Preparation of Ni Nanoparticles-TiO$_2$ Nanotube Arrays Composite and Its Application for Electrochemical Capacitor

Huichao He, Yunhuai Zhang, Peng Xiao,† Yannan Yang,‡ Qing Lou,† and Fei Yang

College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400030, PR China
†College of Physics, Chongqing University, Chongqing 400030, PR China. E-mail: xiaopeng@cqu.edu.cn
‡Environmental Monitoring Station of Ziyang, Ziyang 641300, PR China
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Ni nanoparticles-TiO$_2$ nanotube arrays (Ni/TiO$_2$NTs) composites were prepared by pulsed electrodeposition method and subsequently characterized by means of field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDX). The FESEM results showed that highly dispersed Ni nanoparticles were not only loaded on the top of the TiO$_2$NTs but also within the tubular structure, and the particle size of Ni prepared at different current amplitude (100, 200 and 300 mA·cm$^{-2}$) was in the range of 15 to 70 nm. The electrochemical studies indicated that Ni nanoparticles loaded on the highly ordered TiO$_2$NTs are readily accessible for electrochemical reactions, which improve the efficiency of the Ni nanoparticles and TiO$_2$NTs composite electrode that prepared at a current of 200 mA·cm$^{-2}$, and the electrode also exhibited excellent electrochemical stability.

Key Words : Ni Nanoparticles, TiO$_2$ Nanotubes, Electrochemical capacitor

Introduction

Electrochemical capacitors (ECs), which combining the advantages of high power of dielectric capacitors and high energy density of second batteries, have attracted considerable attention for use in high power energy storage devices in recent years.$^{13}$ ECs can be classified by their reaction mechanisms into electrical double-layer capacitors (EDLCs) and pseudocapacitors. The EDLCs are based on non-faradic charge separation at the electrode/electrolyte interface, whereas the pseudocapacitors are based on the fast and reversible redox reactions at/near the surface of active materials. It is well known that pseudocapacitors show relatively less cycling stability than EDLCs because of the faradic reaction mechanism. However, pseudocapacitor electrodes show promise in asymmetric and/or hybrid configurations owing to their high specific capacitances and high volumetric capacitances as a result of the densely packed active materials. At present, carbon, conducting polymers and transition metal oxides are the most widely used active electrode materials.$^{4,7}$ Among these materials, amorphous hydrated RuO$_2$ exhibits the best properties thus far.$^8$ However, the high cost of RuO$_2$ has limited its commercial attractiveness for ECs applications and stimulated considerable effort on the search for alternative electrode materials.$^{9,10}$

It has been reported that composite electrodes made from Ni nanoparticles and carbon nanotubes or TiO$_2$ nanotubes showed high specific capacitance and rate capability in alkali electrolyte due to the increased surface area, electrochemical utilization of the active materials and ionic transport throughout the internal volume of the electrode.$^{11,12}$ Compared with the carbon nanotubes and TiO$_2$ nanotubes, highly ordered TiO$_2$ nanotube arrays (TiO$_2$NTs) formed on Ti substrate not only offer the direct path for electrons toward the current collector, but also with lower fabrication cost and higher accessible surface for electrochemical reactions. In addition, its large surface areas, high packing densities and ordered pore networks are expected to facilitate rapid charge/discharge kinetics.$^{13,14}$ Consequently, TiO$_2$NTs used as a support to load highly dispersed Ni nanoparticles will possess enhanced capacitance because such composite structure can provide more readily available spaces for electrochemical reactions.

In this study, Ni nanoparticles-TiO$_2$NTs composites were by pulsed electrodeposition method and employed as functional electrode materials. The electrochemical properties of the Ni/TiO$_2$NTs as pseudocapacitor electrodes were investigated by a series of electrochemical tests.

Experimental

Preparation of Ni/TiO$_2$NTs Composite Electrode. TiO$_2$NTs were prepared by anodization method.$^{15}$ Ti foils were degreased by sonication in acetone and methanol, rinsed with deionized water and dried in nitrogen stream. The samples were anodized in 0.15 mol·L$^{-1}$ HF electrolyte with a platinum foil as a counter electrode at 20 V for 2 hrs. And then the as-anodized TiO$_2$NTs were annealed in nitrogen atmosphere at 400 °C for 3 hrs to convert the amorphous TiO$_2$NTs to the crystalline form. Ni nanoparticles were loaded on the as-annealed TiO$_2$NTs by pulsed electrodeposition method.$^{16}$ Deposition experiments were performed in three-electrode system with nickel plate as a counter
electrode and Ag/AgCl electrode as a reference electrode. The deposition bath was a mixture of 300 g·L⁻¹ NiSO₄·6H₂O, 45 g·L⁻¹ NiCl₂·6H₂O, 37 g·L⁻¹ H₂BO₃, pH=4.4. The electrolyte temperature was kept at 38 °C. The Ni/TiO₂NTs composites were prepared at constant current off-time (1000 ms), pulse time of both negative and positive current (8 ms, 2 ms) and different current amplitudes: 100, 200 and 300 mA·cm⁻². Total charge density was fixed at 0.623 C·cm⁻².

Measurements. Morphological characterization was carried out by field emission-scanning electron microscope (FESEM; Nova 400 Nano-SEM). Crystalline structure of the samples was examined by an X-ray diffraction (XRD) with Cu Kα radiation. The content of Ni was identified by an energy dispersive X-ray spectroscopy (EDX; INCA Energy 350).

All electrochemical measurements were carried out in a three-electrode system with a 1.0 mol·L⁻¹ NaOH solution. The as-prepared samples with a geometric area of 1.0 cm² were placed as the working electrode, a platinum foil as a counter electrode and a saturated calomel electrode (SCE) as reference electrode. Electrochemical impedance spectroscopy (EIS) measurement was performed by Autolab PGSTAT32/FRA impedance system. CHI600C electrochemical workstation (Shanghai, China) was employed for the cyclic voltammetry (CV) and chronopotentiometric (CP) tests.

Results and Discussion

Morphology and Crystallization Characterization. Figure 1(a) shows the FESEM image of TiO₂NTs before deposition of Ni nanoparticles. The average interior diameter and tube length of TiO₂NTs were about 100 and 400 nm, respectively, which were advantageous for the ingress of Ni²⁺ and deposition of Ni nanoparticles inside nanotubes. Figure 1(b), 1(c) and 1(d) present the FESEM images of Ni/TiO₂NTs prepared at 100, 200 and 300 mA·cm⁻², respectively. It can be observed that dispersed Ni nanoparticles were loaded uniformly on the top of TiO₂NTs. In addition, some relatively small Ni nanoparticles were observed present into the tubes (inset in Figure 1(c)). Ni/TiO₂NTs with such architecture can provide abundant sites for reversible redox reaction. The particle size of Ni deposited at 100, 200 and 300 mA·cm⁻² is about 70, 15 and 40 nm, respectively. The reduction in particle size with the increase of current amplitudes is due to the higher overpotential and the accompanying increase in nucleation rate. However, when the deposition current increased to 300 mA·cm⁻², the percentage of current for the reduction of H⁺ increased, leading to lower efficiency for nickel deposition. That is, nucleation rate of nickel decreased greatly, resulting in an increase of particle size from 15 to 40 nm (Figure 1(d)), which is consistent with the findings of Yoshimura.

Figure 2 shows XRD patterns of the annealed TiO₂NTs and Ni/TiO₂NTs composites. In the XRD pattern of TiO₂NTs, an anatase characteristic diffraction peak (2θ = 25.3°) was showed evidently. But after nickel deposition, two new characteristic peaks located at 2θ = 44.5° and 51.8° corresponding to Ni (111) and (200), respectively, which is in agreement with previous data reported by Wang’s group. These results confirmed that Ni particles were deposited onto the TiO₂NTs and the composite was Ni/TiO₂NTs.

EDX measurement was carried out to determine the elemental composition in Ni/TiO₂NTs composites. The loading amounts of Ni deposited at 100, 200 and 300 mA·cm⁻² were 9.51, 16.37 and 11.02 at% (atomic percentage), respectively. At the highest current (300 mA·cm⁻²), hydrogen evolution occurred at a high rate, which decreased current electrodeposition and destroyed the surface of Ni/TiO₂NTs electrode. As a result, the Ni loading amounts decreased from 16.37 to 11.02 at%.

Electrochemical Properties. Figure 3 shows cyclic voltammograms of the as-annealed TiO₂NTs and Ni/TiO₂NTs electrodes prepared at 100, 200 and 300 mA·cm⁻². It is obvious that TiO₂NTs shows low current response, which indicates small specific capacitance. For Ni/TiO₂NTs, higher current responses were observed, which suggest the pseudocapacitance is mainly come from Ni nanoparticles on Ni/TiO₂NTs composites. In the anodic scan, non-faradic
adsorption of \( \text{OH}^- \) and possible double-layer charging process would occur at the initial stage from 0 to 0.29 V. Then, owing to the appearance of the redox peak pair, faradic reactions have occurred to cause a good performance of faradic capacitance. This capacitance characteristic of Ni/TiO\(_2\) electrodes could provide a CV curve close to an ideal rectangular shape. Herein the measured capacitance was mainly based on the reversible redox reaction mechanism due to the quasi-reversible electron transfer process. A broad oxidation peak appeared at about 0.34 V ascribed to the oxidation of both Ni deposited to Ni(OH)\(_2\) and the newly formed Ni(OH)\(_2\) to NiOOH. A reduction peak was observed at about 0.21 V, which was associated with the reduction of the NiOOH back to Ni(OH)\(_2\). This reversible redox reaction was written schematically as follows\(^{12,21}\):

\[
\text{Ni(OH)}_2 + \text{OH}^- \rightleftharpoons \text{NiOOH} + \text{H}_2\text{O} + e^- \quad (1)
\]

As shown in Figure 3, the CV current density of Ni/TiO\(_2\) NTs increased with the increase of the deposition current amplitude and reached a maximum when the deposition current was 200 mA cm\(^{-2}\). It can be explained by taking into account that the amount of Ni deposited at this current is at maximum value (15.1 at\%) and the Ni particle size (15 nm) is the smallest, which would provide most abundant active sites for reversible redox reactions. The highest current density indicates that the Ni/TiO\(_2\) NTs composite electrode prepared at 200 mA cm\(^{-2}\) possess a highest specific capacitance than that of 100 and 300 mA cm\(^{-2}\).

Figure 4 presents the impedance spectra in the form of Nyquist plots for the Ni/TiO\(_2\) NTs composite electrodes measured at 0 V. As shown in Figure 4, the depressed semicircles appeared within the entire frequency range in Nyquist impedance plots, which indicated the composite electrodes predominantly conducted a kinetics-controlled electrochemical process, and the impedance was mainly determined by the charge-transfer resistance at the interface of electrolyte/active material/current collector. Regarding three designated Ni/TiO\(_2\) NTs electrodes, the difference of impedance curves at high frequencies was mainly attributed to the limitation degree of the interfacial charge transfer between Ni/TiO\(_2\) NTs composite and the electrolyte. Corresponding resistance of these electrodes could be qualitatively estimated by comparing the diameter of the semicircle-like arc at high frequencies. Impedance analysis shows the diameter of the Nyquist plot on the Ni/TiO\(_2\) NTs composite electrode prepared at 200 mA cm\(^{-2}\) is the smallest, which indicates that the electrode has minimum charge-transfer resistance. It can be attributed to: (1) The maximum amount of electroactive Ni loading on TiO\(_2\) NTs resulted in the composite electrode possesses a highest electrical conductivity; (2) Smallest Ni nanoparticles obtained at 200 mA cm\(^{-2}\) could provide maximum electrochemically active surface area, which decreased the charge-transfer resistance at the interface.

**Electrochemical Capacitance.** Figure 5(a) shows the charge-discharge curves of Ni/TiO\(_2\) NTs composite electrodes at a current density of 0.1 mA cm\(^{-2}\) in a potential window (0 to 0.45 V). The charge process mostly occurred at a potential above 0.34 V till to the designated potential due to the oxidation of both Ni to Ni(OH)\(_2\) and then Ni(OH)\(_2\) to NiOOH, which was in good agreement with the results of the CV curve. The discharge process exhibited a plateau around 0.24 to 0.31 V, corresponding to the reduction of the NiOOH back to Ni(OH)\(_2\). The specific capacitances of Ni/TiO\(_2\) NTs composite electrodes synthesized at different current amplitudes were calculated according to the following Equation:

\[
C_S = \frac{C}{S} = \frac{I \times t}{\Delta V \times S} \quad (2)
\]

Where \( I \) is charge-discharge current; \( t \), discharge time; \( \Delta V \), potential change; and \( S \) is the apparent surface area of Ni/TiO\(_2\) NTs electrode.\(^{24}\) The results show the specific capacitances of the composite electrodes prepared at 100, 200 and 300 mA cm\(^{-2}\) is 5.8, 27.3 and 15.1 mF cm\(^{-2}\), respectively. Obviously, the composite electrode prepared at 200 mA cm\(^{-2}\) has maximum specific capacitance, which can be explained by taking into account that:

![Figure 3. Cyclic voltammograms of TiO\(_2\) NTs and Ni/TiO\(_2\) NTs prepared at different current amplitude in 1 M NaOH at potential sweep rates of 100 mV s\(^{-1}\).](image)

![Figure 4. Electrochemical impedance spectroscopy of Ni/TiO\(_2\) NTs prepared at different current amplitude in 1 M NaOH.](image)
lyte, resulting in more feasible electro-redox reaction at the in-

(1) The Ni nanoparticles with a largest electrochemically active surface area can provide more accessible spaces for the electrolyte, resulting in more feasible electro-redox reaction at the interface of nickel and alkali electrolyte in the charge-discharge process; (2) The maximum amount of electroactive Ni loading on TiO2NTs can form abundant active sites and decrease the charge-transfer resistance at the interface. The electrochemical stability of the Ni/TiO2NTs composite electrode prepared at 200 mA.cm−2 has been further examined by chronopotentiometry. As shown in Figure 5(b), the specific capacitance loss after 250 cycles was about 5%, indicating excellent electrochemical stability.

Conclusions

In summary, Ni nanoparticle-TiO2 nanotube arrays com-

posite electrodes were prepared by pulsed electrodeposition method and constructed for electrochemical capacitor application. It was found that the Ni/TiO2NTs composite electrode prepared at 200 mA.cm−2 had maximum specific capacitance (27.3 mF.cm−2) and excellent cycle stability due to the smallest Ni nanoparticle loaded on TiO2NTs offers highest active surface area for electro-redox reaction. The present study shows Ni/TiO2NTs can act as a promising candidate for the electrochemical capacitor application.

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