

A novel high power symmetric ZnO/carbon aerogel composite electrode for electrochemical supercapacitor

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Abstract

We present, for the first time, a new material of symmetric electrochemical supercapacitor in which zinc oxide (ZnO) with carbon aerogel (CA) was used as active material. Physical properties of ZnO/CA composite were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). It was found that ZnO has single hexagonal structure and the grain size increases with increase of ZnO compository. The result of cyclic voltammetry indicates that the specific capacitance of ZnO/CA composite in 6 M KOH electrolyte was approximately 25 F/g at 10 mV/s for 2:1 composition. AC impedance analysis reveals that ZnO with carbon aerogel powder enhanced the conductivity by reducing the internal resistance. Galvanostatic charge/discharge measurements were done at various current densities, namely 25, 50, 75, and 100 mA/cm². It was found that the cells have excellent electrochemical reversibility and capacitive characteristics in KOH electrolyte. The maximum capacitance of the ZnO/CA supercapacitor was 500 F/g at 100 mA/cm². It has been observed that the specific capacitance is constant up to 500 cycles at all current densities, which implies that the dendrite formation was controlled.

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1. Introduction

Supercapacitors, which are complementary charge-storage devices to conventional batteries, attract growing attention due to their higher power density than batteries and higher specific energy than conventional capacitors [1,2]. Based on the electrode material of supercapacitor, it has been divided into two groups: (i) carbon materials with high surface area, such as activated carbon, carbon aerogel, etc.; (ii) metal oxides such as oxides of Ru, Ni, Co, Zn, etc., and conducting polymers [3]. Ruthenium oxides are widely used in electrochemical supercapacitor due to its high specific capacitance and prominent electrochemical properties [4]. However, the high cost of Ru has retarded its commercial acceptance and a cheap metal oxide with equivalent capacitor characteristics is required. Transition metal oxides with various oxidation states are promising materials for supercapacitor applications. Nickel oxide [5–7], cobalt oxide [8], and manganese oxide supercapacitors [9], are inexpensive and exhibit pseudocapacitive behavior similar to that of ruthenium oxide.

Though the physical properties of the zinc oxide (ZnO) nano particles are available in literature [10–13], but the suitability of the ZnO as a potential candidate for supercapacitor application is not yet been reported. ZnO is a well-known battery active material having high energy density of 650 A/g. But it has the disadvantage of formation of dendrite growth during consecutive cycling, which leads to decrease in cycle life. Because of its good electrochemical activity and eco-friendly nature, we find zinc oxide to be a promising electrode material for supercapacitor. On the other hand, metal oxide/carbon composite electrodes have been investigated widely for supercapacitor applications [14].

Among carbon materials, carbon aerogel (CA) [15,16] has high specific surface area, good chemical stability, and high conductivity to our knowledge. The combination of high surface area carbon aerogel with large specific capacity of ZnO would result in utilizing both the faradaic capacitance of the metal oxide and the double layer capacitance of the carbon. There has not been any report on the electrochemical supercapacitor of ZnO/carbon aerogel composite. In this work, ZnO/carbon aerogel composite electrode has been prepared as a candidate electrode for supercapacitor with two compositions. The capacitive properties of this composite were investigated

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by cyclic voltammetry and charge/discharge methods. The electrical properties of the electrodes were studied through AC impedance electrochemical spectroscopy. The structural and textural characteristics of the ZnO/carbon aerogel compositions were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The effect of addition of ZnO on capacitive properties was also discussed.

2. Experimental

In the present work, ZnO was prepared by co-precipitation method. The stoichiometric quantity of ZnCl_2 was dissolved in triple distilled water. The mixed solution was slowly added into the alkaline KOH solution with constant stirring. The solution was stirred well at 80°C until the precipitate is formed. Then it was filtered and washed copiously using distilled water followed by ethanol. The precursor was then kept in the oven for 2 h at 100°C . The carbon aerogel was used as received which has a specific surface area of $2500\text{ m}^2/\text{g}$. Two different compositions (1:1, 2:1) of ZnO were mixed well with carbon aerogel. The mixture was bound with *N*-methyl pyrrolidine and the slurry was pasted on the nickel foam current collector. Then the electrodes were kept in the oven at 250°C for 1 h and slowly cooled to room temperature. The supercapacitor cells were fabricated by sandwiching the electrodes between the polypropylene separator. The electrochemical behavior of the cells was analyzed in 6 M KOH aqueous electrolyte solution. The cyclic voltammetry was characterized by using the electrochemical analyzer (BAS 100B). The crystalline structure and morphology of ZnO/carbon aerogel were examined by XRD with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056\text{ \AA}$). The morphology of the samples was captured by scanning electron microscope (HITACHI, S-3000H) and transmission electron microscopy (TEM) is viewed on a PHILIPS model CM200 Supertwin transmission electron microscope operated at 200 kV and impedance properties of the cells were characterized by using PARSTAT 2263. The charge/discharge cycling properties of the cells were evaluated for various current densities, namely 25, 50, 75, and $100\text{ mA}/\text{cm}^2$ by using Won-A-Tech Battery Cycler.

3. Results and discussion

3.1. Structural analysis

The crystal structure of the zinc oxide prepared by co-precipitation method was characterized by X-ray diffraction analysis. Fig. 1 shows the XRD pattern of as prepared ZnO and as mixed ZnO/CA of 1:1 and 2:1 compositions. The peaks are sharp, well defined, and reveal the formation of a single-phase hexagonal structure with the lattice parameters $a = 3.2398$ and $c = 5.2066\text{ \AA}$. From the XRD, the lattice parameter and the mean particle size can be calculated by using the Scherer formula:

$$d = \frac{0.9\lambda}{\beta \cos \theta}$$

where λ is the X-ray wavelength (1.5418 \AA), θ is the Bragg diffraction angle, and β is the full width half maximum. The

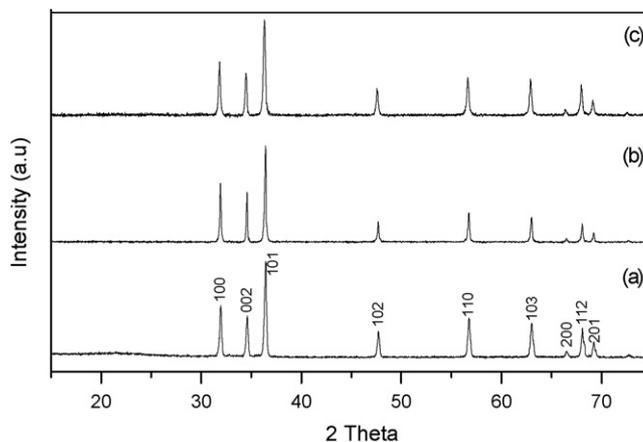


Fig. 1. X-ray patterns of ZnO/carbon aerogel composites: (a) as prepared ZnO; (b) 1:1; and (c) 2:1 compositions.

mean grain sizes of the as prepared sample are 6.505, 8.944 nm (1:1) and 7.1536 nm (2:1) for the compositions, respectively. The mean grain sizes of the samples increase with increase in ZnO compository resulting in the narrowing diffraction peaks. The surface modification of the peaks for the two compositions reveals that the carbon is uniformly coated on the zinc oxide particles. Zinc oxide may be transformed during cycling whereas the carbon aerogel plays a role of stabilizing the crystal lattice and also contribute the double layer capacitance.

3.2. Textural analysis

Fig. 2 shows the SEM microstructures of bare ZnO and ZnO/carbon aerogel compositions of 1:1 and 2:1 ratio before cycling. The micrographs show that the morphology of the compound is highly influenced by the addition of carbon aerogel. The bare ZnO powder shows a fine structure with well faceted crystallites. The crystallites are cubic in shape leaving behind many residual pores. The presence of voids is due to the migration of vacancies from the pore or the neck of the grain boundary. The equal proportion of ZnO/CA photographs (Fig. 2(b)) shows that the ZnO and carbon aerogel powders are in equal distribution. Fig. 2(c) shows the 2:1 composition of ZnO/CA. This microstructure has significantly finer grain size suggesting that the diffusion was impeded when ZnO and carbon aerogel were well mixed. Fig. 3(a) and (b) show SEM for the samples after 500 cycles. The connectivity between the grains for the 2:1 composition is increasing with increase of ZnO, which enhances the electrical conductivity. Also the figures show that there is no dendrite formation even after 500 cycles for the 2:1 sample cycled at different current densities. The particles of the ZnO/CA composite materials become smaller and porous after 500 cycles as shown in Fig. 3(a) and (b), which greatly influence the charge/discharge stability.

3.3. TEM analysis

Fig. 4 shows TEM images and transmission electron diffraction (TED) pattern for ZnO/carbon composite with two different

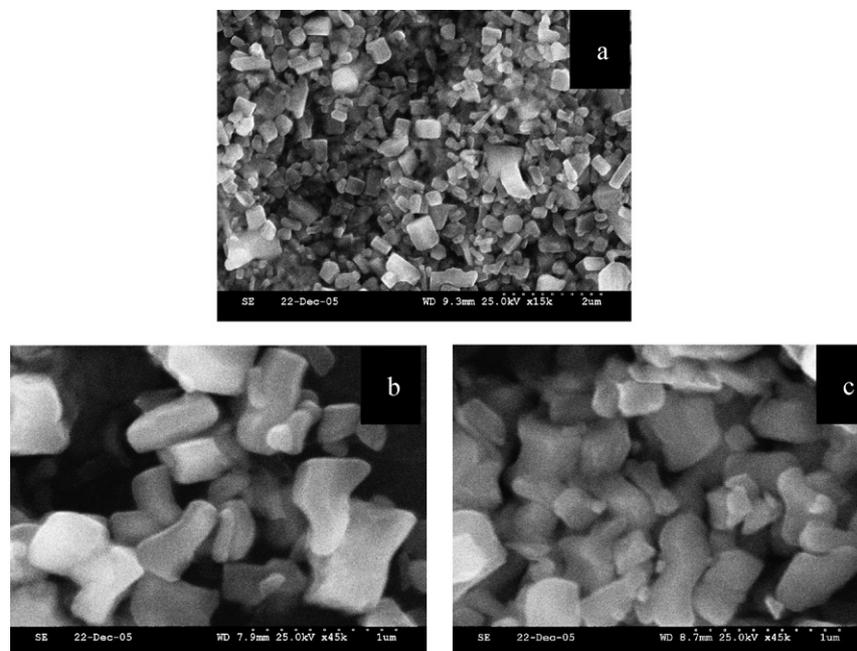


Fig. 2. SEM photographs of: (a) as prepared ZnO; (b) ZnO/carbon aerogel composition of 1:1 ratio; and (c) ZnO/carbon aerogel composition of 2:1 ratio.

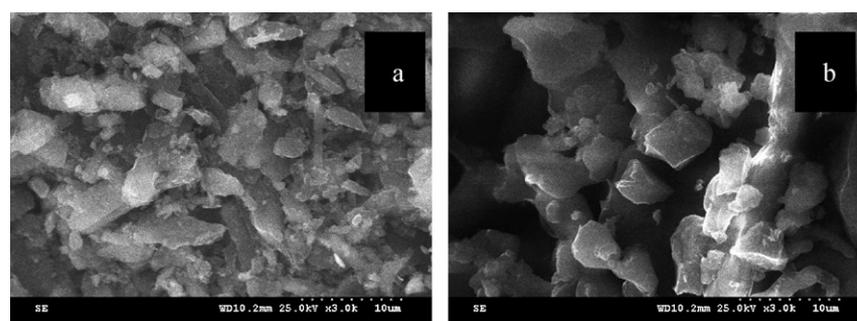


Fig. 3. SEM photographs of ZnO/carbon aerogel composites after cycles: (a) 1:1 and (b) 2:1.

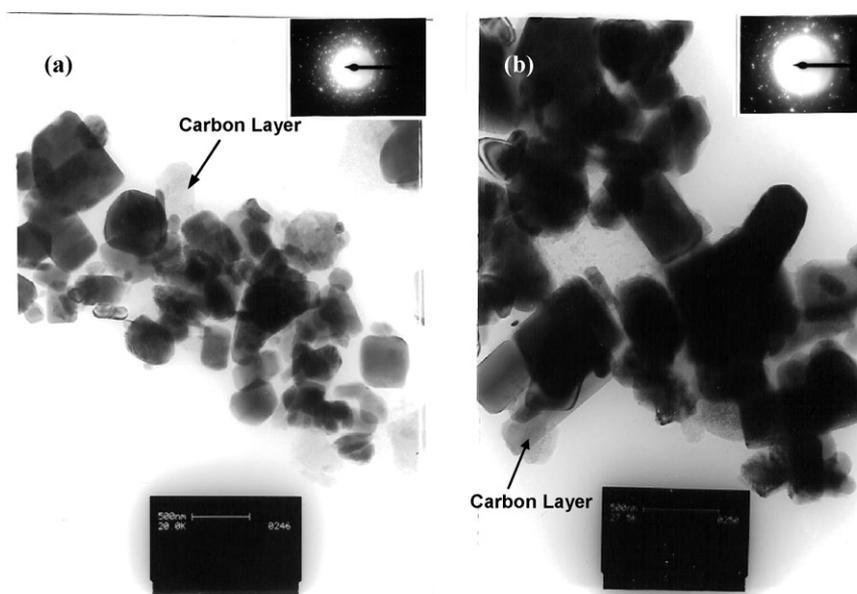


Fig. 4. TEM images of ZnO/carbon aerogel composites: (a) 1:1 and (b) 2:1 compositions. The inset at the top right of each panel represents the transmission electron diffraction (TED).

compositions of 1:1 and 2:1. As shown in Fig. 4, both samples were well dispersed with an average particle size of ~ 100 nm. It also suggests that the particles are cubic in nature having polycrystalline structure due to the presence of uniform central and diffraction spots observed from TED patterns [17]. As the ZnO composition has increased, the diffraction pattern of zinc oxide particles were gradually increased. This indicates that the carbon is well mixed with zinc oxide particles. As the TED (in sets) shows that in 2:1 composition ZnO radius is more dispersed uniformly in a carbon matrix, which is well interconnected and this may be the reason for high conductivity and in this composition there is more of amorphicity compared to 1:1 composition (as is evident from TED pictures). Thus the TEM images are evident for the coating of carbon on ZnO particles.

3.4. Electrochemical properties of ZnO/CA composites

Fig. 5(a) shows the cyclic voltammograms (CV) of bare ZnO in 6 M KOH recorded at 10 mV/s scan rate. Fig. 5(b) and (c) show the CV of ZnO/CA composite electrodes recorded at different

sweep rates, namely 10, 20, and 50 mV/s. All the figures exhibit reversible, symmetric, and capacitive behavior. For ZnO/CA electrode, cyclic voltammogram with rectangular like shape and capacitive current is observed. This implies that ZnO/CA electrode has good capacitive performance. By changing the scan rate of CV, the power property of ZnO/CA composite electrode was evaluated and the results are shown in Fig. 5(b) and (c). It can be seen from the CV curves that the current increases with an increase of scan rate. The curve remains in good rectangular like shape even at high scan rate of 50 mV/s.

The CV curves of the composite electrodes reveal that the mechanism of electrochemical storage could be described by the electrical double theory. Energy storage in these electrodes is the accumulation of ionic charge in the double layer at the electrode/electrolyte interface. This may be due to high surface area and the porosity of the carbon aerogel. Carbon aerogel consist of a three dimensional network of interconnected carbon particles. The high capacitance achieved in these may be due to effective electrical and ionic conductivity. It is suggested that Zn^{2+} and OH^- can occupy some pores within the electrode

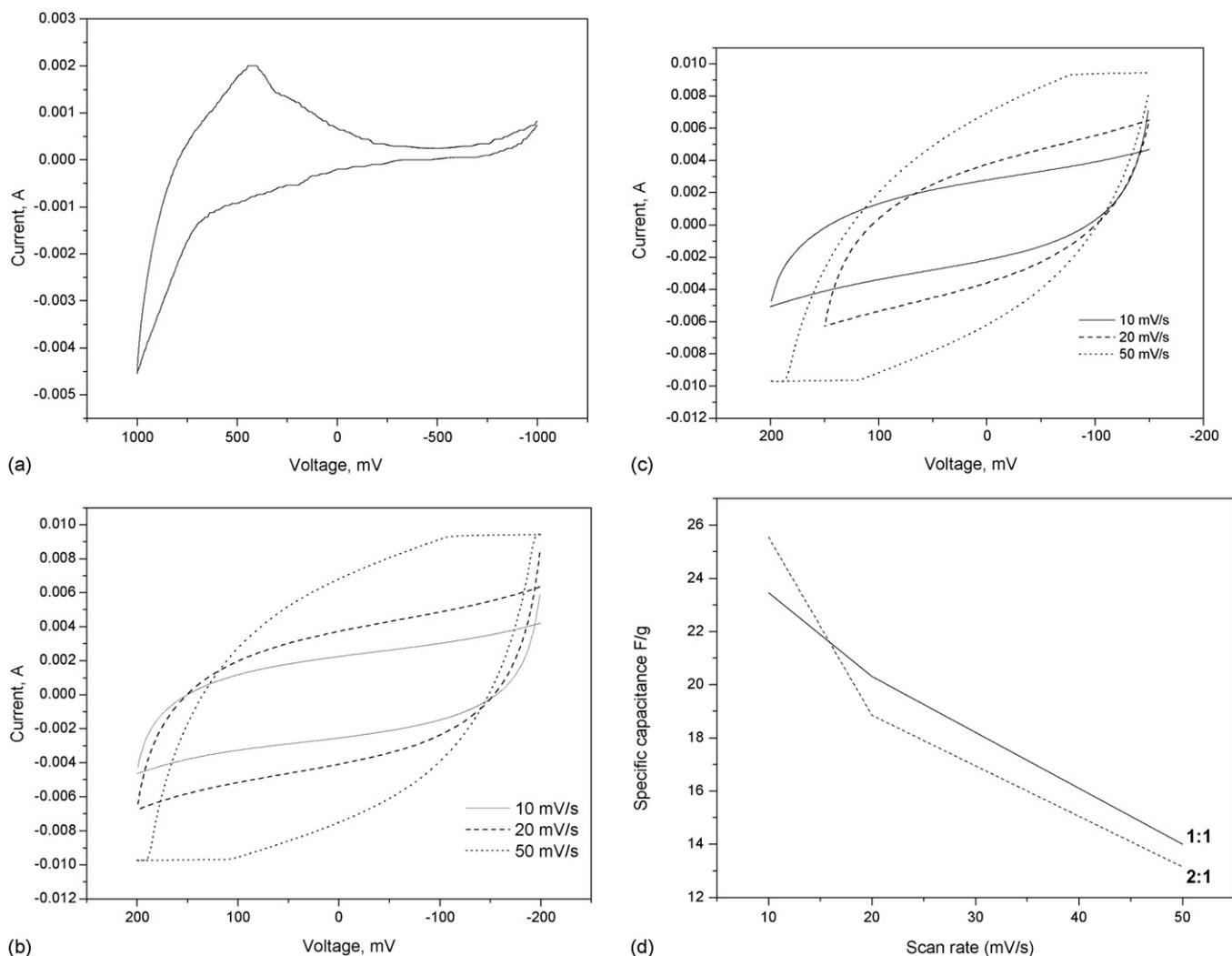


Fig. 5. (a) CV of as prepared ZnO at 10 mV/s scan rate. (b) Cyclic voltammograms of ZnO/carbon aerogel with 1:1 compositions at various scan rates. (c) Cyclic voltammograms of ZnO/carbon aerogel with 2:1 compositions at various scan rates. (d) The relation between specific capacitance and scan rate for different ZnO/carbon aerogel compositions.

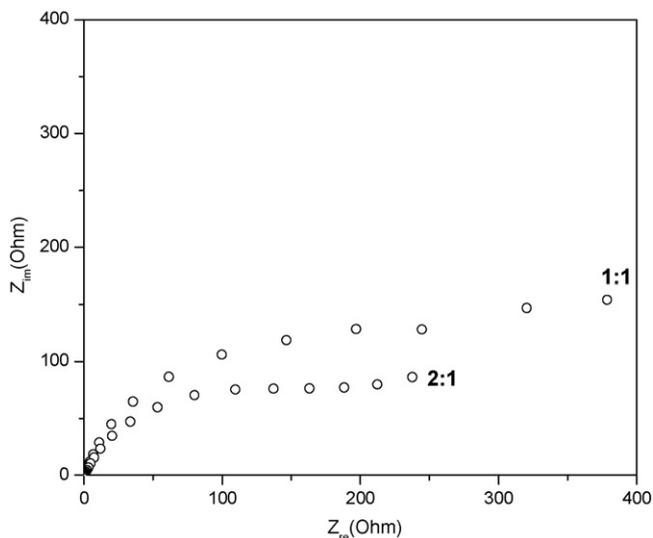


Fig. 6. Nyquist plots of ZnO/carbon aerogel with 1:1 and 2:1 compositions.

to participate in the formation of the electrochemical double layer.

The capacitance observed at the lowest scan rate may be due to highly symmetric nature of the reversible process of adsorption/desorption. As the scan rate increases the profiles gradually depress. This may be due to more transport of ions at the low scan rate. Diffusion rate of ions in pores may be slowed down at higher scan rates.

Fig. 5(d) gives the relation between scan rate and specific capacitance of ZnO/CA electrodes for two different compositions. It implies that ZnO/CA (2:1) composition has good power characteristics. It is because the conductivity and dispersion of ZnO matrix is improved by carbon aerogel and the porous structure of ZnO/CA composite allows the alkaline electrolyte to penetrate deeply into the composite matrix. The specific capacitance of ZnO/CA composite electrodes was calculated from cyclic voltammograms and was found to be 25 F/g for 2:1 composition at 10 mV/s scan rate.

3.5. Electrochemical impedance analysis

The electrochemical impedance measurement was carried out for the two compositions and the typical plot was shown in Fig. 6. As shown in the figure the two compositions presented similar impedance characteristics except the increase in R_{ct} for 1:1 mixture. Two distinct regions are shown depending on the frequency range. In the low frequency region, for the 2:1 composition the impedance of the electrode increases and tends to become purely capacitive. The intermediate frequency region is the 45° line, which is the characteristic of diffusion into the electrode. The charge transfer resistance R_{ct} of the electrode was estimated to be about 180 Ω for 2:1 composition and 500 Ω for 1:1 composition from the point of intercept with real axis in the high frequency range. It is obvious that ZnO with the carbon powder enhanced the conductivity by reducing the internal resistance. The more close to the vertical spike the more will be the supercapacitive behavior. The redox reaction from ZnO which gives rise to pseu-

docapacitance and the double layer capacitance from the carbon matrix combined to increase the conductivity of the electrodes.

3.6. Galvanostatic charge–discharge study of ZnO/CA electrodes

The charge–discharge properties of ZnO/CA composite electrodes in 6 M KOH were investigated from 0 to 1 V at different current densities of 25, 50, 75, and 100 mA/cm² and the corresponding results are shown in Figs. 7 and 8. From the figures, linear and symmetrical feature can be observed for both the compositions. This implies that the cells have excellent electrochemical reversibility and capacitive characteristics. It can be seen that for all the current densities, only a minimum IR drop was observed up to 500 cycles.

From the $E-t$ relationship, which is mostly linear, it is observed that these composite electrodes behave as a good capacitor electrode and highly symmetric charge–discharge curves indicate good cycling stability. Hence this material is a suitable active electrode material for supercapacitor. Increased capacitance may also be due to defect rich zinc oxide, which may help in the movement of ions. In the case of zinc oxide, the deviations in the zinc to oxygen ratio leads to ‘empty’ oxygen sites. These sites are potential wells that can trap either one or two electrons. In addition to this the interstitial occurrence of zinc ions, which are shallow donors, promotes the ionic conductivity. Oxygen vacancies create deep levels of donors, which create bulk extrinsic defects. These involve the presence of heteroatoms by substitution for zinc. Depending on heteroatoms type, they may produce either shallow or deep levels in the band gap of ZnO. In the present investigation the preparation condition of the composite electrodes helps in getting high defect content of zinc oxide with aerogel, in increasing charge carriers, and enhancing double layer capacitance.

The charge–discharge cycle stability of ZnO/CA electrode was also investigated and is given in Fig. 9. As seen from Fig. 9, the specific capacitance value is constant even up to 500 cycles for different current densities. This implies that there is no formation of dendrites of Zn and the ZnO/CA composite electrode has excellent high charge–discharge cycle stability. The surface chemistry of the zinc oxide/carbon aerogel electrodes contributes the superior electrochemical performance of this symmetric supercapacitor. Though the two compositions (1:1 and 2:1) give similar electrochemical activity, the EIS and SEM studies prove that 2:1 composition is giving better performance for charge-storage.

The charge–discharge curves performed the symmetrical triangular wave and the potential behavior was approximately linear. Based on the charge–discharge curves, the capacitance of the mixed oxide electrode/carbon aerogel was calculated to be 375 F/g at 75 mA/cm², which further indicated that ZnO/CA exhibit good electrochemical capacitive characteristics. It is noteworthy that ZnO in carbon matrix shows good electrochemical stability. Hence we proved that ZnO is an active electrode material for supercapacitor applications and due to its combination with carbon aerogel the dendrite formation was controlled as it maintained the stable specific capacitance.

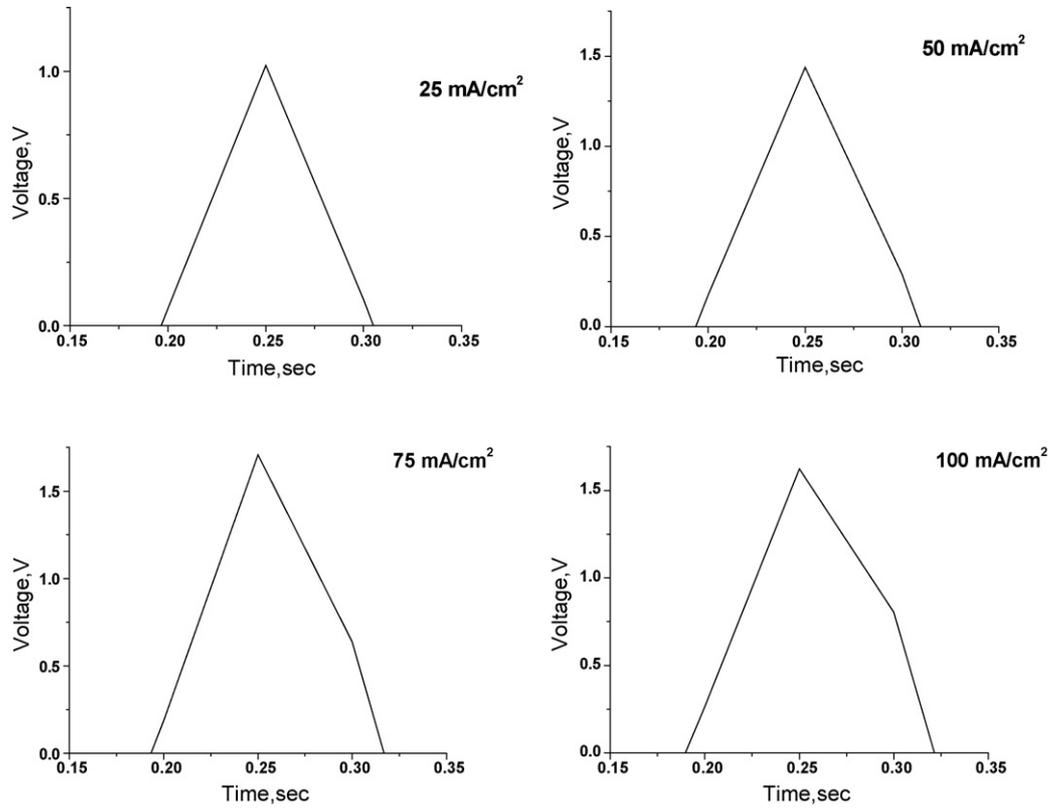


Fig. 7. Typical charge/discharge curves of ZnO/carbon aerogel (1:1) at various current densities.

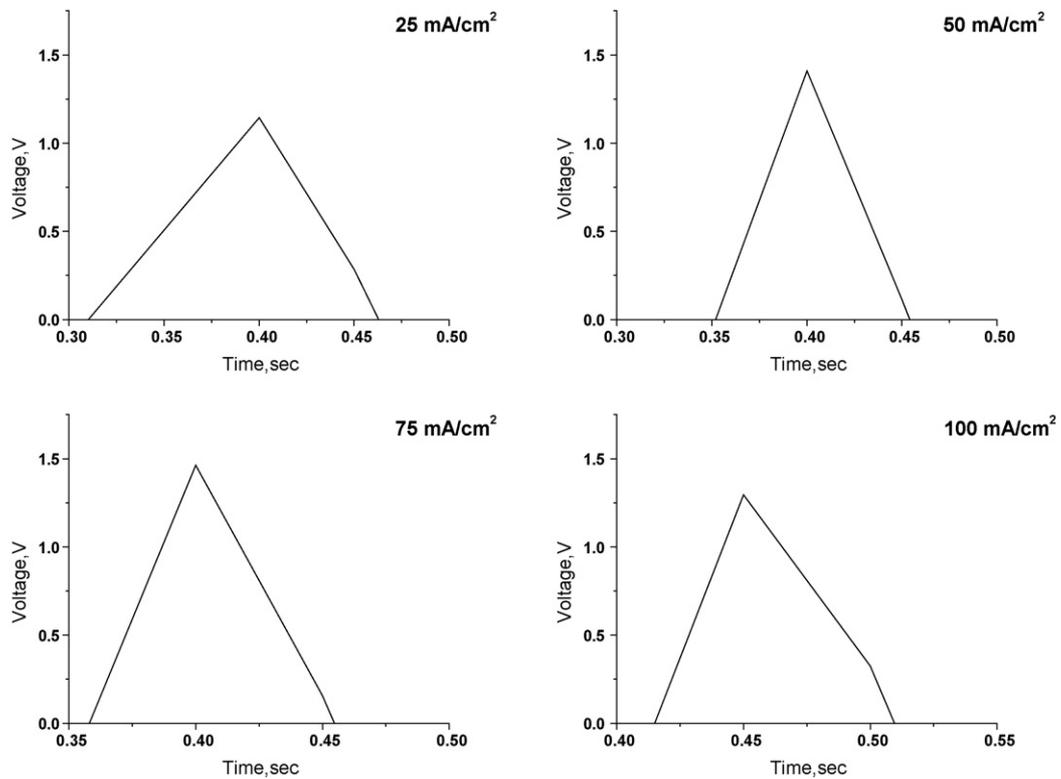


Fig. 8. Typical charge/discharge curves of ZnO/carbon aerogel (2:1) at various current densities.

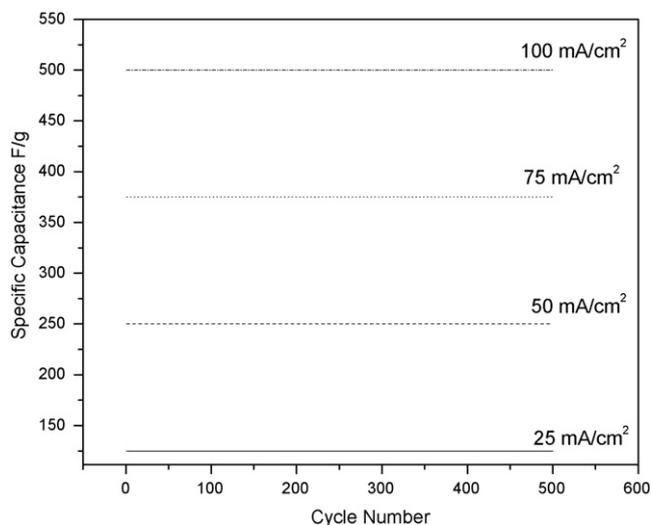


Fig. 9. Cycle number vs. specific capacitance of ZnO/carbon aerogel at different current densities.

4. Conclusion

ZnO was synthesized by a simple co-precipitation process. ZnO has the hexagonal structure and the average grain size is 8 nm. The CV and EIS tests proved that ZnO has good power and capacitive behavior. Since ZnO is cheap, and when it is mixed with carbon aerogel, the zincates formation is prevented

and it delivers excellent capacitive properties. Hence we suggest that ZnO/CA composites are promising super capacitive active materials.

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