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Solution Combustion Synthesis of Fe_2O_3/C, Fe_2O_3-SnO_2/C, Fe_2O_3-ZnO/C Composites and their Electrochemical Characterization in Non-Aqueous Electrolyte for Supercapacitor Application

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Single and mixed metal oxide/carbon composites like Fe_2O_3/carbon, Fe_2O_3-SnO_2/carbon, Fe_2O_3-ZnO/carbon are synthesized by a simple self-propagating solution combustion method. Carbon is introduced in-situ during the preparation of metal oxides in the form of dextrose precursor which act as both fuel and carbon source. The composites are characterized by XRD, SEM-EDAX and elemental CHNS analysis. The carbon content in the composite oxides is found be 19.3%, 17.8%, and 13.1% respectively. Electrochemical characterization is done by cyclic voltammetry in acetonitrile with 0.1 M lithium perchlorate supporting electrolyte. The specific electrochemical double layer capacitances are: Fe_2O_3/carbon, 255 Fg^{-1}; Fe_2O_3-SnO_2/carbon, 78.6 Fg^{-1}; Fe_2O_3-ZnO/carbon, 122 Fg^{-1} respectively.

Keywords: Fe_2O_3/carbon composite; Fe_2O_3-SnO_2/carbon composites; Fe_2O_3-ZnO/carbon composite; Solution combustion synthesis; Super capacitor

1. INTRODUCTION

The research on oxide materials in various combinations and permutations is happening in recent times in view of their phenomenal use as electrode materials in electrochemical double layer capacitor (EDLC) or super capacitor (SCs). They are virtually charge storage devices and can be used as physical batteries. EDLCs fill up the gap between the batteries and the conventional capacitors, allowing applications for various power and energy requirements i.e., back up power sources for electronic devices, load-leveling, engine start or acceleration for hybrid vehicles and electricity storage generated from solar or wind energy. The electrical double layer capacitor (also termed as EDLC) uses carbon as the main electrode material. This device is commercialized by companies like Maxwel, Evans, APCOS, VX, Cooper, ELNA (USA), Matsushita, Asahi glass, Eina Shizuki, Nippon-chemicon, Nichicon, Panasonic (Japan), Tokin, Samsung, Ness (Korea), Tavrima (Canada), ESMA (Russia), and Cap-XX (Australia) [1]. One major disadvantage of carbon based EDLC is the lower specific stored energy. Most of available commercial products have a specific energy below 10 Wh/kg, whereas the lowest figure for batteries is 35-40 Wh/kg, in the case of lead-acid ones, but value as high as 150 Wh/kg is available for rocking chair lithium ion batteries.

Metal oxides present an attractive alternative as an electrode material because of high specific capacitance at low resistance, possibly making it easier to construct high energy, high power supercapacitors. It is proved that the presence of metal oxide improves the capacitance by 10-100 times higher. When metal oxides/ metal oxide and carbon composite/conducting polymer and carbon composite are used as electrodes for the construction of EDLCs, the charge storage mechanism includes both double layer capacitance and pseudo capacitance which result in higher capacitance output. Many researchers have reported on the competence of transition metal oxides and semiconducting oxides (with and without carbon as additive) as electrode materials for EDLCs. A recently published review gives a summary of metal oxides used in these devices [2].

The main aim of the present work is to synthesize single as well as mixed metal oxide/carbon composite by a simple solution combustion method and study their electrochemical properties which would help to screen them as electrode materials in supercapacitors. The chosen oxides were Fe_2O_3/carbon, Fe_2O_3-SnO_2/carbon and Fe_2O_3-ZnO/carbon composites; carbon is introduced in-situ during the preparation of metal oxides in the form of dextrose precursor which act as both fuel and carbon source. Electrochemical characterization was done by cyclic voltammetry in acetonitrile with lithium perchlorate supporting electrolyte. The composites were characterized by XRD (X-ray diffraction), SEM-EDAX (Scanning electron microscopy equipped with energy dispersive X-ray analysis) and elemental CHNS analysis.

2. EXPERIMENTAL PART

2.1. Self-propagating solution combustion synthesis

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 becomes 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. In our earlier work, we reported the synthesis of ZnO/carbon composite using this method [3].

In this method, dextrose was used as a source of carbon as well as the fuel. The molar ratio of chosen precursors was 1:1 in all the composite oxides. For the synthesis of Fe_2O_3/carbon composite, the following chemicals were taken: $Fe(NO_3)_2.9H_2O$, 20 g; dextrose, 8.92 g. For the synthesis of Fe_2O_3-SnO_2/carbon composite, the following chemicals were taken: $Fe(NO_3)_2.9H_2O$, 5 g; $SnCl_2.2H_2O$, 5 g ; dextrose, 5.3 g. For the synthesis of Fe_2O_3-ZnO/carbon composite, the following chemicals were taken: $Fe(NO_3)_2.9H_2O$, 10 g; $Zn(NO_3)_2.6H_2O$, 10 g ; dextrose, 10.5 g. The metal salt precursors and dextrose 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 to give the desired products.

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 and FRA softwares. Both softwares were used for all electrochemical data analysis. The reference electrode was Ag/AgCl (3M KCl) and the counter electrode was a platinum foil supplied along with the instrument. Non-aqueous solvent was acetonitrile (ACN) with 0.1 M $LiClO_4$ supporting electrolyte. Pellets (9 mm dia. 4mm thickness) made by pressing the active materials were used as the working electrodes. 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). SEM-EDAX analysis was done using scanning electron microscope, Leo 440 (Germany) equipped with an Econ 4 detector (EDAX, USA).

3. RESULTS AND DISCUSSION

3.1. Material characterization

Fig. 1 shows the XRD pattern and SEM image of Fe_2O_3/C composite. The XRD pattern confirms the formation of Fe_2O_3 in accordance with JCPDS file No.13-0534. The as prepared powder was amorphous and the XRD image could not be recorded. The powder was calcined at 700º C which shows the crystalline phase. SEM image shows irregular sized and shaped agglomerated particles in the micro-scale range. At the background, one could see on enlargement of the image (~500), a cluster of noodle like particles shaped like hexagons; they are carbon particles retaining the skeleton of dextrose molecules.

Fig. 2 shows the XRD pattern and SEM image of Fe_2O_3-SnO_2/C composite. The XRD pattern can indexed to both Fe_2O_3 (JCPDS file No.84-0307) and SnO_2 (JCPDS file No.41-1445). Peaks of SnO_2 appeared at much higher intensity than that of Fe_2O_3. The SEM image of Fe_2O_3-SnO_2/C composite displays an assorted mass of agglomerated particles with no definite shape or size. This is expected due to the limitation of the technique which allows only short duration of time.

Fig. 3 shows the XRD pattern and SEM image of Fe_2O_3-ZnO/C composite. The XRD pattern of the calcined mixed oxide matches to that of $ZnFe_2O_4$ in accordance with JCPDS file No.22-1012. In contrast to Fe-Sn/C composite, the corresponding zinc based composite has formed a spinel on calcination. The SEM image of the as prepared composite shows large platelets of the ZnO co-existing with irregular mass of Fe_2O_3 particles.

EDAX analysis of the metal oxide/carbon composites revealed the following composition: for Fe_2O_3/C, Fe- 66.9% O- 27.7%; for Fe_2O_3-SnO_2/C, Fe- 8.03%, Sn - 38.5% O-36.2%; for Fe_2O_3-ZnO/C, Fe-18.1%, Zn-26.17%, O-26.1%. CHNS elemental analysis revealed the carbon content in the composites as: Fe_2O_3/C; C = 19.3%, Fe_2O_3-SnO_2/C; C = 17.8%, Fe_2O_3-ZnO/C; C = 13.1%.

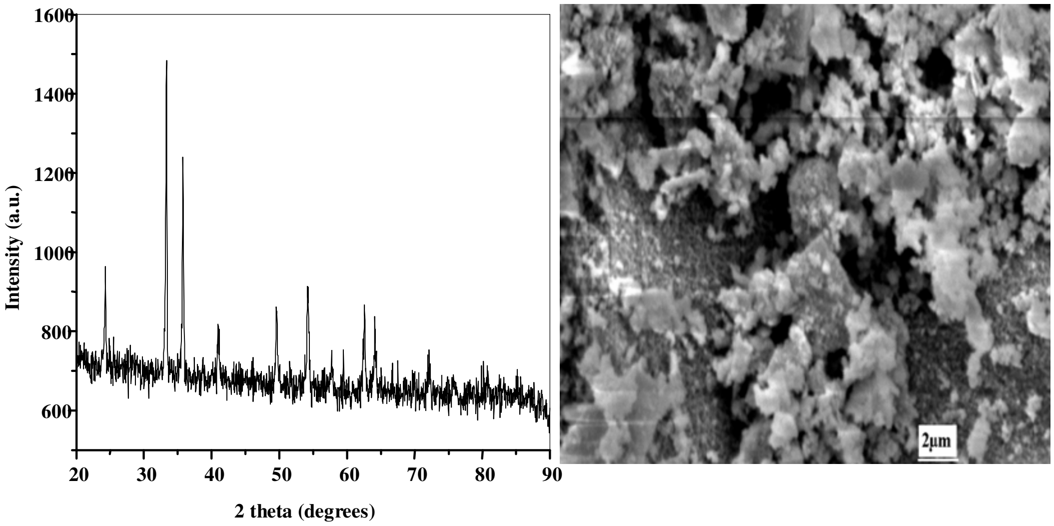

Figure 1. XRD pattern (calcined) and SEM image (as prepared) of Fe_2O_3/C composite

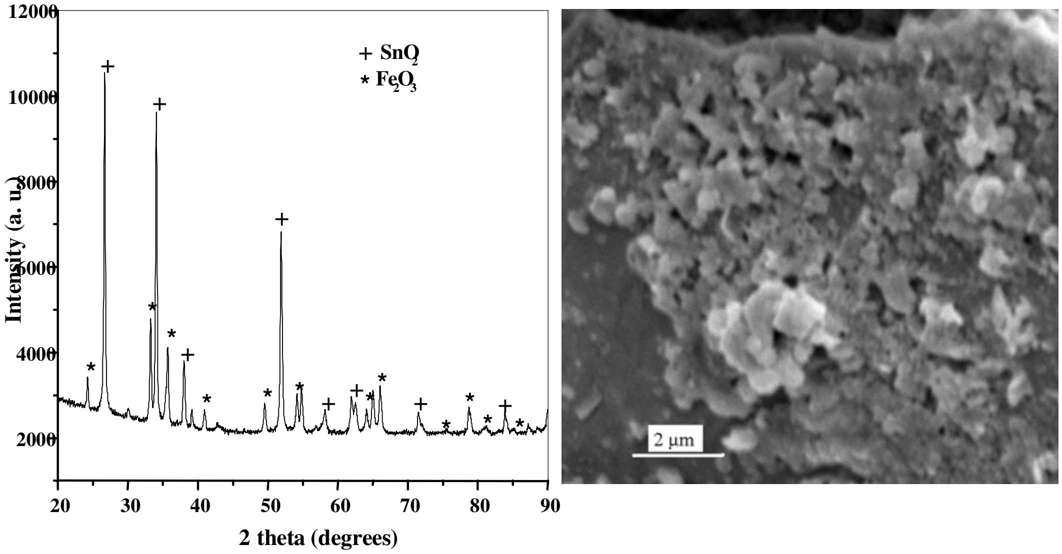

Figure 2. XRD pattern (calcined) and SEM image (as prepared) of Fe_2O_3-SnO_2/C composite

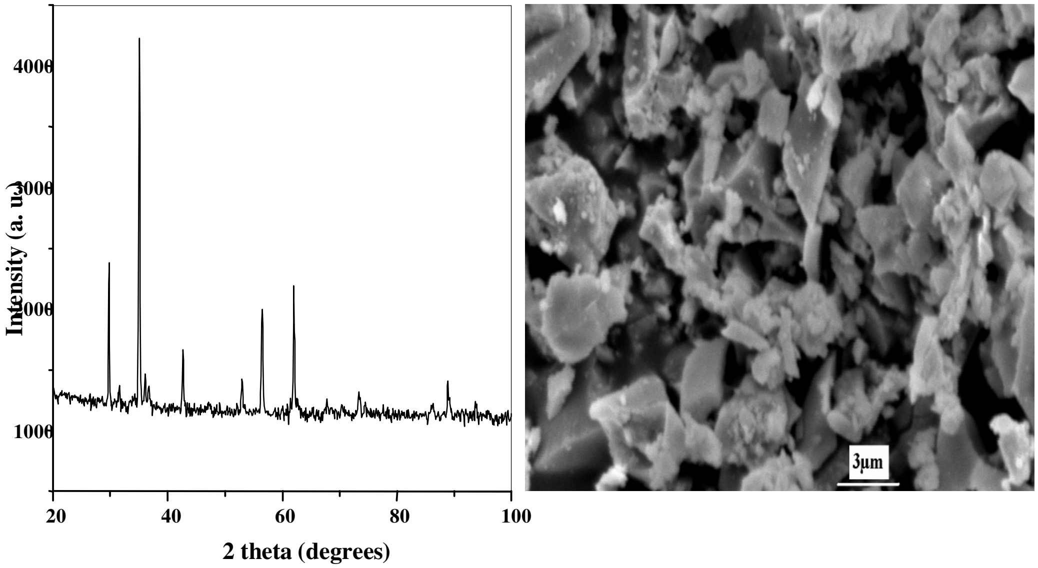

Figure 3. XRD pattern (calcined) and SEM image (as prepared) of Fe_2O_3-ZnO/C composite

3.2. Cyclic voltammetric studies

Fig. 4 shows the cyclic voltammograms (CVs) recorded for Fe_2O_3/C composite in acetonitrile (ACN) with 0.1 M $LiClO_4$ supporting electrolyte at different scan rates. 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 [4]. Capacitance is expressed as,

$$C = dq/dE \text{ or } C = I\, dt/dE$$

For the calculation of specific capacitance (F g^{-1}) from CV measurements, the following equation is used:

$$C = [i(A) \text{ x } t(s)/ w(g) \text{ x } \Delta E(V)]$$

where all the terms has the usual meaning. The cyclic voltmmetric behavior of Fe_2O_3/C conform to the typical capacitive behavior at the scan rates of 200, 500, 700 and 1000 mVs^{-1}; Table 1 shows the specific capacitance values calculated from the forward scan of CV curves at all scan rates. The high values of specific capacitance ~250 Fg^{-1} is due to the charge separation at the electrode/electrolyte interface; such a capacitive behavior of a semiconductor electrode in contact with a conducting electrolyte is usually attributed to potential dependent intrinsic capacitance associated with the electronic state distribution. A combination of several factors such as the particle size, a good electronic conductivity between particles and the presence of a surrounding equipotential surface plays a role which in turn displaces the Fermi level toward the semiconductor conducting band producing a homogeneous increase in the electron concentration in the electrode surface. Once the Fe_2O_3/C electrode is immersed in ACN/$LiClO_4$ electrolyte, primarily physisorption or chemisorption of Li^+ ions on the electrode surface would create a layer of positive charges within the Helmholtz boundary on the solution side. As the energetics of the band edges of Fe_2O_3-C / electrolyte system are controlled by the charges in the Helmholtz inner layer, for charge neutralization a layer of negative charges will be aligned on the solid side (electrode) of the double layer. Such an alignment of charges leads to the formation of an ideal electrochemical double layer which stores charges and acts as a supercapacitor electrode. The extent to which it can hold charge depend on the identity and nature of the electrode material as well as that of the electrolyte.

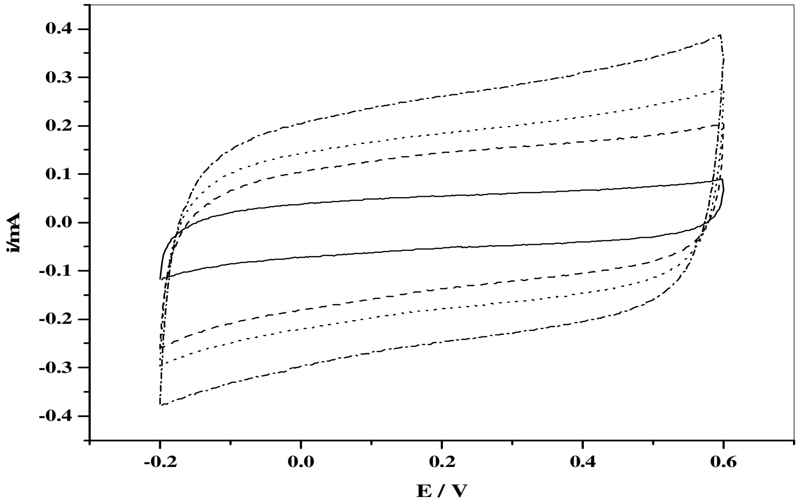

Figure 4. Cyclic voltammograms of Fe_2O_3/C composite in acetonitrile + 0.1 M $LiClO_4$ at different scan rates: — 200 mVs^{-1}; – – 500 mVs^{-1}; ….. 700 mVs^{-1}; -.-.-. 1000 mVs^{-1}

Table 1. Specific capacitance values calculated from the cyclic voltammograms of metal oxide/carbon composites in acetonitrile + 0.1 M $LiClO_4$ electrolyte at different scan rates

Scan rate (mV)	Electrochemical capacitance (Fg^{-1})		
	Fe_2O_3/C	Fe_2O_3-SnO_2/C	Fe_2O_3-ZnO/C
200	254.9	78.6	122.4
500	263.0	79.1	124.8
700	251.6	78.6	123.3
1000	251.5	77.2	122.0

Any change in charge in that layer changes the measured flat band potential and subsequently the energetics of the band edges. For a metal oxide semiconductor electrode, it is proven that the current onset potential can be assigned to the flat band potential and in the presence of double layer capacitance alone and the charging current will start at the flat band potential, becomes constant at a constant scan rate of potential. The rate of charge transfer depends on the diffusion of anions and cations towards the oxide/solution interface as well as the overlap of the electronic levels in the solid with the redox species in the solution [5, 6]. Application of external bias (as in the cyclic voltammogram) to the Fe_2O_3/C electrode subsequently will lead to the following changes: (1) surface charging changes the potential difference across the Helmholtz layer, producing an upward shift of the CB (conduction band) level i.e more free electrons are available; (2) electroneutrality requires that the increase in charge of the particles, due to electrons will be balanced by a corresponding increase in positive lithium ion charge at the Fe_2O_3-C/solution interface; (3) charge accumulation being an indispensable prerequisite to align the band edges, the adsorption of positive ions would shift the band edge (CB) towards positive direction in the forward anodic scan; (4) on the reverse negative scan, the adsorption of negative ions would shift the band edges (VB) towards negative direction. This explains the near constancy of the capacitance values in both anodic and cathodic scans [7].

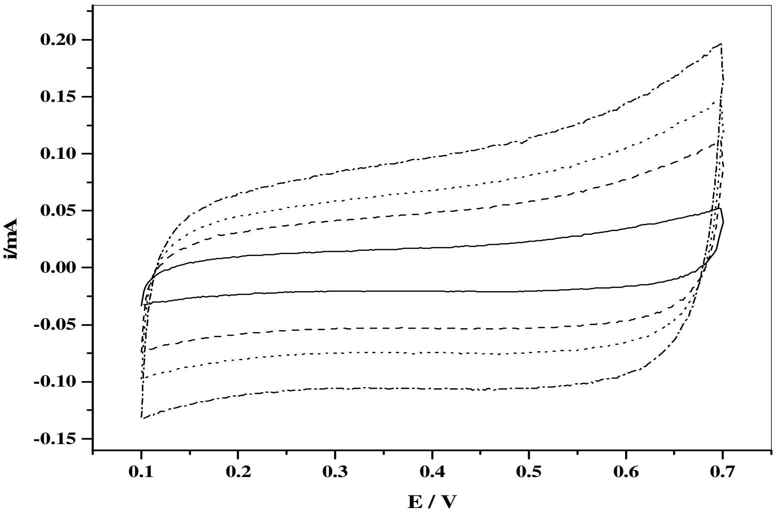

Figure 5. Cyclic voltammograms of Fe_2O_3-SnO_2/C composite in acetonitrile + 0.1 M $LiClO_4$ at different scan rates: — 200 mVs^{-1}; – – 500 mVs^{-1}; ….. 700 mVs^{-1}; -.-.-. 1000 mVs^{-1}

The CVs recorded for Fe_2O_3-SnO_2/C composite electrode in ACN/$LiClO_4$ electrolyte at the scan rates of 200, 500, 700 and 1000 mVs^{-1} were shown in Fig. 5 and Table 1 shows the specific capacitances calculated for the same. The electrochemical capacitance values may be averaged to ~77 Fg^{-1}; this reduction in values in the mixed oxide as against the single iron oxide is singularly interesting. In our previous works on mixed oxides in aqueous electrolytes, presence of SnO_2 to either alumina or V_2O_5 tends to increase the net electrochemical capacitance values [8, 9]. In fact, SnO_2 has been tried as anode material for Li-ion batteries where non-aqueous electrolytes are used [10, 11]. In the earlier works, it was reported that the SnO_2-Fe_3O_4 has a lower specify capacitance of 33 Fg^{-1} as against the single oxide Fe_3O_4 which showed a specific capacitance of 30-510 Fg^{-1} depending on the scan rate; however, the electrolytic system used was aqueous solutions [12, 13].

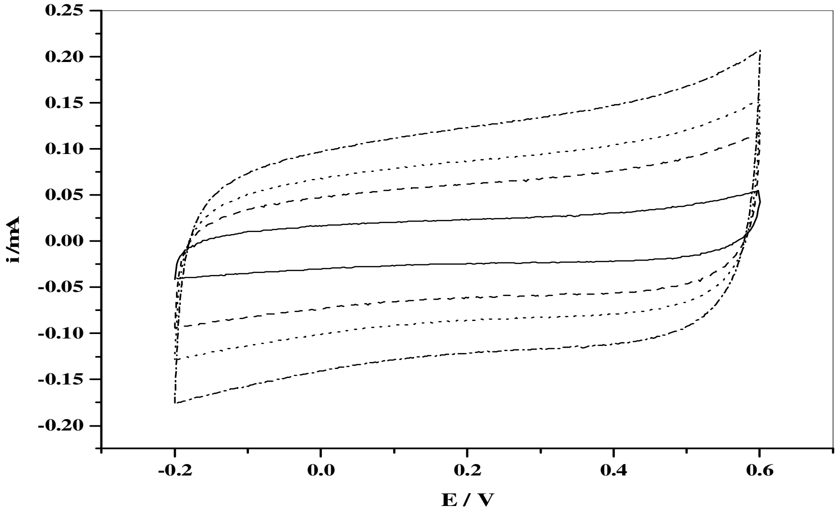

Figure 6. Cyclic voltammograms of Fe_2O_3-ZnO/C composite in acetonitrile + 0.1 M $LiClO_4$ at different scan rates: — 200 mVs^{-1}; – – 500 mVs^{-1}; ….. 700 mVs^{-1}; -.-.-. 1000 mVs^{-1}

Fig. 6 shows the cyclic voltammograms (CVs) recorded for Fe_2O_3-ZnO/C composite in ACN/$LiClO_4$ supporting electrolyte and Table 1 shows the specific capacitance values calculated at various scan rates. The value was ~ 122 Fg^{-1}; for this mixed oxide composite, the specific capacitance value is higher than the Fe_2O_3-SnO_2/C but lower then the Fe_2O_3/C composite. The value of 122 Fg^{-1} was an appreciable capacitance output, but the reason beyond the reduction as against the single iron oxide remains to be explained.

Under the experimental conditions envisaged, i.e the non-faradic charge transfer conditions, the forward (anodic) scan of oxidation produces electrons which accumulates on the solid side of the double layer; on the other hand, Li^+ 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. Reduction in such storage of charge leads to a reasonable assumption that the charge separation at the oxide/solution interface of Fe_2O_3-SnO_2/C or Fe_2O_3-ZnO/C electrode was not as effective as Fe_2O_3/C electrode. The reason for this unexpected and anomalous behavior can be explained by borrowing some basic ideas from semiconductor physics which may not be relevant to the present work. In our earlier works, we explained the undue voltage windows of ZnS in aqueous medium and higher capacitance of SnO_2-Al_2O_3 using the concept of band bending of CB and VB bands associated with the adsorption of positively and negatively charged ions at the semiconductor/solution interface [7, 8].

4. CONCLUSIONS

Among the composite oxides of Fe_2O_3/carbon, Fe_2O_3-SnO_2/carbon, Fe_2O_3-ZnO/carbon composites synthesized by the solution combustion method, Fe_2O_3/carbon gave the best results. Its specific capacitance was 255 Fg^{-1} while the other two mixed oxides 78 and 122 Fg^{-1} respectively. The lesser values in the mixed oxides were attributed to the inhomogeneity in the electronic states of the mixed oxides in the solid matrix, which in turn reduced the charge storage at the double layer.

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