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Ceria deposited titania nanotubes for high performance supercapacitors

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ABSTRACT

The present paper reports the application of a rare earth metal oxide – titania nano tube (TNT) composite for supercapacitor applications. Highly ordered arrays of single walled titanianantubes of length approximately 4 μm were synthesised on titanium metal foil via a modified single step electrochemical anodization method. Nanostructured ceria is deposited on as prepared TNT by simply impregnating in cerous nitrate solution, followed by heat treatment. The characterizations were done by XRD and FE-SEM analysis. Supercapacitive performance is monitored using techniques such as CV, GCD and EIS. The pristine TNT itself shows promising supercapacitive performance (specific capacitance values ~ 6.82 mF/cm^2), which is enhanced significantly by coating psuedocapacitive ceria. Among different ceria deposited samples, 0.075 Ce showed the best results with specific capacitance values ~55.28 mF/cm^2 at scan rate 5 mV/s, owing to its open porous nanotubular morphology (optimal tube diameter around 20 nm) facilitating smooth charge transport and exposure of enormous amount of active material to the electrolyte, marking an enhancement of about 710% as compared to pristine TNT supercapacitors.

1. Introduction

Renewable energy production and its storage are gaining widespread attention for the last decade. Storage systems with high power density and energy density are in strong demand and supercapacitors appears to be the best candidate to meet this requirement than conventional capacitors. Even if the power density and cycle life of supercapacitors is very high compared to batteries, their energy density is comparatively low. Thus supercapacitor research mainly emphasises on increasing energy density. The performance of a supercapacitor mainly depends on the nature of active material, nature of the electrolyte and electrode – electrolyte interface. Supercapacitive performance of titania nanotubes (TNT) has been extensively studied in recent years, owing to their rapid charging-discharging properties, appreciable power/energy density, improved reversibility, long life cycle, wide operating temperature range and low cost per cycle [1,2].

Generally, TiO_2 nanotubes exhibit electrical double layer capacitance in aqueous electrolytes, in contrast to the common faradaic capacitance observed in other metal oxides [RuO_2, MnO_2, Fe_2O_3, V_2O_5, etc.]. Faradaic capacitors involve faradaic charge transfer between the electrode and electrolyte. The hindrance to the Ti^{4+} to Ti^{3+} redox reaction due to the presence of interfacial defects in natural semiconducting titania limits the faradaic contribution of capacitance [3]. There are many reports on the performance of titania nanotubes as a supercapacitor electrode. Salari and co-workers observed specific capacitance of 538 μF/cm^2 in titania nanotube array electrodes at a scan rate 100 mV/s [4]. Kim et al. reported a specific capacitance of 2.4 mF/cm^2 at 50 mV/s scan rate in the case of TNT array electrodes [5]. Anitha et al. improved the specific capacitance of vertically aligned TNT array electrodes to 5.5 mF/cm^2 at 1 mV/s scan rate by reducing the tube diameter [6]. The capacitive performance depended strongly on the length and crystallinity of the nanotubes. The nanotube electrodes showed superior performance over nanoparticle electrodes (around 4 times). The hollow tube morphology allows smooth charge transfer and regular pore size improves interfacial ion movement. The large internal surface area of nanotubes also contributes towards the high specific capacitance. Various techniques like annealing [3,7,8], plasma treatment [9], electrochemical treatment [10–12], nitridation [13], doping/composite formation with other metal/non-metal/metal-oxide, etc. have been attempted [14–21] to improve the capacitance of TNT array electrodes. Transition metal oxides have promising potential as a super capacitor electrode material by virtue of its high faradaic capacitance

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