Electrochemical Deposition of Nanostructured Indium Oxide: High-Performance Electrode Material for Redox Supercapacitors

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Growing demands in digital communication, electric vehicles, and other related devices have created the need for a reliable secondary source of high power. The idea of using an extra battery is rejected since the modern batteries are incapable of providing high powers without performance degradation. Moreover, the modern day battery technology is very expensive to be commercially viable. This led to extensive research in the area of electrochemical capacitors (ECCs). A hybrid system combination of a rechargeable battery and an ECC can provide the overall power and energy without sacrificing the energy density and cycle-life of the battery. Two basic types of electrochemical capacitors can be realized using different charge-storage mechanisms:[1−4] (i) electrical double-layer capacitors (EDLCs), which utilize the capacitance arising from charge separation at an electrode/electrolyte interface, and (ii) redox supercapacitors, which utilize the charge-transfer pseudocapacitance arising from reversible Faradaic reactions occurring at the electrode surface.

The electrodes of redox supercapacitors consist of electroactive materials with several oxidation states. These types of capacitors have been under extensive investigation in recent times because of high-capacitive and high-energy characteristics. Since the pseudocapacitance comes from the reversible redox transitions of the electroactive materials, transition metal oxides[5−15] and conducting polymers[16,17] with various oxidation states are considered to be promising materials for the applications of redox supercapacitors. Hydrous RuO_2 has been extensively studied[5,6] as an active electrode material for supercapacitors as it possesses a capacitance as high as 720 F g^{-1} in aqueous acidic electrolytes. Although RuO_2 gives high specific capacitance, it has disadvantages of high cost and a toxic nature. Recently, Prasad et al.[18] showed that nanostructured MnO_2 can be deposited by a potentiodynamic method at a high scan rate of 200 mV s^{-1}. The same material was found to give very high specific capacitance and power density when employed for redox supercapacitors.[18] Nanostructured In_2O_3 is an important material due to its interesting applications in the areas of photoluminescence, sensors, and microelectronics. Generally employed methods used for the synthesis of nanostructured In_2O_3 are calcinations,[19] laser ablation,[20] and spray pyrolysis.[21]

In the present studies, indium metal was potentiodynamically deposited onto stainless steel (SS)[22] from an electrolyte solution of $InCl_3$ and $Na_3C_6H_5O_7{\cdot}2H_2O$, and the electrode was heated in air at 700 °C for 12 h to form In_2O_3. The mass of In_2O_3 was 0.08 mg cm^{-2} and the In_2O_3/SS electrodes were studied for redox supercapacitor applications in 1 M Na_2SO_3 electrolyte. High specific capacitance (SC) and high power characteristics of In_2O_3 were demonstrated from cyclic voltammetry (CV) at various scan rates. To the best of the authors' knowledge, there are no reports on potentiodynamic deposition of In_2O_3 and applications towards redox supercapacitors. X-ray diffraction patterns of In_2O_3 were recorded (not shown here), which resemble the reported patterns[23] for In_2O_3. This indicates the formation of In_2O_3 by a potentiodynamic method at high scan rates.

Figure 1 shows the SEM images of In_2O_3 electrodes prepared by a potentiodynamic method at a scan rate of 200 mV s^{-1}. It is interesting to note that small nanorods of In_2O_3 were formed with an average length of about 250 nm and an average diameter of about 50 nm. SEM images were also recorded for a bare SS (without deposition) after heating at 700 °C for 12 h and no structure was observed, which also indicates the formation of an In_2O_3 layer on the surface of SS by the present method. Since the successful synthesis of semiconducting oxide nanobelts,[24,25] research in the area of

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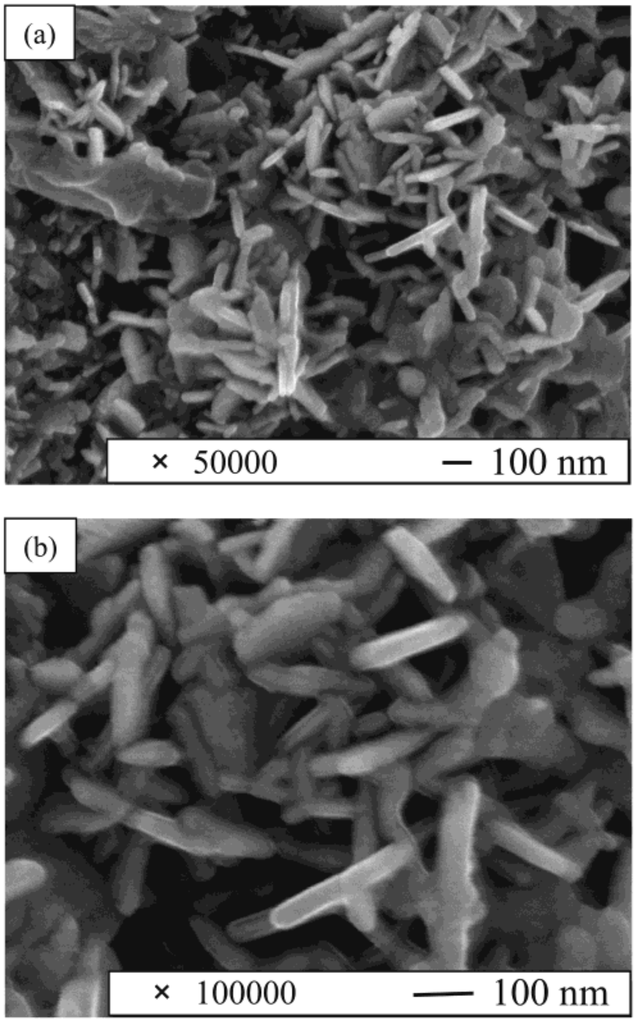

Figure 1. SEM images of In_2O_3 at a magnification of (a) 50000 and (b) 100000. In_2O_3 was prepared by a potentiodynamic method at a scan rate of 200 mV s^{-1}.

oxide nanostructures has attracted considerable attention. Various synthesis methods have been reported in the literature.[26] To the best of the authors' knowledge, there are no reports in the literature on the electrochemical synthesis of nanorods of In_2O_3. Generally nanostructured and three-dimensional materials are expected to perform as active materials for redox supercapacitor applications. Hence, the In_2O_3 electrodes synthesized in the present study were also characterized for the above application.

Figure 2 shows the typical CV (at various scan rates) of In_2O_3/SS electrodes in 1 M Na_2SO_3 between 0.2 and −0.6 V vs. Ag/AgCl. The capacitive behavior of In_2O_3 is clearly seen from this figure with near rectangular-shaped voltammograms and larger CV currents. Cyclic voltammograms were also recorded in the same electrolyte with bare SS electrode heated at 700 °C, which indicate no capacitive behavior with negligible current values compared to that shown in Figure 2. This suggests that the capacitive behavior shown in Figure 2 is because of the existence of an In_2O_3 layer. The cyclic

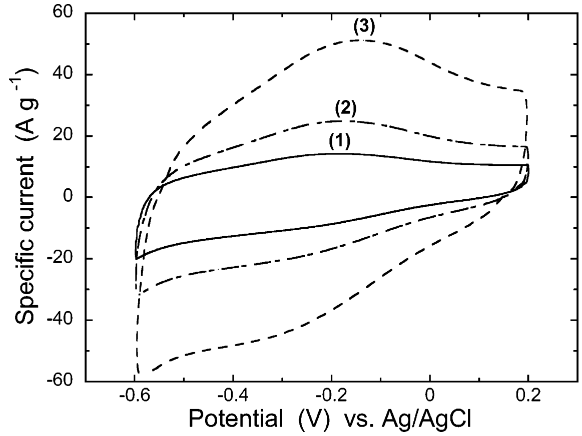

Figure 2. Cyclic voltammograms (CVs) of In_2O_3/SS electrodes in 1 M Na_2SO_3 electrolyte at a scan rate of (1) 100, (2) 200, and (3) 500 mV s^{-1}. Mass of In_2O_3 is 0.08 mg cm^{-2}.

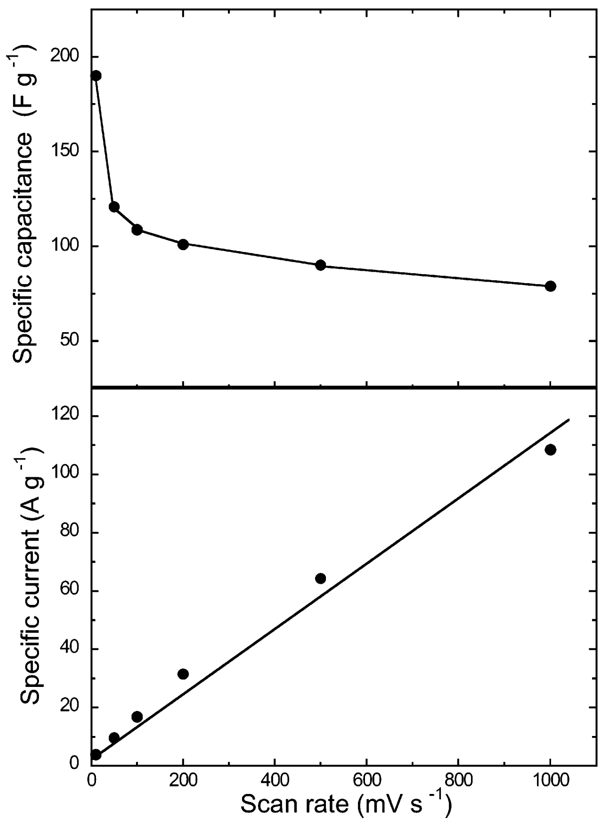

Figure 3. (a) Specific capacitance and (b) CV current of In_2O_3/SS electrodes against the CV scan rate. Mass of In_2O_3 is 0.08 mg cm^{-2}.

voltammetric current densities and the specific capacitance values calculated are shown in Figure 3, as a function of scan rate of CV. It is noteworthy that a SC as high as 190 F g^{-1} has been obtained at a scan rate of 10 mV s^{-1} and a SC of 80 F g^{-1} was obtained even at a very high scan rate of 1000 mV s^{-1}. These values of SC are much higher than the values reported for some other inexpensive oxides at a much lower scan rate. For example, for electrochemically prepared NiO, a SC value of 60 F g^{-1} has been reported[14] at a scan rate of 20 mV s^{-1}. A large decrease in SC (more than 70%) was reported[8] for some other low-cost transition metal oxides, when the scan rate was increased to just 100 mV s^{-1}. However, in the present study a decrease in SC of just 56% was observed when the scan rate was

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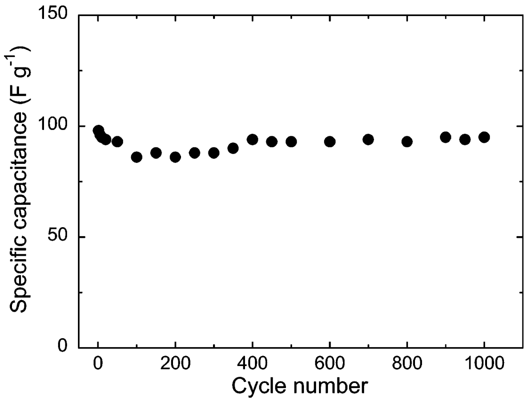

Figure 4. Cycle-life data of In_2O_3/SS electrode. Specific capacitance was calculated from CV at a scan rate of 100 mV s^{-1}. Mass of In_2O_3 is 0.08 mg cm^{-2}.

increased from 10 to 1000 mV s^{-1}. Moreover, this decrease in SC is just 35% between 50 and 1000 mV s^{-1} scan rates. This indicates very high power characteristics of In_2O_3. The high power property of In_2O_3 was also examined in Figure 3b where the CV currents increase linearly with an increase in scan rate. Such a large value of SC at such a high scan rate indicates that In_2O_3 can be a promising material for redox supercapacitors in automobile applications. Moreover, the present method of synthesis and the materials used are highly advantageous from a commercial and economical point of view.

The stability of In_2O_3 was examined by subjecting an In_2O_3/SS electrode for CV for a long number of cycles. The cycling process was performed at a scan rate of 100 mV s^{-1} for 1000 cycles. Figure 4 shows the variation of specific capacitance as a function of cycle number. There is a little decrease in the value of specific capacitance in the first 200 cycles and then, surprisingly, the electrode regains the original SC and there is very minimal SC fade up to 1000 cycles. This very minimal decrease in SC for 1000 cycles indicates very high stability of In_2O_3 for long-term capacitor applications. This decrease in the value of SC is much less compared to that reported in the literature for other low-cost transition metal oxides.[7]

In summary, nanostructured and nanorod-shaped three-dimensional In_2O_3 was prepared by a novel potentiodynamic method at high scan rates and the electrodes were characterized for redox supercapacitor applications. High specific capacitance and high power density were found to be realizable with In_2O_3. The results have shown, by suitably tailoring some more conditions of synthesis, the electrical parameters obtained with inexpensive In_2O_3 could be close to those obtained with highly expensive RuO_2. Extensive studies are underway in our laboratory.

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Supporting Information Available: Method of forming In_2O_3/SS electrode (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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