Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Electroanalytical Chemistry 588 (2006) 140–146

Journal of Electroanalytical Chemistry

www.elsevier.com/locate/jelechem

Mass transport in thin films of $[Fe(CN)_6]^{4-}$ exchanged Ni–Al layered double hydroxide monitored with an electrochemical quartz crystal microbalance

Roto Roto [1], Gilles Villemure *

Department of Chemistry, University of New Brunswick, P.O. Box 45222, Fredericton, NB, Canada E2B 6E2

Received 7 May 2005; received in revised form 26 October 2005; accepted 15 December 2005

Abstract

Changes in the resonant frequency of quartz crystals coated with thin films of a Ni–Al–Cl LDH exchanged with $[Fe(CN)_6]^{4-}$ were monitored. Impedance measurements show no changes in the conductance spectra of the nickel LDH films, before and after adsorption of $[Fe(CN)_6]^{4-}$, or before and after potential scanning, indicating that the films were rigid and that the frequency shifts were due to mass changes. Adsorption of $[Fe(CN)_6]^{4-}$ by a 7.5-μg Ni–Al–Cl films resulted in a frequency drop of −300 ± 10 Hz, corresponding to a mass gain of 260 ± 10 ng. This was attributed to the replacement of 85% of the chloride ions from the LDH interlayer spaces by much heavier $[Fe(CN)_6]^{4-}$ ions. Electrochemical oxidation of $[Fe(CN)_6]^{4-}$ in nickel LDH films was accompanied by a reversible decrease in mass. The mass per electron transferred (MPEs) obtained, −41, −23, and −14 g/mol, in potassium acetate, sodium acetate, and magnesium acetate, respectively, matched the molar mass of the electrolyte cations. This indicates that charge neutralization occurred by the simple loss or gain of electrolyte cations. Similarly, the MPEs obtained for a $[Mo(CN)_8]^{4-}$ exchanged Ni–Al LDH and for $[Fe(CN)_6]^{4-}$ exchanged Zn–Al LDH matched the molar mass of the electrolyte cations. Lost or gain of cations from the electrolyte appears to be a general charge balancing mechanism during the electrochemical reaction of metal cyanides anions in the LDH-modified electrodes.

Keywords: Layered double hydroxide; Hydrotalcite; $[Fe(CN)_6]^{4-}$; Ion exchange; Modified electrodes; EQCM; Mass transport; Charge neutralization

1. Introduction

Layered double hydroxides (LDHs), also known as anionic clays, consist of $M^{II}(OH)_6$ and $M^{III}(OH)_6$ edge sharing octahedrons that form sheets similar to those of brucite [1]. Net positive charges on the sheets are balanced by exchangeable anions [2–5]. For example, the mineral known as hydrotalcite is a Mg–Al LDH with CO_3^{2-} in the interlayer space formulated as $Mg_6Al_2(OH)_{16} \cdot CO_3 \cdot 4H_2O$ [6,7]. LDHs have been studied for possible applications as anion exchangers, acid scavengers, polymer additives, battery cathodes, catalysts, catalyst supports, etc. [5].

The layered structures, large surface areas, and anion exchange capacities of LDHs make them attractive materials as electrode surface modifiers. The electrochemical responses of $[Fe(CN)_6]^{3-}$, $[Mo(CN)_8]^{4-}$, $[IrCl_6]^{2-}$ [8], polyoxometalate ions [9,10], manganese porphyrins [11], and several organometallic [12] and organic anions [13–15] adsorbed in LDH-modified electrodes have been reported. LDH-modified electrodes have been investigated for use as electrochemical sensors [16,17], for electrocatalysis [18], as cathodes for rechargeable batteries [19], as electrochemical capacitors [20,21], etc.

In our study of LDHs containing redox active transition metals, we showed that much larger voltammetric waves could be obtained for electrochemically active anions in

---

* Corresponding author. Tel.: +1 506 453 4998; fax: +1 506 453 4981. *E-mail address:* gvd@unb.ca (G. Villemure).

[1] Present address: Department of Chemistry, Faculty of Mathematics and Natural Sciences, Gadjah Mada University, P.O. Box BLS 21, Sekip Utara Yogyakarta 55281, Indonesia.

0022-0728/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jelechem.2005.12.014

solutions with electrodes modified with redox active LDHs than with redox inactive LDHs [22–24]. To better understand charge transfer in redox active LDHs, we have undertaken a study of mass changes in LDH films during redox processes using an electrochemical quartz crystal microbalance (EQCM). To our knowledge, there was only one prior report on the use of an EQCM to study LDH-modified electrodes. Yao et al. [25] showed that the reduction of $[Fe(CN)_6]^{3-}$ in freshly prepared films of hydrotalcite was accompanied by a mass loss. When the electrodes were allowed to age in the electrolytes prior to the measurements, however, the opposite was found, the reduction of $[Fe(CN)_6]^{3-}$ resulted in a mass gain.

Recently, we reported on mass changes during cyclic voltammetry of Ni–Al–Cl LDH films in blank electrolyte solutions [26]. In this paper, we report on the mass responses of Ni–Al–Cl LDH films during ion exchange with $[Fe(CN)_6]^{4-}$ and during electrochemical oxidation of the adsorbed $[Fe(CN)_6]^{4-}$ ions. The mass per electron transferred (MPEs) obtained were found to match the molar mass of the electrolytes cations. Preliminary results on a Ni–Al LDH exchanged with $[Mo(CN)_8]^{4-}$ are also presented. Results are compared with those obtained with a redox inactive Zn–Al–Cl LDH.

2. Experimental

$NiCl_2 \cdot 6H_2O$ was supplied by Mallinckrodt. $ZnCl_2$ was obtained from BDH. All other chemicals were purchased from Aldrich and used as received.

Ni–Al–Cl was prepared as previously described [26] by titration a mixed solution of the metal ions with NaOH following the procedure of Boclair and Braterman [27]. To improve crystallinity, the slurry was aged in a 300 mL autoclave under argon at an initial pressure 100 psi and a temperature of 150 °C for 18 h [1,26]. The precipitate was collected and the <0.2-μm size fraction separated by centrifugation [28]. The solid was washed with distilled water and dried in vacuum over silica gel for 2 days. The Zn–Al–Cl LDH was prepared the same way except that the hydrothermal aging treatment was omitted.

The layered structure of the products was confirmed by powder X-ray diffraction (XRD). The XRD patterns were obtained on a Philips X-ray diffractometer equipped with a graphite monochromator and a vertical goniometer, using Cu Kα radiation at 40 kV and 20 mA and scanning rate of $0.04° \ 2\theta \ s^{-1}$. Elemental analyses of the LDHs were performed at the Research Productivity Council (RPC), New Brunswick, Canada. Inductively coupled plasma emission spectrometry (ICP) and ion chromatography were used to determine the metals and chloride contents, respectively. The carbonate content was determined as CO_2 in a Leco induction furnace. Some of the LDH films exchanged with $[Fe(CN)_6]^{4-}$ were analysed by SEM/EDX. The SEM/EDX was taken with a JEOL JSM-6400 Scanning Electron Microscope equipped with an Energy Dispersive X-ray Spectrometer (EDS) system EDAX Genesis X-Ray analyser on the 1 mg evaporated film of the LDHs deposited on 1.0 cm^2 polished carbon disk substrates. The accelerating voltage 15 kV, the beam current 1.5 nA, and the spectra collection time 50 s. Matrix corrections were made using the ZAF method. The detection limit was about 0.2% (w/w) [29].

The EQCM measurements were made using an Elchema EQCN-600 system consisting of a Model PS-205 potentiostat, a Model EQCN-601 microbalance and a Model EQCN-602 Faraday cage. The LDH films were deposited on 0.196 cm^2 gold-coated 10 MHz AT cut quartz crystals (Elchema Potsdam, New York). The gold electrode surfaces were washed with 1.8 M sulphuric acid, followed by distilled water, and rinsed with ethanol. A 1.0-g/L suspension of the LDH was prepared by stirring the powder in water for 3 h. 7.5 μL aliquots of this suspension were spread over the gold electrode surfaces and the water was allowed to dry overnight in a desiccator over silica gel. The coated quartz crystals were glued onto the side opening of 100 mL undivided electrochemical cells. A platinum wire was used as the counter electrode. The reference electrode was an Ag|AgCl (3.0 M NaCl) electrode. Metal acetate solutions (0.1 M) were used as electrolytes. They were degassed with nitrogen before the measurements, and all measurements were made at ambient temperature.

Changes in resonant frequency were converted into mass changes using the Sauerbrey equation [30,31]

$$\Delta f = -C_f \Delta m \qquad (1)$$

where Δf is the change in frequency (Hz), Δm is the mass change (ng). The value of the constant C_f, 1.13 Hz/ng, was calculated based on the initial resonant frequency, the surface area, the shear modulus, and the density of the quartz [31]. Its value was confirmed by monitoring the electrochemical deposition of copper from a 5-mM solution of Cu^{2+} in 0.1 M HNO_3 [32].

Impedance measurements around the quartz crystal resonant frequency were made to ensure that the LDH films were rigidly coupled to the gold-coated quartz crystal electrodes [31]. They were done with a Hewlett–Packard HP 8714B RF network analyzer using 250 Hz steps and an ac amplitude of 10 mV rms on crystals coated with 7.5 μg of the LDH.

3. Results and discussions

3.1. Impedance measurements

Fig. 1 shows the conductance spectra near the resonant frequency of quartz crystal electrodes coated with 7.5 μg LDH films. For a film left to equilibrate 2 h in 0.1 M potassium acetate electrolyte (curve a), a relatively sharp conductance peak with a conductance maximum of 2.2 mS and quality factor Q, of 1×10^3 was obtained. A quality factor of approximately 10^3 is comparable to that reported for the other quartz crystals in contact with aqueous solutions [26,31]. Addition of $[Fe(CN)_6]^{4-}$ to the solution did not