Graphene-Based Supercapacitors Using Eutectic Ionic Liquid Mixture Electrolyte

Zifeng Lin[a,b], Pierre-Louis Taberna[a,b,*], Patrice Simon[a,b]

[a] Universite Paul Sabatier Toulouse III, CIRIMAT UMR CNRS 5085, 118 route de Narbonne, 31062 Toulouse, France
[b] Reseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, France

ABSTRACT

Compact graphene films were prepared and electrochemically tested at various temperatures in a eutectic of ionic liquid mixture (1:1 by weight or mole N-methyl-N-propylpiperidinium bis (fluorosulfonyl)imide and N-butyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide) electrolyte. A large temperature window from -30 °C to 80 °C was achieved together with a large potential window of 3.5 V at room temperature and below. A maximum gravimetric capacitance of 175 F.g^{-1} (85 mAh.g^{-1}) was obtained at 80 °C. 130 F.g^{-1} (63 mAh.g^{-1}) and 100 F.g^{-1} (49 mAh.g^{-1}) were still delivered at -20 °C and -30 °C respectively. Besides, a volumetric capacitance of 50 F.cm^{-3} was achieved with a thick graphene film (60 μm). The outstanding performance of such compact graphene film in the eutectic ionic liquid mixture electrolyte makes it a promising alternative to activated carbon for supercapacitor applications, especially under extreme temperature conditions.

1. Introduction

The high theoretical specific surface area (up to 2630 m^{2}g^{-1}) combined with low resistivity (10^{-6} Ω.cm) as well as high mechanical strength and chemical stability make graphene a promising active material for supercapacitors [1,2]. As a result, intensive research efforts have been made to characterize graphene and graphene-based materials in supercapacitors applications [1,3–5]. Specific capacitance beyond 200 F.g^{-1} has been achieved in both aqueous and organic electrolytes [4,6–9], which is similar or even better to many carbon materials like porous activated carbon [10]. However, the low density of graphene often comes with a low volumetric capacitance (F. cm^{-3}), which is a concern in most of applications, especially for micro devices [11]. Besides, restacking of graphene film still remains an issue and blocks the way to higher capacitance [12,13]. Accordingly, efforts have been devoted to synthesize more compact but un-restacked graphene films. In 2013, D. Li's group [7] proposed a method to develop a dense graphene film by capillary compression of graphene gel film in the presence of a nonvolatile liquid electrolyte, where the presence of electrolyte between the layers prevents the restacking of graphene layers.

The energy density being proportional to the voltage square ($E = 1/2 \cdot CV^2$ where E is the energy density, C is the specific capacitance and V is the working potential window), maximizing the cell voltage is of high importance for designing high energy devices. Today, most of the graphene and graphene-based materials have been characterized in aqueous or conventional organic electrolytes [11,12]. As a result, maximum voltage up to 3 V were reported [2,14].

Ionic liquid electrolytes provide a large working potential window (more than 4 V in some cases) [15,16]. In addition, high chemical stability, negligible vapor pressure and non-flammable properties make ionic liquids very promising as electrolytes for both supercapacitors and batteries [15,17]. One of the first report about the use of ionic liquid electrolytes in graphene-based supercapacitors was done by Vivekchand and et al [18], who found a specific capacitance of 75 F.g^{-1} within a 3.5 V potential window. Same group reported a reduced graphene with enhanced capacitance of 258 F.g^{-1} (measured at 5 mV/s) by nitrogen-doped [19]. Ruoff's group synthesized activated graphene materials with extremely high specific surface area – up to 3100 m^{2}g^{-1} – able delivering 200 F.g^{-1} (0.7 Ag^{-1}) in EMIMTFSI ionic liquid [20]. Despite efforts were devoted to improve the performance of graphene-based supercapacitors in ionic liquid electrolytes, less attention was paid to the operation temperature range performance of supercapacitors. Limited by high viscosity and low melting point near room temperature, neat ionic liquids are still

* Corresponding author.
   E-mail address: taberna@chimie.ups-tlse.fr (P.-L. Taberna).

unusable at sub-zero temperatures [15–22]. Therefore, a eutectic of ionic liquid mixture with low viscosity was designed by Lin et al. as an electrolyte for supercapacitors, which turned out to possess a large working temperature range from -50 °C to 80 °C alongside a wide potential window (up to 3.7 V) [21,23]. This eutectic ionic liquid mixture is composed of the same anion (bis(fluorosulfonyl) imide (FSI)) but two different cations (pyrrolidium (PYR) and piperidinium (PIP)) with the same molecular formula. The difference of molecular structure and the associated asymmetry among the cations were thought to hinder lattice formation, thus lowers the melting point while maintaining good miscibility within a large working temperature window. Conductivity values of 28.9 mS/cm and 4.9 mS/cm were measured at 100 and 20 °C, respectively, as reported earlier [23].

In this paper, we propose to use a densified graphene electrode such as proposed by Li's group [7]. in combination with an ionic liquid eutectic mixture as electrolyte to improve both the voltage window – that is the energy density – and the operating temperature range.

2. Experimental

2.1. Electrodes preparation

Commercially available graphite powder (KS44 graphite, purchased from IMERYS Graphite & Carbon Corporation) was used as the raw material. Graphite oxide was prepared by a modified Hummers method [24]. Briefly, a mixture of graphite flakes (1.0 g, 1 wt equiv) and $KMnO_4$ (6.0 g, 6 wt equiv) was added to a 9:1 mixture of concentrated H_2SO_4/H_3PO_4 (120:13 mL). The reaction was then heated to 50 °C and stirred for 12 hours, following by an addition of 200 mL ice with 1 mL 30 wt% H_2O_2. After washing by water, 30% HCl and ethanol, the graphite oxide dispersion was obtained. Graphene oxide dispersion was achieved by 1 hour sonication and 20 minutes centrifugation at 10,000 rpm of graphite oxide water dispersion.

In a first step, graphene dispersion was obtained through the reduction of graphene oxide dispersion by hydrazine solution. 0.2 mL hydrazine (35 wt% in water) and 0.35 mL ammonia (28 wt% in water) solution was added into graphene oxide dispersion (0.5 mgmL^{-1}, 100 mL) in a glass vial for stirring over 1 hour (100 °C). 60 mL 0.5 mgmL^{-1} reduced graphene dispersion was used for vacuum filtration, and an Anodisc© membrane (Whatman company) with an average pore size of 0.1 μm was used. After vacuum filtration, graphene film was carefully peeled off and immersed in deionized water overnight to remove the remaining hydrazine and ammonia [7].

In a second step, the graphene disc films were punched out (7 mm diameter) and transferred into acetonitrile for more than 48 h to totally replace the water with acetonitrile. Films were then immersed in 10 wt% (0.27 M) ionic liquid mixture in acetonitrile for more than 72 hours, to exchange the acetonitrile in graphene film with the ionic liquid solution. Samples were then collected, clipped between two glass plates and moved to a vacuum oven under 80 °C. After 48 hours, the volatile acetonitrile was completely evaporated and nonvolatile ionic liquids remained inside the graphene film, which is expected to limit the restacking of graphene layers. As a result of the densification, the thickness of the graphene film was greatly decreased (from around 180 μm to 60 μm), while the diameter was measured close to 5.4 mm. Herein, the graphene film was well prepared and ready for electrochemical tests.

The weight of the electrodes was measured after electrochemical tests. Specifically, the electrodes were washed by acetonitrile and ethanol to eliminate the trapped electrolyte and then the weight was measured after vacuum drying.

2.2. Electrochemical tests

Graphene films were used as working electrodes directly after vacuum drying without any binders. A eutectic ionic liquid mixture composed of (1:1 by weight or molar ratio) N-methyl-N-propylpiperidinium bis(fluorosulfonyl) imide (PIP$_{13}$-FSI) and N-butyl-N-methylpyrrolidinium bis(fluorosulfonyl) imide (PYR$_{14}$-FSI) was prepared and used as the electrolyte [21]. Both ionic liquids were bought from Solvionic SA (France). Two 25 mm-thick porous Al_2O_3 separators were used together with gold (for RHD cell) or platinum (for Swagelok cell) as the current collector.

For high and low temperature tests, a RHD cell (Figure. S1) was used, which enables finely precise control of the cell temperature from −40 up to 100 °C [25]. After reaching each test temperature, the temperature was held at least two hours before measurements to ensure the cell has reached the desired temperature. Tests were performed by using an Autolab PGSTAT128 N (Metrohm, Switzerland). Besides, three-electrode Swagelok cell were assembled and tested at room temperature, using a silver wire as quasi-reference electrode and tested by using a VMP3 potentiostat (Biologic, S.A.). All supercapacitors cells mentioned above were assembled in a glove box under argon atmosphere (water and oxygen contents less than 1 ppm).

Electrochemical impedance spectroscopy (EIS) measurements were carried out at open circuit voltage (OCV) with an amplitude of 10 mV at the frequency range from 0.01 Hz to 200 kHz. Capacitance was calculated from cyclic voltammograms by measuring the slope of the integrated discharge charge Q versus discharge time (s) plot and divide by scan rate (V/s). Gravimetric capacitance was calculated by dividing the electrode capacitance by the weight of graphene on one electrode, according to equation (1)

$$C = \frac{\Delta Q}{\Delta t \cdot \vartheta \cdot m} \tag{1}$$

Where C is the specific capacitance (F.g^{-1}); $\frac{\Delta Q}{\Delta t}$ is the slope of the integrated discharge charge Q versus discharge time plot (A); ϑ is the scan rate (V/s) and m is the mass of graphene on one electrode (g).

2.3. Characterization

X-ray diffraction patterns were recorded by an X-ray diffractometer (D4 ENDEAVOR, Bruker, Germany) using Cu Kα radiation (λ = 0.154 nm) with an operation voltage of 40 kV and current of 40 mA.

SEM observations of the graphene films were made using a JSM-6510LV Scanning Electron Microscope after completion of
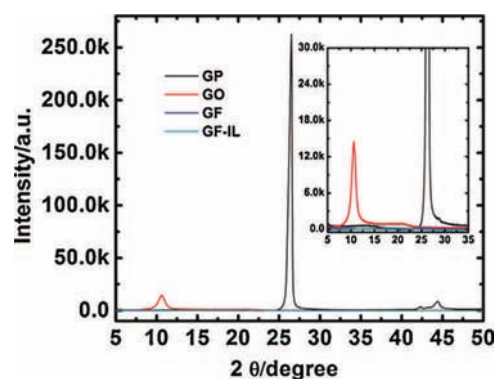
Fig. 1. X-Ray diffraction patterns of graphite (GP), graphite oxide (GO), graphene film (GF) and graphene film filled with electrolyte (GF-IL). Inset: zoom in the 8° - 35° 2θ range.

electrochemical tests, for the sake of accuracy in the film thickness measurement.

3. Results and discussion

X-Ray diffraction patterns of graphite, graphite oxide and graphene films with or without electrolyte are presented in Fig. 1 . GF stands for graphene films without electrolyte, obtained by vacuum filtration that is containing water inside. GF-IL are the graphene films obtained after electrolyte immersion that contain ionic liquid mixture electrolyte after acetonitrile removal. The (0 0 2) peak around 26.0° of pristine graphite (GP) corresponds to an expected interlayer spacing of 0.336 nm. For graphite oxide (GO), the peak shifts to 9.0° as a result of the increased interlayer spacing to 0.976 nm after oxidation [26]. No peaks were observed for graphene film filled or not with electrolyte. It was expected since for graphene film/GF (without electrolyte), which contains more than 90 wt% percent of water inside, the exfoliated graphene flakes were separated from each other by water, therefore no restacking happens [13]. On the other hand, when electrolyte filled graphene films/GF-IL (water replaced by nonvolatile electrolyte), the presence of the electrolyte is assumed to prevent restacking.

SEM observations of the films are shown in Figs. 2 . As can be seen in Fig. 2a graphene films/GF present a homogeneous thickness of 60 μm which enables accurate determination of the volume (1.374×10^{-3} cm^3) to obtain the volumetric capacitance. A layer-by-layer structure was shown in Fig. 2b, as a result of the filtration process. Such a layered structure is assumed to be at the origin of the densification of the films as compared to conventional three-dimensional disordered structure, resulting in a high volumetric energy density [7].

Fig. 3 shows Cyclic Voltammograms (CVs) of an asymmetric 3-electrode Swagelok cell at room temperature, at a scan rate of 20 mV/s, in the ionic liquid mixture electrolyte. The rectangular shape of the CV reveals a capacitive behavior. High gravimetric capacitance (175 F.g^{-1}) was achieved, superior to most of the reduced graphene oxides reported so far in ionic liquid electrolytes or conventional organic electrolytes (Table. S1) [7–28]. In addition, a large potential window of 3.5 V (from -2 V to 1.5 V (vs Ag wire)) make these materials more promising for designing high energy supercapacitors.

A symmetrical two-electrode Swagelok cell was assembled and tested at room temperature. The high frequency loop observed on the Nyquist plot (Fig. 4a) is assumed to originate from the contact resistance between the current collectors and the film [29]. The high frequency series resistance was measured at 40 Ω.cm^2, which is in the same range as previously reported for this electrolyte at room temperature [23]. When going down to low frequencies, the fast increase of the imaginary part of the impedance reveals the capacitive behavior of the electrode. Fig. 4b shows the CVs at different scan rates. High capacitance of 170 F.g^{-1} was obtained at a
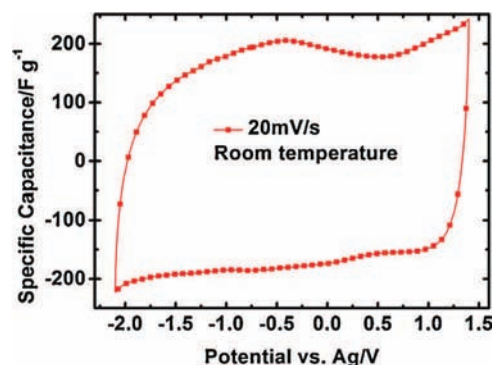

Fig. 3. Cyclic Voltammograms at room temperature in N-Methyl-N-propylpiperidinium bis(fluorosulfonyl) imide (PIP13-FSI): N-Butyl-N-methylpyrrolidinium bis (fluorosulfonyl)-imide (PYR14-FSI) ionic liquid mixture (1:1 by weight or molar ratio). The potential scan rate was 20 mV/s, with a potential window from -2 V to 1.5 V/Reference (using a silver wire as pseudo-reference electrode).

scan rate of 5 mV/s within a 3.5 V potential range, which is beyond most of the conventional carbons reported so far [10–31]. The change of the capacitance with the potential scan rate is shown in Fig. 4c. More than 75% of the maximum capacitance was still preserved at 50 mV/s, thus highlighting the decent power performance of the cell despite using a neat ionic liquid electrolyte. The associated volumetric capacitance, calculated from the electrode thickness, was 50 F.cm^{-3} at 5 mV.s^{-1}, which is also comparable to conventional activated carbon powders [10].

Fig. 5 shows the electrochemical characterization at higher temperature, namely 40 °C, 60 °C and 80 °C. As expected, the high frequency series resistance decreases with increasing temperature (Fig. 5a), due to the decrease of the electrolyte viscosity. The improved capacitive behavior at elevated temperature as can be seen by the sharp increase in the imaginary part at lower resistance; it is associated with the increase of the electrolyte conductivity with the temperature [21,23]. The improved capacitive behavior with the temperature is also visible on the CVs (Fig. 5b), with capacitive electrochemical signatures. However, a limitation in the potential window from 3.5 V down to 3.2 V was observed when the temperature was increased from 40 °C to 80 °C. Such a behavior is associated with the electrochemical activity (oxidation) of the ionic liquid electrolyte at high potential, as already reported elsewhere [21]. Specific capacitance was increased from 160 F.g^{-1} up to 175 F.g^{-1} with increasing temperature because of the viscosity falloff.

Fig. 6 shows the electrochemical characterizations at low and negative (sub-zero) temperature. Owing to the high viscosity under low temperature, a slow scan rate of 1 mV/s was applied. The Nyquist plot (Fig. 6a) shows an important increase of the series resistance at negative temperature, in agreement with the decrease of the electrolyte conductivity [23]. The electrochemical
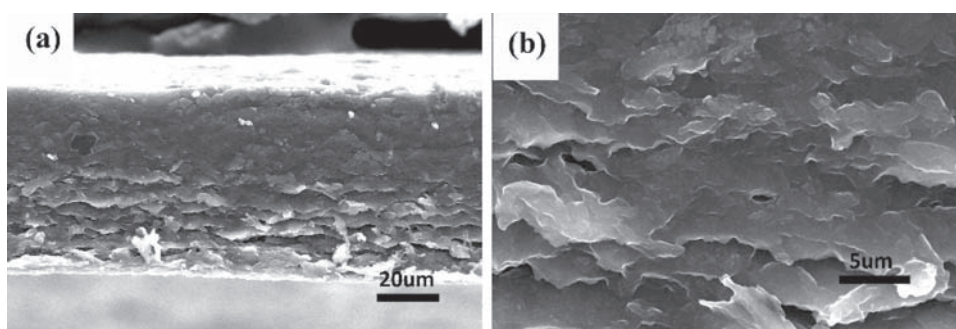

Fig. 2. SEM images of cross-section morphology of graphene film after electrochemical tests. Scale bar: 20 μm (a), 5 μm (b).
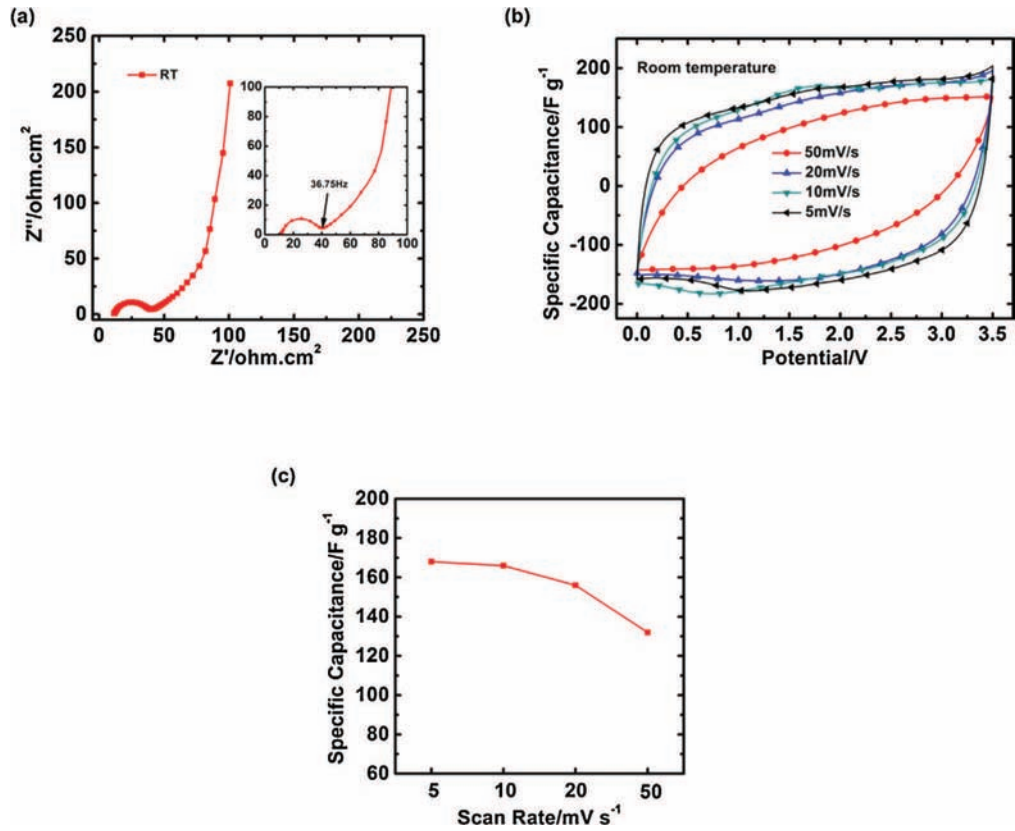
Fig. 4. Electrochemical characterization at room temperature of a 2-electrode cell assembled with dense graphene films, in eutectic mixture electrolyte: EIS Nyquist plot (a), CVs at various scan rates (b), change of the specific capacitance with the potential scan rate (c).
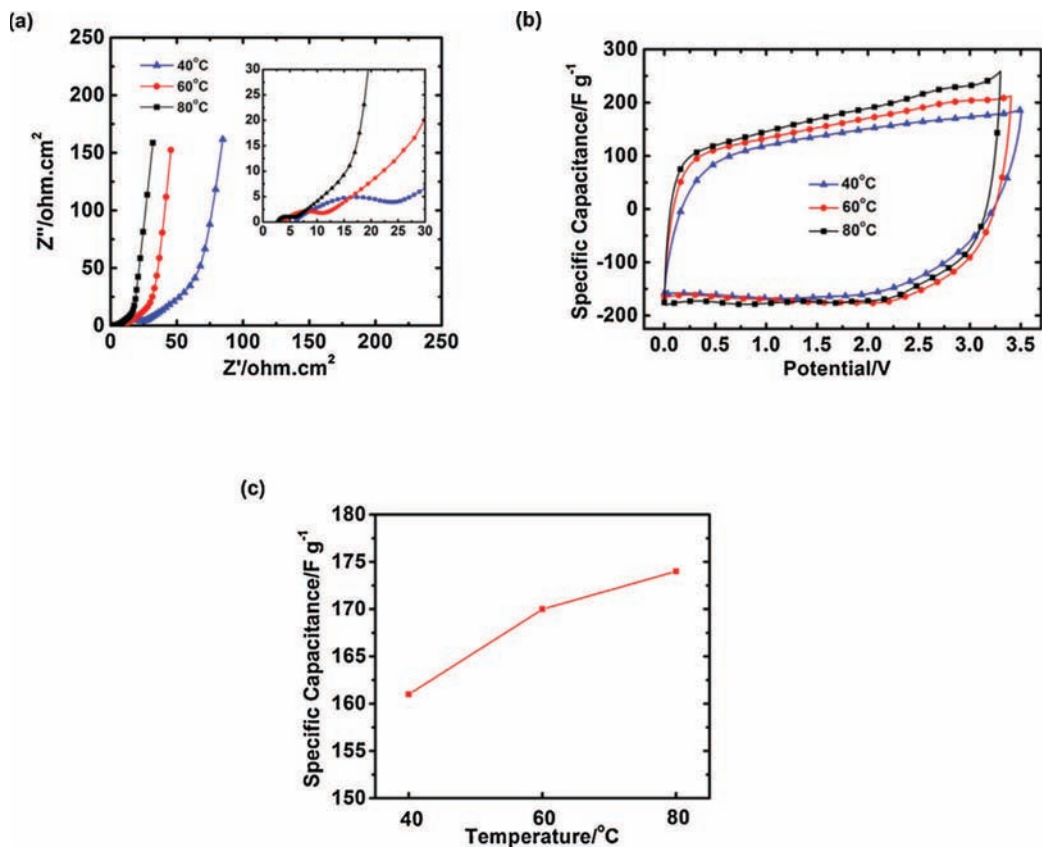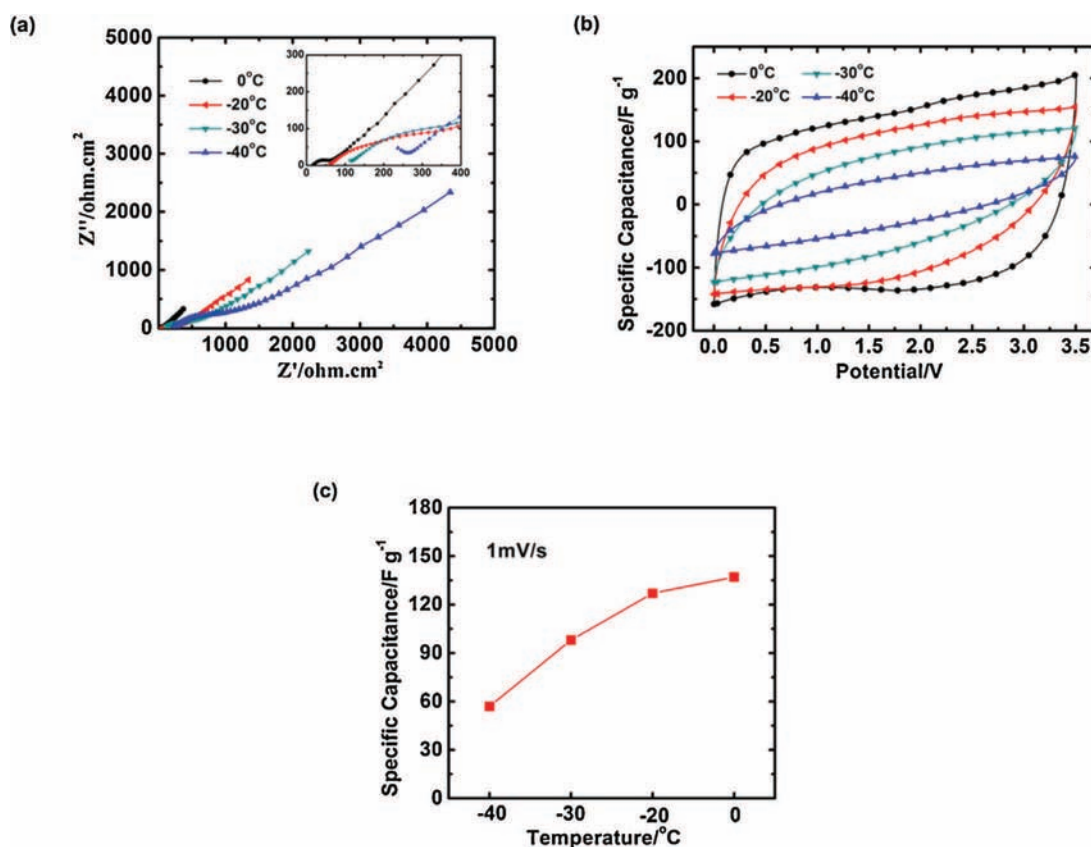

Fig. 5. Electrochemical characterization at 40 °C, 60 °C and 80 °C of a 2-electrode cell assembled with graphene films, in eutectic mixture electrolyte. Nyquist plots (a), CVs (b) and change of the specific capacitance with the temperature (c).

Fig. 6. Electrochemical characterization at 0 °C, -20 °C, -30 °C and -40 °C of a 2-electrode cell assembled with graphene films, in eutectic mixture electrolyte. Nyquist plots (a), CVs at 1 mV.s⁻¹ (b) and change of the specific capacitance with the temperature at a scan rate of 1 mV.s⁻¹ (c).

signature (Fig. 6b) still shows a capacitive behavior down to -30 °C while it becomes too resistive at -40 °C. A capacitance of 135 F.g⁻¹ (63 mAh.g⁻¹) was obtained at 0 °C and 100 F.g⁻¹ (49 mAh.g⁻¹) at -30 °C. When the temperature goes down to -40 °C, the electrochemical behavior is governed by the ohmic drops inside the bulk of the electrolyte.

These results show that the combination of dense graphene films with a eutectic ionic liquid mixture can be promising as an alternative to conventional porous carbons for supercapacitor applications. Beyond the high gravimetric and volumetric capacitance obtained at room temperature (165 F.g⁻¹ and 50 F.cm⁻³, respectively), the large potential window (3.5 V) and temperature operation range (from -30 °C to 80 °C) make them suitable for designing high energy density supercapacitors.

4. Conclusions

Using vacuum filtration, electrolyte immersion and selective evaporation, compact graphene films characterized by a layer-by-layer structure was prepared and used as electrode materials for supercapacitors without binders. Thanks to the use of a eutectic ionic liquid mixture as electrolyte, a large working temperature window from -40 to 80 °C could be explored. A maximum gravimetric capacitance of 175 F.g⁻¹ (85 mAh.g⁻¹) was reached at 80 °C. Despite the capacitance at -40 °C was limited at 60 F.g⁻¹ (30 mAh.g⁻¹), 130 F.g⁻¹ (63 mAh.g⁻¹) and 100 F.g⁻¹ (49 mAh.g⁻¹) were still achieved at -20 °C and -30 °C respectively. The potential window was increased up to 3.5 V at room temperature and 3.2 V at 80 °C, thus leading to substantial improvement in the cell energy density. Additionally, a volumetric capacitance of 50 F.cm⁻³ was also achieved with a thick graphene film of 60 μm. These materials could be a promising alternative to activated carbon operating in conventional electrolytes for supercapacitor applications, especially under extreme temperature conditions.

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