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Studies on the reduction of birnessite thin layers: Influence of medium

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ABSTRACT

This paper describes studies on the reduction of birnessite thin layers electrodeposited onto a cheap transparent semiconductor substrate, tin dioxide (SnO_2), in neutral sulphate solutions. A coupled approach based on electrochemical measurements (cyclic voltammetry and chronoamperometry) and X-ray diffraction (XRD) characterisation allowed us to give information about reduction mechanism of birnessite in presence or absence of Mn(II) in solution. In absence of Mn(II), birnessite is reduced only at low potential ($E = -0.6$ V) into β-MnOOH (feitknechtite), if $Q_{reduction}$ is lower than $Q_{synthesis}$, and in amorphous Mn(II) compound, if $Q_{reduction}$ is equal to $Q_{synthesis}$. In presence of Mn(II) in solution, hausmannite (Mn_3O_4) was detected, and even at high potentials ($E = 0.15$ V). These results signify that a complex between Mn(III), coming from the reduction of Mn(IV) species, and Mn(II) present in solution, can be formed near the surface and leads to the formation of Mn_3O_4, a very resistive compound. These results are important for studies devoted to environmental applications, chemical sensors and also for energy storage.

1. Introduction

Manganese compounds widely exist in soils and sediments in small amounts but with a co-existence of different phases. They participate readily in a variety of oxidation–reduction and cation-exchange reactions or catalysis, due to their low point of zero charge, their large surface area, their strong acid sites and their easily changeable valent states [1,2].

Among these compounds, birnessite (δ-MnO_2) is a major Mn mineral phase in many soils, in desert varnishes and other coatings, and in ocean nodules [3]. Birnessite is a poorly crystallised form of manganese dioxide characterised by a two-dimensional layered structure that consists of edge shared MnO_6 octahedra, with hydrated cations in the interlayer that compensate the small overall negative charge [4,5]. Birnessite is represented by a generalised elemental formula, $A_xMnO_{2-y}(H_2O)_z$ in which A is an alkaline cation (Na^+, K^+, Ca^{2+}, ...) and the average oxidation state of mixed-valence normally falls between 3.6 and 3.8, which represents a predominance of Mn(IV) with minor amounts of Mn(III) or Mn(II). The alkaline cations are naturally inserted into the structure of the birnessite in the environment. But, birnessite-type compounds undergo important cation-exchange reactions, due to their very open structure, and exhibit the largest adsorption capacity on heavy metals than others manganese compounds [6].

Moreover, birnessite-type compounds, due to their microporous nature and/or an irregular stacking of these layers, readily participate in oxidation–reduction reactions via a surface mechanism [7–9]. For these reasons, birnessite attracts always considerable scientific interests as an inexpensive and non-toxic material for potential applications in hazardous waste remediation [10–13], rechargeable battery technology [14–16] or chemical sensors [17,18].

In the past few years, many efforts have been made on the preparation of nanostructured manganese dioxides. These compounds with different morphologies, including nanoparticles, nanowires, and nanosheets have been successfully prepared [19–24]. At contrary, very few studies report the synthesis of birnessite-type compounds as thin films, by oxidation of Mn(II) cations by $KMnO_4$ [25,26], by sol–gel process [27,28] and by electrochemical synthetic procedures [29,30], while layers directly deposited on current collectors present some attractive applications. For example, MnO_2-based thin films grown electrochemically have recently attracted increased interest as redox supercapacitors because of their superior electrochemical performance, environmentally friendly nature, and low cost [31]. Moser et al. demonstrate the feasibility of a transparent electrochemical capacitor using symmetrical electrodeposited MnO_2 thin film electrodes design with

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an appropriate gel-type electrolyte [32]. Recently, we have shown also the good reactivity of birnessite thin layers, electrodeposited onto SnO_2, to degrade phenothiazine dyes (methylene blue, azure B, azure A, azure C and Thionin) allowing potential applications in hazardous water remediation [10].

Previously, we have reported with success electrodeposition of thin layers of various compounds [33–35] and birnessite in particularly [36]. Electrochemistry is a very well adapted method to synthesise adherent, well crystallised and very homogeneous thin layers onto great surfaces, with a good control of the amount and/or the thickness of the layer [37,38]. Moreover, the experimental conditions are generally very soft because the electrodeposition can be made in aqueous solutions at ambient temperature with short duration (from few minutes to some hours). Furthermore, none post-treatment is generally required, in comparison to other methods (e.g. sol–gel).

To the best of our knowledge, the mechanism concerning the redox process, such as the mechanism of electron transfer and the nature of compounds formed during the reduction of thin layers of birnessite made by electrodeposition, has not attracted much attention so far [39–41]. Moreover, these few works have been done in basic media (KOH from 1 M to 9 M), in absence of oxygen and without studied the influence of Mn(II) ions in solution.

In this work, a research relevant to this field will be described and investigated by cyclic voltammetry and chronoamperometry in a medium slightly acidic (pH = 4–6) and in presence of oxygen. The influence of the presence or absence of Mn(II) in solution on the reduction of birnessite will be also studied. In addition, these results will be discussed in relation with the structural properties of the material.

2. Experimental

Reagents, $MnSO_4{\cdot}H_2O$ (ACS Reagent Aldrich), $Na_2SO_4{\cdot}10H_2O$ (ACS Reagent Sigma Aldrich), H_2SO_4 (95–97%, Sigma Aldrich) were used without further purification.

80 mL of a solution (Na_2SO_4 0.4 M; $[MnSO_4] = 1.6 \times 10^{-3}$ M) prepared just before experiments with 18 MΩ cm Milli-Q water was introduced into the electrochemical cell. The pH was measured with a combined pH electrode (WTW SenTix 97/T; pH-meter WTW-Multiline P4), and adjusted, if necessary, by small aliquots of H_2SO_4 solution (0.1 M). For all electrochemical experiments, solutions were used without deaeration. For cyclic voltammetry studies, the solutions were not stirred, but for electrodeposition and reduction experiments, the solutions were gently stirred.

The electrochemical cell was classical with three electrodes. The reference electrode was a MSE electrode (Mercurous Sulfate Electrode REF621 Radiometer analytical, $E_{ref} = 0.656$ V/SHE). All potential values cited in the text are referred to this reference electrode. The counter electrode was a platinum wire, which has been twisted as a "pigtail" to increase its surface. The working electrode was a glass plate covered with tin dioxide (SOLEMS, 120 Ω cm^{-2}, 15 × 60 mm) used as received; the surface in contact with electrolyte was delimited by an adhesive mask (surface $S = 3$ cm^2).

All electrochemical measurements were performed at room temperature using a microautolab potentiostat/galvanostat system (Eco Chemie) controlled by a computer using the GPES software package (version 4.9). After electrodeposition, thin layers were rinsed with Milli Q water and dried in ambient air.

The X-ray powder diffraction experiments were performed with an Inel diffractometer using the Cu Kα radiation ($\lambda = 0.15406$ nm). The surface morphology was observed by a scanning electronic microscopy (SEM) JEOL JSM-6100 directly without preparation.

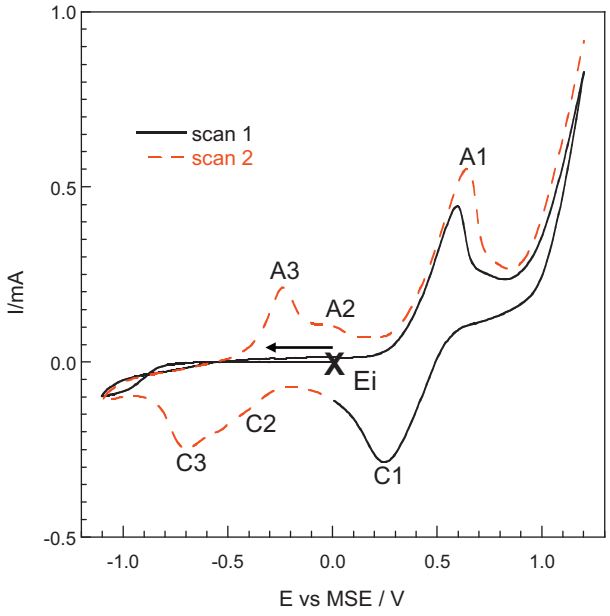

Fig. 1. Cyclic voltammetry initiated in the cathodic direction from E_i, obtained on SnO_2 electrode, in aerated Na_2SO_4 0.4 M–$MnSO_4$ 1.6×10^{-3} M solution, pH free (5.3–5.6), no stirring of solution, $v = 10$ mV s^{-1}.

3. Results and discussion

3.1. Cyclic voltammetry studies

3.1.1. Oxidation of Mn(II) in neutral aerated Na_2SO_4 solution: importance of scan direction

In order to identify the electrochemical conditions of electron transfer of Mn(II) in neutral sulphate solution, a cyclic voltammetry (CV) study was previously performed on SnO_2 substrate [36]. Dissolved oxygen in solution did not modify significantly the shape of cyclic voltammograms compared to in absence of oxygen, but it affects only the peak intensities [36]. The potential scans were initiated in the anodic direction from the rest potential ($E_i = 0.12$ V). In these conditions, a well-defined current appeared corresponding to the oxidation of $Mn(II)_{soluble}$ to a visible brown solid onto SnO_2. The second and third scans have shown the presence of various electrochemical systems. But, it was worthy to note that during the first anodic scan, no peak was visible between 0.1 V and 0.5 V indicating that the electrochemical response was certainly due to the solid present onto SnO_2 [36].

To assess this point, a cyclic voltammetry was done with an inversion of the scan direction, and was initiated in the cathodic direction, Fig. 1. The obtained curve during the scan 1 confirms the importance of the brown solid present onto the working electrode. Indeed, the electrode remained uncoloured and no peak was visible during the first scan. But, just after the formation of the solid, at the potential A1, reduced peaks (C1, C2 and C3) and oxidised peaks (A3, A2) were present again, confirming that all electrochemical peaks observed on the cyclic voltammetry curve are linked to the solid present onto the working electrode.

3.1.2. Comparison of a classical cyclic voltammetry and a cyclic voltammetry made with interruption

From these results, it appears very interesting to study the possibility to synthesise a solid onto SnO_2 during a first scan in the aim to determine the influence of the medium on its electrochemical response, and to understand its redox behaviour. But, it was important to control before the feasibility of this experimental method in standard conditions. That is why, we compared in a first step, and