



Phenolic formaldehyde resin/graphene composites as lithium-ion batteries anode



Lili Wang^a, Yuangang Liu^b, Chuanbin Chong^c, Jing Wang^c, Zhiqiang Shi^{c,*}, Jie Pan^{a,*}

^a School of Environmental and Chemical Engineering, Tianjin Polytechnic University, Tianjin 300387, PR China

^b Intellectuals' Innovation & Entrepreneurship Service Center of Tianjin, PR China

^c Laboratory of Fiber Modification and Functional Fiber, College of Materials Science and Engineering, Tianjin Polytechnic University, Tianjin 300387, PR China

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ABSTRACT

A novel kind of phenol formaldehyde resin and graphene composites were fabricated through spray drying. We synthesized a three-dimensional network structure composites, in which phenol formaldehyde resin offers large lithium storage and graphene layers can provide a highly conductive matrix to enable good contact between particles and facilitate the diffusion and transport of ions. The composite electrodes display a large reversible capacity of 302 mA h g⁻¹ at a current density of 20 mA g⁻¹, and a capacity of 231 mA h g⁻¹ at 100 mA g⁻¹. After 200 cycles, the capacity retention of composite anodes is almost 99%, further confirming the predominance of this new material for lithium storage.

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1. Introduction

Lithium-ion batteries (LIBs) with excellent rate performance and high storage capacities have attracted much attention as a power source for portable devices as well as electric vehicles [1]. Hard carbon (HC) has been considered as a promising anode material owing to its high theoretical capacity (740 mA h g⁻¹), which is approximately twice of graphite material [2]. However, the large irreversible capacity, low pack density and hysteresis in the voltage profile that occur in HC materials during the Li insertion and extraction process severely limit their extensive applications in LIBs. Therefore, modifications to address these issues such as coating with carbon [3], vacuum and oxidation treating [4], or constructing hybrid anodes [5] have been primarily made to modify the surface structure of HC anode.

Graphene, consisting of a single layer or a few layers of graphitic carbon, is regarded as a potential candidate for LIBs due to its large theoretical surface area, good electronic conductivity and high electrochemical stability [6]. Flexible network of graphene could improve the electron conductivity of electrode materials during the charge–discharge processes. However, graphene displayed a relative high irreversible capacity and poor stability at large current density according to recent research [7]. Hence,

plenty of graphene based composite materials as lithium anode have been developed, such as Metal/Graphene hybrids [8], Metal Oxide/Graphene hybrids [9] and Si/Graphene hybrids [10]. Mochen Li et al. [11] grafted hard carbon onto the graphene oxide surface via esterification for application in lithium ion batteries. Here, we present a facile way to synthesize phenol formaldehyde resin/graphene composites.

In this paper, through spray drying the mixture of phenol formaldehyde resin (PF) and graphene oxide (GO), the composites of phenol formaldehyde resin and graphene oxide are prepared. It is believed that the composites can availably utilize the combinative advantage of phenol formaldehyde resin and graphene and obtain LIBs with superior performance.

2. Experimental part

2.1. Synthesis of phenol formaldehyde resin/graphene composites (PF/G)

PF was catalyzed by sodium hydroxide (NaOH). Initially GO was synthesized by a modified Hummers method. Different amounts of PF and GO solution were mixed together and stirred for several minutes, forming homogenous solutions. Then, we synthesize of PF/GO composites through spray drying method by one step. Finally, the pure PF, reduced graphene oxide (RGO) and PF/G were

* Corresponding authors.

E-mail addresses: shizhiqiang@tjpu.edu.cn (Z. Shi), panjie@tjpu.edu.cn (J. Pan).

obtained by heating the materials at 1250 °C under argon and hydrogen flow for 3 h with ramp rate of 5 °C min⁻¹. The composite was prepared by PF and GO, with a GO content of 2 wt%, 10 wt%, 30 wt%, and 50 wt%, which was denoted as PF/G-2, PF/G-10, PF/G-30 and PF/G-50, respectively.

2.2. Material characterizations

The X-ray diffraction profiles of carbons were measured with a Rigaku D/Max2500 X-ray diffractometer using CuK α radiation. Raman spectra were recorded on an Invia Raman spectrometer, with an excitation laser wavelength of 523 nm. Brunauer–Emmett–Teller (BET) date was determined on STA409C. The morphology of the samples was observed by field emission scanning electron microscopy (FESEM, Hitachi S-4800).

2.3. Electrochemical measurement

The electrochemical measurements of the samples were carried out with 2016 coin cells using lithium metal as the counter electrode. The cathode electrodes were prepared as follows: carbon materials were mixed with acetylene black and polyvinylidene difluoride (PVDF) in the weight ratio of 9:1:1 in N-methyl-2-pyrrolidinone (NMP) to form the slurry. The slurry was then spread onto a copper foil and dried in a vacuum oven at 120 °C for 12 h. The solution of 1 M LiPF₆ in ethylene carbonate and diethyl carbonate (1:1 in volume) served as the electrolyte.

3. Results and discussion

The X-ray diffraction (XRD) patterns and Raman spectrum recorded for all samples are shown in Fig. 1 and Table 1. The pure PF exhibited a broad peak around 23° and the graphene showed a peak at 26°. By analyzing the 002 diffraction peak of graphene, the value of d_{002} increase slightly when increasing the weight ratio of PF. The value of d_{002} of PF/G-30 is 0.344 nm, which is a little larger than that of natural graphite (0.335 nm). As presented in Fig. 1b, two distinct peaks are observed around 1360 (D-band) and 1600 cm⁻¹ (G-band) for the carbon samples. The G band is a characteristic feature of graphitic layers, while the D band corresponds to disordered carbon or defective graphitic structure. The Raman band ratio, ID/IG, as shown in Table 1, implied that the graphitic crystalline structure of the PF/G-30 is much better than other samples. The BET date of all sample is summarized in Table 1. Clearly, the specific surface area of RGO is much bigger than the others. However, the BET specific surface area is smaller than the theoretical value of graphene. This is because the oxygen-rich

Table 1
XRD, Raman analysis and BET date.

Sample	PF	PF/G-2	PF/G-10	PF/G-30	PF/G-50	RGO
d_{002} (nm)	0.376	0.389	0.348	0.344	0.343	0.338
ID/IG	1.237	1.114	1.036	1.012	1.283	1.207
BET (m ² /g)	0	54.272	57.069	27.077	21.724	174.18

carbonaceous atomic arrangements of graphene oxide layers were rearranged into highly ordered hexagonal carbon lattices by high-temperature treatment [12].

The SEM images of PF/G composites are shown in Fig. 2. The pure PF is irregular in morphology in Fig. 2a. It is a kind of typical hard carbon materials. We can see from Fig. 2b clearly, while the PF weight occupied for composite highly is around 98%, the graphene sheets stay around PF and appear to be wrinkled. The abundant sheets overlap closely to form a three-dimensional network structure, which enlarge the available liquid-solid interfacial area, leading to a fast and effective path for the insertion and extraction of the electrolyte ion. Fig. 2c is similar to Fig. 2b, while the particles are irregular in shape. SEM images of PF/G-30 and PF/G-50 are presented in Fig. 2d and e. Obviously, the sheet structure of graphene is observed. The surface of sheets appears to be wrinkled and crumpled, which clearly show that the graphene sheets consist of single or double layers. Fig. 2f show that the RGO has several sheets.

Fig. 3 shows the first three cyclic voltammetry (CV) curves of PF/G composites at a scan rate of 0.1 mV s⁻¹. In Fig. 3b, a strong cathodic current peak is observed at around 0.7 V in the first discharge cycle, which is usually ascribed to the formation of the solid electrolyte interface (SEI) film and the decomposition of the electrolyte. In Fig. 3c, we can see a slight peak near 0.13 V during discharge from the second and third cycle onward. The anodic current peak near 0.13 V of PF/G-10 composite emerges at lower potential than PF/G-2 suggesting that lithium ion could easily intercalate and deintercalate carbon lattice when charging/discharging with graphene content increasing in the composites. Cathodic current peak near 1.8 V is present in Fig. 3a, d and e in the first cycle, which is corresponding to the first discharge/charge curve with a voltage drop slope around 2.0 V in Fig. 4a. In Fig. 3f, there are strong cathodic current peaks around 0.5 V and 1.8 V, which are leading to the high irreversible capacity of RGO.

Typical galvanostatic charge/discharge curves of PF/G composite electrodes at a current density of 20 mA g⁻¹ are illustrated in Fig. 4a. The initial discharge capacities of PF, PF/G-2, PF/G-10, PF/G-30, PF/G-50 and RGO are approximately 266, 359, 385, 714, 660 and 1135 mA h g⁻¹, and charge capacities are 125, 237, 256, 282,

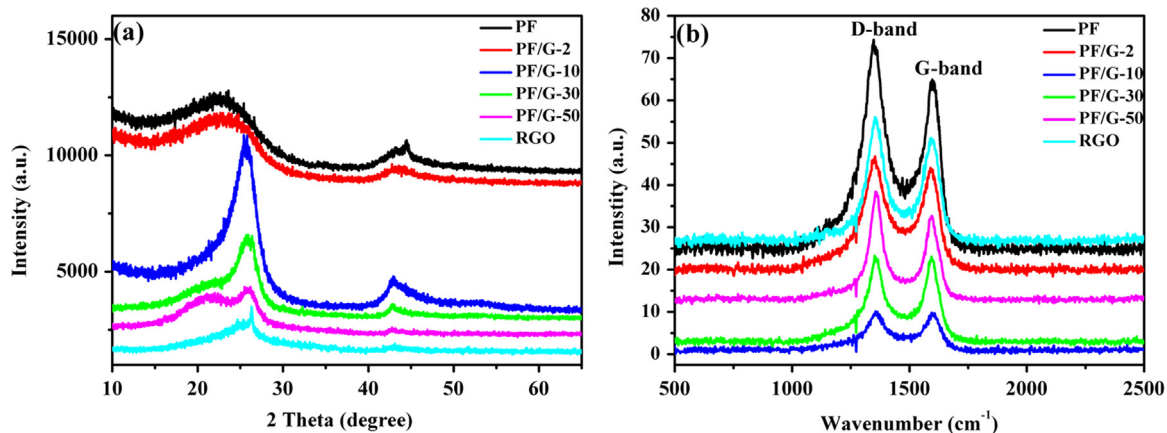


Fig. 1. (a) XRD patterns and (b) Raman spectrum of PF/G composites.

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