

A novel configuration of electrical double layer capacitor with plastic crystal based gel polymer electrolyte and graphene nano-platelets as electrodes: A high rate performance



Manoj K. Singh, Mohd Suleman, Yogesh Kumar, S.A. Hashmi*

Department of Physics & Astrophysics, University of Delhi, Delhi 110007, India

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ABSTRACT

A new, symmetrical, high rate, solid-state EDLC (electrical double layer capacitor) has been fabricated employing a plastic crystal SN (succinonitrile) based GPE (gel polymer electrolyte) and GNPs (graphene nano-platelets) as electrodes. The free-standing GPE film containing poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) exhibits the excellent suitability as electrolyte in EDLC due to its high ionic conductivity ($\sim 2 \times 10^{-3} \text{ S cm}^{-1}$ at 20°C), thermal stability (from -30 to 80°C), electrochemical stability window ($\sim 3.5 \text{ V vs. Ag}$), and excellent mechanical properties. The high rate capability of the EDLC has been observed from the impedance analysis in terms of high knee frequency ($\sim 58 \text{ Hz}$), low response time ($\sim 791 \text{ ms}$) and high pulse power ($\sim 16.4 \text{ kW kg}^{-1}$). The cyclic voltammetric response indicates the capacitive performance up to a substantially high scan rate of 1000 mV s^{-1} , which further confirms the high rate performance of the EDLC. Though the specific energy of the solid-state EDLC is observed to be low ($E_{\text{max}} \sim 8.2 \text{ Wh kg}^{-1}$), its power density is substantially high ($P_{\text{max}} > 4 \text{ kW kg}^{-1}$). After $\sim 20\%$ decrement in specific capacitance during the initial charge–discharge cycles, the EDLC offers almost stable performance up to ~ 3500 cycles.

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1. Introduction

Recently, supercapacitors have attracted global attention as power sources because of their high specific power and long cyclic performance [1–4]. High surface area carbons including activated carbon, CNTs (carbon nanotubes), carbon nanofibers etc. are the excellent electrode materials for a class of supercapacitors referred as EDLCs (electric double layer capacitors) [1–5]. Activated carbons have the limitation of cyclic efficiency, whereas CNTs exhibit low capacitance ($30\text{--}150 \text{ F g}^{-1}$) due to limited surface area [5–7]. To improve the capacitance values, functionalization of CNTs and the formation of composites with conducting polymers or metal oxides are widely reported [6–8], however, these limit their cycling performance. Graphene, an intriguing new class of nanoscale carbon materials with fascinating properties, has many promising applications [9], including its application as an electrode material for lithium ion batteries and supercapacitors [10,11].

EDLCs with graphene electrodes are mostly fabricated with liquid electrolytes [10–12], which limit their performance due to the problems of leakage, corrosion, bulky design, shelf life, etc. GPEs (Gel polymer electrolytes), comprising liquid electrolytes entrapped in suitable host polymers, promise the solution of most of the problems cited above, along with their added advantages including thermal stability and other electro-mechanical properties [5,13,14]. The GPEs employed in batteries and supercapacitors, in general, use organic solvents (EC (ethylene carbonate), PC (propylene carbonate), DEC (diethylene carbon), etc.) or ionic liquids [5,13,14]. The organic solvents suffer from the drawbacks like flammability, volatility etc., whereas the ionic liquids make the ionic transport in GPEs complex due to the conduction of their component ions.

A number of solid-state electrolytes comprising plastic crystal SN (succinonitrile) as a host matrix and a variety of salts have been reported offering high ionic conductivity at room temperature [15]. Some ionic plastic crystals based solid-state ionic conductors have also been reported, in which the plastic crystal acts as solid solvent for ionic salts and supports the ionic transport of doped salt via motions of the matrix ions [16]. Few polymer-based electrolytes have recently been reported incorporating plastic

* Corresponding author. Tel.: +91 1127604881; fax: +91 1127667061.

E-mail addresses: hashmisa2002@yahoo.co.in, sahashmi@physics.u.ac.in (S.A. Hashmi).

crystal SN (succinonitrile), which plays the role of solid-state solvent [17–25]. The ionic conductivities of SN-based electrolytes, doped with salts of lithium, sodium etc. are reported to be in the range of $\sim 10^{-4}$ – 10^{-3} S cm^{-1} at room temperature [15,17–25]. High polarity, high dielectric constant (~ 55 at room temperature) and plastic nature due to large orientational disorder in the temperature range from -39 to 60 °C, the SN molecules assist to obtain high ionic mobility in the polymer-salt systems [15,17,24]. In addition, the SN-based electrolytes possess the ability to accommodate the mechanical stress i.e. volume changes during the charge–discharge process and hence provide better electrode–electrolyte contacts [15].

In this report, we present the studies on a novel configuration of graphene nano-platelets based flexible EDLC incorporated with a GPE added with plastic crystal succinonitrile. Morphological, structural and porosity studies have been carried out to test the suitability of GNPs as EDLC-electrodes. Electrochemical studies on PVdF-HFP (poly (vinylidene fluoride-co-hexafluoropropylene)) based GPE incorporated with SN, to be used as separator/electrolyte, have been performed and compared the results with an organic solvents based GPEs. The performance of EDLC has been characterised using electrochemical impedance spectroscopy, cyclic voltammetry, and charge–discharge test.

2. Experimental

2.1. Preparation and characterization of GNP electrodes

GNP ((Graphene nano-platelet), Grade-3) powder was purchased from Cheap Tubes Inc., USA having 4–5 graphene layers, average thickness of 8 nm and particle diameter < 2 μm . The GNP powder was vacuum dried at ~ 100 °C overnight before its use as EDLC-electrodes. To prepare the electrodes, the GNP powder, AB (acetylene black), and PVdF-HFP (as a binder) with the ratio of 80:10:10 (w/w) were ground in a mortar and pestle with NMP (N-methyl-2-pyrrolidone) to form a slurry. This slurry was spin-coated on the graphite sheet (250 μm thick, Nickunj Eximp Entp., India). These electrodes were dried again at ~ 100 °C overnight in vacuum before fabricating the EDLC cells. The surface area and porosity parameters of GNP powder were evaluated using a surface area analyser (Gemini-V, Micromeritics). SEM (Scanning Electron Microscope) images of GNPs were recorded using Scanning Electron Microscope (Mira-3, TESCAN). TEM (Transmission Electron Microscope) images were obtained using Transmission Electron Microscope (Tecnai G2T30, U-TWIN) in which LiB_6 filament was used as electron source and working voltage range was kept at 50–100 kV. The samples for TEM were prepared on carbon-coated copper grid (Electron Microscopy Sciences, USA). The XRD (X-Ray Diffractometer) patterns were obtained from X-Ray Diffractometer (D8 Brucker, USA) using $\text{CuK}\alpha$ radiation ($\lambda = 1.5406$ Å). A Renishaw Invia Raman Spectrometer, equipped with CCD (charge-coupled device) and a diode LASER (wavelength ~ 784 nm), was used for Raman measurements.

2.2. Preparation and characterization of gel polymer electrolyte

The copolymer, PVdF-HFP (M.W. $\sim 4 \times 10^5$), SN (succinonitrile), and LiTFSI (lithium bis(trifluoromethane sulfonyl)imide) were procured from Sigma–Aldrich, and vacuum-dried overnight at ~ 80 °C. The GPE (gel polymer electrolyte) was prepared by solution-cast method, in which 1 M solution of LiTFSI in SN was immobilised in previously dissolved PVdF-HFP in acetone with a ratio 80:20 (w/w). This solution was stirred magnetically at room temperature for ~ 24 h until the mixture appeared to be homogeneous. Final solution was cast over glass petri-dishes and acetone was allowed to

evaporate slowly. Finally, the free-standing GPE film (thickness ~ 350 – 400 μm) was obtained, and stored in dry atmosphere. A photograph of the flexible GPE film is shown in Fig. 1. Another GPE, comprising 1 M LiTFSI solution in organic solvents (EC:PC 1:1 v/v), entrapped in PVdF-HFP (20 wt%) was also prepared using solution–cast method for comparison.

The possible phase/structural changes in GPE were tested by DSC (differential scanning calorimetry). DSC was performed from -60 to 80 °C at a heating rate of 10 °C min^{-1} in a static N_2 -atmosphere using a DSC system (Q100, TA instruments). The ionic conductivity of the gel film was evaluated in N_2 -atmosphere by impedance spectroscopy using Broadband Dielectric/Impedance Analyser (C-50 Alpha A, Novocontrol). The ESW (electrochemical stability window) of the film was evaluated by LSV (linear sweep voltammetry) using an electrochemical analyser (608C, CH Instruments) at a scan rate of 5 mV s^{-1} .

The mechanical strength of the GPE films was tested using an Instron Microtensile Tester (Model 5848, Singapore) at a strain rate 5 mm min^{-1} with maximum load of 10 N at a room temperature. Each specimen of GPEs was taken in the form of a rectangular sheet (25 $\text{mm} \times 10$ mm) and clamped between the holders of the machine for tensile testing.

2.3. Fabrication and characterization of EDLC cells

EDLC cells were fabricated using the following procedure. The dilute acetone solution of GPE was finely coated on the flat GNP-electrodes. These systems were completely dried in vacuum at room temperature. To form an EDLC in two electrodes geometry, two such electrode/electrolyte systems were stacked over each other and pressed such that the GPE is sandwiched between two symmetrical GNP-electrodes. The entire cell was spring loaded in a holder (Split cell, MTI Corporation, USA) for electrochemical measurements. The performance characteristics of EDLCs were evaluated using EIS (electrochemical impedance spectroscopy), CV (cyclic voltammetry), and charge–discharge tests. The EIS studies were performed using impedance/gain phase analyser (1260A, Solartron). CV responses were recorded at different scan rates using electrochemical analyser mentioned above. The charge–discharge test was performed using a charge–discharge unit (BT2000, Arbin Instruments, USA).

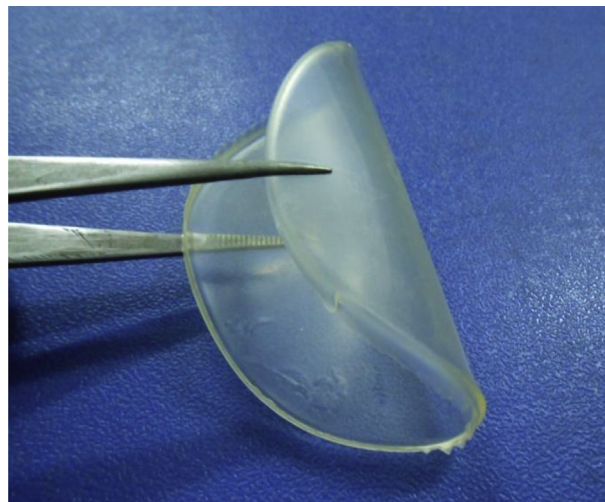


Fig. 1. Photograph of the gel polymer electrolyte flexible film.

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