Electrochemical properties of Co-doped titanate nanotubes for energy storage

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Abstract. Co-doped titanate nanotubes (TNTs) with a nominal composition of CoₓTi₃−ₓO₇(Na₂₋ₓHₓ·nH₂O) (where 0 ≤ x ≤ 0.30) were successfully synthesized by hydrothermal route at a temperature of 130 °C for 24 h. The diameter of nanotubes was found to be on the 7 ∼ 20 nm. The synthesized samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and Brunauer–Emmett–Teller (BET). The electrochemical properties were investigated by using cyclic voltammetry (CV) at different scan rates (2 ∼ 200 mV/s) and galvanostatic charge-discharge (GCD) at different constant current densities in 6 M KOH. The electrochemical measurement showed the variation of the specific capacitances depending on the doping level. The specific capacitances of Co-doped TNTs significantly increased with increasing doping level. The electrochemical properties of TNTs can be improved by Co doping.

1. Introduction

In recent years, low-dimensional nanostructures, i.e., nanoparticles, nanosheets and nanotubes have been intensively studied because of the promising applications in future nanotechnology. Among them, nanotubes are of great interest for the use in potential applications including, Especially, Titanate nanotubes (NaₓH₂₋ₓTi₃O₇·nH₂O; TNTs), material with high dielectric constant [1-3], have been developed for practical applications including photocatalysis [4], support/carriers [5], ion-exchange [6], adsorption [7], photochemistry and electrochemistry [8, 9]. Previous TNT research has been focused on finding novel and appropriate methods to design its nanostructure formation [10-14]. The comprehensive studies based on the exploration and development of their physical and chemical properties for potential applications have been focused. Recently, a number of modifications have been applied to enhance their properties in diverse applications. Recently, supercapacitors have gained intensive attention in renewable energy applications due to the advantages of high-power density, high energy density, long-life cycle, and low cost [15]. Generally, the transition metal oxides-based supercapacitors such as MnO₂ [16], V₂O₅, NiO [17], Fe₃O₄ [18] and Co₃O₄ [15], are the competitive materials for electrochemical capacitors with high specific capacitance. However, the electrochemical properties of TNTs have rarely been studied and is interesting to be explored because of their high specific surface area, good physical and chemical stability and environmentally friendly [15]. Previously, Lee et al. reported the exceptional electrochemical specific capacitance of up to 640 F g⁻¹ with long-term stability in polythiophene infiltrated-TiO₂ nanotubes (TNTs) prepared by the controlled
Co-doped titanate nanotubes (Co-doped TNTs) with a nominal composition of Co$_x$Ti$_{13-x}$O$_7$(Na$_2$$_3$H$_7$nH$_2$O), with $x = 0, 0.05, 0.1, 0.2$ and 0.3 were prepared by a hydrothermal method. In a typical synthesis, the TiO$_2$ anatase (99-100% Riedel-dehean USP) and Co(NO$_3$)$_2$.9H$_2$O (99.9% Kento) were dispersed in 10 M NaOH solution (160 ml) under magnetic stirring at room temperature for 24 h and ultrasonicated for 2 h afterwards. The mixed solution was placed in a Teflon-lined autoclave for hydrothermal process at a temperature of 130 °C for 24 h. After that, the device was then cooled down to room temperature in normal atmosphere. Finally, the obtained sample was dissolved in deionized water and dried in an oven at 70 °C. The crystal phase was identified by X-ray diffraction (XRD) using a CuKα radiation with $\lambda = 0.154060$ nm (D2, Bruker, Germany). The morphology and microstructure were characterized by transmission electron microscopy (TEM), High resolution TEM (HRTEM), selected area electron diffraction (SAED) and energy dispersive X-ray spectroscopy (EDX) using field emission-TEM (FETEM, FEI, Tecnai G$^2$ F20, Netherlands). After degassing at 100 °C for 12 h, the N$_2$ adsorption/desorption isotherms were measured at 77 K using automatic specific surface area/pore size distribution analyzer (BLSORP-miniII). The Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods were used to determine the specific surface area and pore character of the samples. Electrochemical properties were carried out using cyclic voltammetry (CV, Metrohm Autolab PGSTAT302N working station) in a standard three-electrode cell configuration. The as-prepared sample, platinum wire and Ag/AgCl were used as working electrode (WE), counter electrode (CE) and reference electrode (RE), respectively. The working electrode was fabricated by mixing the Co-doped TNTs, polyvinylidene difluoride (PVDF) binder and acetylene black at a weight ratio of 8:1:1 using n-methyl-2-pyrrolidinone (NMP) as a solvent. The slurry was coated on Ni foam with circular shape, baked at 70 °C for 24 h in air and then pressed at 20 MPa to obtained WE. The electrochemical measurement techniques including potentiostatic cyclic voltammetry (CV), and galvanostatic charge/discharge testing (GCD) were employed to evaluate the capacitive performance of all prepared electrodes at room temperature. The CV was measured in 6 M KOH aqueous solution within potential windows of -0.2 to 0.45 V by ranging scan rates between 2 - 200 mV s$^{-1}$. The GCD was carried out at current densities of 0.08, 0.09, 0.1, and 0.2 A g$^{-1}$. The equivalent circuits of the cells were evaluated using Nova 1.10 software. The capacitive properties can be calculated by following equations [21-24]:

\[
C_{CV} = \frac{1}{m\Delta V} \int I(t)dt
\]  

(1)

\[
C_{CD} = \frac{I\Delta t}{m\Delta V}
\]  

(2)

where $C_{CV}$ (F/g) and $C_{CD}$ (F/g) are specific capacitance from CV and GCD techniques. $I$, $m$, $\Delta V$ and $\Delta t$ are current (A), sample mass (g), potential window (V) and duration time (s), respectively.
3. Results and discussion

The XRD patterns of all samples are shown in Figure 1 whose diffraction peaks are corresponded to (001), (110), (310), (203), (11 3 3) and (114) planes of the trititanate (H$_2$Ti$_3$O$_7$) standard data (JCPDS: 4705-61) [25-28] without any impurity phases.

Figure 2 shows the TEM bright-field images of the prepared samples revealing the uniform cylindrical nanotubes. Diameters of the nanotubes were measured to be about 7 - 15 nm with 4 - 5 multiwall layers involved. The distance between each layer was about 0.782 - 0.788 nm. The lengths of nanotubes were estimated to be several hundreds of nanometers up to few micrometers. The SAED patterns exhibit spotty ring patterns corresponding to the (110), (003), (202) and (114) planes of H$_2$Ti$_3$O$_7$ structure consistent with XRD results.

![XRD patterns of TNTs and Co doped TNTs with different concentrations.](image)

Figure 1. XRD patterns of TNTs and Co doped TNTs with different concentrations.

The specific surface area and pore character of all samples were investigated by N$_2$ adsorption/desorption measurement. The nitrogen adsorption isotherms on the surfaces of the undoped and Co-doped TNTs were shown in Figure 3. All samples exhibited hysteresis loops which are the typical type IV isotherms. This is due to capillary condensation of nitrogen in mesopores where some micropores can be attributed by knee-shape at low pressure. In this case, the TNT and Co-doped TNTs at x = 0, 0.05, 0.1, and 0.2 act as type H3 hysterisis loop which is possibly due to nonuniform pores. Whereas, the Co-doped TNT at x = 0.3 exhibits type H4 hysteresis loop indicating the uniform slit-pores shape [23]. Inset of Figure 3 shows the differential pore-volume distributions of all Co-doped TNTs obtained by nitrogen desorption curves using the BJH algorithm at different average tube diameters. The curves show maximum corresponding pore sizes of 2 to 20 nm indicating the mesoporous-scale contribution. The investigated pores may improve the electrode/electrolyte contract area. All significant parameters were calculated and summarized in Table 1.

Figure 4 shows the CV responses of all samples at different scan rates (from 2 to 200 mV s$^{-1}$). The redox peaks were observed which are the pseudocapacitive nature of transition metal oxides. The height of those redox peaks was increased and progressively shifted to higher potential as scan rate increases. This indicates a good reaction ability of our electrodes in the 6 M KOH electrolyte. The typical galvanostatic charge-discharge (GCD) of the samples at various current densities were displayed in Figure 4(b). The observed nonlinear GCD curves confirm the pseudocapacitive behavior of our samples. The discharge time decreases as increasing Co concentration suggesting the significant role of Co doping. The CV curves all Co-doped TNTs at low scan rate of 2 mV s$^{-1}$ were shown in Figure 4(a).
Figure 2. TEM images (left), HRTEM images (middle) and SAED patterns (right) of TNTs and Co-dope TNTs with different concentrations.

Figure 3. N$_2$ adsorption and desorption isotherm of all samples. The inset shows pore volume distribution obtained from nitrogen desorption curves.
The CV curves of all electrodes present a pair of cathodic and anodic peaks corresponding to the oxidation and reduction processes, but their height and position are different depending on Co concentration. It was found that the height of those redox peaks was increased as increasing Co doping concentration. Additionally, it can be seen that the redox reversibility of the Co-doped TNTs at x > 0 is higher than that of the TNTs. This indicates that the presence of Co in the TNT structures can improve their electrochemical response. Figure 4(b) presents the linear voltage-time profiles of GCD measurement of all electrodes at the current density of 0.2 A g⁻¹. Among all samples, the TNTs electrodes showed the longest ions charge-discharge time at each current density. This time duration is decreased with increasing Co doping concentration. The specific capacitance decreased with increasing current density and then remained approximately constant at I = 0.2 A g⁻¹. Figure 4(c) shows corresponding specific capacitance of all samples at different scan rates where the Co-doped TNTs at x = 0.2 demonstrates a maximum specific capacitance of about 30 F g⁻¹ at a scan rate of 2 mV s⁻¹. This behavior is similar to the previous research of Al-doped LiNi₀.₈Co₀.₂O₂ which can stabilize its layered-structure and greatly improve the electrochemical cycling ability [30]. The specific capacitance of all Co-doped TNTs decreased as scan rate increases. This is attributed to the presence of inner active sites, which partly inhibited the redox transitions at higher scan rates, probably owing to the diffusion effect of protons within the electrode. However, the specific capacitance is significantly decreased in x = 0.3. This should be related to the reduction of its surface area and volume which is apparently decreased from 202 to 160 m² g⁻¹ and 0.8 to 0.5 m³ g⁻¹ s for x = 0.2 and x = 0.3, respectively. The lower surface area (and volume) may affect the reduction of electrolyte-electrode contract area, leading to the decrease in specific capacitance. These results not only indicate that specific capacitance is dependent on the surface area but also subject to other factors such as pore size distribution and pore volume.

The specific capacitance as a function of scan rates of all samples was represented in Table 2. The maximum specific capacitance of 11 F g⁻¹ at a current density of 0.08 mV s⁻¹ was obtained in the Co-doped TNTs at x = 0.2. 70% of the maximum specific capacitance were retained at I = 0.2 mA cm⁻² compared to that of the 0.08 mA cm⁻². This indicates a good rate capability of the Co-doped TNTs electrodes.

| Table 1. Summary of BET analysis of TNTs and Co-doped TNTs by N₂ adsorption. |
|-----------------|-----------------|-----------------|-----------------|
| Doping Level    | Mean pore diameter (nm) | BET surface area (m² g⁻¹) | Pore volume (m³ g⁻¹) |
|-----------------|-----------------|-----------------|-----------------|
| x = 0           | 15.2            | 210.4           | 0.8             |
| x = 0.05        | 15.3            | 209.3           | 0.8             |
| x = 0.1         | 17              | 214.7           | 0.9             |
| x = 0.2         | 15.4            | 202             | 0.8             |
| x = 0.3         | 12.2            | 159.3           | 0.5             |

| Table 2. Summary specific capacitance of Co-doped TNTs at different scan rates. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Scan rate (mV/s)| Specific capacitance (F g⁻¹) |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| 2               | x = 0.05        | x = 0.1        | x = 0.2        | x = 0.3        |
| 5               | 21.6            | 25.4            | 29.5            | 26.2            |
| 10              | 11.0            | 20.0            | 23.1            | 21.5            |
| 20              | 8.3             | 16.4            | 18.1            | 17.5            |
| 50              | 6.8             | 12.0            | 12.9            | 13.2            |
| 100             | 5.1             | 7.8             | 8.2             | 8.5             |
| 200             | 4.0             | 5.9             | 6.2             | 6.2             |
|                 | 3.2             | 4.5             | 4.9             | 4.8             |
Figure 4. (a) CV curves at 2 mV/s scan rate, (b) GCD curves at 0.2 A/g current density (c) specific capacitance as a function of scan rate, and (d) specific capacitance as a function of current density of TNTs and Co-doped TNTs.

4. Conclusions
The Co-doped TNTs were successfully synthesized by hydrothermal route. The XRD patterns indicated that all samples possess a trititanate structure (H₂Ti₃O₇). The Co-doped TNTs were 7–10 nm in diameter with several hundreds of nanometers in length. Doping Co into TNTs can significantly improve their capacitive properties with the specific capacitance of up to 30 F g⁻¹.

Acknowledgements
This work was supported by Suranaree University of Technology, for financial support and providing facilities. The authors would like to thank Rajamangala University of Technology Isan and Advance Materials Physics Group (AMP).

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