Random shaped ZnO supported on a porous substrate as supercapacitor

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Abstract

Potentiostatic depositions of zinc oxide (ZnO) on titania (TiO₂) nanotube substrate have been observed to demonstrate remarkable enhancement in the supercapacitance behavior as reported in this study. Systematic evaluation of the morphology and crystal structure of the electrodeposited ZnO phase was carried out using scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques, respectively. The cyclic voltammetry and galvanostatic charge-discharge experiments indicated that the electrode can attain a maximum specific capacitance of 304 F g⁻¹ that was partly attributed to the electro-active ZnO phase and partly to the highly permeable, porous, and unidirectional nanotubular TiO₂ substrate.

1. Introduction

Nanotubular morphology of TiO₂ (T-NT) is of particular interest for various applications, especially because of its certain peculiar properties: high surface area, good chemical stability and non-toxicity [1, 2]. As supercapacitor electrode, the specific capacitance of T-NT is quite low (~0.1 mF cm⁻²) [3], however its presence as a supporting base/substrate in combination with

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various electro-active metal oxides has proven to produce substantial enhancement in the supercapacitance behavior [4-6]. Metal oxides such as NiO, Bi₂O₃, and Co₂O₃ were used previously to fabricate composite electrodes with T-NT in order to promote the overall capacitance properties [4-6]. Recently, ZnO based electrodes were studied for their capacitance properties [7,8]. It has been argued that high electrochemical capacitance behavior (typically of the order of 100-200 F g⁻¹) observed in this class of oxide material is due to its good electrochemical attributes as well as favorable electronic properties [7,8].

This study has been conducted to evaluate the supercapacitance behavior of T-NT/ZnO composite electrode. The composite electrodes were synthesized using a simple, easy to implement electrodeposition technique. The fabricated T-NT/ZnO electrode indeed showed promising supercapacitance properties due to the favorable combinations of an electro-active oxide phase and porous supporting nanotubular substrate.

2. Experimental studies

2.1 T-NT Substrate Fabrication

Titanium samples (0.1 mm thickness and 10 mm x 15 mm) were roughly polished (with 600 grit SiC emery paper) and ultrasonically cleaned in a solution of acetone and isopropyl alcohol (1:1). Subsequently, the coupons were anodized potentiostatically in an electrolyte (0.5 wt % ammonium fluoride and 10% H₂O) at 40 V for 1 hour. Subsequently, the anodized titanium samples were annealed in air at 500°C for 2 hours.

2.2 Electrochemical Deposition of ZnO

Potentiostatic deposition of ZnO on T-NT surface was carried out in an aqueous solution of 10 mM zinc chloride and 0.5 M KCl at 60°C. A 3-electrode based electrochemical workstation

(Gamry Reference 600) with annealed T-NT coupon as working electrode, platinum coil as counter electrode and a saturated Ag/AgCl electrode as reference constituted the electrochemical deposition setup. Depositions were carried out at a constant potential ($-1.25V_{\text{ref Ag/AgCl}}$) for various durations of time (5-20 min).

2.3 Characterization

Examination of the surface and cross sectional morphology of T-NT and T-NT/ZnO samples was performed using a field emission scanning electron microscope (FE-SEM, Hitachi S-4800). The XRD analysis of the samples was carried out using SIEMENS D5000 diffractometer with copper K- α radiation.

2.4 Electrochemical Measurements

The electrochemical properties of the T-NT/ZnO electrodes were evaluated by conducting cyclic voltammetry (CV) and galvanostatic charge-discharge experiments in 0.1M Na₂SO₄ using a potentiostat (Gamry Reference 600), connected to a 3-electrode setup consisting of the T-NT/ZnO sample as the working electrode, platinum coil as the counter electrode, and saturated Ag/AgCl electrode as a reference electrode.

3. Results and Discussion

Anodization of Ti produced self-organized and vertically aligned nanotube array (T-NT) as shown in Fig. 1a. The nanotubes were found to have an average diameter of ~ 90 nm, length of ~ 1.5 μm (inset Fig. 1a) and wall thicknesses in the range of 15-20 nm.

Potentiostatic deposition of ZnO on T-NT substrate resulted in the formation of irregular shaped morphology of the oxide phase after various deposition times. Fig. 1(b-e) shows the ZnO deposits obtained after the deposition times of $t = 5, 10, 15,$ and 20 minutes. Some important

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4 observations can be made from these micrographs. In general, the deposits appeared to be
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6 irregular, although occasional hexagonal nano-sized crystals as well as rod-shaped oxide phases
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8 were visible from the micrographs which were also observed in a previous study [9]. As the
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10 deposition time was increased, the amount of oxide deposits was also increased. One interesting
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12 observation was that the size of the ZnO crystals decreased after the deposition time was
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14 increased from 10 to 15 minutes. For example, after deposition for 10 minutes, the ZnO crystals
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16 were approximately 0.5-1 μm (Fig. 1c), however, after 15 minutes, the crystals became 200-500
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18 nm (Fig. 1d). One possible reason for the decreased ZnO crystal size could be due to the change
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20 in the concentration of the Zn^{2+} in the deposition electrolyte after prolonged deposition time [9].
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22 Also evident from the micrograph in Fig. 1d, the deposits became more uniformly distributed on
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24 the surface of the T-NT after 15 minutes of deposition. Such distribution of the oxide phase is
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26 important for electrochemical charge storage application as it provides well-balanced optima of
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28 sufficient electroactive material for the redox reactions as well as a good accessibility for the
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30 electrolyte to permeate through the porous T-NT substrate for efficient intercalation. Further
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32 increase in the deposition time to 20 minutes, the ZnO crystal density was increased although
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34 size of the oxide phase remained the same as that obtained after 15 minutes (Fig. 1e). In Fig. 1e,
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36 agglomeration of the ZnO crystals was also visible after 20 minutes of deposition.
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47 The XRD analysis conducted on the T-NT/ZnO electrode prepared for $t=15$ min indicated the
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49 formation of crystalline ZnO phase. The XRD profile presented in Fig. 2 indicated the presence
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51 of diffraction peaks from (110) and (103) planes of the ZnO phase agreeing well with the
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53 literature reported data [7,8]. Please note that some of the peaks from the anatase phase of the T-
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55 NT as well as Ti-substrate can also be observed in the XRD profile.
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The cyclic voltammetry (CV) profiles, recoded at 200 mV s⁻¹ for the electrodes prepared for various deposition durations are shown in Fig. 3a. The profiles, irrespective of the deposition time, appeared to be the mixture of the pseudo as well as EDL type capacitance behavior. The pseudo nature of the electrodes is due to the redox reactions that might have occurred at around 0.4V (vs Ag/AgCl ref. electrode) as evident in the CV profiles. Moreover, the current responses in the CV profiles exhibit mirror-image behavior about the zero-current line with rapid current reversals at each potential limit [1,2]. It is also interesting to note that the electrodes prepared for $t = 15$ min showed relatively higher capacitance compared to all other electrodes — a relatively higher enclosed CV area for this electrode can be observed in comparison to the other electrodes. The reason for the increased capacitance for this electrode can be argued based on the ZnO morphology/distribution observed for this electrode (Fig. 1c). The uniform distribution of the ZnO crystallites (no agglomeration) along the entire T-NT substrate resulted significantly higher intercalation with the electrolyte during the CV process along with the optimum access of the electrolyte for efficient permeation into the porous T-NT substrate that lies beneath the oxide phase. The deposition processes for shorter durations ($t = 5, 10$ min) resulted in lesser weight fraction of ZnO, while with increased deposition time ($t = 20$ min) agglomeration of the oxide phase was observed leading to the incomplete intercalation of the oxide phase. From the CV curves, the specific capacitance (C) of the electrodes was calculated using the following equation [3,5,10-12],

$$C = Q/\Delta Vm \quad (1)$$

Where Q = half of the total charge from the integrated CV area, ΔV =voltage window, m = mass of ZnO deposit. Using Eqn. 1, the specific capacitance were calculated to be about 92, 103, 154

and 139 F g^{-1} for the electrodes prepared for $t = 5$ -20 minutes, respectively and plotted in the inset of Fig 3(a).

Further, CV experiments were performed at different scan rates for the electrode prepared for $t = 15$ min and presented in Fig. 3(b). It is apparent from the figure that the shape of the CV curves did not vary with the change in the scan rates demonstrating good stability of the electrode material. The specific capacitance of the electrode were 302, 198, 154 F g^{-1} at the scan rates of 20, 100 and 200 mV s^{-1} . The specific capacitance decreased by about 50% upon increase in the scan rate from 20 to 200 mV s^{-1} – such decrease in capacitance can be attributed to the incomplete intercalation between the ZnO and the electrolyte at higher scan rates as described previously in more details [3,5].

Fig. 3(c) shows the representative charge-discharge profile for the electrodes prepared for $t = 15$ min of deposition obtained after conducting galvanostatic charge-discharge cycle test at a current density of 3 mA cm^{-2} . The experiments were conducted for 1000 continuous cycles and the specific capacitance obtained were plotted and presented in Fig. 3(d). The tests demonstrated that the capacitance retention for the electrode was excellent with only 10% fading of the capacitance value after 1000 continuous charge-discharge cycles.

4. Conclusion

The synthesis of composite electrodes comprising of zinc oxide (ZnO) and titania nanotubes (T-NT) using a simple electrodeposition process has been carried out. SEM and XRD analysis on the composite electrodes suggested evolution of various morphologies (random, hexagonal rounded and rod shaped) and crystalline phases of the ZnO deposit. The cyclic voltammetry and

galvanostatic charge discharge tests conducted using the electrodes suggested that a high capacitance value ($\sim 300 \text{ F g}^{-1}$) can be achieved in the electrode by suitably optimizing the electrodeposition parameters.

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Figure 1: (a) The top view of the T-NT after anodization (inset shows the cross-sectional view), morphologies of the ZnO deposit after deposition time (t) of (b) 5 min, (c) 10 min, (d) 15 min and (e) 20 min.

Figure 2: XRD profile of the T-NT/ZnO electrode prepared for $t = 15$ min

Figure 3: (a) CV profiles of the T-NT/ZnO electrodes prepared for $t = 5$ -20 min (inset shows the variations in the specific capacitance (C) with t) (b) CV curves recorded at various scan rates for the T-NT/ZnO electrode prepared for $t = 15$ min (c) Representative galvanostatic charge-discharge profiles obtained at a current density of 3 mA cm^{-2} on the T-NT/ZnO electrode prepared for $t = 15$ min. (d) Variations in the C of the T-NT/ZnO electrode prepared for $t = 15$ min. as the function of cycle number.