



Metal/graphene oxide batteries



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ABSTRACT

Based on the spontaneous redox reaction between metal and graphene oxide, a novel type of metal/graphene oxide (M/GO) batteries is developed to convert chemical energy into electricity, including Li/GO, Na/GO, Zn/GO, Fe/GO, and Cu/GO batteries. They are fabricated via the simple assembly of metal foils with GO films, in which M plays the role of anode, and GO acts as both cathode and separator. Among them, Li/GO battery generates the highest specific capacity of 1572 mAh cm^{-3} (about 1604 mAh g^{-1}). The energy density of M/GO battery is determined by the contact area of M with GO. Therefore, three-dimensional (3D) M/GO battery will deliver higher energy in comparison to 2D planar M/GO battery. As expected, a semi-solid 3D-Cu/GO redox flow battery (RFB) is assembled by 3D Cu foam with flowing GO/ionic-liquid catholyte. Its specific capacity is ca. 97 times that of Cu foil/GO RFB. Besides, a compressible, all-solid-state, and pressure-responsive 3D-GO/Zn battery is also fabricated. It can accurately control the energy output in response to pressure stimulations without the aid of conventional battery management system. Beyond those demonstrated in this work, the concept of M/GO battery will shed light on the design of similar electrochemical power sources.

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1. Introduction

Graphene is a two-dimensional (2D) honeycomb lattice of sp^2 -bonded carbon atoms [1]. Graphene oxide (GO) is a graphene derivative with abundant oxygen-related functional groups attaching to its basal plane and sheet edge, such as hydroxyl, epoxy, and carboxyl groups [2]. It can be cheaply obtained in large quantities via the chemical exfoliation of graphite [3–7]. GO could be reduced by active metal, such as zinc (Zn) [8,9], ferrum (Fe) [10], and copper (Cu) [11], upon inserting metal foil into aqueous GO dispersion at ambient condition. As illustrated in our previous work [8–11], the contact of GO with metal induced the redox reaction: $M + GO \rightarrow rGO + M_xO_y$, where rGO and M_xO_y were reduced graphene oxide and the resultant metal oxide, respectively. Electrons could spontaneously transfer from metal to GO, leading to the reduction of GO and the oxidation of metal. Based on the redox reaction between active metal and GO, a series of metal/GO galvanic batteries are developed by the simple assembly of active metal foils and solid-state GO(s) films. They can directly output available electricity resulted from the conversion of chemical

energy. The active metals can be further extended to lithium (Li) and sodium (Na). There are no separation membranes existing in those M/GO batteries. This is because GO(s) acts as both cathode and separator to avoid the short circuit of the battery due to its insulating nature. Meanwhile, M plays the role of anode in offering electrons, so that electrical current is allowed to flow in external circuit. As expected, Li/GO battery generates a specific capacity of $\sim 1572 \text{ mAh cm}^{-3}$ (corresponding to 1604 mAh g^{-1}). Beyond the 2D planar structure of M/GO battery, constructing 3D M/GO battery with higher energy density and controlled energy release is very important and significant. Accordingly, a semi-solid 3D-Cu/GO redox flow battery (3D-Cu/GO RFB) is achieved by using Cu foam as anode and flowing GO/ionic-liquid as cathode, whose specific capacity is ca. 97 times that of Cu foil/GO RFB. Besides, a compressible, all-solid-state, and pressure-responsive 3D-GO/Zn battery is also developed, in which GO-coated sponge and Zn foil serve as cathode and anode, respectively. The 3D-GO/Zn battery can be repeatedly compressed and released to accurately control its energy output in response to pressure stimulations without need of conventional battery management system.

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2. Experimental

2.1. The fabrication of GO^{0.3} and GO^{0.6}

The aqueous GO dispersion was prepared through the oxidation exfoliation of graphite according to the modified Hummer's method [22]. In this context, two kinds of GO with O/C atomic ratios of 0.3 and 0.6 were denoted as GO^{0.3} and GO^{0.6}, respectively. The preparation of GO^{0.3} was as follows: First, 80 mL concentrated H₂SO₄ was added to 250 mL flask filled with 3 g graphite in an ice bath with mechanical agitation, and then 3 g NaNO₃ and 9 g KMnO₄ were slowly added, respectively. Second, the flask equipped with condensing system was transferred to 36 °C oil bath and vigorously stirred for 1 h, followed by the addition of 150 mL deionized water. Successively, the reaction system was heated up to 90 °C and maintained for 20 min, followed by the dropwise addition of 5 mL H₂O₂ (30%). Third, the suspension was cooled to room temperature, which was then filtered and washed with about 1.2 M HCl aqueous solution to remove metal impurity. The obtained solid was further filtered by adding deionized water and then dispersed in 400 mL water, followed by stirring overnight. Finally, the as-produced GO dispersion was centrifuged at 10,000 r.p.m. for 20 min to remove the unexfoliated particles, followed by the dialysis in deionized water for one week using dialysis bags.

The preparation of GO^{0.6} was identical to that of GO^{0.3} except changing the dose of KMnO₄ into 18 g and prolonging the oxidized time to 16 h at a higher temperature of 50 °C.

2.2. The fabrication of M/GO batteries

GO film with a density of ~0.98 g cm⁻³ was obtained by the freeze-drying of aqueous GO dispersion and subsequent tableting with a pressure of ca. 20 MPa. The thickness of GO film was about 30 μm. The M foil (*i.e.*, Li, Na, Zn, Fe, Cu) and GO film were sandwiched between the lower battery shell and stainless steel (SS) foil plated with Au, then encapsulated into CR2032-type coin cells in Ar-filled glove box (Fig. S1). The electrolytes for Li/GO battery and Na/GO battery were 1 M LiPF₆ dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:1:1 in volume), and 1 M NaPF₆ in a 1:2 (v/v) mixture of EC and DEC, respectively. Zn/GO battery, Fe/GO battery, and Cu/GO battery used 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF₄) as electrolyte. The voltage and current outputs were recorded by a Keithley 2400 sourcemeter. The circuit parameters of the open circuit voltage test were current = 0 mA and step index = 5 points per s. The circuit parameters of the short circuit current test were voltage = 0 mV and step index = 5 points per s. The specific capacity of M/GO battery was calculated from I-T curve (Fig. 2d and Figs. S5a, b, d, f) by using the following formula:

$$C = \int i dt$$

where C was the volume capacity (mAh cm⁻³), i was the discharging current density (mA cm⁻³) based on the volume of GO film, and dt was the discharging time (h) [13].

2.3. The fabrication of 3D-Cu/GO RFB

The catholyte was obtained *via* adding freeze-drying GO monoliths into BMIMBF₄ to form 2 mg mL⁻¹ dispersion, and then poured into a beaker. Afterward, a piece of fresh Cu foam was inserted into catholyte with Au foil as the current collector to construct a two-electrode system (Fig. S17b). A magnetic stirring bar was placed into the beaker to enable GO catholyte to flow when

the RFB was in operation. The electrical signals were recorded by Keithley 2400 sourcemeter.

2.4. The fabrication of 3D-GO/Zn battery

Commercial polyurethane (PU) sponge was cut into cuboids and then immersed into 2 mg mL⁻¹ GO solution by a squeezing procedure. Subsequently, the lyophilization was carried out to obtain GO-coated PU sponge using liquid nitrogen, whose density was about 16.1 mg cm⁻³. GO accounted for ~16% of the whole sponge weight. The 3D-GO sponge was mounted on the fresh Zn foil to form 3D-GO/Zn battery in the absence of electrolyte (Fig. S18). To investigate the controllable power output behavior, the 3D-GO/Zn battery was sandwiched in a CR2032-type coin cell without encapsulation. The lower battery shell laminated to a nonconductive polyethylene terephthalate (PET) film was fixed to the pressure testing system, while the upper shell with PET film was able to move up and down during the compression/decompression cycles.

2.5. The fabrication of lab-made coin battery

The home-built coin battery was composed of Li₂TiO₃ (LTO), Li foil, and commercial separator membrane (celgard 2400 microporous polypropylene membrane). The LTO electrode was prepared by mixing Li₂TiO₃, acetylene black, and polyvinylidene fluoride (PVDF) binder with weight ratios of 8:1:1 into N-methylpyrrolidone (NMP) to form monodispersed slurry. Then the as-produced slurry was pasted onto a Cu foil and dried at 120 °C for 12 h under vacuum. For one electrode, it typically had a loading of ~0.65 mg cm⁻². The electrolyte was 1.0 M LiPF₆ in ethylene carbonate/dimethyl carbonate/diethyl carbonate (EC: DMC: DEC = 1:1:1 in volume). The assembly of coin cell was performed in an argon-filled glove box, where moisture and oxygen concentrations were strictly limited below 1.0 ppm. The cells were then aged for 12 h before measurement. The galvanostatic discharge/charge test was carried out over a voltage range of 0.01–2.5 V versus Li⁺/Li on the LAND CT2001A battery system at room temperature. Electrochemical impedance spectral measurements were carried out in the frequency range from 100 kHz to 0.01 Hz on CHI760D electrochemical workstation.

2.6. Characterization

Field-emission scanning electron microscopy (FE-SEM) and X-ray energy dispersive spectroscopy (EDS) of the samples were carried out on a JSM-7001 F SEM unit (Japan Electron Optics Laboratory Co., Ltd, Japan). Transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) were conducted using a TecnaiG2 20ST (T20) at an acceleration voltage of 120 kV (FEI corporation, USA). High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was operated at 200 KV (FEI, Technai G2 F30). X-ray photoelectron spectroscopy (XPS) data were carried on an ESCALab220i-XL electron spectrometer using 300 W AlK irradiation (VG Scientific Co., Ltd, UK). The base pressure was about 3 × 10⁻⁹ mbar. Powder X-ray diffraction (XRD) patterns were performed on a Bruker D8 advance X-ray diffractometer (Bruker Corporation, Germany) using a Netherlands 1710 diffractometer with a Cu Kα irradiation source (λ = 1.54 Å) and a self-calibration process was performed with a SiO₂ internal standard sample prior to target measurement. Raman spectra were recorded using a RM 2000 Microscopic Confocal Raman Spectrometer (Renishaw PLC, England) with a 514 nm laser. The repeated compression/decompression tests of 3D-GO/Zn battery were conducted with an Instron material testing system (Instron 3342), and the current variation was recorded in real time using a

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