



Preparation and capacitance properties of Mn-doped TiO₂ nanotube arrays by anodisation of Ti–Mn alloy



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ABSTRACT

Ti–Mn (Mn: 3.0, 7.0, 10.0 wt%) alloys were prepared by a power metallurgical method. Mn-doped TiO₂ nanotube arrays have been achieved directly by anodising the Ti–Mn alloys. Morphologies, crystal structure, chemical composition, supercapacitor performances of samples were characterised by scanning electron microscopy, X-ray diffraction, inductively coupled plasma optical emission spectrometry, and electrochemical analysis, respectively. The effects of manganese content, scan rate, current density, and annealing temperature on the capacitive properties were studied. Results show that doping Mn into TiO₂ nanotube arrays obviously enhanced their capacitive properties. The nanotube arrays prepared from Ti–Mn alloy (Mn: 7.0 wt%) exhibited the best capacitive performance and after annealed at 300 °C, the areal capacitance reached up to 1662.5 μF/cm² at a current density of 5.0 μA/cm². The retention of capacitance was 89.0% when the current density changed from 5.0 to 12.5 μA/cm² and capacitance retention was 84.6% after 2000 cycles. The factors that contributed to the superior areal capacitance of the film have also been discussed.

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1. Introduction

Titanium dioxide (TiO₂) is an important function material with good chemical stability, low cost, low toxicity, natural abundance and environmentally friendly nature [1–3]. It is currently being intensively studied for various applications in environment and energy areas, such as, photocatalysts, pollutant cleansers, lithium ion batteries, supercapacitors, gas sensors, solar energy cells, and so forth [4,5].

The materials' morphology has a great influence on their performance [6]. TiO₂ nanotube arrays fabricated by anodisation, with highly ordered structures and large specific surface areas, are of enhanced or new properties compared to other morphologies. For example, the TiO₂ nanotube arrays showed significantly higher charge-collection efficiencies and light-harvesting efficiencies than those of the nanoparticles [7]. Especially, TiO₂ nanotube arrays can be employed directly as supercapacitors because of the back-contacted nanotube layers on the substrate [4,8–13]. Modified TiO₂ nanotube arrays, with better performances, have a wider

range of applications, such as dye sensitized solar cell [14], catalyst [15], etc. In order to further improve the capacitive properties, numerous research efforts concerning modification of TiO₂ nanotube arrays have been made. Previously reported modification methods included annealing the TiO₂ nanotube arrays in Ar [10], NH₃ [16], or H₂ atmosphere [17], electrochemical hydrogenation treatment [1] and combination the nanotube arrays with other oxides [18–20].

As MnO₂ is one of the most promising pseudocapacitive materials with high theoretical specific capacitance and it is suitable for a pseudocapacitive electrode in hybrid system with other active electrode materials like TiO₂ [21]. For example, the composites of TiO₂ nanotube arrays with MnO₂ exhibited a remarkable specific capacitance [22,23].

Metal ions doping is one of the effective approaches to improve the properties of TiO₂ nanotube arrays [24–26]. Whereas, to the best of our knowledge, there are few reports on the capacitance properties of Mn-doped TiO₂ nanotube arrays. In this research, Mn-doped TiO₂ nanotube arrays were prepared by the anodisation of Ti–Mn alloys and their morphologies, structures and capacitance were discussed in detail. In addition, as a comparison, the TiO₂ nanotube arrays were also prepared and characterized.

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2. Experimental

Ti–Mn (99.9% purity, Mn: 3.0, 7.0, 10.0 wt%) alloys prepared by a power metallurgical method were cut into 20 mm × 40 mm × 2 mm foils, and then polished with metallographic abrasive paper, ultrasonically washed in twice-distilled water and ethanol before use. Anodisation was carried out using a program-controlled DC source (Dahua Coop., Beijing, China). The anodisation set-up consisted of a two-electrode configuration with a Ti–Mn alloy foil as the anodic electrode and a platinum foil (30 mm × 50 mm × 0.1 mm) as the cathodic electrode. The electrolyte used in this process was an ethylene glycol solution containing 0.25 wt% NH₄F and water. All chemical reagents were analytical grade. The anodisation experiments were conducted at 40 V for 3 h. After anodisation, the samples were rinsed in deionised water, air-dried, and then characterized. For brevity, the Mn-doped TiO₂ nanotube arrays prepared from Ti–Mn alloys with 3.0 wt% Mn, 7.0 wt% Mn and 10.0 wt% Mn were denoted by TiO₂–Mn (3%), TiO₂–Mn (7%), and TiO₂–Mn (10%), respectively. In addition, as a comparison, the TiO₂ nanotube arrays were prepared by the same method (denoted by TiO₂).

Morphologies, structures, and chemical composition of the samples were investigated using a scanning electron microscope (SEM, Hitachi, S-4800), an X-ray diffractometer (XRD, Rigaku, D/MAX-2500), and an inductively coupled plasma optical emission spectrometer (ICP-OES, Leomon, Prodigy Xp), respectively. The electrochemical properties of the samples were investigated by cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) testing using an LK2005 electrochemical analyser (Lanlika, China). The electrochemical measurements were conducted in a standard three-electrode configuration composed of a sample as the working electrode, a platinum foil as the counter-electrode, a saturated calomel electrode (SCE) as the reference electrode, and 0.5 M Na₂SO₄ as the electrolyte. The analysis of the capacitive performance of each sample was based on the geometric area of the working electrode [17,27].

3. Results and discussion

Previous studies showed that TiO₂ and ion-doped TiO₂ nanotube arrays could be prepared in ethylene glycol electrolyte [28–30]. In this work, by changing experiment conditions, the TiO₂ and Mn-doped TiO₂ nanotube arrays with similar morphologies were successfully prepared respectively and the SEM images are shown in Figs. 1 and 2, the diameter being about 110 nm and the length about 3.5 μm.

The preparation conditions of nanotube arrays were shown in Table 1, it can be seen that the preparation conditions changed along with alloy composition. When the voltage, oxidation time and NH₄F concentration was constant, the water concentration and reaction temperature decreased with the increasing manganese contents. Lower water concentration and reaction temperature resulted in lower dissolution ability of the electrolyte [29–31]. The solubility of the oxides increased with the increasing manganese contents. Therefore, only by reducing the dissolution ability of the electrolyte, nanotube arrays with similar morphology could be obtained.

ICP-OES analysis indicated that the mass ratios of Mn/(Mn + Ti) in TiO₂–Mn (3%), TiO₂–Mn (7%), and TiO₂–Mn (10%) were 2.05%, 3.02%, and 5.44%, respectively, which were significantly lower than those in the Ti–Mn alloys. The reason might be that manganese oxide was more easily to be dissolved in the electrolytes than that of titanium oxide.

To study the effect of the manganese contents on the capacitive properties, the CV curves of TiO₂ and Mn-doped TiO₂ nanotube

arrays film annealed at 300 °C with a scan rate of 10 mV/s were tested and the results are shown in Fig. 3. According to Fig. 3, it could be calculated that the areal capacitance values of TiO₂, TiO₂–Mn (3%), TiO₂–Mn (7%) and TiO₂–Mn (10%) were 141.9, 389.7, 415.8, 324.1 μF/cm², respectively. The areal capacitance of Mn-doped TiO₂ nanotube arrays was obviously higher than that of TiO₂ nanotube arrays. With the increasing manganese contents, the areal capacitance first increased and then decreased. The areal capacitance of TiO₂–Mn (7%) reached up the highest value.

Manganese oxides were promising pseudocapacitive materials with high theoretical specific capacitance. Doping manganese into TiO₂ materials could obviously enhance their capacitive properties [32,33]. The electrical conductivity of TiO₂, TiO₂–Mn (3%), TiO₂–Mn (7%) and TiO₂–Mn (10%), tested under same conditions, were 0.674, 0.631, 0.629 and 0.532 mS/cm, respectively. Apparently, doping manganese would introduce defects into oxide lattice. For TiO₂–Mn (3%) and TiO₂–Mn (7%), the doping content of manganese was relatively low. The small number of defects existed in Mn-doped TiO₂ nanotube arrays would have little effect on electrical conductivity compared with that of TiO₂. Therefore, the areal capacitance would increase with the increasing manganese content. However, for TiO₂–Mn (10%), the doping content of manganese was high, too much defects would lead to reduced electrical conductivity and decreased areal capacitance consequently.

The annealing temperature exerted a significant influence on the capacitive performance, CV curves of the TiO₂ and TiO₂–Mn (7%) samples annealed under different temperatures ranging from 100 to 500 °C are shown in Fig. 4. According to Fig. 4, it could be calculated that the areal capacitance of TiO₂ sample annealed at 100, 300, and 500 °C were 93.1, 141.9 and 26.3 μF/cm², respectively. The areal capacitance of TiO₂–Mn (7%) sample annealed at 100, 300, and 500 °C were 257.8, 415.8 and 235.3 μF/cm², respectively. The areal capacitance of Mn-doped TiO₂ was obviously higher than that of TiO₂ nanotube arrays. Both of the TiO₂–Mn (7%) and TiO₂ nanotube arrays film obtained the highest areal capacitance when annealed at 300 °C.

XRD analysis of TiO₂ and TiO₂–Mn (7%) samples annealed at 100, 300, and 500 °C were conducted and the results are shown in Fig. 5. When the samples were annealed at 100 °C, no diffraction peaks was detected, indicating that the oxides were amorphous. When the samples were annealed at 300 °C and 500 °C, the diffraction peaks of both TiO₂ and TiO₂–Mn (7%) were indexed only to anatase TiO₂ (pdf Card no. 65-5714). The intensity of the diffraction peak increased at 500 °C. At 300 °C, the calculated grain size of TiO₂ and TiO₂–Mn (7%) were 19.7 nm and 20.8 nm; at 500 °C, the grain size increased to 31.5 nm and 24.2 nm respectively.

No characteristic peaks of manganese oxide have been detected in Mn-doped TiO₂ nanotube arrays, which indicated that element manganese was doped into the crystal structure of TiO₂ because of its high dispersion and lower manganese concentration.

The influence of annealing temperature has two aspects. Along with the increase in annealing temperature, on the one hand, the conductivity of the oxides increased with the improved crystallinity and degree of structure order, thus the capacitive performance increased accordingly. On the other hand, the hydrophilicity would decrease with the decreased amount of surface hydroxyl groups [31], thus the capacitive performance decreased accordingly. The film annealed at 300 °C would be more conducive to balancing the conductivity and hydrophilicity. Therefore, the most suitable annealing temperature was 300 °C, and thus the film was annealed at 300 °C for subsequent measurements.

Fig. 6A shows the CV curves of TiO₂–Mn (7%) sample annealed

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