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SHORT COMMUNICATION

Observation of mixed valency in electrosynthesized nickel hydroxide

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1. Introduction

Electrogeneration of base by cathodic reduction of the nitrate ion [1] is widely used as a one step synthetic route [2, 3] for the preparation of nickel hydroxide electrodes for use in nickel-cadmium batteries. Electrosynthesized nickel hydroxide (ESN) designated as α-$Ni(OH)_2$ has been found to have superior electrochemical properties compared to chemically prepared β-$Ni(OH)_2$ [4]. The electrochemical properties of ESN are found to improve on the addition of up to 5% Co and several studies have been reported in the literature concerning the effect of cobalt on the mechanical [5, 6], chemical [7] and electrochemical [8–10] properties of ESN.

In this paper we have attempted to characterize ESN in the bulk state by employing X-ray diffraction, infrared spectroscopy, BET and 'ferrometry" (reaction with Fe^{2+}). We report, for the first time, that ESN is a partially oxidized form of nickel hydroxide and participates in the oxidation of Fe^{2+} to Fe^{3+}. On doping with cobalt, the oxidizing power of ESN is enhanced and a maximum value of 0.07 equivalents per mole is achieved at a 5% Co concentration.

2. Experimental details

Electrosynthesis of nickel hydroxide was carried out by cathodic reduction of a 0.2 M Ni $(NO_3)_2$ solution (pH 3.5) in a divided electrochemical cell potentiostatically at -1.0 V with respect to a saturated calomel electrode, using a three electrode assembly. A platinum flag of 2 cm^2 area was used as the cathode. A platinum wire was used as the anode; 0.2 M KNO_3 was used as the electrolyte in the anodic chamber. Prior to deposition, the cathode was first cleaned with a detergent and then electrochemically cleaned as described elsewhere [11].

Deposition of ESN was carried out at a temperature of 25° C at a current density which varied between 5 to 35 mA cm^{-2} for a period of 8 to 10 h. The ESN film was removed by sonication from time to time to collect the material in the form of a powder. The powder was filtered and washed repeatedly with water and dried to constant weight at 55° C.

Cobalt-doping was carried out by nitrate reduction of mixed $Co(NO_3)_2$ and $Ni(NO_3)_2$ solutions taken in appropriate proportions. As nickel and cobalt hydroxides have nearly equal solubility products [12], it is expected that the film composition would be very close to the composition of the bath. Co doped samples containing 1, 5, 10 and 25% Co were prepared. All ESN samples were handled in an identical fashion. Pure cobalt hydroxide was obtained by cathodic reduction of a $Co(NO_3)_2$ solution.

Chemical nickel hydroxide samples were prepared by literature methods. Merlin's nickel hydroxide [13] was prepared by evaporation of a solution of nickelammine complex. The solid was filtered and washed free of nitrate and ammonium ions. Brauer's nickel hydroxide [14] was prepared by adding strong alkali (1 M KOH) to a nickel nitrate solution at 35° C. Turbostratic $Ni(OH)_2$ [15] was prepared by addition of ammonia to nickel nitrate and by rapid centrifugation of the precipitate.

All chemically prepared samples were dried to constant weight at 55° C. All X-ray diffractograms were recorded on a Jeol X-ray diffractometer (model JDX8P) using a copper anode. Infrared spectra were recorded on a Perkin Elmer model 684 infrared spectrometer in KBr pellets at a resolution of 3 cm^{-1}.

Estimation of excess charge in the nickel hydroxide samples was carried out by adding an accurately weighed amount (100 mg) of the sample to 10 ml of an acidified standard ferrousammonium sulphate solution (0.01 M). The compound was dissolved by prolonged stirring at room temperature. ESN samples were found to be less readily soluble than the chemically prepared samples. The excess Fe^{2+} was then estimated by titrating it against standard $K_2Cr_2O_7$ (0.01 M) potentiometrically. The minimum detectable change in the oxidation state under the experimental conditions was 5×10^{-4}. Blank titrations were carried out under identical experimental conditions to correct for the air oxidation of Fe^{2+} to Fe^{3+}.

3. Results and discussion

Figure 1 shows the X-ray diffraction (XRD) pattern for ESN. The pattern reported here matches well with that reported by other authors [16–18] and attributed to α-$Ni(OH)_2$. The infrared spectra are identical to those reported in the literature [16] and the BET surface areas range from 17 to 21 $m^2\,g^{-1}$, which are typical of values obtained from nickel hydroxide electrodes. Thus the electrosynthesized nickel hydroxide obtained can be definitely identified as α-$Ni(OH)_2$.

Nickel hydroxide exists in a variety of phases, the diffraction data of which have been documented [19] extensively. All these phases have been indexed

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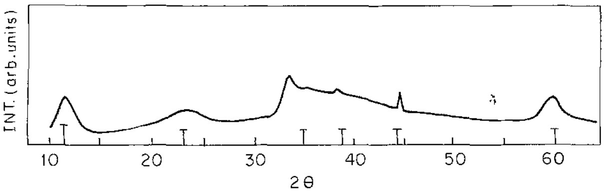

Fig. 1. X-ray diffractogram of electrosynthesized nickel hydroxide. The vertical lines mark the positions and intensities of the lines reported as PDF pattern No. 6–0044.

according to the hexagonal unit cell and four of the PDF pattern numbers 1–1047, 2–1112, 3–0177 and 14–117 have been assigned to $Ni(OH)_2$. Two phases, PDF pattern numbers 6–0141 and 6–0075 have been assigned to nickel oxide-hydroxides of the formula NiO(OH). Two more phases, PDF pattern numbers 6–0044, and 6–0144 have been assigned to mixed valent compositions $4Ni(OH)_2 \cdot NiO(OH)$ and $Ni_3O_2(OH)_4$ respectively.

On comparing the XRD pattern recorded for ESN with the reported patterns, we find that ESN corresponds most closely to the PDF pattern number 6–0044 assigned to $4Ni(OH)_2 \cdot NiO(OH)$ (see Fig. 1). ESN obtained under various electrodeposition conditions in this work and in refs [16–18] shows a characteristic first line at $d = 0.769$ nm in close agreement with the first line $d = 0.77$ nm reported for the mixed-valent phase. All other nickel hydroxide phases have their first lines at d values well below 0.5 nm, with the exception of γ-NiO(OH) whose d_{003} appears at 0.69 nm.

The close correspondence between the structures of ESN and the phase identified as $4Ni(OH)_2 \cdot NiO(OH)$ throws open the possibility of ESN also being mixed valent in character. Accordingly the excess charge on ESN was estimated by reacting it with acidified ferrousammonium sulphate and by back-titrating the excess Fe^{2+} potentiometrically with a standard $K_2Cr_2O_7$ solution. The results are given in Table 1. It can be seen that ESN has 0.03 equivalents of oxidizing power per mole of the compound. Electrosynthetically prepared nickel hydroxide appears to be partially oxidized. Oxidation of nickel hydroxide is known to proceed through proton extraction [20, 21] so that the oxidized forms of nickel hydroxide can be written as $H_{2-x}NiO_2$ where x represents the oxidizing power in equivalents per mole of nickel. ESN can therefore be represented as $H_{1.97}NiO_2$. This is in keeping with the formulation of $4Ni(OH)_2 \cdot NiO(OH)$ as $H_{1.8}NiO_2$ [20]. The close correspondence between the two structures becomes understandable as they can be visualized as bronzes of the parent quadrivalent nickel oxide NiO_2 [20, 21].

Table 1. Measurement of excess charge on pure and Co-doped ESN and chemically prepared nickel hydroxide samples

Sample	*Co (%)*	*Mass of ferrous ammonium sulphate consumed by 100 mg of sample (mg)*	*Oxidation state of Ni*
ESN	0	14.42	2.03
	1	22.69	2.05
	5	28.18	2.07
	10	23.25	2.06
	25	20.99	2.05
Merlin's $Ni(OH)_2$	–	0.0	2.00
Brauer's $Ni(OH)_2$	–	0.0	2.00
Turbostratic $Ni(OH)_2$	–	0.0	2.00

Chemically prepared nickel hydroxide samples, on the other hand do not show any oxidizing power indicating that they are in the fully reduced state. Whether this difference is responsible for the different electrochemical properties of chemically and electrosynthetically prepared nickel hydroxide electrodes is difficult to say. Nevertheless the presence of vacancies in the proton layers in ESN can certainly account for the higher proton diffusion coefficients observed for electrosynthetic nickel hydroxide and thereby, the faster kinetics of the α-$Ni(OH)_2 \rightleftharpoons \gamma$-NiO(OH) redox reaction compared to the β-$Ni(OH)_2 \rightleftharpoons \beta$-NiO(OH) reaction [16] of chemically prepared samples.

ESN electrodes usually contain 5% cobalt hydroxide [5–10] and the effect of cobalt on the oxidizing power of ESN was examined (see Table 1). Cobalt doping is known to improve electrochemical activity of the ESN electrodes, especially its coulombic efficiency and conductivity. Accordingly, doping with cobalt is found to increase the oxidizing power of ESN, a maximum of 0.07 equivalents per mole is observed for 5% Co concentration. The ESN at this composition can be formulated as $H_{1.93}NiO_2$. Understandably the larger number of vacancies in the proton layers enhance the conductivity of ESN in the presence of cobalt. Beyond 5% no further increase is observed. Pure $Co(OH)_2$ on the other hand deposits as a rose red powder with negligible oxidizing power. It appears that cobalt promotes the partial oxidation of electrosynthesized nickel hydroxide.

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