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High performance quasi-solid-state supercapacitors with peanut-shell-derived porous carbon

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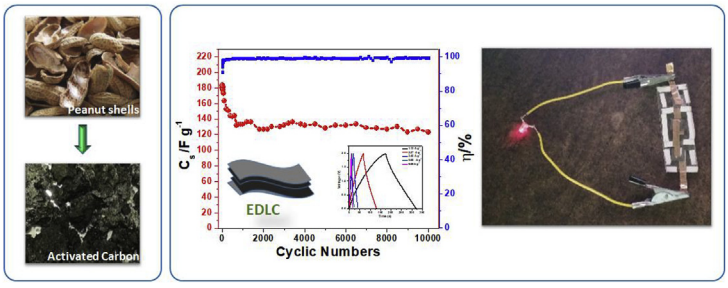
HIGHLIGHTS

- AC powder is synthesized from bio-waste peanut-shells by two different routes.
- Ethanol-soaked peanut-shell-derived AC (EPAC) shows high meso-porosity.
- EPAC electrodes show specific capacitance of ~189 F g^{-1} in solid-state-EDLCs.
- EDLC is stable for ~10^4 cycles with ~28% fading and 100% Coulombic efficiency.
- Capacitor offers specific energy 26 Wh kg^{-1} and specific power 57 kW kg^{-1}.

GRAPHICAL ABSTRACT



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ABSTRACT

We present high performance symmetric quasi-solid-state electrical double layer capacitors (EDLCs) with activated carbon (AC) electrodes produced from peanut-shells. Two different (ethanol soaking and hydrothermal) pre-treatments were given to peanut-shells to tailor ACs' microstructure and comparative supercapacitive performance have been evaluated with Mg-salt (magnesium trifluoromethanesulfonate, Mg $(Tf)_2$) and ionic liquid, IL (1-ethyl-3-methylimidazolium-trifluoromethanesulfonate, EMITf) incorporated gel polymer electrolytes (GPEs). Morphological and porosity studies indicate larger content of mesoporous interiors in ACs obtained from ethanol pre-soaking, offering superior capacitive performance over hydrothermally-treated ACs. The high room temperature ionic conductivity (~3.8×10^{-3} S cm^{-1}), good electrochemical stability window (~3.7 V) and flexible nature of the free-standing films of GPEs Mg $(Tf)_2$/IL/poly (vinylidinefluoride-*co*-hexafluoropropylene) (PVdF-HFP) show their excellent compatibility with AC-electrodes. Electrochemical impedance spectroscopy and cyclic voltammetry indicate high-rate capability of the device. The AC-electrodes, prepared via ethanol-soaking offer superior performance during charge-discharge tests in terms of specific capacitance (~189 F g^{-1}), energy (~26 Wh kg^{-1}) and maximum power (~57 kW kg^{-1}) with Mg-salt/IL incorporated GPE-film as compared to the devices with only IL-based GPE-film. The EDLC shows stable performance up to ~10,000 charge-discharge cycles with ~28% initial fading in specific capacitance. The EDLC is thermally stable in the temperature range from −50 to 70 °C.

1. Introduction

Over the last few decades, market for the portable electronic devices and electrical vehicles with hybrid power system is growing rapidly, for which, there is an urgent need of efficient energy-storage devices like rechargeable ion-batteries and supercapacitors [1,2]. Significant

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research and development is globally ongoing on electric double layer capacitors (EDLCs), which is an important and most reported class of supercapacitors. They have attracted world-wide attention due to their high power delivering ability and excellent charge-discharge cycling performance [2]. High surface area porous carbons including activated carbon, carbon aerogels, carbon nanotubes (CNTs), carbon nanofibers (CNFs), graphene, etc. are important electrode materials for EDLCs [3–8]. In this race, the activated carbons are still potential candidates, which are prepared from various organic compounds such as poly acrylonitrile (PAN) [9], coal-tar pitch [10], carbides [11], etc. However, the production processes of activated carbon from these compounds are hazardous and costly.

In order to develop 'green' energy storage systems like EDLCs and to make them cost-effective, waste biomass materials are reported to be used to produce activated porous carbon for EDLC electrodes. Biomass-based activated carbons can be produced from a variety of sources namely coconut shell [12,13], coffee shell [14], almond shell [15], tea-leaves [16], rice husk, poplar wood [17], etc. and are reported to develop high performance EDLCs. Recently, peanut-derived carbon is reported in various energy storage applications namely EDLCs [18], sodium-ion batteries and capacitors [19] etc. The peanut-shell based activated carbons offer high surface area ($\sim 2100\ m^2\ g^{-1}$), graphene-like flakes etc., suitable for efficient EDLC-electrodes, while being environment friendly and cost-effective at the same time. It may be noted that peanut industry generates considerable quantities of shells (~ 6 million tons) each year, which are entirely discarded as bio-waste.

Peanut-shell is ligno-cellulosic material, containing cellulose macro-fibril bundles, made of a number of micro-fibrils. Each micro-fibril is a crystalline, longitudinal arrangement of cellulose sheets parallel to each other. These sheets are further made of longitudinally arranged chains of cellulose. The crystalline fibrils are the packing of a number of flat sheets made of uniformly arranged cellulose chains, bonded with each other by van der Waal's forces [20]. Lignin and hemi-cellulose are present in the space between macro-fibrils and give the overall structural strength to the fiber. The content of cellulose, lignin, and hemi-celluloses in peanut-shell is 34–45%, 27–33% and 12–16% (w/w), respectively [21,22]. It may be noted that different processes of pretreatments, before carbonization and activation, affect the above-mentioned components of peanut-shells in different ways, so, different porous textures of the activated carbon are obtained.

In general, the high surface area activated carbon has the ability to store large amount of charges, however, mostly nonlinear relationship has been observed between the capacitance shown by the material and its specific surface area [23]. This is due to the possibility that not all the pores of the electrodes are necessarily accessible to the electrolyte ions. Generally, micro- and mesopores of carbon electrodes, which greatly affect the performance of the EDLCs, are controlled by the activation processes [24,25]. Various activation processes such as physical, chemical, or a combination of both are described in literature [15,26]. The carbon materials are generally activated chemically followed by physical activation to modify their various properties such as porosity, microstructure and surface area. For the chemical activation, different activating agents are employed, namely: H_3PO_4, $ZnSO_4$, $ZnCl_2$, K_2CO_3, Na_2CO_3, NaOH, KOH, $CaCl_2$, etc. [15,26]. Recently, Satlewal et al. reported that soaking of biomass in ethanol for longer duration before chemical and physical activation processes is an important approach to observe improved performance of carbon electrodes [27].

EDLCs of latest generation employ, in general, quasi-solid-state films of gel polymer electrolytes (GPEs) instead of liquid electrolytes. GPEs comprise liquid electrolyte (e.g. aqueous H_2SO_4, KOH, etc. or salts dissolved in organic solvents, or ionic liquids or their mixture with salts) entrapped in host polymers e.g. PVdF-HFP, PMMA, PEO, PVA, etc. EDLCs/supercapacitors based on liquid electrolytes mostly suffer from various common drawbacks such as leakage, corrosion, self-discharge, etc. On the other hand, GPEs have proven to be potential separators/electrolytes due to many advantageous reasons such as flexibility, mouldability, and high ionic conductivity, almost comparable to liquid electrolytes. Particularly, ionic liquid-based GPEs offer excellent thermal and electrochemical stability, in addition to the other advantageous properties, mentioned above [28,29]. From safety point of view also, ionic liquid based GPEs are attractive due to non-volatile and non-flammable nature of ionic liquids. GPEs, employing organic solvents or ionic liquids, used for EDLC applications, mostly contain Li-salts [30]. The Mg-salts (e.g. magnesium trifluoromethane sulfonate, Mg $(Tf)_2$, magnesium bis(trifluoromethan sulfonyl)imide, Mg $(TFSI)_2$, $Mg(ClO_4)_2$, etc.), on the other hand, may be a better substitute to incorporate in GPEs, as Mg-ions are doubly charged cations with ionic sizes comparable to Li-ions. Few recent studies indicate that GPEs containing Mg-salts are equally suitable for supercapacitor-like applications [31,32].

In this paper, a comparative performance study has been presented on EDLCs, fabricated with peanut-shell derived activated carbon electrodes (prepared by two processes) and ionic liquid incorporated Mg^{2+}-ion conducting GPE film. To prepare activated carbons, raw peanut-shell powder was treated by two different processes i.e. soaking in ethanol for long duration and hydrothermal treatment, before their chemical and physical activations. These two pretreatments have different impacts on the nanoscale structure, which ultimately define the content and quality of meso- and micropores in the carbon, which greatly influence the performance characteristics of EDLCs. The GPE, employed as flexible electrolyte, comprised of 0.3 M solution of magnesium triflate (Mg $(Tf)_2$) in ionic liquid 1-ethyl-3-methylimidazolium trifluoromethane-sulfonate (EMITf), entrapped in a host polymer poly (vinylidene fluoride-*co*-hexafluoropropylene (PVdF-HFP). The characteristics of EDLCs have been studied based on electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and galvanostatic charge-discharge techniques over numerous cycles. Role of porosity in carbon-electrodes and effect of Mg-salt in gel electrolyte in the performance of EDLCs has been specifically discussed.

2. Experimental

2.1. Materials

Ethanol (C_2H_5OH; AR grade) and zinc chloride ($ZnCl_2$; purity $\sim$95%) were procured from Merck Chemicals. Acetylene black (AB), co-polymer poly (vinylidinefluoride-*co*-hexafluoro-propylene) (PVdF-HFP), magnesium trifluoromethanesulfonate (Mg $(Tf)_2$), and ionic liquid (IL) 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMITf) were procured from Sigma-Aldrich. All the chemicals were used without further purification. The un-roasted peanuts (with shells) were purchased from a local market.

2.2. Preparation and characterization of porous activated carbon

Peanut shells were washed with de-ionized water, and vacuum dried at $\sim$110 °C, for 12 h before use. The porous activated carbon was prepared following two procedures where the peanut shells were given two different treatments before their chemical and physical activations. The preparation processes of activated carbons are schematically represented by Fig. 1. The pre-treatments were either soaking in ethanol, or a hydrothermal treatment. In the first process, peanut shells were soaked with ethanol for 30 days and then dried in vacuum oven at $\sim$110 °C for 14 h. Thereafter, the material was crushed into powder form using mortar and pestle for chemical and physical activation. The powder was then mixed in 20 ml deionised water with activation agent $ZnCl_2$ in the ratio of 1:2 w/w. The mixture was then stirred thoroughly followed by drying it overnight at $\sim$110 °C [12]. The material was then placed into a tube furnace and heated up to $\sim$800 °C with heating rate $\sim$5 °C per min under constant flow of nitrogen for chemical activation. This process was followed by CO_2 flow for 2 h for its physical activation. After natural cooling to room temperature, the resulting material was