



Design and electrochemical investigation of a novel graphene oxide–silver joint conductive agent on LiFePO_4 cathodes in rechargeable lithium-ion batteries



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ABSTRACT

We designed a novel graphene oxide–silver (GO–Ag) joint conductive agent to improve the low electronic conductivity of LiFePO_4 (LFP) and attempted to replace the commercial carbon black. The phase evaluations of fabricated cathodes have been characterized using X-ray diffraction and it shows no additional peaks from GO–Ag. The morphological and elemental analysis depicts that the joint GO–Ag enwraps the LFP with uniform distribution of elements. The electrochemical profiles corroborate the stable cycleability and better capability. The optimized electrode gives the better initial charge–discharge capacity of $\sim 155 \text{ mAh/g}$ and $\sim 150 \text{ mAh/g}$ at a 0.5C rate, respectively.

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Introduction

Gentle developing of rechargeable Li-ion batteries are being considered for various applications, including portable electronics and high-power hybrid vehicles due to their high volumetric and gravimetric energy densities compared to those of other known secondary batteries. LFP has been extensively studied as a cathode material in spite of its low cost, environmentally benign, thermally stable and high theoretical capacity ($\sim 170 \text{ mAh/g}$) [1,2]. However, it has a poor intrinsic electronic conductivity ($\sim 10^{-8} - 10^{-10} \text{ S/cm}$) and Li-ion diffusivity ($\sim 10^{-18} \text{ cm}^2/\text{s}$) [3,4]. To rectify the intrinsic properties, several efforts have been attempted by metal doping and coating with carbons, metal oxides, or polymers [5–8]. Among them, carbon coated LiFePO_4 has excellent improvement in terms of electronic conductivity, and rate capability [9]. On the other hand, implementing carbon derived additives promisingly increases the cathode active materials performance [10]. In general, the conductive agent is used as a mediator to transfer an electron between the Li metal and current collector [11]. Mostly, commercial carbon black (CC) has been used as a conductive agent in Li-ion batteries [12]. So far, carbon nanotubes (CNT) and graphene (G) have been introduced as a conductive agent instead of CC [13,14]. Among them, the unique and high surface area of

graphene could make a superior electronic conductivity than CC. Moreover, the LFP/G provides an enhanced conductive properties than other carbon composites [15,16]. Recently, CNT and Ag hybrid conductive materials have been used with cathode material and resulted in excellent electronic conductivity [17]. With best of our cognition, there is no report regarding the GO–Ag joint conductive agent in Li-ion batteries. In this paper, we designed a novel GO–Ag conductive agent, for the first time, and their physical and electrochemical performances have been discussed.

Experimental

Preparation of GO–Ag joint conductive agent

GO was synthesized by modified hummer's method [18]. In brief, 1.5 g of graphite flakes were dispersed in 36 ml of concentrated sulfuric acid followed by adding of 4 ml hydrochloric acid. The solution was stirring at room temperature for 12 h. Then, the potassium permanganate was added to the above solution and kept in an ice bath stirring for 2 h, and followed by heating at 90°C for 12 h. Again 150 ml of deionized water contained 2.5 ml (30%) of hydrogen peroxide added to above solution. The resulting suspension was filtered and washed with distilled water for several times. The GO–Ag joint conductive agent has been prepared by a facile wet chemical process as follows; as-prepared GO and Ag particles were dispersed in acetone and kept

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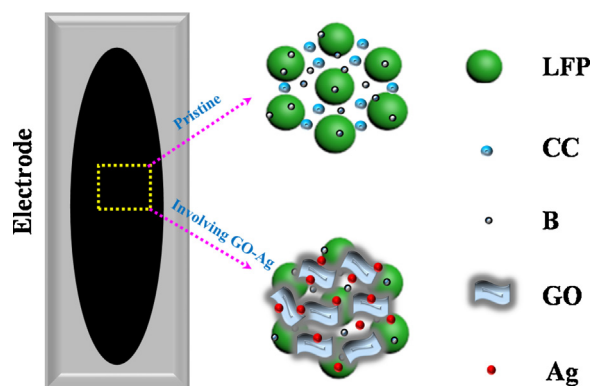


Fig. 1. Schematic diagram of surface view of the materials used for electrode preparation.

ultrasonication for 1 h followed by drying until the solvent evaporation. To optimize the amount of GO–Ag, we repeated the same experimental procedure.

Cell fabrication

The cathode consists of 85 wt% active material LFP (JingRui Battery Co., Ltd.), 10 wt% conductive agent (GO–Ag) and 5 wt% binder (B) (polyvinylidene fluoride). The cathode was fabricated by blending of LFP, GO–Ag and B in a proper amount of N-methyl-2-pyrrolidone to form a homogeneous slurry. The slurry was spread on aluminum foil, and dried in a vacuum at 120 °C for 12 h. Finally, the cathode was punched in a required size for cell fabrication. Typical 2032-type coin cells were assembled in a highly pure argon-filled glove box using Li metal as an anode, Celgard 3501 as the separator and 1 M LiPF₆ in an ethylene carbonate (EC): dimethyl carbonate (DMC) (1:1 vol%) as an electrolyte. In order to prepare pristine cathode, CC has been used as a conductive agent and the cathode is named as LFP:CC:B (85:10:5 wt%). Additionally, cathodes involving GO–Ag joint conductive agents instead of CC are named as LFP:GO:Ag:B (85:5:5:5 wt%), LFP:GO:Ag:B (85:8:2:5 wt%), and LFP:GO:Ag:B (85:9:1:5 wt%), respectively. Fig. 1 illustrates the schematic diagram of surface view of the materials used for electrode preparation.

Material characterization

The cathodes were physically characterized by an X-ray diffractometer (XRD, D8Discover with GADDS, Bruker AXS) in the 2θ range between 5° and 85° with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$), and high resolution field emission scanning electron microscope (HR-FESEM, MERLIN, Carl Zeiss) with energy dispersive spectroscope (EDS). Then the electrochemical impedance spectroscopy (EIS, IVIUM), and galvanostatic cyler (ARBIN) were used to study the electrochemical properties.

Results and discussion

Structure and morphology

Fig. 2 shows the XRD patterns of (a) LFP:CC:B (85:10:5 wt%), (b) LFP:GO:Ag:B (85:8:2:5 wt%), (c) GO, (d) Ag samples. Fig. 2(a) and (b) diffracted patterns can be indexed to orthorhombic Pnma space group (JCPDS 81-1173). There is no peaks for impurity were observed which demonstrates the addition of GO and Ag does not affect the core phase of LFP. For evaluation, the GO and Ag patterns were displayed at same diffracted regions as shown in Fig. 2(c) and (d). The GO shows the sharp peak at $2\theta = 12^\circ$ and corresponding d-spacing of 7.4 Å [19] and Ag can be indexed to cubic face-centered

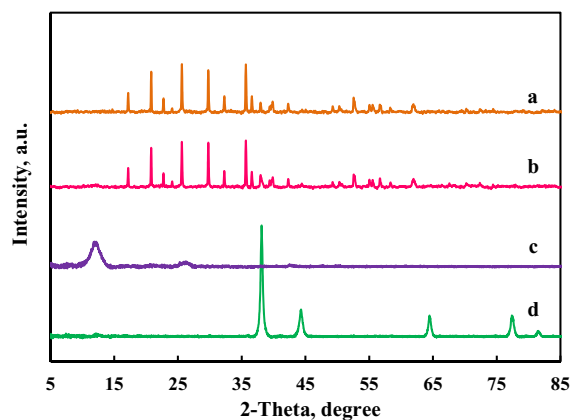


Fig. 2. XRD patterns of (a) LFP:CC:B (85:10:5 wt%), (b) LFP:GO:Ag:B (85:8:2:5 wt%), (c) GO, and (d) Ag, respectively.

with Fm3m space group (JCPDS 89-3722). Evidently, the GO–Ag joint conductive agent does not alter the LFP original phase due to the small amount of existence. Fig. 3(a) and (b) represents the surface morphologies of LFP:CC:B (85:10:5 wt%) cathode at high and low magnifications. The representative morphologies of LFP:GO:Ag:B (85:8:2:5 wt%) cathode were shown in Fig. 3(c) and (d). It can be seen that the surface morphologies of LFP particles are not uniformly formed by CC whereas the GO–Ag joint conductive agent completely wrapped on the LFP. On the account of small surface area of CC does not cover all over LFP. But the two dimensional GO decidedly covered over LFP. This phenomenon will give better conductive network between the LFP particles. Further, to know the elemental distributions, we carried out EDS as shown in Fig. 4. The EDS mapping of the LFP:GO:Ag:B (85:8:2:5 wt%) cathode indicated the existence of Fe (iron), P (phosphorous), C (carbon), O (oxygen), and Ag (silver). In particular, the presence of Ag is evenly distributed in the cathode. From EDS results, we could confirm that our material does not have foreign elements.

Electrochemical studies

To diagnose the nature of interfacial resistance for all the attempted cathodes, we observed EIS behavior for the fresh cells just after fabrication. Fig. 5(a) shows the electrochemical impedance response of all cathodes. The Nyquist plots are clearly showing that all cathodes defined traditional semicircle patterns. The diameter of the semicircles decreased with the decrease of inter-particle electric contact resistances, which is approximately equal to the charge transfer resistance [20]. The semicircle denotes to charge transfer resistance, and the straight line indicates Warburg equation for the Li-ion diffusion [21–23]. The impedance values are $\sim 490 \Omega$, $\sim 360 \Omega$, and $\sim 430 \Omega$ which corresponds to LFP:GO:Ag:B (85:5:5:5 wt%), LFP:GO:Ag:B (85:8:2:5 wt%), and LFP:GO:Ag:B (85:9:1:5 wt%) cathode at real axis in lower frequency regions whereas the pristine LFP:CC:B (85:10:5 wt%) cathode shows $\sim 620 \Omega$ in the same region. In specific, the ratio of electrode materials was playing an important role in reducing the charge transfer resistance. The kinetic process has been increased when making graphene with LFP [24]. Moreover, GO has unique functional groups at unorganized carbon sites. So it is very useful for reversible Li-ion insertion process during the electrochemical reactions [25]. Moreover, Ag modified or composited with cathode powerfully reduce the resistance and thereby electronic conductivity improved which reported previously [26,27]. According to this mechanism, the approached novel binary conductive material possessed a significant electronic conductivity. Fig. 5(b) displays the initial charge–discharge curve of LFP:CC:B (85:10:5 wt%) and LFP:GO:Ag:B (85:8:2:5 wt%) cathodes obtained at the current rate

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