The role of re-aggregation on the performance of electrochemically exfoliated many-layer graphene for Li-ion batteries

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A B S T R A C T

Two potential pathways for Li$^+$ diffusion occur within graphitic carbon with typically in-plane diffusion dominating ($\sim$10^{-7} cm^2 s^{-1}) over diffusion along the crystallite grain boundaries ($\sim$10^{-11} cm^2 s^{-1}). Reducing the flake thickness of microcrystalline graphite powders via electrochemical exfoliation offers a method to overcome the latter, sluggish grain boundary Li$^+$ diffusion, thereby increasing the overall rate capability of the graphite negative electrode in a Li-ion battery. Six micron particulate graphite was electrochemically exfoliated to give flakes of which $\sim$90% had a thickness of <10 graphene layers. This exfoliated material was then prepared as an ink and allowed to dry prior to forming a battery electrode. Analysis of the electrode and dried exfoliated powder using powder X-ray diffraction, scanning electron microscopy and Brunauer–Emmett–Teller isotherm analysis show that the material has, apart from a significant reduction of the rhombohedral fraction from 41% to 14%, near-identical properties to that of original starting graphite powder. Thus, once the exfoliated powder has been dried from the exfoliation process, as anticipated, major restacking of the multi-layer graphene flakes had occurred. Likewise there was no significant improvement in using the exfoliated material at high rates of delithiation and lower specific capacity, when tested within a half cell vs. lithium metal. In situ Raman analysis showed that the exfoliated material displayed similar spectral features to the pristine sample during lithiation, as did multi point measurements on differently disordered areas shown from the varying I_D/I_G-band intensity ratios, indicating that local surface disorder does not influence the course of lithium insertion. The re-aggregation of graphenic material is widely recognised, but seldom evaluated. This work shows the importance of keeping graphenic material dispersed at all stages of production.

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1. Introduction

There are presently no guidelines for designing carbon-based electrode architectures for lithium-ion batteries, particularly for high-power applications. A prospective avenue of development would be to modify or fabricate graphitic flakes to take best advantage of their Li$^+$ diffusion properties. It has been reported that Li$^+$ diffusion through graphitic carbon can occur via two pathways: typically in plane diffusion dominates ($\sim$10^{-7} cm^2 s^{-1}) over diffusion along the crystallite the grain boundaries ($\sim$10^{-11} cm^2 s^{-1}) (Fig. 1a) [1]. A design that efficiently utilises the fast in-plane lithium diffusivity has been previously postulated. It is based upon graphitised natural graphite (MCMB – mesocarbon microbeads)

with a typical crystalline domain size of around 45 nm, which could be intercalated/deintercalated in less than 0.2 ms [1]. Such a rate would compete with the fastest-rate cathode materials seen to date [2]. As described, a rate-promoting design could potentially be achieved by creating graphite particles with radially aligned crystallites, where the graphene planes are parallel to each other in radial direction. Herein we present work towards a different concept to generate very thin high aspect ratio graphitic flakes in order to overcome sluggish grain boundary diffusion of Li$^+$. Reductive electrochemical exfoliation has been shown to be an effective method in generating single and multi-layer graphene sheets greater than one micron diameter [3–5]. In this method tetraalkylammonium cations are electrochemically inserted into graphitic carbons in order to exfoliate them to produce flakes down to a monolayer. As the method is reductive, the resultant flakes have low oxygen content, and therefore are of potential interest for Li-ion negative electrodes.
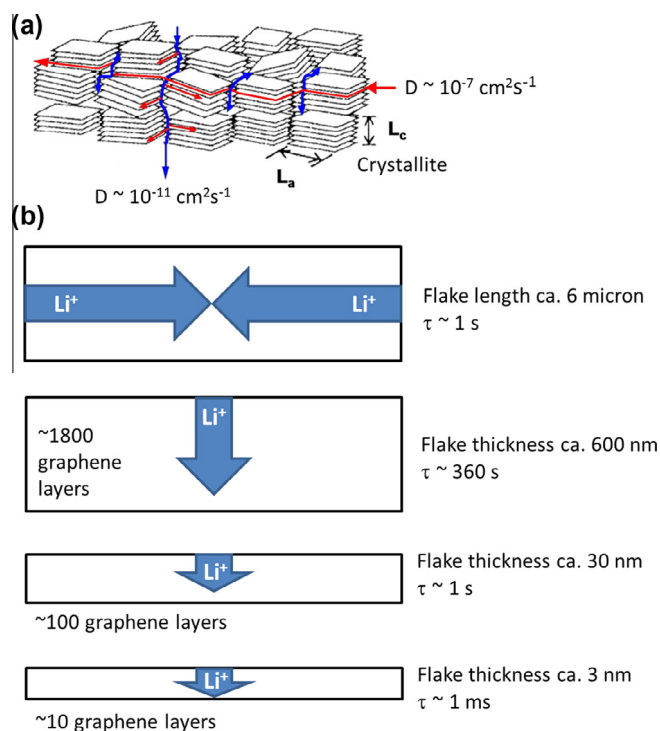
Fig. 1. (a) Figure showing the diffusion pathways of Li$^+$ through a graphite particle (b) design principle and diffusion times for higher rate graphitic particles from controlling flake thickness.

Fig. 1a illustrates an idealised picture of a graphitic particle comprised of crystallites with lateral and thickness dimensions of L_a and L_c respectively. The effect of anisometric Li$^+$ diffusion on diffusion times with respect to particle dimensions is shown in Fig. 1b. Li$^+$ diffusion time, τ is calculated by $\tau = L^2/D$, where D is the diffusion coefficient (cm^2 s^{-1}) and L is the diffusion length (cm). Thus, for a particle with an aspect ratio of 10:1 where the particle length is 6 μm and thickness is 600 nm, the Li$^+$ diffusion time along grain boundaries is 360 times slower than between the graphene sheets. Reducing the particle thickness will allow Li$^+$ diffusion through grain boundary pathways to become more significant. Thereby decreasing the thickness down to 100 graphene layers brings parity of the diffusion times, and reducing further to 10 layers decreases the grain boundary diffusion time to 1000× faster than between the graphene sheets. In this paper the effect of modification of synthetic graphite via reductive exfoliation on structure is studied and the resultant Li electrochemistry is presented.

It is however, acknowledged that graphenic material re-aggregates, if allowed to dry out. It is the intension of this paper to characterise the structural changes that have occurred during exfoliation and subsequent restacking. As well as to examine whether such rearrangements have any significant effect on electrochemical performance of the material, as the active component of a Li-ion battery negative electrode, via the introduction of stacking faults that may provide shorter grain boundary diffusion path lengths.

2. Experimental

2.1. Electrochemical reduction method for producing exfoliated graphite and Raman characterisation of product

The experimental setup and process for electrochemical exfoliation of graphite is illustrated in Fig. 2. A two electrode system was used for the process, a ca. 6 micron-sized synthetic graphite carbon SFG6 (Timcal, AG) was selected and pressed into a pellet and used as working electrode, the electrolyte was composed of dimethyl sulfoxide (DMSO) saturated with lithium chloride (LiCl) and tri-ethylammonium hydrochloride (Et$_3$NHCl), and a graphite rod was used as counter electrode. A negative voltage (−10 V) was applied to the working electrode for 8 h, during this process the graphite pellet dissociated and spread into the solution due to the intercalation of Li$^+$ and triethylammonium ions [3]. Afterwards, the exfoliated graphitic material was dispersed in water, then collected by vacuum filtration and washed repeatedly with water to remove the residual ions. Finally, the obtained powder was dried in an electric oven at 80 °C for 5 h to ensure that the sample was completely moisture free to prevent any hydration of the lithium in the battery testing. This process can be repeated to achieve a higher exfoliation level.

2.2. Characterisation of graphite powders

Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance operating in transmission mode with a copper source ($\lambda = 1.5418$ Å). The average crystallite size along the crystallographic c-axis (L_c) and the a-axis directions (L_a) were determined from the XRD data by peak fitting the (1 0 0) and the (0 0 2) peaks for both the SFG6 and the exfoliated-SFG6.

These peaks were then analysed using the Scherrer equation:

$$L \text{ (nm)} = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

where L is the average crystallite size along the analysed plane, K (the dimensionless shape factor) is a constant (here 0.9), λ is the wavelength of the X-rays, θ is the Bragg diffraction angle of the analysed plane and β is the full width at half-maximum (FWHM) of the analysed peak. By determining L for the (1 0 0) and (0 0 2) fitted peaks, it was possible to determine the values for L_a and L_c respectively. The rhombohedral fraction (3R phase) was then determined by comparison of the ratio of the intensities of the (1 0 1) hexagonal and rhombohedral diffraction peaks. Relative surface disorder was determined via Raman spectroscopy from the average intensity ratio of D and G bands (I_D/I_G) of the graphite powders taken from 400 points on the powder surface across an area of 95 μm × 95 μm. Surface area measurements were conducted using a Quantachrome NOVA 4200e Volumetric Gas Sorption Analyser, employing high purity nitrogen (99.9995) at 77.35 K. Approximately 400 mg of each of the powders were degassed overnight at 350 °C to 10^{-3} mbar dynamic vacuum. The surface area of the powders were calculated via the multipoint Brunauer–Emmett–Teller (BET) analysis of the isotherm using five data points with relative pressures ranging from 0.1 to 0.3. Graphite powder morphologies were characterised using a JEOL 6610 scanning electron microscope operating at an accelerating voltage of 20.0 keV.

2.3. Electrochemical testing

Composite electrodes were prepared from a slurry of 90 wt.% active material (SFG6, Timcal AG or exfoliated-SFG6) and 10 wt.% poly(vinylidene fluoridehexafluoropropylene) co-polymeric binder (Kynarflex, Arkema) cast onto a copper foil current collector. Typical electrodes had a thickness of ∼30 μm and mass loading of 2–3 mg cm^{-2}. CR2032 coin cells were assembled in an argon filled glove box (O$_2$, H$_2$O < 1 ppm) with 1 M LiPF$_6$ in EC-DMC (BASF) impregnated glass fibre separators (Whatman) and a Li metal counter electrode.

Electrochemical charge/discharge measurements were carried out at 30 °C (Maccor Series 4200 battery cycler). An asymmetric cycling procedure was developed whereby an initial galvanostatic