Preparation and Characterization of Glassy Carbon Monolithic Electrode for Electrochemical Analysis

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Abstract

Carbon monoliths have the advantage of being conductive materials and were therefore also investigated as electrode materials for electrochemical analysis. A glassy carbon monolithic electrodes (GCME) has been successfully prepared using an adapted method of Liang *et al.* [1]. The sample has a high specific surface area and a large pore volume. Electrochemical analysis indicated that it has fine electrochemical double-layer performance.

Electrochemical measurements obtained on the anodised glassy carbon monolithic electrodes (GCME) showed a more reproducible surface relative to the polished GCME. The electrode was investigated using cyclic voltammetry following electrochemically induced oxidation to impart hydrophilicity. The surface oxidation was studied to generate oxygen-containing surface functional groups. The electrochemical oxidation of GCME was carried using 2M NaOH and 1 M H_2SO_4, respectively. Cyclic voltammetry was investigated using a solution containing $K_3Fe(CN)_6$ and KCl between -0.2 and +1.1 V. The scan rate used for the above characterisations was 20 – 100 mV/s.

Key words: Carbon monoliths , electrode materials , electrochemical analysis

1. Introduction

Porous carbon materials have been attracting a lot of attentions due to their extensive applications in the fields of hydrogen-storage, catalysis, electrochemistry, etc. Hierarchical porous materials containing both interconnected macroporous and mesoporous structures have enhanced properties compared with single-sized pore materials due to increased mass transport through the material and maintenance of a specific surface area on the level of fine pore systems [2] and [3]. Hierarchical porous carbon materials have also been attracting attention because of their emerging applications. Shi and co-workers synthesized a carbon monolith with trimodal pores using a novel silica monolith as the template [4]. However, the macropore structure of the product was disordered. Chai and co-workers synthesized the ordered macroporous carbon with mesoporous walls by template replication of aggregates of small silica particles, which were themselves templated by a self-assembled lattice of larger monodisperse polystyrene spheres [5]. However, this method requires a complicated process.

In the present work, we synthesized ordered meso/macroporous carbon monoliths by an easy method. Our strategy is using SiO_2 opal to create three-dimensionally interconnected macroporosity, block copolymer (Pluronic F127) macromolecular templating to produce a mesoscale porosity. The as-prepared sample has a very high Brunauer-Emmett-Teller (BET) surface area and specific pore volume. Electrochemical studies showed that this meso/macroporous carbon has good electrochemical double-layer capacitance properties.

2. Experimental

2.1 Materials and Reagents.

The two reagents needed in this experiment are potassium chloride and potassium ferricyanide (III), 99% (Aldrich). Reagent water was obtained from a Millipore Milli-Q water purification unit (Millipore, Bedford, MA, USA) and was 18.2 MΩ. Class A volumetric pipets and flasks were used to prepare solutions.

2.2 Instrumentation.

Cyclic voltammetry and electrochemical oxidation were performed using a CH Instruments Model 660 Electrochemical Workstation and a three-electrode cell. All potentials quoted are with respect to a Ag/AgCl reference electrode (in 3.0 M KCl). Working electrode was GCME (5 x 17 mm), 68 mg and counter electrode was platinum mash. Potential data were saved as BIN files and plotted using a spreadsheet such as Excel.

2.3 Electrode preparation, charecterisation and electrochemical measurements

The GCME was prepared by polishing with successive slurries of 0.3 and 0.05 μm alumina in Millipore Milli-Q water on a polishing microcloth (Beuler). The electrodes were sonicated in distilled/deionized water for 15 min between slurries. GCME was characterised by cyclic voltammetry in a solution containing 10 mM $K_3Fe(CN)_6$ and 2 M KCl between -0.2 and +1.1 V. Cyclic voltammetry was performed at scan rates of 0.02–0.1 mV s^{-1}. The oxidation procedure involved poising a polished electrode at +1.80 V for a selected period of time in 1 M NaOH. A three-electrode cell was used with a Ag/AgCl/KCl(sat) reference electrode and a Pt mesh counter electrode. The cell was connected to a Model 660 potentiostat. Cyclic voltammograms of 10 mM $K_3Fe(CN)_6$ (2 M KCl) were obtained after an oxidation time of 20, 40 and 60 min, respectively.

GCME was synthesized by acid-catalysed polymerisation of a resorcinol/iron(III) complex and formaldehyde in the presence of silica beads 10 μm as a template. This rod was carbonised and graphitised under inert atmosphere with a programmed temperature cycle from room temperature to 1250 °C. Subsequently, the silica beads along with iron catalysts were removed, leaving a porous carbon rod. The precursor solution was prepared by Liang *et al.* method [1]

The mixture solution was slowly transferred into 7-mm-i.d. glass tube which was capped when filled. These tube was then placed in a 90 °C hot water bath. The mixture was soon polymerized into a solid rod inside the glass tube. The rod detached from the tube wall because of the shrinking caused by polymerisation. The polymer rod was aged in the glass tube by keeping it in the hot-water bath overnight. The crack-free phenolic resin/silica rods were removed from the glass tubes by shaking each tube toward its open end. The wet rod was kept under the hood for 3 days to evaporate the solvent, and finally, it was thoroughly dried in a vacuum oven at 80 °C overnight. The dried rods were further cured at 135 °C for 4 h to ensure complete polymerisation.

The precursor rods were placed into a programmed horizontal tube furnace and purged with N_2 (45 mL/min). The temperature was first ramped from room temperature to 800 °C at 2.5 °C/min, and then holds at 800 °C for 2 h, to ensure complete carbonisation. A second ramp took place from 800 to 1250 °C at 10 °C/min. The temperature was kept constant at 1250 °C for 1 h. Afterwards, the furnace was allowed to cool naturally to ambient temperature. The silica beads and the iron catalyst were removed by etching in concentrated hydrofluoric acid (38-40%) and washed away with copious amounts of distillated water. The porous carbon rod obtained was thoroughly dried under vacuum at 80 °C. The encapsulated glassy carbon monolithic rod 30mm was then glued into a silver wire with epoxy glue to make it as an electrode.

2.3 Scanning Electron Microscopy/Energy Dispersive X-ray Microanalyses (SEM/EDX)

Surface morphologies were examined using an Hitachi S-3000N VP (SEM/EDX) at an accelerating voltage of 20 kV. Imaging of this monolithic rod by SEM/EDX revealed a highly interconnected bimodal porous structure.

2.4 BET surface area measurements

Further investigation of the sample surface area and the pore volume was performed using Brunauer-Emmett-Teller (BET) surface area measurement equipment (Micromeritics Gemini Ltd. 2375, Georgia, USA).

Full nitrogen absorption/desorption measurements were performed. Typically, a 0.05-g piece of carbon monolith was used. The pore size distribution and the surface area of the sample were derived from the BET isotherm by using the supporting software of the instrument.

3. Results and discussion

A photograph of the glassy carbon monolithic structure is shown in figure 1. Figure 1a shows the SiO_2 template was well replicated. Figure 1b shows the SEM image of the SiO_2 template, which was dispersed in 1.5 g of 1-Butanol by sonication for 1h before the polymerisation reaction of a resorcinol/iron (III) complex and formaldehyde took place. Macropores are clearly observed in figure 1c. Figure 2a shows a glassy carbon monolithic rod (GCMR) and 2b a glassy carbon monolithic electrode (GCME). The pore diameter was estimated as about 10 nm. Energy-dispersion X-ray spectra (EDX) shows (Figure 3) that the product is constructed by pure carbon without any detectable Si element.

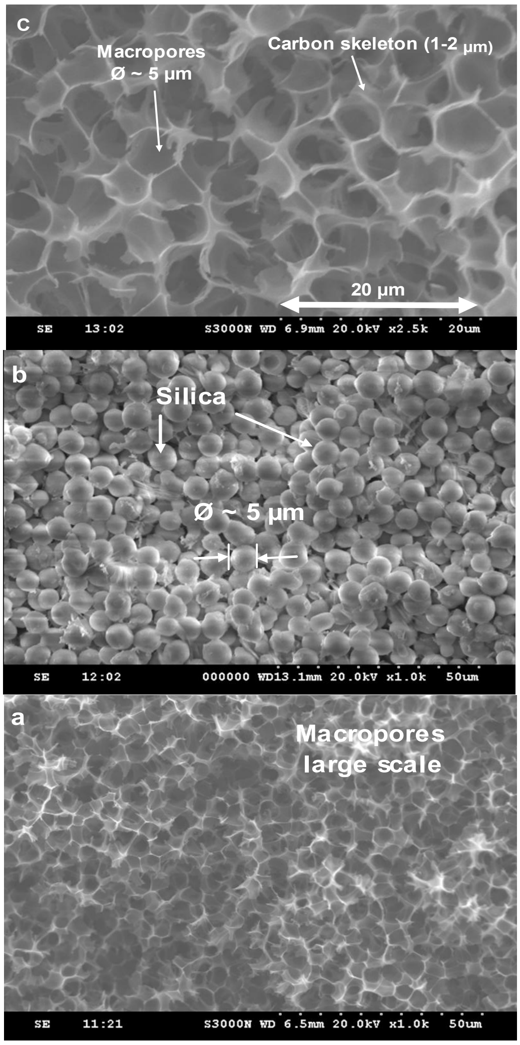

Figure (1a and **c**) SEM images of carbon monolith structure; and (**b**) SiO_2 template

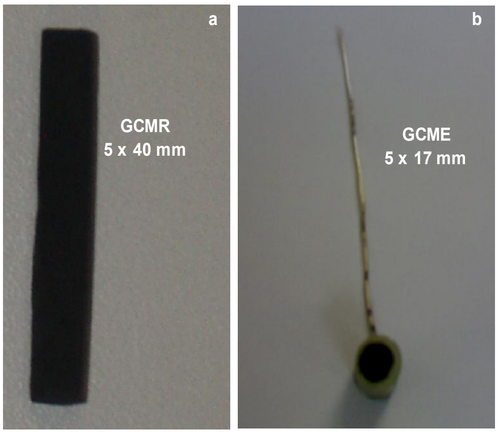

Figure 2(a). Glassy carbon monolithic rod (GCMR). (**b**) Glassy carbon monolithic electrode (GCM

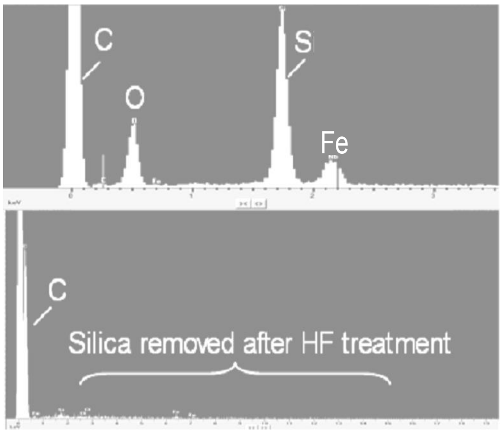

Figure 3. EXD analysis showing elimination of silica following HF treatment

The N_2 sorption isotherms (Figure 4a) of meso/macroporous carbon show typical curves for mesoporous materials, with a sharp capillary condensation step at high relative pressures (P/P_0=0.8–0.9), which is similar to large-pore mesoporous silica FDU-12 [6]. The pore size distributions from the adsorption and desorption branch are shown in figure 4b. The adsorption average pore diameter is about 10nm [7], which was basically consistent with the results of SEM and TEM. The meso/macroporous carbon had a large BET surface area of 124 $m^2 g^{-1}$, and a pore volume of 0.32 $cm^3 g^{-1}$.

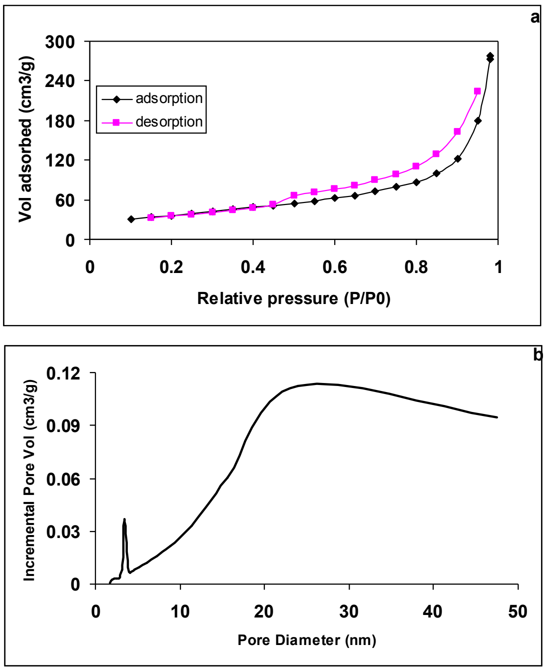

Figure 4: (a) BET nitrogen adsorption-desorption isotherm 10 µm carbon Monolith, **(b)** The pore size distributions

The unique porous system, the large BET surface area and the large pore volume of macroporous carbon are expected to favor electrolyte transfer in the pore system and increase the carbon–electrolyte interfacial area. Therefore, we use macroporous carbon to fabricate the electrode of electrochemical capacitors. The working electrode was prepared according to the literature [1]. Cyclic voltammograms and potentiostatic charge/discharge cycling measurements were carried out in 2 M KCl in a half-cell setup configuration at room temperature. A platinum mash electrode and a saturated Ag/AgCl electrode served as the counter electrode and reference electrode, respectively. Figure 5a shows the cyclic voltammetric behavior of the electrodes at different CV scan rates, which is the typical shape of electric double-layer capacitance. The Potentiostatic charge/discharge curve of the sample was shown in figure 5b. Almost no internal resistance drop can be detected, which indicated that the sample has good conductivity and small resistance [8]. The triangle shape also proves its good capacitive behavior. The corresponding specific capacitance of the sample is calculated from the following expression: $C = (It) / (mV)$, where I is the discharge current, t the total discharge time, m the mass of active material, V the potential drop during discharging and C the specific capacitance. The intrinsic capacitance of GCME is calculated to be about 130 F g^{-1} at a constant potential of 1.8 V, which is larger than those of commercially available active carbon (19 F g^{-1}), carbon black (10 F g^{-1}) and carbon aerogel (23 F g^{-1}) [9]. This high value is probably attributed to the novel structure of GCME. The unique GCME can facilitate electrolyte transfer to the mesopore, which could make full use of the inner surface of the electrode materials.

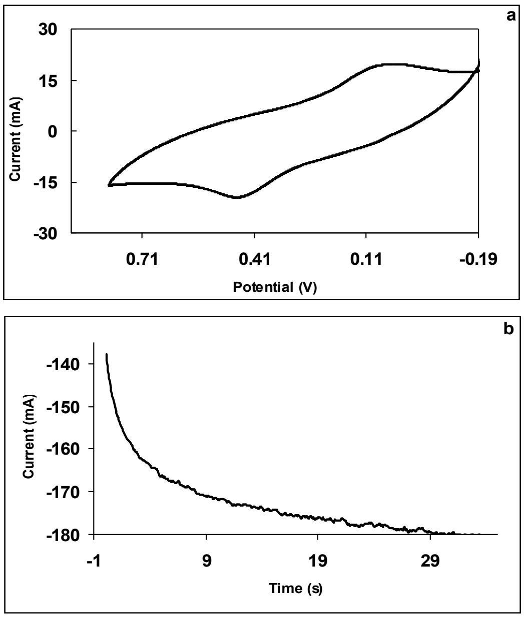

Figure: 5 (a) Cyclic voltammetry of 1 mM $[Fe(CN)_6]^{3-}$ (1 M KCl), at scan rate 20 mV/s, **(b)** Potentiostatic charging–discharging curve of the GCME at a constan potential of 1.8 V.

4. Conclusions

In summary, GCME has been successfully prepared using Nucleosil 10 µm as template by a facile method. The sample has a high specific surface area and pore volume. Electrochemical analysis indicated that it has good electrochemical double-layer performance. It is anticipated that these novel materials will have potential applications in electrode materials, catalysis, adsorption and other fields.

Acknowledgement

This work has been supported by the Science Foundation of Ireland (SFI).

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