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Macroporous carbon from human hair: A journey towards the fabrication of high energy Li-ion capacitors

Rohit Satish[a], Vanchiappan Aravindan[b], Wong Chui Ling[b], Ng Kee Woei[a], Srinivasan Madhavi[a,b,*]

[a] School of Materials Science and Engineering, Nanyang Technological University, 639798, Singapore
[b] Energy Research Institute @ NTU (ERI@N), Nanyang Technological University, Research Techno Plaza, 50 Nanyang Drive, 637553, Singapore

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ABSTRACT

Human hair is a cheap and easily available source of carbon to be used as high performance electrode for electrochemical energy storage devices. In the present work, human hair is pre-treated and then activated using NaOH before being employed as electrode. The resulted activated carbon (ACHH) exhibits a high specific surface area of 1116 $m^2 g^{-1}$ which is one of the pre-requisite for it to be used as an electrode for supercapacitor applications. ACHH delivered a specific capacitance of ~115 F g^{-1} at a current density of 100 mA g^{-1} in single electrode configuration with Li in the presence of organic medium. This result was followed by the fabrication of symmetric supercapacitor and delivered an energy density of 19.2 Wh kg^{-1}. The energy density has been further improved by introducing an insertion type electrode, $Li_4Ti_5O_{12}$ in Li-ion hybrid electrochemical capacitor (Li-HEC) assembly. The combined battery-supercapacitor type reactions in Li-HEC recorded the maximum energy density of 23 Wh kg^{-1}. An excellent cycleability is noted for both symmetric and Li-HEC in an organic medium.

1. Introduction

Today, there is a growing need of energy and this need encompasses a broad spectrum ranging from mobile electronics to large scale applications like hybrid electric vehicles (HEV) and electric vehicles (EV). Energy storage devices for these applications also vary in terms of cost, energy density, power capabilities and safety. The two predominant energy storage technologies existing today are Li-ion batteries and supercapacitors. However, for technologies like Plug–in hybrid electric vehicles (P-HEV) and small automated industry machinery which need an intermediate of these two technologies Li-ion hybrid electrochemical capacitors (Li-HEC) are a step towards providing a solution.

Li-HEC devices are electrochemical cells which are composed of two electrodes, one of the electrode stores charge *via* a Faradaic mechanism (battery type) and the other electrode stores charge using a non-Faradaic process (supercapacitor). This combination allows the device to exploit the higher energy density of batteries and the excellent high power performance of supercapacitors [1,2]. A large amount of research has gone into the pin pointing of a material that can be a suitable battery type electrode including materials like $Li_4Ti_5O_{12}$(LTO) [2,3], $LiMn_2O_4$ [3], $Li_3V_2(PO_4)_3$ [4], TiP_2O_7 [5], Li_2MnSiO_4 [6], $LiTi_2(PO_4)_3$ [7], Li_2FeSiO_4 [8] and V_2O_5 [9] etc., the difficulty in finding a suitable intercalation host for Li–HEC's are the stringent requirements that are put on the materials including extremely high stability and exceptional high rate performance. Although the intercalation electrode is the more studied of the two electrodes in a Li-HEC configuration, the supercapacitor electrode mainly consisting of high surface area carbonaceous materials like activated carbon (AC) is the limiting factor in achieving a high energy density [10].

AC has long been the material of choice for supercapacitor applications irrespective of the electrolyte medium [11,12]. This can be attributed to its exceptionally high specific surface area, tuneable pore size and being environment friendly. AC is made from a variety of sources ranging from fossil fuels to renewable and biodegradable sources. Biodegradable sources are of special interest [13–20] as these are cheaper to use and easier to obtain.

In the case of commercial AC, the increased surface area can be attributed to the presence of a large fraction of micropores [11]. These micropores are predominantly less than 0.5 nm which are not accessible to the larger ions in organic electrolytes [21]. As a consequence, inferior performances are resulted for the electrodes. In order to get optimum performance of activated AC, the pore size

* Corresponding author. Tel.: +65 85390807; fax: +65 6776126.
E-mail addresses: aravind_van@yahoo.com (A. Vanchiappan), Madhavi@ntu.edu.sg (M. Srinivasan).

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needs to be controlled so as to keep a high surface area but at the same time allow for facile adsorption de–adsorption kinetics.

Keeping all this in mind, we report the preparation of high surface area, macroporous carbon from human hair (ACHH), it is a readily available waste generated from barber shops and salons [22,23]. The chemical makeup of human hair is approximately 51% carbon, 17% nitrogen, 21% oxygen, 6% hydrogen, 5% sulphur and trace amounts of metals like magnesium, arsenic, chromium and other minerals. We look at the preparation of hetero-doped AC from hair using a chemical activation using NaOH process followed by a carbonization process. From the preliminary characterisation it can be deduced that the processed material has a high surface area (1116 m^2g^{-1}), and a relatively large average pore size (50–100 nm). These properties were indicative of good performance in a supercapacitor configuration [12,24–28]. The material was further investigated in a Li-HEC configuration with LTO as the counter electrode. Because of the larger pore size, faster Li-ion kinetics was observed during charge-discharge with a maximum energy density of 23 Wh kg^{-1}. A thorough discussion of the results and findings are given in the forthcoming sections.

2. Experimental

2.1. Synthesis

The AC was derived from the human hair obtained from the barber shops located in Singapore. The hair was initially cut into 2–5 mm pieces and thoroughly washed using iso-propanol and dried at 100 °C for 12 h. The dried hair was then pre-carbonized in the presence of Ar at 300 °C for 90 min. The pre–carbonized sample was mixed with NaOH (Sigma-Aldrich) in a mass ratio of 1:2. The sample was later carbonized at 750 °C for 3 h in an Ar atmosphere. The ACHH obtained was repeatedly washed with hot water to remove any traces of sodium from the sample and the washed product was then dried at 80 °C for 6 h for further studies.

2.2. Electrode preparation

The ACHH was mixed with conductive carbon (Super P Li TIMCAL) and a binder (Teflonized acetylene black, TAB–2) in a ratio of 8:1:1. It was then pressed on a 200 mm^2 stainless steel mesh (0.25 mm thickness, Goodfellow, UK) current collector. All electrodes were dried in vacuum overnight at 60 °C. All the electrochemical studies were performed using CR 2016 coin-cell configuration. Half-cells were assembled using metallic Li as the reference and counter electrode. 1 M $LiPF_6$ dissolved in 1:1 ratio of ethylene carbonate (EC): di-methyl carbonate (DMC) (Tomiyama Pure Chemicals, Japan) was used as the electrolyte and glass fibre (Whatman Cat. No. 1825–047, UK) was the separator. Symmetric and hybrid capacitors were assembled in the same way. The Li-HEC was assembled with ACHH as the cathode and commercial LTO (Sigma Aldrich) as the anode material by adjusting the mass loading.

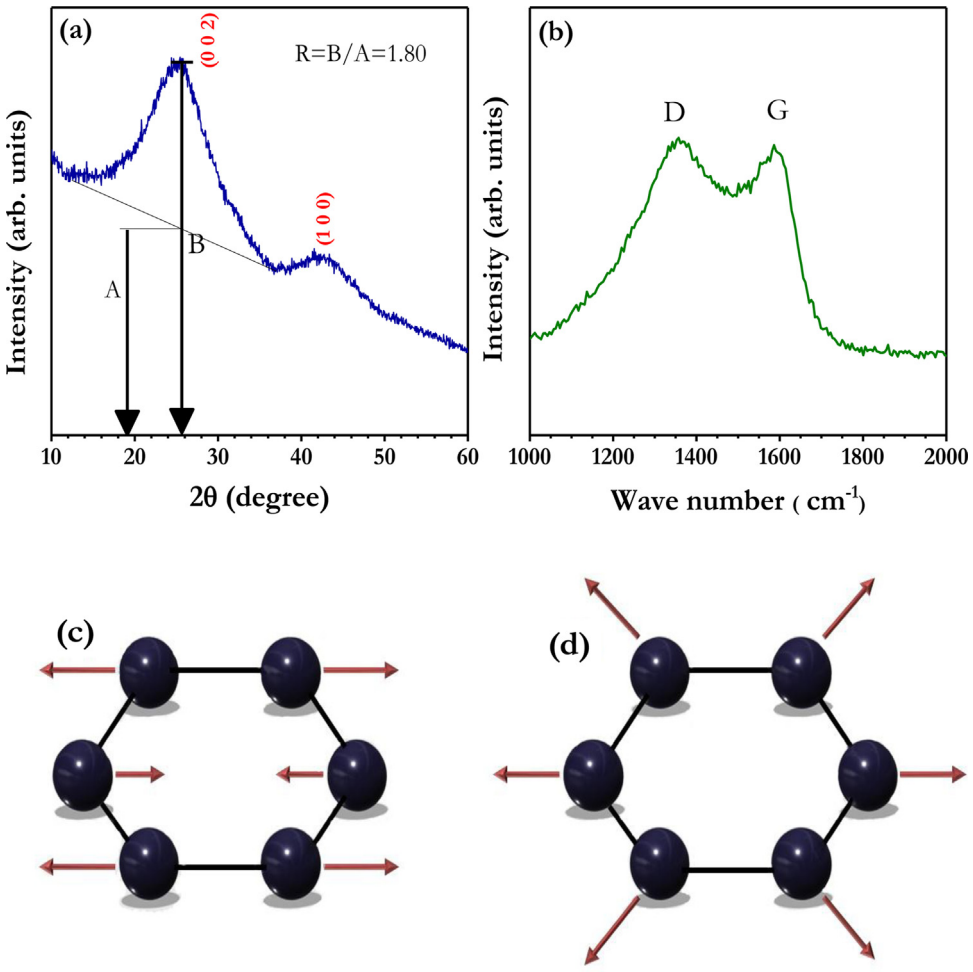

Fig. 1. (a) X–ray diffraction pattern of ACHH; (b) Raman spectra of ACHH indicating D and G bands. Schematic representing the allowed vibrations for carbon atoms. (c) E_{2g} vibrations, (d) A_{1g} vibrations.