

# Capacitive behaviour of thermally reduced graphene oxide in a novel ionic liquid containing di-cationic charge



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## ABSTRACT

A novel ionic liquid (IL) with di-cationic group was synthesized and used to evaluate the supercapacitive behaviour of a thermally reduced graphene oxide (rGO) in comparison with aqueous LiClO<sub>4</sub> electrolyte. The morphological properties of GO and thermally reduced GO were characterized by XRD, TEM, Raman spectroscopy, and rGO was found to have a typical structural nature after thermal reduction. The electrochemical performance of the GO and rGO were studied using cyclic voltammetry, impedance spectroscopy and galvanostatic charge/discharge in two different aqueous electrolytes, 0.1 M C<sub>6</sub>(TMA)<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub> and 0.1 M LiClO<sub>4</sub>, respectively. Superior capacitive properties were observed from rGO in both the electrolytes than that of GO electrode. Maximum specific capacitances of 102 F g<sup>-1</sup> and 155 F g<sup>-1</sup> from rGO were obtained in 0.1 M LiClO<sub>4</sub> and C<sub>6</sub>(TMA)<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub>, respectively, at a scan rate of 10 mV s<sup>-1</sup>, and that are higher than that of GO (12 F g<sup>-1</sup> and 23 F g<sup>-1</sup> in 0.1 M LiClO<sub>4</sub> and C<sub>6</sub>(TMA)<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub>, respectively). The charge transfer resistances of the rGO electrode were 18.3 Ω for 0.1 M LiClO<sub>4</sub>, and 12.8 Ω for 0.1 M C<sub>6</sub>(TMA)<sub>2</sub>(BF<sub>4</sub>)<sub>2</sub>. The rGO electrode also exhibited a desirable profile and maintained over 90.6% of its initial capacitance after 2000 cycles, while 63.8% retention was observed in 0.1 M LiClO<sub>4</sub>, indicating that it has an excellent cycling performance and structural stability in IL compared with the other electrolyte.

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## 1. Introduction

Electrochemical capacitors, also known as supercapacitors or ultracapacitors, have attracted wide attention recently due to their high power density, fast charge and discharge characteristics, long cycle life, and environmental friendliness compared with traditional batteries [1,2]. Recently, graphene a single layer of two-dimensional nanostructure sp<sup>2</sup> carbon material and its derivatives have been extensively used for the fabrication of supercapacitor electrodes owing to its high aspect ratio, excellent electrical conductivity, extremely large surface area and good mechanical properties [3,4]. Stoller et al. fabricated a symmetric supercapacitor based on chemically reduced graphene oxide (GO) and obtained a specific capacitance value of 135 F g<sup>-1</sup> in KOH and 99 F g<sup>-1</sup> in an

organic electrolyte [5]. Le et al. fabricated a supercapacitor using thermally-reduced GO, which has a specific capacitance of 132 F g<sup>-1</sup> in 1 M H<sub>2</sub>SO<sub>4</sub> electrolyte [6]. In addition an electrochemically-reduced GO film was found to have a specific capacitance of 128 F g<sup>-1</sup> in 1 M NaNO<sub>3</sub> [7]. Apart from this several researches has been focused to improve the capacitance of the graphene towards its theoretical capacitance value (<500 F g<sup>-1</sup>).

Techniques including micromechanical cleavage of highly oriented pyrolytic graphite (HOPG) [8], chemical exfoliation [9], chemical vapour deposition (CVD) [10,11], and arc discharge method [12] have been used to prepare graphene oxide. Among them, the chemical exfoliation method is considered to be one of the most effective ways for large-scale and low-cost preparation of GO from graphite. The formation of GO paper by simple filtration has been reported for the fabrications of flexible devices [13,14]. As-prepared GO can be converted to reduced graphene oxide (rGO) via reduction of GO using hydrazine or other chemical reductants [15–17]. Electrochemical reduction [7], thermal reduction [18], ion implantation [19], and flash-light induced reduction

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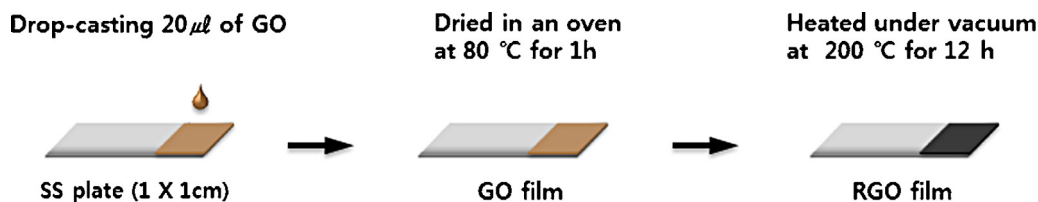


Fig. 1. rGO preparation by thermal treatment.

[20] have also been used to convert GO to rGO. Recently, supercapacitors based on graphene and aqueous electrolytes have been fabricated and the remarkable results illustrate the exciting potential for high-performance and environmentally friendly electrical energy storage devices [21,22].

In the recent past organic electrolytes, like tetraethylammonium tetrafluoroborate [23] and triethylmethylammonium tetrafluoroborate [24] in organic solvents, have been used for supercapacitors because of their relatively large potential windows. Currently, aqueous electrolyte solutions have been mostly utilized owing to their better stability, low cost and eco-friendliness [25]. But properties such as the electrolyte depletion upon charging, narrow operational temperature range, and low safety are three main drawbacks. Ionic liquids (IL) have been used to replace the organic electrolytes in a wide range of applications. Recent research demonstrated that the performances of IL-based supercapacitors are enhanced [26–28]. The physical and chemical properties of ILs can be tuned by altering the cation, anion, and attached substituents. Recently, dicationic ionic liquids have been developed by Armstrong and co-workers [29]. Some electrochemical experiments to applying these dicationic analogues have been reported to obtain the above 4 V electrochemical window [30] and an improved specific capacitance value [31].

In our previous work we reported the electrochemical capacitance behaviour of few ionic liquids with activated carbon electrodes [32]. In this present work we report the preparation of a reduced graphene oxide (rGO) electrode by a thermal reduction of GO coated directly on stainless steel (SS) without the need for a binder. A novel dicationic ionic liquid, 1,6-bis(trimethylammonium-1-yl)hexane tetrafluoroborate was synthesized and used, as the electrolyte for the evaluation of electrochemical performances of the electrodes. For a comparative study, aqueous  $\text{LiClO}_4$  is used as a supporting electrolyte.

## 2. Experimental

### 2.1. GO preparation

The experimental set-up and procedure for the synthesis of graphene oxide (GO) were based on the modification of previously reported synthesis methods [33,34]. Naturally expandable graphite flakes (3772, Asbury Graphite Mills, US) were thermally treated at 1050 °C for 15 s to produce expanded graphite (EG) and then used as the precursor for GO synthesis. In a typical GO synthesis, 1 g of EG and 200 ml of sulphuric acid were mixed and stirred in a three neck flask for 24 h. 5 g of  $\text{KMnO}_4$  was added to the mixture and stirred at room temperature for 24 h. The mixture was then cooled in an ice bath and 200 ml of deionized water and 50 ml of  $\text{H}_2\text{O}_2$  were poured slowly into the mixture resulting in a colour change to light brown followed by stirring for 30 min. The resulting dispersion was washed and centrifuged three times with a HCl solution (9:1 volume water:HCl). Repeated centrifugation-washing steps with deionized water were carried out until a solution  $\text{pH} \geq 6$  was achieved. Large GO sheets were re-dispersed in deionized water by gentle shaking.

### 2.2. Fabrication of rGO electrode

The fabrication of rGO electrode is schematically depicted in Fig. 1. The GO film was prepared by drop-casting 20  $\mu\text{l}$  of GO suspension on the stainless steel (SS) substrate ( $1 \times 1 \text{ cm}^2$ ) and dried in an oven at 80 °C for 1 h. The obtained GO film was reduced by a heat treatment under vacuum at 200 °C for 12 h. After heat treatment the film shows a colour change from deep brown to black representing the formation of reduced graphene oxide.

### 2.3. IL synthesis

Trimethylamine (Aldrich) was mixed with 1,6-dibromohexane in ethanol, and the mixture was refluxed for 48 h at 40 °C. Then, the solvent ethanol and residue were removed using a vacuum evaporator maintained at 70 °C. The synthesized sample was collected and dissolved in acetone, and mixed with an anion source ( $\text{NaBF}_4$ ). Then metathesis was performed at room temperature for 24 h with stirring, and then a white precipitate was formed which was isolated by filtration. After that the collected solution was dried in a vacuum oven at 70 °C for 24 h. Finally, the sample was purified using  $\text{Al}_2\text{O}_3$  in ACN to remove inorganic ion residues such as  $\text{Na}^+$  and  $\text{Br}^-$ . The structure of the produced IL was elucidated using  $^1\text{H-NMR}$  spectroscopy (Fig. 2). For instance 1,6-bis(trimethylammonium-1-yl)hexane tetrafluoroborate ( $\text{C}_6(\text{TMA})_2(\text{BF}_4)_2$ ) was identified as follows: *m.p.* 340–350 °C  $^1\text{H-NMR}$ , 300 MHz (DMSO- $d_6$ ):  $\delta$  (ppm) 3.36 (t, 4H), 3.09 (s, 18H), 1.72 (q, 4H), 1.32 (q, 4H).

### 2.4. Evaluation of supercapacitive properties of rGO in 0.1 M $\text{LiClO}_4$ and 0.1 M $\text{C}_6(\text{TMA})_2(\text{BF}_4)_2$ each in water

Electrochemical measurements were performed using a two or three electrode configuration using a potentiostat (Won-A Tech, Korea) system using GO and rGO electrode coated on stainless steel substrate ( $\text{SS}$ ,  $1 \times 1 \text{ cm}^2$ ) as the working electrode, and  $\text{Ag/AgCl}$

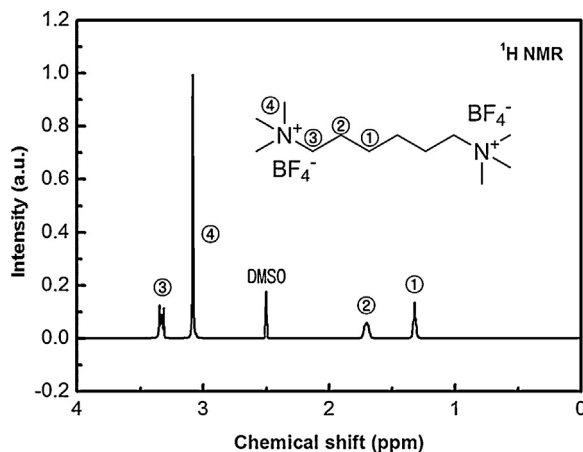


Fig. 2. NMR spectrum of  $\text{C}_6(\text{TMA})_2(\text{BF}_4)_2$ .

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