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Single Step Solution Combustion Synthesis of ZnO/carbon Composite and its Electrochemical Characterization for Supercapacitor Application

M. Jayalakshmi[*], *M. Palaniappa, K. Balasubramanian*

Non-ferrous Materials Technology Development Centre, Kanchanbagh Post,
Hyderabad - 500 058, India.
[*]E-mail: jayalakshmi@nftdc.res.in

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Zinc oxide/carbon (ZnO/C) composite is synthesized by self-propagating solution combustion method using dextrose as fuel and carbon source. By this method, carbon is added in-situ to the metal oxide. The powders are characterized by XRD, SEM, CHNS analysis and cyclic voltammetry. Electrochemical capacitive behavior of ZnO/C is studied in aqueous KNO_3 solution. In dilute 0.1 M KNO_3 solution, ZnO/C showed a specific capacitance of 21.7 Fg^{-1} at a scan rate of 50 mVs^{-1} and further increase in concentration of electrolyte solution decreased the electrochemical capacitances. A comparative evaluation of ZnO/C with pure nano ZnO (synthesized) and commercial ZnO (microsize particles) is also done.

Keywords: Zinc oxide/carbon composite; Dextrose; combustion synthesis; Electrochemical capacitance

1. INTRODUCTION

The storage of electrical energy based on the separation of charged species (supporting electrolyte) by adsorption on electrode surfaces in electrolytic double layers is simple compared with rechargeable batteries. Such devices are called electrochemical double-layer capacitors (EDLCs). Recently, EDLCs have been proposed as the sub-power source for the hybrid electric vehicle because of its higher power density (larger than 1000 W kg^{-1} or 1000 Wl^{-1}) and fast charge-discharge ability. Because the energy density of EDLC is much lower than that of rechargeable batteries, an improvement in the capacitance of EDLC is required [1]. In view of this logical reasoning, attempts are made to recognize new electrode materials that have the dual benefits of cost effectiveness and higher performance. Carbon is known for its high surface area, porosity and conductivity. Hence researchers aim to prepare electrode materials with carbon as additive either by in-situ or ex-situ to enhance the performance and durability. In our earlier works on super capacitor electrode materials, especially on mixed oxides, ex-situ added carbon nanotubes (CNTs) to SnO_2-V_2O_5 (i.e CNTs added to the mixed oxide after hydrothermal synthesis) gave very good results [2]. In the case of SnO_2-Al_2O_3 carbon composite where the carbon was added in-situ during the hydrothermal synthesis of mixed oxide using the carbon precursor tetrapropyl ammonium hydroxide did not fulfill the expectation that the added carbon would enhance the electrochemical performance [3]. So a generalized view on the behavior of carbon cannot be taken as it changes with the nature of source, condition of synthesis and to the metal oxide it is added.

Many researchers have highlighted the importance of carbon as additive/support in rechargeable batteries, fuel cells, catalysis and super capacitors. Also exhaustive literature is available for the synthesis of ZnO (Zinc oxide) in the nanoscale range. To our knowledge, only limited work is done on the ZnO/C composite for the application of supercapacitors. In an earlier work on this material, ZnO was prepared by co-precipitation method and purchased carbon aerogel (2500 m^2/g) was mixed with it and used as electrode. A specific capacitance of 25 F/g at 10 mVs^{-1} in 6 M KOH solution was reported [4]. The focus of the present work was to synthesize ZnO/carbon (ZnO/C) composite in-situ using dextrose as fuel and carbon source by solution combustion method and study the electrochemical behavior in aqueous KNO_3 electrolyte for super capacitor application. A comparative evaluation on the electrochemical capacitances of commerical ZnO vs. synthesized nano ZnO and as prepared ZnO/C composite vs. calcined ZnO is also discussed. The nano-composite was characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM) and Carbon Hydrogen Nitrogen Sulphur (CHNS) elemental analysis.

2. EXPERIMENTAL PART

2.1. Self-propagating solution combustion synthesis

Self-propagating high temperature combustion synthesis is a novel technique that has been used successfully for the preparation of ceramic and phosphor materials. This method was successfully employed to prepare $LiNiO_2$, $LiCoO_2$ and $LiMnO_4$ [3,4]. The main advantage of this method, compared to the solid state sintering method, is that the experiment is completed within 10 min. The basic principle of the method is the decomposition of an oxidizer, e.g., a metal nitrate, in the presence of a fuel. The fuel gets ignited by the oxidizer to yield oxide materials derived from the metal salts. The fuel used in the present study was dextrose which acts both as fuel and carbon source.

Zinc nitrate (10 g) and dextrose (3.6 g) were dissolved in 25 ml of water contained in a beaker and placed on a hot plate for 15 minutes as the solution dehydrates to form a disposition like a gel. Then the beaker was placed in a preheated muffle furnace at 400°C. The solution boils, ignites with a flame and the entire reaction was completed within 5 minutes. The powder was highly amorphous, a portion of the sample was calcined at 650° C and the XRD pattern of this powder confirms the formation of ZnO.

2.2. Instrumentation

All electrochemical experiments were conducted with a PGSTAT 302 Autolab system (Ecochemie, Utrecht, The Netherlands). It was connected to a PC running with Eco-Chemie GPES software. GPES software was used for all electrochemical data analysis. The reference electrode was Ag/AgCl (3M KCl) and the counter electrode was a platinum wire supplied along with the instrument. Paraffin impregnated graphite electrodes (PIGE) were used as working electrodes with the surface immobilized with the active electrode materials. A few micrograms of composite oxide nano-particles were placed on a clean glass plate and the surface of PIGE electrode was pressed over the nano-material which would mechanically transfer the nano-particles to the tip of the electrode [5].

Powder XRD data of the samples were obtained by means of a Philips X-Pert diffractometer with Bragg–Brentano geometry and having Cu Kα radiation (λ = 1.5418°A). Scanning electron microscope (SEM) images were obtained with a Hitachi (Japan) model. Carbon content in the metal oxide is determined by CHNS analysis

3. RESULTS AND DISCUSSION

3.1. Synthesis and characterization of nano ZnO/carbon composite

Fig. 1a shows the XRD of ZnO (calcined) sample. The peaks are quite sharper indicating the crystalline nature of the particles. On the other hand, the as-prepared ZnO/C composite powder was amorphous with fine particles in the nanoscale range. The XRD pattern matches the standard file of ZnO (JCPDS card no. 79-0206). Fig. 1b shows the SEM image of as-prepared composite; the particles were agglomerated and their sizes lie in the range of 35-85 nm. The agglomerated particles neck with their neighbors; they form elongated spindle-like shapes intermitted with voids, ensuring high surface area. CHNS analysis of the as-prepared composite showed the carbon content in the sample to be 10.1%.

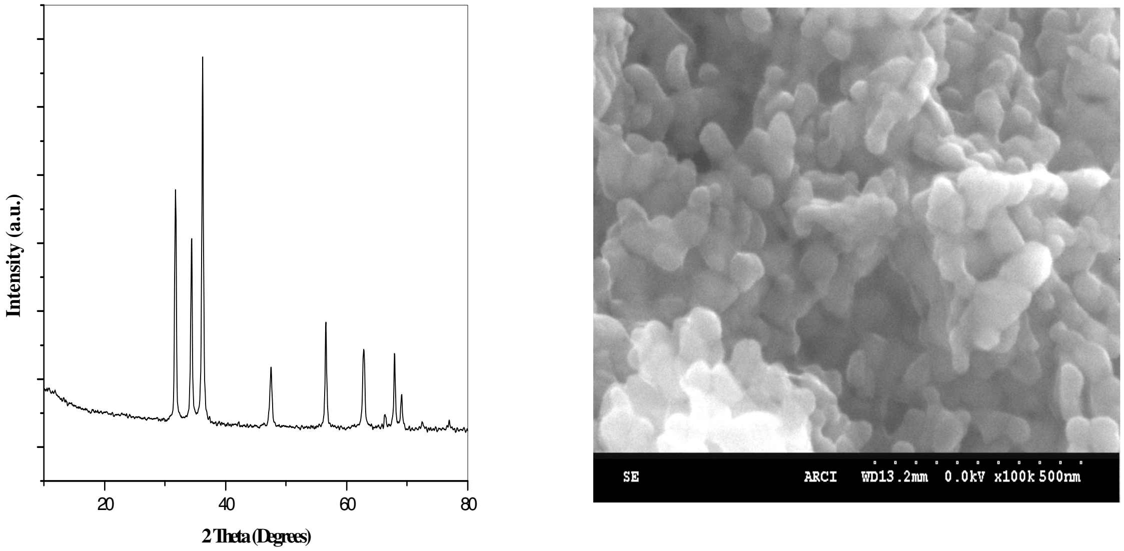

Figure 1. X-Ray Diffraction (a); SEM microstructure (b) of nano ZnO/C composite powder.

3.2. ZnO/carbon composite behavior in aqueous electrolytes

Cyclic voltammaograms (CVs) recorded for ZnO/C in 0.1 M KNO_3 electrolyte solutions at the scan rate of 50 mVs^{-1} are shown in Fig. 2. The CVs were cycled up to 500 times to study the chemical and electrochemical stability of the composite. As one can see, after the initial scan, the electrochemical response remained the same for the entire 500 scans confirming the robust nature of the material. They show clearly the rectangular and symmetric current-potential (I-V) characteristics of a capacitor. The reason for the appearance of rectangular shaped CV for a typical capacitative behavior has been well documented [6]. The equivalent circuit of double layer capacitor electrodes can be represented by a serial combination of equivalent series resistance (R) and double layer capacitance (C). The shape of the voltammogram was duly determined by the time constant, τ (RC) of the electrochemical cell. If τ (RC) $\neq 0$, then the shape of the CV would be non-rectangular indicating a current containing a transient part as well as a steady state part. As s becomes larger, the transient part lasts longer and hence more time is required to charge the capacitor resulting in the collapse of the rectangular current profile. As evident from Fig. 2, a large capacitance was observed for ZnO/C electrode as against the blank PIGE electrode. Such a behavior is a characteristic feature of semiconductor oxides permeated with a conductive phase which has the ability to accumulate a large number of injected electron charges in the solid matrix. In the present case of nanosized ZnO/C composite, a combination of several factors such as the nanosize, a good electronic conductivity enriched by the necking between the neighbours, a probable increase in surface area attributable to the presence of in-situ formed carbon and the presence of equipotential surface contributed to the displacement of Fermi level towards the conducting band producing a homogeneous increase in the electron concentration in the electrode surface. Such a process increases the electrochemical capacitance behavior as the rate of charge transfer depends on the diffusion of anions and cations towards the ZnO-C/solution interface and the overlap of the electronic levels in the ZnO with the redox species in the solution [7].

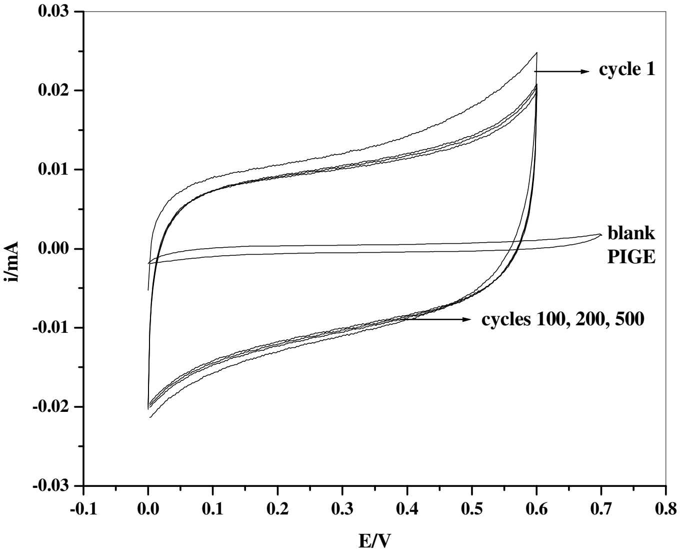

Figure 2. Cyclic voltammaograms of ZnO/C immobilized on PIGE and cycled in 0.1 M KNO_3 solution for 500 scans; Scan rate = 50 mVs^{-1}.

Capacitance is expressed as,

$$C = dq/dE \text{ or } C = I\, dt/dE \qquad (1)$$

For the calculation of specific capacitance (Fg^{-1}) from CV measurements, the average anodic capacitive current is considered. It was calculated from the following expression:

$$C = [\ i(A) \times t(s)/w(g) \times \Delta E(V)\ ], \qquad (2)$$

where all the terms has the usual meaning.

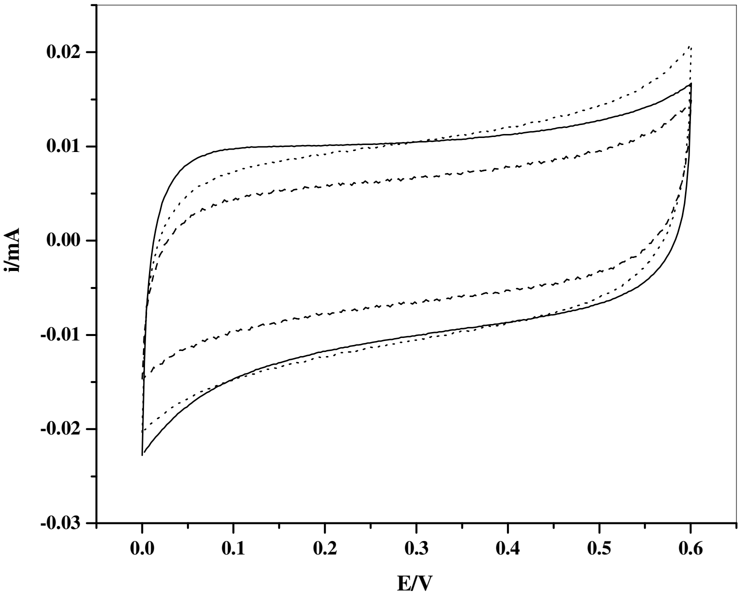

Figure 3. Cyclic voltammaograms of ZnO/C immobilized on PIGE and recorded in different concentrations of KNO_3 solutions; Scan rate = 50 mVs^{-1}; — 0.01 M; …… 0.1 M; - - - 0.5 M.

Fig. 3 shows the CVs recorded for ZnO/C composite in KNO_3 solutions of three different concentrations. It could be seen that there is no significant difference in the I-V curves of the composite in 0.01 M and 0.1 M KNO_3 solutions. The specific capacitance values calculated from the curves were 21.6 and 20.8 Fg^{-1} respectively. Interestingly, the specific capacitance value has decreased to 14.2 Fg^{-1} on increasing the concentration of the electrolyte to 0.5 M and further down to 12.1 Fg^{-1} for 1.0 M KNO_3 (Figure not given) solution. Under the experimental conditions envisaged, i.e the non-faradic charge transfer conditions, the forward scan of oxidation produces electrons which accumulates on the solid side of the double layer; on the other hand, K^+ ions tend to accumulate on the solution side of the double layer due to the attractive forces. This polarizable double layer acts as the ideal electrochemical capacitor which do not have current leakage pathway or self-discharge and hence can remain charged indefinitely. However this condition is attained only in dilute electrolyte solutions. In concentrated solutions, the double layer is no more intact, as evident from the decrease in specific capacitances; this is because the population density of electrons on the solid side remains a constant factor but that of K^+ ions on the solution side of double layer increases. This would lead to a decrease in ΔG° for the specific adsorption of K^+ ions so that adsorption of K^+ ions becomes increasingly difficult with increasing K^+ ion concentration. There may be a decrease in effective negative potential on the inner Helmholtz plane i.e. the potential which the K^+ ion encounters as it approaches the surface due to the previous surface coverage by K^+ ion or a repulsive potential between adsorbed K^+ ions and the K^+ ions about to be adsorbed [8, 9]. In other words, higher population density of the K^+ ions disturbs the double layer in such way that it becomes a leaking capacitor.

The beneficial role of carbon in enhancing the capacitance can be understood from the CVs shown in Fig. 4. Calcination at high temperature removes carbon from the ZnO/C composite and the calcined product consist of pure ZnO only. It could be seen that the removal of carbon decreased the specific capacitance almost three times. The specific capacitance of as prepared ZnO/C was 21.7 Fg^{-1} while that of calcined ZnO was 7.38 Fg^{-1}. Our results are consistent with a recent report by D. Kalpana et al who reported a value of 25 Fg^{-1} for ZnO/C synthesized by aerogel method [4].

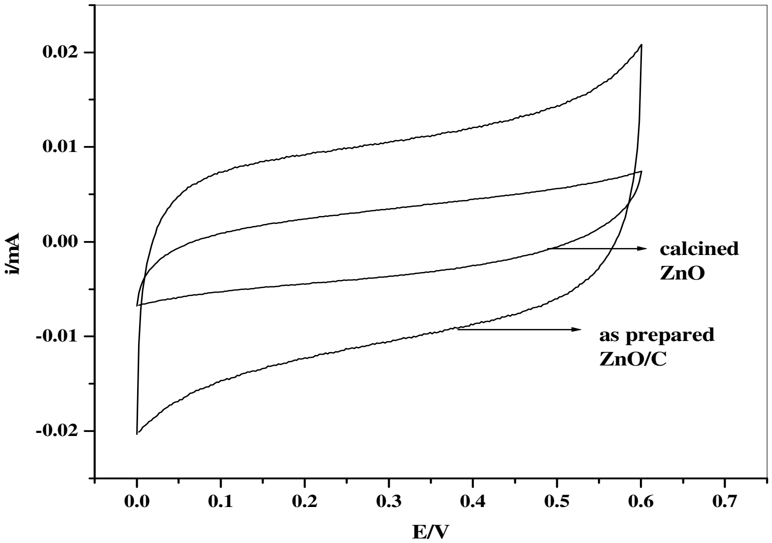

Figure 4. Cyclic voltammograms of as-prepared ZnO/C and calcined ZnO nanopowders C immobilized on PIGE and recorded in 0.1 M KNO_3 solution; Scan rate = 50 mVs^{-1}.

Fig. 5 shows the CVs of mcirosized ZnO (commercial) and nano ZnO emphasizing the effect of particle size on the electrochemical capacitance of ZnO powders. The specific capacitances determined from the anodic scan of the CVs were of 1.78 and 7.38 Fg^{-1} respectively. The major advantage of ZnO nanoparticles over conventional materials is the high surface area to volume ratio. Electrochemistry plays a key role in nanoparticle science as it paves a way for coupling particle activity to external circuitry. In the microsized particles, the depth of space charge layer is insignificant compared to the grain size and the electrical conduction on the application of an external bias is largely governed by the grain boundaries. On the other hand, in nanosized particles, the space charge layer is in par with grain size, so that the application of external bias of same magnitude would have a profound effect on the intergrain conduction, leading to an increase in electronic conduction and thereby, the capacitance. The nanoparticulate surface not only enhances current due to the high surface area but also the scale of surface roughness removes the requirement for a solution phase species to mediate electron transfer to the active redox site of the electrode material. Under these conditions, an increase in the electronic and ionic conductance should be inversely proportional to the particle size; i.e. smaller the particle size, higher the conductance and hence the capacitance [10].

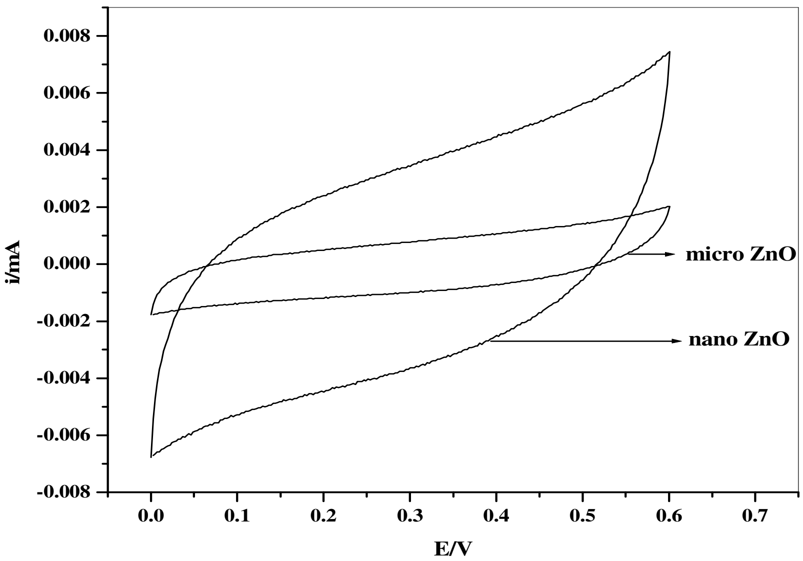

Figure 5. Cyclic voltammograms of micro- and nano-sized ZnO powders immobilized on PIGE and recorded in 0.1 M KNO_3 solution; Scan rate = 50 mVs^{-1}.

4. CONCLUSIONS

Zinc oxide/carbon (ZnO/C) composite synthesized by self-propagating solution combustion method using dextrose as fuel and carbon source was shown to give electrochemical capacitance of 21.7 Fg^{-1} in par with carbon aerogel used in the earlier work by Kalpana et al. We used dilute neutral solution and higher scan rates as compared to 6 M KOH and very slow scan rate used in the earlier work. It is well known that this simple combustion method is the easiest route to synthesize inorganic materials and used in industries for scaling up. Hence we conclude that ZnO/carbon composite synthesized by this method gives good electrochemical capacitance and the results of this study could be easily extended to technological applications.

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