Mass changes accompanying the electrochemical reaction of sol-gel formed 50:50 Ni–Co oxide films

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Abstract

Cyclic voltammetry (CV) and the electrochemical quartz crystal microbalance (EQCM) technique have been employed to monitor the mass changes during potential cycling of sol-gel (SG) formed 50:50 Ni–Co oxide films in 0.5 M NaOH solutions. The experimentally determined pH dependence, together with the EQCM measurements, have confirmed that charging and discharging of SG Ni–Co oxide films is accompanied by the injection/expulsion of mobile ions, suggested to be OH^- and Na^+ . Although an unambiguous identification of the species involved in the mass transport within the oxide films cannot be made by CV and EQCM alone, these studies provide a deeper insight into morphological changes of the SG oxide films which occur with time of cycling in alkaline solutions. A model involving water exchange during the redox process of these films is proposed, with water being expelled during oxidation and injected upon reduction. An increased amount of exchanged water with longer cycling times may indicate the early stages of the degradation of SG-formed 50:50 Ni–Co oxide films. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Considerable interest in the structural and electrochemical properties of Ni, Co and Ni–Co oxide films has been driven by their numerous practical applications. Thus, many studies have been devoted to the better understanding of the redox reactions of Ni oxide electrodes during potential cycling, primarily because of their use as the positive electrode in Ni/Cd, Ni/metal hydride and Ni/Fe batteries [1,2]. Co oxide electrochemistry in alkaline solutions has been extensively investigated due to its applications as an insertion cathode in Li batteries [3] and in electrochromic devices [4]. Both Co and mixed Ni–Co oxide materials, $\text{Ni}_x\text{Co}_y\text{O}_4$, are considered to be promising electrocatalysts for the oxygen evolution (oer) [5,6] and reduction (orr) [7,8] reactions.

The main reaction during the charge/discharge of the Ni oxide electrode in alkaline solutions is generally expressed by the following equations [9],

In alkaline solutions, reaction (1) has been suggested to be valid only within the film [10]. At the film|solution interface, protons, which are released during film oxidation, would react rapidly with OH^- to form water. In the present work, reaction (2) is considered as the more reasonable reaction, being valid both within the oxide film and at the film|solution interface. For Co oxide electrodes, the suggested reactions are [11]:

The reactions given above for Ni and Co oxide are still oversimplified. Numerous studies have shown that the stoichiometry of these reactions is more complex

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and, similarly to other hydrous transition metal oxides [12,13], cyanometallates [14] and conducting polymers [15], it may involve cationic counter-ions (e.g. Na^+) and solvent exchange. This is based partly on one of the previously reported characteristics of hydrous oxide films formed at electrodes such as Ir [13], Ni [16], Co [17] and their alloys [18], namely their super-Nernstian pH dependence (> -59 mV per pH unit). This indicates the involvement of more than one proton or hydroxyl ion per electron in the redox reaction and the concurrent flux of counter ions is required to maintain electroneutrality within the oxide film. The reaction for Ni–Co oxide materials in alkaline solutions should therefore be more correctly written as [19]:

Prior electrochemical quartz crystal microbalance (EQCM) [20] and probe beam deflection [21] studies of Ni oxide films have indicated that cations and/or solvent molecules are indeed exchanged during the redox reaction. In related publications [22–24], we have reported the electrochemical behavior and structural properties of pure Ni and 50:50 Ni–Co oxide films formed by the SG technique. In the present work, the stoichiometry of the 50:50 Ni–Co SG oxide redox reaction was determined from the pH dependence measurements. Mass changes during oxidation and reduction of these SG oxide films have been monitored by means of the EQCM technique and a reaction model, involving the injection/expulsion of ions and water, is proposed.

2. Experimental

2.1. Electrodes and solutions

The sols, containing an equimolar mixture of Ni and Co, were formed as described elsewhere [25]. In the EQCM studies, 5 MHz AT-cut quartz crystals (2.5 cm in diameter, Valpey–Fisher) were employed as the working electrode (WE) substrates. The crystals were cleaned in hydrogen peroxide, rinsed with distilled water and air-dried. The crystals were then sputter-coated on both sides in the typical keyhole pattern, first with a thin film of Ti for adherence and then with a thin film of Pt, employing a Denton Vacuum DV–502A system. Au wires were attached to the edges of the sputtered Pt with conducting Ag epoxy (2400 circuit works, cardinal) to provide electrical contact.

The SG oxide films were dip-coated on Pt sputter-coated quartz crystals (EQCM work), or on Pt foil substrates embedded in soft glass tubing (used in the pH dependence studies), employing a substrate withdrawal rate of 6 cm min^{-1} and drying at 200° for 15

min. The Au contact wires and the unused side of the quartz crystals were masked with Teflon tape during the dip-coating procedure. For the 5 MHz crystals used in the present work, a uniformly distributed mass increase of $1 \mu\text{g cm}^{-2}$ resulted in a frequency decrease of 56.6 Hz [26].

The SG formed Ni–Co oxide films were equilibrated by soaking in 1 M NaOH overnight. In the CV experiments, their equilibrium charge density was determined by integrating the cathodic peak between 1.0 and 1.55 V versus RHE at a slow sweep rate of 5 or 10 mV s^{-1} , and using the double layer charging current of the underlying Pt substrate as the baseline. After the electrochemical experiments were complete, the SG oxide films were dissolved from the Pt substrates by potential cycling in 1 M H_2SO_4 .

A high area Pt mesh electrode served as the counter electrode (CE), while a reversible hydrogen electrode (RHE) was generally employed as the reference electrode (RE) in this work. For the EQCM measurements, a saturated sodium calomel electrode (SSCE, $E^\circ = 0.236$ V versus SHE) was used during the highly sensitive frequency measurements to eliminate possible noise originating from the bubbling of hydrogen in the RHE.

NaOH solutions (0.5 and 1 M) were used for the electrochemical studies of the SG formed Ni–Co oxide films. The pH dependence of the equilibrium potential of the SG formed Ni–Co oxide films was determined by transferring the 50:50 Ni–Co oxide films between 0.01–0.1 M OH^- solutions of identical ionic strength ($\mu = 2$ M), prepared by adding appropriate amounts of NaClO_4 to the NaOH solutions. A constant ionic strength ensured a constant activity coefficient, so that while the exact pH for each solution was not known, the H^+/OH^- activity could be assumed to change by an exact amount.

Solutions used in the electrochemical experiments were deoxygenated by purging with nitrogen before each experiment and then by passing nitrogen over the solution for the duration of the experiment. All chemicals used in this work were ACS analytical grade and all solutions were made with triply distilled water. All experiments were carried out at r.t. ($22 \pm 1^\circ\text{C}$).

2.2. Instrumentation

The electrochemical experiments were carried out using an EG&G PARC 173 potentiostat/galvanostat, coupled with an EG&G 175 programmer. The voltammetric responses were plotted on a Hewlett–Packard 7044B X–Y recorder.

The EQCM measurements allowed the measurement of mass changes during the oxidation/reduction of the SG oxide films by monitoring small changes in the resonant frequency of an oscillating quartz crystal. The oscillator (constructed by M. Bertram, Department of

Geology and Geophysics, University of Calgary) was driven by a 3 V power supply. Changes in the resonant frequency of the crystal were tracked using a Phillips PM 6654C frequency counter. A resolution of 0.1 Hz could be achieved. The frequency changes were plotted as a function of potential on a Goerz Servogor 790

Fig. 1. CVs (50 mV s^{-1}) of 50:50 Ni-Co oxide film with an equilibrium charge density of 38 mC cm^{-2} in solutions of different OH^- concentration. Film was dip-coated on a Pt foil substrate (0.53 cm^2) at 6 cm min^{-1} , dried at 190°C for 15 min and equilibrated by immersion in 1 M NaOH for 19 h. Solutions were composed of NaOH, with NaClO_4 added to maintain constant ionic strength of 2 M.

Fig. 2. pH dependence of cathodic peak potential of a 50:50 Ni-Co oxide film of Fig. 1 at different sweep rates in solutions of constant ionic strength ($\mu = 2 \text{ M}$). Film formed at 6 cm min^{-1} and dried at 190°C for 15 min.

X–Y recorder. To ensure the reproducibility of the frequency measurements, a standard crystal (5 MHz, FOX 05A Korea, Radio Shack) was employed to calibrate the EQCM system. The stability of the EQCM setup was checked by ensuring that the resonant frequency of the standard crystal was stable ($\pm 1 \text{ Hz}$) over a period of 5 min before each experiment.

3. Results and discussion

3.1. pH dependence of redox reaction of SG formed Ni-Co oxide films

Fig. 1 shows a series of CVs ($s = 50 \text{ mV s}^{-1}$) for a 50:50 Ni-Co SG oxide film having an equilibrium charge density of 38 mC cm^{-2} . With decreasing $[\text{OH}^-]$ concentration, the equilibrium potential of the Ni-Co oxide peaks shifts positively, consistent with the predictions of the Nernst equation. The observed decrease in the equilibrium charge densities of films at lower OH^- concentrations, particularly at $< 0.1 \text{ M}$ NaOH, is similar to what has been reported in the prior literature for Ni, Co [27] and mixed Ni-Co oxide films [18]. Unfortunately, it is not yet certain why this occurs, although it does indicate that, at lower pH, an increasing number of oxide film sites become inactive.

As the cathodic peak potential remains essentially unchanged with long periods of potential cycling in each solution, and as the anodic peaks partially overlap with the oxygen evolution reaction (oer), the experimental pH dependence was calculated from the slope of the plot of the cathodic peak potential as a function of the OH^- concentration (activity coefficient not known, but the OH^- concentration, and therefore the pH, is changed by an exact amount). As can be seen from Fig. 2, the slope does not change significantly with the sweep rate. This analysis yields a pH dependence of $-86 \text{ mV per pH unit}$ versus a pH-independent reference electrode (SSCE). This value is similar in magnitude to the results published in the literature for Ni oxide films formed using a variety of methods. Lian and Birss [18] reported values ranging between -75 and $-80 \text{ mV per pH unit}$ for oxide films grown electrochemically on amorphous Ni-Co alloys. Singh et al. [17] found a pH dependence of -70 and $-85 \text{ mV per pH unit}$, respectively, for Co_3O_4 and NiCo_2O_4 films prepared by the spray pyrolysis method.

The observed shift of the redox potential by $-86 \text{ mV per pH unit}$ indicates that, for these 50:50 Ni-Co SG oxide films, for every electron accepted during reduction, 1.45 hydroxyl ions are expelled from the film, and vice versa during oxidation. To maintain electroneutrality within the oxide film, the co-injection/co-expulsion of counter-ions (Na^+) is necessary. The proposed stoichiometry of the redox process for the

Fig. 3. The equilibrium charge density of 50:50 Ni-Co SG oxide films as a function of film mass. All films were formed at a withdrawal rate of 6 cm min^{-1} and dried at 190°C for 15 min. Mass of SG films immersed in 0.5 M NaOH solution was calculated from the resonant frequency shift of the crystal, while charge density was obtained by integrating cathodic CV peaks (5 or 10 mV s^{-1}).

50:50 Ni-Co SG oxide film studied in this work can therefore be represented by the following reaction, without, as yet, considering any changes in the water content of the film:

To investigate further the suggested involvement of ions and solvent in the redox reaction of SG oxides, the EQCM experiments described below were carried out.

3.2. Mass changes during oxidation/reduction of 50:50 Ni-Co SG oxide films

To ascertain that the EQCM technique could be used reliably in the study of these SG-derived oxide materials, the mass of the films measured in 0.5 M NaOH solution was first correlated with their equilibrium charge density (Fig. 3). The resonant frequency of the quartz crystal was measured before and after SG film deposition. The change in the frequency was converted to the film mass using the Sauerbrey equation, which is valid for thin and rigid films [26]. Although only three points are shown, the linearity of the plot in Fig. 3 does suggest that the frequency shifts can be reliably converted to mass changes via the Sauerbrey equation for the SG oxide films under study.

EQCM measurements during the oxidation/reduction of the SG formed Ni-Co oxide films were performed in

0.5 M NaOH solutions. The SG oxide films were dip-coated on the Ti/Pt sputter-coated crystals from a 50:50 Ni-Co sol at a withdrawal rate of 6 cm min^{-1} , dried at 200°C for 15 min and stabilized by soaking in base overnight. Film loading ranged between 15 and $100 \mu\text{g cm}^{-2}$, with the equilibrium charge densities being between 12 and 30 mC cm^{-2} . Fig. 4(a) shows a typical CV and a simultaneously recorded voltmassogram for a freshly formed 50:50 Ni-Co oxide film during the first cycle in 0.5 M NaOH solution. It can be seen that the mass of the SG oxide film increases (frequency decreases) during oxidation and decreases (frequency increases) when the oxide is reduced. The experimental data of Fig. 4 are in agreement with much of the past literature reports for Ni and Ni-Co oxide films [20,28,29].

As was stated in the introduction, various reaction schemes have been proposed to describe the redox behavior of Ni, Co and Ni-Co oxide films, including the exchange of protons, hydroxyl ions, alkali metal cations and water [20,28,30]. Stress measurements [31,32] have indicated a decrease in the film volume during Ni oxide oxidation, which the authors related to the expulsion of a large number of protons simultaneously with the intercalation of a few heavy cations (Na^+), and vice versa during reduction. In the present work, the observed mass changes have been attributed to the injection of OH^- and hydrated Na^+ ions during the anodic cycle and their expulsion during oxide reduction, consistent with the proposed reaction scheme (reaction 6). The injection/expulsion of ions during oxidation/reduction could be the diffusion-limited process observed at high sweep rates for the SG Ni-Co oxide films under study [22].

It is of interest that, while the characteristics of the 50:50 Ni-Co SG oxide film CVs remain unchanged with time of cycling, the mass response changes significantly (Fig. 4(a-c)). At long cycling times, e.g. after 2 h (Fig. 4(c)), the mass of the oxide film during oxidation initially decreases (frequency increases), contrary to the case for fresh films and the predictions of reaction (6). When the potential is scanned positive of the anodic peak, the mass of the film increases (frequency decreases), consistent with the injection of Na^+ and hydroxyl ions. In the reverse scan, the mass of the film decreases as ions leave the film. However, the mass increases again, as the potential is scanned negative of the cathodic peak potential (Fig. 4(b-c)), and then levels off. These anomalous mass changes become more pronounced at longer cycling times (Fig. 4(b-c)), probably indicating the gradual occurrence of structural and/or morphological transformations of the SG Ni-Co oxide film. It has been suggested in the literature for Ni oxide films [33] that these types of changes are likely related to a change in the water content and cation concentration within the oxide film. Gradual

changes in the composition and structure, not detected by either CV or galvanostatic measurements, were also shown to take place during potential cycling of anodically formed Ni hydroxide films, studied in situ using the second harmonic generation technique [34].

Cordoba-Torres et al. [20] have reported a similar anomalous mass decrease as oxidation commences during cycling of freshly-formed electron beam evaporated pure Ni oxide films. This was explained by the suggested presence of some Ni^{3+} sites and OH^- ions in the as-formed NiO_x film, in which Ni is mainly in the +2 oxidation state. The mass loss, seen at the start of

the oxidation scan, was proposed to be caused by the departure of a certain number of hydroxyl ions accompanying the reduction of some retained Ni^{3+} sites. Following this, the film is oxidized again at the potential corresponding to the anodic current peak in the CV, reflected by the more typical mass increase characteristic of Ni oxide film oxidation (reaction 6).

Several recent reports have indicated that the EQCM behavior of electrochemically deposited Ni and Ni–Co hydrous oxide films is determined by the structural/compositional characteristics of these materials. Mo et al. [35] and Kim et al. [36,37] reported a complete

Fig. 4. Typical CVs (10 mV s^{-1}) and voltammograms of a 50:50 Ni–Co oxide film with time of cycling: (a) freshly formed film, (b) after 1 h and (c) 2 h of potential cycling in 0.5 M NaOH. Film was formed at withdrawal rate of 6 cm min^{-1} , dried at 190°C for 15 min, has a loading of $41 \mu\text{g cm}^{-2}$ and an equilibrium charge density of 12 mC cm^{-2} .

Fig. 5. Mass to charge ratio, calculated over 50 mV segments, as a function of the applied potential during reduction of a 50:50 Ni–Co SG oxide film, after various times of cycling (10 mV s^{-1}) in 0.5 M NaOH . Film has a mass loading of $81 \mu\text{g cm}^{-2}$ and an equilibrium charge density of 30 mC cm^{-2} . Film formed at 6 cm min^{-1} and dried at 190°C for 15 min.

reversal of the direction of mass change with potential scan direction after extensive cycling of Ni hydroxide films in alkaline solutions, i.e. a loss of mass during oxidation, followed by a mass gain during the subsequent reduction scan. This unique effect was correlated with a shift in the position of the CV oxidation peak potential towards more positive values. The mass reversal was attributed to the transformation of $\alpha\text{-Ni(OH)}_2$ to $\beta\text{-Ni(OH)}_2$ [35] and its different charge compensation mechanism.

Kim and Kim [37] used the proton transport model to describe the redox reactions of Ni hydroxide films (reaction 1). Based on X-ray diffraction, CV and EQCM measurements, it was shown that, in the case of $\alpha\text{-Ni(OH)}_2$, which has a long inter-sheet distance between the Ni(OH)_2 layers ($8.6 \text{ \AA}$), the mass of the film increases during oxidation and decreases during reduction [36,37]. It was suggested that, while the large inter-sheet distance of $\alpha\text{-Ni(OH)}_2$ readily allows cations to enter and protons to exit the film during oxidation, the mass increase due to the injection of heavy cations, overwhelms the mass decrease caused by the expulsion of protons from the film. For $\beta\text{-Ni(OH)}_2$, having a small inter-sheet distance ($4.7 \text{ \AA}$), a reversal of the direction of mass change is seen [36,37], perhaps as the smaller inter-sheet distance of $\beta\text{-Ni(OH)}_2$ restricts cation movement. The mass loss during oxidation (gain upon reduction) was suggested to be caused by proton transport through the lattice only. However, it was shown that, for mixed Ni–Co oxide films, the addition of 10 [35] and 16.7% [37] of co-precipitated Co to pure Ni oxide prevents the reversal of the mass change, indicating that Co may stabilize the $\alpha\text{-Ni(OH)}_2$ phase.

It should be noted that none of the above-mentioned prior studies [28,35–37] included the determination of the pH dependence of the Ni and Ni–Co oxide redox reaction, and therefore the participation of the cationic counter ion cannot be ruled out in interpreting the $\beta\text{-Ni(OH)}_2$ redox behavior.

Electron diffraction and IR spectroscopy investigations of the Ni and Ni–Co SG materials under study in the present work [38] have demonstrated that, as-formed, the films are fcc NiO and/or CoO with a rock salt structure. We suggest that the Co atoms replace every other Ni atom in the unit cell with a lattice parameter of 0.42 nm [39]. Films consist of nanoparticles, ca. $1\text{--}1.5 \text{ nm}$ in diameter. It is suggested that the mechanism of their charge/discharge in alkaline solutions involves the transport of hydrated Na^+ and OH^- , which diffuse in the voids between the SG oxide nanocrystallites. The structural differences between layered Ni and Ni–Co hydroxide materials investigated by other researchers [35,37] and the nanocrystalline SG materials under study here suggest that the mechanism responsible for the partial inversion of the mass changes at negative potentials may be different.

The change of the film mass per mole of electrons passed (mass to charge ratio) during the reduction of SG formed 50:50 Ni–Co oxide films between -0.2 and 0.5 V versus SSCE was calculated using the Sauerbrey equation [26]. This ratio was determined for the reduction reaction only, in order to eliminate error arising from the contribution of the oer to the anodic charge. In the present work, the value of the mass to charge ratio ranges between 2 and $4.5 \text{ g per mole of electrons}$ (further abbreviated as $\text{g mol}^{-1} \text{ e}^-$). This is similar in magnitude to the results reported in the literature for Ni, Co and Ni–Co oxide films formed by various other techniques. Faria et al. [31] reported a $5 \text{ g mol}^{-1} \text{ e}^-$ ratio, calculated during the reduction of rf sputtered Ni oxide films in 0.1 M NaOH , while Mo et al. [35] reported a value of $7 \text{ g mol}^{-1} \text{ e}^-$ for electrodeposited Ni oxide films. However, the proposed stoichiometry of the 50:50 Ni–Co oxide film redox reaction (reaction 6), obtained from the pH dependence of the reaction and involving 1.45 OH^- and 0.45 Na^+ per each electron, predicts a mass change of $35 \text{ g mol}^{-1} \text{ e}^-$. This discrepancy between the theoretically predicted and experimental $\text{g mol}^{-1} \text{ e}^-$ ratios has led to the more detailed analysis of the EQCM data over narrow ranges of potential, which follows.

3.3. Analysis of the mass/charge ratio over narrow potential ranges

The CVs and voltammograms of 50:50 Ni–Co SG oxide films have been analyzed in 50 mV potential segments during the reduction reaction only, in order to eliminate possible errors from the contribution of the

over charge, as discussed above. Fig. 5 shows the calculated $\text{g mol}^{-1} \text{e}^{-}$ ratio during the reduction of a 50:50 Ni–Co oxide film, plotted as a function of potential for various cycling times. Each point on the graph represents the $\text{g mol}^{-1} \text{e}^{-}$ ratio calculated over a 50 mV range, and is plotted at the potential in the middle of each 50 mV segment.

During the first few cycles of potential, the mass/charge ratio is approximately constant over the entire range of potentials (Fig. 5). Its value is ca. -2 to $-4 \text{ g mol}^{-1} \text{e}^{-}$, indicating that 2–4 g of the film mass is lost for each mole of electrons injected during the reduction of the 50:50 Ni–Co oxide film, as Na^{+} and OH^{-} ions are expelled from the SG oxide (reaction 6). At longer cycling times (e.g. after 15 cycles), at potentials positive of ca. 0.2 V versus SSCE, the mass to charge ratio in the negative scan is still within this range. However, as the potential is scanned more negatively, the ratio takes on the opposite sign. The magnitude of this mass inversion seen at negative potentials becomes more pronounced with longer cycling times (Fig. 5, cycle 40). As stated above, this likely reflects structural/morphological changes within the film, not detected by the CV response, and which remain essentially unchanged throughout these experiments.

As has been discussed above, the loss of mass upon reduction of a 50:50 Ni–Co SG oxide film, predicted by

the reaction stoichiometry (reaction 6), is expected to be $35 \text{ g mol}^{-1} \text{e}^{-}$. However, the experimentally determined mass to charge ratio is much smaller and even of the opposite sign after long cycling times. To explain the low values of the mass to charge ratio, it is proposed that, as ions (Na^{+} and OH^{-}) leave the SG oxide film during reduction, a neutral species, such as water, is injected to counterbalance the mass loss. During oxidation of the SG oxide, as OH^{-} and counter ions (Na^{+}) enter the film to maintain electroneutrality, water would then be expelled. Consistent with this, it has been suggested by Burke and Lyons [16] and Biwer et al. [34] that Ni oxide films, formed by electrochemical cycling of Ni substrates in alkaline solutions, dehydrate at the positive and rehydrate at the negative end of the sweep. Also, based on EQCM results, a similar model of water exchange during the oxidation/reduction of electrochemically grown hydrous Ir oxide films has been proposed by Bock and Birss [13].

The redox process in Ni–Co oxide films [40], similar to that in conducting polymers such as polyaniline [15], is coupled with an exchange of ions and/or solvent, which cause changes in the micro and macroscopic dimensions of the active material. Indeed, AFM studies of electrodeposited [41] and anodic [42] Ni oxide films have indicated an increase in volume/thickness of these films upon reduction and a corresponding shrinkage during oxidation.

From the difference between the predicted and experimental values of the mass/charge ratio, the amount of water injected during 50:50 Ni–Co SG oxide film reduction can be calculated (Fig. 6). In these calculations, it has been assumed that the pH dependence of SG Ni–Co oxide films is not influenced by the potential or the cycling time, which is consistent with experiment (the peak potentials do not change after long cycling times in any one solution). Therefore, it can be concluded that the reaction stoichiometry in terms of injected/expelled OH^{-} and Na^{+} ions (reaction 6) also remains unchanged. The observed changes in the mass/charge ratio with potential and cycling time are then attributed entirely to variations in the extent of water exchange. As can be seen from Fig. 6, during the initial period of potential cycling (solid circles), ca. 2–2.5 water molecules per electron, depending on the potential, enter the film during reduction as the ions (OH^{-} and Na^{+}) leave the film. The amount of injected water does not change significantly with potential. At longer cycling times (squares), the water exchange process displays a notable potential dependence, with a larger number of water molecules, up to ca. 3.5, injected at more negative potentials during SG film reduction, while only ca. 1.5 are injected at more positive potentials.

Although the origin of the proposed potential and time-dependent water exchange is not known at this

Fig. 6. Water injection (right-hand scale) during reduction of a 50:50 Ni–Co SG oxide film of Fig. 5 as a function of the applied potential, after first cycle (●) and after 3 h (□) of cycling (10 mV s^{-1}) in 0.5 M NaOH. Film has a mass loading of $81 \mu\text{g cm}^{-2}$ and an equilibrium charge density of 30 mC cm^{-2} . Film formed at 6 cm min^{-1} and dried at 190°C for 15 min.

time, it is clearly related to structural/morphological changes of the SG oxide film during cycling, not detectable by cyclic voltammetry. The increasing amount of water injected during reduction at longer cycling times can be linked to the slow, but progressive degradation of the SG-formed Ni–Co oxide film. Natarajan et al. [43] have recently shown that heat-treatment of anodically deposited electrochromic Ni hydroxide thin films increases their durability from 500 cycles (for as-deposited films) to more than 5000 cycles (for the heat-treated films). With longer cycling times, the Ni–Co SG oxide films may swell and their adhesion to the Pt substrate may deteriorate, which would explain the observed slow decrease in the charge density.

4. Summary

A combination of CV and EQCM techniques has been employed to monitor mass changes during potential cycling of 50:50 SG-formed Ni–Co oxide films in 0.5 M NaOH solutions. The films were dip-coated on Pt sputtered quartz crystals or on Pt foil electrodes at a withdrawal rate of 6 cm min⁻¹ and dried in air at ca. 200°C for 15 min. The experimentally determined pH dependence of –86 mV per pH unit versus a pH-independent reference electrode (SSCE), together with the results of the EQCM measurements, suggests that charging and discharging of the SG Ni–Co oxide films is accompanied by the injection/expulsion of mobile ions (found to be 1.45 OH⁻ and 0.45 Na⁺ per electron passed). The proposed stoichiometry of the redox reaction predicts that the film mass should change by 35 g mol⁻¹ e⁻ passed. However, the experimental values determined during the reduction of the SG Ni–Co oxide films ranged between 2 and 4.5 g mol⁻¹ e⁻.

The discrepancy between the theoretically predicted and experimental mass/charge ratios suggest that, as ions (Na⁺ and OH⁻) leave the film during reduction, between 1.5 and 3.5 moles of water per mole of electrons, are injected to counterbalance the mass loss in fresh SG-formed Ni–Co oxide films. During oxidation of the SG oxide, as OH⁻ and counter-ions (Na⁺) enter the film to maintain electroneutrality, water is then expelled. An increased amount of exchanged water (up to 3.5 moles of water per each mole of converted Ni/Co sites) at longer cycling times and, particularly at negative potentials, may indicate the early stages of SG film degradation. Although an unambiguous identification of all of the species involved in the mass transport within the oxide film cannot be determined by CV and EQCM, these studies provide a deeper insight into the morphological changes of the Ni–Co SG oxide films which occur with time of cycling in alkaline solutions.

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