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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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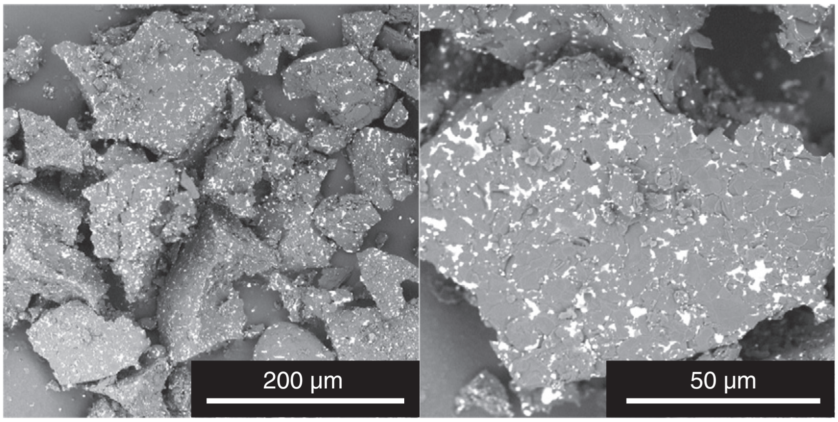

Fig. 1. SEM images of CGSC powder at different magnifications.

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.

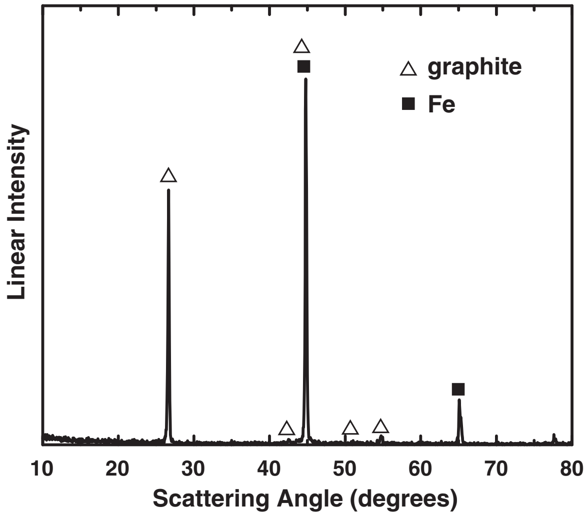

Fig. 2. XRD pattern of CGSC powder. (Graphite: JCPDS 96-901-2231; Fe: JCPDS 00-006-0696).

X-ray diffraction (XRD) patterns were collected using a Rigaku Ultima IV diffractometer with a CuKα radiation source (λ = 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

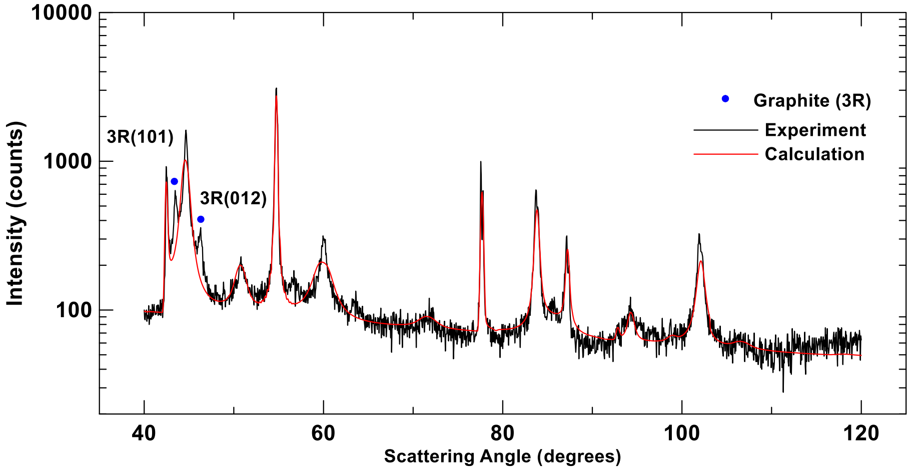

Fig. 3. XRD pattern plotted on a logarithmic scale of CGSC powder after the Fe catalyst was removed in acid. Also shown is a fit to the XRD pattern using the two-layer model of the CARBONXS software, as described in the text.

and trickled discharged to C/40 during the first cycle, and a C/5 rate and trickled discharged to C/20 for all subsequent cycles, in a voltage range of 0.005–2.0 V.

3. Results and discussion

3.1. Structural and morphological characterization of CGSC

Fig. 1 shows an SEM image of CGSC. It comprises 50 μm–100 μm composite particles composed of graphite flakes roughly 7 μm in diameter. Dispersed amongst the graphite grains are small bright Fe regions that are smaller than 5 μm in size. TGA analysis of the CGSC sample resulted in a 25.8% weight loss after heating in air at 900 °C. This indicates an initial carbon content of 81.2 mol%, assuming all the carbon formed CO_2 and the Fe formed Fe_2O_3 during the TGA experiment. The density of this sample was measured to be 3.1 g/ml, which is close to the theoretical value of 3.3 g/ml based on the TGA result. The carbon composition measured by TGA is slightly lower in carbon content than the starting hard carbon content of 87.5 mol%. Evidently, a small amount of carbon was lost during pyrolysis. Therefore, a carbon content based on the TGA measurements was used for all subsequent calculations.

Fig. 2 shows the XRD pattern of CGSC. It contains sharp peaks characteristic of a highly graphitized carbon, and peaks from the iron catalyst particles. To determine the degree of graphitization, the XRD pattern of CGSC with the iron removed by acid was fit using the CARBONXS software developed by Shi et al. [8] and their two-layer model. The resulting fit is shown in Fig. 3 and is a characteristic of a very high degree of graphitization, with some rhombohedral graphite (3R) peaks visible. The probabilities of random stacking (0.084) and 3R stacking (0.086) from this fit are close to those reported for conventional artificial graphites prepared at temperatures as high as 2800 °C [9]. This indicates that CGSC shows a high degree of graphitization, and may have excellent potential for application as a negative material for lithium ion batteries.

3.2. Electrochemical characterization of CGSC in Li cells

The first cycle voltage curve and differential capacity of CGSC are shown in Fig. 4(a) and (b), respectively. For both of these curves the capacity is shown with respect to the weight of carbon in the sample, so that it may be compared to that of conventional graphite negative electrodes. The reversible capacity obtained for CGSC was 366 mAh/(g carbon). This high capacity is indicative of a high degree of graphitization and low turbostratic disorder [9]. The voltage curve and differential capacity show sharp staging plateaus, also characteristic of highly graphitized carbon. Such characteristics are unprecedented for a carbonaceous material made at this temperature [2]. However, the irreversible capacity is high compared to a commercial graphite, leading to an initial coulombic efficiency (ICE) of about 87% (95% is typical for commercial graphite). The cycling performance and coulombic efficiency (CE) of CGSC are shown in Fig. 5 and are excellent for the 30 cycles measured. There is little fade in the 30 charge/discharge cycles measured and a CE of about 99.7% is achieved, as measured with the 16 bit resolution of the Maccor charger.

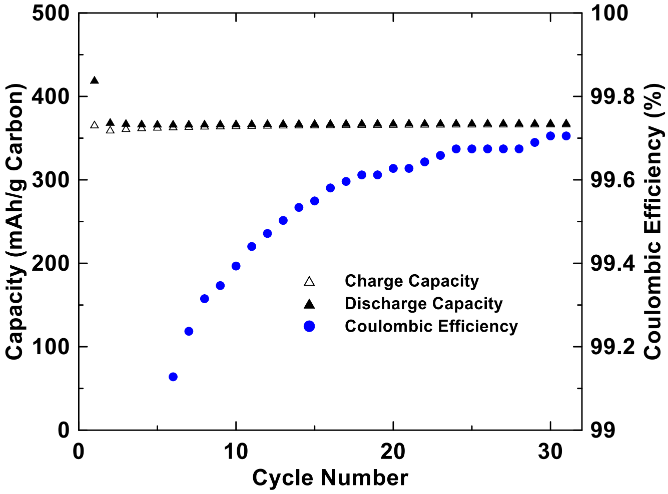

Fig. 5. The cycling performance and coulombic efficiency of CGSC.

4. Conclusions

Hard carbon derived from glucose was found to form a highly ordered graphite, when heated in the presence of Fe powder at 1200 °C in only three hours. This temperature is about 1800 °C lower than the temperatures needed to synthesize conventional artificial graphites for Li-ion cells. Furthermore, the source of carbon is from green and renewable plant material. The performance of CGSC is similar to that of artificial graphites, however a higher irreversible capacity was obtained. More efforts must also be made to remove the iron catalyst from the carbon, if it is to be used in commercial Li-ion cells. Nevertheless, the performance of CGSC shown is unprecedented for any carbon material made at such a low temperature. We believe that catalytic graphitization opens up exciting new directions of research into the development of high performance negative electrodes for Li-ion batteries.

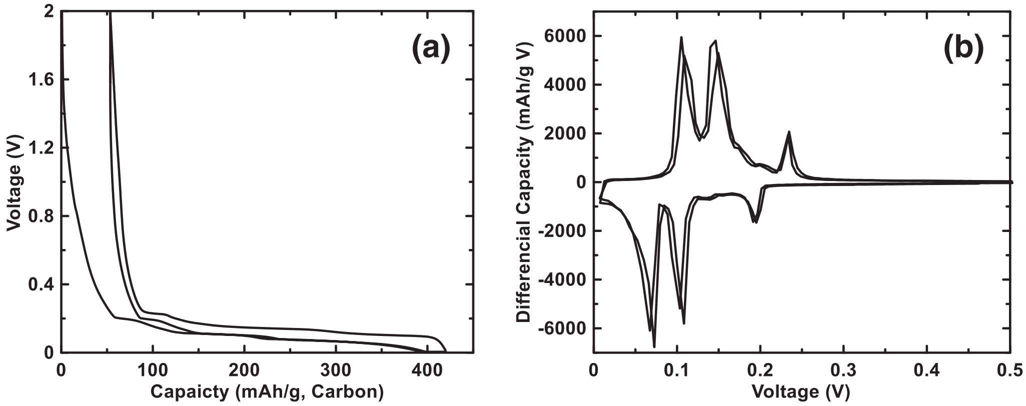

Fig. 4. (a) Voltage curve and (b) differential capacity of CGSC.

Acknowledgments

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