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Ionic Liquid Electrolytes with Various Constituent Ions for Graphene-based Supercapacitors

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ABSTRACT

Although activated carbon shows a higher maximum capacitance than that of graphene nanosheets (GNSs) in a conventional organic electrolyte, the latter material, characterized by high conductivity and a unique planar structure, is more suitable for use in an ionic liquid (IL) electrolyte for supercapacitors. IL electrolytes consisting of various cations (1-ethyl-3-methylimidazolium (EMI^+) and N-butyl-N-methylpyrrolidinium (BMP^+)) and anions (bis(trifluoromethylsulfony) imide ($TFSI^-$), tetrafluoroborate (BF_4^-), and dicyanamide (DCA^-)) are systematically studied. Among them, BMP-DCA IL is found to be the superior electrolyte, in which the GNS electrode exhibits a capacitance of 235 F g^{-1} and a satisfactory rate capability within a potential range of 3.3 V at 25 °C. This electrolyte is even more promising for elevated-temperature applications. At 60 °C, a symmetric-electrode GNS supercapacitor with BMP-DCA IL is able to deliver maximum energy and power densities of 103 Wh kg^{-1} and 43.3 kW kg^{-1} (based on the active material on both electrodes), respectively, which are much higher than 19 Wh kg^{-1} and 17.6 kW kg^{-1} for a control cell with a conventional organic electrolyte.

1. Introduction

With the upcoming depletion of fossil fuels coupled with growing concerns about pollution and global warming, the development of clean and effective energy conversion/storage systems that can meet future power requirements has become increasingly important [1,2]. Supercapacitors, including electric double-layer capacitors (EDLCs) and pseudocapacitors, are promising energy storage devices owing to their higher power density, wider operation temperature window, superior cyclic stability, and greater charge–discharge efficiency compared to those of batteries [3]. EDLCs, which are based on a storage mechanism of non-faradaic charge separation at the electrode/electrolyte interface, are commonly used in practical applications because they are stable, inexpensive, and easily mass-produced [4]. Activated carbon (AC) electrodes and organic electrolytes are typically used in traditional EDLCs [5]. The development of a more effective carbon material and a compatible electrolyte to further improve EDLC performance has attracted a lot of research attention.

Increasing the energy density of supercapacitors to approach that of batteries is an important topic as it extends the application domain of supercapacitors [6–8]. One effective way to achieve this is to find an advanced electrode material. Traditional AC, despite its high surface area, typically has unsatisfactory electric conductivity (and thus is unfavorable for high-rate performance). Moreover, its small pores may not be easily accessible to electrolytes, leading to a low double-layer capacitance. Carbon aerogels, ordered mesoporous carbon, and hierarchical porous carbon are attractive new materials for EDLCs [9–11]. Nevertheless, their high cost and low yield limit widespread application. Graphene nanosheets (GNSs), characterized by a two-dimensional (2-D) architecture with large accessible area, have excellent conductivity and high double-layer capacitance and thus have become a recent research focus [12,13]. Moreover, it was reported that GNSs can be manufactured in ton quantities at low cost and high uniformity [14]. It is noted that to optimize an EDLC electrode, an appropriate design of the corresponding electrolyte (type and composition) is of great significance. However, this issue has not been well explored for GNS electrodes, and thus further investigation is needed.

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To increase the energy density (ED) and power density (PD) of a supercapacitor, increasing the cell voltage (V) is an effective strategy because both ED and PD are proportional to the square of V [3]:

$$ED = (C_{cell} \times V^2)/2 \quad (1)$$

$$PD = (C_{cell} \times V^2)/(2 \times t) \quad (2)$$

where C_{cell} is the specific cell capacitance and t is the discharge time. Therefore, an alternative electrolyte with a large potential window compared to that of a conventional organic electrolyte (such as propylene-carbonate-based solution, which has a potential window of ~2.5 V) is highly desired. Ionic liquids (ILs) are excellent electrolyte candidates [15,16]. Besides having large potential windows, they possess intrinsic ionic conductivity and a high concentration of cations/anions. Using ILs can also eliminate the safety and environmental concerns raised by organic electrolytes, since ILs have excellent thermal stability, non-flammability, and non-volatility [17]. Similar drawbacks (safety and environmental issues) of the organic electrolyte in other electrochemical devices (such as Li batteries and dye-sensitized solar cells) have also been concerned [18,19]. A combination of GNS electrodes and IL electrolytes has shown promising results. 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF_4) [20–24] and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfony) imide (EMI-TFSI) [25–27] are the most commonly used IL electrolytes. However, it was found that their performance varies. For instance, the reported potential windows for EMI-BF_4 range from 3.5 to 4 V and the measured GNS capacitances are between 90–230 F g^{-1} [20–24]. Moreover, most previous studies have focused on only one kind of IL. The lack of a systematic comparison makes it difficult to tell which IL is most suitable for GNS electrodes. To have a further insight into this subject, the present study investigates various IL electrolytes. The effects of the constituent cations and anions on C_{cell},V, ED, and PD are systematically discussed. The BMP-DCA IL is found to be a promising electrolyte for GNS-based EDLCs.

2. Experimental procedure

GNSs were synthesized using a modified Staudenmaier method; the preparation details can be found in our previous papers [28,29]. Briefly, graphite oxide (GO), chemically oxidized from natural graphite (Alfa Aesar; particle size: ~70 μm; purity: 99.999%), was reduced and exfoliated by heating (~1 °C min^{-1}) to 300 °C in an inert Ar atmosphere, yielding GNSs. Besides GNSs, AC (Kuraray, YP-50F) was used in this study for comparison.

The microstructure of the GNSs was examined with transmission electron microscopy (TEM; JEOL 2100 F). X-ray diffraction (XRD; Bruker D8 Advance) was used to explore the crystallinity. In the analyses, the X-ray detector was scanned at a speed of 1° min^{-1}. A Raman spectrometer (UniRAM MicroRaman) was employed to study the bonding structure of GNSs. The spectrum was excited by a diode-pump solid-state laser with a wavelength of 532 nm. The GNS thickness was characterized using atomic force microscopy (AFM; Veeco/DI NanoMan D3100CL).

To make a supercapacitor electrode, a slurry, prepared by mixing 70 wt% graphene (or AC), 20 wt% Super P, and 10 wt% poly (vinylidene fluoride) in *N*-methyl-2-pyrrolidone solution, was pasted onto nickel foam and vacuum-dried at 110 °C for 8 h. The active material loading was approximately 0.5 mg cm^{-2}. EMI-TFSI, N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfony) imide

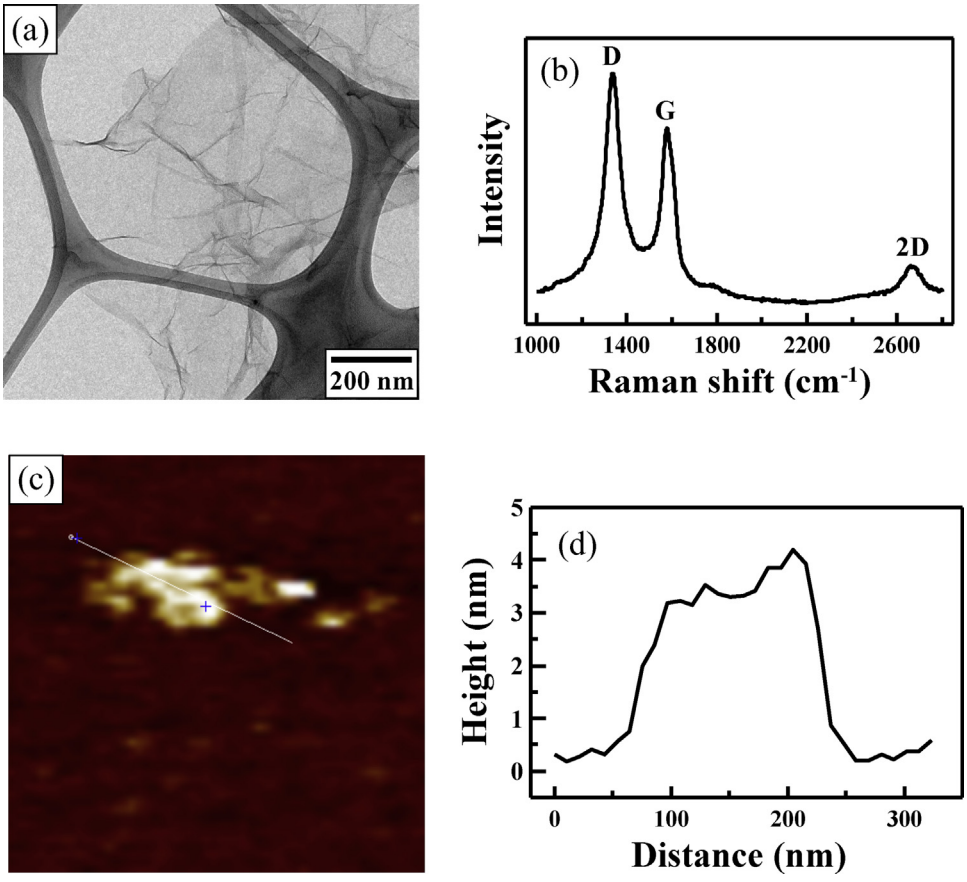

Fig. 1. (a) TEM image, (b) Raman spectrum, (c) AFM image, and (d) height profile across the marked line in (c) of synthesized GNSs.