

Capacitance studies of cobalt oxide films formed via electrochemical precipitation

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Abstract

Cobalt oxide films were prepared by electrochemically precipitating the hydroxide and heating it in air to form Co_3O_4 . The resulting oxide films behave as a capacitor. The materials were studied emphasizing their use as either positive or negative electrodes in devices. The capacitance of the material was estimated at different heating temperatures and insight was gained into the charge storage mechanism. It was seen that the charge storage in cobalt oxide was similar to that of nickel oxide, although their capacitances were different. While, the material was shown to be inferior to nickel hydroxide/oxide when used as a positive electrode, it was seen to be superior as a negative. An asymmetric capacitor with NiO as a positive electrode and Co_3O_4 as a negative promises adequate capacitance over a large voltage window. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

With the prominence gained by hybrid electric vehicles (HEV) in recent years, high power energy storage systems have received much attention [1–3] for use in acceleration and charge storage during regenerative braking. While carbon-based devices, where the charge storage is confined to the double layer formed at the electrode/electrolyte interface, have been commercialized, the low utilization of the active material (~10%) [4], has driven the need to identify more suitable materials. One promising route is the use of transition metal oxides for these devices. The ability to achieve high specific capacitance with materials like RuO_2 [5,6] and IrO_2 [6], with values as large as 760 F/g [5], has spurred research in this area. These class of materials, which exhibit a current–voltage response similar to a double layer albeit with charge transfer process similar to batteries, are referred to as Faradaic or pseudocapacitors. However, the high cost of these materials has necessitated the need to identify low cost alternatives with similar characteristics.

Recently, Liu and Anderson [7–10] reported the pseudocapacitance of nickel oxide films that were made by heating

sol–gel-derived nickel hydroxide ($\text{Ni}(\text{OH})_2$) in air at 300 °C. Subsequently, we investigated similar nickel oxide films, where the nickel hydroxide was produced via electrochemical deposition [11,12]. Both techniques yield materials with specific capacitance as high as 260 F/g. Although, from a capacitance standpoint these materials are similar to activated carbon [4], their advantage is the ability to make them into thin films, whereby high power densities can be achieved. In addition, the materials were seen to have excellent cycle life and high current utilization [11].

However, the capacitance of nickel oxide was found to be potential dependent with a voltage range of ~0.5 V. In other words, while NiO is suitable as a positive electrode in devices, its use as a negative electrode would limit the voltage window significantly. Therefore, another material needs to be identified which exhibits capacitance in negative potentials. In addition, it is desirable to study the generality of the electrochemical precipitation technique as a means of fabricating other oxide films for use in capacitor applications. Hence, here we study cobalt oxide prepared using a similar electrochemical deposition technique. The study was conducted on two potential windows, one between –0.15 and +0.35 V versus saturated calomel electrode (SCE) and other between –0.35 and –0.05 V versus SCE.

The possibility of CoO_x being a candidate for capacitor application was explored by Lin et al. [13], who prepared cobalt oxide xerogels using a sol–gel technique, followed by

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a heating step to different temperatures. The materials exhibit excellent cycle life with no significant change in the cyclic voltammogram (CV) for up to 10,000 cycles. However, the material did not possess the box-shape characteristic of capacitors, but rather battery-like behavior was observed. Using the charge passed, the capacitance of the material was estimated to be 290 F/g for a single electrode. However, no capacitance was seen at potentials less than 0.0 V versus SCE.

While, the above method involves making bulk materials using the sol–gel technique, Liu et al. [14] demonstrate the use of cobalt metal as a charge storage material. Here, the metal is cycled in NaOH solution for ≈ 3000 cycles, whereby an oxide film formed on the surface grows with cycling. Such a technique was previously demonstrated by Simpraga [15] with the motive of understanding the redox processes better. Although peaks are clearly visible, the overlapping reactions leads to the current–voltage signature similar to that of a capacitor. However, no capacitance values are reported.

2. Experimental

Thin films of cobalt hydroxide were deposited on gold foils masked with a sealant (SiliconeTM) so as to expose an area of 1.0 cm². The films studied here were deposited at room temperature in a bath containing 0.175 M Co(NO₃)₂ and 0.075 M NaNO₃ in a solvent of 50 vol.% ethanol in a procedure described in detail elsewhere [16,17]. A cathodic current density of 1.0 mA/cm² was applied for 8 min, which resulted in 360 $\mu\text{g}/\text{cm}^2$ films, as measured using an electrochemical quartz crystal microbalance (EQCM). The expected capacity was confirmed by performing cyclic voltammetry on cobalt hydroxide in 3 wt.% KOH and integrating the area under the reduction peak of a stable CV.

For subsequent studies in KOH, the cycled cobalt hydroxide films were again rinsed in de-ionized water, heated in air to the desired temperature at a rate of 5 °C/min, maintained at that temperature for 3 h and subsequently cooled at 5 °C/min to room temperature. The oxide films were then cycled in the electrolyte for approximately 25 cycles and the steady-state capacitances were measured.

A SCE and a platinum mesh were used as the reference and counter electrode, respectively, in all experiments. Deposition and CV studies were conducted on a computer controlled EG&G M273 potentiostat/galvanostat using the M270 software. The capacity of the films were estimated by integrating the area under the CVs using the software.

3. Results and discussion

Fig. 1 shows the first two cycles of an as-deposited cobalt hydroxide film from -200 to $+350$ mV versus SCE at a sweep rate of 5 mV/s. While, the first oxidation cycle results in a charge transfer of ~ 363 mC, the subsequent reduction

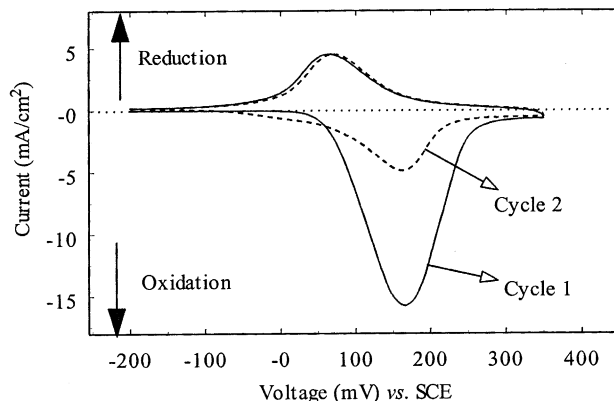


Fig. 1. CV of a as-deposited 360 $\mu\text{g}/\text{cm}^2$ cobalt hydroxide film at a sweep rate of 5 mV/s. Note the decrease in charge storage after the first oxidation cycle.

and oxidation steps correspond to only ~ 130 mC (a 64% loss in capacity). Continued cycling shows that the film is stable with little loss in capacity with cycling. This suggests that while Co can be oxidized to a higher oxidation state in the first cycle, the reverse reaction is not completely reversible.

When this material is heated to different temperatures between 100 and 350 °C, as shown in Figs. 2 and 3, the capacity of the film is reduced even further to approximately 50 mC even at 100 °C. For films heated to 300 °C and below, the CVs in this positive potential window show the presence of a redox reaction in addition to capacitance. The ratio of the redox peak current to the capacitive current decreases with increasing temperature. At 350 °C, the CV is completely capacitive, resembling the “box-shape” seen in capacitor materials.

In investigating sol–gel-precipitated cobalt oxide electrodes, Lin et al. [13] show using TGA evidence that at ~ 160 °C cobalt hydroxide decomposes to form cobalt oxide by removal of chemisorbed water according to,

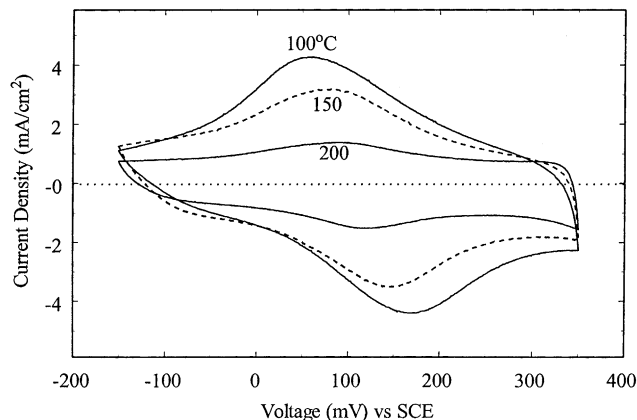
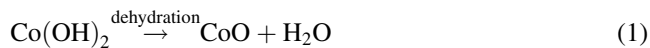


Fig. 2. CV of a cobalt oxide film heated to temperatures less than 200 °C when used as a positive electrode at a sweep rate is 20 mV/s. The Faradaic reaction seen in the figure is due to the reaction (3).

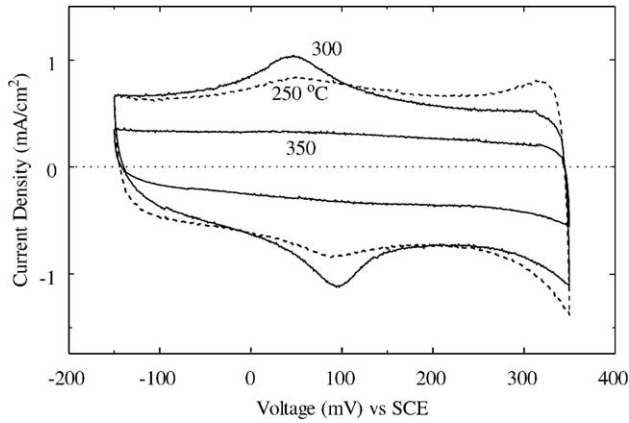


Fig. 3. CV of a cobalt hydroxide film heated to temperatures, above 200 °C when used as a positive electrode at a sweep rate is 20 mV/s. Note the capacitor-like behavior.

As the electrode is heated further, the authors found an additional weight loss beyond 200 °C, which was attributed to the cobalt oxidation reaction



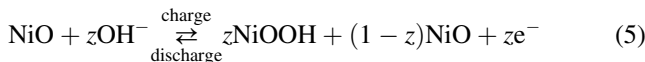
Reaction (2) proceeds until 400 °C, although at these temperatures, primary CoO_x particles aggregate to form larger crystallites thus reducing the surface area of the material [13]. Based on the TGA evidence, the redox peaks seen in Fig. 2 at temperatures less than 200 °C can be attributed to [13,18]



Above 200 °C, the redox peaks seen in Fig. 3 can be attributed to [13,18]



Note that reaction (4) is comparable to the redox reaction seen in nickel oxide material when heated above 300 °C, represented by [12]



In summary, it would appear that while $\text{Co}(\text{OH})_2$ exhibits a battery-like behavior (similar to $\text{Ni}(\text{OH})_2$), Co_3O_4 exhibits a capacitor-like behavior (similar to NiO).

Fig. 4 shows that at temperatures lower than 200 °C when the material is cycled in negative potentials, the behavior of the electrode is unlike that of a capacitor. Although the CVs appear to resemble a capacitor during the initial few cycles (not shown), the behavior is not stable and after 50 cycles all capacitive behavior is lost. Previous researchers have indicated the presence of a redox reaction at this potential range in cobalt oxide electrodes according to [19]

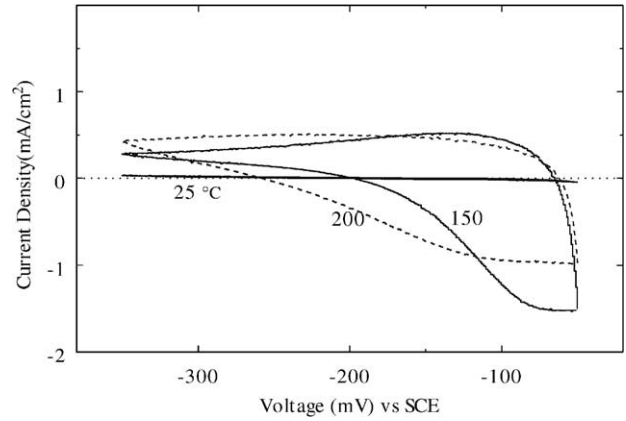
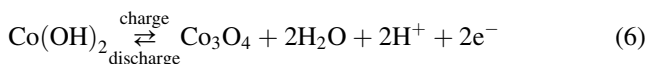


Fig. 4. CV of a cobalt hydroxide film heated to temperatures less than 200 °C when used as a negative electrode at a sweep rate of 20 mV/s. The CVs, which exhibit a capacitor-like behavior initially, are unstable on extended cycling.

Although no peaks were apparent in this study, the shoulder in Fig. 4 may be a result of such reactions. However, at temperatures above 200 °C, in agreement with the results in Fig. 3, the CVs in Fig. 5 resemble that of a capacitor with a fairly constant current over the voltage window of operation. One difference between the CVs in Figs. 3 and 5 are the lack of a redox peak at lower temperatures in Fig. 5 (i.e. no redox peaks when heated between 250 and 300 °C and cycled in the more negative potential window). The second difference is the tilt seen in the CVs at all temperatures in Fig. 5. A consequence of this tilting current is that cycling below -350 mV versus SCE did not provide much capacitance during the reverse sweep as the currents remained cathodic. Such a tilt in a CV may be caused by Ohmic resistance in the oxide film.

The specific capacitance of the material was estimated from the CVs by integrating the area under the current–potential curve and then dividing by the sweep rate, the mass

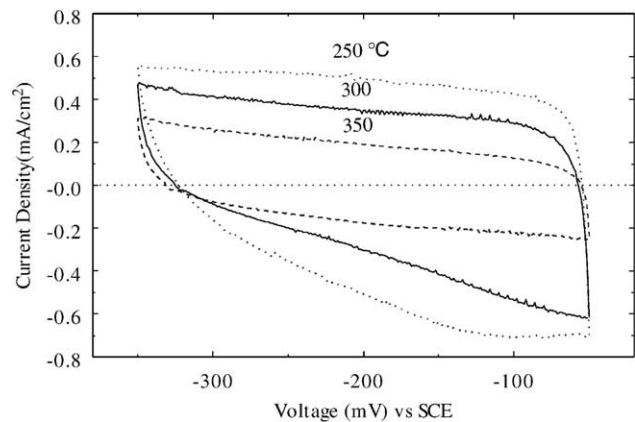


Fig. 5. CVs of a cobalt oxide film heated temperatures above 200 °C when used as a negative electrode at a sweep rate of 20 mV/s. Note the capacitor-like behavior of the material.

of the film and the potential window according to the equation

$$C = \frac{1}{mv(V_a - V_c)} \int_{V_a}^{V_c} I(V) dV \quad (7)$$

where $(V_a - V_c)$ represents the potential window. Similar to NiO [12], the weight of this material is also dependent on the heating temperature, as discussed below.

Unlike nickel hydroxide, cathodically precipitated cobalt hydroxide is stoichiometric (i.e. does not contain cobalt vacancies). For example, when a 70 μg cobalt hydroxide film is deposited using an EQCM and then oxidized according to reaction (3), the charge passed is consistent with a one electron transfer when the moles of cobalt are calculated using the molecular weight of cobalt hydroxide (92.93 g). This is also consistent with TGA experiments on the material [13] where no weight losses due to lattice water is seen, in contrast to nickel hydroxide. Therefore, when the material is heated to temperatures above 150 $^{\circ}\text{C}$, it was assumed to be predominantly Co_3O_4 . Although the presence of CoO is seen at intermediate temperatures, this reaction is neglected as the weight change occurring from CoO to Co_3O_4 conversion is negligible ($\sim 6\%$). Therefore, the weight of the material is calculated using the difference between the molecular weights of $\text{Co}(\text{OH})_2$ (92.93 g) and Co_3O_4 (80.26 g)—a loss of 14%. This is consistent with the TGA results of Lin et al. [13], where a weight loss of $\sim 15\%$ was seen above 150 $^{\circ}\text{C}$.

Fig. 6 shows a plot of the specific capacitance versus the temperature for cobalt oxide materials when used as a positive electrode. Less than 200 $^{\circ}\text{C}$, the charge storage behavior corresponds to a redox reaction. Eq. (7), which is applicable for a system exhibiting capacitance, results in a large capacitance of ~ 750 F/g for the as-deposited material

after the first cycle. Similarly, when the precursor of NiO (i.e. nickel hydroxide, the active material in nickel batteries) is evaluated using Eq. (7) in the potential window 0.0 and 0.45 V versus SCE, a capacitance of ~ 2000 F/g is obtained. This high “capacitance” is due to the bulk intercalation of protons into the solid phase, which is represented by the following overall reaction



This indicates that as-deposited, nickel hydroxide is a considerably better charge storage material compared to cobalt hydroxide, but neither should be classified as a capacitor. When heated to temperatures higher than 200 $^{\circ}\text{C}$, the CV of Co_3O_4 resemble that of a capacitor and the region shows as much as 50% drop in capacitance compared to the lower temperatures. Fig. 6 also shows the specific capacitance of NiO cycled between 0.0 and 0.35 V versus SCE for comparison [12] for values above 275 $^{\circ}\text{C}$. This potential window was chosen in a previous study as it was seen to avoid the redox peaks due to reaction (8). Increasing the potential window would result in higher capacitance, especially at temperatures lower than 275 $^{\circ}\text{C}$ as the reaction (8) will dominate. In other words, it can be misleading to calculate a capacitance below 275 $^{\circ}\text{C}$ for NiO and below 200 $^{\circ}\text{C}$ for the Co_3O_4 as charge storage under these conditions correspond to redox reactions. However, in the voltage windows used, the specific capacitances of the two materials are comparable and both show a drop in capacitance at higher temperatures.

The estimation of the intrinsic capacitance (F/cm^2 of total surface area) provides a means of understanding the nature of the charge storage mechanism in these materials. Using

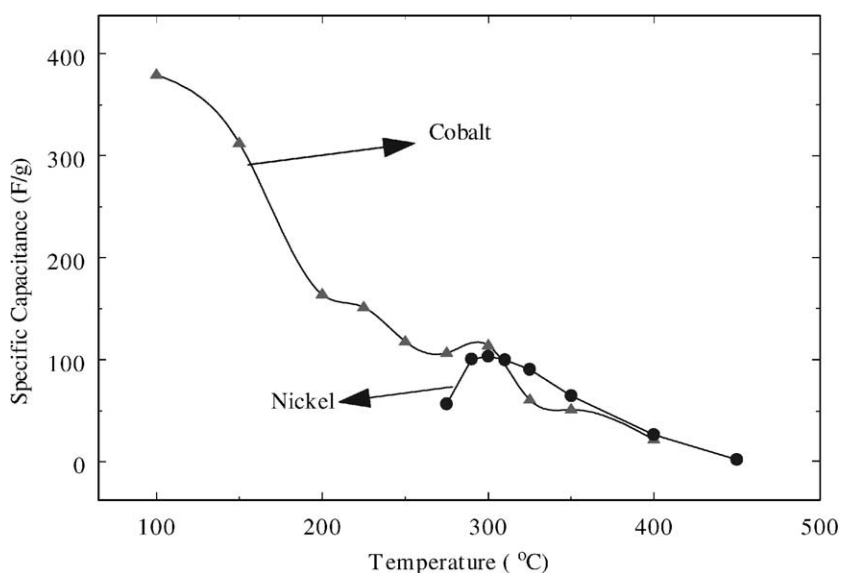


Fig. 6. Capacitance vs. temperature for the cobalt hydroxide material when used as a positive electrode (cycled between -0.15 and $+0.35$ V vs. SCE). The capacitance was calculated from the CVs and the mass of the film at that temperature as detailed in the text. The capacitance of NiO cycled between 0.0 and 0.35 V vs. SCE is also shown for comparison.

the BET surface area measurements performed by Lin et al. [13] on sol–gel-derived cobalt oxide material at 200 °C, namely, 180 m²/g with the capacitance (164 F/g) the intrinsic capacitance was estimated to be 90 μF/cm². This high capacitance is unrealistic from a Helmholtz double layer and hence can be attributed to a redox reaction (4). This is similar to NiO, where an intrinsic capacitance of 70 μF/cm² was estimated at 300 °C [12].

Assuming that reaction (4) represents the mechanism of charge storage in these materials, the utilization of the active material can be gauged by Faraday's law using the equation

$$z = \frac{CM \Delta V}{F} \quad (9)$$

where C is the specific capacitance, M the molecular weight and ΔV the potential window. In other words $z = 1$ means that all the active material is utilized. Using the molecular weight of Co₃O₄ (80.26 g), the specific capacitance at 200 °C (164 F/g) and the voltage window (0.5 V), z is estimated to be 0.06. In other words, 6% of the total active material is seen to participate in the charge storage at 200 °C, suggesting a surface phenomenon. A similar analysis at 100 °C assuming the material to be Co(OH)₂ shows that as much as 18% of the material is utilized. In other words, while low temperatures lead to more bulk utilization, charge storage at higher temperatures is restricted to the surface. However, this decrease is accompanied by a change in the behavior from a battery to that of a capacitor. A similar trend was also seen in nickel hydroxide and nickel oxide, where only 2.5% of the material was seen to be active at 300 °C.

Fig. 7 shows the specific capacitance calculated using Eq. (7) and Figs. 4 and 5 for the negative electrode. The mass of the material was estimated in the same manner as described above. The graph shows an increase in capacitance at lower temperatures with a peak at 225 °C. Based on the TGA evidence [13], it would appear that the capacitive behavior corresponds to the formation of Co₃O₄. On further heating the specific capacitance decreases, consistent with

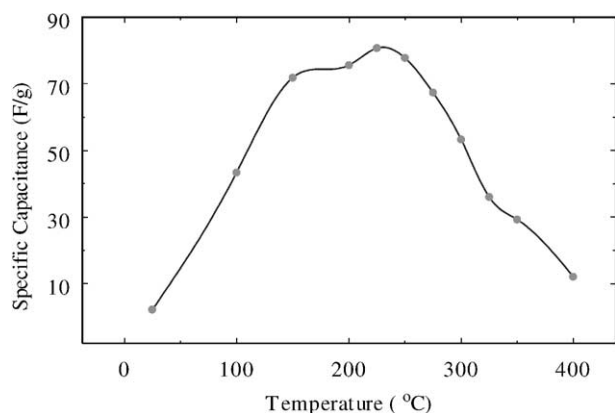


Fig. 7. Capacitance vs. temperature for the cobalt hydroxide material when used as a negative electrode (cycled between 0.35 and –0.05 V vs. SCE). The capacitance was calculated from the CVs and the mass of the film at that temperature as detailed in the text.

results on the positive electrode. Using the surface area of Co₃O₄ (180 m²/g) estimated by Lin et al. [13] and the specific capacitance (76 F/g) at 200 °C the intrinsic capacitance was estimated to be 42 μF/cm², again a value at least twice larger than that expected for the Helmholtz double layer, suggesting a pseudocapacitive mechanism possibly based on reaction (4). In addition, an analysis based on Eq. (9) suggests that at 200 °C only 1.9% of the material is accessed as opposed to 6% estimated for the positive electrode. It should be noted that nickel oxide exhibits no charge storage capability in this region.

In summary, while at low temperatures cobalt hydroxide is seen to exhibit a large capacitance when used as a positive electrode, its charge storage is that of a battery and is considerably smaller than nickel hydroxide. When converted to Co₃O₄ by heating, the material starts to behave more as a capacitor with capacitance comparable to NiO when cycled in a positive potential window. However, the cost difference between the two materials makes Co₃O₄ a less desirable candidate as a positive electrode. However, as a negative electrode, cobalt-based materials provide an attractive proposition. In this region the charge storage in this material is far greater than that in NiO. This is seen clearly in Fig. 8, where CVs of NiO heated to 300 °C and Co₃O₄ heated to 250 °C are shown over their whole range of charge storage. The 0.5 V potential window for the NiO material is extended to 0.9 V when used with Co₃O₄ as a negative electrode in a hybrid capacitor.

Both cobalt and nickel oxide show considerable similarities in their charge storage mechanism. At low temperatures, when H⁺ diffusion causes the charge storage in the two materials (corresponding to reactions (3) and (8)) more of the bulk is utilized and the charge storage mechanism resembles that of a battery. On heating to the oxide, the charge storage is that due to OH[–] ions and the reaction shifts to more of a surface phenomenon. Considering the size differences between the proton and the OH[–] ions, it is not surprising that no bulk utilization occurs. This change to a

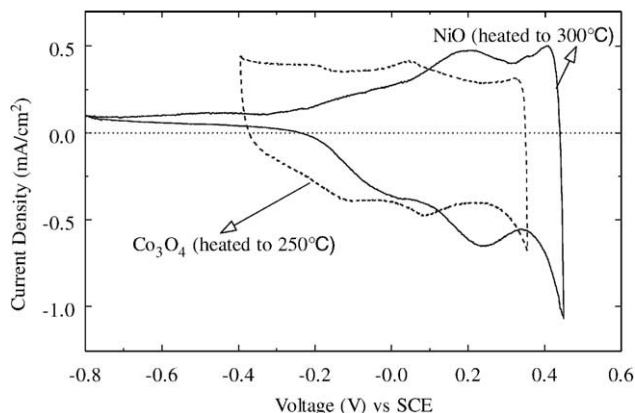


Fig. 8. CV of NiO heated to 300 °C and Co₃O₄ heated to 250 °C over a wide potential window. The mass of the as-deposited film was 350 μg for both the films. Note the comparable capacitance over the different voltage regimes.

surface reaction results in the signature of the material changing to that of a capacitor. However, this is in contrast to RuO₂ where the current–voltage response is representative of capacitance even when 85% of the bulk is accessed.

Considering that the reaction is limited to the surface, in order to enhance the capacitance of these materials, the particle size would have to be reduced such that more of the surface is accessed by the electrolyte. The electrochemical route offers a possible solution, as the current and the solution composition can be changed to change the rate of deposition—a possible method to control the particle size.

4. Conclusions

The paper illustrates the behavior of electrochemically precipitated cobalt hydroxide films when heated to different temperatures. Studies were conducted in two potential windows to gauge the use of this material as both a positive and negative electrode. As a positive electrode, the charge storage capacity of Co₃O₄ was similar to that of NiO. However the low cost of Ni compared to Co makes the former more attractive as a positive electrode in devices. As a negative electrode, Co₃O₄ exhibited capacitive behavior far superior to NiO. Although the capacitance is smaller in this region (76 F/g in the negative, compared to 164 F/g in the positive), the value is comparable to carbon capacitors as negative electrodes.

The charge storage mechanism in cobalt was seen to be analogous to nickel. While at room temperature proton diffusion occurs resulting in bulk being accessed, on heating the reaction shifts to OH[−] adsorption on the surface. The study indicates that an asymmetric device with NiO as a positive electrode and CoO as a negative would occur a adequate capacitance with a large potential window (0.9 V) at a reasonably low cost.

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