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In situ XANES measurements during electrodeposition of thin film: Example of birnessite, a promising material for environmental applications

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ABSTRACT

This paper highlights the potentialities of a very simple electrochemical set-up for studying the electrodeposition of thin film in real time by in situ XANES measurements. This study focuses on birnessite, a promising non-toxic manganese oxide for various applications. The main originality of this device comes from its window used as a counter electrode allowing the electrodeposition on large surfaces (some cm^2), exactly like in a classical electrochemical cell. The quality of the in situ XANES measurements is comparable to that of ex situ measurements demonstrating the real interest of this continuous flow electrochemical cell for characterising compounds during electrochemical measurements. Moreover, the electrodeposited thin films are similar to those obtained in a classical electrochemical cell, as illustrated by the ex situ characterizations (XANES, XRD and SEM). Thus, this promising set-up will allow the studies of numerous materials in the future.

1. Introduction

Birnessite is a natural manganese oxide, which has important redox and sorption properties. This non-toxic mineral presents interests for many fields such as environment and energy [1–4]. But, natural birnessite is not pure and poorly crystallised that is why numerous methods of preparation, as powder or thin film, can be found in the literature [5–9]. Among them, electrodeposition is a very well adapted and reproducible method for obtaining adherent, homogeneous and nanostructured thin films of pure birnessite [9]. Moreover, the syntheses are rapid (less one hour), performed in very soft conditions (ambient temperature, in aqueous solution, without deaeration) with a very good control of the amount [9].

Furthermore, such thin films of birnessite seem particularly interesting for potential applications. For example, some papers report the real potentialities of the used of birnessite thin films for water splitting by photo(electro)oxidation for hydrogen production [10–12]. Birnessite thin films can be also used for energy storage for the development of rechargeable lithium batteries [7,8]. Such electrodeposited thin films seem also particularly interesting for the development of innovating wastewater treatments. Indeed, they can degrade and mineralize significantly pollutants by simple contact such as organic dyes (methylene blue, indigo carmine), pesticides like glyphosate (the active ingredient of Roundup®), or AMPA, its main metabolite [13–15]. Moreover, when the reaction is coupled to electrochemistry, the degradation becomes very important even for very high concentrated solutions of persistent pollutant such as AMPA, but with a very low energy input [16–18].

But, birnessite is a complex material with possible multiple structures [1,19], variable Mn (III)/Mn (IV) proportions and vacancies [20–22], which can influence its reactivity [3,4]. That is why, precise characterisations of the material are important after synthesis or uses. X-ray Absorption Spectroscopy (XAS) is a very powerful analytical method for giving information on oxidation states and local coordination of a central atom in a molecular structure. Indeed, this method is particularly well appropriated for characterising such material, as reported in the literature by a lot of studies performed by ex situ measurements [23–28].

Measurements performed in real conditions (e.g. in presence of aqueous solutions), could give more precious information for a better understanding of interfacial processes. However, very few

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studies are reported in the literature because in situ measurements are complex to implement for an efficient exploitation of the powerful tool capabilities of X-ray Absorption Spectroscopy (XAS) [29]. One of these crucial points is the development of the cell, and especially if the measurements are coupling with electrochemistry (e.g. electrodeposition, electro-catalysis).

Over the years, various cell designs have been investigated during many variety of in situ synchrotron studies [29–31]. Some works report the development of electrochemical cells allowing in situ XANES measurements during electrochemical characterisations of various organic and inorganic compounds, and birnessite in particular [32–36]. In the same way, some cells were used during electrodeposition of different materials onto small electrodes ($\leq$1 cm^2). For example, studies about nickel oxide and nickel hydroxide [37,38], zinc oxide [39], magnesium [29] and palladium [40] are reported in the literature. But, as far as we know, no study concern in situ XANES measurements during electrodeposition of birnessite, and particularly onto large surfaces like in classical electrochemical cells (some cm^2).

In this context, this paper highlights for the first time in situ X-ray Absorption Near-edge Spectroscopy (XANES) measurements performed in real time during the electrodeposition of birnessite thin films. For that, we used the special electrochemical cell, developed in our laboratory for in situ XRD characterisations by reflection, and used previously during electrodeposition of birnessite [41] and electrochemical characterisation of Layered Double Hydroxides (LDH) [42]. But the challenge was greater for XANES measurements because the aqueous solution thickness above the sample must be largely inferior to 1 mm to avoid the signal absorption.

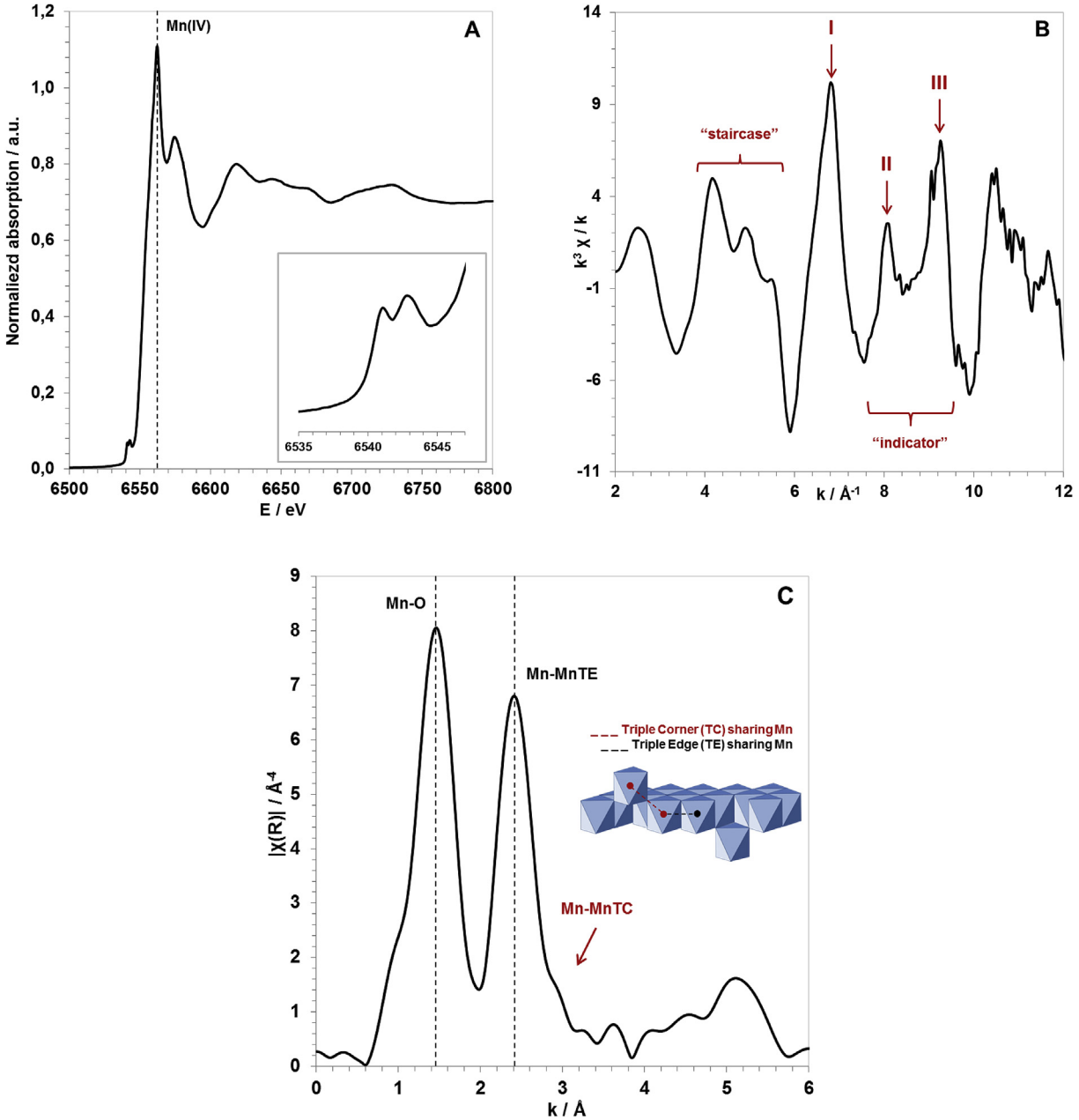

Fig. 1. Ex situ XAS spectra of H-birnessite thin film electrodeposited in a classical electrochemical cell in standard conditions. **1A**- Ex situ XANES (***Inset***: pre-edge feature); **1B**- Mn K-edge EXAFS; **1C**- Fourier transformed. **Inset**: schematic illustration of bonds in H-birnessite structure.