Vanadium is another element commonly found in groundwater, and is potentially harmful to humans [6]; moreover, it often correlates positively with arsenic [7]. Vanadium, usually found as anionic species, can also adsorb onto iron oxides, and V removal using a Fe oxohydroxide has been reported [8,9]; thus V, besides its own toxicity, is a potential interference in As removal using iron oxides. Consequently, the knowledge of the interaction of V species with iron oxo- or oxohydroxides, including redox behaviour, is important to understand the competence of As and V and ultimately such remediation methods.

There are very few studies of V adsorption onto iron oxides. Jin et al. [10,11] studied by density functional theory (DFT) the adsorption of V onto idealized hematite crystal faces, concluding that it forms mainly threefold bonds with O atoms. Peacock and Sherman [12] investigated experimentally and theoretically the adsorption of V(V) species onto goethite; EXAFS measurements indicated the presence of bidentate inner-sphere surface complexes, attributed to corner-sharing species through DFT ab-initio calculations. On the basis of such results a surface complexation model was proposed that predicted satisfactorily the adsorption edge experiments.

The electrochemistry of Vanadium has received more attention. This element has a complex redox-pH behaviour (Fig. 1) [13] which reflects in its electrochemical response. Israel and Meites [14] studied by polarography, amperometry and chronocoulometry the reactions between V(II), V(III), V(IV) and V(V) species, concluding that the formation of polynuclear species led to the complex behaviour observed. Goto and Ishii [15] studied the chronopotentiometry of V(V) in phosphoric acid solutions, reporting the presence of two couples, V(V)/V(IV) and V(IV)/V(III), reversible and irreversible, respectively. The V(III)/V(II) couple was investigated by several authors [14,16,17] and generally considered reversible; the V(IV)/V(III) couple, on the other hand, was reported to be reversible on Pt but irreversible on Hg [18]. The electrochemical response of metallic V has also been studied [19,20]. There are no reports, to the best of our knowledge, on the electrochemistry of V on non-metallic surfaces.

The electrochemistry of magnetite has been studied quite extensively, mostly in connection with its role in iron passivity and corrosion; also, the oxygen evolution on Fe_3O_4 surfaces has received attention in the literature ([21,22] and references therein). Albeit most studies have been conducted in alkaline media, in acidic media it was found, at pH = 1, a relatively low polarization current between oxygen

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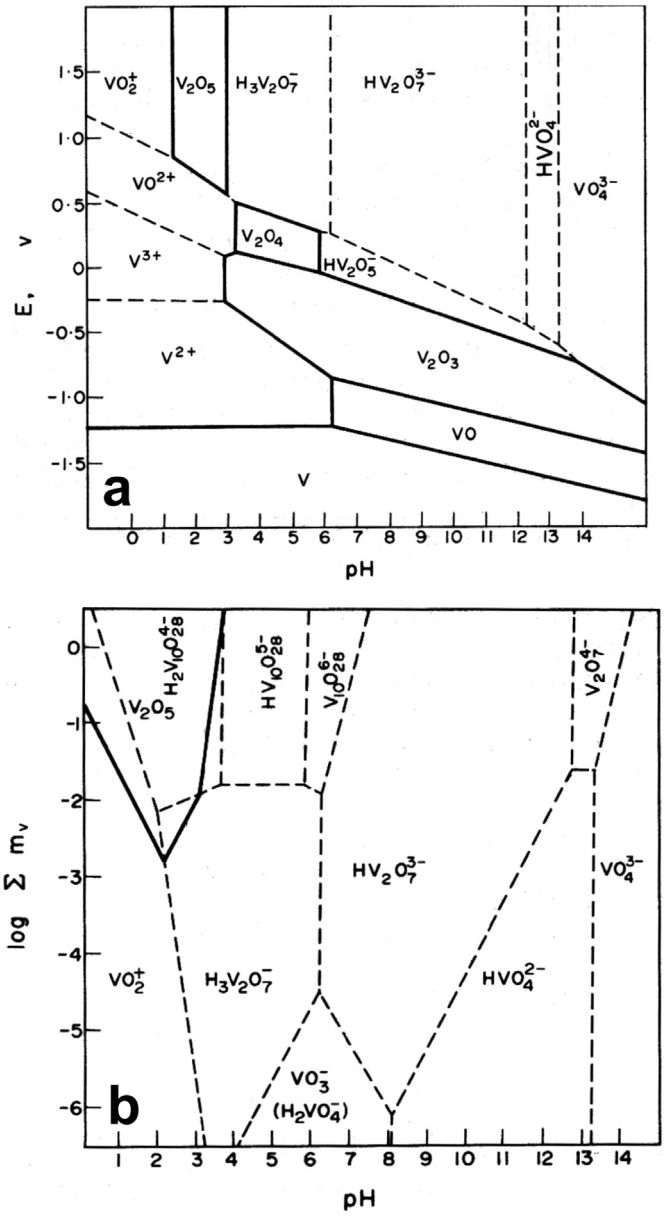

Fig. 1. (a) The potential/pH diagram for the vanadium-water system at 298.15 K and total V concentration of 0.01 m; (b) Log(total concentration) vs pH diagram for the V(V) system at 298.15 K. Reprinted from Ref [13], with permission from Elsevier. Copyright Elsevier 1976.

evolution at about -1.9 V and hydrogen evolution at ~ -0.6 V, both vs NHE [23].

The electric conductivity of magnetite allows its use as substrate for electrochemical measurements. Thus, it can be expected that the interaction between Fe_3O_4 and V can be examined through electrochemical methods.

Here, a voltammetric study of V(V) electrochemical response on magnetite film electrodes (MFE) is reported, with the aim of investigate the electroactivity of magnetite towards vanadium. Fe_3O_4 films are grown electrochemically. For solid ion selective electrodes, it was reported that a layer of a hydrophobic conducting polymer improved stability by avoiding the formation of a thin water layer in the electrode/film interphase [24]. Therefore, the same approach was taken in the present work: the electrochemically formed Fe_3O_4 films are deposited on polythiophene (PT) films, in turn electrochemically grown on glassy carbon (GC) electrodes.

2. Experimental

2.1. Chemicals and materials

AR grade chemicals and high purity water from a Milli-Q system were employed throughout. V(V) was added in the form of ammonium metavanadate. The electrochemical experiments were conducted in a three electrode cell, with working and auxiliary electrodes placed in the same compartment; the working electrodes were 0.3 cm diameter glassy carbon (GC) disks, polished with alumina of decreasing sizes up 0.3 μm, cleaned in an ultrasonic bath with acetone, thoroughly rinsed with high purity water and dried in air. The reference electrode was a saturated calomel electrode (SCE); all potentials are referred to it. The counterelectrode was a Pt foil. A Teq-04 (S. Sobral, Buenos Aires, Argentina) potentiostat under computer control was employed in all the experiments.

2.2. Electropolymerization of thiophene

The PT base films were synthesized galvanostatically following Bobacka et al. [25]. The GC disks were immersed in a 0.1 M thiophene + 0.1 M $LiClO_4$ propylene carbonate solution. A 1.43 mA cm^{-2} current was applied for 80 s with the GC electrode acting as anode; after that the electrode was removed and rinsed thoroughly with high purity water, and allowed to dry in air.

2.3. Magnetite film formation

The Fe_3O_4 films were also obtained galvanostatically, following Abe and Tamaura [26]. The cell was initially filled with ultrapure water, degassed with 99.98% N_2 and heated to 80 °C in a thermostatic bath; then, $FeSO_4$, NH_4CH_3COO and KOH are added so as to reach concentrations of 0.028 M, 0.026 and 0.057 M, respectively. Immediately, an anodic constant current of 0.25 mA cm^{-2} is applied for a 2 h period. Finally, the electrode is removed and carefully rinsed with water. A dark, homogeneous surface is observed. The procedure is reproducible, resulting in electrodes with good conductivity.

2.4. Film characterization

Microscopical observation was performed on MFEs grown with the procedure given above on ITO surfaces, so as to be fitted into the SEM chamber. The base surfaces, the PT films and the final magnetite films were observed by scanning electron microscopy (SEM) with a Zeiss Supra 40 Gemini microscope.

The formation of Fe_3O_4 was verified by grazing incidence X-ray diffraction (GIXRD). A Siemens D5000 difractometer was employed, at an angle of 2°, 0,02° theta steps and 5 s per step; Cu-Kα radiation was employed.

Further characterization was performed through ATR-FTIR spectra determination of the base surface, PT and magnetite films, using a Nicolet 8700 equipment fitted with a diamond crystal ATR accessory.

The acid-base behaviour of Fe_3O_4 films was characterized by titration with 0.1 M KOH solution in KNO_3 0.01 M supporting electrolyte, after addition of HNO_3 to bring the pH to a sufficient acidic media, simultaneously recording the solution pH and the potential difference, ΔE, against a saturated calomel electrode (SCE). Numerical fitting of the results is performed with the aid of the Mathematica package (Wolfram Research Inc., www.wolfram.com).