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Deficiencies of Chemically Reduced Graphene as Electrode in Full Li-Ion Cells

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ABSTRACT

In spite of the good electrochemical performance of graphene as electrode vs. lithium (half-cell configuration), graphene does not work in a full Li-ion cell as the delivered capacity continuously fades on cycling. The high irreversible capacity (IC) of the electrode observed in the former configuration, which is caused by the solid-electrolyte interface (SEI) formation, can be one of the causes of this shortcoming. As a remedy to this drawback, the graphene electrode was subjected to a lithiation process to form the SEI before assembling the full cell. Two lithiation methods were implemented: 1) precycling the electrode vs. a Li foil, and 2) placing the electrode in contact with a Li foil that was wetted with the electrolyte. Both methods improved the performance of the full cell, particularly the contact treatment, but the capacity retention on cycling was moderate. Moreover, not only does the electrode activation govern the electrochemical response, but factors such as the synthesis method and particle dimensions can also affect the cell performance.

1. Introduction

At present, graphite is the most commonly used material for manufacturing the anode of Li-ion batteries (LIB). Its main drawback is the low delivered capacity compared with that of disordered carbons, the capacity of which sometimes exceeds 1000 mAh g^{-1} [1–3]. However, these carbons possess a high irreversible capacity (IC), which is attributed to the solid-electrolyte interface (SEI) formation coming from electrolyte decomposition, as well as the blurring of plateaus and a higher polarization than graphite between the discharge and charge curves. Dozens of articles have been published regarding the electrochemical properties of these carbons for LIB, most of them in a half-cell configuration (versus the Li electrode) [3–6]. In general, after the strong capacity fading that is observed in the first cycle, the capacity retention tends to stabilize upon cycling. However, in the full-cell configuration, the capacity fades continuously with cycling [7,8], which makes the electrode unattractive for commercial Li-ion batteries.

IC is one of the factors responsible for this behavior. A way to palliate this drawback is to form the SEI before assembling the full cell. Two procedures are effective for this process: either precycling the electrode vs. a Li foil [8,9], or placing it in contact with a Li foil that is wetted with the electrolyte [10,11]. In both cases, electrolyte decomposition is induced with subsequent SEI formation on the electrode surface. To our knowledge, no comparative studies on the effectiveness, efficiency, and advantages/disadvantages of these procedures have been reported, and this is the purpose of this article. For this study, we chose graphene nanosheets (GNS), an emerging material that is frequently reported in the literature as a candidate to replace graphite in LIB [5,12]. Graphene doubles the graphite capacity due to its ability to store Li^+ on both sides of the sheet; it also possesses a high electronic conductivity. Usually, its performance in the half-cell configuration is outstanding. However, like other disordered carbons, GNS exhibit an unavoidable high IC, as well as strong polarization between the discharge and charge curves. Here, commercial $LiFePO_4$ (LFPO) was used as the cathode for the full-cell configuration.

2. Experimental

2.1. Materials

A full description of the GNS synthesis is reported elsewhere [3]. GNS were prepared in two steps from commercial graphite:

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graphitic oxide was first synthesized by a modified Hummers method, followed by a reduction step with a 1 M aqueous solution of N_2H_4. Commercial $LiFePO_4$ was supplied by Phostech Ltd.

2.2. Sample characterization

XRD patterns were recorded on a Siemens D5000 X-ray diffractometer using non-monochromated Cu Kα radiation and a graphite monochromator for the diffracted beam. The scanning conditions for structural analysis were 5–55° (2θ), a 0.03° step size, and 12 s per step. Raman measurements were carried out with a Renishaw inVida Microscope equipped with a Renishaw CCD Camera (578 × 400) as the detector, and a laser of 532 nm edge in Linefocus mode. TEM images were obtained with a Philips CM-10 microscope operating at 100 keV, while HRTEM images were obtained with a Philips CM-200 microscope operating at 200 keV. XPS recordings were obtained on a Physical Electronics PHI 5700 spectrometer, using non-monochromatic Mg Kα radiation and a multichannel detector. All spectra were fitted to Gauss–Lorentz curves in order to better identify the different functional group in each material. Elemental analyses were carried out on a LECO CHNS-932 microanalyzer.

2.3. Electrochemical measurements

The GNS and LFPO electrodes were prepared in a weight proportion of 80:10:10 of GNS (LFPO), PVDF binder, and carbon Super P, respectively. These mixtures were treated with 1-methyl-2-pyrrolidinone (Sigma–Aldrich) to obtain a slurry that was then deposited on Al (LFPO) and Cu (GNS) foils using the "doctor blade" technique. The full cells were assembled with an anode-to-cathode average capacities ratio (N/P) of around 0.9, and the average capacities were 600 mAh g^{-1} for GNS [3] and 150 mAh g^{-1} for LFPO [7]. The mass loading, therefore, was around 2.4 mg cm^{-2} for the cathode and four times lower for the anode. Such an N/P value was chosen based on the results of Zhang et al. as the best ratio for full cells with graphite as the anode [13]. The electrolyte was 1 M $LiPF_6$ in EC:DMC (1:1, by weight) and Whatman paper was used as the separator. All of the tests were carried out in three-electrode Swagelok T-type cells, with a Li foil as the reference electrode, in order to record the half-cell potential throughout cycling. Cycling tests were performed on an Arbin BT2000 potentiostat–galvanostat system within the potential window 3.9–1.5 V, using a current density of 34 mA g^{-1}, corresponding to C/5 regarding the cathode mass. The specific capacity values also refer to the cathode mass.

3. Results and Discussion

3.1. Sample characterization

The strong chemical treatment applied to the graphite for its transformation to GO causes a disruption to its structure as a result of the intercalation of different functional groups, which increases the interlayer spacing as observed in the XRD patterns of Fig. 1a. Thus the characteristic peak of graphite at ca. 27° (2θ) migrates to ca. 11° (2θ), and the lower intensity reflections disappear. Chemical treatment of GO with hydrazine implies the reduction of the functional groups with a concomitant contraction in the interlayer spacing as revealed by the movement of the characteristic peak to a higher angle (2θ∼26°), which corresponds to the (002) diffraction peak of graphene. The (002) interlayer spacing of GNS, 0.365 nm, is consistent with the majority of reported values for this system [14–16].

Splitting of the graphite layers was also revealed by Raman spectroscopy, since the spectra gave rise to a couple of bands in the range 1200–1800 cm^{-1}, and the relative intensity of which has been proposed as an indicator of graphene disorder [17]. The Raman spectra for graphite, GO, and GNS are shown in Fig. 1b. The G (at ca. 1600 cm^{-1}) and D (at ca. 1350 cm^{-1}) peaks are associated with the in-plane vibrational mode that involves sp^2-hybridized carbon atoms and to the breathing modes of sp^2 carbon rings, respectively. The latter band, D, is generally weak in graphite and high-quality graphene as the presence of defects is required for its activation.

The morphological properties of graphene were studied by TEM. The particles adopted the typical shape, i.e., entangled and scrolled sheets that resemble crumpled paper (Fig. 2a). According to some researchers [18], sheet thickness can be estimated by using high-resolution images to inspect a folded region that is assumed

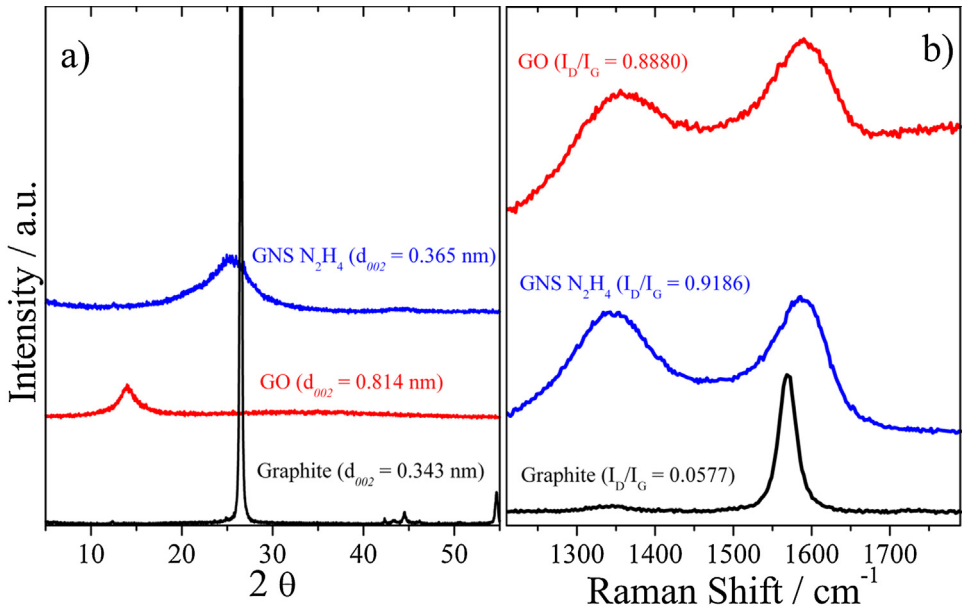

Fig. 1. a) XRD pattern, and b) Raman spectra of graphite, graphitic oxide, and GNS.