Electrochimica Acta 218 (2016) 237–242

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Large-Scale Fabrication of Graphene-like Carbon Nanospheres for Lithium Ion Battery Application

Wei Ding[a], Li Xu[b], Xin Chen[b], Yu Han[b], Shuangyu Liu[b], Peng Sheng[b], Bo Wang[b], Guangyao Zhao[b], Hui Bi[a,*], Fuqiang Huang[a,c]

[a] *State Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, 200050, PR China*
[b] *State grid smart grid research institute, Future Science & Technology Park, Changping, Beijing, 102211, PR China*
[c] *State Key Laboratory of Rare Earth Materials Chemistry and Applications and Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, PR China*

ARTICLE INFO

Article history:
Received 5 June 2016
Received in revised form 5 September 2016
Accepted 25 September 2016
Available online 26 September 2016

Keywords:
graphene-like carbon
nanosphere
large scale
lithium ion battery

ABSTRACT

Large scale preparation of graphene-like carbon nanospheres (GCNSs) was performed by direct-current arc discharge using C_2H_2 as carbon resources. The morphology and structure of the obtained products were investigated by field-emission scanning electron microscope, high-resolution transmission electron microscope, Raman spectroscope, X-ray diffraction and nitrogen adsorption. The GCNSs consist of quasi-spherically concentric graphitic shells with high purity and quality, and its size distribution is in the range of 30–50 nm. The high-quality GCNSs also exhibit highly electrical conductivity of $\sim$30.3 S cm^{-1}, and can act as conductive agent to significantly improve the electrochemical performance of $LiFePO_4$ (LFP) cathode, compared with the conventional carbon black (CB). Discharge capacity of the LFP (GCNSs) cathode reaches up to 155.6 mAh g^{-1} at 0.1 C, which is slightly higher than that of the LFP (CB). However, The LFP (GCNSs) cathode still delivers high capacities of 114.9 mAh g^{-1} and 65.2 mAh g^{-1} at 1 C and 10 C rates, respectively, which are much higher than those of the LFP (CB). At the same time, the discharge capacities reach up to 114.9 mAh g^{-1} and 80.9 mAh g^{-1} at 1 C and 5 C discharge rates for the first discharge, and the corresponding capacities decrease down to 108.5 mAh g^{-1} and 79.9 mAh g^{-1} after 100 cycles, respectively. This indicates excellent cyclic stability, especially at high rate charge/discharge cycles. Thus, the mass production, high crystalline and highly electrical conductivity may make the GCNSs find applications in energy conversion and storage.

1. Introduction

Lithium ion batteries (LIBs) as the promising power sources have been applied for mobile phones, renewable energy storage and other portable electronic devices due to their advantages of high energy density, good cycle and absolute security [1–3]. With the rapid development of LIBs, how to gain mass, environment friendly, low cost electrode materials become more and more important. Hence, researchers have turned from lithium cobalt and nickel oxide to focus on lithium iron phosphate, $LiFePO_4$ (LFP). However, LFP exists some inherent shortages, such as inferior electrical conductivity and limited Li-ion diffusivity, which severely limited the capabilities and cycling stability of LIBs [4,5]. Therefore, developing a new and excellent conductive agent has become a hot topic in the field of LIBs. Huang et al. adopted carbon nanotubes as conductive additive to study the performance of LFP [6]. The initial discharge capacity of LFP was 142.6 mAh g^{-1} at 0.1 C, which was only 85% of theoretical capacity. Moreover, the LFP electrode had good rate capability and the discharge capacity could reach up to 133.8 mAh g^{-1} at 1 C. Kalaiselvi et al. studied that super P carbon was used as conductive agent in preparing LFP cathode to gain high discharge capacity (152 mAh g^{-1} at 0.1 C) [7]. Hence, we found that the conductive agent had seriously affected the electrochemical performance of LFP cathode. To date, it remains a great challenge to develop a novel conductive agent for LFP cathode to improve capacity and rate capability.

However, compared with the traditional conductive agents, graphene as a regular hexagonal crystalline form has remarkable

---

* Corresponding author. Tel.: +86 21 5241 1620.
E-mail address: huangfq@mail.sic.ac.cn (F. Huang).

http://dx.doi.org/10.1016/j.electacta.2016.09.125
0013-4686/© 2016 Published by Elsevier Ltd.

electron mobility and low resistivity, exhibiting huge potential in LIBs [8–10]. Various types of graphene have been developed by oxidation-reduction method [11], chemical vapor deposition (CVD) [12], liquid-phase exfoliation from graphite [13], *etc*. Recent research results have shown that graphene can clearly improve the electrochemical performance of LFP. For example, Hu et al. employed electrochemical exfoliation method to incorporate few-layer graphene into LFP, and its capacity exceeded theoretical capacity, which was attributed to the reversible reaction between electrolyte and graphene flakes [14]. In our previous work, defect-free and highly crystalline graphene sheets were synthesized by CVD technique to modify LFP cathode, and its capacity reached up to 132 mAh g^{-1} at 1 C, which was much larger than that of LFP (commercial carbon black, CB) [15]. Moreover, three-dimensional graphene was fabricated by CVD on porous Ni template as conductive framework to load LFP materials, which has excellent electrical conductivity of ~600 S cm^{-1} to significantly improved the rate performance of LFP cathode, and its discharge capacity achieved 109 mAh g^{-1} at 10 C [16]. Although the CVD graphene has high quality and electrical conductivity to obviously improve the electrochemical performance of LFP cathode, compared with commercial CB, the preparation method is relatively complex and expensive, and the yield is rather low. Chemical reduced graphene oxide had more functional groups and more defect, greatly limiting the performance of LFP [17].Therefore, adopting a way to synthesize mass-production, high-quality and highly conductive graphene for LIBs is becoming more urgent.

In this study, we have developed a simple, efficient and low-cost route for large scale fabrication of graphene-like carbon nanospheres (GCNSs) with uniform morphology, size, high conductivity and high crystalline quality. The GCNSs were obtained via direct-current arc discharge at 120 A, which can achieve mass production as a controlled way. In addition, the electrochemical properties of the cathode electrode consisting of LFP and GCNSs for LIBs application have also been investigated.

2. Experimental

2.1. GCNSs preparation

The GCNSs were prepared by adopting direct-current arc discharge. The reaction was carried out in a water-cooled stainless steel chamber consisting of two pure graphite rod (diameter: 8 mm) electrodes. The cathode was fastened on the water-cooled copper pedestal. The equipment was first vacuumized to 5 Pa, then He and C_2H_2 (1: 1 molar ratio) mixture was bubbled into the chamber to make the pressure reach 100 Pa. The rods moved close together, and discharge occurred (the current: 120 A), which produced the plasma. Both rods would keep at a constant distance of approx. 2 mm, when the anode was consumed. The reaction time was about 5 minutes and the anode graphite rod was consumed. Finally, the soot was collected under ambient conditions.

2.2. Fabrication of LIB

Commercial active materials LFP (80 wt.%), conductive additive GCNSs (10 wt.%) and polyvinylidene fluoride (PVDF, 10 wt.%) were mixed in N-methyl-2-pyrrolidone and stirred for 4 h. The resultant slurry, pasted on Al foil, was dried at 70 °C for 1 h. The film was punched into disc, and dried at 100 °C for 12 h in vacuum. The CR2016 coin cells were then assembled in an argon-filled glove box using Li metal as the anode, Celgard 2600 as the separator, and 1 M $LiPF_6$ (dissolved in ethylene carbonate and dimethyl carbonate with a 1: 1 volume ratio) as the electrolyte. Reference cells were fabricated by the same method, using 80 wt.% LFP, 10 wt.% commercial CB and 10 wt.% PVDF.

2.3. Characterization and measurement

The morphology and structure of GCNSs were investigated with field emission scanning electron microscope (FESEM, Hitachi S-4800), high resolution transmission electron microscopy (HRTEM, JEOL 2100F) and selected area electron diffraction (SAED). X-ray photoelectron spectroscopy (XPS) analysis (Thermo VG Scientific) was undertaken under high vacuum on GCNSs using Al-Ka 1486.6 eV radiation at 400 W (15 kV). Raman spectra of GCNSs and CB were obtained with Raman spectroscopy having laser excitation energy of 532 nm. The crystalline structure and phase identification of GCNSs and CB were performed by X-ray diffraction (XRD, Bruker D8) with a monochromatized source of Cu $K_{\alpha 1}$ radiation ($\lambda = 0.15405$ nm) at 1.6 kW (40 kV, 40 mA). Nitrogen sorption measurements were performed with ASAP 2020 M (Micromeritics) to obtain BET-specific surface area. The electrical conductivities were measured by the Van der Pauw method with an Accent HL5500. Electrochemical impedance and cyclic voltammetry (CV) measurements were performed on a CHI 660 electrochemistry workstation. Charge-discharge characteristics were tested at various rates in the voltage range of 2.5–4.2 V (vs. Li^+/Li) on a CT2001A cell test instrument (LAND Electronic Co.) at room temperature.

3. Results and discussion

We could obtain approx. 100 g of the powder-like GCNSs per batch (reaction time: 5 min) using the direct-current arc discharge, as shown in Fig. 1a. The quantity is very easily scaled up by using larger reaction container, high concentrated carbon resource and long reaction time. In addition, the GCNSs are well dispersed in the N-Methyl pyrrolidone at about 1.0 mg ml^{-1} with the presence of polyvinyl alcohol at 0.5 wt.%. After 30 days, the GCNSs dispersion is homogeneous without agglomeration, which is very important for the future practical applications.

Fig. 1b & c shows that the as-obtained GCNSs have quasi-sphere morphology with the diameters of 30–50 nm, and these GCNSs connect each other to form three dimensional porous nanostructure. Furthermore, HRTEM images (Fig. 1d and e) demonstrate that the GCNSs have a hollow and irregular core of about 10–25 nm in diameter, and the nanospheres' wall is short-range order graphene sheets with few layer structure. The inter-planar spacing of 0.34–0.38 nm corresponds to that of the (002) plane of graphite, and the corresponding SAED pattern (Fig. 1f) reveals the polycrystalline structure of the GCNSs.

XPS spectrum taken from the GCNSs reveals that there are no any impurities except for C and a little O (only 0.21 wt.%), as shown in Fig. S1, indicating the high purity of the GCNSs. The C 1s XPS spectrum shows a highly intensive peak associated with the binding energy (~284.5 eV) of sp^2 hybridised carbon atoms (Fig. 2a) and two very weak peaks at ~286.0 eV and ~291.3 eV associated with sp^3 carbon atoms, respectively[18,19]. Raman spectra were obtained to identify the microstructure of the GCNSs and commercial CB, as shown in Fig. 2b. The three broad peaks centered at ~1343 cm^{-1}, ~1579 cm^{-1} and ~2676 cm^{-1} are ascribed to D, G and 2D bands, respectively [20,21]. The intensity ratio of GCNSs of 2D band to G band (I_{2D}/I_G) is ~0.55, and the full width at half-maximum (FWHM) of the 2D band is ~84 cm^{-1}, obviously suggesting typical few-layer structure of graphene. For the comparison, the CB hardly observe the 2D band, which indicates typical amorphous carbon nanostructure of the CB. In addition, the I_D/I_G ratio of the GCNSs is about 1.1, and the large I_D/I_G may be due to a finite size of sp^2 hybridized crystallites and some amount of structural defects in the GCNSs. These results reveal the relatively short range order with high graphitization degree for the graphene sheets, in good agreement with the HRTEM results.