A comparative evaluation of differently synthesized high surface area carbons for Li-ion hybrid electrochemical supercapacitor application: Pore size distribution holds the key

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ABSTRACT

We report a comparative evaluation of carbonaceous cathodes synthesized by different protocols in the context of Li-ion hybrid electrochemical supercapacitors (Li-HEC) application. The four cathode materials compared include hierarchically perforated graphene (HPGN), Polymer (Poly (4-styrene sulfonic acid-co-maleic acid) sodium salt) derived Graphene (PDG), dead Neem leaves derived carbon (LDC) and commercial activated carbon (CAC). All these carbons exhibit high specific surface area with excellent porosity. In the single electrode configuration (vs. Li), HPGN shows maximum specific capacitance of $\sim$155 F g^{-1} with good cycleability over 1000 cycles (99.5% retention). On the other hand, there is no obvious distinctive difference between the specific capacitance values for the rest of the carbonaceous materials tested. The Li-HEC is constructed with spinel phase Li$_4$Ti$_5$O$_{12}$ anode and carbonaceous materials described above as cathode in a non-aqueous medium. Amongst the various cases the Li-HEC with HPGN delivered maximum energy and corresponding power density of 65 Wh kg^{-1} and 0.5 kW kg^{-1}, respectively with excellent cycleability as compared to the rest of the materials, tested in the same configuration under the same testing conditions.

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1. Introduction

As of today, in the frame of energy storage, the major scientific efforts have been expended in the area of electrochemical double layer capacitors (EDLC) [1–3]. However, the most important question of limited energy density has remained unsolved for prospective advanced applications such as hybrid electric vehicles (HEV) and electric vehicles (EV) [4]. In the conventional EDLC configuration, carbonaceous materials such as activated carbon (AC) [5–7], carbon nanotubes (CNT) [2,6,8] and graphene nanosheets (GNS) [9,10] have dominated as electro-active materials irrespective of the electrolyte medium owing to their high specific surface area, excellent chemical stability in electrolyte solutions with different pH levels, low cost and amphoteric nature which allows rich electrochemical properties from donor to acceptor state with wide operating temperatures [5]. Although, EDLC delivers excellent power density it fails to display practical energy density beyond $\sim$10 Wh kg^{-1} [11]. Therefore, EDLC alone is not truly capable of powering HEV and EV [12]. On the other hand, Li-ion batteries (LIB) offer high energy density, but lack the desired power density to drive such vehicles [1,4,13–15]. In this scenario, it is very challenging to overcome the limitations of individual systems like EDLC and LIB. One of the best solutions to solve this problem is to integrate both systems to obtain higher energy and power densities and such a configuration is called Li-ion hybrid electrochemical capacitor (Li-HEC). The Li-HEC is expected to bridge the huge gap between EDLC and LIB. Similar to EDLC, utilization of aqueous medium is not appreciated due to the water

splitting issues (~1.23 V). Therefore, exploitation of non-aqueous solutions is anticipated and such concept is originally proposed by Amatucci et al. [16,17]. Generally, Li-HEC consists of Li-insertion type electrode (battery component) coupled with high surface area carbonaceous materials preferably AC as counter electrode (supercapacitor component) in Li-ion conducting non-aqueous electrolytes. There are numerous Li-insertion type materials such as pre-lithiated graphite [1], $Li_4Ti_5O_{12}$ [12,18–22], $LiCrTiO_4$ [23,24], MnO_2 [25], TiO_2-B [26,27], β-$FeOOH$ [28], TiP_2O_7 [29], $LiTi_2(PO_4)_3$ [30], Li_2MnSiO_4 [31], Li_2FeSiO_4 [32], $Li_3V_2(PO_4)_3$ [33], $LiFePO_4$ [34], $LiCoPO_4$ [35], $LiMn_2O_4$, $LiNi_{0.5}Mn_{1.5}O_4$ [36,37], V_2O_5 [38], Li_2CoPO_4F [39], which have been explored along with carbonaceous counter electrodes in non-aqueous medium. Among them, spinel phase $Li_4Ti_5O_{12}$ is found to be appealing due to its salient features like no volume variation during Li-insertion/extraction (Zero strain host), appreciable theoretical capacity (~175 mAh g^{-1}) with high reversibility, thermodynamically flat operating potential (~1.55 V *vs.* Li), easy synthesis and eco-friendliness [40]. Although pre-lithiated graphite anode delivers very high energy density in Li-HEC configuration, the tedious pre-lithiation and solid electrolyte interface during such lithiation process hinders the mass production [12,21,22]. Hence, much attention is paid to develop insertion type transition metal oxides for Li-HEC applications. Compared to the Li-insertion type materials, there is not much work reported on the development of carbonaceous electrodes, except AC. However, the energy density is limited to ~14 Wh kg^{-1} when coupled with $Li_4Ti_5O_{12}$ anode, in spite of its high specific surface area. This may be due to the poor conductivity (poor degree of graphitization) and random pore structure. Currently, great attention is being paid to the development of high surface area carbonaceous materials with porous nature. Among the carbonaceous materials, graphene is found noteworthy due to its high specific capacitance with good cycleability in EDLC configuration, high surface area (2630 m^2 g^{-1}), excellent electrical conductivity and good chemical and thermal stabilities [9]. Recently, Stoller et al. [41] first reported the performance of KOH treated microwave exfoliated graphene oxide (a-MEGO) with $Li_4Ti_5O_{12}$ anode in Li-HEC assembly with a delivered energy density of 40.8 Wh kg^{-1}. Recently, tailoring of graphene into 3D form, functionalized graphene, nano-perforated graphene, porous graphene derived by pyrolysis of polymer and porous carbon derived from dead leaves have been explored as outstanding electrode material for EDLC [42–44]. Owing to the extraordinary performance in EDLC configuration and easy synthesis protocol, we set out to examine these forms for the construction of high energy density Li-HEC. We optimized the mass loading for constructing Li-HEC based on the electrochemical performance of HPGN, PDG, LDC and commercially available activated carbon (CAC) in a single electrode configuration *vs.* Li. The detailed structural and electrochemical performances were carried out along with the spinel phase $Li_4Ti_5O_{12}$ anode in Li-HEC configuration and are described in detail.

In this work we demonstrate that amongst the four materials under study *viz.* three novel carbon nanoforms (HPGN, PDG and LDC) and one conventional form CAC, the HPGN material performed well in terms of impressive electrochemical properties in Li-HEC. We highlight the importance of HPGN electrode in perspective energy storage context. For example, in the single electrode configuration (*vs.* Li), HPGN displayed high specific capacitance of ~155 F g^{-1} with 99.5% retention in the initial capacitance over 1000 cycles with maximum energy density and corresponding power density of 65 Wh kg^{-1} and 0.5 kW kg^{-1}, respectively. The other three materials PDG, LDC and CAC showed limited performance with specific capacitance values of 86, 74 and 72 F g^{-1}, respectively. The observed results for HPGN are almost double as compared to the other electrodes. The reasons for the best performance of HPGN are discussed.

2. Experimental

2.1. Materials

Spinel phase $Li_4Ti_5O_{12}$ nanaoparticles (particle size < 100 nm with a surface area of 32.6 m^2 g^{-1}) and CAC (surface area of 880 m^2 g^{-1}) were procured from Sigma–Aldrich, USA and Norit, The Netherlands, respectively and used without any further treatment.

2.2. Synthesis of hierarchically nano-perforated graphene (HPGN)

Initially graphite oxide (GO) was prepared by harsh oxidation of graphite powder by using the modified Hummer's method. The step by step synthetic process of GO and its purification is discussed in our previous report [45]. Briefly, 100 mg of GO was homogeneously dispersed in 100 ml de-ionized (DI) water by means of strong sonication (~1 h). To the above homogeneous brown dispersion of GO 100 ml of Ludox (colloidal solution of 12 nm silica nanoparticles) solution was added. The above mixture was stirred (24 h) and finally the product was separated by centrifugation. The attached SiO_2 particles were removed by adding sufficient amount of HF. The product was then washed several times with DI water and finally re-dispersed in 100 ml DI water and reduced using hydrazine hydrate to yield HPGN.

2.3. Synthesis of polymer derived graphene (PDG)

3D hexaporous graphene was synthesized according to the process proposed by Yadav et al. [43]. In a typical procedure Poly (4-styrene sulfonic acid-co-maleic acid) sodium salt was pyrolyzed at 1000 °C for 4 h in Ar atmosphere. The obtained black powder was washed several times with DI water to remove associated inorganic impurities and finally the product was dried in vacuum oven to obtain polymer derived graphene (PDG).

2.4. Porous carbon derived from dead leaves (LDC)

The details of the process used to obtain this form of carbon and the choice of precursor are described in our recent publication [44]. Briefly, dead leaves of Neem tree were collected from CSIR-NCL campus. These leaves after proper drying process were crushed into fine powder and heated using a split tube furnace in an inert atmosphere at 1000 °C for 4 h. The obtained black product was then subjected to ball milling to obtain fine porous carbon powder, which is now termed as leaves derived carbon (LDC).

2.5. Characterizations

In this paper we focus mainly on the use of three porous carbons (HPGN, PDG and LDC) as cathode materials for highly efficient advanced Li-HEC application. Therefore, in the characterization section we have mainly emphasized the properties as revealed by the electrochemistry techniques used for the Li-HEC study along with some added physical characterizations such as thermogravimetric analysis (TGA in N_2 gas atmosphere) and X-ray photo electron spectroscopy (XPS, by using ESCA-3000, VG Scientific Ltd. to analyze surface functionality). All the rest characterizations of the powdered samples by different physical techniques such as X-ray diffraction, Raman analysis, BET surface area analysis, morphological studies by using high resolution transmission electron microscopy (HR-TEM) and field emission scanning electron microscopy (FE-SEM) for all the three materials have been fully discussed in our previous reports [42–44]. The key techniques like XRD and Raman were applied to all the three porous carbon materials and the data are presented in the Electronic Supplementary Information (Fig. S1a,b). In order to reveal the porous structures in