



# A phenylenediamine-mediated organic electrolyte for high performance graphene-hydrogel based supercapacitors

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## ABSTRACT

We prepare a novel redox-additive organic electrolyte containing phenylenediamine for a graphene-hydrogel supercapacitor. By adopting this electrolyte, significant capacity enhancement (47–596% increase) is achieved. At the concentration of  $0.02 \text{ mol l}^{-1}$ , the specific capacity value of the graphene-hydrogel electrode reaches  $171 \text{ mAh g}^{-1}$ ,  $287 \text{ mAh g}^{-1}$ , and  $353 \text{ mAh g}^{-1}$  at  $1 \text{ A g}^{-1}$  for o-phenylenediamine (OPD), m-phenylenediamine (MPD), and p-phenylenediamine (PPD), respectively. The enhancement by PPD is more significant than OPD and MPD at concentrations higher than  $0.02 \text{ mol l}^{-1}$ . This behavior is likely caused by the para-amino groups, which exhibits less stereo-hindrance during the absorption of phenylenediamine onto the graphene surface. In the electrolyte containing  $0.04 \text{ mol l}^{-1}$  of PPD, specific capacity of  $516 \text{ mAh g}^{-1}$  at  $1 \text{ A g}^{-1}$  and energy density of  $143 \text{ Wh kg}^{-1}$  with power density of  $1.11 \text{ kW kg}^{-1}$  are achieved. Meanwhile, 93.8% of the electrode's initial capacity ( $433 \text{ mAh g}^{-1}$ ) is retained after 5000 cycles at  $2 \text{ A g}^{-1}$ , demonstrating its excellent cycling stability.

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## 1. Introduction

The electrochemical capacitors, also known as supercapacitors (SCs), exhibits high power density (allowing fast charging and discharging) and long cycling life (>100,000 cycles). These advantages over traditional batteries have attracted considerable research interest from both academia and industry [1,2]. However, relatively low energy density has limited its application as the sole power source in various applications (e.g., portable electronics, electric or hybrid electric vehicles, aircraft, and smart grids) [3–7]. Currently, the commercial SCs exhibit energy density value of  $5\text{--}10 \text{ Wh kg}^{-1}$  [8,9], lower than that of lead acid batteries ( $25\text{--}35 \text{ Wh kg}^{-1}$ ) and lithium ion batteries ( $200\text{--}400 \text{ Wh kg}^{-1}$ ) [10]. Significant research effort has been devoted to improve the energy density of SCs without sacrificing their power density and cycling stability [5,6,8,9].

Recent research has shown that adding redox-active compound into the electrolytes can effectively improve the specific capacitance. In this type of devices, the electrochemical characteristics consists of electric double-layer capacitance (EDLC) and diffusion-controlled faradaic reaction of the adsorbed active compound on the electrode [11,12]. The latter is closely related to electrochemical behavior of flow batteries [13,14].  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  [15] and iodine/iodide [16] are the first redox mediators studied by researchers. The iodine/iodide couple demonstrates specific capacitance as high as  $1000 \text{ F g}^{-1}$  ( $222 \text{ mAh g}^{-1}$ ). Yoo et al. study pentylviologen/bromide redox pair and fabricate an asymmetric supercapacitor exhibiting energy density of  $48.5 \text{ Wh kg}_{\text{dry}}^{-1}$  at  $0.5 \text{ A g}_{\text{dry}}^{-1}$ . Phenyl compounds and their relatives, such as phenylenediamine [17,18] and hydroquinone [19,20], have also been studied as redox additives. In particular, phenylenediamine is a promising choice because of its low-cost and the highly reversible two-electron redox reaction, which results in significant pseudocapacitive contribution. Zhang and coworkers adopted phenylenediamine-mediated aqueous electrolyte with 1,4-dichlorobenzene derived carbon, demonstrating a specific capacitances of  $504.1 \text{ F g}^{-1}$  ( $140 \text{ mAh g}^{-1}$ ) at  $3 \text{ A g}^{-1}$  [17]. Wu et al. studied aqueous KOH/PPD electrolyte and show a specific capacitance of  $605.2 \text{ F g}^{-1}$  ( $168 \text{ mAh}$

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$\text{g}^{-1}$ ) [18]. However, when using organic electrolyte for higher operating voltages, the capacitance enhancement decreased drastically. Yu and coworkers investigated the phenylenediamine-mediated acetonitrile electrolyte with activated-carbon electrode but only found the specific capacitance to be  $68 \text{ F g}^{-1}$  ( $51 \text{ mAh g}^{-1}$ ) [21]. Because high cell voltage leads to high energy density, developing a phenylenediamine-mediated organic electrolyte is important for pursuing low-cost and high-performance supercapacitors.

The difference in the enhancement between aqueous and organic electrolytes likely originates from the interaction between phenylenediamine and the carbon-based electrodes. In 1990s, the interaction of aromatic compounds via inter-molecular forces, especially  $\pi$ - $\pi$  interaction, has been widely studied [22,23]. The above-mentioned researches on the phenylenediamine-mediated electrolytes are all based on activated carbon electrodes. As we known, the solvation energy needs to be compensated as the redox-mediator is absorbed onto the electrode from the electrolyte. The irregular surface of the activated carbon electrode exhibits limited  $\pi$ -electron characteristics, incapable of compensating the energy for phenylenediamine desolvation, especially in organic solvent.

As a promising alternative carbonaceous material, graphene demonstrates high electrical conductivity while exhibiting high surface area and good chemical stability [24,25]. Its electrochemical properties can be further improved by forming 3D structure, such as foams [26], hydrogels [27], or sponges [28]. These different architectures effectively prevent the restacking between graphene sheets and preserve the  $\pi$ -electron characteristics of the graphene surface [29,30]. Interestingly, graphene can be functionalized non-covalently (such as via  $\pi$ - $\pi$  interaction) without interrupting the electrical conductivity of graphene architectures [31,32]. The functionalization further improves the specific capacitance of graphene electrodes.

Herein, by adopting the strategy of non-covalent functionalization of graphene, we prepare a phenylenediamine-containing organic electrolyte for graphene-hydrogel (GH) based supercapacitors. The electrochemical properties of GH electrodes are characterized to reveal significant capacity enhancement by the phenylenediamine addition. The GH electrode exhibits large specific capacity of  $516 \text{ mAh g}^{-1}$  and high energy density of  $143 \text{ Wh kg}^{-1}$  at  $1 \text{ A g}^{-1}$ . Moreover, 93.8% of the electrode's capacity are retained after 5000 cycles at  $2 \text{ A g}^{-1}$ , demonstrating great potential in practical applications.

## 2. Experimental section

### 2.1. Preparation of electrodes and redox-additive organic electrolytes

All reagents used in this work are of analytical grade unless mentioned otherwise. Graphene-hydrogel electrodes are prepared by hydrothermal-chemical reduction of graphene oxide (GO). GO is prepared from high-purity graphite flakes (Aladdin, 99.99%, 8000 mesh) according to the Hummers' method [33]. For the hydrothermal-chemical reduction,  $\text{NaHSO}_3$  is added into the  $2 \text{ mg ml}^{-1}$  homogeneous aqueous GO dispersion as the reducing agent. A mass ratio of 3:1 between  $\text{NaHSO}_3$  and GO is adopted according to a reported method [34]. After sufficient stirring, 1.5 ml of the mixture is sealed in a 20-ml glass vial and heated at  $95^\circ\text{C}$  in an oven for 3.5 h to form the graphene-hydrogel (GH). The as-prepared GH disc is dialyzed in deionized water for 12 h to remove the residual inorganic compounds. After the dialysis, the GH disc is pressed onto a piece of 16-mm round nickel-foam current collector under 5 MPa pressure. The electrode is dried at  $100^\circ\text{C}$

for 12 h. The mass loading of GH on each electrode is approximately 1.5 mg.

$\text{MeEt}_3\text{NBF}_4$  is chosen as the supporting electrolyte in acetonitrile. o-phenylenediamine (OPD) (Aladdin, AR), m-phenylenediamine (MPD) (Aladdin, AR), and p-phenylenediamine (PPD) (Aladdin, AR) are used as the redox additives. As an example, to 40 ml of  $1 \text{ mol l}^{-1}$   $\text{MeEt}_3\text{NBF}_4$  acetonitrile solution, 0.0864 g ( $0.02 \text{ mol l}^{-1}$ ) of p-phenylenediamine (Aladdin, AR) is dissolved to make the redox organic electrolytes [ $1 \text{ M MeEt}_3\text{NBF}_4 + 0.02 \text{ M PPD}$ ]. Electrolyte solutions contain different amount of OPD ( $0\text{--}0.03 \text{ mol l}^{-1}$ ), MPD ( $0\text{--}0.03 \text{ mol l}^{-1}$ ), and PPD ( $0\text{--}0.06 \text{ mol l}^{-1}$ ) are also made according to the same method.

### 2.2. Characterizations and measurements

The microstructure and morphology of the as-obtained GH electrodes are characterized by scanning electron microscopy (SEM; Hitachi SU8010). X-ray diffraction (XRD) patterns are collected on a Rigaku Miniflex diffractometer equipped with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). XPS spectra are obtained from a Thermo Scientific ESCALAB 250Xi X-ray Photoelectron Spectrometer with  $\text{Mg K}\alpha$  radiation as the excitation source. Raman spectra are collected on LabRAM HR Evolution (France).  $\text{N}_2$  adsorption-desorption test is done on a Micromeritic ASAP 2020 M.

Cycle voltammetry (CV) measurements are conducted on a PINE electrochemical workstation (Wavedrive 10). The electrochemical characterization of individual electrodes are performed in a three-electrode cell configuration, with a platinum counter electrode and an  $\text{Ag/AgCl}$  reference electrode ( $0.241 \text{ V vs. SHE}$  at  $25^\circ\text{C}$ ). The galvanostatic charge-discharge (GCD) tests are carried out on a Neware Battery Measurement System (Neware, China) at various current densities within the voltage window of  $0.01\text{--}2.7 \text{ V}$ . A sealed electrolytic beaker cell in two-electrode configuration is adopted for GCD tests. The cell contains two pieces of GH electrodes and phenylenediamine-mediated electrolyte to form a symmetrical supercapacitor. Prior to the supercapacitor assembly, CV scan is run on the GH electrodes from  $-1.35 \text{ V}$  to  $1.35 \text{ V}$  (vs.  $\text{Ag/AgCl}$ ) at  $20 \text{ mV s}^{-1}$  for 100 cycles in the corresponding phenylenediamine-mediated electrolyte.

Electrochemical impedance spectroscopy (EIS, in a frequency range from 100 KHz to 0.01 Hz) of supercapacitors are performed on a Chenhua CHI660 electrochemical workstation. The specific capacity ( $Q_m/\text{mAh g}^{-1}$ ) of the GH electrodes is calculated based on Equation S(1) (for CV) and S2 (for GCD) in the supporting information. The supercapacitor energy density ( $\text{E/Wh kg}^{-1}$ ) and power density ( $\text{P/W kg}^{-1}$ ) are calculated according to Equations S(3) and S(4).

## 3. Results and discussions

### 3.1. Characterizations of the GH electrodes

The appearance of the as-obtained GH and GH electrode is shown in Fig. 1a. The interconnected graphene sheets form a three dimensional hydrogel structure (Fig. 1b), effectively prevent the accumulation and restacking of graphene layers in the GH [35]. The powder XRD patterns of the pristine graphite, GO, and freeze-dried GH are shown in Fig. 1c. As we can see, GH exhibit a weak and broad diffraction hump near  $26.1^\circ$ , corresponding to an interlayer spacing of 0.38 nm, showing little restacking of the graphene sheets [36]. Meanwhile, the characteristic signal of GO at  $10^\circ$  disappears in GH, indicating the successful reduction of GO to graphene. The Raman spectra (Fig. 1d) of GH exhibits two peaks at about  $1348.7$  and  $1579.3 \text{ cm}^{-1}$ , corresponding to the D band and G band of carbon material [37]. The intensity ratio between the D band and the G

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