



Fabrication and characterization of titania nanotube/cobalt sulfide supercapacitor electrode in various electrolytes



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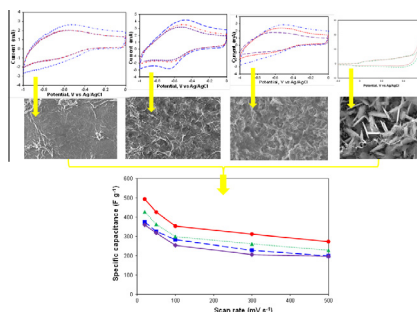
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HIGHLIGHTS

- Synthesis of titania nanotube (T-NT)/cobalt sulfide (CoS) composite electrode by simple electrodeposition method.
- Evaluation of supercapacitance behavior of the composite electrode in various electrolyte: KOH, KCl, Na₂SO₃, Na₂SO₄.
- Highest specific capacitance (~400 F g⁻¹) at galvanostatic charge-discharge current density of 5 mA cm⁻².
- More than 80% capacitance retention even after 1000 cycles of continuous charge-discharge in all electrolytes.

GRAPHICAL ABSTRACT



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ABSTRACT

A facile electrochemical technique has been employed to fabricate titania nanotube (T-NT)/cobalt sulfide (CoS) composite electrode for high performance supercapacitor application. The morphology and phase evaluation of the electrode were analyzed using scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) techniques. The pseudocapacitance behavior of the T-NT/CoS composite electrode has been evaluated in four different aqueous electrolytes: KOH, KCl, Na₂SO₄ and Na₂SO₃. Cyclic voltammetric studies in aqueous KOH electrolyte indicated that a very high specific capacitance (370 F g⁻¹) can be achieved in this electrolyte together with excellent cycle stability even after 300 consecutive CV cycles. Further, the capacitance behavior of the T-NT/CoS electrode in KCl, Na₂SO₄, and Na₂SO₃ electrolytes exhibited a mixture of electric double layer (EDL) and redox-induced supercapacitance as displayed in the cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopic (EIS) experiments. It was also observed that the capacitance behavior of the composite material is not greatly dependent on the electrolyte used except for Na₂SO₃ electrolyte where the capacitance value attained is relatively higher than the other electrolytes i.e. 400 F g⁻¹ at a fairly high charge-discharge current density of 5 mA cm⁻². Galvanostatic charge-discharge experiments conducted on the composite electrode suggested stable capacitance behavior with excellent capacitance retention (~80%) even after 1000 continuous charge-discharge cycles in KCl, Na₂SO₄, and Na₂SO₃ electrolytes.

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1. Introduction

Electronic advancements continue to press the need for energy storing devices with high power and high specific energy density [1]. Electrochemical capacitors (EC) are being developed to satisfy this demand as they not only possess higher energy density but also demonstrate longer cycle life compared to batteries and dielectric capacitors [1,2]. EC can be categorized into two primary types by their charge storing mechanism: electric double-layer (EDL) and fast Faradic redox type (pseudocapacitors or supercapacitors) capacitors. In the EDL capacitor, electric energy is stored through the non-faradic charge separation at the electrode/electrolyte interface [2]. EDL based capacitors have been fabricated using carbon, graphene and aerogel, however, they all display relatively low energy densities and poor cycle stability [2,3]. On the other hand, in case of pseudocapacitors, which are based on Faradic mechanism, redox reactions are largely responsible for the energy storage [3,4]. Generally, transition metal oxides (e.g. RuO_2 , NiO , Co_2O_3) have received immense attention for preparation of redox oxide based ECs [4,5]. The presence of multiple valence states in the transition metals can lead to efficient redox-based reaction with the electrolyte, thereby enhancing the specific capacitance in this class of material. Supercapacitors synthesized using hydrous ruthenium oxide have been reported to show high power and energy density coupled with high cycle stability; however, scarcity and higher cost associated with ruthenium prohibits its application in mass/commercial applications [6]. Several other transition metal oxides have been investigated as more economical alternative to ruthenium oxide including manganese oxide [7], nickel oxide [8], cobalt oxide [9,10], molybdenum oxide [11], vanadium oxide [12], and iron oxide [13,14].

Transition metal sulfide based ECs, specifically cobalt and nickel sulfide supercapacitors [15–26] also exhibit remarkably high specific capacitance. Specifically, cobalt and nickel sulfide supercapacitors are studied extensively for this purpose [15–23]. For example, CoS nanowires synthesized through biomolecule-assisted method produced a specific capacitance of 508 F g^{-1} in 3 M KOH electrolyte with high specific energy, good discharge rate and excellent stability [17]. Similarly, nickel sulfide composite supercapacitors, such as nickel sulfide/Ni-foam as well as nickel sulfide/graphite electrodes, also demonstrated remarkable capacitance properties ($>500 \text{ F g}^{-1}$) [25,26]. It has been observed in these studies that the presence of a porous substrate (graphite, Ni-foam, etc.) can produce remarkable enhancement in the supercapacitance behavior in many composite electrodes [25,26]. The porous substrate facilitates easy migration/diffusion of electrolytes into the electrode during the electrochemical processes, thereby increasing the reactivity between the electrode/electrolyte systems.

In line with the above discussions, the focus of the present study is to evaluate the supercapacitance behavior of titanium nanotube (T-NT)/CoS composite electrode fabricated by electrodeposition method. T-NT substrate demonstrates several advantages – easy fabrication, high and uniform surface area coupled with excellent chemical stability, and non-toxic in nature [27–32]. The presence of porous substrate like T-NT has been reported to show remarkable enhancement in the supercapacitance behavior in many composite electrode materials [3,33]. The enhancement in capacitance was found to be due to the fact that highly ordered architecture and high surface area of the T-NT substrate facilitated enhanced reaction sites as well as improved charge and mass transfer through the tubular tunnels, thus increasing the capacitance of the composite structure. Here, the capacitance properties of the T-NT/CoS composite electrode were studied in the following electrolytes: KOH, Na_2SO_4 , Na_2SO_3 and KCl. It is to be noted that the capacitance properties of transition metal sulfide supercapacitors have only been evaluated in KOH electrolyte so far. An early

attempt to study the pseudocapacitance of CoS in Na_2SO_4 electrolyte rendered fruitless as the authors reported very less specific capacitance in this electrolyte [20]. There is a need to explore the applicability of sulfide based supercapacitors in other electrolytes beside KOH. Therefore, we have studied the capacitance of the composite electrode in various other electrolytes using CV, galvanostatic charge–discharge and EIS techniques. These experiments suggested that the composite electrode can attain very high supercapacitance properties in all of the above mentioned electrolytes. The capacitance of the electrode was attributed to a mixed type behavior (EDL + redox) in these electrolytes. Very high specific capacitance and good stability of the electrode material indicated the feasibility of its applicability as supercapacitor in all electrolytes studied here.

2. Experimental studies

2.1. T-NT substrate fabrication

Titanium foil (99.9% purity) of 0.1 mm thickness was cut into $10 \times 15 \text{ mm}$ coupons. The coupons were roughly polished for 2 min. (with 600 grit SiC emery paper) and ultrasonically cleaned in a solution of acetone and isopropyl alcohol (1:1) for 10 min. Subsequently, the coupons were anodized potentiostatically in an

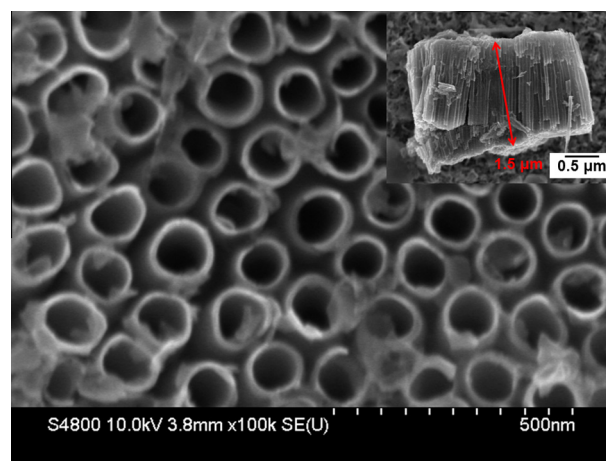


Fig. 1. The top view of the T-NT arrays formed after anodization at 40 V for 1 h, the inset shows the cross-sectional view.

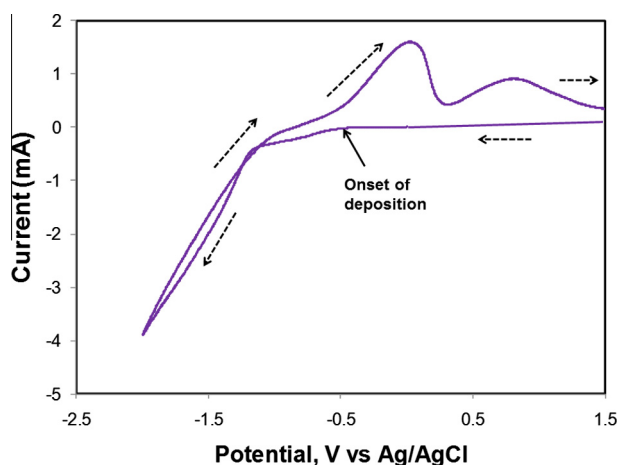


Fig. 2. Cyclic voltammetry of the T-NT substrate in aqueous solution of 10 mM cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) and 0.5 M thiourea ($(\text{NH}_2)_2\text{CS}$) at a scan rate of 20 mV s^{-1} .

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