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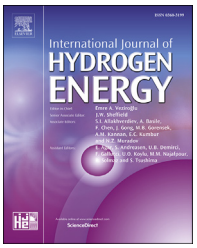

Electrochemical performance of controlled porosity resorcinol/formaldehyde based carbons as electrode materials for supercapacitor applications

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ABSTRACT

Controlled porosity carbons aerogels were synthesized by sol–gel polycondensation of resorcinol (R) and formaldehyde (F) using sodium-carbonate as the catalyst (C). The Effect of variation of R/C ratio and carbonization temperature on the porous structure of resultant gels and carbons was investigated by characterizing the porous structure of the materials using nitrogen adsorption–desorption measurements at 77 K. It was shown that carbons with surface areas ranging between 537 and 687 $m^2\ g^{-1}$ and average pore size in the range of 1.80–4.62 nm can be produced when controlling the resorcinol to catalyst (R/C) molar ratio between 100 and 500 and carbonization temperature in the range of 800–1000 °C.

The resultant polymeric carbons were used as the electroactive material for the fabrication of electrodes for electrochemical cells. Contact angle measurements were performed to study the wettability of the electrodes using 6 M KOH as the probing liquid. The contact angles were in the range of 106°–125° indicating the carbon based electrodes are hydrophobic in nature and no significant change in contact angles was observed with the change in R/C ratio.

XRD patterns of the carbon electrodes show a typical broad peak at 2θ of about 23 indicating a disordered structure corresponding to the amorphous nature of the materials as expected for polymeric based hard carbons with crosslinked structure. These results are in line with Raman spectra of carbons which indicate two peaks in 1590 cm^{-1} and 1340 cm^{-1} wavenumber.

The electrochemical performance of the electrodes was investigated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements. The CV results showed that high specific capacitance of 136 Fg^{-1} can be achieved for the carbon with average pore diameter of 1.80 nm at a scan rate of 5 mV s^{-1} when using 6M KOH as the electrolyte. Electrochemical impedance (EIS) measurements also revealed that the capacitance of the cell deteriorates with increase in pore size of the carbon probably due to pore flooding by the electrolyte. The results of this study show the applicability of these carbons as potential electrode materials for supercapacitor applications.

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Introduction

As the world's energy forecast shows, the global energy demand is going to be doubled in next 50 years [1]. With increase in energy requirement of upcoming systems and associated concerns on the depletion of fossil fuels and their environmental related effects in the planet, deployment of renewable energy sources such as wind, wave and solar will play a key role in our future energy demands. Study suggests that at the end of 2013 global renewable energy generation capacity reached 1560 GW, almost double than the estimated figure of 895 GW at the start of the year 2004 [2]. The capacity of global renewable energy generation is currently at 1707 GW [3] indicating a significant increase in the contribution of renewable energy resources to our energy demands. However due to the unpredictable and intermittent nature of these energy resources and as the security of the supply is crucial in any energy system, employment of the renewables is only possible when effective energy storage technologies commensurate with each application are developed. Batteries, fuel cells and supercapacitors are in the forefront of energy storage technologies. However due to their energy storing and releasing capabilities in limited time scales, they cannot respond to all energy requirements of future devices. Batteries and fuel cells are only effective for the storage and delivery of energy at slow rates over a long period of time [4,5]. While in high power applications when a surge of energy in a short time is required, storage technologies such as electrochemical capacitors become imperative to respond to the short term fluctuations in energy outputs and improve the quality of the energy supply. Properties such as rapid charge/discharge, exceptionally high capacitance retention and long cycle life make electrochemical capacitors as ideal candidates to complement other primary storage devices when a wide spectrum of energy and power is required [6,7]. The performance of electrochemical capacitors depends on the type of electrode and electrolyte materials used in their manufacture.

Due to its chemical inertness, exceptionally high specific surface area, electrical conductivity and tailored pore size, carbon is the most widely used electroactive material for the fabrication of electrodes in supercapacitor industry [8–10].

Polymeric carbons obtained from the pyrolysis of resorcinol–formaldehyde (RF) aerogels have been used as active material for various energy storage devices due to their desirable properties such as high porosities (>80%), high specific surface area (700–2600 $m^2\ g^{-1}$), pore volume (0.179–2.195 $cm^3\ g^{-1}$) and exceptional conductivity as a result of their three dimensional cross-linked structure. Their properties and particularly their porous structure can be tuned by the control of synthesis parameters during gel preparation and also through the control of processing conditions during carbonization and activation processes [11–13].

In this work, we have synthesized RF based carbon aerogels with controlled porosity by controlling the resorcinol to catalyst molar ratio (R/C) during the preparation of the gel precursor and also controlling the carbonization temperature during the production of carbons. The effect of porous structure of the resultant carbons when used as the electrode material with 6M KOH solution as the electrolyte in an electrochemical cell on the capacitance of the device is investigated by cyclic voltammetry (CV) measurements. Electrochemical impedance (EIS) measurements are also carried out to elucidate the effect of electrode's porosity and electrode/electrolyte interfacial resistances on the performance of the electrochemical cell.

Experimental

Synthesis of RF gels

Resorcinol (R) formaldehyde (F) aerogels were prepared by polycondensation reaction between resorcinol and formaldehyde according to the procedure explained elsewhere [13,14]. Predetermined amount of resorcinol and sodium carbonate as catalyst (C) were mixed in distilled water (W) under vigorous stirring for 45 min. Formaldehyde was added and the stirring was continued for another 45 min at room temperature. The resorcinol to formaldehyde molar ratio (R/F) and the ratio of the amount of resorcinol to the amount of water used (R/W) in g ml^{-1} were kept constant at 0.5 and 0.1 respectively whereas the resorcinol to catalyst molar ratio (R/C) was varied in the range of 100–500. The homogenous solutions were transferred into the sealed glass vails to prevent the evaporation of water during the gelation process and placed in the oven where temperature was controlled first at 25 °C for 24 h to initiate gelation process followed by increasing it to 60 °C for 72 h and further increase to 80 °C for 48 h for the completion of the gelation process. This long gelation time ensures a well-developed three dimensional gel structure. The resultant dark opaque aqua-gels were broken into small pieces and immersed in acetone for 4 days for solvent exchange to extract water from the porous structure of hydrogels completely prior to their drying. The gels then were dried under vacuum at 5 mbar and 40 °C for 4 days to completely remove acetone from the internal pores of the gel without any shrinkage [14].

Carbonization of RF aerogels

The dried RF aerogels were carbonized at different temperatures to investigate the effect of pyrolysis conditions on the porous structure of carbon aerogels. A sample of gel (≈3 g) in a ceramic boat was placed in the middle of a tubular furnace and purged with Ar at room temperature for 30 min prior to the pyrolysis. The temperature was increased at a rate of 5 °C min^{-1} to 150 °C and maintained for 30 min. The temperature was further increased to 450 °C at a rate of 5 °C min^{-1} and held for 30 min. Finally it was increased to 800 °C at 10 °C min^{-1} and the sample was kept at this temperature for 3 h before cooling it down to the room temperature. The entire process was performed under Ar flowing at rate of 240 ml min^{-1}.

Electrode preparation

Electrodes for electrochemical measurements were prepared using carbon in the form of well grinded powder. Approximately 80 wt% active carbon material, 10 wt% Cabot carbon black XC72 as conductivity enhancer and 10 wt% Kynar 2801

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