



Effect of polymer binders on graphene-based free-standing electrodes for supercapacitors

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ABSTRACT

As the rapid growth of supercapacitor industry, there are increasing demands for aqueous dispersible and environmentally friendly polymer binders to manufacture graphene electrodes with high capacitance, long lifetime, and great mechanical flexibility. Here, four different binders were selected to study the effect on structural and electrochemical performance of the reduced graphene oxide (rGO) thin film electrodes. The four binders include two fluorinated polymers, a conductive binder formulation, and a water-based elastomeric binder. The morphology, crystallinity, thermal stability, and hydrophilicity of the electrode films were characterized. Electrochemical measurements were carried out to compare capacitance, resistance, and frequency response of the electrodes with various binders. Results reveal that the rGO with conductive binders showed the highest capacitance with low internal resistance in both aqueous and organic electrolytes; while the rGO bound by elastomeric binder exhibited excellent cycling stability, low charge transfer resistance, and low relaxation time constant in aqueous electrolyte. Moreover, it was found that that binders with high conductivity and enhanced compatibility with electrolytes can facilitate ionic diffusion within the porous structure of electrodes, which leads to faster frequency response and better capacitive properties.

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1. Introduction

The high demand for portable electronics and renewable energy sources has driven the research towards efficient and environmentally friendly energy storage systems [1–4]. Supercapacitors, also known as electrical double layer capacitors (EDLCs), have developed as emerging energy storage devices for electric vehicles, micro-electronics, and memory back-up [5–8]. Supercapacitors storage energy via the reversible adsorption/desorption of ions at the electrode/electrolyte interface under bias, thus making it stand out in high power density, long-term stability, and non-toxicity compared to conventional electrochemical batteries [9,10].

Carbon nanomaterials, such as activated carbon (AC), carbon nanotube (CNTs), and graphene, have been applied as electrode materials for EDLCs to accommodate large ion adsorption on electrode surface [11]. Particularly, graphene electrodes have demonstrated excellent electrochemical properties due to high conductivity, large surface area, and mechanical stability [12–14]. To fabricate high density thin film electrodes, carbon particles or graphene sheets have to be bridged together by polymer binders to form compact and mechanically stable films. In addition, binders must be inert to electrolytes, be electrochemically stable over wide potential window, and must not impose any degradations to internal structures of electrodes [15]. Generally, polymer binders are electrically insulating and their concentrations are kept at around 5–10 wt%. Excessive amount of binder added can increase the internal resistance and block the open pores of the electrodes for ionic transport, thus lowering down the electrochemical performance of the device [16,17].

Several quality metrics have been considered for the selection of

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appropriate binders, such as adhesion strength, hydrophilicity, toxicity, mechanical flexibility and electrical conductivity. Polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) are two commonly used inert binders. PTFE has a high operating temperature up to 270 °C, while PVDF can provide strong adhesion to metal current collectors with improved chemical and mechanical stability in carbon pastes [15,18]. However, problems remain for PVDF including their electrically insulating nature and the necessity to use the toxic organic solvent, N-methyl pyrrolidone (NMP). Therefore, it is of great advantage to introduce some water-soluble, conductive and environmentally friendly binder for electrode fabrication. Recently, several aqueous dispersible binders have been developed, such as polyvinyl alcohol (PVA), poly (3,4-ethylenedioxythiophene) (PEDOT:PSS), and carboxymethyl cellulose (CMC) [19–22]. Particularly, an elastomeric binder can be made by mixing the stiff CMC with a styrene butadiene rubber (SBR) as thickening agent [23,24]. In CMC/SBR, the ratio of these two components can be tuned to make the electrodes flexible and compatible with various electrode processing configurations. As a conductive and water-dispersible binder, commercial Electrodag has been formulated containing PVP (primary binder), carbon black, graphite and other additives (detailed compositions listed in Table S1) [25]. The introduction of conductive components in binder slurries can improve the conductivity of electrodes while facilitating the electrode mixing process. However, for this multi-component binder, the amount of binder should be carefully adjusted to ensure the best capacitive performance.

Previous reports on the binder study have mainly focused on the AC-based electrodes cast on current collectors [26–30]. Due to the unique nanostructures of 2D graphene sheets [31], it is necessary to select optimal binders to make large scale thin film graphene electrodes for supercapacitor applications. In this work, chemically reduced graphene oxide (rGO) was used as a benchmark material. Four types of binders, PTFE, PVDF, Electrodag and CMC/SBR, were employed to fabricate free-standing thin film graphene electrodes, and their corresponding structural and electrochemical properties were discussed. Specifically, the effect of binders on surface morphology, crystalline structures, thermal stability, and surface energy of these graphene electrodes were investigated. The electrochemical behavior of the electrodes using different binders were also compared and analyzed in both aqueous and organic electrolytes using a symmetric two-electrode coin cell configuration.

2. Experimental description

2.1. Reagents

Graphite flakes (230U) were provided by Asbury Carbons. PTFE condensed liquid binder (PTFE solid content: 60%), PVDF powder, CMC powder, and SBR glue (solidity: 50%) were purchased from MTI Inc. Electrodag EB-012 binder was obtained from Ladd Research Industries Inc. The KOH pellets, tetraethylammonium tetrafluoroborate (TEABF₄), N-Methyl-2-pyrrolidone (NMP), and acetonitrile (AN) were purchased from Sigma Aldrich and used without further treatment. The salt and solvent for organic electrolyte (TEABF₄ and AN) were stored and processed in a glovebox.

2.2. Electrode preparation

Reduced graphene oxide (rGO) was used as the active electrode material. To prepare rGO powders, graphene oxide (GO) was first made by modified Hummers' method, followed by the chemical reduction of GO using hydrazine [32]. Typically, 100 mg of GO was dispersed in 100 mL DI water and ultrasonicated for 1 h followed by the addition of 1 mL hydrazine monohydrate. The solution was

stirred at 90 °C for 24 h and purified by filtration. The collected powder was dried in oven at 75 °C overnight before use. The synthesized rGO powders had a bulk conductivity around 250 S/m with a few layers of stacking, and the specific surface area was determined to be 170 m²/g based on BET measurements (Fig. S1) [3].

For the binder preparation, a 5 wt% PVDF solution was made by dissolving PVDF powder into NMP. For CMC/SBR binder, the weight ratio of CMC: SBR was kept at 1:2 to ensure high binding efficiency and sufficient elasticity. Generally, CMC/SBR mixture were diluted in DI water to make 1.5 wt% aqueous solution. PTFE and Electrodag binder solutions were used without additional treatment. To prepare rGO films, rGO powders were mixed with different binders at 9:1 ratio with respect to the solid content of binders except Electrodag binder. The rGO/binder mixture was thoroughly blended until a uniform paste was formed (Fig. S2). For Electrodag binder, different rGO to binder ratios were studied, and best electrochemical performance was achieved for rGO films containing 25 wt % of solid binder content (3.1 wt% PVP). After homogeneous mixing, rGO pastes were sandwiched between two parallel plates and rolled through a rolling machine to make free-standing electrodes with an average thickness of 80 μm. After drying in a vacuum oven, thin film electrodes were punched into a round disk (6 mm in diameter, (2 ± 0.2) mg in mass) before assembled into coin cell for electrochemical testing. The mechanical flexibility of the electrodes was tested by rolling the films (18 × 18 cm²) around a cylinder (12.9 mm in diameter) for 100 cycles (Fig. S3).

2.3. Materials and electrochemical characterization

Surface morphology of the samples was studied using a Hitachi SU8010 field-emission scanning electron microscope (SEM). X-ray diffraction (XRD) patterns were acquired from Panalytical X'Pert PRO Alpha-1 system using Cu K α radiation (1.5418 Å). Fourier transform infrared spectroscopy (FTIR) spectra were obtained from a Nicolet Magna IR 560 spectrometer. Thermogravimetric analysis (TGA) was conducted with a TGA system (Q5000, TA Instrument) in air at a heating rate of 10 °C/min. Contact angle measurements were carried out on a Rame-Hart goniometer. Electrochemical characterizations including cyclic voltammetry (CV), galvanostatic charge/discharge (CD), and electrochemical impedance spectroscopy (EIS) were performed on a 2-channel system (Princeton Applied Research) using symmetric two-electrode coin cells in both aqueous (2 M KOH) and organic (1 M TEABF₄/AN) electrolytes. The coin cell consists of two pairs of symmetric current collectors and electrode films in sandwich structures with glass microfibers in between as separators. Electrolyte solutions were degassed by sonication for several times under vacuum to remove dissolved oxygen before use. The specific capacitance was calculated from CV curves using Equation (1)

$$C_{sp} = \frac{2 \int I dv}{vmV} \quad (1)$$

where C_{sp} is the specific capacitance, I is the applied current, V is the potential window, v is the scan rate, and m is the total mass of two electrodes. All the capacitance was normalized based on the content of active rGO materials. The frequency-dependent capacitance was derived based on Equation (2),

$$C = \frac{1}{2\pi fZ''} \quad (2)$$

where f is the frequency, and Z'' is the imaginary part of the impedance.

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