

Preparation and characterization of the electrodeposited Ni-Co oxide thin films for electrochemical capacitors

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Abstract—Nickel-cobalt (Ni-Co) oxide thin films were electrodeposited onto copper substrates in an electrolyte containing cobalt chloride and nickel chloride, and the electrochemical capacitor behaviors of these films were investigated. The XRD pattern revealed that the electrodeposited Ni-Co oxide thin film was comprised of NiCo_2O_4 . In the SEM image, the electrodeposited Ni-Co oxide film was covered with hexagonal and cubical shaped particles. The electrodeposited Ni-Co oxide electrode exhibited a specific capacitance of 148 F/g at a scan rate of 20 mV, and the current density was fairly stable over 200 cycles. The charge-discharge test confirmed that capacitance of the electrodeposited Ni-Co oxide electrode resulted from the electric double layer capacitance and pseudocapacitance.

Key words: Ni-Co Oxide Thin Films, Electrodeposition, Electrochemical Capacitor, Specific Capacitance, Charge-discharge

INTRODUCTION

Electrochemical capacitors, which are also called supercapacitors or ultracapacitors, deliver a high power density and exhibit excellent reversibility and long cycle life. These capacitors can be applied in electronic devices such as power electronics, lightweight electronic fuses, starting power devices for fuel cells, space flight technology, and so on [1-5]. Electrochemical capacitors are classified by either electric double layer capacitance or pseudocapacitance based on the electrode materials and the charge storage mechanism. Electric double layer capacitance arises from a non-faradic way or charge separation at the electrode/electrolyte interface, whereas pseudocapacitance arises from reversible faradic redox reactions of the electroactive materials with several oxidation states. Electroactive materials with a high reversibility for fast charge transfer reactions are needed to store energy for faradic processes. The electrode materials in electrochemical capacitors are generally highly porous activated carbon for electric double-layer capacitors (EDLCs) or hydrous transition metal oxides for electrochemical pseudocapacitors [1-5].

Materials require a large surface area, a capacitive behavior, and an electrochemical stability for electrochemical capacitor electrode applications. Ruthenium oxide (RuO_2) is a well known electrode material with a high electrochemical reversibility and a high specific capacitance of above 700 F/g [6,7]. However, ruthenium oxide is very expensive and toxic. Hence, considerable efforts have been devoted to the development of new and cheaper materials with improved performances to replace ruthenium oxides. Transition metal oxides (oxides of Mn, Co, Ni, Cr, Fe) with several oxidation states and structures are considered promising electrode materials for electrochemical capacitors [8-11]. Among them, Co and Ni oxides are interesting for current technologies.

He et al. prepared nickel and cobalt mixed oxides on a carbon

nanotube substrate and investigated the effect of the plating bath composition for Ni-Co binary oxides on the specific capacitance of the composite electrode [12]. Gupta et al. compared cyclic voltammetric behavior for the nanocrystalline cubic spinel NiCo_2O_4 thin films synthesized at different temperatures on stainless-steel by electrodeposition. They found that specific capacitance was high at low temperatures due to high porous morphology of the film while specific capacitance decreased at high temperatures due to decrease in porosity with increasing crystallinity [13].

Ni-Co oxide thin films have been prepared on a variety of substrates using various methods including thermal decomposition, coprecipitation, spray pyrolysis, electrodeposition, etc. [14-19]. Among these methods, electrodeposition offers lower processing temperature, better control over the deposition technique, and thus wide range of compositions.

In this work, Ni-Co oxide thin films with a porous morphology were synthesized as the electrode material for electrochemical capacitors on copper substrates using an electrodeposition method at room temperature. The structural and morphological characteristics of these films were examined. Additionally, the electrochemical capacitive behavior of the electrodeposited Ni-Co oxide electrode was investigated using cyclic voltammetry (CV) and galvanostatic charge-discharge tests.

EXPERIMENTAL

The Ni-Co oxide thin films were prepared on a copper substrate through electrodeposition in an electrolyte containing 0.5 M cobalt chloride and 0.5 M nickel chloride. The solution was complexed with 30% aqueous ammonia by adjusting the pH to around 10. The copper substrate was polished with a zero-grade polish paper and then ultrasonically washed with double-distilled water for 20 min.

The electrodeposition was conducted at a constant potential of -1.2 V using a standard three electrode cell with the copper substrate as the working electrode, a platinum-coated titanium mesh as

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the counter electrode, and saturate Ag/AgCl as the reference electrode. After the electrodeposition, the copper substrate was dried in air. Then the amount of Ni-Co oxide that was loaded onto the substrate was weighed with a microbalance.

A microstructural analysis of the electrodeposited Ni-Co oxide thin films was carried out by using an X-ray diffractometer (XRD). The surface morphology of the films was examined by scanning electron microscopy (SEM). The supercapacitive behavior of the films was examined by using cyclic voltammetry and electrochemical impedance spectroscopy in a 2 M KOH electrolyte. The charge-discharge behavior of the Ni-Co oxide electrode was studied with a galvanostatic charge-discharge method at a constant current of 1 mA/cm².

RESULTS AND DISCUSSION

Fig. 1 shows the XRD spectrum of the electrodeposited Ni-Co oxide thin film on the copper substrate. The small intensity peaks at $2\theta=44.34^\circ$ and 47.47° were due to the (400) and (422) planes of NiCo₂O₄, respectively [JCPDS: 73-1704]. Additionally, three distinct

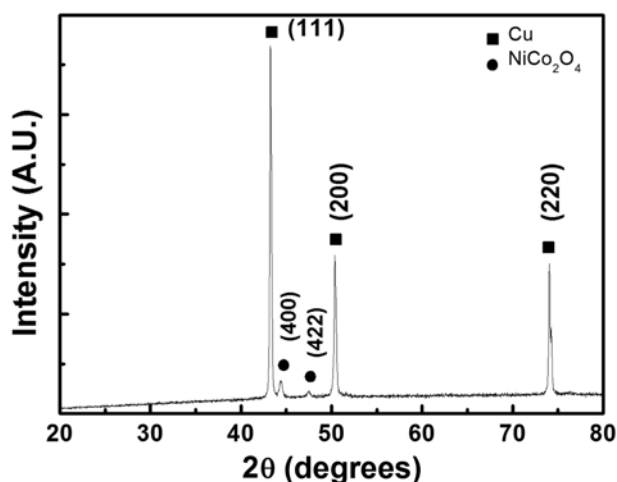


Fig. 1. XRD pattern of the Ni-Co oxide thin film that was electrodeposited on the copper substrate.

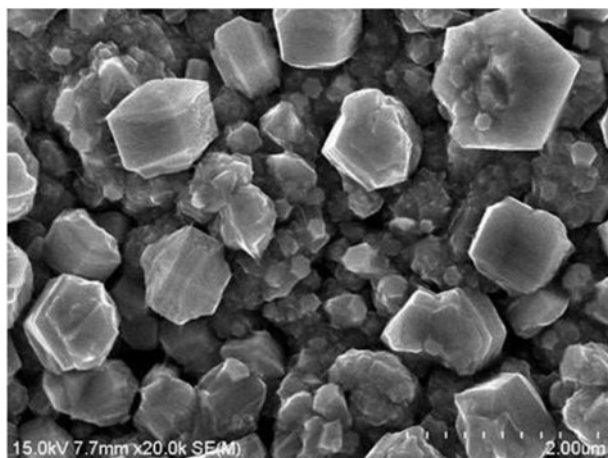


Fig. 2. SEM image of the electrodeposited the Ni-Co oxide thin film.

peaks were at $2\theta=43.33^\circ$, 50.49° and 74.05° for the copper substrate, corresponding to Cu (111), Cu (220) and Cu (200) planes, respectively [JCPDS: 04-0836]. The XRD spectrum revealed that the electrodeposited Ni-Co oxide thin film was nanocrystalline NiCo₂O₄.

Fig. 2 shows the SEM image of the electrodeposited Ni-Co oxide thin film. The substrate was well covered with fine cubical- and hexagonal-shaped particles having different sizes. The apparent size of the particles was in the range of 0.2 to 1 μm . Some micro porous spaces were also observed between the fine particles. The redox process was facilitated by the high porosity and large pore size of the films because of the high packing density of the active material. This process may lead to a large surface area and porous volume, which are important requirements in electrochemical capacitor applications.

The electrodeposited Ni-Co oxide thin films were used as the electrodes for the electrochemical capacitors. The supercapacitive behavior of the electrodes was tested by cyclic voltammetry (CV). Fig. 3 shows the CV curve of the electrodeposited Ni-Co oxide electrode at a scan rate of 20 mV/s in a 2 M KOH electrolyte. Small anodic and cathodic peaks were observed at 0.27 and 0.20 V, respec-

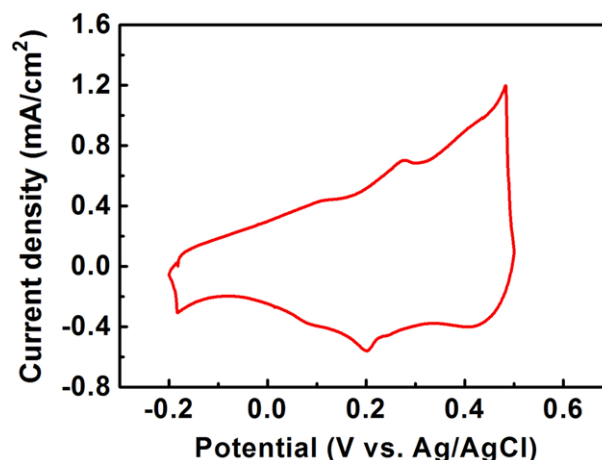


Fig. 3. CV curve of the electrodeposited the Ni-Co oxide electrode in the 2 M KOH electrolyte at a scanning rate of 20 mV/s.

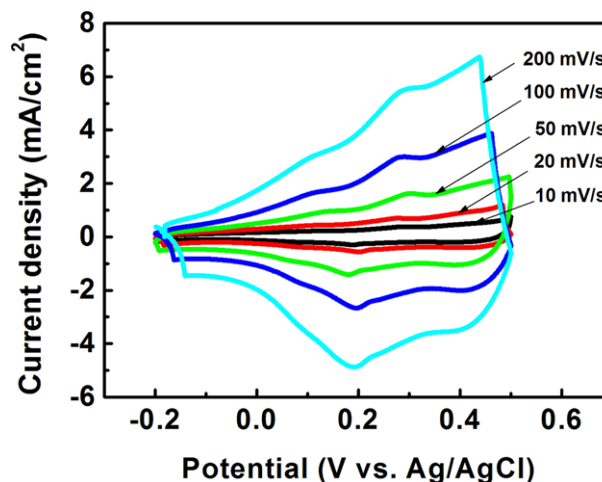


Fig. 4. CV curves of the electrodeposited Ni-Co oxide electrode at various scanning rates in the 2 M KOH electrolyte.

tively, indicating that the capacitance arose from the redox transition and the EDLC at the electrode/electrolyte and electrolyte/electrode interfaces, respectively.

The capacitance (C) was calculated from

$$C = \frac{I}{dV/dt} \quad (1)$$

where I is the average current and dV/dt is the scanning rate. The specific capacitance of the electrode was obtained by dividing the capacitance by the weight of the electrode that was dipped in the electrolyte. The specific capacitance of the electrodeposited Ni-Co oxide electrode was 148 F/g in the 2 M KOH electrolyte.

Fig. 4 shows the cyclic voltammograms of the electrodeposited Ni-Co oxide electrode at various scan rates. The current under the curve slowly increased with respect to the scan rate. Therefore, the voltammetric current was proportional to the scan rate, corresponding to an ideally capacitive behavior [20]. The specific and interfacial capacitance values decreased from 162 to 29 F/g and 0.194 to 0.035 F/cm², respectively, as the scan rate increased from 10 to 200 mV/s.

The stability of the electrodeposited Ni-Co oxide electrode in 2 M KOH was evaluated at various CV cycles. Fig. 5 shows the CV curves of the 5th, 100th and 200th cycles. The current under the curve decreased around 3% after 200 cycles, illustrating the stability of the electrodeposited Ni-Co oxide electrode in energy storage applications. The specific and interfacial capacitance values slightly decreased with respect to the number of cycles because of the loss of the active material.

The charge-discharge behavior of the electrodeposited Ni-Co oxide electrode was studied by using the galvanometric charge-discharge method. Fig. 6 shows the charge-discharge behavior of the Ni-Co oxide electrode at a current density of 1 mA/cm². The shape of the discharge curve did not correspond to the capacitance characteristics of a pure double layer capacitor. During the discharge period, two regimes existed in the curve. The non-linear dependence of the potential (0.25 to 0.4 V) indicated a typical pseudocapacitance behavior, which resulted from the electrochemical redox reaction at

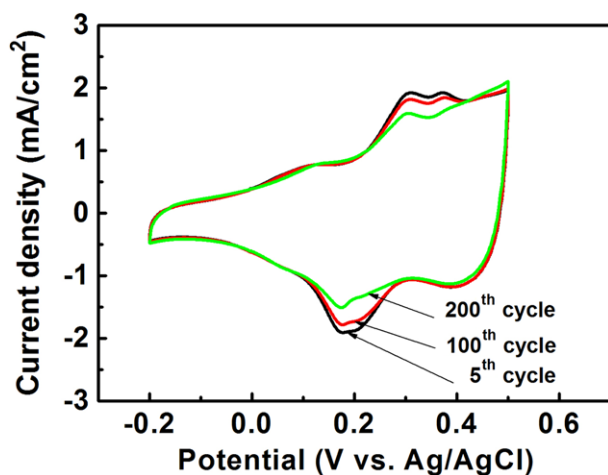


Fig. 5. CV curves of the electrodeposited Ni-Co oxide electrode after the 5th, 100th, and 200th cycles. The scanning rate and the KOH concentration were 50 mV/s and 2 M, respectively.

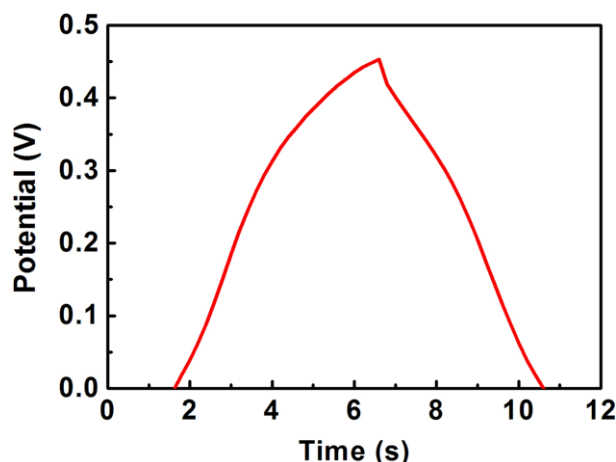


Fig. 6. Charge-discharge curve of the electrodeposited Ni-Co oxide electrode in the 2 M KOH electrolyte at a charging current of 1 mA/cm².

the electrode/electrolyte interface. The linear dependence of the potential (0 to 0.25 V) indicated an electric double-layer capacitance, which originated from the charge separation across the interface between the electrode and the electrolyte.

CONCLUSIONS

The Ni-Co oxide thin films were electrodeposited onto the copper substrates. The XRD measurements revealed that the electrodeposited Ni-Co oxide thin film was nanocrystalline NiCo₂O₄. The SEM image showed that the electrodeposited Ni-Co oxide thin film was covered with cubical- and hexagonal-shaped particles. Microporous spaces between the particles were also observed. The cyclic voltammetry study revealed that the electrodeposited Ni-Co oxide electrode had a specific capacitance of 148 F/g at a scan rate of 20 mV/s. As the scan rate increased, the voltammetric current increased, while the specific capacitance decreased. The current density decreased around 3% after 200 cycles, indicating that the electrodeposited Ni-Co oxide electrode was fairly stable. The charge-discharge test confirmed that the capacitance of the electrodeposited Ni-Co oxide electrode resulted from the electric double layer capacitance and pseudocapacitance. Consequently, the electrodeposition method was promisingly used to fabricate a nanostructured Ni-Co oxide thin film for electrochemical capacitors.

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REFERENCES

1. A. Lewandowski and M. Galinski, *J. Power Sources*, **173**, 822 (2007).
2. P. Simon and Y. Gogotsi, *Nat. Mater.*, **7**, 845 (2008).

3. S.-W. Lee, D. K. Park, J. K. Lee, J. B. Ju and T. W. Sohn, *Korean J. Chem. Eng.*, **18**, 371 (2001).
4. Y. Zhang, H. Feng, X. Wu, L. Wang, A. Zhang, T. Xia, H. Dong, X. Li and L. Zhang, *Int. J. Hydrog. Energy*, **34**, 4889 (2009).
5. A. Burke, *J. Power Sources*, **91**, 37 (2000).
6. J. P. Zheng, P. J. Cygon and T. R. Jow, *J. Electrochem. Soc.*, **142**, 2699 (1995).
7. Y.-Z. Zheng, H.-Y. Ding and M.-L. Zhang, *Thin Solid Films*, **516**, 7381 (2008).
8. D. P. Dubal, D. S. Dhawale, R. R. Salunkhe and C. D. Lokhande, *J. Alloy. Compd.*, **496**, 370 (2010).
9. S. G. Kandalkar, D. S. Dhawale, C.-K. Kim and C. D. Lokhande, *Synth. Met.*, **160**, 1299 (2010).
10. U. M. Patil, R. R. Salunkhe, K. V. Gurav and C. D. Lokhande, *Appl. Surf. Sci.*, **255**, 2603 (2008).
11. G. Lota, E. Frackowiak, J. Mittal and M. Monthieux, *Chem. Phys. Lett.*, **434**, 73 (2007).
12. K.-X. He, Q.-F. Wu, X.-G. Zhang and X.-L. Wang, *J. Electrochem. Soc.*, **153**, A1568 (2006).
13. V. Gupta, S. Gupta and N. Miura, *J. Power Sources*, **195**, 3757 (2010).
14. D. P. Lapham and A. C. C. Tseung, *J. Mater. Sci.*, **39**, 251 (2004).
15. V. Gupta, S. Gupta and N. Miura, *J. Power Sources*, **175**, 680 (2008).
16. B. Chi, J. Li, Y. Han, Y. Chen, *Int. J. Hydrog. Energy*, **29**, 605 (2004).
17. J.-J. Deng, J.-C. Deng, Z.-L. Liu, H.-R. Deng and B. Liu, *J. Mater. Sci.*, **44**, 2828 (2009).
18. Z.-A. Hu, Y.-L. Xie, Y.-X. Wang, H.-Y. Wu, Y.-Y. Yang and Z.-Y. Zhang, *Electrochim. Acta*, **54**, 2737 (2009).
19. J.-M. Luo, B. Gao and X.-G. Zhang, *Mater. Res. Bull.*, **43**, 1119 (2008).
20. D. P. Dubal, D. S. Dhawale, R. R. Salunkhe and C. D. Lokhande, *J. Electroanal. Chem.*, **647**, 60 (2010).