Synthesis and electrochemical properties of porous tubular TiN powders prepared via ammonia reduction nitridation of nonhydrolytic TiO₂ powders

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Porous tubular TiO₂ powders were prepared first via a novel facile and non-template route of the nonhydrolytic sol-gel method. The as-prepared TiO₂ powders could then be directly converted into porous tubular TiN powders through an ammonia reduction nitridation process. The results indicated that the obtained TiO₂ powders consisted of a pure, well-crystallized anatase TiO₂ phase of porous tubular morphology, with a Brunauer-Emmett-Teller (BET) specific surface area of 39 m²/g and an average pore size of 11 nm and pore volume of 0.012 cm³/g. After the porous tubular TiO₂ powders were calcined at 800°C for 2 h under an ammonia (NH₃) gas atmosphere, TiN powders maintaining their porous tubular architecture were obtained, with a BET specific surface area of 35 m²/g and an average pore size and pore volume of 12 nm and 0.096 cm³/g, respectively. The electrochemical performance of the porous tubular TiN powders demonstrated that TiN powders could be a promising electrode material for supercapacitors.

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Key-words : Tubular TiN, Porous, Nonhydrolytic sol-gel, Ammonia reduction nitridation, Ethanol

[Received April 4, 2017; Accepted June 5, 2017]

1. Introduction

Titanium nitride (TiN) materials possess such excellent properties as super-hardness, corrosion resistance, high electrical/thermal conductivity, and chemical/thermal stability.^{1)–3)} They are therefore widely applied as catalysts and catalyst-support materials in dye-sensitized solar cells,^{4)–6)} fuel cells, batteries,^{7)–12)} and supercapacitors.^{13)–15)} Particular attention is being paid to powders with porous architectures due to their high surface-to-volume ratios, which could improve the permeability and charge transport for distinctive physicochemical properties.¹⁶⁾ Special interest has developed, moreover, in controlling synthetic approaches to porous and tubular TiN materials. Liu et al. synthesized hierarchical nanotubular TiN by magnesiothermic reduction of TiO₂ replicas of a cellulose substance (filter paper) in N₂,¹⁷⁾ for example, Xie et al. prepared TiN nanotubes by an anodization process of TiO₂ in ethylene glycol solution, and a subsequent nitridation process in an NH₃ gas atmosphere.¹⁸⁾ However, these approaches generally require a complicated and long-term fabrication process to prepare TiO₂ precursors. Thus, it is more efficient to prepare TiO₂ precursors with various ultrastructures by exploring facile, easily controlled and lower-cost synthetic routes.

Recently, a novel simple and template-free technique, the nonhydrolytic sol-gel method, has been developed to prepare TiO₂ materials with versatile morphologies.^{19)–22)} The use of anhydrous ethanol as the oxygen donor, in particular, contributes

to the formation of tubular TiO₂ materials.^{22),23)} However, there are lower reports on synthesis of porous tubular TiN powders using an ammonia reduction nitridation process based on the nonhydrolytic sol-gel method.

In this paper, we describe a new route to synthesis of porous tubular TiN powders via ammonia reduction nitridation of nonhydrolytic TiO₂ powders using ethanol as an oxygen donor. It is demonstrated that porous tubular structured TiN powders can be proposed as a promising electrode material for supercapacitors.

2. Experimental

2.1 Sample preparation

The following reactants were used for the synthesis of TiO₂ powders: titanium tetrachloride (TiCl₄) as a titanium resource, anhydrous ethanol (C₂H₅OH) as an oxygen donor and dichloromethane (CH₂Cl₂) as a solvent. All chemicals were used as received without further purification. Porous tubular TiO₂ powders were prepared by the nonhydrolytic sol-gel method. First, 8.8 mL of TiCl₄ and 30 mL of CH₂Cl₂, respectively, were added slowly to 9.3 mL of C₂H₅OH solution under vigorous stirring at room temperature. The obtained mixture was heated in an autoclave at 110°C for 38 h to form TiO₂ gelations (gels). Second, the gels were dried at 80°C in air and then calcined to obtain TiO₂ powders at a heating rate of 5 °C/min to 600°C for 30 min. The as-prepared TiO₂ powders were then placed in the quartz boat reactor of a tube furnace. The reduction nitridation of the TiO₂ powders proceeded as follows: the furnace was flushed with N₂ gas at a flow rate of 100 mL/min for 30 min to remove O₂ at room temperature. The N₂ gas was then replaced with dry NH₃

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gas. The flow rate of NH_3 gas was kept at about 400 mL/min at 300 to 500°C. When the temperature reached 500°C, the flow rate of NH_3 gas was adjusted to 800 mL/min up to 800°C and then held there for 2 h. During the furnace cool down, the same nitridation gas flow rate procedure was applied with a corresponding elevating temperature process. Finally, TiN powders were obtained.

2.2 Characterization techniques

The X-ray diffraction (XRD) patterns of the samples were recorded with a Rigaku X-ray diffractometer (D/MAX2500PC, Japan) using a $\text{Cu-K}\alpha$ radiation from 10 to 80° at a scanning speed of 10 °C/min. The morphological structure of the synthesized TiN material was observed by scanning electron microscopy (SEM, S-4800, Japan). The specific surface area was measured using a Brunauer–Emmett–Teller (BET) technique (Quantachrome Inst., NOVA2200e). And the Barrett–Joyner–Halenda (BJH) model was used for determining the pore diameter distribution of the synthesized TiN material.

As the battery testing system, a LIR2032 button-type supercapacitor was employed to study the electrochemical performance of the porous tubular TiN powders. The TiN powders as the active material were mixed with acetylene black and PVDF (wt %, 16:3:1, respectively). The mixed samples were pasted on nickel foam, dried at 80°C for 24 h, and formed under a pressure of 10 MPa. A LIR2032 button-type supercapacitor was then assembled using two identical TiN electrodes, 1M Na_2SO_4 as an aqueous electrolyte and polypropylene as the diaphragm. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements of the TiN material were evaluated using an electrochemical workstation instrument (CHI Instrument Inc., CHI604E). And galvanostatic charge/discharge (GCD) testing was performed with a battery-testing system (LAND Instrument Inc., CT2001A).

3. Results and discussion

3.1 Characterization of nonhydrolytic TiO_2 powders

XRD patterns of as-prepared nonhydrolytic TiO_2 gels after calcination at 600°C for 30 min are shown in Fig. 1. These indicate that pure anatase TiO_2 is formed in the powders. No trace of rutile is detected. Anatase phase TiO_2 favors further reduction nitridation of as-prepared TiO_2 powders.²⁴⁾

In our experiment, when TiCl_4 was added to a $\text{C}_2\text{H}_5\text{OH}$ solution at room temperature, it interacts first with the $\text{C}_2\text{H}_5\text{OH}$ to produce titanium alkoxide $\text{TiCl}_2(\text{OR})_2$ ($\text{R} = \text{CH}_2\text{CH}_3$) with the liberation of HCl .²⁴⁾ The corresponding reaction can be written as:

The nonhydrolytic nucleophilic substitution reaction among the titanium alkoxide $\text{TiCl}_2(\text{OR})_2$ precursors to form titanium gels can be written as:

The microstructure of as-prepared nonhydrolytic TiO_2 powders was characterized by SEM imaging as shown in Fig. 2. It was found that anatase TiO_2 crystals grow mainly into tubular cluster-like structures in the SEM image at high magnification (inset). As explained by other reports in the literature,²⁵⁾ the dramatic change in crystal morphology can be explained based on selective interaction of the solvents with surface ions, which exhibits the growth of specific lattice planes and thus results in the expression of these lattice planes in the final crystal form. The resultant morphologies of nonhydrolytic TiO_2 products could have an inherent relation with the chelate precursors between TiCl_4 and $\text{C}_2\text{H}_5\text{OH}$.²⁴⁾

SEM images at high magnification revealed that a number of pores were also formed on the surface of tubular TiO_2 , and quantities of tubular TiO_2 were also formed. The average inner diameter of tubular TiO_2 was about 350 nm and the length was approximately 1.5 μm .

The results of the investigation of the surface area, pore size, and the BET surface area of nonhydrolytic TiO_2 powders were recorded as shown in Fig. 3. The N_2 adsorption–desorption curves of TiO_2 powders showed a Type IV isotherm characteristic of mesoporous materials,²⁶⁾ featuring an H2 hysteresis loop.²⁷⁾ It could be seen that the N_2 adsorption capacity increased with increases in the relative pressure below the $p/p_0 = 0.7$ region and formed a thin hysteresis, which could be related to the N_2 adsorption on the inside surface of mesoporous channels. In the relative pressure range $0.7 < p/p_0 < 1$, the N_2 sorption isotherms of TiO_2 powders showed a strong hysteresis with a steep rise in the adsorption region, which is associated with capillary condensation of mesoporous channels.

Testing showed the BET surface area of nonhydrolytic TiO_2 powders to be 39 m^2/g , the average BJH pore diameter of the desorption branch of the isotherm to be about 11 nm, and the total pore volume to be 0.012 cm^3/g . All these data clearly confirmed that the as-prepared TiO_2 powders possessed a mesoporous structure that may be favorable for enhancing the reduction nitridation of TiO_2 powders.

Fig. 1. XRD patterns of as-prepared TiO_2 powders.

Fig. 2. SEM images of as-prepared TiO_2 powders.

Fig. 3. (a) N₂ adsorption-desorption isotherms of as-prepared TiO₂ powders and (b) the pore diameter distribution obtained from the desorption branch of the isotherm using the BJH method.

Fig. 4. (a) XRD patterns of TiN powders and (b) multi-peak Gaussian fitting results of (111), (200) and (220) XRD lines of TiN powders.

3.2 Characterization of porous tubular TiN powders

Figure 4 shows the XRD patterns of the TiN powder samples after reduction nitridation of nonhydrolytic TiO₂ powders at

Fig. 5. SEM images of TiN powders.

800°C for 2 h. As shown in Fig. 4(a), the results showed that the diffraction peaks of the nitridation product did not exactly match the cubic TiN corresponding to the (111), (200), (220), (311) and (222) plane reflections. However, the peaks of the (111), (200) and (220) planes showed a broad pattern in the absence of shoulder-peaks. It is indicated that the obtained phases are not of truly pure TiN but of a titanium oxynitride (TiN_{1-x}O_x) with a face-centered cubic arrangement of atoms (NaCl structural type) similar to the TiN structure. Therefore, multi-peak Gaussian fitting processing of (111), (200) and (220) XRD lines is shown in Fig. 4(b). The results indicate that a part of the TiN-TiO solid solution corresponding to TiN_{0.6}O_{0.4} (PDF card No. 49-1325) is formed in addition to the stoichiometric TiN phase.²⁸⁾ The lattice constant of the TiN sample calculated from the XRD patterns was 4.193 Å, moreover, which was smaller than the value of the stoichiometric TiN (4.2417 Å from PDF card No. 38-1420). And the chemical compositions of TiN_{1-x}O_x were calculated as TiN_{0.71}O_{0.29}. For reasons of convenience, the nitridation product is still called “TiN”.²⁹⁾ The chemical molecular of TiN_{1-x}O_x was determined using the following formula:³⁰⁾

$$x = (\alpha - 4.175 \text{ Å}) / (4.238 \text{ Å} - 4.175 \text{ Å})$$

The overall ammonia reduction nitridation reaction can be described as follows:

The formation and intermediate products of TiN through ammonia reduction nitridation of the as-prepared TiO₂ have been suggested to proceed by the following reactions:³¹⁾

The morphological structures of the TiN powder samples were observed as shown in Fig. 5. The morphological structures of TiN powders are consistent with those of porous tubular TiO₂ powders before reduction nitridation treatment (Fig. 2). This could be explained by suggesting that O oxygen atoms of the O-Ti bonding of TiO₂ are gradually displaced in situ with N nitrogen atoms of NH₃ during the reduction nitridation process, and thus the morphological structures of porous tubular TiO₂ powders are maintained.³²⁾ Porous tubular TiN powders present a layered outer wall structure, moreover, with an average inner diameter of about 440 nm and length of above 1.2 μm.

Fig. 6. (a) N_2 adsorption-desorption isotherms of TiN powders and (b) the pore diameter distribution obtained from the desorption branch of the isotherm using BJH method.

Fig. 7. CV curves of TiN powders (scan rate: 10–100 mV/s).

The porosity characteristics of the tubular TiN powder samples were determined by N_2 adsorption-desorption measurement as shown in Fig. 6. The adsorption and desorption isotherms of the TiN samples showed a Type IV isotherm above the $p/p_0 = 0.45$ region. The TiN powders still maintained the characteristics of typical mesoporous structures of tubular TiO_2 samples after the reduction nitridation treatment in NH_3 . BJH analyses of the desorption branch of the isotherm for the tubular TiN powders exhibited a mean pore diameter of 12 nm, a BET specific surface area of $35 \text{ m}^2/\text{g}$, and a pore volume of $0.096 \text{ cm}^3/\text{g}$.

3.3 Electrochemical measurements of porous tubular TiN powders

CV tests were carried out to estimate the electrochemical properties of the porous tubular TiN powder electrodes at different scan rates of 10, 20, 50, and 100 mV/s. As shown in Fig. 7,

Fig. 8. Specific capacitance curves of TiN powders (scan rate: 10–100 mV/s).

Fig. 9. Charge/discharge curves of TiN powders (current density: 0.05–0.5 A/g).

with increases in the scan rate, the CV curves were all estimated to be rectangle-like shapes reflecting the ideal capacitive behavior of TiN. It is indicated that the behavior of porous tubular TiN powder electrodes resembles the response representative of typical electric double-layer capacitors. However, an increase in current between 0.4 and 0.8 V shows the presence of a redox reaction of TiN in Fig. 7. Hence, the capacitance of the porous tubular TiN powders was attributed to a combination of an electric double-layer capacitor and pseudocapacitance through a faradaic reaction.³³⁾ The charge storage mechanism could be based on continuous chemisorption of Na^+ in the applied potential range, according to the following reaction process:

The specific capacitance of the TiN is calculated by the below equation:

$$C = \frac{\int_{V_1}^{V_2} IdV}{m \cdot v \cdot (V_2 - V_1)} \quad (10)$$

Where m is the mass of the active material, and I , v , $(V_2 - V_1)$ are the average current of charge and discharge, scan rate, and potential difference, respectively. The overall specific capacitances of the porous tubular TiN at progressive scan rates (10–100 mV/s) were tested as shown in Fig. 8. The highest specific capacitance of the TiN electrode was shown to be 82.4 F/g at a scan rate of 10 mV/s. With an increase in the scan rate, the corresponding specific capacitance retention of porous tubular TiN electrodes was 62%.

Fig. 10. Specific capacitance curves of TiN powders (current density: 0.05–0.5 A/g).

Fig. 11. Cycling performance of TiN powders at a current density of 0.5 A/g.

The GCD curves of porous tubular TiN powder electrodes in the range of 0.05–0.5 A/g are shown in **Fig. 9**. It can be clearly seen that the GCD curves of the TiN electrode present a good symmetry, indicating good electrochemical reversibility of the TiN electrode material. The charge/discharge times were prolonged with a decrease in the charge/discharge current density. This suggests that the porous tubular structure of TiN electrodes allows rapid ion diffusion and presents an excellent rate capability. The values of the specific capacitance of the porous tubular TiN powders as a function of charge/discharge current density are depicted in **Fig. 10**. The specific capacitance gradually decreased from 83.4 to 63.8 F/g as the current density increased from 0.05 to 0.5 A/g, indicating a capacity retention of 77%. This indicates that the specific capacitance is inversely proportional to the charge/discharge current density. It is considered that the decrease in capacitance can be attributed mainly to a relationship in which the higher the current density, the shorter the formed time of the electric double-layer capacitor, a result of the difficulty of electrolyte invasion into micropores of the porous tubular TiN powders.

The electrochemical stability of porous tubular TiN powder electrodes at a current density of 0.5 A/g is shown in **Fig. 11**. It can be seen that a capacity retention of about 92% is exhibited after 1000 cycles, indicating an ability of TiN powder electrodes to maintain an acceptable cycle. This suggests that there is little electrochemical dissolution or structural collapse of the porous tubular TiN powder electrodes during continuous GCD processes.

EIS was used to investigate the resistance changes in porous tubular TiN electrodes. The Nyquist plot is shown in **Fig. 12**. A

Fig. 12. Nyquist plot of a TiN powder electrode.

depressed semicircle in the middle and a high-frequency region were observed. The internal resistance of the porous tubular TiN electrode was 0.9 Ω, a result corresponding to the point intersection with the real axis in the high-frequency range. At low frequencies, the straight line had a finite slope near 45°, which implies diffusive behavior of electrolytes in the pores of the porous tubular TiN electrode. The pore structure characteristic of tubular TiN powders might therefore promote adsorption of Na⁺ from Na₂SO₄ electrolytes. The tubular structure and pores on the walls of TiN electrodes would thus promote rapid ion diffusion and/or possible contributions of electrochemical supercapacitors.

4. Conclusions

In conclusion, we have synthesized porous tubular TiN powders via ammonia reduction nitridation of nonhydrolytic TiO₂ powders. Using anhydrous ethanol as an oxygen donor, nonhydrolytic porous tubular TiO₂ was transformed directly into porous tubular TiN at high temperature in an NH₃ atmosphere. The synthesis of TiN powders was achieved without an external template. And the accessible porous tubular structures of TiN powders contributed to good electrochemical performance of the TiN electrodes. The specific capacitance of the TiN electrodes was 83.4 F/g at a current density of 0.5 A/g. The capacity retention was maintained at 77% at different current densities. The internal resistance was only 0.9 Ω. Furthermore, the results indicate that porous tubular TiN materials could potentially be beneficial for application in supercapacitors.

Acknowledgments The authors are grateful to the National Natural Science Foundation of China (51272066) and Natural Science Foundation of Hebei Province (E2013209183) for their financial support.

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