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Reversible lithium insertion in catalytically graphitized sugar carbon

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ABSTRACT

A highly ordered graphite was derived from the low temperature (1200 °C) graphitization of sugar carbon using an iron catalyst. This graphite has electrochemical performance that is similar to artificial graphites made at temperatures over 2500 °C, although its irreversible capacity is somewhat higher. Graphite made by the catalyzed pyrolysis of low cost and renewable plant derived precursors represents a new avenue for research in the development of high performance negative electrodes for Li-ion batteries.

1. Introduction

High performance graphites for commercial Li-ion battery negative electrodes can be derived from the high temperature graphitization (>2800 °C) of soft carbon precursors, such as petroleum pitch [1,2]. Such graphites are dense, have high gravimetric (~350 mAh/g) and volumetric (~720 Ah/L) capacities, low average voltage (~125 mV vs Li/Li^+), low surface area, good rate capability, and pack well during electrode calendering. High temperature processing adds to the cost of artificial graphites [1]. Because of this, the use of lower cost natural graphites is desirable, but such graphites can suffer from reduced rate capability [1]. Carbons from the low temperature (~1000 °C) pyrolyzation of hard and soft carbons have also been suggested for use as Li-ion battery negative electrodes [1,2]. However, hard carbons suffer from low density and a large voltage range, while low temperature carbons derived from soft carbon precursors can have high average voltages, low capacity from turbostratic disorder, and significant hysteresis from residual hydrogen [2].

Another pathway to the formation of graphites is to introduce metal catalysts during pyrolysis [3,4]. Catalytic graphitization can significantly lower the graphitization temperature of carbons and both soft and "non-graphitizable" hard-carbon precursors can be graphitized by this method [3,4]. Skowroński and Knofczyński showed that glassy carbon could be partially graphitized with an iron catalyst, resulting in the formation of a graphite with turbostratic disorder and a capacity of about 276 mAh/g [5,6]. Complete graphitization could not be achieved even after 100 h of heating. Recently we reported that non-graphitizable ball-milled carbon can be graphitized in the presence of an Fe catalyst [7]. At 2000 °C catalytically graphitized ball-milled carbon had excellent performance in Li-ion cells and low turbostratic disorder. In fact, we found this graphite to be similar in its characteristics to artificial graphites made at 2800 °C. Nevertheless, the 2000 °C temperature of catalyzed graphitization is still rather high. Although ball-milled carbon could also be graphitized at 1100 °C, at this temperature the graphite had increased turbostratic disorder, resulting in very low reversible capacity in Li cells [7]. We know of no other reports of the use of catalytically derived graphite as negative electrodes in Li cells.

Here we report the catalytic graphitization of hard carbon derived from glucose. We have found that using a hard carbon remarkably reduces the temperature at which a highly ordered graphite can be formed, compared to ball-milled carbon, by almost 1000 °C. We believe that such green-sourced graphites present an exciting new avenue for research in the development of high-performance Li-ion negative electrodes.

2. Materials and methods

2.1. Synthesis and characterization of catalytically graphitized sugar carbon (CGSC)

Glucose (Aldrich) was first dewatered by heating at 180 °C in air for 24 h. The dewatered glucose was then heated at 1100 °C for 3 h under argon flow to form hard carbon. The hard carbon was graphitized by first grinding it by hand with iron powder (Alfa Aesar, 99.9% pure, <10 μm) in a 87.5:12.5 carbon:iron mole ratio, and then heating the mixture for 3 h at 1200 °C under a flow of argon using an induction furnace or a tube furnace. To dissolve the iron catalyst, 0.1 g of the graphite powder was placed in a 20 ml solution of concentrated HCl (Aldrich) containing a few drops of ethanol (98%, Aldrich) for 12 h. The ethanol reduced the surface tension of the acid solution, increasing its wetting ability. The graphite was then collected by centrifuging and the above

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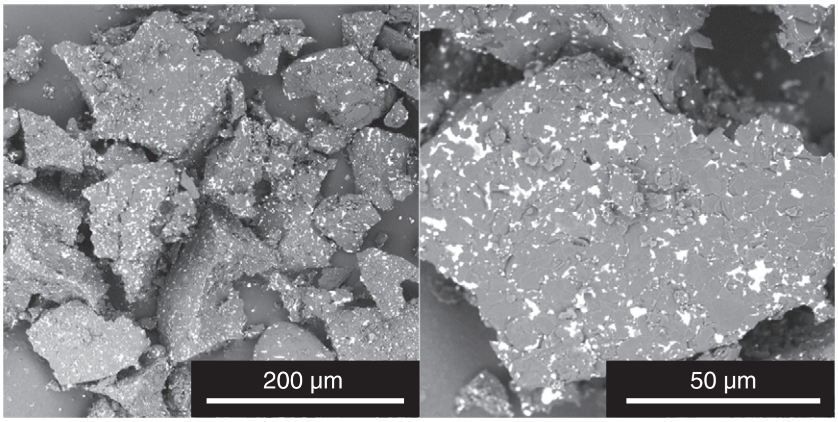

Fig. 1. SEM images of CGSC powder at different magnifications.

procedure was repeated seven times. Finally, the graphite was collected by centrifuging and washed repeatedly with distilled water and ethanol before drying at 120 °C in air for 1 h.

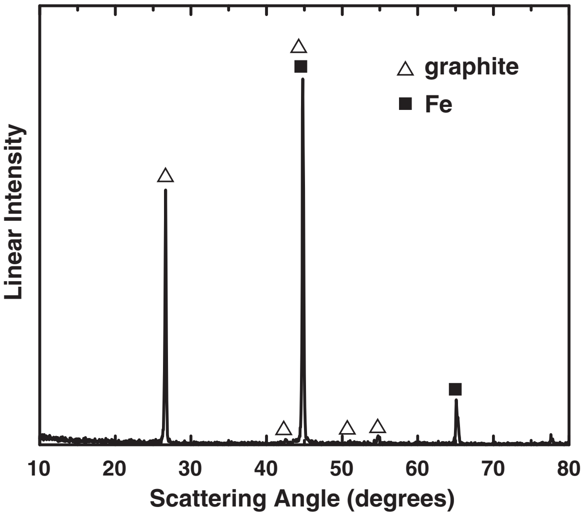

Fig. 2. XRD pattern of CGSC powder. (Graphite: JCPDS 96-901-2231; Fe: JCPDS 00-006-0696).

X-ray diffraction (XRD) patterns were collected using a Rigaku Ultima IV diffractometer with a CuKα radiation source ($\lambda = 1.54$ Å), a diffracted-beam graphite monochromator and a scintillation detector. A Phenom G2-pro Scanning Electron Microscope (SEM, Nanoscience, AZ) was used to observe the morphology of the samples. Density was measured using a Micromeritics AccuPyc II 1340 Pycnometer. To evaluate the carbon content, thermogravimetric analysis (TGA) was carried out on a TG 209F3 thermo-microbalance (NETZSCH, Germany) between 25 °C and 900 °C with a heating rate of 5 °C/min in an atmosphere of flowing dry air.

2.2. Electrochemical measurements

Electrode slurries containing 90 wt.% CGSC, 2 wt.% Super-P carbon black (MMM Carbon, Belgium), and 8 wt.% polyvinylidene difluoride (KYNAR) binder in 1-methyl-2-pyrrolidinone (Sigma-Aldrich, 99.5%) were mixed using a Kurabo Mazerustar planetary mixer/deaerator for two cycles (600 s total). A thin layer of slurry was coated on Cu foil using a Teflon coating bar with a 0.004 inch gap. The resulting electrodes were dried in vacuum at 120 °C overnight before use.

The CGSC electrodes were evaluated in 2325-type coin cells using 1 M $LiPF_6$ dissolved in ethylene carbonate/diethyl carbonate/monofluoroethylene carbonate (30/60/10 v/v/v) electrolyte, two Celgard 2300 separators and a lithium foil counter/reference electrode. Cells were assembled in an argon-filled glove box. Theoretical capacities were calculated assuming that only carbon is active with a theoretical capacity of 372 mAh/g and that Fe is inactive to lithium. Cells were cycled with a Maccor Series 4000 Automated Test System at a C/10 rate

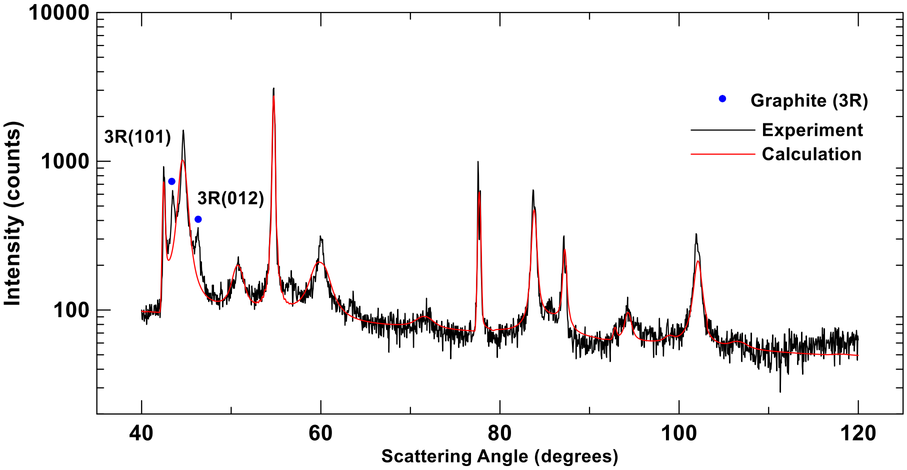

Fig. 3. XRD pattern plotted on a logarithmic scale of CGSC powder after the Fe catalyst was removed in acid. Also shown is a fit to the XRD pattern using the two-layer model of the CARBONXS software, as described in the text.