



Graphite, Graphite Oxide, Graphene Oxide, and Reduced Graphene Oxide as Active Materials for Electrochemical Double Layer Capacitors: A comparative Study

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Abstract: In this paper report we compare the properties and the performance of four different carbonaceous materials, namely graphite, graphite oxide, graphene oxide and reduced graphene oxide, as active materials for electrochemical double layer capacitors (EDLCs). Compared to ordinary graphite, and graphite oxide, rGO have superior capacitive behavior and power output in EDLCs due to their unique nanoporous structure, porosity and enormous BET surface area close to $1200 \text{ m}^2\text{g}^{-1}$. The electrochemical properties of these carbonaceous materials were determined by cyclic voltammetry. The result of this investigations indicate reduced graphene oxide as a very promising candidate for the realization of high performance EDLCs, able to display high energy and high power. In the potential range of (0 to -0.8) V, rGO has the specific capacitance of 85.9 Fg^{-1} in $1 \text{ molL}^{-1} \text{ LiNO}_3$ solution using three-electrode system. A further analysis of the electrochemical behavior in different electrolytic aqueous media showed that in Li^+ solution rGO have the highest capacitance, as we compare to Na^+ and K^+ solutions.

INTRODUCTION

Electrochemical capacitors (or supercapacitors) are very attractive power sources for portable electronic systems and automotive applications due to their high specific power and very long durability (Conway, 1999; Kotz and Carlen, 2000; Frackowiak and Beguin, 2001). Electric double layer capacitors (EDLCs) are advantageous over modern secondary batteries in power capability and long cycle life. There are two energy storage mechanisms for supercapacitors: double-layer capacitance and pseudocapacitance. Although the energy densities of devices based on pseudocapacitance are greater than those on double-layer capacitance, the phase changes in the pseudocapacitance materials limit their lifetime and power density due to the faradaic reaction. As we know, carbon materials,

commonly corresponding to double-layer capacitance, are the most ideal materials for supercapacitors (Pandolfo and Hollenkamp, 2006; Simon and Gogotsi, 2008).

The performance of porous carbons as EDLCs is strongly dependent on a number of factors which include carbon material properties (such as porosity, surface chemistry and electrical conductivity), preparation method of the electrode and electrolyte characteristics (such as ions dimensions, dielectric constant, etc.). A unit cell of EDLC works on the principle of double-layer capacitance at the electrode/electrolyte interface where electric charges are accumulated on the electrode surfaces and ions of opposite charge are arranged in the electrolyte side. Since this phenomenon is controlled by

the surface area of the interface, activated carbons are the most widely used electrode materials for EDLSs. Considering that only charging of the double-layer is involved, it should be expected that higher the specific surface area of the carbonaceous material, higher the capacitance (Castello *et al.*, 2003; Shi, 1996).

Although a high specific surface area is regarded as a primary requirement for carbon electrodes to be used in EDLCs, some other aspects of the surface physicochemical properties can be critical for the electrochemical performance. Beside the pore size distribution, the electric conductivity of the carbon material is a key parameter, and there is a possibility that heteroatoms as oxygen or nitrogen can induce pseudocapacitance effects. The foreign atoms in the graphene layers modify also their electron donor/acceptor character, and are consequently expected to affect the charging of the electrical double layer (Qu and Shi, 1998; Martinez *et al.*, 2005).

Graphene based materials have shown immense theoretical and practical advantages among carbonaceous materials, such as a high surface area, excellent conductivity and capacitance, and relatively low production costs (mass production) (Brownson and Banks, 2010).

Graphene is two-dimensional one atom-thick planar sheet of sp^2 bonded carbon atom, which is considered as the fundamental foundation for all fullerene allotropic dimensionalities. Chemically, graphene oxide is similar, if not identical, to graphite oxide, but structurally it is very different. Rather than retaining a stacked structure, the material is exfoliated into monolayers or a few stacked layers, and graphene oxide contains a range of reactive oxygen functional groups (Dreyer *et al.*, 2010). It is graphene oxide that is the product obtained by Hummers method, and hence it is graphene oxide that undergoes the reduction to graphene, or more precisely GO is reduced to r-GO.

The present work is focused on an advanced understanding of the electrochemical behavior of different carbonaceous materials as candidate for electrode material for supercapacitors in aqueous media.

EXPERIMENTAL

Preparation of working electrode and electrochemical characterization

The composite carbon electrodes used in this paper were prepared by mixing the pure carbon material with poly (vinylidene fluoride) binder, 5% nafion solution and of a conductive additive carbon. The ration of carbon material to other ingredients is 9:1. The suspension was made in water-alcohol mixture.

Electrochemical measurements were carried out in three-electrode setup with PAR 263A Potentiostat/Galvanostat workstation operating at room temperature. The working electrode was glassy carbon which consists of added composite carbon materials as active material. Before CV measurements, suspension is put under vacuum treatment to remove an excess oxygen from the solution and its fine suspended using ultrasound treatment. Ag /AgCl electrode and Pt wire served as reference electrode and counter electrode, respectively. 1M LiCl, NaCl, and KCl aqueous solution was used as electrolyte. The cyclic voltammetry (CV) curves were acquired at scan rates of 50, 100, 200 and 500 $mV s^{-1}$ in potential window (-1 to 0.8 V).

RESULTS AND DISCUSSION

In first series of experiments, cyclic voltammetry at various scan rates were carried out for EDLCs with graphite and graphite oxide as active materials using 1M Li^+ , Na^+ and K^+ aqueous electrolytes. Figure 1 shows the results of these CV measurements exemplary for a different scan rates of 50, 100, 200 and 500 mVs^{-1} in potential window (-1 to 0.8 V). At the low voltage sweep rate of 50 mVs^{-1} , graphite and graphite oxide roughly maintains the rectangular shape indicative of an acceptable capacitive behavior. However, the voltammograms become distorted dramatically with the increase of voltage sweep rate, which indicates that graphite and graphite oxide are not suitable for quick charge-discharge operations. In positive potential window there is a significant influence of the pseudocapacitance for both graphite and its oxide form.

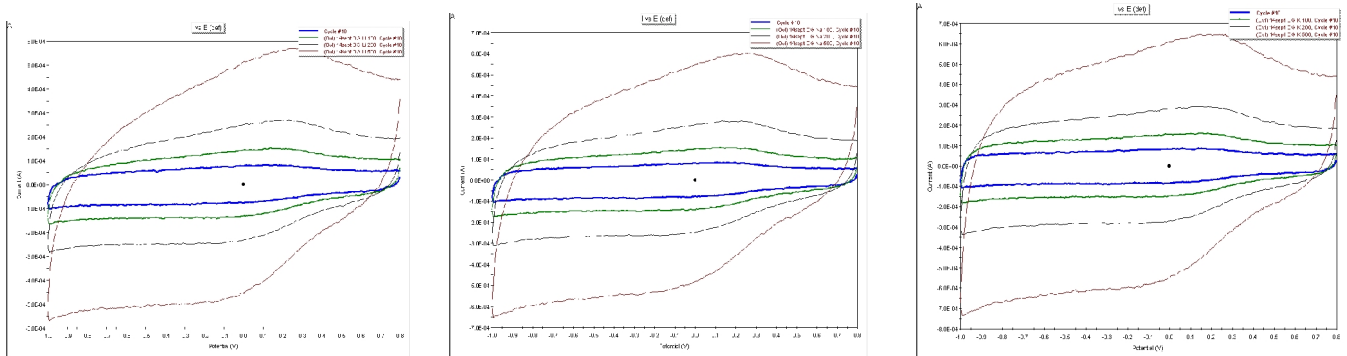


Figure 1. Different sweep rates (50 - smallest rectangular, 100, 200, 500 mV/s – biggest rectangular) of cyclic voltammetry for graphite oxide in 1M Li^+ , Na^+ and K^+ aqueous electrolyte. Voltammogram for graphite material is very similar to its oxide form.

The voltammograms of graphene oxide with voltage sweep rates from 50 mV/s to 500 mV/s are presented in Fig. 2.

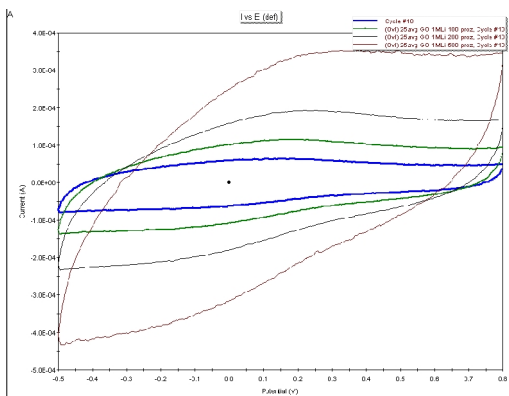


Figure 2. Different sweep rates (50-smallest rectangular to 500-biggest rectangular) mV/s of cyclic voltammetry for graphene oxide (GO) in 1M Li⁺, Na⁺ and K⁺ aqueous electrolyte.

As in case for graphite materials, voltammogram for graphene oxide become distorted dramatically with increase of voltage sweep rate, which indicates that graphene oxide is not suitable for quick charge-discharge operations. The rectangular shape of voltammogram of GO is less distorted with increase voltage sweep rate than that of graphite and graphite oxide, which means that GO possesses better capacitive behavior than GO.

From the electrochemical point of view, the three-electrode cyclic voltammograms of GO (Fig. 2) and rGO (Fig. 3) are very comparable. Since the functional groups on graphene cannot undergo redox reactions thoroughly during the fast charge/discharge process and the fact that GO contains more functional groups, more significant double-layer capacitance drop can be observed at higher scan rates compared to that of r-GO. However, the presence of additional pseudocapacitance from GO still contributes to the higher total specific capacitance (tab 1).

The voltammogram of r-GO (Fig. 3) maintain good box-like shape at all voltage sweep rates from 50 mV/s to 500 mV/s, which indicates the excellent capacitive behavior even in quick charge-discharge operations. Generally, the better accessibility of the ions to the electrochemically active surface, the better capacitive at high voltage sweep rate.

Table 1. Summary of maximum total capacitance ($C_{S,T,M}$), double-layers capacitance (C_{dl}), and pseudocapacitance (C_p) for graphite, graphite oxide, GO and r-GO in Li⁺ aqueous electrolyte

Sample	$C_{S,T,M}$ (Fg ⁻¹)	C_{dl} (Fg ⁻¹)	C_p (Fg ⁻¹)	$C_p/C_{S,T,M}$
Graphite	17.04	5.12	11.92	69.91
Graphite oxide	17.35	4.71	12.64	72.86
Graphene oxide (GO)	87.62	13.51	74.10	84.57
Reduced graphene oxide (r-GO)	85.90	65.56	20.34	23.68

The total specific capacitance in LiCl (85.90 Fg⁻¹) is a little bit higher than that in NaCl (77.70 Fg⁻¹), revealing that the reversible adsorption of Li⁺ can gain access to almost all available pores or voids of the r-GO electrode, leading to a higher occupancy and, thereby, a higher $C_{S,T,M}$ value.

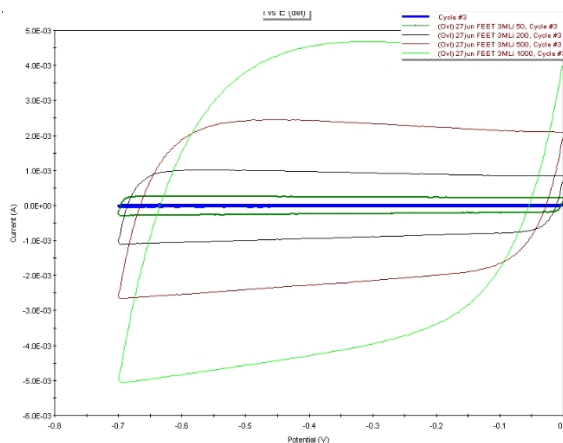


Figure 3. Different sweep rates (50-smallest rectangular to 500-biggest rectangular) mV/s of cyclic voltammetry for graphene oxide (GO) 1M Li⁺, Na⁺ and K⁺ aqueous electrolytes.

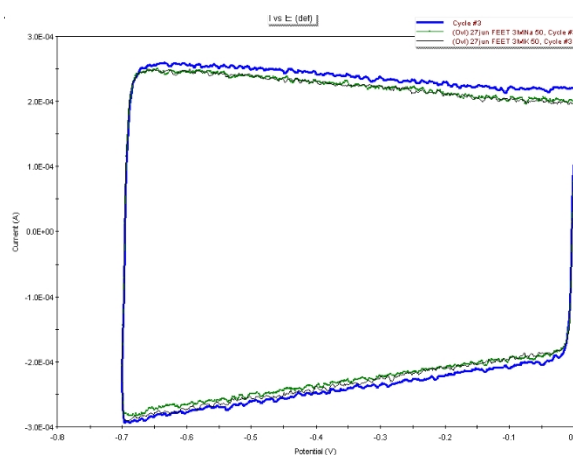


Figure 4. Shows the voltammogram of r-GO at sweep rate of 100 mV/s which compares rectangulars in Li⁺, Na⁺ and K⁺ aqueous electrolyte.

The total specific capacitance in LiCl (85.90 Fg⁻¹) is a little bit higher than that in NaCl (77.70 Fg⁻¹), revealing that the reversible adsorption of Li⁺ can gain access to almost all available pores or voids of the r-GO electrode, leading to a higher occupancy and, thereby, a higher C_{S,T,M} value. There may be an explanation for that on the basis of the different ionic sizes. First, the sizes of Li⁺ and Na⁺ ions are 0.74 and 1.02 Å, respectively. In an aqueous electrolyte, each ion is assumed to attract four water molecules on the outer shell, and the radii of hydrated cations for Li⁺ and Na⁺ are estimated to be 3.49 and 3.77 Å, respectively. This is based on the fact that one water molecule has an average diameter of 2.75 Å. Thus, the area occupied by the hydration molecules, S_o, can be determined by

$$S_o = \frac{C_s N A V \sigma}{F} \quad (1)$$

where N is Avogadro's number, σ is the cross-sectional area of hydration molecule, and F is the Faraday constant. Higher value for Li⁺ demonstrates that r-GO plane provides a higher surface accessibility for the Li ions than the Na ions in aqueous electrolyte. The n_s value is a crucial factor in evaluating the electrochemical charge density on the r-GO sheets. The n_s values for both Li⁺ and Na⁺ are 1.21 and 0.68, respectively. This finding reflects that the Li-containing molecules tend to stack dual layers, whereas Na⁺ hydration molecules favor monolayer adsorption on the partially oxidized graphene planes. Voltammogram is often used to calculate the specific capacitance value of the electrode materials. Capacitance value expressed in Farads (F) is given by the following formula:

$$C = \frac{I}{m \left(\frac{dV}{dt} \right)} \quad (2)$$

where I is the applied current, m is the mass of active electrode material, and dV/dt is the slope of the discharge curve. The obtained capacitance values of all investigated materials are listed in table 1. The GO shows the highest total specific capacitance but r-GO shows the highest double-layer specific capacitance which is of great importance due to fast charge-discharge processes in supercapacitors. Generally the higher the specific surface area of carbon, the higher the ability for charges accumulation. At slow sweep rate, the ions have enough time to diffuse into the micro and mesopore surface of GO, while at high voltage sweep rate the ions can only penetrate into some external large pores, which explain why the total capacitance of GO changes so much with the variation of voltage sweep rate compared to r-GO.

Summary / Sažetak

Superkondenzatori su uređaji za pohranu energije koji posjeduju veliku gustinu energije. Zasnivaju se na upotrebi karbonskih materijala. U ovom članku je napravljeno poređenje između raznih vrsta karbonskih materijala i to grafita, grafena kao i njihovih oksidovanih oblika. Vršena su elektrohemijska mjerenja, a najbolje se pokazao redukovani grafen oksid čiji je voltamogram na cikličnoj voltametriji pokazivao oblik pravougaonika, što je indicacija da se radi o kapacitivnim strujama. Izmjerena vrijednost njegovog kapaciteta je 85.9 Fg⁻¹ u vodenoj sredini serije elektrolita alkanih metala u radnom prozoru potencijala od 0 do -0.8V.

CONCLUSION

In this work we presented a comparison of different active materials, namely graphite, graphite oxide, graphene oxide and reduced graphene oxide for EDLCs. Electrochemical studies show the superior electrochemical performances for GO, and especially for r-GO. Cyclic voltammograms show that r-GO possesses the highest capacitance at slow sweep rate, such as 50 mV/s and it seems to be a promising alternative to other active materials. This material also shows the best performance in terms of energy and power. The worst capacitive behavior of graphite and graphite oxide is believed to be due to both its disordered pore structure, and small available surface area. These results indicate that r-GO active material may find applications in diverse fields, such as negative electrode for supercapacitors, flexible batteries, seawater desalination, and biomedical applications.

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