Journal of Applied Electrochemistry **34**: 235–240, 2004.

Composite nickel hydroxide – polyelectrolyte films prepared by cathodic electrosynthesis

I. ZHITOMIRSKY
Department of Materials Science and Engineering, McMaster University, 1280 Main Street West, Hamilton, Ontario, Canada L8S 4L7
(fax: +1-905-528-9295, e-mail: zhitom@mcmaster.ca)

Received 30 April 2003; accepted in revised form 24 September 2003

Key words: composite, electrolytic deposition, electrophoretic deposition, film, nickel hydroxide, poly(diallyldimethylammonium chloride), polyethylenimine

Abstract

Composite films consisting of nickel hydroxide and cationic polyelectrolytes, such as polyethylenimine (PEI) and poly(diallyldimethylammonium chloride) (PDDA) were obtained via cathodic electrodeposition. Films up to 3 μm thick were obtained on Pt, graphite and carbon felt substrates. By varying the concentration of the polyelectrolytes in solutions and deposition time, the amount of the deposited material and its composition can be varied. The deposits were studied by thermogravimetric analysis, X-ray diffraction analysis and scanning electron microscopy. The mechanisms of electrochemical intercalation of the cationic polyelectrolytes into nickel hydroxide deposits are discussed.

1. Introduction

Electrodeposition of oxide and hydroxide materials is an area of intense interest [1–11]. Novel electrochemical strategies have been developed for deposition of individual oxides, such as ZnO [3], Cu_2O [4], ZrO_2 [5], Nb_2O_5 [2], TiO_2 [7], WO_3 [8], complex titanates $ZrTiO_4$ [2] and PZT [9], manganites $La_{1-x}Ca_xMnO_{3+\delta}$ [10] and composites TiO_2–RuO_2 [11]. The co-deposition of these materials with polymers has created opportunities in the preparation of novel nanocomposites [12]. A number of advances have recently contributed to the use of cationic polyelectrolytes for electrodeposition of composite materials [13–18]. Electrodeposition offers important advantages compared to layer-by-layer assembly currently used for preparation of such films [19–21]. The advantages of electrodeposition are short processing time and process simplicity. Moreover, uniform films can be formed on substrates of complex shape as well as on selected areas of the substrates. Cathodic electrodeposition enables the formation of inorganic nanoparticles *in situ* in a polymer matrix, preventing particle agglomeration. Therefore, this method offers novel opportunities, which are beyond the capabilities of layer-by-layer assembly. An important development was the electrodeposition of hybrid films based on Fe_3O_4 and poly(diallyldimethylammonium chloride) (PDDA) [14]. It was demonstrated that PDDA promotes room temperature crystallization of Fe_3O_4 nanoparticles and prevents their agglomeration. As a result, prepared films exhibited superparamagnetic properties [14]. It was shown that composition, properties, nanostructure and morphology of the hybrid films can be tailored by variation of bath composition, deposition parameters, and mass transport conditions for organic and inorganic components.

Polyelectrolytes can be categorized into two groups: strong polyelectrolytes, for which the degree of ionization is independent of the solution pH, and weak polyelectrolytes, for which the degree of ionization is determined by the solution pH. PDDA, because of the quaternary ammonium group, is a strong polycation, and the degree of dissociation of the ionic groups is nearly pH-independent over a wide pH range. In contrast, polyethylenimine (PEI) is a weak cationic polyelectrolyte. The charge of PEI decreases with increasing pH.

In a series of papers [12–18], the intercalation of PDDA and PEI into electrolytic deposits has been studied. An important task is the further extension of this method to deposit novel composite materials. Nickel hydroxides and oxides in their various forms are important functional materials for various applications, including rechargeable batteries, electrochromic devices, supercapacitors [22–24]. This paper presents results of cathodic electrodeposition of novel composites based on nickel hydroxide and cationic polyelectrolytes, such as PDDA and PEI.

2. Experimental procedures

Commercial purity $NiCl_2 \cdot 6H_2O$, PDDA (M_w 400 000–500 000) and PEI (80% ethoxylated, M_w 70 000) (Aldrich) were used as starting materials. Solutions of 5 mM $NiCl_2$ containing 0–1 g l^{-1} PEI or PDDA in methanol – water (5 vol % water) solvent were prepared for electrodeposition. The solution of $NiCl_2$ turned deep blue after addition of PEI. Cathodic deposits were obtained by the galvanostatic method on Pt foils, graphite plates and carbon fiber felts (Lydall) at a current density of 5 mA cm^{-2}. The area of the vertically oriented electrodes was in the range of 20–30 cm^2. The electrochemical cell for deposition included a cathodic substrate centered between two parallel platinum counterelectrodes. Deposition was performed without stirring. Deposit weights were obtained by weighing the Pt substrates before and after deposition experiments followed by drying at room temperature for 48 h. After drying at room temperature, the electrolytic deposits were scraped from the Pt electrodes for thermogravimetric analysis (TG) and X-ray diffraction analysis (XRD). The thermoanalyzer (Netzsch STH-409) was operated in air between room temperature and 1200 °C at a heating rate of 5 °C min^{-1}. The phase content was determined by XRD with a diffractometer (Nicolet I2) using monochromatized CuK_α radiation at a scanning speed of 0.5° min^{-1}. The microstructures of the deposited films were studied using a Philips 515 scanning electron microscope (SEM).

3. Experimental results

Electrodeposition experiments performed from 5 mM $NiCl_2$ solutions containing PEI and PDDA resulted in formation of cathodic deposits. Figure 1 shows deposit weight as a function of deposition time for 5 mM $NiCl_2$ solutions, containing 0.4 g l^{-1} PEI. The results given in Figure 1 indicate that the deposit weight increases with deposition time at a constant current density. Similar dependences were obtained for deposits prepared from $NiCl_2$ solutions containing PDDA.

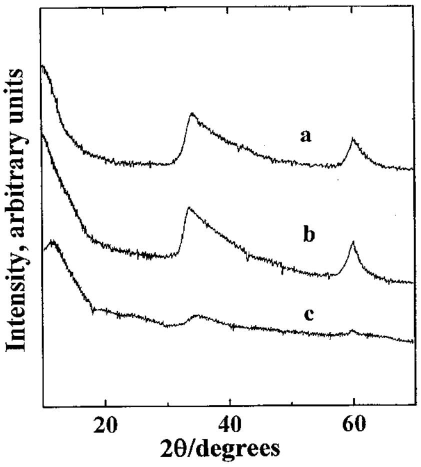

Fig. 2. X-ray diffraction patterns for deposits prepared from 5 mM $NiCl_2$ solutions without additives (a) and containing 0.5 g l^{-1} (b), and 1 g l^{-1} PDDA (c).

X-ray diffraction patterns of deposits prepared from pure $NiCl_2$ solutions (Figure 2) showed peaks of α- $Ni(OH)_2$ [25]. The peaks are considerably broadened due to poor crystallinity of the deposits. XRD spectra taken from the deposits prepared from $NiCl_2$ solutions containing PDDA also displayed peaks of α-$Ni(OH)_2$ (Figure 2), however the intensity of the peaks decreased with increasing PDDA concentration in the solutions. TG data for the deposits prepared from pure $NiCl_2$ solutions exhibited weight loss, which was attributed to dehydration of nickel hydroxide (Figure 3). The total weight loss in the temperature region up to 1200 °C was found to be 30.1% of the initial sample weight. It is important to note that most of the weight loss (27.2%) occurred below 300 °C, no significant weight change was observed at temperatures exceeding 400 °C. TG records for deposits prepared from 5 mM $NiCl_2$ solutions, containing 1 g l^{-1} PDDA exhibit several distinct steps in weight loss (Figure 3). A sharp reduction of the sample weight was observed up to 400 °C, an additional

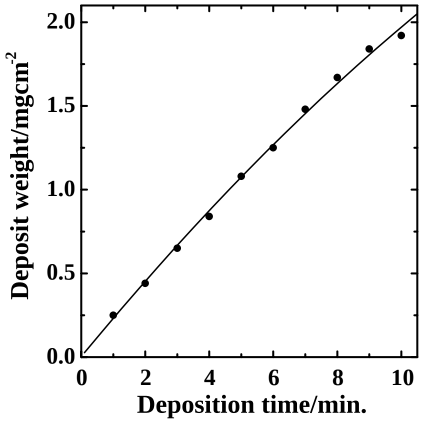

Fig. 1. Deposit weight vs deposition time for deposits prepared from 5 mM $NiCl_2$ solutions containing 0.4 g l^{-1} PEI.

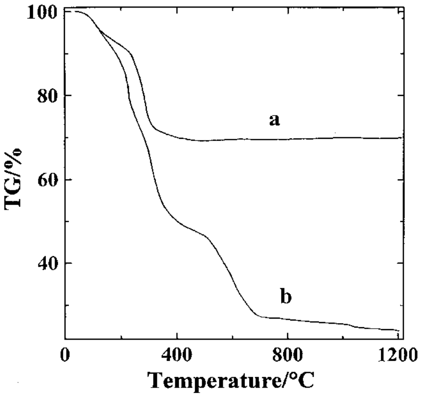

Fig. 3. TG data for deposits prepared from 5 mM $NiCl_2$ solutions without additives (a), and containing 1 g l^{-1} PDDA (b).

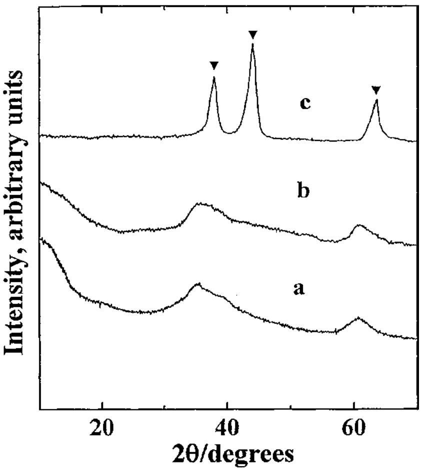

Fig. 4. X-ray diffraction patterns for deposit prepared from 5 mM $NiCl_2$ solution containing 0.4 g l^{-1} PEI: as prepared (a) and after heat treatment at 200 (b) and 400 °C (c) during 1 h (▼: peaks of NiO [26]).

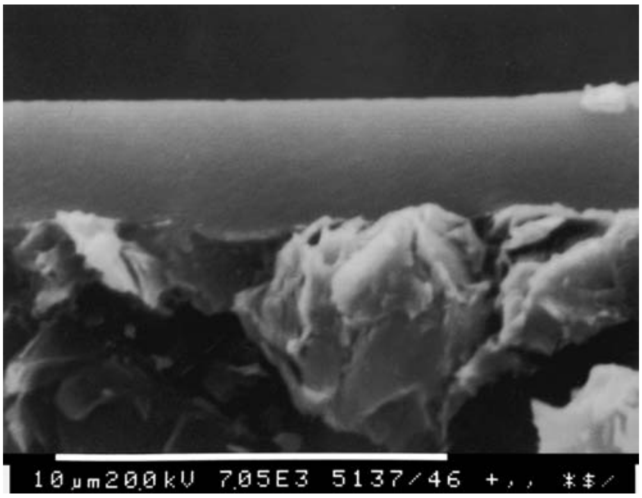

Fig. 6. SEM picture of sectioned nickel hydroxide–PDDA deposit on graphite substrate.

step in weight loss was recorded in the region of 520–650 °C, then the weight fell gradually. Weight loss at 400 and 700 °C was found to be 50.6 and 73.1%, respectively. The total weight loss in the temperature range up to 1200 °C was found to be 75.4%. TG data for pure PDDA were obtained in a previous paper [16]. Heat treatment resulted in burning out of the polymer. TG data showed different weight loss for deposits prepared from pure $NiCl_2$ solutions and $NiCl_2$ solutions containing PDDA. These results indicate the possibility of electrochemical co-deposition of PDDA and nickel hydroxide and formation of composite films. The total weight loss for the composite films is attributed to dehydration of nickel hydroxide and burning out of an organic phase. When considering the deposits as a mixture of nickel hydroxide and PDDA, the amount of organic phase can be evaluated as 64.8 wt %.

Figure 4 shows X-ray diffraction pattern of fresh deposits prepared from 5 mM $NiCl_2$ solutions containing 0.4 g l^{-1} PEI. The peaks corresponding to nickel hydroxide are considerably broadened. The deposits heated at 200 °C also exhibited broad peaks. In Figure 4 it can be seen that deposits displayed peaks of NiO [26] after heat treatment at 400 °C. Figure 5 shows TG data for two different deposits prepared from solutions containing 0.4 and 0.75 g l^{-1} PEI. The TG curves obtained at a heating rate of 5 °C min^{-1} indicate that weight loss occurs in several steps. No appreciable weight change was observed at temperatures exceeding 500 °C. The total weight loss in the temperature range up to 1200 °C was found to be 59.1 and 76.6% for PEI concentrations of 0.4 and 0.75 g l^{-1}, respectively. These results coupled with the TG data for pure nickel hydroxide (Figure 3) indicate the possibility of electrochemical co-deposition of PEI and nickel hydroxide. The deposits prepared from solutions containing PEI show weight loss (Figure 5), attributed to dehydration of nickel hydroxide and burning out of an organic phase to form nickel oxide. From the TG data shown in Figure 5 it may be concluded that the deposition process resulted in formation of composite films, containing different amounts of PEI. The increase in PEI concentration in solutions resulted in higher PEI content in the deposits. When considering the deposits as a mixture of nickel hydroxide and PEI, the amount of organic phase can be evaluated as 41.5 and 66.5 wt % for films prepared from solutions containing 0.4 and 0.75 g l^{-1} PEI, respectively.

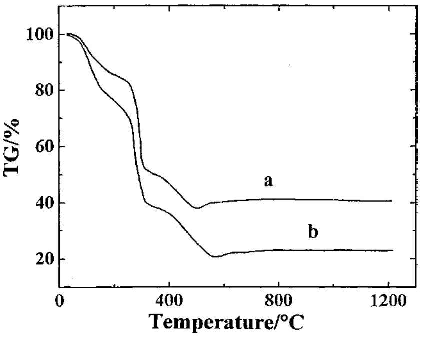

Fig. 5. TG data for deposits prepared from 5 mM $NiCl_2$ solutions containing 0.4 g l^{-1} (a), and 0.75 g l^{-1} PEI (b).

Deposits of various thickness in the range up to ~3 μm were obtained. Figure 6 shows a typical SEM picture of nickel hydroxide–PDDA deposit on a graphite substrate. SEM observations indicate that the method enables film formation on substrates of complex shape, such as carbon felt. Figure 7 shows nickel hydroxide–PDDA and nickel hydroxide–PEI films on individual carbon fibers. Tape tests indicate that obtained films adhered strongly to the Pt substrates.

4. Discussion

Experimental results show the possibility of co-deposition of nickel hydroxide and cationic polyelectrolytes.

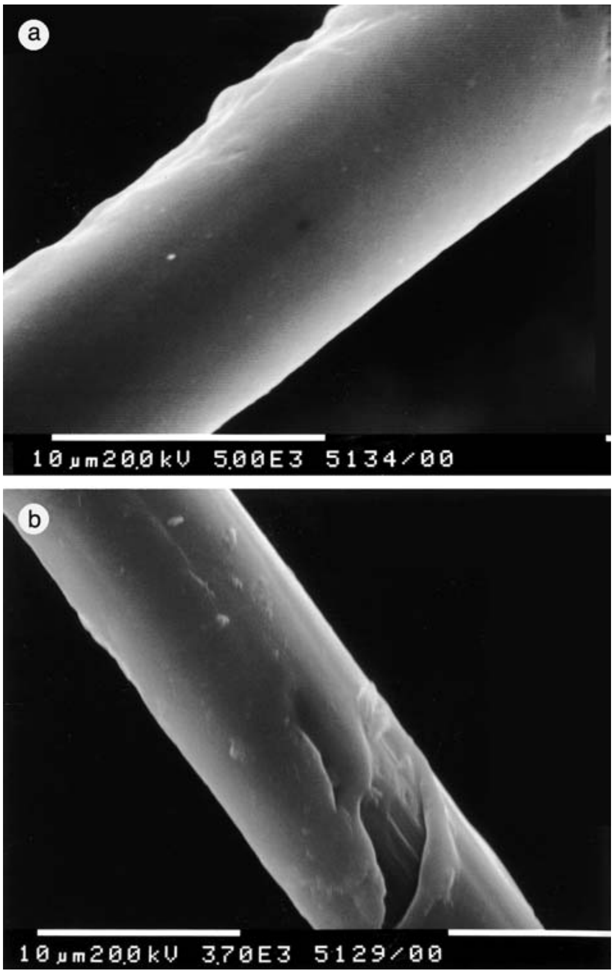

Fig. 7. SEM picture of nickel hydroxide–PDDA (a) and nickel hydroxide–PEI, (b) deposits on carbon fibers.

The mechanism of nickel hydroxide electrodeposition has been widely investigated [27–32]. Deposit weight for deposits prepared from $NiCl_2$ solutions was studied as a function of deposition time and other parameters [6, 30]. Formation of NiO from hydroxide precursor was observed at temperatures exceeding 250 °C. An important point to be discussed is the mechanism of polymer intercalation into nickel hydroxide deposits. In previous works [13, 16], it was suggested that intercalation of PDDA particles into electrolytic deposits was achieved by their adsorption on the surface of colloidal particles, which are produced near the cathode and form a cathodic deposit. A model has been developed based on electrostatic attraction of oppositely charged colloidal particles of hydroxide materials and PDDA. In the cathodic electrodeposition process, metal ions or complexes are hydrolyzed by an electrogenerated base to form deposits on the cathodic substrate. The cathodic reactions that generate OH^- are:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{1}$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{2}$$

It is important to note that the surfaces of hydroxide particles may become positively or negatively charged depending on pH:

$$\mathrm{M{-}OH} + H^+ \rightarrow \mathrm{M{-}OH_2^+} \tag{3}$$

$$\mathrm{M{-}OH} + OH^- \rightarrow \mathrm{M{-}O^-} + H_2O \tag{4}$$

The pH in the bulk solution is low, whereas cathodic reactions 1, 2 result in a significant pH increase near the cathode [13]. Therefore the charge of hydroxide particles formed at the electrode surface depends on their isoelectric point and pH at the electrode surface.

PDDA is a strong cationic polyelectrolyte, which maintains a positive charge under basic conditions. However, no electrophoretic deposition was observed from pure PDDA solutions in water [16]. It was suggested that the electrostatic repulsion of PDDA macromolecules prevents their deposition. On the other hand, co-deposition of PDDA and zirconium hydroxide was achieved from aqueous solutions [16]. It is important to note that the isoelectric point of hydrous zirconia was reported to be 6.7 [33]. Therefore, zirconium hydroxide particles formed near the cathode surface are negatively charged. In this case, film formation is achieved via heterocoagulation of oppositely charged PDDA and hydroxide particles formed at the cathode surface. However, in the case of nickel hydroxide the use of the charge compensation mechanism presents difficulties. Indeed, the isoelectric point of nickel hydroxide was reported to be in the range of 11–12 [33].

The important strategy to reduce electrostatic repulsion of PDDA macromolecules is related to the choice of a solvent [34]. It is in this regard that the thickness of polyelectrolyte multilayers deposited by layer-by-layer assembly [34] increased with increasing ethanol content in a mixed water–ethanol solvent. On the other hand the polymer can be adsorbed on the surface of colloidal particles when its solubility in the dispersion medium is low. Therefore, another benefit of using poor solvent is that it promotes adsorption of PDDA on colloidal particles. It is important to note that the attraction of polyelectrolytes and colloidal particles could be electrostatic or nonelectrostatic or a combination of both. Moreover, forces of other origins can also act between the particles and polymer macromolecules near the electrode [13]. These forces can result in heterocoagulation of nickel hydroxide and PDDA and formation of composite films.

In this work electrodeposition was performed using a mixed methanol–water solvent. The deposition process needs a certain amount of water for base generation in reactions 1, 2. On the other hand lower dielectric constant of methanol compared to that of water can result in reduced dissociation of ionizable PDDA groups and reduced chain expansion, related to repulsion between the charged groups. It is suggested that the use of methanol–water solvent resulted in reduced electrostatic and steric repulsion of PDDA macromolecules and provided better adsorption of PDDA on nickel hydroxide particles. As a result composite nickel hydroxide–PDDA films were obtained. It is suggested that the mechanism of deposition of nickel hydroxide–PDDA composites is based on electroprecipitation of nickel hydroxide and electrophoretic deposition of PDDA, followed by heterocoagulation of nickel hydroxide particles and PDDA macromolecules.

The mechanism of deposition of nickel hydroxide–PEI composites is not clearly understood. PEI has a positive charge over a wide pH range below pH 11. It is known that electric field can provide electrophoretic motion [13] of positively charged PEI macromolecules from the bulk of low pH solutions towards the cathode. The decrease of PEI charge with increasing pH at the cathode surface reduces electrostatic repulsion of PEI macromolecules and promotes their deposition. However, PEI is a polybase. The pH of the 1 wt % PEI solution was found to be about 11 [35, 36] and the PEI molecule has no charge [36]. It achieves its cationicity through protonation of the amine groups in acidic solutions [35]:

$$[\mathrm{-CH_2-CH_2-NH-}]_n + \mathrm{H_3O^+} \rightarrow [\mathrm{-CH_2-CH_2-NH_2^+-}]_n + \mathrm{H_2O} \tag{5}$$

The degree of ionization of PEI depends on the amount of acid added. On the other hand it is known that Ni^{2+} ions have remarkable binding affinity towards PEI and its derivatives. The formation of PEI complexes with Ni^{2+} and other ions was studied in several papers [37–40]. The results of these works indicate the formation of positively charged complexes in solutions. The extent of binding of the ions by PEI depends on the concentration of Ni ions in solutions, PEI concentration, solution pH and other factors [37–40].

The formation of PEI–Ni^{2+} complexes was indicated by the strong coloration of mixed PEI–$NiCl_2$ solutions. Moreover, TG results indicate electrochemical intercalation of PEI into nickel hydroxide deposits. It is suggested that PEI macromolecules acquire a positive charge as a result of complex formation with Ni^{2+}. In this case, electric field provides electrophoretic motion of PEI macromolecules and bonded Ni^{2+} ions towards the electrode surface. It is suggested that these ions participate in cathodic reactions to form nickel hydroxide. Indeed, the results of X-ray analysis indicate formation of the nickel hydroxide phase, which converted to nickel oxide after heat treatment and dehydration. On the other hand, it is possible [40] that free nickel species, which are not complexed by PEI, also exist in solutions and contribute to the electrosynthesis of nickel hydroxide.

In this investigations the amount of an organic phase in the composite films was evaluated from TG analysis of the composite films and pure hydroxide deposits. However, it is possible that the composite deposits cannot be considered as a simple mixture of inorganic and organic phases. Therefore, more detailed investigation is necessary to study the composition and microstructure of the prepared films. The electrochemical strategies developed pave the way for fabrication of other composite materials. It is in this regard that PEI and its derivatives forms complexes with Cu^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+} and other ions [37–40].

5. Conclusions

The feasibility of electrochemical co-deposition of nickel hydroxide and cationic polyelectrolytes has been demonstrated. Experimental conditions were determined for electrochemical intercalation of PDDA and PEI into the hydroxide deposits. XRD and TG studies indicate formation of composite films containing nickel hydroxide and organic phases. The amount of an organic phase in the deposits can be changed by variation of polyelectrolyte concentration in solutions. The amount of deposited material increases with increasing deposition time. Films up to 3 μm thick were obtained on various conductive substrates. It was established that films prepared from solutions containing PEI and PDDA with inherent binding properties, adhered well to the substrates and exhibited enhanced resistance to cracking. The method enables deposition on substrates of complex shape. The results pave the way for deposition of other composites, based on cationic polyelectrolytes and metal oxides or hydroxides.

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