A Study of Effect of Electrolytes on the Capacitive Properties of Mustard Soot Containing Multiwalled Carbon Nanotubes

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Abstract

Specific capacitances of a low-cost multiwalled carbon nanotubes produced in mass level by pyrolysing mustard oil, are being evaluated by means of cyclic voltammetry in 1M solution of various electrolytes. The carbon nanotubes with an average diameter of 30 nm have been functionalized and dispersed in polystyrene matrix to obtain thin film of the electroactive species. A comparative study of single and binary mixtures of various electrolytes as well as the effect of scan rates on the electrochemical performance of the functionalized carbon nanotubes (MS-CNT) was carried out. Even if the capacitance value obtained were not very high, but the production of carbon nanotubes in mass level and the use of the CNTs-insulating PS mixture on Teflon substrate provides an economical and easily available electrode material.

Keywords: Specific capacitance, cyclic voltammetry, MS-CNTs, electrolytes.

Introduction

Supercapacitors, occupying a region between batteries and dielectric capacitors have been touted as a solution to the mismatch between the fast growth in power required by devices and the inability of batteries to efficiently discharge at high rates[1-10]. A number of reviews have discussed the science and technology of supercapacitors for various configurations and electrode materials[11-13]. Carbon in its various forms, is currently the most extensively examined and widely utilised electrode material, achieving high surface-area with low matrix resistivity.

Incidentally discovered carbon nanotubes, now have been recognized as potential electrode material for electrochemical super capacitors[14-16]. However, due to microtexture defects, micropore volume and catalyst contamination, its specific capacitance is restricted to low values. Several works have been reported in the literature[17-21] to increase the specific capacitances of the carbon nanotube electrodes by oxidation[17,18], plasma treatment[21], and by the formation of carbon nanotube - conducting polymer composites[16,18,21].

There is another aspect of super capacitors, related to the effects of the electrolytes which is in practical use. In the present work, the super capacitive behavior of the multiwalled carbon nanotube, produced by pyrolyzing mustard oil (MS-CNTs) was studied in the presence of different electrolytes using cyclic voltammetry at different scan rates in order to optimize the conditions. The work was mainly focused on a comparative study of several electrolytes individually, and also using their combinations. Since, the mesoporous character of as-received nanotubes essentially determine their electrochemical properties, hence in this paper, we have tried to see the effect of increase of microporosity of nanotubes using nitric acid.

Material and methods

Preparation of carbon nanotubes based electrode material: The carbon nanotube was synthesized by pyrolyzing mustard oil in presence of air, purified and functionalized and the carboxylated MS-CNTs with an average diameter of 10-30 nm was confirmed by SEM and TEM images. Weighed amount of MS-CNT was dispersed in a solution of polystyrene in dichloroethane in 9:1 ratio and sonicated. A drop of the sonicated slurry, containing a known concentration of MS-CNT was dropped on Teflon substrate having dimensions of 3.4 x 1.0 x 0.05 cm, dried in air and used as electrode material.

Type of electrolytes taken: The electrochemical measurements were conducted using five electrolytes viz. potassium carbonate (K_2CO_3), potassium chloride (KCl), sodium chloride (NaCl), sodium sulphate (Na_2SO_4) and magnesium sulfate ($MgSO_4$) individually, as well as with their binary mixtures. In order to investigate the actual role of different electrolytes on the capacitive behavior of MS-CNT and to optimize the measurement conditions, 1M aqueous solution of each of the electrolytes has been maintained.

Instrumentation: The cyclic voltammetric (CV) measurement was performed using the DropSens portable minipotentiostat (µStat100), employing a three electrode experimental set up. The minipotentiostat consisted a hand-held USB powered instrument, connected to a PC by means of an USB cable, for use with electrochemical sensors or electrochemical cells. The MS-CNT coated on Teflon substrate served as the working as well as the counter electrode. Silver was used as the reference electrode and for all electrical contacts.

Results and discussion

The effect of different electrolytes was carried out with respective aqueous solution of five electrolytes viz. 1MK_2CO_3, 1M KCl, 1M NaCl, 1M Na_2SO_4 and 1M $MgSO_4$ as well as four sets of their binary mixtures, viz. 1M KCl - 1M K_2SO_4, 1M KCl - 1M $MgSO_4$, 1M KCl - 1M Na_2SO_4 and 1M NaCL - 1M Na_2SO_4, at varied scan rates from 10 to 1000 mVs^{-1}.

The voltammetric responses of MS-CNT electrode in 1M aqueous solution with single electrolytes are shown in Fig.1. Nearly same profile was observed for all the five samples showing the linear dependence of the voltammetric currents on the scan rate of CV. The figure also represents the specific capacitances of MS-CNT electrode as a function of the scan rate. As expected the capacitance decreases with increasing scan rates. This phenomenon, in fact, is found in the case of all single and binary mixtures of electrolytes indicating that the charge- discharge currents are typically capacitive-like.

The decrease of capacitance value with the increase in scan rate has been attributed to the resistance of ion diffusion with certain micropores (especially the micropore surface partially accessible to electrolytes) which becomes significant under relatively high scan rate due to the differential depletion of the electrolyte concentration. In addition, the proportion of these inaccessible micropores also increased with increasing the scan rate of CV, therefore a monotonous decrease in the specific capacitance is observed accordingly. In this case, the decrease is more pronounced, when the scan rate was increased from 10 mVs^{-1} to 30 mVs^{-1}.

It is almost clear that a maximum capacitance value in the case of all types of electrolytes (single or mixture) can be obtained at the lowest scan rate of 10mVs^{-1}. The specific capacitance value of a single electrolyte follows the order 1M $MgSO_4$> 1M NaCl> 1M Na_2SO_4,> 1M KCl> 1M K_2CO_3 at the same scan rate. Here the conductivity, mobility of cations and anions, and size of the hydration spheres may be determining factors for such a behavior of MS-CNT electrode in different electrolytes. A comparison of the specific capacitance of MS-CNT electrode in five individual electrolytes indicates the lowest capacitance value in the case of 1 M K_2CO_3. Since K_2CO_3 is a weak electrolyte hence ionic dissociation is also poor, which is responsible for its lower ionic mobility, conductivity and hence its specific capacitance.

At the scan rate of 10 mVs^{-1} the 1 M $MgSO_4$ electrolyte showed unexpectedly the highest capacitance value of 153 Fg^{-1}. However the decrease in such a value was more pronounced in $MgSO_4$, as compared to other electrolytes over fast scan rates. In case of a mixture of NaCl and Na_2SO_4, nearly similar values of specific capacitance was observed up to the scan rate of 100 mVs^{-1}, indicating neither the cation nor the anion dominates. When KCl and NaCl were compared although NaCl showed high capacitance value of 144 at 10 mVs^{-1} but at higher scan rate KCl dominates in that over NaCl which is due to higher conductivity of K^+ ions when compared to Na^+ or Mg^{+2} ion.

Figs. 2-5, present the CV responses of the MS-CNT electrode in case of four set of binary mixtures of the five different electrolytes showing their shape closer to rectangular shape with no peaks. The linear dependence of voltammetric currents on the scan rate as well as the specific capacitance as a function of scan rate of these binary combinations are shown in Fig. 6. In case of binary mixtures the value of specific capacitance follows in the order: 1M NaCl - 1M Na_2SO_4 > 1M KCl - 1M Na_2SO_4 > 1M KCl - 1M $MgSO_4$ > 1M KCl - 1M K_2SO_4 at a scan rate of 10 mVs^{-1}. After that the specific capacitance decreases but this decrease was more pronounced when the scan rate was increased from 10 to 30 mVs^{-1}. The specific capacitance of 1M NaCl-1M Na_2S0_4 was found to be highest at all scan rates even of low mobility, low conductivity and higher hydration number of Na^+ ion as compared to K^+. This suggests that there may be some kind of interactions between the MS-CNTs and the electrolytic mixtures which reduces the hydration number of Na^+ ion thereby increasing the conductivity as well as capacitance.

In the case of binary mixture of 1M KCl-1M $MgSO_4$ although comparative low value of capacitance (144 Fg^{-1}) was observed at 10 mVs^{-1} but after that the values were somehow become nearly equal to the values obtained with 1M NaCl - 1M Na_2SO_4. Here the higher mobility and conductivity of both K^+ and Mg^+ ions predominates over Na^+ ion, resulting similar values of capacitance. The mixture of 1M KCl - 1M Na_2SO_4 although showed a high specific capacitance value of 165 Fg^{-1} at a scan rate of 10mVs^{-1} as compared to 1M KCl - 1M K_2SO_4 yielding a value of 138 Fg^{-1} but both showed nearly similar behavior on increasing the scan rate, even 1M KCl - 1M K_2SO_4 showed slightly increased capacitances value at the higher scan rate. It is due to the overall effect of the presence of K^+ ion when anions are same in both the cases.

Conclusion

In the present work we did a study on the role of electrolytes on specific capacitance of carbon nanotubes produced in mass level, using cyclic voltammetry. The results showed that a highest value of specific capacitance of 212 Fg^{-1}can be achieved in the case of 1M NaCl - 1M Na_2SO_4 electrolyte, at a scan rate of 10 mVs^{-1}. The mixture of 1M KCl - 1M $MgSO_4$ although showed comparative low value of capacitance (144 Fg^{-1}) at 10 mVs^{-1} but at higher scan rate its CV response was nearly the same as observed with 1M NaCl - 1M Na_2SO_4. Hence, the overall study suggests that no single electrolyte can meet all of the essential requirements for supercapacitor applications. A suitable combination of electrolytes as well the scan rate of CV can serve the purpose and a judicious selection of both can make the process simple which may increase the potential application for the fabrication of carbon nanotube based supercapacitors.

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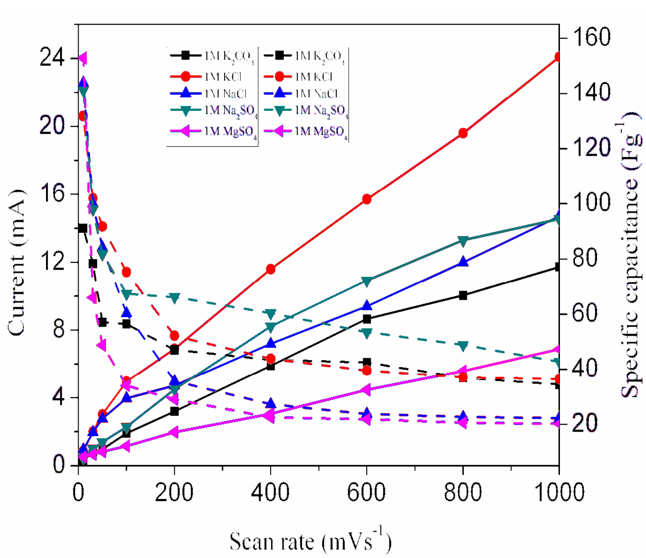

Figure-1: Specific capacitance and current of the single electrolytes as a function of scan rate (10-1000 mVs^{-1})

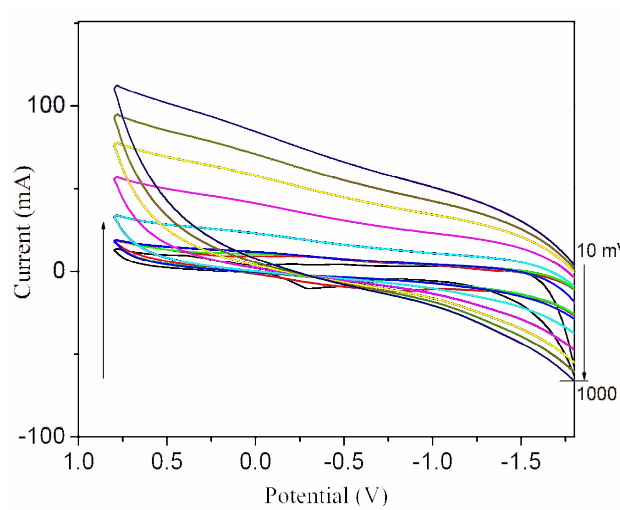

Figure-2: Cyclic voltammogram of 1M KCl-1M K_2S0_4 on CS-CNT electrode at different scan rate (10-1000 mVs^{-1})

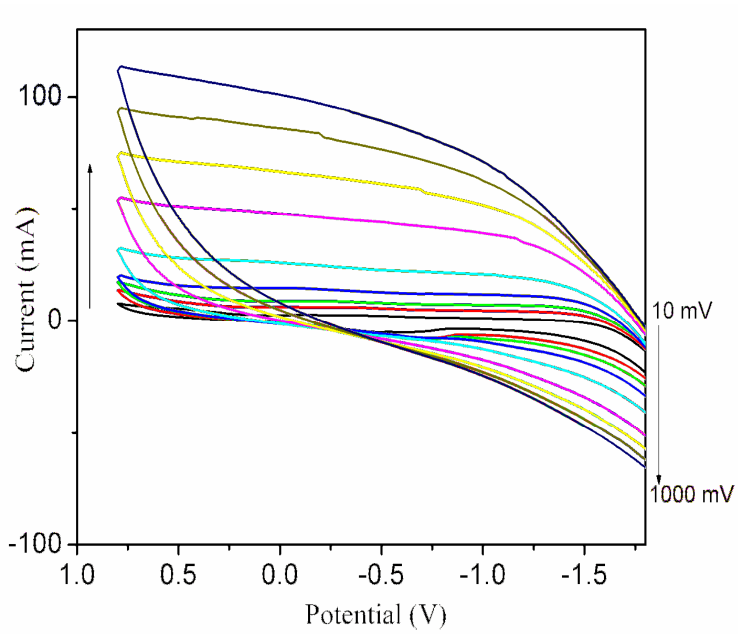

Figure-3: Cyclic voltammogram of 1M KCl-1M $MgS0_4$ on CS-CNT electrode at different scan rate (10-1000 mVs^{-1})

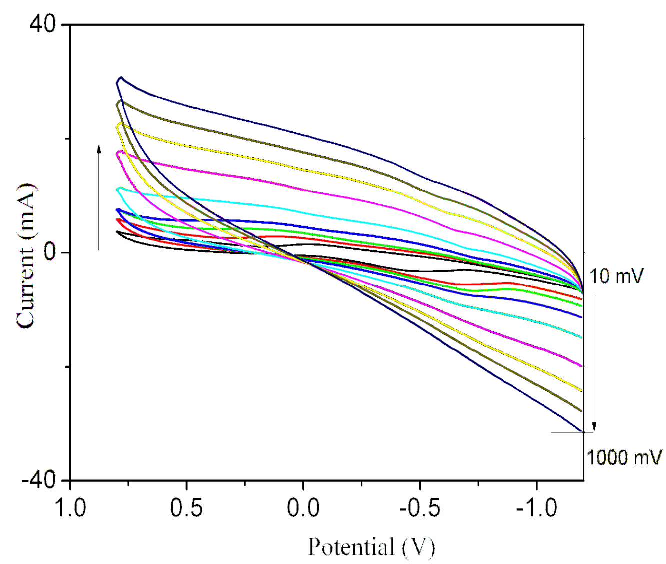

Figure-4: Cyclic voltammogram of 1M KCl-1M Na_2SO_4 on CS-CNT electrode at different scan rate (10-1000 mVs^{-1})

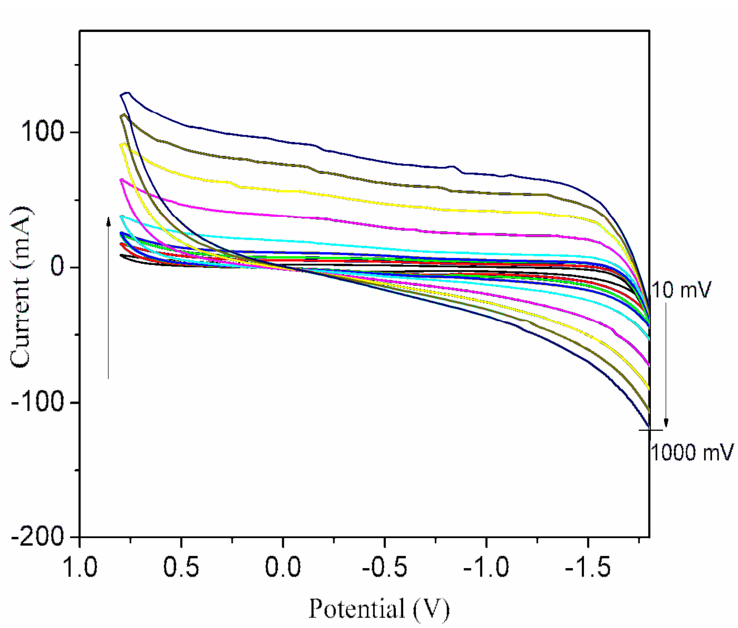

Figure-5: Cyclic voltammogram of 1M NaCl-1 M Na_2SO_4 on CS-CNT electrode at different scan rate (10-1000 mVs^{-1})

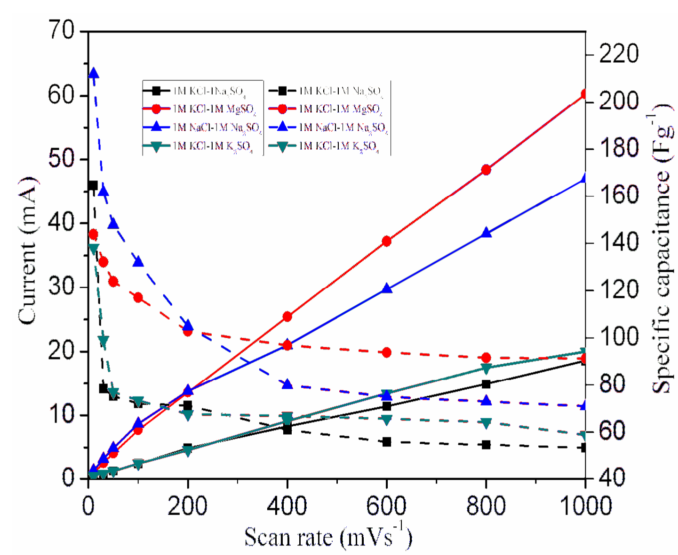

Figure-6: Specific capacitance and current values in case of four set of binary mixture of electrolytes as a function of scan rate