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Hard Carbon Wrapped in Graphene Networks as Lithium Ion Battery Anode

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ABSTRACT

Hard carbon enveloped with graphene netwo[illegible] was fa[illegible]by a facile and scalable method. In the constructed architecture, hard carbon offers l[illegible] li[illegible]um storage and flexible graphene layers can provide a highly conductive ma[illegible] enabli[illegible]od contact between particles and facilitate the diffusion and transport of ele[illegible]s and ions. As [illegible]onsequence, the hybrid anode exhibits enhanced reversible capacity (500 mAh [illegible] at current density [illegible]20 mA g^{-1}), rate capability (400 mAh g^{-1} at 0.2 C, 290 mAh g^{-1} at 1 C, 250 mAh [illegible] at 2 C, and 2[illegible] mAh g^{-1} at 5 C, 1C = 400 mA g^{-1}) and cycle performance. We believe that the o[illegible]tstand[illegible]ynergetic e[illegible]t between the graphene networks and the hard carbon structures induces t[illegible]perio[illegible]hium st[illegible]ge performance of the overall electrode by maximally utilizing the electroche[illegible]lly act[illegible]ne and hard carbon particles. As far as we know, the hard carbon/graphene hybrids w[illegible] firstly fabricated as anode in lithium-ion batteries.

1. Introduction

Lithium-ion batteries (LIBs) are the po[illegible]so[illegible]e of choice not only for popular consumer elec[illegible]ics bu[illegible]o for upcoming electric vehicles. So far, various ma[illegible]ls, suc[illegible] carbon based materials (graphite [1–3], h[illegible]rd carbon [illegible]7], car[illegible] fiber [8–10], graphene [11,12]), transitio[illegible]etal oxides [illegible]O$_4$ [13], Fe_3O_4 [14]), chalcogenides (TiS_2 [15], Mo[illegible]6]), and [illegible]ir composites have been exploited as th[illegible]de ma[illegible]ls of [illegible]s. Among them, hard carbon (HC) has [illegible]een [illegible]onstra[illegible] be one of the most promising an[illegible] materials [illegible] Li-ion batteries due to its high theoretical cap[illegible] (740 mAh [illegible]^{1}), two times larger than that of graphite (372 mA[illegible]^{1}), whic[illegible]re expected to meet the requirements of future en[illegible] st[illegible]ge systems [17–19]. Unfortunately, due to considerable [illegible] atoms or radicals in hard carbon, absorbed species and formation of solid electrolyte interphase (SEI) on the active material surface, the irreversible capacity is commonly too high (>150 mAh g^{-1}) during the first lithium ion insertion/extraction. In addition, HC characterized with the disordered texture and large paticle size (>15 μm) behaves lower conductivity than those organized carbon lattice, thereby leading to poor rate performance. To overcome these issues, substantial efforts have been made to modify the surface structure of HC anodes, such as vacuum and oxidation treating [6,20], pyrocarbon coating [21] and constructing hybrid anodes [5,22]. Though these surface modification methods can improve the Coulombic efficiency of HC to some extent, the rate performance and cyclability, two of the most significant properties as electrode material, are far from satisfactory. Therefore, to keep large reversible capacity combined with high Coulombic efficiency, achieving long cycling life and good rate capability of hard carbon electrode material still remains a great challenge.

Recently, a novel two-dimensional graphitic carbon, graphene, has drawn special attention due to its outstanding electrical conductivity, superior mechanical flexibility, large specific surface area, and high thermal/chemical stability [23–26]. Hence, plenty of graphene based composite materials as lithium anode have been developed, such as Sn/Graphene hybrids [27,28], SnO_2/Graphene hybrids [29,30], Metal Oxide/Graphene hybrids (Co_3O_4 [31,32], $CoMoO_4$ [33], $ZnCo_2O_4$ [34]) and Si/Graphene hybrids [35,36]. It has been demonstrated that graphene based anode materials have large initial discharge capacity (600∼2042 mAh g^{-1}) and reversible capacity (540∼1264 mAh g^{-1}), although they suffer from large irreversible capacity, low initial Coulombic efficiency, and fast capacity fading [11,12,37]. More importantly, the ultrathin flexible

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graphene layers can provide a highly conductive matrix for enabling good contact between particles. Core-shell graphene@amorphous carbon composites were also prepared by Hui Wu et al. for application in polymer electrolyte membrane fuel cells [38]. Therefore, it is believed that the composite of flexible and electrically conductive graphene wrapped around surface of hard carbon particles can efficiently utilize the combinative merits of hard carbon and graphene and obtain LIBs with superior performance.

Herein, we report a facile strategy to synthesize such composite of hard carbon wrapped in conducting graphene networks as an advanced anode material for high performance LIBs. This HC/graphene composite displays superior LIB performance with large reversible capacity, high Coulombic efficiency, improved cyclic performance, and good rate capability, highlighting the importance of the hard carbon enveloped by graphene sheets for maximum utilization of electrochemically active hard carbon and graphene for energy storage applications in high-performance LIBs.

2. Experimental Part

2.1. Synthesis of Hard Carbon (HC)

Epoxy novolac resin (Hunan Jiashengde Materials Technology CO.) and Maleic anhydride (Sinopharm, China) as the hardener were thoroughly mixed at 80 °C and then cured overnight in air at 180 °C. The cured precursor was heated at 500 °C for 1 h and then ground to powders less than 37 μm in diameter after cooling down under Argon atmosphere. Finally, the powders were heated at 1000 °C under Argon flow for 1 h with ram[illegible]te of 10 °C min^{-1}.

2.2. Synthesis of Hard Carbon/Graphene composite (HC/G) Graphene Oxide (GO)

was prepared from graphite powder ac[illegible]ing to [illegible]odifie[illegible] Hummers' method [25]. Firstly, different [illegible] GO (0[illegible]0.[illegible], or 0.3 g) and 1 g HC were sonicated f[illegible]5 h in [illegible] mL de[illegible]ed water and 20 mL ethanol to disperse G[illegible]eets [illegible] HC powders. In addition, 0.1 g polyvinyl pyrroli[illegible]ne (PV[illegible]) was dissolved in the resulting suspending liquid by [illegible]gnetic [illegible]ing for 5 h at room temperature. Due to the hydrophob[illegible] of HC [illegible] hydrophilia of GO, the polyvinyl pyrroli[illegible]e is used a[illegible]factants to prepare hard carbon coated by Graphen[illegible]ide. Mixtu[illegible] of hard carbon and GO were obtained by suction [illegible]ation o[illegible]he suspending liquid followed by dryi[illegible]ht at [illegible]he air. Finally, composite of HC and red[illegible]d Graph[illegible] Oxide ([illegible]O) was obtained by heating the mixtur[illegible]000 °C und[illegible] Argon flow for 1 h with ramp rate of 10 °C min^{-1}. G[illegible]ene Oxid[illegible]an be reduced by annealing in inert or reducing at[illegible]heres [illegible]d the process is named thermal annealing reduction[illegible]. The composite prepared by 1 g HC and 0.1, 0.2 or 0.3 g GO wa[illegible] denoted as HC/G-10, HC/G-20 and HC/G-30 respectively.

2.3. Characterization

The carbon weight percentages of the samples were determined on CS-600. The hydrogen and oxygen weight percentages of the samples were determined on an ONH analyser. The XRD profiles of carbons were measured with CuKα using D/Max2550VB + diffractometer. Raman spectra were recorded on an Invia Raman spectrometer, with an excitation laser wavelength of 514.5 nm. The morphology and microstructure of the samples were characterized by field emission scanning electron microscopy (FESEM, Hitachi S-4800) and TEM (JEOL-2100F) respectively.

Table 1
Elemental analysis and structural parameters of HC and HC/G samples

Sample	Elemental analysis (wt. %)			R	I_D/I_G
	C	H	O		
HC	97.81	0.37	1.05	2.2	2.86
HC/G-10	96.35	0.35	1.77	2.3	2.70
HC/G-20	96.05	0.28	1.93	2.5	2.46
HC/G-30	95.78	0.20	2.12	3.1	1.84

2.4. Electrochemical measurement

The electrochemical measurements of the samples were carried out with 2016 coin cells using lit[illegible]n metal as the counter electrode. The cathode electrodes [illegible]re prepared as follows: the carbon materials were mixe[illegible]ith p[illegible]nylidene difluoride (PVDF) in the weight ratio of [illegible] in [illegible]methyl-2-pyrrolidinone (NMP) to form the slurry. T[illegible]lurry [illegible] then sp[illegible]d onto a copper foil and dried in a vacu[illegible]ven at 12[illegible] for [illegible]our. The solution of 1 M $LiPF_6$ in ethyl[illegible]nate, dieth[illegible]bonate and dimethyl carbonate (1:1:1 i[illegible]olum[illegible]rved as the electrolyte. The cells were galvanostatically charg[illegible]d discharged at various current densities of 20 mA g^{-1} (C/20, [illegible]400 mA g^{-1}) to 2 A g^{-1} (5 C) between 0[illegible]V (*vs.* Li/Li^+) on a LAND battery testing station at room temp[illegible]ture[illegible] voltammograms (CV) were obtained with voltage[illegible]n r[illegible]0.[illegible]mV s^{-1} and electrochemical impedance spectro[illegible] (EIS) measurements were performed by [illegible]plying an [illegible] voltage of 5 mV amplitude in the frequency range of 0.01 to [illegible]kHz at the CHI660 electrochemical station.

[illegible]. Results [illegible]d discussion

[illegible]tal analysis data of all the samples are summarized in Table 1. The C content and H content of samples decrease as the [illegible]ight ratio of GO to HC increases, whereas the O content [illegible]creases slightly. On one hand, these are ascribed to the existence of abundant O atoms in GO. On the other hand, it is proved that oxygen cannot absolutely be removed or the GO completely be reduced just by thermal treatment in Ar atmosphere at 1000 °C, which is in accordance with other reported results [23,40]. In addition, no extra more H content are introduced into composites with increasing weight percentages of GO.

The X-ray diffraction patterns of the pure hard carbon and varied HC/G composites are shown in Fig. 1. These characteristic features are typical of poorly organized carbons [41]. The XRD diffractogram for the as-prepared samples contains well-pronounced diffraction peaks at 23∼26° and 43∼45° 2θ angle which

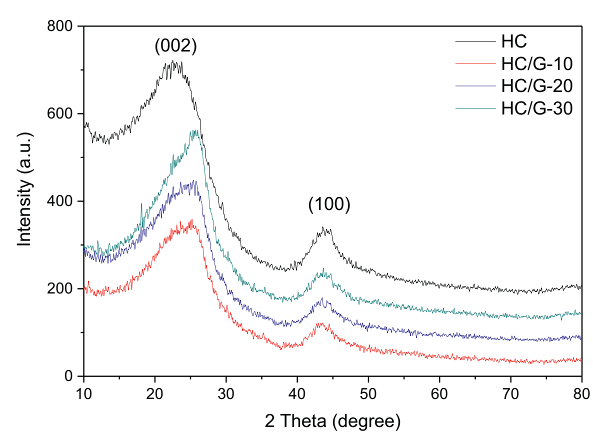

Fig. 1. XRD patterns of hard carbon (HC) and HC/G composites. The data has been offset sequentially by 100 counts for clarity.