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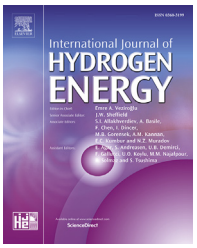

Preparation and properties of MnO_2–TiO_2 nanotube array composite electrodes using titanium foam as the current collector

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ABSTRACT

MnO_2–TiO_2 nanotube array composite electrodes were prepared through depositing MnO_2 onto TiO_2 nanotube arrays obtained by anodization of the titanium foam and the effect of morphologies of TiO_2 nanotube arrays on the performance of the electrode was investigated. Results show that the wall thickness, the tube diameter and the tightness among the nanotubes affected the performance of composite electrodes. The areal, quality and volume capacitance value of the optimized sample reached up to 436.2 mF/cm^2, 1470.8 mF/g and 5452.5 mF/cm^3, respectively, at a current density of 0.1 mA/cm^2, which were significantly higher than those of the MnO_2–TiO_2 nanotube array composite electrodes using planar titanium foil as the current collector. The capacitance retention was 85.7% after 3000 cycles. In addition, the influences of the cations (Li^+, Na^+, K^+, NH_4^+) and anions (Cl^-, Br^-, I^-, $CH3COO^-$) in the testing electrolytes on the capacitance properties were also studied in detail.

Introduction

Supercapacitors have many special features, such as rapid charging-discharging rates, long cycle life, high power density, energy saving and environmental compatibility, etc. Based on the factors including the charge storage mechanism and the type of active materials, supercapacitors can be classified as double-layer capacitors and pseudocapacitors and the latter has a higher energy density than the former [1–3].

The supercapacitor electrode, mainly composed of the current collector and active material, is one of the most important factors that directly influence its performance. MnO_2 is a promising pseudocapacitive material and has attracted a great deal of attention among many active materials for its low cost, natural abundance, wide electrochemical potential window and high theoretical capacitance value (1370 F/g) [4–6]. However, the intrinsically poor electrical conductivity and easy dissolution of MnO_2 hinder the achievement of high electrochemical performance. Combining MnO_2 with other materials (e.g. C [7–9], TiO_2 [10], Co_3O_4 [11,12], ZnO [13], Ag [14] and Fe_2O_3 [15]) is an effective way to overcome these problems.

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TiO_2 nanotube arrays with large specific surface area and highly ordered structures can be fabricated in situ by anodisation of titanium which can be directly employed as the current collector. The unique structure is conducive to the energy storage and the rapid transfer of the ions during the electrochemical process, therefore, the MnO_2–TiO_2 nanotube array composite electrodes often exhibited an excellent electrochemical performance [16–19], moreover, the anodization method could greatly simplify the manufacturing process of the electrode.

Current collectors also have a great influence on the performance of the supercapacitor. Using metal materials with large specific surface area (e.g. nickel foam [20–28], foam copper [29], three-dimensional nanostructured stainless steel [30], nickel nanocone arrays [31], nickel nanowire arrays [32], and nanoporous metals [33,34]) as the current collectors can improve the contact area between the current collector and active material, reduce the internal and interface resistance of electrode, and obviously improve the performance of electrode.

As one of the hot spots in the research of foam metals, titanium foam material has excellent mechanical properties, low density, high specific surface area, excellent corrosion resistance and biocompatibility, thus, it has been widely used in these fields such as structural materials [35,36], biology [37,38], filters, energy absorbers [39], etc. Using titanium foam as the current collector, high-capacity electrode materials can also be prepared [40,41].

However, as far as we know, titanium foam has not been reported as the current collector for MnO_2–TiO_2 nanotube array composite electrodes. In this paper, the titanium foam was firstly anodised to prepare TiO_2 nanotube arrays on the surface of titanium foam, then, MnO_2 was deposited onto TiO_2 nanotube arrays by a one-step redox precipitation method to prepare MnO_2–TiO_2 nanotube arrays composite electrodes with the titanium foam as the current collector. The

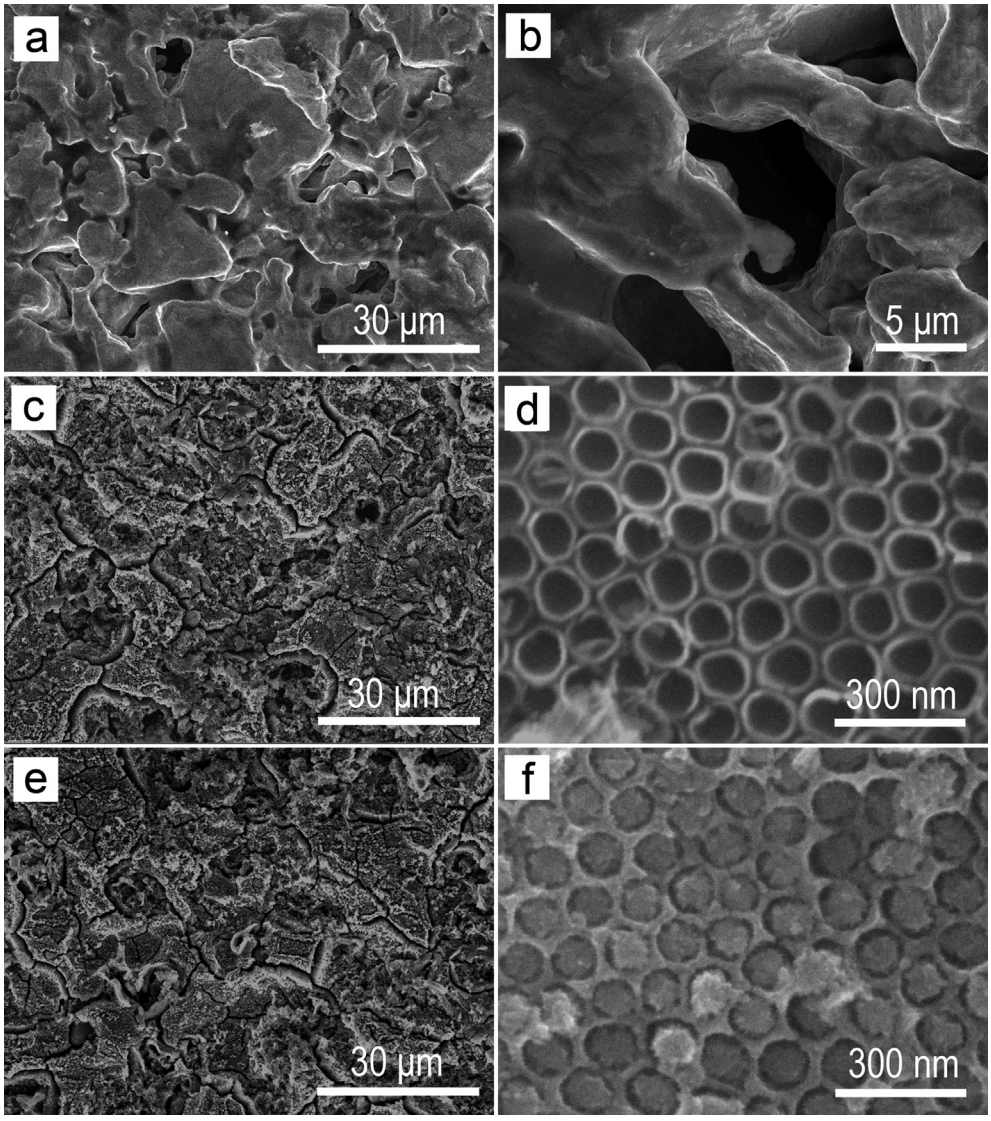

Fig. 1 – SEM images of different samples: (a and b) titanium foam at low and high magnification, (c and d) TNTA-5 at low and high magnification, (e and f) MnO_2-TNTA-5 at low and high magnification.

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