Recognizing Nano SnO as an Electrode Material for Electrochemical Double Layer Capacitors

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In this communication, we recognize the electrochemical capacitance behavior of SnO (tin(II) oxide) nanoparticles in aqueous solutions. TEM image shows the SnO nanoparticles synthesized via hydrothermal method to be in the nano scale range. The nanomaterial was immobilized on paraffin-impregnated graphite electrode to preserve the high surface area of SnO nanoparticles which plays a crucial role in preserving the electrochemical activity. In 0.1 M NaCl solutions, nano SnO provided a high cell voltage of 1.65 V vs Ag/AgCl and the nanomaterial was chemically and electrochemically stable over 1000 cycles of potentiodynamic and charge–discharge measurements.

Current interest in developing new materials to be used as electrodes in electrochemical capacitors (ECs) arises because of the need for energy storage devices which give short high power pulses. They are complementary to batteries as they deliver high power density and low energy density.[1] To increase the performance of ECs in terms of energy, power and voltage, metal oxides like RuO_2, MnO_2, and TiO_2 in combination with carbon powder were investigated to utilize both advantages of double layer capacitance and pseudocapacitance.[2] Recently, in lithium-ion secondary battery, SnO has been recognized as a potential anode material.[3] In the present work, we report the hydrothermal synthesis of SnO by urea hydrolysis in an autoclave and the SnO nanoparticles were characterized by XRD, TEM, and cyclic voltammetry. Nanomaterials have the inherent advantage of having high surface area and that would be lost if the SnO nanomaterial was palletized or screen-printed on a conducting substrate. To avoid the problem, we employ paraffin-impregnated graphite electrode (PIGE) technique used successfully in our earlier works to evaluate $LiNiO_2$, $LiCoO_2$, and $LiMnO_2$ electrode materials for reversible battery applications and nano SnS for super capacitors.[4]

Typically, 0.04 moles of $SnCl_2 \cdot 2H_2O$ and 0.24 moles of urea were dissolved in 300 mL of deionized water in an autoclave. The autoclave was programmed to reach 180 °C in 1 h (ramp time) and at this temperature, the reaction was kept for 2 h (soak time) with stirring speed of 400 RPM. In situ pressure developed was 14 atm. When autoclave temperature reached to RT, the solution with precipitate (pH $\approx$ 9) was filtered and washed with distilled water to get neutral pH. The solid was dried overnight in oven at 120 °C. For electrochemical measurements, PGSTAT 30 Autolab system (Ecochemie, Netherlands) was used. The reference and counter electrodes were an Ag/AgCl (3 M KCl) and a platinum foil, respectively. Nano SnO immobilized on PIGE was the working electrode.

Figure 1 shows the TEM and XRD results of SnO nanoparticles. TEM reveals the SnO particles in the nanoscale range (<40 nm) while the XRD pattern was of SnO phase (JCPDS card No. 6-395) with high degree of crystallinity. The crystallite size calculated as per Scherrer equation at d_{101} was 28.1 nm. An XPS measurement also confirms the formation of this tin monoxide. It is very interesting that the nanoparticles shown by TEM produce sharp peaks in XRD; though, no explanation was offered, similar results have been published earlier for SnO_2 prepared by different routes.[3,5] However, the inset of d_{101} peak in Figure 1b was a zoomed version of the original peak and it certainly shows peak broadening which was a landmark of nanoparticles.

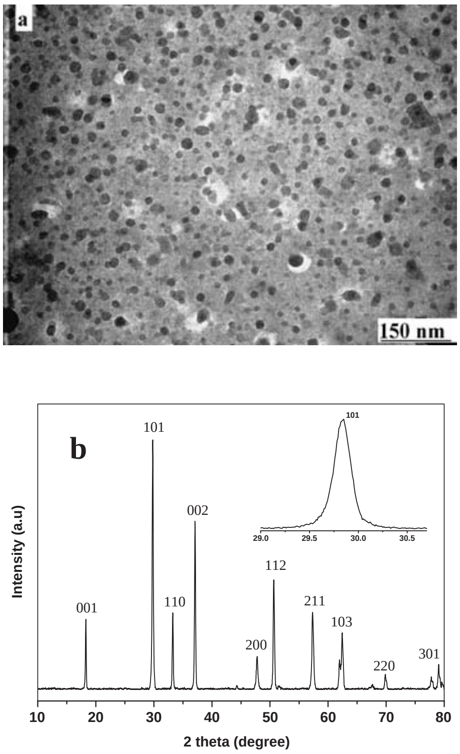

Figure 1. TEM image (a) and XRD pattern (b) of SnO nanoparticles.

Figure 2 shows the cyclic voltammograms (CVs) recorded in 0.1 M NaCl solutions. The potential window was of 1.65 V. The CVs, especially at slow scan rates reflect the almost rectangular current–potential profile of an electrochemical double layer capacitor. The equations used to calculate specific capacitance have been mentioned in our recent earlier work.[4] With increase in scan rates, capacitance values decrease (Table 1). This difference occurs because at high scan rates diffusion limits the movement of Na^+ ions into the SnO pores because of time constraint and only the outer active surface is utilized for the charge storage. However at low scan rates, all the active surface area can be utilized for charge storage.[6]

The electrochemical stability of the nano SnO was tested by continuous cycling for 1000 cycles at a scan rate of $50\,mVs^{-1}$ and the capacitance values (anodic) obtained from the cyclic vol-

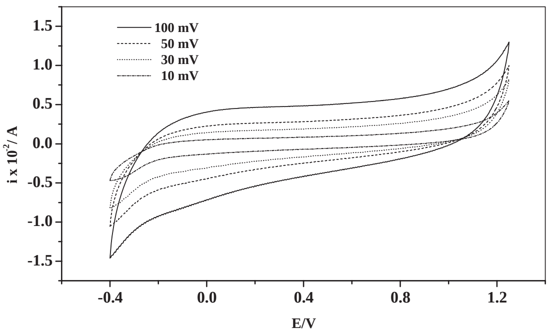

Figure 2. Cyclic voltammograms of SnO at various scan rates.

Table 1. Effect of scan rate on specific capacitances of nano SnO

Scan rate /mV s^{-1}	Specific Capacitance values (C_{dl}) from	
	Anodic charges (Q_+) /F g^{-1}	Cathodic charges (Q_-) /F g^{-1}
10	5.474	4.703
30	3.392	3.096
50	2.785	2.579
100	2.165	2.019

tammograms at 100th, 300th, 600th, 800th, and 1000th cycles were of 2.16, 4.99, 6.21, 6.87, and 7.22 F g^{-1}, respectively. This increase in anodic charges may be due to faradaic pseudocapacitive behavior involving surface oxidation of SnO to SnO$_2$; after 600 cycles, the CV response gets almost stabilized.

The galvanostatic charge–discharge behavior of SnO electrode was studied by double step chronopotentiometry by applying a constant current of 100 μA. In the forward charging step, a positive current of 100 μA was applied between the potential ranges 1.2 to −0.4 V in a time scale of 60 s. At the completion of 60 seconds, current reversal occurs; a negative current of −100 μA flows between −0.4 to 1.2 V and the resultant chronopotentiogram represents a typical charge–discharge curve. The charge–discharge curves in the 1st, 500th, and 1000th runs of the experiment were shown in Figure 3. There was a tremendous increase in charges as compared to the recorded first and 500th cycle; it was a similar response as in CVs due to the oxidation of SnO to SnO$_2$.

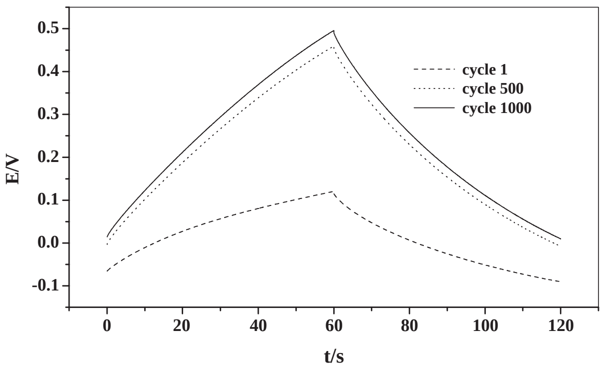

Figure 3. Glavanostatic charge–discharge curves of SnO in 0.1 M NaCl solutions.

The specific capacitance values calculated for the stabilized 1000th cycle for the charging forward step of the chronopotentiogram was 24.58 F g^{-1} and that of backward discharging step was 17.3 F g^{-1}. On comparison with the earlier works, we found that our values were consistent for SnO$_2$ prepared by sol–gel methods which was reported to be 16 F g^{-1} at the scan rate of 4 mV s^{-1} and they differ to be 285 F g^{-1} at the scan rate of 10 mV s^{-1} for SnO$_2$ synthesized by electrochemical deposition.[7,8] An order of increase in capacitance values was obtained in chronopotentiograms which are essentially a current step measurement where the output is linearly related to the voltage. On the other hand, in cyclic voltammograms, basically a potential step technique, the output current is an exponentially decaying one. The robust stability of the nano SnO on continuous charge–discharge cycles was very good and proves its ability to perform as a super capacitor material.

In conclusion, we identify SnO (tin(II) oxide) as a good electrode material for supercapacitors. As success of any material's application depending on the economy of the synthesis, hydrothermal synthesis proves to be an economically viable route because of its simplicity and noncomplicated chemistry. Though the specific capacitance values were comparable, the high voltage was a huge beneficial factor for short spikes of high power pulses. SnO was shown to have chemical and electrochemical stability over 1000 cycles of persistent cycling by cyclic voltammetry and charge–discharge techniques.

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