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# 4–10 V capacitors with graphene-based electrodes and ionic liquid electrolyte

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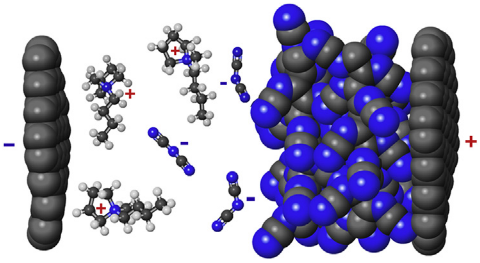
## HIGHLIGHTS

- Graphene electrodes passivate in dicyanamide-based ionic liquids.
- High voltage graphene-based capacitor construction is proposed.
- 4.5, 5, 6.3, and 10 V capacitors with reduced graphene oxide electrodes are tested.
- Graphene-based capacitors have higher energy densities than Ta capacitors.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Atomically thin graphene is a promising capacitor electrode material, but the cell voltages achieved so far with various electrolytes are too low for a typical capacitor's application. In this paper it is demonstrated that in a dicyanamide-based ionic liquid electrolyte a graphene electrode passivates at 10 V and at the same time the conductivity of the single-layer graphene sheet increases more than 5 times. The protective self-healing nanolayer formed is a new carbon–nitrogen material with dielectric constant value up to 9.8. In the cell voltage range from 4 to 10 V, capacitors with large surface area reduced graphene oxide electrodes outperform any commercial capacitor technology by better energy density.

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## 1. Introduction

The energy density of capacitors depends on the quality of dielectric material used – it is a linear function of the dielectric constant ($\varepsilon_r$), but a square root function of the dielectric strength [1]. An electrical double layer capacitor, often called a supercapacitor (SC), does not have a dielectric layer and has the highest energy density. However, the ~1 s time constant is too high for a typical capacitor's application – smoothing ac ripple in dc voltage converters [2–4]. Lately, faster graphene-based SCs have been introduced, but the limitation is still low cell voltage, only up to 0.8–2.5 V [5–7] (3.5 V have been achieved in slower graphene-based capacitors [2]). Modern electronic devices, such as computers, USB chargers, or mobile phones, have a typical rail voltage of 3.3 or 5 V and use capacitors within range of 4–10 V. Unfortunately, series electrical connection of SCs reduces useable high frequency range and increases complexity of the electrical circuit [5]. Therefore, because of low cell voltage, lower efficiency, higher time constant, and worse high temperature stability, SC market

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share is only 4%, whereas the total capacitor annual market is approximately $18 billion [8].

In the cell voltage range from 4 to 10 V the highest energy densities (before current work) can be obtained with tantalum capacitors, followed by aluminum and ceramic capacitors [1]. However, because the metal nanostructures and a few nm thick dielectric films are not very stable, the energy densities are ridiculously low, for example only 0.015 J $g^{-1}$ for a 4 V tantalum capacitor (Supplementary methods S2.4). What is even worse, in real applications capacitor voltages are usually further derated 50% in order to get longer lifetime [9], but half voltage results in 4 times lower energy density. The surface roughness of aluminum foil electrodes is less than 200 [10] or specific surface area of sintered tantalum anodes is below 10 $m^2$ $g^{-1}$ [11], but carbon forms stable atomically thin graphene sheets with surface area more than 2600 $m^2$ $g^{-1}$ [2]. However, unlike tantalum and aluminum, graphene does not form a protective dielectric oxide layer; thus, high voltage graphene electrolytic capacitors are not known yet.

1-Butyl-1-methylpyrrolidinium dicyanamide (BMPDCA) ionic liquid (IL) has excellent properties for charge-storage devices, because of relatively low viscosity of 50 cP at 25 °C, high ionic conductivity of 12.4 mS $cm^{-1}$, low melting point of −55 °C, high decomposition temperature of 300 °C, negligible vapor pressure, and cathodic limit of −2.2 V vs. Ag|AgCl [12–17]. Furthermore, it has been found that the ILs containing DCA anions are less toxic than widely used ILs containing $BF_4^-$ anions [18]. Wu et al. studied germanium electrodeposition from BMPDCA and noted the formation of an isolating layer at the positive electrode surface, which obstructs Ge electrodeposition process [19].

This article describes passivation (*i.e.* formation of protective layer) of graphene and other flat carbon electrodes by an anodic polymerization reaction in BMPDCA and demonstrates the high voltage capacitor properties with large surface area reduced graphene oxide (RGO) electrodes.

## 2. Experimental

### 2.1. Preparation of electrode materials

Graphene electrodes were prepared from CVD-grown (chemical vapor deposition) single layer graphene films on copper foil (from Graphenea, additionally confirmed by an intensive Raman peak at 2633 $cm^{-1}$, measured using a 633 nm laser [20]), which were attached onto glass plates using an epoxy glue, followed by dissolution of the Cu layer with 1 M $FeCl_3$ solution during 40 min at 60 °C. 10 μm thick highly oriented pyrolytic graphite (HOPG) films were ripped from a HOPG (0001) cube (Veeco). 20 nm thick amorphous carbon films (aC) were magnetron sputtered onto glass plates with the following parameters: base vacuum $5\times10^{-9}$ Torr, 3 mTorr Ar pressure, 200 W pulsed DC source (100 kHz, 3 msek), 50 W bias at the sample, sample temperature 190 °C, 3″ graphite (99.999%) target [21]. RGO electrodes were produced from graphene oxide (GO), synthesized in our lab using a modified Hummer's method [22]. Thermal reduction was carried out by heating GO quickly up to 500 °C. Dispersion of GO (2.5 mg $mL^{-1}$), multiwall carbon nanotubes (MWCNT) (0.8 mg $mL^{-1}$), and RGO (5 mg $mL^{-1}$) was prepared by first applying ultrasonic bath (for 30 min) to GO and MWCNT solution in ethanol and then mixing with the RGO powder. An RGO electrode was prepared by dropping 10 μL of the solution onto a microscope glass support heated to 225 °C and gently roll-pressing the material; this process was repeated once more to yield 40–60 μm thick electrode with diameter of 4–5 mm (spray-pyrolysis gives similar results and can be used in scaling up the electrode sizes). Next, the electrode material was heated in vacuum up to 550 °C to increase the electronic conductivity and after cooling down it was coated with 1 μm thick aluminum layer by magnetron sputtering for good electrical contact.

### 2.2. Spectroscopy equipment

Atomic force microscopy (AFM) data were obtained by Agilent Technologies™ Series 5500 system. Raman spectra were measured with Renishaw inVia Raman Microscope. Scanning electron microscopy images were taken with Zeiss EVO MA15. The infrared spectroscopic measurements were performed using a PerkinElmer Spectrum GX FT-IR system equipped with a liquid nitrogen-cooled mid-range MCT detector. The details for *in situ* infrared absorption spectroscopy measurements have been provided elsewhere [21]. The electrochemical measurements were conducted using an Autolab PGSTAT 30 potentiostat. The maximum cell voltage for the developed capacitor was restricted to 10 V due to limitation of the Autolab potentiostat and the impedance measurements were limited to 5 V.

### 2.3. Electrochemical measurements

Electrochemical measurements with graphene, aC, HOPG, and 40–60 μm thick RGO electrodes were conducted in a three-electrode glass cell, which holds 0.35 mL of IL and also includes a Pt spiral counter electrode [21]. An Ag|AgCl wire in the same IL was used as a reference electrode and it was connected to the cell with a Luggin capillary. The cell was pressed against an electrode using a silicon seal. Conveniently, 0 V also represents the zero charge potential as the actual values for the untreated RGO and passivated RGO or graphene electrodes are 0 ± 0.1 V vs. Ag|AgCl in IL (detected from the minima of capacitance, potential curves for unmodified RGO electrodes and by comparing capacitance values from impedance and from constant current discharge curves for the passivated electrodes). It is important to note that the measurements were carried out in an argon glove-box and before experiments the BMPDCA (Solvionic; purity 99.5%; density 0.95 g $cm^{-3}$) was additionally dried in ultra high vacuum at 110 °C for 24 h, until reaching a pressure of $5 \times 10^{-9}$ Torr and water content below the detection limit of Karl-Fischer method (<10 ppm).

The electrochemical data for the 4–6 mm diameter capacitor electrodes were measured after the electrodes were completely passivated at 23 °C. Flat electrodes were usually passivated using three cyclic voltammetry scans at scan rate of 10 mV $s^{-1}$ from 0 V to a passivating potential ($E_{pass}$), followed by holding the electrode at the $E_{pass}$ for 16–24 h. RGO electrode passivation procedure started with a 2 s pulse at 2.9 V, followed by three cyclic voltammetry scans at scan rate of 10 mV $s^{-1}$ from 0 to the $E_{pass}$, and then the electrode was held at the $E_{pass}$ for 24 h.

It must be noted that because decomposition products form at the negative electrode during passivation of the positive electrode, it is recommended to carry out the passivation procedure with a separate counter electrode and also replace the ionic liquid electrolyte for a 2-electrode cell. However, tightly packed 2-electrode cells were not assembled in this work and all electrochemical measurements were carried out in the 3-electrode cell without changing the electrolyte.

## 3. Results and discussion

### 3.1. Passivation of carbon surfaces

Single-layer graphene sheet was used as the electrode and dried BMPDCA ionic liquid as the electrolyte in the following experiments. The first excursion of electrode potential $E$ toward the

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