

Formation and Characterization of Carbon and Nickel Oxide/Carbon Composites for Supercapacitors

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In this study a carbon and NiO/carbon electrodes were prepared and investigated. The surface roughness increases with the increase of the torch power. The addition of the NiO changes the surface structure from a snowflake-like to a mesh-like. It was demonstrated that the addition of the nickel oxide to amorphous carbon increases the specific capacitance of composite electrode. However, the NiO/carbon electrodes have a lower breakdown voltage values and longer charge–discharge cycles.

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1. Introduction

Supercapacitors have been extensively studied in recent years due to their high power density, long cycle life, and short charge time [1, 2]. The transition metal oxides (NiO, RuO₂, MnO₂, IrO₂), conducting polymers, and carbon based materials (carbon black, carbon nanotubes, glassy carbon, activate carbon) are widely used as the electrode materials of supercapacitors [1–5]. The application of carbon materials is very attracting due to high surface porosity leading to high surface area. The other advantages are: high temperature stability, conductivity, and chemical resistance [1, 3]. Recently much attention is focused on the investigation of supercapacitors where electrode material combines the metal oxides (RuO₂, IrO₂, NiO, MnO₂ and etc.) and carbon based materials [2, 4, 5]. The addition of metal oxide on the carbon surface improves the capacitance values and increases the energy density. The nickel oxide due to its inexpensive price and pseudo capacitance behavior similar to RuO₂ can be successfully used to improve the capacitance value of the carbon electrodes [4–6].

In this paper an experimental work was done to investigate the effects of torch power and NiO layer on the surface morphology and electrical parameters (capacity, breakdown voltage, and charge–discharge time) of carbon and NiO/carbon electrodes.

2. Experimental setup

The carbon was deposited on the stainless steel 1X18H9T substrates at the atmospheric pressure using a direct current plasma torch. More details about the

plasma torch and deposition process can be found elsewhere [7]. Argon (Ar) was used as the plasma working gas with a flow rate of 6.6 l/min. An acetylene (C₂H₂) was used as precursor with a flow rate of 0.165 l/min. The distance between the plasma torch and substrate was 0.005 m, the coatings deposition time — 300 s, and torch powers were 750 W and 870 W. The NiO layer was deposited by the magnetron sputtering. The magnetron voltage was 280 V, current — 1 A, pressure of the oxygen gas 1.36 ÷ 1.85 Pa. The deposition time was 60 s, and it led to the growth of nickel oxide film with thickness of 72 nm, or ≈ 300 μg.

The surface morphology was analysed by scanning electron microscopy (SEM) model JEOL JSM-5600. The structure was characterized by the Raman scattering spectroscopy (Ivon Jobin spectrometer using Spectra-Physics Nd:YAG laser (532.3 nm, 50 mW, spot size 0.32 mm)) and X-ray diffraction (XRD) (DRON-UM1, BRUKER D8Advance). Concentrated potassium alkali 10 M KOH was used as electrolyte. The charge–discharge curve measurements at a constant current (150 mA) were carried out on unit cell capacitor.

3. Results and discussion

The surface morphology of the carbon structure consists of ≈ 30 μm diameter columns. Each column is composed of the fuzzy and snowflake-like structure. The column diameters become large (up to 50 μm), however the surface structure remains unchanged when the torch power increases. The deposited carbon structure contains deep holes between the individual columns (Fig. 1a). It was observed that the increase of torch power increases the surface roughness. The surface consists of a mesh-like structure after the deposition of NiO layer (Fig. 1b).

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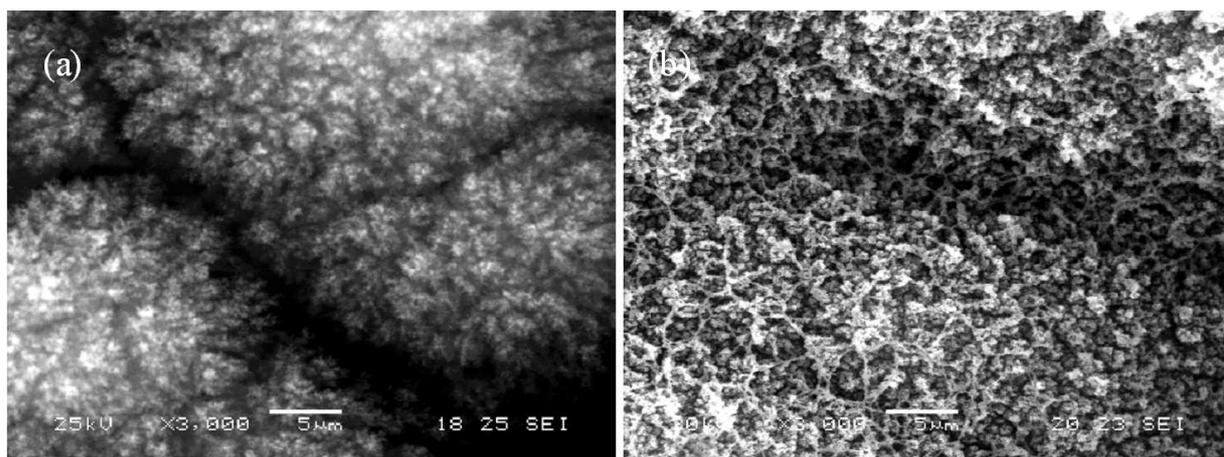


Fig. 1. The surface morphology of carbon coatings deposited at 870 W torch power (a) without NiO, (b) with NiO.

The XRD patterns of carbon electrodes show only a very broad peak indicating the amorphous carbon phase. The XRD analysis indicated a low intensity peak at $2\theta \approx 43.2^\circ$, corresponding to (200) diffraction plane of cubic structure of nickel oxide after loading the NiO on the carbon. The Raman spectra of carbon coatings are presented in Fig. 2. The coating prepared at 750 W power consists of the two separated peaks; *D* centred at 1336 cm^{-1} and *G* at 1581 cm^{-1} (Fig. 2). The full width at half-maxima (FWHM) of the *D* is around $\approx 301 \text{ cm}^{-1}$ and *G* is $\approx 122 \text{ cm}^{-1}$. The ratio of I_D/I_G intensities is approximately 1.32. The carbon layer deposited at 870 W shows the *D* peak situated at 1370 cm^{-1} and *G* at 1596 cm^{-1} . The increase of the torch power influences the narrowing of the FWHM for *D* (274 cm^{-1}) and *G* (86 cm^{-1}) peaks. As a result the I_D/I_G ratio increases up to 2.51. The higher I_D/I_G ratio demonstrates the increase of the graphite-like component in the amorphous carbon coatings and the sp^2 -bonded carbon clusters size [8]. It may be noted that both deposited carbon coatings are amorphous and consist of the sp , sp^2 , and sp^3 carbon site mixtures.

The specific capacitances of the carbon layers were equal to 1.82 F/g at 750 W and 1.80 F/g at 870 W. It may be noted that the specific capacitance increases more than sixth times (up to 11.8 F/g) when the nickel oxide was deposited on the carbon electrode prepared at 750 W. Meanwhile, the specific capacitance of the NiO/carbon composite, when the carbon coating was prepared at 870 W reached even 53.6 F/g value. Tai and Teng [4] and Ito et al. [6] also demonstrated that the specific capacitance of the carbon based materials increases with the addition of the NiO. The increase of the specific capacitance for the NiO/carbon electrodes is explained in such way. The impregnation of the carbon by the NiO produces the Faradaic pseudo-capacitance. At the same time the carbon structure due to a high specific area can provide a large double-layer capacitance. Thus, the spe-

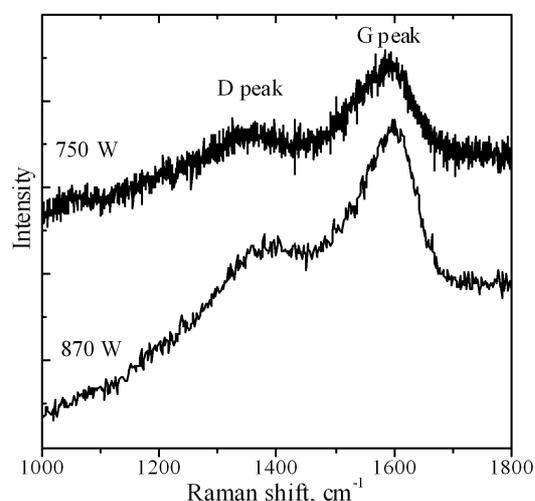


Fig. 2. The Raman spectra of carbon coatings.

cific capacitance of nickel oxide/carbon composite electrode increases [1].

The measurements indicated that the breakdown voltages of the carbon coatings deposited at 750 W and 870 W are 0.54 V and 0.52 V , respectively. Meanwhile, when the NiO was deposited, the breakdown voltage decreases up to 0.36 V and 0.40 V for the carbon coatings prepared at 750 W and 870 W, respectively. So, the charge-discharge behaviour of the carbon electrodes in the potential range between 0 V and 0.5 V at 150 mA was measured considering the breakdown voltage results. The charge-discharge times of the carbon electrodes are very similar due to almost the same capacity values (Fig. 3). It may be noted that the curves vary nearly linearly with the time demonstrating a good capacitive behaviour [9]. The charge-discharge curves of the NiO/carbon electrodes were measured in the poten-

tial range between 0 V and 0.35 V at 150 mA current. It was found that the charge–discharge cycle of the NiO/carbon electrodes prepared at 750 W and 870 W lasts 70 s and 320 s, respectively. Also the NiO/carbon curve was not as well-shaped triangle. This happens when the redox pseudo-capacitance arises and due to the existence of ohmic resistance of the cell [1].

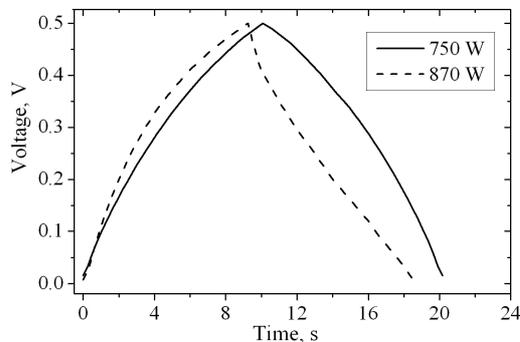


Fig. 3. The charge–discharge curves of carbon capacitors.

4. Conclusions

The carbon and nickel oxide/carbon composite electrodes were obtained and investigated. It was demonstrated that the increase of the torch power increases the surface roughness and the sp^2 carbon sites fraction in the carbon electrodes. However, it has no effect on the specific capacitance values. The impregnation of the

nickel oxide changes the surface morphology from the snowflake-like to the web-like. The highest specific capacitance (up to 53.6 F/g) was obtained for the NiO/carbon composite, when the carbon was deposited at 870 W. The breakdown voltages of the carbon electrodes are higher than the NiO/carbon composites. The charge–discharge cycle of the NiO/carbon composite electrodes lasts longer compared to the carbon electrodes.

Acknowledgments

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References

- [1] A. Pandolfo, A. Hollenkamp, *J. Power Sources* **38**, 11 (2006).
- [2] R. Kotz, M. Carlen, *Electrochim. Acta* **45**, 2483 (2000).
- [3] V.V.N. Obreja, *Physica E* **40**, 2596 (2008).
- [4] Y.L. Tai, H. Teng, *Carbon* **42**, 2329 (2004).
- [5] H. Li, Y. Li, R. Wang, R. Cao, *J. Alloys Comp.* **481**, 100 (2009).
- [6] E. Ito, S. Mozia, M. Okuda, T. Nakano, M. Toyoda, M. Inagaki, *New Carbon Mater.* **22**, 321 (2007).
- [7] L. Marcinauskas, A. Grigonis, V. Valincius, P. Valatkevičius, *Mater. Sci.* **13**, 269 (2007).
- [8] J. Robertson, *Mater. Sci. Eng. B* **37**, 129 (2002).
- [9] Y.F. Su, Y. Wu, L.Y. Bao, Z.H. Yang, *New Carbon Mater.* **22**, 53 (2007).