



# Improved contrast between the coloured and transparent states in electrochromic Ni–Al layered double hydroxide films in mixtures of electroactive ions



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## ABSTRACT

The simultaneous addition of  $[\text{Ru}(\text{bpy})_3]^{2+}$  and  $[\text{Co}(\text{bpy})_3]^{2+}$  to the electrolyte was found to greatly improve the contrast between the bleached and coloured states in electrochromic Ni–Al layered double hydroxide (LDH) films. The relative transmittance of an LDH film recorded *in situ* during potential scans dropped to 35% on oxidation and returned to 90% on reduction, corresponding to an optical density change ( $\Delta\text{OD}$ ) of 0.41, four times larger than the 0.10 obtained in presence of only  $[\text{Co}(\text{bpy})_3]^{2+}$ . This improvement is attributed to mediation of the electrochemical oxidation of the LDH Ni(II) sites by  $[\text{Ru}(\text{bpy})_3]^{2+}$ . The redox potential of  $[\text{Ru}(\text{bpy})_3]^{2+}$  is higher than that of Ni(II) in the LDHs. The oxidized form of the ruthenium cation can accept electrons from these Ni(II) sites during the anodic scans, resulting in more extensive oxidation of the LDH films. The potential of  $[\text{Co}(\text{bpy})_3]^{2+}$  is lower than that of the LDH Ni(II) sites.  $[\text{Co}(\text{bpy})_3]^{2+}$  can donate electrons to the oxidized Ni sites, ensuring the full reduction of the films back to the transparent state during the cathodic scans. In presence of only  $[\text{Co}(\text{bpy})_3]^{2+}$ , oxidation of the film was not as extensive, and the coloured state was not as dark. Similar results were obtained in presence of  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Ru}(\text{bpy})_3]^{2+}$ , or of  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Ru}(\text{CN})_6]^{4-}$  when the pH of the electrolyte solution was raised to 10.  $[\text{Fe}(\text{CN})_6]^{4-}$  was a more efficient mediator for the reduction of the LDH films than  $[\text{Co}(\text{bpy})_3]^{2+}$ . The colour changes were more reversible with transmittance returning to nearly 100% at the end of each individual scan. However, the coloured state was not as dark. Contrasts in the  $[\text{Fe}(\text{CN})_6]^{4-}$ – $[\text{Ru}(\text{bpy})_3]^{2+}$  and  $[\text{Fe}(\text{CN})_6]^{4-}$ – $[\text{Ru}(\text{CN})_6]^{4-}$  mixtures were lower, with  $\Delta\text{OD}$ s of 0.30 and 0.27, respectively.

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## 1. Introduction

Electrochromism is a reversible change in the optical properties of a material upon electrochemical oxidation or reduction [1–5]. It occurs when the two redox states have different electronic absorption bands in the visible region. Electrochromic materials have applications for information displays, light shutters, smart windows, variable-reflectance mirrors, variable-emittance thermal radiators [6–9], etc. Many transition metal oxides and hydroxides are electrochromic, typically going from a transparent state to a coloured state upon oxidation or reduction. This includes NiO and  $\text{Ni}(\text{OH})_2$  films that go from transparent to dark brown upon electrochemical oxidation [10–17].

Nickel containing layered double hydroxides (LDHs) consist of sheets formed by edge-sharing  $\text{Ni}^{\text{II}}(\text{OH})_6$  and  $\text{Al}^{\text{III}}(\text{OH})_6$  octahedrons,

with hydrated, exchangeable, charge balancing counter anions intercalated between the layers [18–22]. Oxidation of Ni–Al-LDH films is accompanied by a colour change from clear to black [6]. However, this colour change is not easily reversed because complete electrochemical reduction of nickel sites in partially oxidized LDH films back to Ni(II) is difficult and requires long reduction times. The conductivity of fully reduced Ni–Al-LDH films is much lower than that of the partially oxidized films [23,24]. The onset of electrochemical reduction of an oxidized LDH film generates an insulating phase at the base of the film, at the interface between the LDH and the substrates that slows the progress of reduction of the remaining nickel sites in the bulk of the films [25–27]. This very slow bleaching back to the transparent state makes Ni–Al LDHs impractical for use in electrochromic devices.

In a previous publication, we reported that the addition of small amounts of electroactive  $[\text{Co}(\text{bpy})_3]^{2+}$  ions to the electrolyte solution greatly improved the rate and extent of bleaching of the Ni–Al LDH films [28]. This was attributed to an efficient electron

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transfer between the  $[\text{Co}(\text{bpy})_3]^{2+}$  ions and the oxidized nickel sites in the LDH films, despite the fact that the cations were not adsorbed by the positively charged LDHs. More recently, we showed that a wide range of electroactive anions with redox potentials below that of the LDH nickel sites, when added to the electrolyte, or adsorbed in the LDH interlayer spaces, were also effective at mediating the full reduction of Ni–Al LDH films [29]. However, reversibility of the colour change is only one of the features of a good electrochromic material. Another desirable property is contrast between the bleached and coloured states. In the case of LDH films, increasing contrast requires making the oxidized coloured state darker, since the reduced state is already fully transparent.

We report here the effect of the addition of  $[\text{Ru}(\text{bpy})_3]^{2+}$  on the electrochromic response of Ni–Al LDH films. Addition of this ion was found to result in a darker coloured state than in blank electrolyte. In presence of both  $[\text{Co}(\text{bpy})_3]^{2+}$  and  $[\text{Ru}(\text{bpy})_3]^{2+}$  a greatly increased contrast between the bleached and coloured states was observed. Similar results were obtained in a mixture of  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Ru}(\text{bpy})_3]^{2+}$ , or in a mixture of  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Ru}(\text{CN})_6]^{4-}$  when the pH of the electrolyte was increased to 10.

## 2. Experimental section

$[\text{Co}(\text{bpy})_3]\text{Cl}_2$  was prepared by reacting  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  with excess bipyridyl in hot ethanol as described by Nyholm and Burstall [30].  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  was obtained from Mallinckrodt. All other chemicals were from Aldrich and were used as received.

The Ni–Al–LDH was prepared by titration of a mixed solution of the metal ions with NaOH, as described by Boclair and Braterman [31]. Briefly, a solution 0.075 M in Ni(II) and 0.025 M in Al(III) was prepared by dissolving the metal chlorides in carbonate free water. The solution was brought to boil and titrated with 0.8 M NaOH under nitrogen to approximately 92% of the end point required for the formation of a 3:1 LDH. To improve crystallinity, the LDH slurry was aged in an autoclave under argon at an initial pressure 100 psi, at 150 °C for 18 h [32]. The precipitate was collected and the  $<0.2 \mu\text{m}$  size fraction separated by centrifugation [33]. The solid was washed with distilled water and dried in a vacuum over silica gel for 2 days.

The powder X-ray diffraction (XRD) patterns of the LDH films were obtained with a Bruker D8 X-ray diffractometer using  $\text{Cu K}\alpha$  radiation at 40 kV and 20 mA and a scanning rate of  $0.04 \text{ } 2\theta \text{ s}^{-1}$ . Elemental analysis of the LDH powder was done at the Research Productivity Council, New Brunswick, Canada. Inductively coupled plasma emission spectrometry (ICP) and ion chromatography were used to determine the metals and chloride contents, respectively. The total carbon content of the LDH was determined as  $\text{CO}_2$  in a Leco induction furnace. Results were used to calculate a structural formula for the LDH,  $[\text{Ni}_{0.783} \text{Al}_{0.217}(\text{OH})_2] [\text{Cl}_{0.135}(\text{CO}_3)_{0.04}]$ .

For the electrochromic studies, a  $1 \times 2 \text{ cm}$  quartz cuvette polished on all four sides was used as electrochemical cell. It was placed in the beam of a Hewlett Packard model 8452 diode array spectrophotometer. The LDH films were deposited by the solvent evaporation method on tin-doped indium oxide coated glass substrates (ITO) (Delta Technology, Stillwater, MN). The ITO substrates were cut into  $0.7 \times 5 \text{ cm}$  strips, cleaned by sonication in water and in ethanol. A 10 g/L suspension of the LDH was prepared by stirring the powder in water for 3 h. Twenty microliter aliquots of this suspension, containing 200  $\mu\text{g}$  of the LDH powder were spread over  $0.80 \text{ cm}^2$  areas of the substrates and the water was allowed to evaporate in air overnight. The LDH coated ITO working electrodes were placed in the cuvette in such a way that the film surfaces were parallel to the  $1 \times 2 \text{ cm}$  faces of the cuvette. An  $\text{Ag}|\text{AgCl}|3 \text{ M NaCl}$  reference electrode (BAS MF-2063) and a Pt wire counter electrode were placed in the cuvette to the sides out of the path

of the beam. Changes in the UV–Visible absorbance of the LDH films were recorded *in situ* during the electrochemical measurements. Unless otherwise stated, the reported transmittances are the average transmittances of the films between 400 and 500 nm, using the fully reduced as prepared film on the ITO substrate as reference.

The electrochemical measurements were made with a Princeton Applied Research PARC Model 273 potentiostat. The supporting electrolyte was a 0.1 M potassium borate buffer pH 8.0, except in the studied of the  $[\text{Fe}(\text{CN})_6]^{4-}$ – $[\text{Ru}(\text{CN})_6]^{4-}$  mixtures where the pH of potassium borate buffer was increased to 10. All the solutions were degassed with  $\text{N}_2$  prior to the measurements and all measurements were made at room temperature. The average oxidation state of nickel in the Ni–Al–Cl LDH films before and after the potential scans or potential steps was determined by iodometry [34]. Briefly, the films were immersed in a solution containing 0.1 M acetic acid, 0.1 M potassium acetate and 0.1 M potassium iodide for 15 min. The iodine formed was determined from the absorbance of this solution at 352 nm ( $\epsilon = 12,000 \text{ M}^{-1} \text{ cm}^{-1}$ ). All solutions were degassed with  $\text{N}_2$  and the measurements done under a nitrogen atmosphere.

## 3. Results and discussions

### 3.1. $[\text{Co}(\text{bpy})_3]^{2+}$ – $[\text{Ru}(\text{bpy})_3]^{2+}$ mixtures

Fig. 1 shows the transmittance of a Ni–Al LDH film as a function of the applied potential recorded *in situ* during a potential scan in pH 8 borate buffer containing 0.015 mM  $[\text{Ru}(\text{bpy})_3]^{2+}$ . It is not significantly different from what was obtained for a film scanned in the blank electrolyte [27]. The transmittance dropped rapidly with the onset of oxidation of the LDH nickel sites around 1.0 V in the anodic scan, and continued to drop until reduction of the nickel began in the cathodic scan. This change was not reversible. Transmittance at the end of the scan was only about 75% of the initial value. As a result, when the film was subjected to multiple potential scans rapid darkening was observed (see Fig. 3). The corresponding current potential curve shows only one prominent peak for the reduction of the nickel sites near 650 mV.

Fig. 2 shows the same measurements when a mixture of  $[\text{Ru}(\text{bpy})_3]^{2+}$  and  $[\text{Co}(\text{bpy})_3]^{2+}$  was added to the electrolyte solution. Curves a and b are the transmittance versus potential and current versus potential curves, respectively. The transmittance versus potential obtained in electrolyte containing  $[\text{Co}(\text{bpy})_3]^{2+}$  but no  $[\text{Ru}(\text{bpy})_3]^{2+}$  was added for comparison (curve c). In the first scan (Fig. 2A) the difference between curves a and c was not dramatic. In presence of both cations, the films got slightly darker, with a minimum transmittance of 47%, compared to 52% in presence of only  $[\text{Co}(\text{bpy})_3]^{2+}$ . In both cases, the bleaching occurred in two distinct stages beginning around 1000 and 50 mV respectively in the reverse scan. The transmittance change in presence of both cations was also not as fully reversible as in presence of only  $[\text{Co}(\text{bpy})_3]^{2+}$ . Transmittance of the film at the end of the scan in the  $[\text{Ru}(\text{bpy})_3]^{2+}$ – $[\text{Co}(\text{bpy})_3]^{2+}$  mixture was 88% compare to 98% in presence of only  $[\text{Co}(\text{bpy})_3]^{2+}$ .

Fig. 2B shows the same set of curves for the fifth potential scan. The current potential curve (curve b) is very similar to the current potential curve in Fig. 2A. However, in the mixture of  $[\text{Ru}(\text{bpy})_3]^{2+}$  and  $[\text{Co}(\text{bpy})_3]^{2+}$  the films got significantly darker upon oxidation. The minimum transmittance in the fifth scan was 36% compared to 47% in the first scan. The opposite was observed in presence of only  $[\text{Co}(\text{bpy})_3]^{2+}$  with a minimum transmittance 70% in the fifth scan compare to 52% in the first scan. Combined, these two differences resulted in a much larger contrast between the oxidized and reduced states of the film. In presence of  $[\text{Ru}(\text{bpy})_3]^{2+}$  and

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