Storage capacity in Graphene and blends of Graphene EDLC

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ABSTRACT

Solid State EDLC's, Electrochemical Double Layer Capacitor, form excellent energy storage device for high power applications with added advantage of electrolyte leaks avoidance, increased reliability and convenient packaging to suit various applications. We can use activated carbon to Graphene, with varying particle size, surface area, pore size and pore distribution as the active material for charge storage. The emphasis is to optimize the Graphene to carbon blend in the electrodes which would provide appreciable storage density of the EDLC. We have used perflurosulfonic acid polymer as the solid electrolyte in the EDLC assembly. They have high ionic conductivity, good thermal stability, adequate mechanical strength and excellent chemical stability. Carbon is widely used for many practical applications**,** especially for the adsorption of ions and molecules, and because it is possible to synthesize one-, two-, or three-dimensional (1-, 2-, or 3-D) carbons. Some of the problems in activated carbon like varying micro or meso pores, poor ion mobility due to varying pore distribution, low electrical conductivity, can be circumvented by using Graphene and blends of Graphene with carbon of the right pore dimension. Graphene in various structural nomenclatures have been used by various groups for charge storage. Graphene nanoplates (GNP), with narrow mesopore distribution have been effectively used to for EDLCs. EDLCs assembled with GNP and Blends of GNP with Vulcan XC and Solid polymer electrolyte like Nafion show exceptional performance. The cyclic voltammetric studies show that they support high scan rates with substantial smaller capacitance drop as we increase scan rates. Optimization of the electrode structure in terms of blend percentage, binder content and interface character in the frequency and time domain provides excellent insight to the double layer interface.

Keywords: Graphene, storage capacity, double layer, solid state.

1 INTRODUCTION

In this era when we are on the lookout for high density and efficient energy storage devices for Electric vehicles/Hybrid electric vehicle (EV/HEV) and solar Photo voltaic application, carbon based solid state EDLC's appears to be a very economical and viable option. The EDLC's can be used as stand alone energy storage banks or the can be used as storage support with battery systems.

The EDLCs are electrochemical capacitors where carbon acts as an active electrode material for storage. Carbon in its various forms is extensively studied and is a widely utilized electrode material in EDLCs. [1, 2] The emphasis has been to develop carbon electrodes with suitable surface area to achieve high storage density using non Faradaic charge separation at the electrode/electrolyte interface.

Solid electrolytes are elegant to use and improves the reliability of the EDLCs. They can also be shaped and sized to suit the application. All solid EDLCs using proton conducting polymer electrolyte and various composites have been studied by different groups (3-10).

Using the proton conducting polymer solid polymer electrolyte it was possible to achieve high scan rates (≈ few 100V/s). D. Pech et. al. [9], Subramaniam [5], Gao [6], Miller [10]. The have reported high scan rates which suggests usefulness in EV/HEV applications.

The reduction of ionic and electronic resistance in EDLC through nano architectural design has become an increasingly important part of research in power applications. This simply means that the storage capacity depends on the micro texture of the carbon used and the construction of the electrodes. The parameters that affect the EDLC electrode design are pore size, surface area, wettability, and conductivity. The gravimetric capacitance Cg is strictly determined by the electrode material and electrode structure. No simple relation exists between Cg and specific surface area (SSA). This may also be due to ion size effects.[5]

Some of the limitations in performance and in electrode structure can be circumvented by using ordered mesoporous carbons (OMC) or highly ordered mesoporous carbon (HOMC). In these systems, high specific capacitance can be obtained and the capacitance show negligible dependence on potential sweep rate.

Carbon based EDLCs store charge electrostatically by the adsorption of ions on to electrodes that have high accessible surface area. Therefore, a high specific capacitance active electrode plays a vital role in efficient energy storage. Various forms of porous carbon, for instance CNT,

mesoporous carbon, activated carbon and carbide derived carbon have been studied for electrodes. Graphene and RGO have been as electrodes due to very high specific surface area (2630 m2/g), chemical stability, excellent electrical, thermal conductivity and low cost [2, 11-19]. Interestingly, graphene has demonstrated intrinsic capacitance near 21F/cm2, that set new upper limit for capacitance. Stoller *et al.* [14] They have also pioneered the use of chemically reduced graphene, CRG, in super capacitor.

We present in this paper electrochemical performance of solid state EDLCs using carbon meso porous carbon Graphene and blends of carbon with Graphene as electrodes with solid ionic polymers of perfluoro sulphonic acid as electrolyte.

2 EXPERIMENTAL

The assembly of the EDLC has been described in detailed elsewhere. [3-5] Carbon fiber paper was used as the base matrix for the electrodes. The typical size of the electrode used was 5 cm^2. 2.5 mg/cm^2 of the active material was coated on the surface of this matrix. Solution of the ionic polymer was used as binder in the fabrication of the electrodes. The performance of the electrode is very sensitive to the amount of binder used for a particular active material. Two carbon electrodes were assembled on either side of the solid electrolytes. The electrodes and the electrolyte were laminated by standard lamination process at elevated temperatures below the glass transition temperature of the solid polymer electrolyte. This assembly was placed between two grafoil® end plates which were used as current terminals. Insulating gaskets were placed on both the internal faces of the end plates to prevent lateral shorting and to delimit the central capacitor portion and to seal the cell assembly.

3 RESULTS

The results are presented in the follfwing figures.

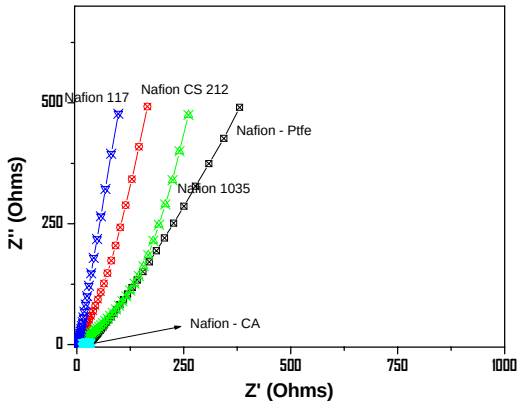

Figure 1: **Nyquist plots for the EDLC assembly with different forms of the solid polymer electrolyte. The solid polymer thickness varies from 50 to 125 microns. (Nafion 112 to 117) Nafion – PTFE and Nafion –CA are composites of Nafion in PTFE (microporous poly tetra fluoro ethylene) an CA (micro porous Cellulose Acetate)**

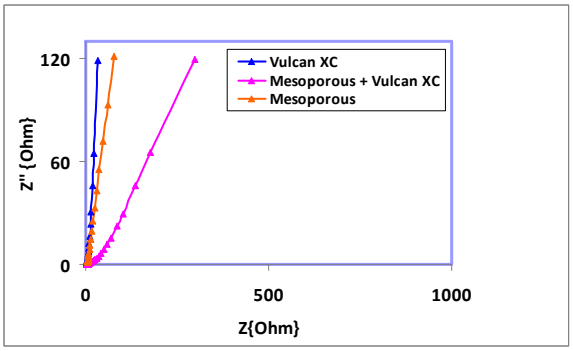

Figure 2 : **Nyquist plots for the EDLCs with various carbons Vulcan XC, Mesoporous and Mesoporous + Vulcan XC blend using Nafion 112 as solid polymer electrolyte.**

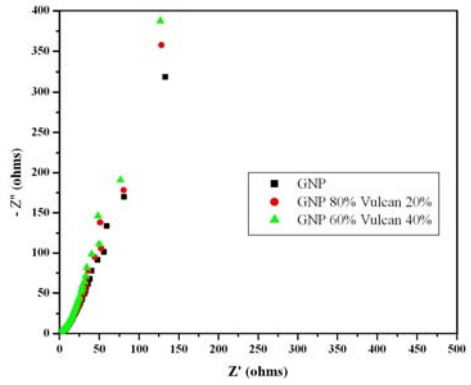

Figure 3 : **Nyquist plots for the EDLCs with Graphene nano plates, and blends with Vulcan XC.**

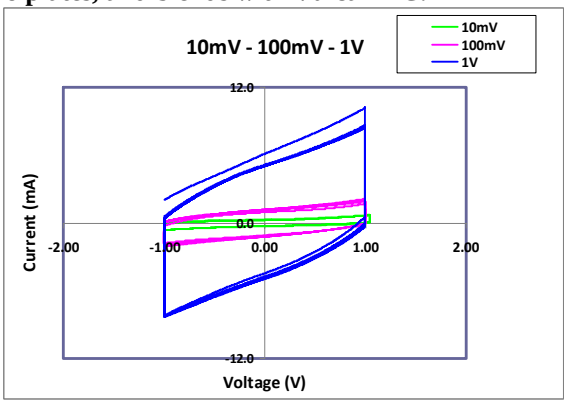

Figure 4 : **Cyclic voltammograms at scan rate of 10 mVs^{-1}, 100 mVs^{-1} and $1Vs^{-1}$ for Vulcan XC carbon electrodes.**

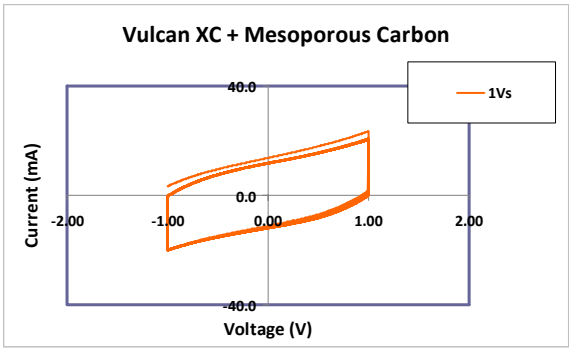

Figure 5 : **Cyclic voltammograms at scan rate of $1Vs^{-1}$ for Vulcan XC and meso porous carbon blended electrodes**

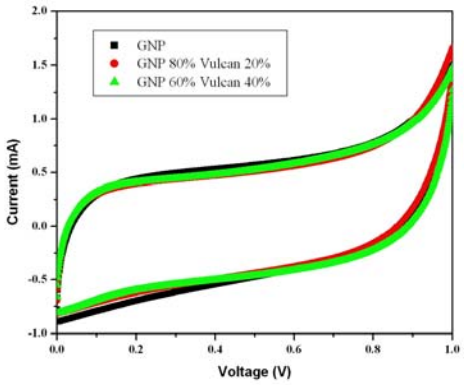

Figure 6 : **Cyclic voltammograms at scan rate of 10 mVs-1 for Graphene and blends of Graphene with Vulcan XC**

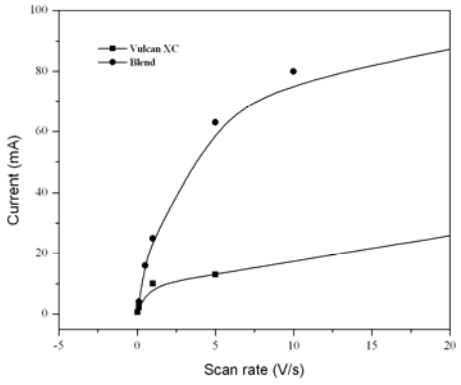

Figure 7 : **Variation of Current with scan rate for Vulcan carbon and blends**

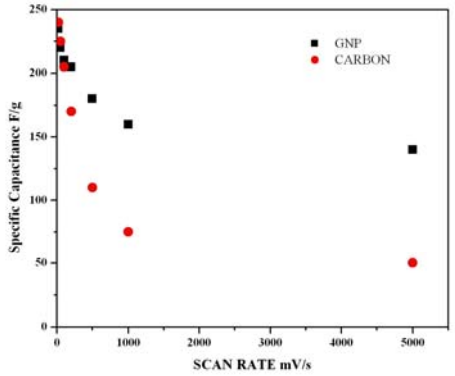

Figure 8 : **Variation of specific capacitance with scan rate for Graphene and Vulcan carbon**

4 DISCUSSIONS

From the present study we can state that EDLCs assembled with carbon and Solid polymer electrolyte like perfluoro sulfonic acid we can fabricate solid state EDLCs with high charge density which can support high scan rates. There exist two distinct regions of scan rates where we can operate depending on the application. The meso pores introduced has a definite influence on the double layer interface. The high scan rate emphasizes the ESR component of the EDLC, an important parameter in EDLC fabrication. The pore volume and pore size distribution needs to be scrutinized further for solid state EDLCs, in order to fabricate EDLCs for different applications. These parameters also depend on the scan rate. The EDLCs assembled with Graphene and Blends of Graphene with Vulcan XC and Solid polymer electrolyte like show appreciable energy storage capabilities. They can also support high scan rates with substantial smaller capacitance drop at higher scan rates. There exist different distinct regions of scan rates like low medium or high scan rates where we can operate depending on the application. Blending Graphene with carbons like Vulcan XC improves the double layer interface. However, optimization of the electrode structure in terms of blend, binder and interface character in the frequency and time domain [21], would provide a very commercially viable solid state EDLC.

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