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Enhanced charge-discharge characteristics of RuO$_2$ supercapacitors on heat-treated TiO$_2$ nanorods

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Electrochemical capacitors based on RuO$_2$ were prepared onto electrospun TiO$_2$ nanorods. Further heat treatment of the TiO$_2$ at 800 °C under nitrogen was found to greatly improve the electrochemical performance of the RuO$_2$ electrodes, especially at fast charge-discharge rates. The specific capacitance was found to decrease by only 33% when the scan rate increased from 10 to 1000 mV s$^{-1}$ (from 687 to 460 F g$^{-1}$). The characteristic response time of the RuO$_2$ electrode was found to be 0.15 s when a heat-treated TiO$_2$ substrate was used, which is 20 times better than that of the pristine TiO$_2$ used. © 2007 American Institute of Physics. [DOI: 10.1063/1.2715038]
Ag/AgCl reference electrode (with saturated KCl solution). The precursor solution was stirred during the deposition, and the temperature was maintained at 50 °C. RuO₂ was potentiodynamically deposited by cycling the heat-treated TiO₂ electrode between 0.25 and 1.45 V versus the Ag/AgCl reference in RuCl₃ solution. The scan rate used for deposition was 300 mV s⁻¹. After deposition, the electrode was heat treated at 175 °C for 1 h. The RuO₂ deposited electrodes were examined using cyclic voltammetry in aqueous 0.5 M sulfuric acid solution.

After calcination of the hot-pressed electrodes at 450 °C (A450), the original web structure of the as-spun TiO₂ fibers was found to be retained, with each fiber composed, of TiO₂ nanorods, as shown in Fig. 1(a). The Brunauer-Emmet-Teller surface area of the pristine TiO₂ web after calcination was found to be 138 m² g⁻¹. After the heat treatment at 800 °C under dry nitrogen, the surface area of heat-treated TiO₂ decreased to 20 m² g⁻¹ due to the crystal growth as well as the coalescence, as shown in Fig. 1(b). The mesopores between nanorods were found to decrease after heat treatment from Barrett-Joyner-Halenda analysis. However, the fibrous structure of TiO₂ was found to be retained also after heat treatment, as shown in Fig. 1(b). Figure 1(c) shows the RuO₂ deposited on the N800 substrate. The macropores between each fiber were found to be retained after RuO₂ deposition. These pores provide a diffusion path for electrolyte into the inner part of the electrode. Figure 1(d) shows the x-ray diffraction patterns of the A450 and N800 substrates. The A450 only produces anatase peaks, whereas rutile peaks of TiO₂ were found in the x-ray diffraction pattern of the N800 after heat treatment at 800 °C under dry nitrogen. The color of the A450, calcined at 450 °C in air, was white, but the N800 was gray. The energy dispersive spectra analysis revealed that the atomic ratio of N800 was Ti(1) vs O(1.91), while the pristine one was Ti(1) vs O(2.01). Thus, the oxygen in the titanium dioxide is only partially removed (~5%), and the oxide is not reduced completely to the metallic state. How-

ever, partial deoxidation at an early stage of reduction results in the formation of an electrically conductive oxide phase. The apparent resistance of TiO₂ nanorods was measured using Pt-grid-patterned Al₂O₃ substrates with a 200 μm gap. As presented in Table I, the resistance decreased from 2.5 × 10¹⁰ Ω (A450) to 3.9 × 10⁸ Ω (N800) after heat treatment, which corresponds to 64 times improvement in conductivity.

Cyclic voltammetry is the appropriate technique for examining a capacitive behavior. It is desirable that the electrochemical capacitor exhibit a rectangular shape and symmetry in the anodic and cathodic sweeps, and a current density of large magnitude in the cyclic voltammogram (CV). Figure 2 shows the CVs of the RuO₂ electrodes. At slow scan rates, the cyclic voltammograms (CVs) of the two different electrodes have a similar shape and current density, as shown in Fig. 2(a). At fast scan rates, however, the shapes of the CVs are quite different. The RuO₂ deposited on the N800 electrode (N800Ru) was found to exhibit a rectangular CV outline even at scan rates faster than 500 mV s⁻¹, whereas the RuO₂ deposited on the A450 electrode (A450Ru) was found to produce a linear shape at that scan rate. Thus, the average current density of the N800Ru electrode was found to be larger than that of the A450Ru electrode. This leads to a substantial difference in the specific capacitances of the electrodes at fast scan rates, as shown in Fig. 3(a). The average specific capacitance was calculated according to

$$C_{sp} = \frac{i}{uvw},$$

(1)

where $i$, $v$, and $w$ are the average current (mA), the scan rate (mV s⁻¹), and the weight of deposited RuO₂ (g), respec-

<table>
<thead>
<tr>
<th>TABLE I. Preparation conditions and properties of TiO₂ substrates.</th>
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<tbody>
<tr>
<td>Substrate</td>
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<tr>
<td>Temperature (°C)</td>
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<tr>
<td>Atmosphere</td>
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<tr>
<td>Resistance (Ω)</td>
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<tr>
<td>Surface area</td>
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FIG. 2. Cyclic voltammograms of the RuO₂ electrodes based on pristine (A450) and heat-treated TiO₂ (N800) substrates in 0.5M H₂SO₄ electrolyte at a scan rate of (a) 50 mV s⁻¹ and (b) 500 mV s⁻¹.

FIG. 3. (a) Variation of specific capacitance calculated from cyclic voltammograms and (b) galvanostatic charge-discharge voltage profiles of pristine (A450Ru) and heat-treated TiO₂ (N800Ru) electrodes at 15 mA cm⁻².
tively. The variation of specific capacitance of A450Ru and N800Ru electrodes is shown in Fig. 3(a). The specific capacitance of the A450Ru electrode was found to decrease from 593 F g⁻¹ at a scan rate of 10 mV s⁻¹ to 62 F g⁻¹ at 1000 mV s⁻¹ (an 89% decrease). However, the specific capacitance of the N800Ru electrode is decreased by only 33% by the use of fast scan rates (from 687 F g⁻¹ at 10 mV s⁻¹ to 460 F g⁻¹ at 1000 mV s⁻¹). Similar results were obtained in galvanostatic charge-discharge tests, in which symmetric full cells (2 × 2 cm²) containing these two electrodes and a rayon separator were used. The separator was immersed in 0.5 M H₂SO₄ before each symmetric cell was assembled. Figure 3(b) shows the galvanostatic charge-discharge voltage profiles for the RuO₂ electrodes at 15 mA cm⁻². The specific capacitances at this current density of the A450Ru and N800Ru electrodes were found to be 454 and 164 F g⁻¹, respectively. The decrease in the iR drop of N800Ru at this current density compared to A450Ru indicates that the N800 has higher electrical conductivity.

Electrochemical impedance spectroscopy (EIS) was also used to characterize the charge-discharge properties of the pseudocapacitors. The EIS analysis was conducted using an IM6e ( Zahner-elektrik) over a frequency range of 10 mHz to 1 MHz at an ac amplitude of 10 mV. Figure 4(a) shows the Nyquist plots for the RuO₂ electrodes. Both the A450Ru and N800Ru electrodes were found to exhibit an almost purely capacitive behavior at low frequencies, as indicated by the vertical lines in these Nyquist plots. These electrodes were found to exhibit different behaviors in the high frequency region. The semicircle at high frequencies is found to disappear by using N800Ru electrode. The semicircle at high frequencies is associated with the porous structure of electrode, namely, the semicircle disappeared due to the decrease of mesopores after heat treatment of TiO₂ nanorods. Figure 4(b) shows the Bode plots for the TiO₂-based electrodes. The characteristic response frequency f₁(θ=45°), which is the frequency at the phase angle (θ) is 45°, is used to characterize the transition from capacitive to resistive behavior. The characteristic response time τ was also defined as the inverse of f₁(θ=45°) and characterizes the charge-discharge rate of the system. τ was found to be 3.33 and 0.15 s for the A450Ru and N800Ru electrodes, respectively. Thus, the response time was found to improve by a factor of 20 with the use of the N800Ru.

In summary, we have shown that the heat treatment of the TiO₂ substrate enhances the electrical conductivity, hence substantially improving the response time of the RuO₂ electrode. The heat treatment of the TiO₂ substrate not only increases the maximum specific capacitance but greatly enhances the performance at fast charge-discharge rates. The RuO₂ electrode deposited on heat-treated TiO₂ maintains a high capacitance, with only a 33% decrease at a fast scan rate of 1000 mV s⁻¹ with respect to the value at 10 mV s⁻¹. Furthermore, the use of the heat-treated TiO₂ enhances the capacitance and the charge-discharge rate by a factor of more than 20 over that of the pristine TiO₂. These results demonstrate the remarkable supercapacitor performance of RuO₂ electrodes deposited on the heat-treated TiO₂ at very fast scan rates and high current densities.