Enhanced Capacitance of Porous Carbon Electrodes through Deposition of Small Amounts of NiO

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Amorphous carbon and NiO/carbon composites were used as an electrode material for supercapacitors. The investigations were performed to evaluate the influence of the Ar/C_2H_2 ratio on the capacitance values of carbon and NiO/carbon electrodes. The surface morphology of the carbon electrodes changes from snowflake-like to columnar with the increase of the Ar/C_2H_2 ratio. The Raman scattering spectroscopy results demonstrated that the I_D/I_G ratio decreases from 1.33 to 0.91 with the increase of the Ar/C_2H_2 ratio. It indicates the decrease of the sp^2 bonded carbon in the coatings. The specific capacitance of the carbon electrodes increases with the increase of the Ar/C_2H_2 ratio. The NiO/carbon electrodes show capacitance values 10 times larger as those of carbon electrodes. The largest specific capacitance of 27.7 F/g was obtained for NiO/carbon electrode, when carbon coating was deposited under $Ar/C_2H_2 = 27$.

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1. Introduction

In recent years, a great deal of attention has been devoted to the research of supercapacitors since they exhibit some excellent properties: extremely large capacity (up to 780 F/g), high power density, and high efficiency of discharge [1–3].

Various carbon-based materials (carbon black, carbon nanostructures, glassy carbon, carbon films, activated carbon) are used as electrodes for supercapacitors. Such interest of carbon-based materials is related due to high total surface area, porosity, high temperature stability, conductivity, and chemical resistance [2–5]. This type of supercapacitors are called electric double-layer capacitors. The capacitance of electric double-layer capacitors very largely depends on the conductivity, surface area, and pore size of carbon material [1–5]. Variation and optimization of these parameters should be done in order to obtain capacitors with desirable electrical parameters.

It was reported [1, 6–11] that the capacitive behaviour of the carbon-based materials can be further improved by the presence of various metal oxides (ruthenium oxide, nickel oxide, manganese oxide) or conductive polymers. These electrochemical supercapacitors combine the advantages of both double-layer capacitance and pseudocapacitance. The specific capacitance of the RuO_2/carbon composites could reach even 1000 F/g values [1]. However, the high cost of RuO_2 limits its commercialization.

Meanwhile, nickel oxide is inexpensive, exhibits pseudocapacitance behaviour similar to that of ruthenium oxide, and has a large surface area. These properties make NiO suitable and promising material for improvement of carbon based supercapacitors [7–11]. Li et al. [9] demonstrated that the specific capacitance of the NiO/carbon composite is higher than that of carbon electrode, despite the decrease of the surface area. Ito et al. [10] found that the addition of NiO increases the capacitance of cypress charcoal by about 13% in the gravimetric value. The authors point to the fact that the structural properties of carbon material and NiO content amount have the main influence on the capacitance values [7–12]. So it is very important to find relationship between the structure of the carbon material and the electrical parameters of supercapacitors. The second challenge is to investigate the effect of NiO loading on different structure amorphous carbon electrodes.

The objective of the present study is to find the influence of the carbon structure on the capacitance values and examine how the NiO addition can improve the performance of a carbon electrode.

2. Experimental setup

The carbon layers were deposited on the stainless steel 1X18H9T substrates (2.5×2.5 cm^2) using a direct current plasma torch at atmospheric pressure. A detailed description of the carbon deposition process has previously been described [13]. The plasma is ignited in Ar gas with a flow of 6.6 l/min, and when the acetylene with

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a flow of 0.12–0.245 l/min is injected through anode. The ratio of Ar/C_2H_2 was equal to 27, 40, and 55. The arc voltage value was 38 V, current — 20 A, and the distance between the plasma torch outlet and the sample — 0.005 m. The deposition time varied in the 75–150 s range, which leads to ≈ 2.7 mg.

The NiO layer was deposited by the magnetron sputtering. A water cooled substrate holder and a shutter were located in front of a nickel magnetron. The target--to-substrate distance was 0.06 m. The chamber was evacuated to a pressure of 10^{-5} to 10^{-4} Pa by a pumping unit. The deposition parameters of the nickel oxide layers were following: magnetron voltage — 280 V, current — 1 A, pressure of the oxygen gas $1.36 \div 1.85$ Pa. The deposition time was 60 s, which leads to growth of nickel oxide film with the thickness of 72 nm, or ≈ 300 μg.

The surface morphology analysis was carried out using a scanning electronic microscope (SEM) JSM-5600. The bonding structure of carbon coatings was characterized by the Raman scattering (RS) (Ivon Jobin spectrometer). RS was investigated using Spectra-Physics Nd:YAG laser (532.3 nm, 50 mW, spot size 0.32 mm). The electrodes were analyzed by X-ray diffraction (XRD) (DRON-UM1, BRUKER D8Advance) with standard Bragg–Brentano focusing using Cu K_α ($\lambda = 0.154059$ nm) radiation. Concentrated potassium alkali 10 M KOH was used as an electrolyte. The electrical characteristics of fabricated supercapacitors were measured using a typical electrical circuit. The charge–discharge curves measurements at constant current (150 mA) were carried out using the unit cell capacitor.

3. Results and discussion

The surface morphology of the carbon and NiO/carbon composites electrodes are presented in Fig. 1. The surface of the carbon coating deposited at Ar/C_2H_2=27 is composed of the snowflake-like structure. The surface morphology is very porous and uneven (Fig. 1a). The surface roughness decreases and snowflake-like structure changes to columnar with the increase of the Ar/C_2H_2 ratio. It may be noted that the diameter of each column is 10–20 μm. The individual columns consist of the agglomerated 0.5 μm size granules. The deposition of NiO on the carbon surface results in the changes of surface topography. The snowflake-like structure disappears and mesh-like one appears (Fig. 1c). Meanwhile, the films deposited at higher Ar/C_2H_2 ratios show a columnar structure, but the diameters of the columns become smaller and the bonds between the individual grains become less pronounced (Fig. 1d).

The carbon coating deposited at $Ar/C_2H_2 = 27$ consists of two separate G (1583 cm^{-1}) and D (1340 cm^{-1}) bands (Fig. 2). The full width at half-maxima (FWHM) of the D and G peaks is 309 cm^{-1} and 120 cm^{-1}, respectively. The intensity ratio between the D and G peaks (I_D/I_G) of the film is 1.33. The increase of Ar/C_2H_2 influences slight narrowing of FWHM for D (301 cm^{-1}),
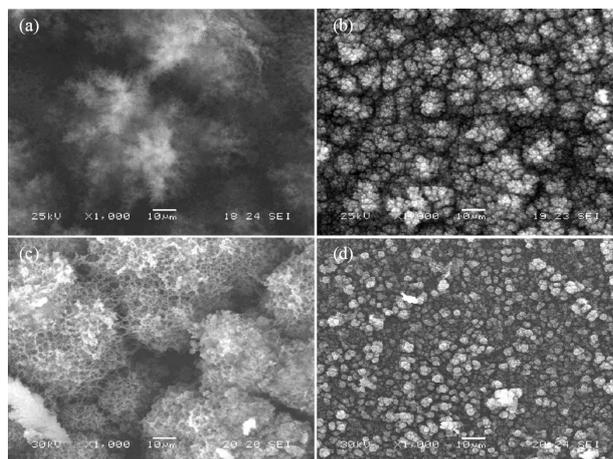

Fig. 1. Surface morphology of carbon (a, b) and NiO/carbon (c, d) electrodes, (a, c) $Ar/C_2H_2 = 27$ and (b, d) $Ar/C_2H_2 = 55$.

and slight broadening for the G (122 cm^{-1}) peak. As a result, I_D/I_G decreases to 1.32. Meanwhile, the carbon film obtained at Ar/C_2H_2=55 has D peak at 1332 cm^{-1} (with FWHM 234 cm^{-1}) and G at 1581 cm^{-1} (with FWHM = 133 cm^{-1}), while the I_D/I_G ratio is 0.908. The RS results demonstrated that with the increasing Ar/C_2H_2 ratio from 27 to 55, the carbon structure becomes less disordered as evident from the decrease in the FWHM values of D-band. FWHM of the G-peak slightly broadens (from 120 to 133 cm^{-1}), but the position of the G-peak remains unchanged. It is well known that higher I_D/I_G values show the increase of the graphite--like component in the a-C:H films and the sp^2-bonded carbon clusters size [13–15]. Generally, separation of the D and G peaks indicates that carbon coatings have glassy carbon phase inserts [14].
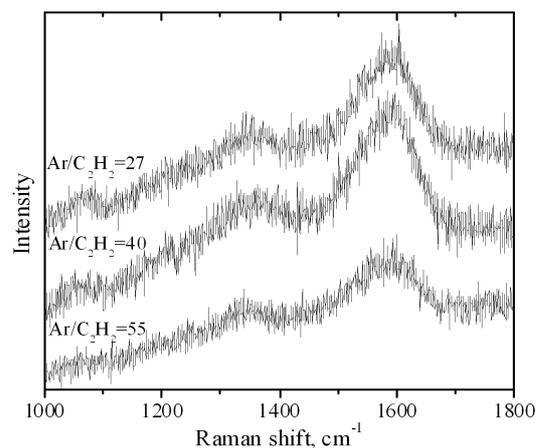

Fig. 2. Raman spectra of carbon electrodes.

The XRD profiles of carbon electrodes show only a very broad peak indicating the amorphous phase. The XRD

measurements demonstrated a broad low intensity peak at $2\theta \approx 43.2°$, corresponding to (200) diffraction plane of NiO cubic structure after loading the nickel oxide on the carbon. The width of the NiO peak demonstrates an amorphous structure.

The specific capacitance of the carbon electrode obtained at $Ar/C_2H_2 = 27$ shows the lowest value ≈ 1.63 F/g. Meanwhile, with the increase of the Ar/C_2H_2 ratio, the capacitance increases up to 2.25 F/g. The specific capacitance increases when NiO is added on the top of amorphous carbon electrode (Fig. 3). The highest value (27.7 F/g) of the specific capacitance was obtained at $Ar/C_2H_2 = 27$. Meanwhile, the specific capacitance of the NiO/carbon composites when the Ar/C_2H_2 ratio is 40 and 55 are lower but very similar, 11.8 and 11.7 F/g, respectively.
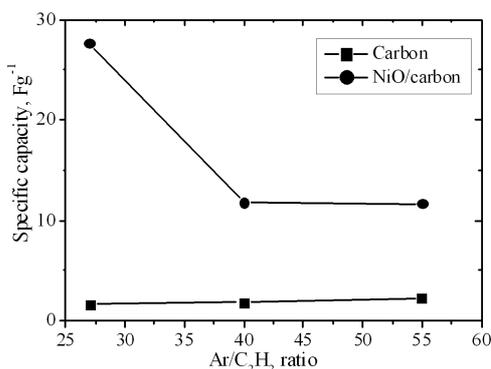

Fig. 3. Dependence of specific capacity of carbon and NiO/carbon electrodes on Ar/C_2H_2 ratio.

The capacity increase of carbon electrodes is probably related to changes of pores size and structure. The carbon electrodes with higher surface porosity and sp^2 sites fraction usually have higher capacity values [2]. In this research the opposite tendency was obtained. Probably the fraction of the macropores in the carbon electrode deposited at $Ar/C_2H_2 = 27$ is the highest. When the Ar/C_2H_2 ratio increases, the fraction of mesopores and micropores becomes higher, and as a result, the specific capacitance increases. The addition of 10% of NiO increases the specific capacity of electrodes. The increase of capacitance is due to the Faraday pseudo-capacitance, which was derived from the NiO redox reaction in the KOH electrolyte [9]. So, the capacitance of the composite electrode is promoted by combination of double-layer capacitance (produced by a carbon layer) and Faraday pseudo-capacitance (produced by NiO) [1]. It may be noted that the bonding structure of the carbon electrodes deposited at $Ar/C_2H_2 = 27$ and $Ar/C_2H_2 = 40$ is very similar, but the specific capacitance after the NiO addition is different. The difference values of capacitance are the results of surface morphology.

The charge–discharge behaviour of the carbon and NiO/carbon electrodes in the potential range between 0 and 0.35 V at 150 mA is given in Fig. 4. It can be found
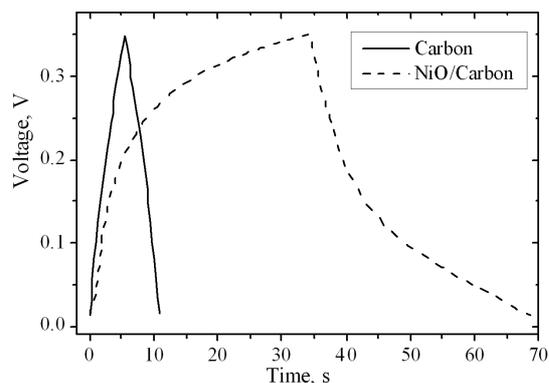

Fig. 4. Charge–discharge curves of carbon and NiO/carbon electrodes when Ar/C_2H_2 ratio was 40.

from the curves that the carbon capacitor voltage varies nearly linearly with the time, which indicates good capacitive behaviour [6]. The NiO/carbon curve was not as well-shaped triangle as an ideal capacitive behavior should be, which is caused by the redox pseudocapacitance and ohmic resistance of the cell [8].

4. Conclusions

The carbon and NiO/carbon composite electrodes were formed by plasma jet and magnetron sputtering techniques. The influence of Ar/C_2H_2 ratio on surface morphology and bonding structure of carbon electrodes was investigated. The SEM results demonstrated that the surface roughness increases with the Ar/C_2H_2 ratio. RS measurements indicated the increase of the sp^2 carbon sites with the decrease of the Ar/C_2H_2 ratio. The capacitance increases from 1.63 up to 2.25 F/g with the increase of the Ar/C_2H_2 ratio. The loading of the NiO changes the surface morphology and increases the specific capacitance up to 17 times.

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