

1997

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Publication Info

Journal of the Electrochemical Society, 1997, pages L210-L213.

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<http://www.electrochem.org/>

Publisher's link: <http://dx.doi.org/10.1149/1.1837859>

DOI: 10.1149/1.1837859

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Acknowledgment

This work was carried out with financial support from the U.S. Air Force Office of Scientific Research and Development and from the Israel Ministry of Defense.

Manuscript submitted March 3, 1997; revised manuscript received May 27, 1997.

Tel Aviv University assisted in meeting the publication costs of this article.

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An Electrochemical Route for Making Porous Nickel Oxide Electrochemical Capacitors

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ABSTRACT

Porous nickel oxide films were prepared by electrochemically precipitating nickel hydroxide and heating the hydroxide in air at 300°C. The resulting nickel oxide films behave as an electrochemical capacitor with a specific capacitance of 59 F/g electrode material. These nickel oxide films maintain high utilization at high rates of discharge (*i.e.*, high power density) and have excellent cycle life. Porous cobalt oxide films were also synthesized. Although the specific capacitances of these films are approximately one-fifth that of the nickel oxide films, the results demonstrate the versatility of fabricating a wide range of porous metal oxide films using this electrochemical route for use in capacitor applications.

Introduction

Electrochemical capacitors have generated wide interest in recent years for use in high power applications^{1,3} (*e.g.*, in a hybrid electric vehicle, where they are expected to work in conjunction with a conventional battery). Presently, most commercial electrochemical capacitors function by extracting the energy stored in the double layer formed at the electrode/electrolyte interface. The capacitance of an electrochemical double layer is typically in the range of 10 to 40 $\mu\text{F}/\text{cm}^2$ ⁴ and the voltage is limited by the electrochemical stability of the electrolyte (*e.g.*, 1.2 V for an aqueous electrolyte). One strategy for increasing the energy of an electrochemical double-layer capacitor is to use high surface area materials such as activated carbon. Unfortunately, about 90% of the available surface area is not used owing to the significant fraction of micropores that cannot be wetted by the electrolyte.⁵

Another means of increasing the energy of an electrochemical capacitor is to use faradaic pseudocapacitance (*i.e.*, electrosorption or redox processes¹⁻³). For example, metal oxide based capacitors, such as RuO_2 or IrO_2 , exhibit faradaic pseudocapacitance.^{1,6,7} Nevertheless, the high cost of ruthenium and iridium have been an impediment to the commercialization of these systems.

Recently, Liu and Anderson developed an electrochemical pseudocapacitor using porous films of nickel oxide prepared using the sol-gel technique.^{8,9} The first step in this process is to prepare a sol by stirring a solution of nickel hydroxide and water for 2 days to hydrolyze the salt. Once the sol is formed, thin films of nickel hydroxide and nickel acetate are prepared by dipping a nickel foil into the sol. The films are then heated in air to 300°C to produce nickel oxide xerogel films $\sim 0.4 \mu\text{m}$ thick. Liu and Anderson report-

ed a specific capacitance of ~ 50 to 65 F/g electrode, a value comparable to that of activated carbon.⁵ Even though the specific capacity, and hence the energy density, of the nickel oxide film is comparable to activated carbon, the ability to make thin films via the sol-gel process enables high power devices to be fabricated. However, the sol-gel technique used by Liu and Anderson is tedious and difficult to control. For example, in this process the withdrawal rate of the foil from the sol controls the thickness of the nickel hydroxide films.

We report here a relatively inexpensive and highly controllable method for making a porous nickel oxide capacitor using an electrochemical precipitation technique followed by the heating step used by Liu and Anderson.⁹ The resulting nickel oxide films behave as an electrochemical capacitor with a specific capacitance of 59 F/g electrode material which is comparable to electrodes made via the sol-gel method. The advantage of the electrochemical precipitation technique is that the mass, and consequently, the thickness of the nickel hydroxide film can be controlled with relative ease and accuracy by controlling the current, bath chemistry, and temperature,¹⁰⁻¹² thus making the process attractive for device fabrication. Films of cobalt hydroxide have also been deposited electrochemically and heated to assert the generic nature of the method as a means to fabricate metal oxide electrodes for high power applications.

Experimental

Thin films of nickel hydroxide were deposited electrochemically onto a 0.2 cm^2 gold substrate sputtered on a quartz crystal in a procedure described in detail elsewhere.¹⁰⁻¹¹ An electrochemical quartz crystal microbalance was used to measure the mass of the deposited films. The films studied here were deposited at room temperature in a bath containing 1.8 M $\text{Ni}(\text{NO}_3)_2$ and 0.075 M NaNO_3 in a solvent of 50 volume percent (v/o) ethanol using a

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cathodic current density of 5 mA/cm². The deposition times for a 7.0 and 70.0 μg film were 2.0 and 27.0 min, respectively. The film thickness can be estimated by dividing the mass by the product of the density and the cross-sectional area. For a $\text{Ni}(\text{OH})_2$ density of 3.5 g/cm³¹³ and an area of 0.2 cm², the corresponding film thicknesses for the 7 and 70 μg films are 0.1 and 1 μm , respectively. Cobalt hydroxide films were deposited at room temperature in a bath containing 0.175 M $\text{Co}(\text{NO}_3)_2$ in a solvent of 50 v/o ethanol. A cathodic current density of 5 mA/cm² for 2.0 min was used to produce a 70 μg cobalt hydroxide film.

The deposited films were washed in deionized water and heated in air at either 200 or 300°C for 2 h and allowed to cool for an additional 3 h. Heated films were characterized electrochemically in a 3% KOH solution using a Ag/AgCl reference and a platinum counterelectrode. Cyclic voltammetry and galvanostatic charge/discharge experiments were conducted on the films using an EG&G M273 potentiostat/galvanostat.

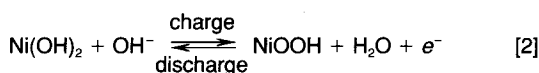
Results and Discussion

Thermogravimetric analysis was conducted on electrochemically precipitated nickel hydroxide to reveal that ~50% of the weight is lost when the film is heated to 300°C.^{14,15} This behavior is attributed to the loss of the water of hydration and adsorbed water at ~200°C and further by the conversion of the hydroxide to the oxide at ~300°C according to the reaction¹⁴⁻¹⁶



Therefore, the 7.0 and 70 μg films will have masses of ~3.5 and 35 μg , respectively, after heating to 300°C.

The change in the electrochemical response of the film resulting from the loss of water at 200 and 300°C is seen in Fig. 1. Three different cyclic voltammograms are shown in this figure: (i) the freshly deposited 7 μg film, (ii) the film heated to 200°C, and (iii) the film heated to 300°C. In all figures, reduction currents are positive. The anodic and cathodic peaks in voltammograms (i) and (ii) correspond to oxidation and reduction of the active material according to the reaction



Heating the film to 200°C does not significantly affect the electrochemical response of the materials which is consistent with the statement that only adsorbed water is lost when $\text{Ni}(\text{OH})_2$ is heated to 200°C.^{14,15} In contrast, when the film is heated to 300°C a fundamentally new structure with significantly less capacity than the fresh film is formed. The cyclic voltammogram reveals that the film heated to 300°C resembles a capacitor.

The capacitive behavior of the nickel oxide film is seen more clearly in Fig. 2 where a 35 μg film is compared to the 3.5 μg film shown in Fig. 1. Again, the voltammograms from the films heated to 300°C do not contain distinct oxidation and reduction peaks characteristic of reaction 2. The redox reaction of nickel oxide is thought to be^{8,16,18}

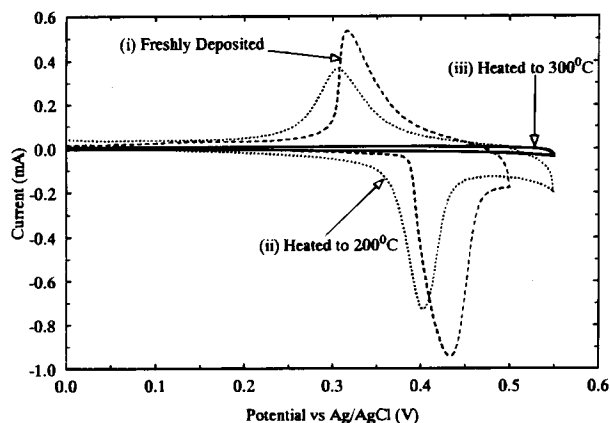


Fig. 1. CVs of nickel hydroxide films heated to different temperatures. (---) Corresponds to a freshly deposited film, (····) corresponds to a film heated to 200°C, and (—) to a film heated to 300°C. The fresh film was 7 μg and the film heated to 300°C was ~3.5 μg . In all three cases the sweep rate was 20 mV/s.

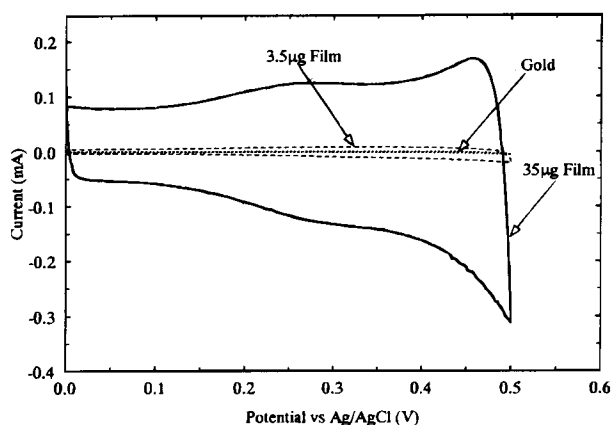


Fig. 2. CVs of nickel oxide films of varying masses. (····) Corresponds to a CV on gold, (---) to a 3.5 μg film, and (—) to a 35 μg film.

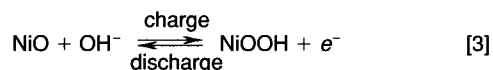


Figure 2 also shows a voltammogram on gold for comparison to assert that the capacitance effect is not associated with charging of the double layer across the 0.2 cm² electrolyte/film interface. Rather the capacitance results from the three-dimensional nature of the oxide films. This is further evident because the 35 μg film shows a capacitance approximately ten times that of a 3.5 μg film. If the capacities of the heated films were due only to their projected surface area then there would be no change in capacity with a change in mass.

The average capacitance of the 35 μm nickel oxide films shown in Fig. 2 is estimated to be 5.8 mF from the cyclic voltammograms. This value was obtained by using the current at 0.25 V and dividing by the sweep rate. The specific capacitance of a device fabricated from these films has a value approximately four times smaller than that for a single electrode, a factor of two to account for the mass of the positive and negative electrodes, and another factor of two to account for the two capacitors being in series. Therefore, the specific capacitance of a device consisting of two 35 μm thick nickel oxide films is ~42 F/g active material (*i.e.*, excluding the mass of the electrolyte, current collector, or device packing).

The capacitive behavior of the electrochemically deposited films is similar to those observed on sol-gel derived films.⁸ Liu and Anderson speculated that the capacitance may be associated with the formation of micropores during the heating process as water is lost from the lattice spacing according to reaction 2. They measured a Brunauer, Emmett, and Teller method (BET) surface area of ~120 m²/g. Although this value is significantly less than the surface area of ~1000 m²/g for activated carbon,⁵ the nickel oxide film exhibits a specific capacitance equivalent to activated carbon.

An advantage of using the sol-gel process is that the microstructure of the resulting material can be controlled precisely. However, changes in the microstructure of the porous nickel oxide films also can be achieved using the electrochemical route by changing the current, temperature, and alcohol content during the deposition process. A previous study has indicated that variations in the deposition process lead to films with varying nickel-to-solvent ratio.¹¹ In addition, it may be that the heating process rather than the deposition process ultimately controls the microstructure. For example, Natarajan *et al.*¹⁶ have shown that their heating process produced nickel oxide films that on cycling showed distinct oxidation and reduction peaks corresponding to reaction 2. Therefore, the temperature and time for which the films are heated have a marked effect on the electrochemical response of the films. Also, work on other oxide materials has indicated that the drying temperature has a significant effect on the microstructure of the resulting films.¹⁹ Thus, the electrochemical route is faster and offers better control over the film mass in addition to producing oxide films of equivalent quality to those made via the sol-gel process.

Further, the electrochemical route can be easily adapted to synthesize mixed oxide capacitors using a coprecipitation technique similar to that demonstrated for the nickel hydroxide deposition where metals such as cobalt and manganese have been incorpo-

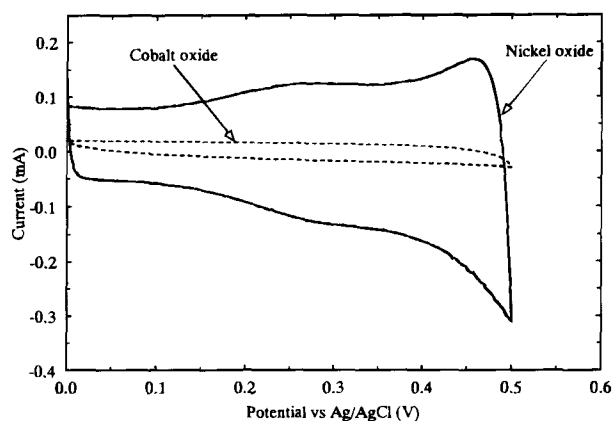


Fig. 3. CVs of hydroxide films following heating to 300°C. The mass of both porous oxide films was 70 μg before heating. The sweep rate was 20 mV/s.

rated into the film.^{10-12,17} To test the applicability of the method in fabricating other metal oxide capacitors, films of cobalt oxide were prepared and subjected to similar electrochemical tests. Figure 3 shows the cyclic voltammogram (CV) of a heated 70 μg cobalt hydroxide film compared to a nickel oxide film. The heated cobalt hydroxide film clearly exhibits a capacitance effect, but of a smaller magnitude compared to the nickel oxide film. Assuming similar weight losses as in the nickel hydroxide system, the capacitance of a device consisting of two cobalt oxide electrodes is ~ 10 F/g electrode material.

For these materials to be suitable for use in electrochemical capacitors, they should exhibit the following two characteristics: (i) maintain high utilization at high currents and (ii) have long cycle life. Therefore, galvanostatic discharge experiments were conducted on the nickel oxide films to quantify the loss in capacity at high discharge rates, and CVs were used to test cycle life. Figure 4 shows ohmically corrected discharge curves as a function of discharge rates for the heated films (*i.e.*, nickel oxide films). At a given discharge rate the nickel oxide film has significantly less capacity as compared to the nickel hydroxide film. However, the oxide film loses only 7% of its capacity at 30 mA/cm². In contrast, a 70 μg nickel hydroxide film loses $\sim 20\%$ of its capacity at 30 mA/cm².²⁰

The discharge curves shown in Fig. 4 can be used to estimate the energy density of a device constructed from these films with a voltage span of 1 V (*i.e.*, aqueous electrolyte). For example, the energy density is estimated by finding the area under the voltage-time curve from 0.5 to 0.0 V, multiplying this by the current, and dividing by the weight of the positive and negative electrodes. The power density is determined by multiplying the voltage of the device at the start of discharge (1 V) by the current and dividing by the weight of the positive and negative electrodes. Using the data

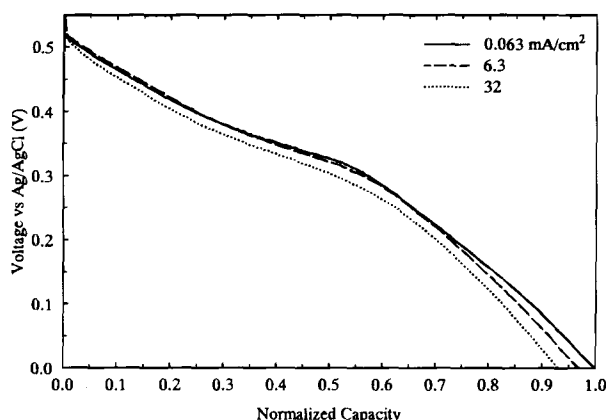


Fig. 4. Discharge curves as a function of discharge rate for a porous nickel oxide film. The curves were normalized using the capacity at the lowest current. The mass of the film was 35 μg .

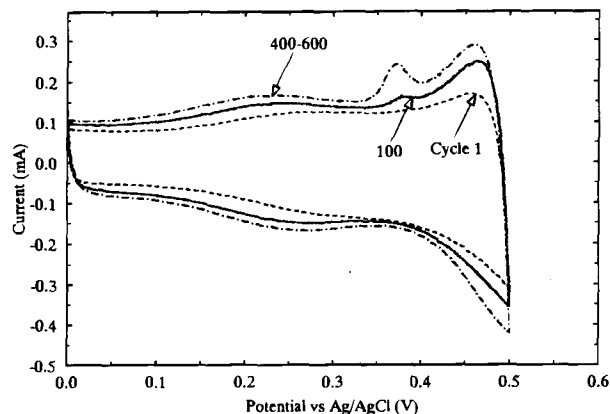


Fig. 5. Cycle life studies of a 35 μg porous nickel oxide film. (---) Corresponds to the first cycle, (—) corresponds to the hundredth cycle, and (---) to cycles from 400 to 600.

in Fig. 4, a device constructed from nickel oxide films and discharged at 0.063 mA/cm² has an energy density of 3.4 Wh/kg active material and a peak power density of 0.2 kW/kg. At 32 mA/cm², the peak power density increases to 90 kW/kg while the energy density decreases only 7% to 3.1 Wh/kg. Although these power densities exclude the resistance of the separator, it does indicate the promise of thin porous metal oxide films in high power applications.

To study the cycle life of the films, cyclic voltammetry experiments were conducted. The fresh film and the one heated to 200°C lost 50% of their capacity after 15 cycles. In contrast, the film in Fig. 5, which was heated to 300°C, shows a 40% increase in capacity to 59 F/g during the first 400 cycles. This increase in capacitance results in a device with energy densities 40% higher than those given above. As the cycle number increases, cathodic peak currents become more prominent. These peaks may be due to: (i) nickel oxide redox processes occurring via reaction 3; (ii) the oxidation and reduction of Ni³⁺ to the plus four oxidation state²¹; or (iii) rehydration of the oxide film and subsequent redox processes occurring via reaction 2. Voltammograms between 400 and 600 cycles were visually indistinguishable from one another. Spectroscopic information is currently being collected to understand the redox chemistry of these films on cycling.

Conclusion

A novel electrochemical route to fabricate porous metal oxide capacitors has been investigated with particular reference to nickel oxide. The nickel oxide films have a specific capacitance comparable to those made via sol-gel methods (~ 59 F/g), but this electrochemical route is faster and offers better control over film mass. The porous oxide films maintained high utilization at high discharge rates (*i.e.*, high power density) and they showed excellent cycle life. The capacitance, for example, increased by 40% during the first 400 cycles and then showed no sign of degradation up to 600 cycles. Improvements in the electrochemical performance of the metal oxide are being pursued by: (i) varying the deposition conditions, and (ii) varying the heating process. Either or both of these fabrication steps may alter the microstructure of the resulting metal oxide. Consequently, the electrochemical route possesses the main advantage of the sol-gel process, the ability to control the microstructure of the hydroxide, while being faster and offering easier control of the film mass.

Acknowledgment

The authors gratefully acknowledge financial support from the U.S. Department of Energy under Cooperative Agreement No. DE-FC02-91ER75666.

Manuscript submitted Feb. 18, 1997; revised manuscript received May 9, 1997.

University of South Carolina assisted in meeting the publication costs of this article.

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Studies on a Novel Secondary Battery: MH/MnO₂ Rechargeable Battery

II. Characteristics of the MnO₂ Cathode

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ABSTRACT

The characteristics of the MnO₂ cathode of a MH/MnO₂ battery have been studied by cyclic voltammetry, x-ray diffraction, and potentiostatic techniques. It was found that the addition of Ni(OH)₂ to the MnO₂ can prevent overcharge of the MnO₂ and decrease the imbalance of the charge/discharge states of the positive and negative electrodes, raise the working voltage of the MH/MnO₂ cell, and prevent the formation of Mn₃O₄, thereby improving the rechargeability of the MnO₂ electrode. The discharge mechanism is also discussed.

Introduction

Nickel/metal hydride (Ni/MH) and alkaline zinc/manganese dioxide rechargeable batteries (rechargeable alkaline manganese, RAM) have been the subject of recent work. The Ni/MH system is attractive because of its high energy density, nontoxicity, good rate capability, overcharge protection, and lack of a memory effect. However, the disadvantages of the Ni/MH battery are its relatively high self-discharge rate and low volumetric energy density, which thus make it unsuitable for some applications.¹⁻² The zinc-manganese dioxide rechargeable battery has been widely studied because of its low cost, abundant raw materials, and because its production can easily substitute for that of the primary alkaline manganese battery.³ However its development has been restrained, owing to the growth of zinc dendrites, the production of soluble (ZnO₂)²⁻ and the use of mercury. For these reasons, we have tried to substitute the zinc anode of the Zn/MnO₂ secondary battery with the anode active material of the Ni/MH battery, giving a novel secondary battery: the MH/MnO₂ rechargeable battery. The possibility of its development has been studied.

During this study, we found that the working voltage of MH/MnO₂ cell is low (1.1 to 0.7 V). In addition, since MnO₂ is in the charged state and MH is in the discharged state, there is a mismatch between the anode and cathode during fabrication. These difficulties can be solved by adding an appropriate amount of nickel hydroxide and catalysts⁵ to the cathode, which cannot only decrease the mismatch but also raise the working voltage of MH/MnO₂ cell to the level obtainable with a Ni/MH or Ni/Cd battery. We have constructed a 3.5 Ah prismatic MH/MnO₂ battery. A series of performance experiments was conducted, including discharge at 20 and -18°C, overdischarge, charge retention, and shelf-life. The results show that its discharge performance is superior to that

of the Zn/MnO₂ cell and its charge retention and shelf-life are better than that of Ni/MH and Ni/Cd secondary batteries. Figure 1 displays discharge curves of the 3.5 Ah MH/MnO₂ cell at the C/5 discharge/recharge rate. It shows that the capacity of 129th and 208th cycles corresponds to 84 and 78.4% of the initial capacity, respectively, which indicates that the MH/MnO₂ rechargeable battery has good charge/discharge performance. Details of a practical cell will be published in another paper.⁶ In this paper, we introduce results for the cathode.

Experimental

Preparation of Bi-EMD⁷.—Commercially pure sandblasted titanium and graphite were used as the anode and cathode, respec-

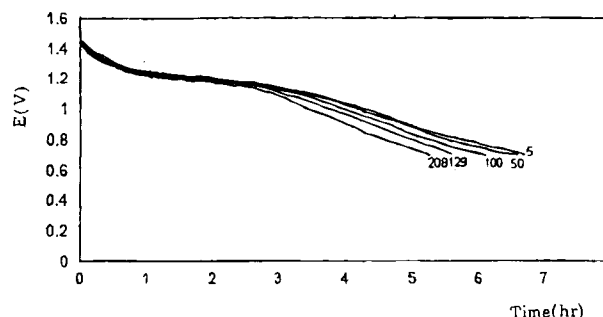


Fig. 1. Constant current discharge curves of a 3.5 Ah MH/MnO₂ cell at C/5 discharge rate for the 5, 50, 100, 129, and 208th cycle.

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