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# Electrochemical Behavior of Sol-Gel Produced Ni and Ni-Co Oxide Films

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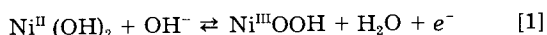
## ABSTRACT

Ni and mixed Ni-Co oxide films were formed at Pt substrates by the sol-gel technique and studied electrochemically in 1 M NaOH solutions. All sol-gel films under study have to be found amorphous. The charge densities of these films are quite high compared to oxides formed by the anodic oxidation of metallic substrates. Mixed Ni-Co oxide films display higher charge densities, broader CV peaks, and negatively shifted equilibrium potentials *vs.* pure Ni oxide films. At slow sweep rates, all films studied showed kinetically reversible surface electrochemical behavior. At higher sweep rates, the redox reactions became kinetically irreversible, being either surface reactions with no diffusion limitations or controlled by the diffusion rate of species inside the film. The effect of the oxide film formation conditions, *i.e.*, the withdrawal rate of the substrate from the sol solution and the firing temperature, on the electrochemical efficiency of the oxide films was also studied.

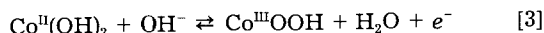
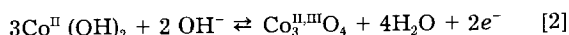
## Introduction

Nickel oxide/hydroxide and mixed Ni-Co oxide films have been extensively studied in the past, primarily due to their numerous promising applications. These include their use as battery electrodes,<sup>1</sup> both in aqueous and non-aqueous media, with much work having been focused on the addition of Co to Ni oxides in order to improve their performance. The electrochromic oxidation/reduction in both cobalt and nickel oxide/hydroxide films, which occurs with the injection and expulsion of mobile ions,<sup>2</sup> has facilitated their applications in "smart windows,"<sup>3</sup> display panels,<sup>4</sup> and rearview mirrors.<sup>4</sup> Ni-Co-based alloys also appear to be very promising materials for water electrolysis because of their good electrocatalytic properties and reported stability for the oxygen<sup>5-8</sup> and hydrogen<sup>9-11</sup> evolution reactions. Cobalt based films are also widely used in recording media.<sup>12</sup>

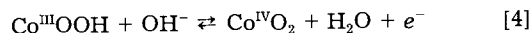
The most important electrochemical process for Ni oxide electrodes, which occurs in alkaline solutions, can be described as<sup>2</sup>



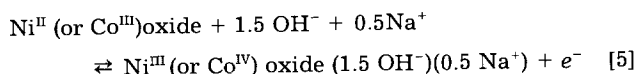
A similar reaction can be written for cobalt oxide electrodes<sup>13</sup>



and



However, it is a well-established fact that these redox reactions are more complex than indicated here<sup>1,14</sup> and that they involve the intercalation/deintercalation of cations in basic solutions<sup>15</sup> in which the oxides are stable, *i.e.*, in simplified form<sup>16</sup>



Nickel and cobalt oxide-hydroxide films can be prepared by the anodic oxidation of the metallic substrate,<sup>1,5</sup> cathodic precipitation,<sup>1</sup> electron-beam evaporation,<sup>2,17</sup>

electrodeposition,<sup>3,12</sup> etc. Chemical deposition,<sup>18</sup> electrolytic deposition,<sup>8,11</sup> spray pyrolysis,<sup>19,20</sup> etc. are utilized to make mixed nickel-cobalt oxide films, which can also be formed by the anodic oxidation of polycrystalline and amorphous Ni-Co alloys.<sup>10</sup>

Our interest in nickel-cobalt based materials has arisen from the unique and promising properties of oxide films formed electrochemically in our laboratory at amorphous melt-spun Ni-Co based alloys.<sup>16,21,22</sup> It was found that, even in the presence of fairly high Co contents, the cyclic voltammetric (CV) response appeared to be primarily that of Ni. However, the amount of oxide which could be formed at these alloys with potential cycling was very high compared to that at pure nickel, with the growth characteristics, electrochromic properties, and film stability being much more similar to that of hydrous oxide films formed electrochemically at Co metal.<sup>23</sup> We therefore developed an interest in studying the properties of similar amorphous oxide films, this time formed by the sol-gel technique.

The sol-gel (SG) method was initially introduced as an energy saving approach in the preparation of glasses and ceramics.<sup>24</sup> The innovative aspect of the method involves mixing all components in solution, thus achieving homogeneity on the molecular scale. The gelation process results in the formation of an oxide network containing substantial amounts of water and organic residues. These are eliminated by the use of suitable drying techniques, yielding amorphous materials with a high degree of porosity.<sup>25</sup> The gels can be shaped into fibers, powders, or can be easily coated on a substrate.<sup>25</sup> SG techniques have been utilized to form single-component oxide materials,<sup>26</sup> as well as oxide mixtures, having an overall composition tailored by varying the ratios of the precursors in solution.<sup>27</sup> SG methods are very convenient for the preparation of thin films of high surface area amorphous oxide materials.

While quite a number of coatings have been formed using SG routes,<sup>26,28,29</sup> to our knowledge, there have been few reports as yet regarding the electrochemical response of oxide films produced in this manner. El Baydi *et al.*<sup>30</sup> prepared high surface area powders of LaNiO<sub>3</sub> and NiCo<sub>2</sub>O<sub>4</sub> via the SG route and, while the oxidation/reduction characteristics of these materials were not examined, their catalytic activity for the oxygen evolution reaction in alkaline media was investigated. Liu *et al.*<sup>31</sup> investigated sol-gel formed nickel oxide films for use in electrochemi-

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cal capacitors. Atik *et al.*<sup>32</sup> carried out potentiodynamic studies of the corrosion behavior of stainless steel coated with sol-gel formed TiO<sub>2</sub>-SiO<sub>2</sub> films in sulfuric acid solutions. Le Goff *et al.*<sup>33</sup> compared the structural and electrochemical properties of manganese dioxides formed by precipitation and sol-gel routes. Cyclic voltammetry and quartz crystal microbalance techniques were used by Park *et al.*<sup>34</sup> to study the intercalation of lithium into V<sub>2</sub>O<sub>5</sub> xerogel films. In the present note, we report the electrochemical behavior of Ni-based oxide films formed by the sol-gel technique and investigate the influence of the preparation conditions on their electrochemical properties.

### Experimental

Nickel, cobalt, and mixed Ni-Co oxide solutions were prepared as described elsewhere<sup>35</sup> and were used for 2 to 3 weeks before being discarded. The working electrode (WE) was a Pt foil (*ca.* 0.53 cm<sup>2</sup>) embedded in soft glass tubing and coated with the SG-formed oxide film. The WE was prepared by dip-coating the Pt foil in the sol-gel solution of Ni, Co, or Ni-Co oxides and withdrawing it at a constant rate of 0.1 to 1 cm/s. The coating was then fired in an oven at 60 to 400°C for 15 min. The counterelectrode (CE) was a large area Pt gauze. The reversible hydrogen electrode (RHE), separated from the WE cell compartment by a closed wet stopcock and a Luggin capillary, was used as the reference electrode (RE). After the electrochemical experiments, the Ni and Ni-Co oxide films were removed by chemical or electrochemical dissolution in 1 M sulfuric acid. The complete removal of the oxide coating was ascertained from the CV of the Pt WE in 1 M H<sub>2</sub>SO<sub>4</sub>.

CV experiments were carried out utilizing an EG&G PAR 173 potentiostat and EG&G 175 programmer and plotted on a Hewlett-Packard 7044B X-Y recorder. Solutions of 1 M NaOH were deaerated by purging with nitrogen for 5 min before recording the CVs and then passing it over the solution. Triply distilled water was used to prepare all solutions. All experiments were carried out at room temperature. All potentials are referred to the RHE. X-ray diffraction measurements were performed on a 2000 Scintag diffractometer (Philips), using Cu K<sub>α</sub> radiation as the source. To measure the infrared spectra of the sol-gel formed oxides, films were dip-coated on KBr disks which were then fired at temperatures ranging from 100 to 400°C. The transmission IR spectra were recorded using a Fourier transform infrared (FTIR) Mattson 5000 spectrometer.

### Results and Discussion

**General electrochemical behavior.**—Figure 1 shows a typical set of CVs observed with a fresh sol-gel prepared Ni oxide coated Pt electrode in a 1 M NaOH solution, all at a sweep rate of 100 mV/s. With continuous cycling, the current peaks reflecting the Ni(II)/Ni(III) equilibrium initially increase somewhat, particularly after the first full cycle of potential, and then increase by another factor of *ca.* up to two, probably as more Ni(II) sites become accessible to the solution with increased wetting of the film. The maximum charge obtained from the integration of the cathodic CV peak for the pure Ni oxide film in Fig. 1 is *ca.* 30 mC/cm<sup>2</sup>, considered to be equivalent to 200 to 300 monolayers of Ni oxide film (assuming one monolayer of Ni oxide would yield 0.10 to 0.15 mC/cm<sup>2</sup> in the Ni(II)/(III) redox peaks<sup>31</sup>). This is a relatively large charge density as compared to the typical charge densities seen for oxide films formed electrochemically at a polycrystalline Ni substrate,<sup>36</sup> suggesting a distinct advantage of forming the oxides via the SG route. With further cycling, a slow decrease (eventually to 50% of the maximum initial values) in both the cathodic and anodic peaks is observed at all sweep rates. The loss of charge for the Ni(II)/Ni(III) redox processes with potential cycling may reflect an alteration in the film structure, such as a sintering effect, or may be caused by the mechanical loss of oxide material from the electrode surface.

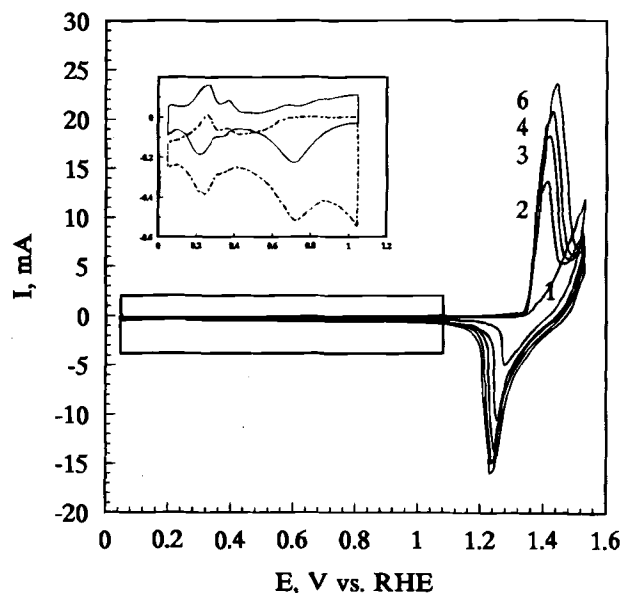


Fig. 1. CVs (100 mV/s) of a fresh SG formed Ni oxide film on Pt in 1 M NaOH with cycling time. Film formed at 24 cm/min withdrawal rate and fired at 190°C for 15 min. Electrode area 0.53 cm<sup>2</sup>. The inset shows CVs of the bare Pt WE (solid line) and Pt coated with the SG Ni oxide film (dashed line).

The loss of charge which was observed on freshly formed SG oxide films after the time of potential cycling was found to be significantly reduced by pretreating the electrode by soaking in the 1 M NaOH solution for 10 to 24 h before commencing any electrochemical experimentation. For example, while untreated Ni-Co films usually showed a *ca.* 30% decrease of the cathodic peak charge after 4 h of continuous potential cycling, the cathodic peak charge of a film pretreated first for 24 h was reduced by only 12% of the initial value after a day of cycling at different sweep rates. After the electrode was left in solution for another 72 h, the charge increased again to *ca.* 92% of its initial value. Therefore, it appears that the loss of charge with cycling reflects an unstable film structure resulting from electrochemical oxidation/reduction of a film which was inadequately equilibrated with and wetted by the solution, and can be avoided by the type of preconditioning described above.

At all stages of cycling in Fig. 1, the surface exhibits electrochromic behavior, with the surface being dark brown in the oxidized state and light brown in the reduced. It is interesting that no evidence is seen for the reduction of any Ni(II) oxide to Ni metal, even when the potential was cycled negatively to -0.2 V, or for the subsequent Ni metal/Ni(II) oxide transition (or Ni hydride oxidation) at 0.3 V, even after relatively long times spent at potentials negative of the onset of the hydrogen evolution reaction (HER). For Ni oxide films formed at polycrystalline Ni metal substrates, however, it is common to observe an anodic peak corresponding to the Ni/Ni(II) transition, which corresponds to the oxidation of either Ni metal or of Ni hydride.

The inset in Fig. 1 shows that, surprisingly, the hydrogen adsorption/desorption peaks seen on the Pt substrate between 0 and 0.4 V, as well as the onset and subsequent reduction (at *ca.* 0.7 V) of a Pt oxide film, are almost unaffected in magnitude by the presence of the sol-gel oxide film. As well, potential holding at values greater than 1.0 V yields an enhanced Pt oxide reduction peak at *ca.* 0.7 V, exactly as would be expected for a bare Pt electrode. These are interesting results, indicating that the solution can readily access the Ni oxide film, even to the Pt substrate. This is perhaps not surprising, as sol-gel techniques are known to yield highly porous materials. It also demonstrates that, while the adhesion of the sol-gel oxide is good

enough to pass electrons freely between the Pt and the Ni sites in the film, the oxide is either contacted only through a limited number of points to the Pt electrode surface or it is weakly adsorbed, allowing for essentially complete Pt oxidation/reduction and hydrogen adsorption/desorption to occur. The only indication of the presence of the sol-gel film is that the hydrogen peaks are sometimes somewhat altered in shape and that a persistent cathodic offset to the CVs can be seen. This current may reflect the reduction of oxygen or of organics, present from the sol-gel preparation solutions, in the pores of the SG film.

Figure 2 shows a typical CV for an oxide film formed from an equimolar (0.23 M each) Ni-Co solution, as well as CVs for the pure Co and Ni oxide films, also formed by the SG technique. The CV for the equimolar (50:50) Ni-Co oxide mixture shows a single pair of peaks, similar to the CV of pure Ni oxide, but with the anodic peak potential shifted slightly negatively from that for pure Ni oxide ( $E_{p,an}$  shifts from 1.4 to 1.45 V for Ni to 1.35 to 1.38 V for the 50:50 oxide). Also, compared with pure Ni oxide films (0.3 M), the peaks of the 50:50 Ni-Co oxide film are substantially broader and the charge is larger. The fact that redox peaks characteristic of Co are not seen in these mixed Ni-Co SG films is in agreement with past reports of electrochemically formed oxides of this kind.<sup>22,37</sup> It has been suggested,<sup>37</sup> that once Co(III) is generated, the Co sites remain inactive regardless of the oxidation state of the Ni sites in the film, as seen by extended x-ray absorption fine structure (EXAFS). In the present case, Co(III) could be formed during oxide synthesis or could be generated in the first anodic scan. However, the larger charges observed in the case of mixed Ni-Co oxides *vs.* for pure Ni oxide could imply that the Co oxide redox chemistry occurs in the same potential range as the Ni(II)/Ni(III) transition,<sup>38</sup> and therefore cannot be resolved separately. The stability of the Ni-Co oxide films is superior to that of the pure Ni sol-gel oxide, as seen by the fact that the loss of charge with longer times of potential cycling is less pronounced. In addition, the removal of the Ni-Co oxide films from the Pt substrate by electrochemical dissolution in sulfuric acid is more difficult to achieve than that of the pure Ni oxide films.

The CV of the pure Co oxide film shows a pair of peaks at ca. 1.42 V *vs.* RHE which, in the literature,<sup>5,13</sup> is usually

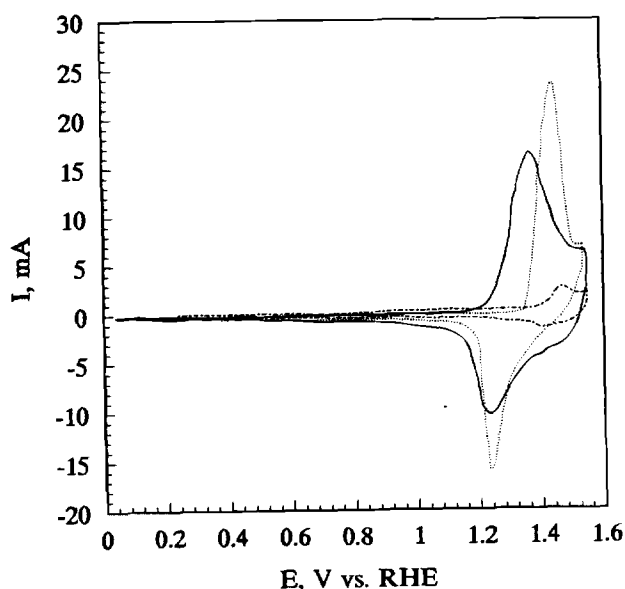


Fig 2. CVs (100 mV/s) of the equimolar Ni-Co oxide film (solid line), pure Ni oxide (dotted line), and pure Co oxide (dashed line) films in 1 M NaOH. All films formed by the SG method at 24 cm<sup>2</sup>/min withdrawal rate and fired at 190°C. The electrode area is 0.53 cm<sup>2</sup>.

attributed to the Co(III)/Co(IV) redox reaction. The peaks for the oxidation/reduction of Co(II)/(III), usually seen at 1.05 to 1.1 V *vs.* RHE,<sup>5,13</sup> in all probability overlap with the Pt oxide formation plateau. The relatively low charges observed for Co oxide films formed using identical SG procedures to those employed in the formation of Ni and Ni-Co films is a real effect, and has been seen in many repeat experiments. This may indicate that Co oxides formed via the SG route have a lower electrochemically active surface area than do Ni or mixed oxides. As in the case of both Ni and Ni-Co oxide films, the Pt substrate is seen to be fully accessible to solution, as the hydrogen adsorption/desorption and Pt oxide formation/reduction peaks can be readily detected in the presence of the overlying Co oxide films (not shown in Fig. 2).

*Effect of sol-gel coating formation conditions on electrochemical behavior.*—At slow sweep rates, the electrochemical response generally became noisier due to what appears to be some roughening of the coating, and therefore, a sweep rate of 100 mV/s was selected for studies of the effect of oxide preparation conditions on the film properties. These studies were initially carried out with Ni oxide films and later extended to the equimolar Ni-Co oxide mixtures. Figure 3 shows the effect of several important experimental variables in the preparation of the sol-gel oxide films. The rate of withdrawal (Fig. 3a) of the Pt electrode from the solution is important in terms of altering the quantity of film produced, consistent with the known fact that faster withdrawal rates produce thicker sol-gel coatings.<sup>39</sup> Consistent with this, a faster withdrawal rate generally resulted in higher charges observed in the Ni(III)/Ni(II) redox peaks, *i.e.*, a greater number of electrochemically active Ni(II) sites do appear to be present. In contrast, the time spent in the sol-gel deposition solution plays almost no role in affecting the amount of oxide film deposited, as can be inferred from the amount of charge passed in the CV experiments as a function of time in the SG solution.

Another very important variable in terms of the electrochemical response is the temperature used to dry the SG oxide films. The firing temperature determines the density of the coating, with the film shrinking laterally and pores reducing in size as the solvent evaporates.<sup>39</sup> Thus, when the substrate is withdrawn at a constant rate from the same solution, thinner coatings are obtained after firing at higher temperatures. Under otherwise identical preparation conditions, an increase in the firing temperature of Ni oxide films from 100 to 150°C produced a ca. twofold increase in the cathodic peak charge density (results not shown). The increased electrochemical efficiency with increased film density in this temperature range suggests that not all of the Ni sites in the oxide film participate in the redox process. Similar behavior has been recently reported<sup>40</sup> for chemically precipitated Ni(OH)<sub>2</sub> films having a gel-like structure, where only material close to the Pt substrate surface was suggested to be electroactive.

A maximum efficiency for the equimolar Ni-Co oxide mixtures was achieved at temperatures between 180 and 250°C (Fig. 3b). The wide scatter in the data shown is reflective of the fact that the sol-gel films are difficult to form reproducibly. The loss of water, as well as the possible collapse of the oxide structure, may result in fewer active sites at higher firing temperatures and the observed decrease in the electrochemical efficiency at temperatures above 250°C.

*Structural/compositional studies of SG oxide films.*—X-ray diffraction was employed in an attempt to establish the structural properties of the SG oxide films. Films were formed on Pt substrates and fired at temperatures ranging from 200 to 400°C. The x-ray diffraction patterns of all films formed indicated that they were amorphous in nature. Figure 4 shows a typical result for a pure Ni oxide film, fired at 200°C. Only a very broad peak is seen, so that it was not possible to establish the composition (oxide *vs.*

hydroxide) of the film material. The observed sharp peaks originate from the polycrystalline Pt substrate.

Sol-gel Ni and Ni-Co oxides were also studied by means of IR spectroscopy. The films were formed on KBr disks and studied as formed or after heating at temperatures ranging from 100 to 400°C. The IR transmission spectrum of a Ni oxide film fired at 200°C is shown in Fig. 5. Bands at 1380 and 825  $\text{cm}^{-1}$  were assigned to the nitrate ion<sup>41</sup> retained in the films from the SG preparation step. The shoulder at *ca.* 2900  $\text{cm}^{-1}$  is induced by the presence of the methyl and methylene groups.<sup>41</sup> A broad O-H stretching band of hydrogen bonded water and possibly of retained alcohols is seen at *ca.* 3360  $\text{cm}^{-1}$ .<sup>42</sup> Water bending vibrations produce the band at *ca.* 1620  $\text{cm}^{-1}$ .<sup>42</sup> Both water bands disappeared when the films were fired at 400°C. We have assigned the broad band at *ca.* 650  $\text{cm}^{-1}$ <sup>43,44</sup> to metal-oxygen interactions. The presence of free water in these SG films makes it difficult to distinguish between Ni (Ni-Co) oxides and their hydroxides by IR spectroscopy.

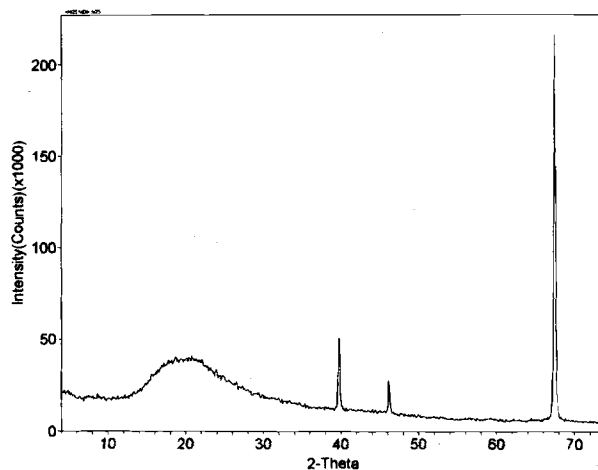


Fig. 4. X-ray diffractogram of Ni oxide film formed on Pt substrate at 24 cm/min withdrawal rate and fired at 200°C.

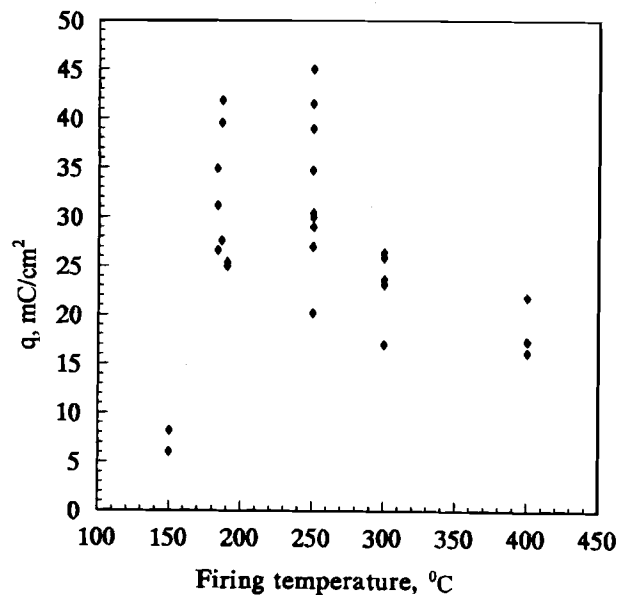
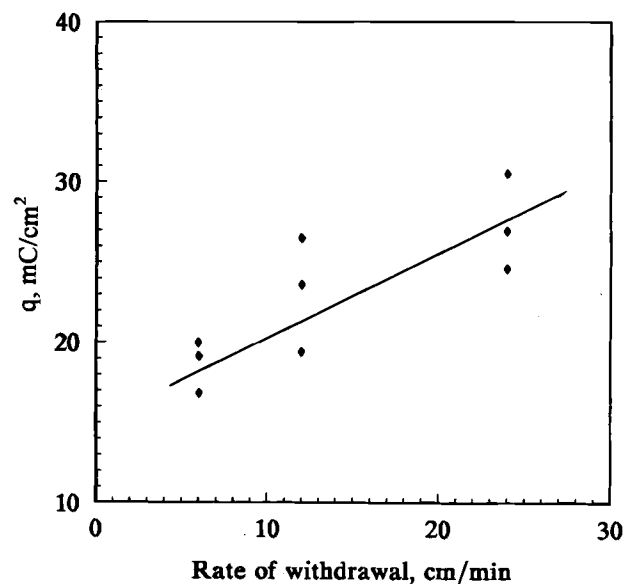


Fig. 3. Effect of (a, top) the withdrawal rate of the Pt WE from the Ni oxide sol solution and (b, bottom) firing temperature of the coated electrode on the cathodic peak charge density of sol-gel oxide films. (a) Ni oxide fired at 155°C; (b) equimolar Ni-Co oxide films formed at 24 cm/min withdrawal rate. 1 M NaOH solution, sweep rate 100 mV/s. The electrode area is 0.53  $\text{cm}^2$ .

However, the breadth of the M-O band suggests that these SG oxide films are hydrated metal oxide materials.

*Kinetic behavior of sol-gel oxide films.*—The kinetics of the oxidation/reduction of sol-gel oxide films were studied in 1 M NaOH solution using a lower potential limit of either 0.05 or 0.8 V vs. RHE. The upper potential limit was maintained at 1.55 V at all times. As the anodic peak was significantly perturbed by the onset of the oxygen evolution reaction (OER), primarily the cathodic peak current was analyzed as a function of sweep rate. All peak currents and charge densities are given with respect to the apparent surface area of the Pt substrates.

Initial experiments focused on relatively thin Ni oxide films which were cycled between 0.8 and 1.55 V and were not preconditioned. For a typical film formed at a withdrawal rate of 6  $\text{cm/min}$ , the cathodic charge density was *ca.* 30  $\text{mC/cm}^2$  at slow sweep rates (1 to 2 mV/s), and *ca.* 25  $\text{mC/cm}^2$  at faster sweep rates of up to 100 mV/s. Figure 6a shows the sweep rate dependence of the cathodic peak current density for this particular Ni oxide film. A linear dependence is seen, consistent with the

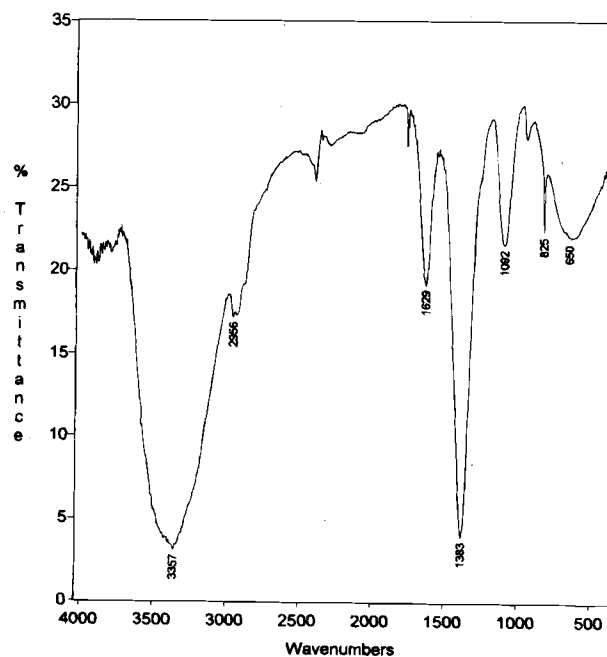


Fig. 5. IR transmission spectrum of freshly formed Ni oxide film on KBr disk; withdrawal rate 6  $\text{cm/min}$ , firing temperature 200°C.

behavior of surface films such as hydrous oxides<sup>36</sup> and conducting polymers,<sup>45</sup> although the slope of the plot is different at low *vs.* high sweep rates. Efforts to plot this data *vs.*  $s^{1/2}$  clearly show that this is inappropriate, *i.e.*, that there are no diffusion limitations under these conditions. The change in slope in Fig. 6a suggests that the reaction is fully reversible at sweep rates less than *ca.* 10 mV/s, becoming irreversible (but not diffusion controlled) at higher sweep rates. Figure 6b shows a plot of both the anodic and cathodic peak potentials *vs.*  $\log s$  for the data of Fig. 6a, which confirms this interpretation, *i.e.*, the peak potentials are independent of sweep rate at less than *ca.* 10 mV/s (reversible surface reaction), and then shift *ca.* 120 mV per decade of sweep rate, at least for the cathodic peak which can be more reliably studied, at sweep rates higher than this. This is consistent with the predicted peak potential *vs.* sweep rate relationship for initially reversible, and then (at  $s > 10$  mV/s) fully irreversible one-electron surface reaction.<sup>46</sup>

In another set of experiments, when thin Ni oxide films were first preconditioned (stabilized) by immersion in 1 M NaOH for several hours prior to carrying out the electrochemical experiments, a linear dependence of the cathod-

ic peak current on sweep rate was observed only up to *ca.* 5 to 10 mV/s, followed by a square root sweep rate dependence above 35 mV/s (Fig. 7a). Peak potentials were again independent of sweep rate at slow sweep rates and then shifted by 60 mV/decade at higher sweep rates (Fig. 7b), suggesting that the reaction was responding as a fully reversible surface process at slow sweep rates, becoming an irreversible process, controlled by diffusion, at higher sweep rates. Notably, agitation of the solution did not affect any of the observed currents, confirming that the mass transport limitations are of species inside the oxide film. It is notable that the stabilized oxides of Fig. 7 yield higher charges than those in Fig. 6, *i.e.*, a greater proportion of the film sites appear to react after preconditioning, which may explain the development of diffusion-controlled conditions.

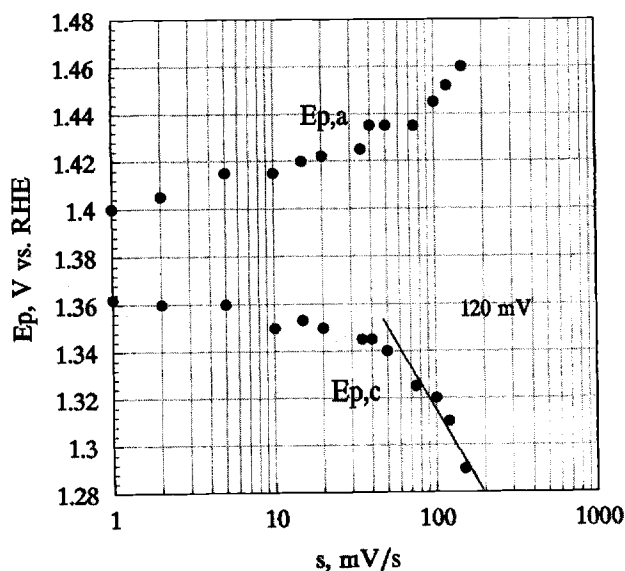
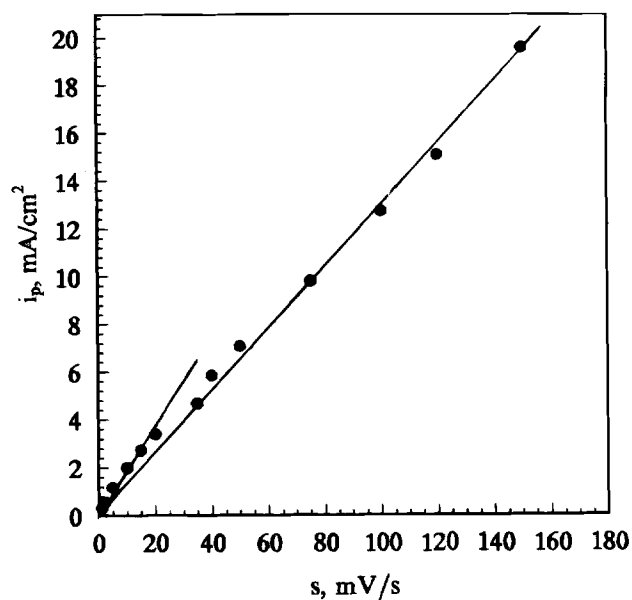


Fig. 6. Dependence of (a, top) the cathodic peak current density and (b, bottom) both cathodic and anodic peak potentials, on the sweep rate for a thin Ni oxide film formed at 6 cm/min withdrawal rate and fired at 190°C. 1 M NaOH solution,  $E_- = 0.8$  V, electrode area 0.53 cm<sup>2</sup>.

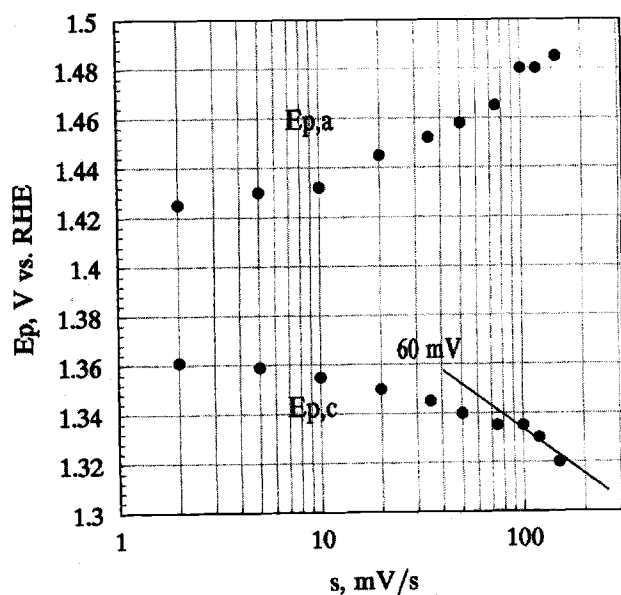
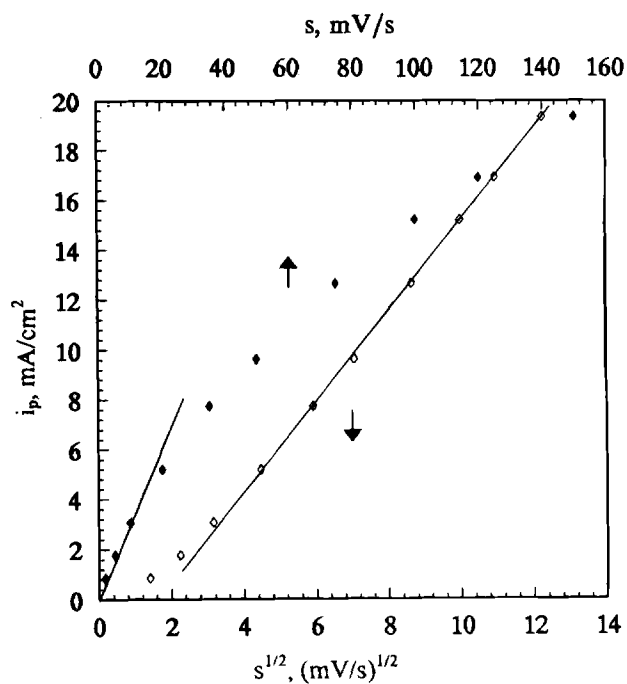


Fig. 7. Dependence of (a, top) the cathodic peak current density and (b, bottom) both cathodic and anodic peak potentials, on the sweep rate for a Ni oxide film, stabilized by soaking in NaOH. Oxide coated on Pt substrate at 6 cm/min withdrawal rate and fired at 195°C. 1 M NaOH,  $E_- = 0.8$  V, electrode area 0.53 cm<sup>2</sup>.

The existence of a steady-state peak separation at slow sweep rates, but peak potentials independent of sweep rate (Fig. 6b and 7b), is one indication that the oxidized and reduced forms of the sol-gel formed Ni oxide films are thermodynamically (*i.e.*, structurally and/or compositionally) different. In particular, it is possible that the ion and water content of the films is different in the two cases, being more depleted of these species in the reduced state (see reaction 5). In turn, this may result in a more swollen and more contracted internal film structure in the oxidized *vs.* reduced states. Indeed, recent AFM studies of the electroprecipitated Ni oxide films<sup>47</sup> showed large structural rearrangements during oxidation/reduction which were attributed to the differences in the densities of nickel hydrous oxide films in these two states.

Thin, preconditioned 50:50 Ni-Co oxide films, formed using identical SG conditions to those for Ni oxide, also

showed a linear dependence of the peak current on the sweep rate at slow sweep rates, *i.e.*, up to 5 mV/s (charge density *ca.*  $45 \pm 3$  mC/cm<sup>2</sup>), followed by a  $s^{1/2}$  dependence above *ca.* 35 mV/s (Fig. 8a). Again, solution stirring did not influence the currents, indicating that species within film are diffusion controlled. The linearity of the peak current *vs.* sweep rate plot at slow sweep rates and the constant value of peak potentials again suggest a fully reversible surface reaction, similar to the behavior of thin, preconditioned Ni oxide films (Fig. 7). The slopes of the peak potentials *vs.*  $s$  plots are *ca.* 60 mV/decade for the anodic peak and *ca.* 35 mV/decade for the cathodic one (Fig. 8b), indicating that the cathodic reaction, in particular, is still not fully irreversible under these conditions. It is of interest that Ni-Co oxides formed under conditions which should yield relatively thick film coatings yield similar charge densities as for thinner oxide films, *i.e.*, *ca.* 50 mC/cm<sup>2</sup> at 5 mV/s. For efficiency reasons, thin oxide films formed at slower withdrawal rates should therefore be preferred.

## Conclusions

Ni and mixed Ni-Co oxide films were formed on polycrystalline Pt substrates by the sol-gel (SG) technique and were studied electrochemically in 1 M NaOH solutions. The charge densities of these films are very high compared to those of oxides formed anodically at metallic substrates. Preconditioning of the SG-formed films by immersion in the 1 M NaOH solution for *ca.* 10 to 24 h prior to electrochemical experimentation stabilizes the oxide film response. Mixed Ni-Co oxides display higher charge densities, broader CV peaks, and a slightly negatively shifted redox potential *vs.* pure Ni oxides formed by the SG method. Pure Co oxides yield comparatively low charge densities, perhaps indicating a lower active surface area.

All SG oxide films under study are amorphous. Faster withdrawal rates of the substrate from the SG solution yield higher charge densities as thicker oxide films are formed, while time spent in the SG solution plays no role on the subsequent response of the films. An increase in the SG firing temperature produced an increase in the cathodic charge densities, which decreased as temperatures were raised further. The initial increase might be attributed to the increased density of the oxide films. The decrease in efficiency at higher temperatures may be associated with the loss of water and structural changes.

At slow sweep rates, all films studied showed kinetically reversible surface electrochemical behavior, although the anodic and cathodic peak potentials remain *ca.* 40 to 70 mV apart, indicative of structural and/or compositional differences in the oxidized and reduced forms of the film. At higher sweep rates, the reaction becomes kinetically irreversible, being either a surface reaction with no diffusion limitations or controlled by diffusion of species inside the film.

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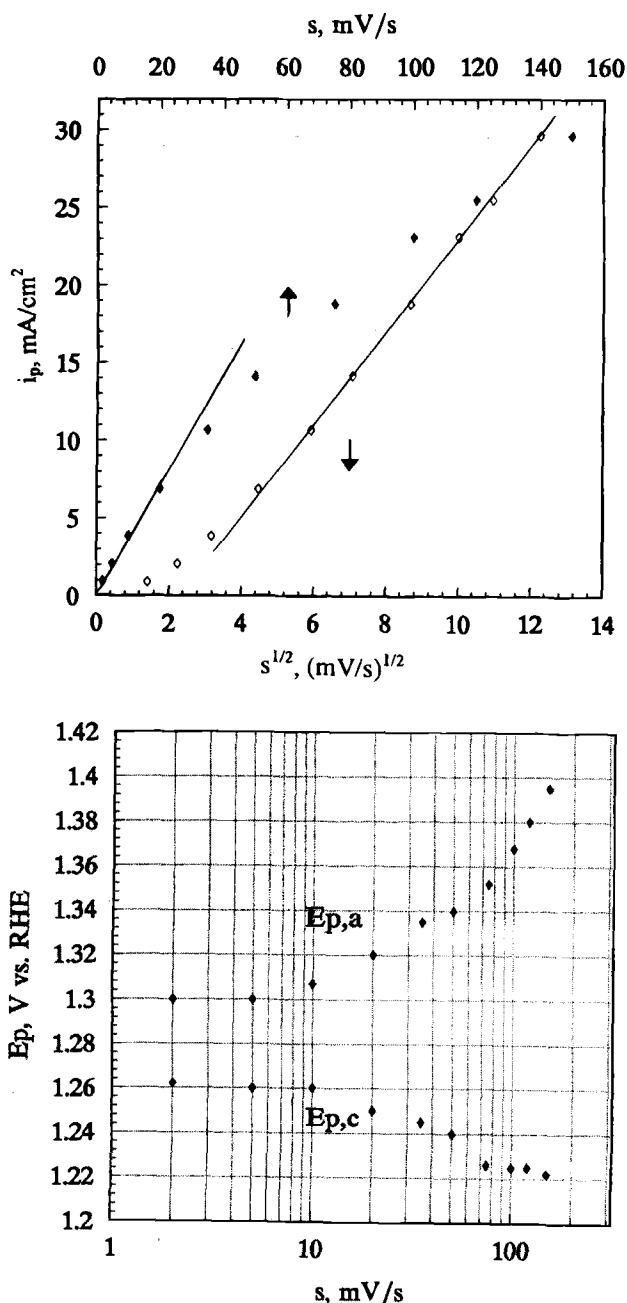


Fig. 8. Effect of the sweep rate on (a, top) the cathodic peak current density and (b, bottom) cathodic and anodic peak potentials, for a thin equimolar Ni-Co oxide film, stabilized by presoaking in 1 M NaOH solution. Oxide formed at 6 cm/min withdrawal rate and fired at 195°C, electrode area 0.53 cm<sup>2</sup>.

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