Fabrication and Characterization of Titania Nanotube/Cobalt Sulfide Supercapacitor Electrode in Various Electrolytes

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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

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except for Na_2SO_3 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 ($\sim 80\%$) even after 1000 cycles of continuous charge-discharge cycles in KCl , Na_2SO_4 , and Na_2SO_3 electrolytes.

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 3M 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 in to 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, Na₂SO₄, Na₂SO₃ 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 Na₂SO₄ 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 (ELD + 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 mm x 15 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 ten minutes. Subsequently, the coupons were anodized potentiostatically in an electrolyte consisted of ethylene glycol with 0.5 wt % ammonium fluoride and 10% H₂O. The anodization was carried out at a constant voltage of 40 V for 1 hour at room temperature.

Annealing was performed in a muffle furnace in air at 500°C. The temperature was raised at a rate of 1.5°C/min to the set point and maintained for 2 hours. After holding the anodized sample at the elevated temperature, the samples were allowed to cool within the furnace by natural convection.

2.2 Electrochemical Deposition of CoS

Electrochemical deposition of cobalt sulfide on T-NT surface was carried out in an aqueous solution of 10 mM cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) and 0.5 M thiourea ($(\text{NH}_2)_2\text{CS}$). A 3-electrode based electrochemical workstation (Gamry Reference 600) with annealed T-NT coupon as working electrode, platinum coil as counter electrode and a saturated Ag/AgCl electrode as reference constituted the electrochemical deposition setup. Electronic noise was minimized by isolating the system within a Faraday cage. Potentiostatic depositions were carried out at two different potentials of -0.5 V to -1.5 V. CV deposition was performed by cyclically varying the potential between -0.5 V to -1.5 V for 10 cycles at a scan rate of 20 mV s^{-1} . The deposition bath was constantly stirred at 170 rpm during experiments. Electrochemical deposition was performed at standard conditions.

2.3 Characterization

Examination of the surface and cross sectional morphology of T-NT and T-NT/CoS samples was performed using a field emission scanning electron microscope (FE-SEM, Hitachi S-4800). The XRD analysis of the samples was carried out using SIEMENS D5000 diffractometer with copper K- α radiation. The diffraction tests were done by θ to θ scan from 20° to 80°. X-ray photoelectron spectroscopy (XPS) study was carried out using monochromatic Al K α source (PE = 1600 eV) on a Kratos Axis Ultra DLD instrument, with a 300 -700 μm spot size. Dwell time was set to 200 ms with three sweeps and a step size of 1 eV (0.1 eV for regional scans).The

weight of the deposited CoS was determined using a Satorius microbalance with the accuracy of 0.01 mg. The mass of the deposited CoS was determined as follows: The initial weight (m_1) of the T-NT was measured after annealing. Then, after deposition of CoS on to the T-NT substrate, the composite electrode was dried at 110°C for 2 hours and the weight (m_2) of the composite electrode was measured. By subtracting m_1 from m_2 , the weight of the deposited CoS was obtained.

2.4 Electrochemical Measurements

The electrochemical properties of the T-NT/CoS samples were evaluated by conducting cyclic voltammetry (CV) and galvanostatic charge-discharge experiments using a potentiostat (Gamry Reference 600), connected to a 3-electrode setup consisting of the T-NT/CoS sample as the working electrode, platinum coil as the counter electrode, and saturated Ag/AgCl electrode as a reference electrode. CV tests were performed in 2M KOH, 2M KCl, 1M Na₂SO₃ and 1M Na₂SO₄ electrolytes. Galvanostatic charge/discharge tests were performed in 2 M KCl, 1M Na₂SO₃ and 1M Na₂SO₄ electrolytes. Potentiostatic EIS tests were carried out using a Parstat 4000 (Applied Princeton Research) at -0.5 V (vs reference) with perturbation amplitude of 10 mV in the frequency range of 100 Hz to 25 mHz. Prior to the EIS measurements, the electrodes were equilibrated with the electrolyte for 30 minutes.

3. Results and Discussion

3.1 Morphology and Phase of T-NT/CoS:

Figure 1 shows the self-organized and vertically aligned T-NT array formed on the titanium foil after anodization at 40V for 1 hr. The nanotubes were found to have an average diameter of ~ 90 nm, length of ~ 1.5 μ m (inset Fig. 1) and wall thicknesses in the range of 15-20 nm.

Prior to deposition, CV analysis was carried out in an aqueous solution of 10 mM cobalt chloride and 0.5 M thiourea to establish suitable deposition parameters. The CV profile was recorded at 20 mV s⁻¹ scan rate between +1.5 to -2.0 V vs Ag/AgCl reference electrode as shown in Figure 2. From the plot, the deposition of the cobalt sulfide phase appeared to start at a potential close to -0.5V, while the deposition might as well continue up to -2.0 V of the reference electrode.

The following reactions could be attributed for the deposition process [34]:

Based on the CV analysis, we have carried out both potentiostatic and cyclic voltametric deposition to see the effect of the deposition parameters on the morphology of the CoS phase. Generally, it has been emphasized that relatively more porous structure can be achieved through CV deposition compared to the potentiostatic and potentiodynamic deposition processes [35]. To investigate this, the potentiostatic depositions were carried out at -0.5 V and -1.5 V, and the CV deposition was conducted by cyclically varying the potentials between these two potential limits. The deposition time was kept the same in all deposition conditions (16 min).

Figure 3 shows the morphology of the deposited CoS layer on T-NT substrate under various deposition conditions. The CoS layer appeared to non-uniform after deposition at -0.5 V (Fig. 3a) may be due to the fact that this potential is close to the onset potential for deposition as observed in the prior CV study (Fig. 2). On the other hand, when deposition was performed at -1.5V, the sulfide layer appeared to be very dense (Fig. 3b) in comparison to the one observed at -

0.5V. However, after the CV deposition, the layer appeared to be much uniform than that obtained at -0.5V and relatively more porous compared to the one achieved after deposition at -1.5V (Fig 3c). Therefore, further analysis and electrochemical tests were performed on the sample obtained through the CV deposition technique and for more clarity, this sample will be referred to as “T-NT/CoS electrode” in further discussions. It is to be noted that the CoS phase did not penetrate through the titania nanotubes during the deposition process. For example after deposition at -0.5V, the inside of the nanotube pores appeared to be devoid of any CoS phase (Fig 3a). However, deposition at -1.5V and the CV deposition resulted in formation of CoS nanoparticles decorating the rims of the nanotubes as shown in Figure 3(d&e). Notice that still there is no penetration of CoS particles in the pores at these deposition conditions. The weight of the cobalt sulfide deposit in the T-NT/CoS electrode was found to be approximately 0.15 mg cm^{-2} .

The XRD profile obtained for the T-NT/CoS electrode is shown in Figure 4. The peaks from the (220) and (330) planes of the CoS phase thus indicate the formation of crystalline phase of the deposited sulfide. Also these peaks reveal that the CoS phase is hexagonal in nature consistent with previous reported studies (JCPDS no. 19-366) [17, 18]. Please note that some of the peaks from the anatase phase of the T-NT as well as Ti-substrate can also be observed in the XRD profile. Further, the oxidation states of Co and S in the deposited sulfide phase were investigated by conducting XPS analysis on the T-NT/CoS electrode. High resolution XPS spectra of Co 2p, and S 2p peaks are presented in Figure 5(a&b). The Co 2p spectrum, shown in Figure 5a, contains a main peak located at a binding energy value of 779.8eV and a shake-up feature at higher binding energy. These peaks can be assigned to Co^{2+} of CoS phase as supported by the literature [36-39]. Further, the Co-spectrum can be de-convoluted into couple of more constituent components corresponding to the following chemical states: CoO and Co(OH)_2 . The presence of

CoO is also attributed due to the presence of signal at 780 eV. The $2p_{3/2}$ peak observed at 786.1 eV can be attributed to a shake-up satellite of CoO [40]. It has been suggested in many studies that electrodeposition of transition metal based oxide or sulfide phases often results in co-existence of many of these species (CoO, Co(OH)_2 , Co, CoOOH etc) in the deposited layer [41, 42]. Figure 5b shows that the binding energy value of S 2p is around 162 eV, indicating that most of the S species exist as S^{2-} . Therefore, the XPS analysis indicated the deposited layer to be consisted of mostly CoS phase.

3.2 Pseudocapacitance of T-NT/CoS in KOH Electrolyte:

The supercapacitance behavior of the T-NT/CoS electrode was first evaluated using cyclic voltammetric studies in 2M KOH electrolyte. The CV profiles, recorded at various scan rates (20 to 500 mVs^{-1}) within a potential window of -0.2 V to 0.6 V are presented in Figure 6a. With increase in scan rate, the area under CV curve increases. This is concomitant with the increase in the current response in the CV profiles with increase in scan rate. Further, the shape of the CV curves did not display the conventional electric double-layer capacitance behavior as these profiles deviated from the ideal rectangular shape. In these plots, indications of redox processes are evident, suggesting that the capacitance mainly resulted from the redox reactions between the electrode and the electrolyte. These redox peaks are rather broad and shallow. However, at a very slow scan rate (1 mV s^{-1}), the redox peaks became very evident (Inset of Fig. 6a). It was suggested [16] that the redox peak potentials of CoS are very close to those of Co(OH)_2 and the electron transfer process of CoS in alkaline media should take place between different valence states of cobalt, such as Co^{2+} , Co^{3+} and Co^{4+} . Further, both sulfur and oxygen belong to the same group. In this case also, anodic peaks, marked as Oxidation 1 and Oxidation 2 in inset of Figure 6a, are believed to be because of the oxidation of CoS to CoSOH and CoSOH to CoSO ,

respectively, as argued previously [16, 20]. The cathodic peaks (Reduction 1 and Reduction 2, inset of Fig. 6a) are assumed to be due to the reverse processes occurring at the CoS electrode as shown in the reactions below [16, 20],

The anodic-cathodic reverse processes are the characteristic signatures of the pseudo capacitance behavior of CoS electrode as observed in many other research work [16, 20]. Further, the overall shape of the CV curve did not change with increase in the scan rate suggesting a good capacitance behavior of the electrode material.

Based on the CV results, the specific capacitance (C) of the T-NT/CoS electrode was calculated as the function of the scan rate using Eqn. 7 (shown below) and presented in Figure 6b.

$$C = Q/\Delta Vm \quad (7)$$

Where Q = half of the total charge from the integrated CV area, ΔV =Voltage window, m = mass of CoS deposit.

Usually, reduction in specific capacitance is observed at higher scan rates [3], a normal trend associated with the higher resistance and circuitous diffusion tracks of the porous electrode material. At a lower scan rates, the entire electrode material (both outer and inner pore surfaces) is utilized for charge migration, while at higher scan rates only outer regions of the electrode can be accessed by the electrolyte. Therefore, as shown in Figure 6b, the specific capacitance of the composite electrode decreased by 45% at the scan rate of 500 mV s^{-1} compared to the value at 20 mV s^{-1} .

Repetitive CV experiments were conducted on the composite electrode a scan rate of 300 mV s^{-1} for up to a total of 300 cycles. The comparative CV profiles after 1st and 300th cycles are shown in Figure 6c. The CV profiles appeared nearly the same with remarkable shape and area retention suggesting that the depletion of capacitance was insignificant even after a large number of CV cycles. Therefore, it is a clear demonstration of the excellent cyclic stability and superior capacitance behavior of the electrode material.

The surface morphology of the T-NT/CoS electrode was analyzed after undergoing 300 cycles of CV in the KOH electrolyte. As shown in Figure 7, the morphology of the CoS deposit underwent drastic change from a porous layer (as observed in the as-deposited condition, Fig. 3c) to a platelet like morphology after the CV cycles (Fig. 7). The inset in Figure 7 showed that the thickness of the platelet was about 80 nm. The XPS data for the Co 2p, and S 2p spectra were also obtained for the electrode after the repetitive CV cycling and presented in Figure S1 (Supp. Info.). The presence of peaks at 779.8 eV and a shake-up feature at higher binding energies for Co^{2+} and peak at around 162 eV for S^{2-} are indicative of the presence of CoS phase. These peaks and their positions are similar to that of the as deposited condition (Fig. 5) suggesting that although the shape/morphology of the sulfide phase changed, the crystal phase remained unchanged after the CV experiments.

3.3 Pseudocapacitance of T-NT/CoS in KCl, Na_2SO_4 and Na_2SO_3 Electrolytes:

The supercapacitance behavior of the T-NT/CoS electrode has also been studied in three other electrolytes: 1M Na_2SO_4 , 1M Na_2SO_3 and 2M KCl. The CV experiments were performed in the same potential window of -1.0 to 0 V in all the above electrolytes. The resultant CV profiles recorded at various scan rates of 20-500 mV s^{-1} are presented in Figure 8(a-c). Irrespective of the

electrolyte, it can clearly be observed from these profiles that the capacitive nature of the T-NT/CoS electrode is a mixture of both EDL as well as pseudo-behavior. The curves appeared to have indications of cathodic and anodic redox peaks suggesting the influence of pseudo nature in the overall capacitance behavior of the electrode (the inset figures shows the CV profiles obtained at 1 mV s^{-1} - demonstrating clearly the redox-humps). It is worth noting here that CV studies of many cobalt sulfide supercapacitor electrodes demonstrated rather broad redox peaks [17, 20, 43-45]. Although the specific reasons for such behavior has not been communicated yet, one possibility could be the co-existence of various phase in the deposit as observed in the XPS analysis (Fig 5a). Nevertheless, in all electrolytes, the cathodic peaks were observed between -0.8 to -0.6 V, while the anodic peaks were present between -0.6 to -0.4V. There was an increase in current values in the CV curves with increase in scan rate. Also, the sharp change in current at each terminal potential of the CV profile is also concomitant with the pseudo capacitance behavior of electrode material. Further, the shape of the CV curves did not change with increase in the scan rate in all electrolytes demonstrating an excellent pseudocapacitive response of the electrode material. A brief comparison of shape/size of CV profiles (Fig. 8d) indicated that they are rather similar for the cases of Na_2SO_4 and KCl electrolytes; however a slight variation was observed in the case of Na_2SO_3 electrolyte. For instance, the area under the CV curves was slightly smaller in the former electrolytes compared to the later one (Fig. 8a). Also the redox peaks in the Na_2SO_3 electrolyte were relatively sharper. The maxima of the redox peaks are observed around -0.7 V in the Na_2SO_3 electrolyte. Therefore, it appears that the specific capacitance of the electrode in Na_2SO_3 electrolyte was relatively higher. In order to demonstrate the enhancement in capacitance of the T-NT/CoS electrode due to the presence of the porous T-NT substrate along with the electro-active CoS phase, CV experiments were also carried out

using Ti/CoS electrode as well as bare T-NT electrode (no CoS phase). The comparative CV studies, presented in Figure S2 (Supporting Information), demonstrates clearly the enhancement due to the presence of the T-NT substrate in the T-NT/CoS electrode.

Figure 9a shows the variations in anodic peak current values from the CV curves (Fig. 8) obtained in these electrolytes plotted as the function of the scan rate. The anodic current values demonstrated linear relationship in all electrolytes corroborating the occurrence of surface redox reactions and the pseudocapacitance nature of CoS electrode [46]. The CV profiles also show that the change in peak current positions is rather small with increase in scan rates. The linear relationship of peak current with scan rate as well as small shifts in peak potentials suggested good rate capabilities and excellent reversibility of the electrode in these electrolytes [46].

Figure 9b shows the specific capacitance (calculated using Eqn. 7) of the T-NT/CoS electrode at various scan rates obtained in these electrolytes. The figure shows decrease in the specific capacitance with increase in scan rate. The decreasing trend of capacitance in the case of electrochemical capacitor is very common and the reason for such has been discussed above. In short, it can be attributed to the non-accessible inner active sites in the T-NT/CoS electrode by the electrolytic ions at higher scan rate due to diffusion limitations. Therefore, a complete redox transition is not achieved at higher scan rate, leading to a decrease in the specific capacitance. However, the specific capacitance obtained in the Na_2SO_3 electrolyte was highest among the three electrolytes, while it was least in the Na_2SO_4 electrolyte. For example, there was nearly 30% increase in specific capacitance in Na_2SO_3 electrolyte compared to that of Na_2SO_4 at the scan rate of 20 mV s^{-1} (Fig. 9b).

The electrochemical capacitance of the T-NT/CoS electrode is appeared to be more dependent on the type of anions (SO_3^{2-} , SO_4^{2-} , Cl^-) present in the electrolyte compared to the cations (K^+ , Na^+ etc). Similar behavior of anion-dependent supecapacitance properties has been also observed in case of magnetite/carbon-black composite electrode [47]. In their study, they have witnessed that the specific capacitance of the electrode was highest in the Na_2SO_3 compared to Na_2SO_4 and NaCl electrolytes partly due to enhanced redox activities between the electrode and the SO_3^{2-} species of the former electrolyte. They explained their findings based on the rest potentials and the anion concentrations in the electrolyte— for example, the enhanced pseudo-behavior in the Na_2SO_3 electrolyte was due to stronger dependence of rest potentials on the concentration of anions in the solution. Similar argument may also prevail in this case as the dependence of the specific capacitance of the T-NT/CoS electrode appeared to have followed similar pattern as observed in their work.

The stability of the composite electrode in different electrolytes have been evaluated by employing consecutive CV up to 300 cycles at a scan rate of 100 mV s^{-1} . Figure 10(a-c) shows the comparative CV profiles of T-NT/CoS electrode in Na_2SO_4 , Na_2SO_3 and KCl electrolytes after 1st, 100th and 300th CV cycles. In all electrolytes, the redox peaks were clearly observed even after 300th CV cycle indicating sustained redox-based reactions between the electrode/electrolyte systems. The CV plots indicate decrease in specific capacitance of the T-NT/CoS electrode with increase in number of CV cycles. The decrease in current response with number of cycles is slightly higher in Na_2SO_4 electrolyte, compared to Na_2SO_3 and KCl electrolytes. Up to 100th CV cycle, there has been some decrease in current response in all electrolytes; however the current level remained unchanged afterwards. The CV profiles after the 100th and the 300th cycles appeared to be nearly the same in all electrolytes. Therefore, it can be

observed that substantial amount of capacitance was retained even after large number of CV cycles in all electrolytes.

To study the integrity of the T-NT/CoS electrode after undergoing consecutive CV cycles, the microstructural and compositional analysis of the electrode was carried out by SEM and XPS analysis, respectively. Figure 11 shows the SEM images of the electrode after the repetitive CV experiments. The micrographs suggested that the morphological aspects of the CoS deposit did not change to any significant degree after the repetitive CV cycles. In fact, the CoS phase deposit appeared to be foamy and porous similar to that observed in the as-deposited condition (Fig. 2a). The compositional analysis also suggested remarkable stability of the electrode after the CV studies. Figure S3 (Supp. Info.) shows the XPS spectra for Co 2p, and S 2p obtained for the electrode after the repetitive CV in various electrolytes. The positions of the peaks for Co 2p, and S 2p suggested that the phase composition of the sulfide phase was unaltered in comparison to Figure 3, suggesting excellent stability of the electrode material.

The galvanostatic charge-discharge behavior of T-NT/CoS electrode was evaluated in the Na_2SO_4 , Na_2SO_3 and KCl electrolytes at constant current densities of 1, 3 and 5 mA cm^{-2} in the voltage window of 0 to -1 V. Figure 12 (a-c) shows the charge-discharge profiles for the electrode in these electrolytes. The profiles, in terms of voltage-time (V-t), appeared to be non-symmetric. However, in all the electrolytes, the shape of the charge-discharge profiles appears to be similar. Specially, the discharge curves consisted of two parts: (i) a steep voltage drop due to the internal resistance and (ii) a relatively curved part with gradual decrease in voltage due to the change in energy within the capacitor. Furthermore, charge-discharge time decreased with

increase in current density. Using the following relationship, the specific capacitance of the electrode materials was calculated as:

$$C = It/\Delta Vm \quad (8)$$

where, I is the charge-discharge current density, t is the discharge time from the $V-t$ plots, ΔV is the voltage window, m is the mass of the electrode. The calculated specific capacitance of the electrodes in various electrolytes were plotted as the function of the charge-discharge current density and shown in of Figure 12d .The specific capacitance decreased by about 20-27% in all electrolytes upon increase in charge-discharge current density. Specifically, the capacitance of the electrode in the Na_2SO_3 electrolyte decreased from 487 F g^{-1} to 389 F g^{-1} upon increase in current density from 1 to 5 mA cm^{-2} . Similar trend was also observed in the other two electrolytes. These results are in strong agreement with the CV analysis in these electrolytes (Fig. 8).

The stability of the electrode was also evaluated by imposing continuous charge-discharge cycles up to 1000 cycles in the three electrolytes at a charge-discharge current density of 5 mA cm^{-2} . Figure 13a shows the variations in specific capacitance of the electrode as the function of cycle number in various electrolytes. The inset figure shows the representative charge-discharge curves ($V-t$) for the electrode during the beginning of the charge-discharge experiment in various electrolytes. Consistent with the CV results (Fig. 10), the capacitance behavior of the electrode was found to be very stable even after a large number of charge-discharge cycles. The specific capacitance was highest in the Na_2SO_3 electrolyte among all electrolytes investigated in this study. On the other hand, only about 20% of the capacitance faded after the 1000 cycle irrespective of the electrolyte used. This decrease in capacitance could be attributed to the small

dissolution of the electroactive material (CoS) in to the electrolytes [25]. Figure 13 (b-d) shows the charge-discharge cycles of the electrode after the end of 1000 cycles in various electrolytes.

A brief comparison of the capacitance of the T-NT/CoS electrode can be made with some of the literature reported values for CoS electrodes. Justin *et al* [16] reported that their porous sphere-like CoS electrode demonstrated low charge-transfer resistance and good reversibility with a specific capacitance of 363 F g^{-1} . Wang and co-workers [18] also observed high specific capacitance (555 F g^{-1}) in their flower-liked nanostructured $\text{CoS}_{1.097}$ electrode along with excellent cycle stability. In another study, supercapacitor electrode comprising of hollow Co_3S_4 nanospheres on reduced graphene oxide substrate showed a specific capacitance of 521 F g^{-1} with very high Columbic efficiency [19]. Tao *et al.* [20] reported capacitance behavior of micro-sized CoS_x using 6M KOH electrolyte and obtained a high value of specific capacitance (475 F g^{-1}). In comparison to these studies, it is evident that that overall capacitance property of the T-NT/CoS electrode observed in this study is at par with many of the earlier literature reported values. Hence, the feasibility of using T-NT/CoS composite electrode in these electrolytes is quite viable as demonstrated successfully through this study.

3.4 EIS study of T-NT/CoS electrode:

Figure 14 shows the Nyquist plot for the T-NT/CoS electrode in various electrolytes. All EIS profiles show capacitance arc/depressed semicircle at high frequency domain and a linear curve at lower frequencies as observed in these plots. The semicircular profiles indicate that irrespective of the electrolytes, there is some amount of interfacial charge transfer resistance between the electrode/electrolyte systems. This behavior has also been observed in the case of CoS electrode in earlier studies [16, 17]. Further, it has also been suggested that a vertical line in the Nyquist plot leaning towards the imaginary axis suggests EDL type capacitance behavior

[16,17,42]. However, in our case, the EIS profiles (Fig. 14a&b) showed considerable deviations from the imaginary axis in all electrolytes. This represents the ionic diffusion into the pores of the electrode suggesting the capacitive nature of the electrode in these electrolytes. These observations are also supported well by the CV and charge-discharge results discussed in the previous sections. Therefore, higher conductivity and reduced charge transfer resistance observed in the EIS studies support the higher capacitive performance obtained in the T-NT/CoS composite electrode.

4. Conclusion

In this study, we have demonstrated a simple and economical electrodeposition process (potentiostatic and CV depositions) to synthesize titania nanotubes (T-NT)/CoS composite material for supercapacitance applications. The morphology and phases of CoS deposit were analyzed using various characterization tools, such as SEM, XRD, and XPS. The electrochemical tests on the composite materials were carried out in four different electrolytes: 2M KOH, 1M Na₂SO₄, 1M Na₂SO₃ and 2M KCl using a three electrode experimental set-up. More emphasis was given on the supercapacitance studies in the 1M Na₂SO₄, 1M Na₂SO₃ and 2M KCl electrolytes as transition metal sulfide based supercapacitors have never been studied in these electrolytes. The CV analysis indicated that the capacitance of the composite electrode emanated partly from the fast and reversible faradic-redox reactions occurring in the electrode/electrolyte interface in all electrolytes. From the CV studies, the highest specific capacitance values achieved were about 493, 427, 374, and 360 F g⁻¹ for the Na₂SO₃, KCl, Na₂SO₄, and KOH electrolytes, respectively. The galvanostatic charge-discharge experiments were also carried out on the composite electrode in the 1M Na₂SO₄, 1M Na₂SO₃ and 2M KCl electrolytes. The results

in fact reinforced the findings of the CV analysis, suggesting that the specific capacitance of the composite materials can reach very high value in all electrolytes. The galvanostatic charge-discharge experiments also resulted in the maximum specific capacitance in the range of 450-500 F g^{-1} for all electrolytes. This high capacitance for the electrode was attributed to the combined effect of the redox reactions associated with the CoS in the electrolytes as well as the high surface area associated with the nanotubular nature of the substrate material. The stability of the composite material was also evaluated by employing continuous charge-discharge cycle up to 1000 cycles. A very high percentage (~80%) of capacitance retention was achieved in the composite material even after successive charge-discharge cycles. Therefore, this study successfully demonstrated the feasibility of T-NT/CoS electrode to be used as high performance supercapacitor material in various electrolytes.

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

Figure 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} .

Figure 3: Morphology of the CoS deposit on T-NT obtained after potentiostatic deposition at (a) -0.5 V, (b) -1.5 V, and (c) CV deposition (10 cycles between -0.5 V and -1.5 V). The underneath T-NT substrate showing CoS nanoparticles decorating the rim of the tubes after deposition (d) CV (10 cycles between -0.5 V and -1.5 V), (e) -1.5V

Figure 4: XRD profile for the T-NT/CoS electrode prepared by CV deposition.

Figure 5: (a) Co 2p XPS spectra of the T-NT/CoS electrode, (b) S 2p XPS spectra obtained in the T-NT/CoS electrode

Figure 6: (a) CV profiles of the T-NT/CoS electrode in 2M KOH electrolyte at various scan rates (inset shows the profile at 1 mV s^{-1}) (b) Variations in the specific capacitance of the T-NT/CoS electrode as the function of scan rate. (c) The 1st and 300th CV profiles recorded at a scan rate of 300 mV s^{-1} for the composite electrode. Excellent stability of the capacitance behavior can be observed from the CV profiles.

Figure 7: Morphology of the T-NT/CoS electrode after 300 numbers of repetitive CV cycles in 2M KOH electrolyte. The CoS deposit changed to a plate-like morphology with approximate plate thickness of 80 nm (inset figure).

Figure 8: CV profiles of the T-NT/CoS electrode in (a) 1M Na₂SO₄, (b) 1M Na₂SO₃, and (c) 2M KCl electrolytes at various scan rates (insets show the profile at 1 mV s⁻¹). (d) Comparison of CV profiles in these electrolytes at 20 mV s⁻¹.

Figure 9: (a) Anodic current peaks from the CV profiles in Figure 8(a-c) obtained for the T-NT/CoS electrode in 1M Na₂SO₄, 1M Na₂SO₃, and 2M KCl electrolytes as the function of scan rate. (b) Variations in the specific capacitance of the T-NT/CoS electrode in 1M Na₂SO₄, 1M Na₂SO₃, and 2M KCl electrolytes as the function of scan rate.

Figure 10: Comparisons of CV profiles (1st, 100th, and 300th cycles) of the T-NT/CoS electrode in (a) 1M Na₂SO₄, (b) 1M Na₂SO₃, and (c) 2M KCl electrolytes at a scan rate of 100 mV s⁻¹.

Figure 11: Morphology of the T-NT/CoS electrode after 300 cycles of repetitive CV cycles in (a) 1M Na₂SO₄, (b) 1M Na₂SO₃, and (c) 2M KCl electrolytes at a scan rate of 100 mV s⁻¹.

Figure 12: Galvanostatic charge-discharge (V-t) profiles obtained at a current densities of 1, 3, and 5 mA cm⁻² for the T-NT/CoS electrode in (a) 1M Na₂SO₄, (b) 1M Na₂SO₃, and (c) 2M KCl electrolytes. (d) Variations in the specific capacitance of the T-NT/CoS electrode in 1M Na₂SO₄, 1M Na₂SO₃, and 2M KCl electrolytes as the function of charge-discharge current density.

Figure 13: (a) The variations in the specific capacitance of the T-NT/CoS electrode obtained at a charge discharge current density of 5 mA cm⁻² in 1M Na₂SO₄, 1M Na₂SO₃, and 2M KCl electrolytes. Inset is the representative charge-discharge (V-t) profiles recorded at the current density of 5 mA cm⁻² for the composite electrode in these electrolytes. The V-t profiles obtained towards the end of the charge discharge cycles in (b) 1M Na₂SO₄, (c) 1M Na₂SO₃, and (d) 2M KCl.

Figure 14: Nyquist plot of the T-NT/CoS electrode in (a) KOH (inset shows the semi-circle domain at high frequency), (b) Na₂SO₄, Na₂SO₃, and KCl electrolytes.

Figure S1: (a) Co 2p XPS spectrum, (b) S 2p XPS spectrum of the T-NT/CoS electrode after repetitive CV cycles in 2M KOH electrolyte

Figure S2: Comparative CV profiles of the T-NT, Ti/CoS, and T-NT/CoS electrodes in (a) 1M Na₂SO₄, (b) 1M Na₂SO₃, (c) 2M KCl and (d) 2M KOH electrolytes recorded at 100 mV s⁻¹.

Figure S3: (a) Co 2p XPS spectra, (b) S 2p XPS spectra of the T-NT/CoS electrode after repetitive CV cycles in 2M KCl, 1M Na₂SO₃, and 1M Na₂SO₄ electrolytes

Figure 1

Figure 2

Figure 3a

Figure 3b

Figure 3c

Figure 3d

Figure 3e

Figure 4

Figure 5a

Figure 5b

Figure 6a

Figure 6b

Figure 6c

Figure 7

Figure 8a

Figure 8b

Figure 8c

Figure 8d

Figure 9a

Figure 9b

Figure 10a

Figure 10b

Figure 10c

Figure 11a

Figure 11b

Figure 11c

Figure 12a

Figure 12b

Figure 12c

Figure 12d

Figure 13a

Figure 13b

Figure 13c

Figure 13d

Figure 14a

Figure 14b