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Modification of Graphene Anode Morphologies via Wet and Dry Milling

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Abstract

Graphene, an individual graphite monolayer, is being considered for use in lithium ion anodes as there is a technological drive to make batteries thinner, lighter and more flexible whilst maintaining or increasing cell capacity and cyclability. Due to its mono/few-layer platelet structure graphene may potentially be affected by mechanical processing routes. Here the effects that dry milling and wet milling have on graphene nanoplatelets and graphene anode solutions have been investigated. It was found that dry milling for 15 minutes causes graphene nanoplatelets to form agglomerated graphite, but that wet milling of graphene anode solution results in reduced porosity and smoother electrodes without visibly destroying the nanoplatelets.

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Keywords: Lithium-ion batteries; graphene; battery anode

1. Introduction

Since their initial commercialisation by Sony in 1991 [1], rechargeable, electrochemical, lithium ion batteries have become essential for handheld, portable, consumer electronics. They exhibit high energy densities relative to both the volume of space they occupy and their mass [2]. As a result, they are now considered to be the most suitable battery for numerous applications, replacing lead-acid in the process. However, lithium ion batteries still have scope for

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development when compared to lead-acid and nickel-metal hydride batteries (NiMH) which have been commercialised for over a century and since the early 70s respectively. There is a strong drive to make them thinner, lighter or more flexible whilst maintaining high cyclability and increasing cell performance.

The vast majority of commercial anodes are carbonaceous in nature and the most prevalent of which is graphite which was the first carbon-based material utilised as an anode in rechargeable lithium ion batteries [3]. Graphite has a theoretical maximum capacity of 372 mAh/g which corresponds to the formation of LiC_6 , and a cycling capacity of 320 mAh/g in commercial cells [4]. LiC_6 forms as the cell is charged due to the Li^+ ions being inserted between the individual graphene planes that compose graphite [3]. The lithiation of graphite is an intercalation process and LiC_6 which forms contains approximately 0.167 Li per C [5]. Graphite is the preferred commercial anode due to its high cyclability across hundreds of cycles and its relative inexpensiveness.

A modern alternative to graphite is graphene. It is a two-dimensional, one atom thick, individual graphite monolayer consisting of hexagonal sheets of hybridised sp^2 bonded carbon. Graphene has a high surface area, exhibits good electrical conductivity [6] and a theoretical maximum capacity up to double that of graphite due to Li^+ ions being stored as LiC_3 on either side of the graphene sheets, resulting in approximately 0.33 Li per C [7].

During the fabrication of batteries, it is common practice when constructing cells to dry mill the active component and conductive additive elements of an electrode together, prior to electrode production to improve mixing and the electrical conductivity across the electrode. Dry milling is advantageous when using graphite as the active anode component, but potentially detrimental when using graphene as the active anode component due to the possibility that the mechanical processing will result in the formation of graphitic carbon or other carbon allotropes. Where dry milling is a destructive processing route, wet milling of the electrode solution prior to coating the current collector is an alternative. In this work graphene powder used in the construction of battery anodes has been characterised by scanning electron microscopy (SEM) before and after dry milling to evaluate the changes in the graphene nanoplatelet structure. The dry milling process is compared to wet milling a graphene anode solution and the subsequent electrode morphology is characterised.

2. Methodology

2.1 Materials

Li-ion battery anode materials have been fabricated using Elicarb Premium Grade Graphene Powder (Thomas Swan Ltd) as the active component. It is considered “few layer graphene” (FLG) and is a significantly cheaper alternative to monolayer graphene which is currently produced by time and energy intensive processes resulting in excessive costs. The graphene as-received is in the form of nanoplatelets, approximately 1000 nm in width of varying thicknesses between 5 and 7 carbon layers (see Fig. 1(a)).

Timcal C-Nergy Super C65 Conductive Carbon Black (C65) was used as a conductive additive for this study. C65 particles are carbon nanospheres structure 65 nm in diameter. Relative to other conductive additives C65 has lower electrode resistance, is easier to disperse and has fewer trace elements and impurities. To bind the graphene and C65 together, Poly(acrylic acid) (PAA) is used. In 2010, Huebner et al. demonstrated that PAA can function as a binder with increased stability and more tuneable mechanical properties when compared to polyvinylidene fluoride (PVDF) and carboxymethyl cellulose (CMC). PAA is soluble in both water and ethanol for fabricating anode solutions, and battery anodes fabricated with PAA have demonstrated improved cycling over both PVDF and Na-CMC [8].

2.2 Battery anode material processing

Dry milling of graphene powder was carried out for 15 minutes in a SPEX Sample Prep 8000M Mixer/Mill High Energy Ball Mill. In addition, a mix of Graphene and C65 in a ratio of 87.5:12.5 (70:20) was also dry milled using the same milling parameters for 15 minutes to evaluate the effect of the C65 additive on the graphene dry milling process.

Two graphene-based electrodes were constructed using standard centrifugal mixing of anode solutions; one underwent subsequent wet milling for 15 minutes whereas the other did not. The electrodes were prepared from a mixture of active material graphene (A), binder PAA (B) and conductive additive C65 (C). The mass ratio between materials A:B:C was 70:20:10. First a polymer solution of poly(acrylic acid) and ethanol was produced and centrifugally mixed for 15 minutes at 1500 rpm. The mix of active material and conductive additive was added to the

binder solution and mixed again for up to 30 minutes at 1500 rpm to form an ‘ink’. For one sample, this ink was wet ball milled for 15 minutes with the same mill as before. Both inks were then separately applied to carbon coated copper foil using a drawdown table and doctor blade at a thickness of 200 microns. The coating was left to dry before being transferred into a vacuum oven to dry further at 120 °C overnight. Both constructed electrodes and dry milled graphene-based anode materials and were characterised by SEM (FEI Nova NanoSEM 450).

3. Results

3.1 Dry milling graphene

Few-layer graphene powder was dry milled to evaluate the effect of the processing procedure on the graphene nanoplatelets. SEM images of the graphene structure before and after dry milling are shown in Figure 1. Prior to milling, the FLG graphene platelets are approximately 1 μm across and under 7 layers (<2.5nm) thick. After milling, the particles are noticeably much larger and rounder in shape (Fig 1(b)), appearing more similar to graphite. Although individual graphene platelets can still be identified after 15 minutes dry milling (Fig 1(b)), there are significant agglomerated carbon particles in the size range 2-15 μm diameter generated by the mechanical impacts.

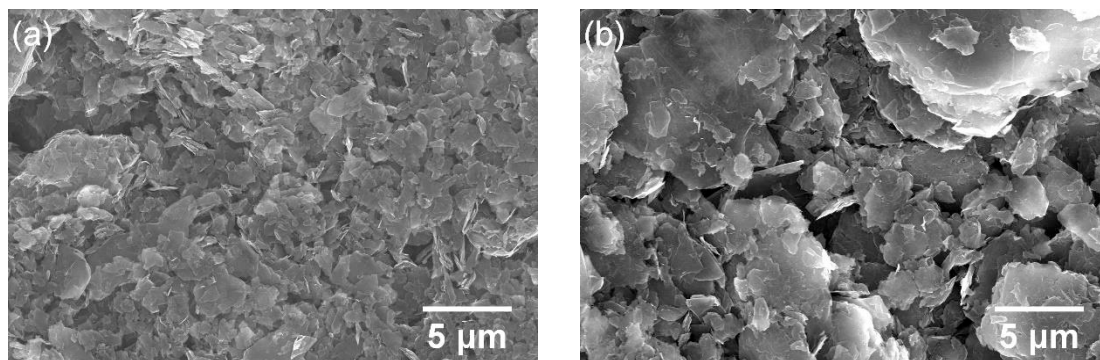


Figure 1. Graphene before and after 15 min dry milling. (a) As-received graphene. (b) Graphene after 15 min dry mill.

The effect of dry milling FLG graphene with 12.5 wt% C65 carbon nanospheres is shown in Figure 2. The graphene particles increase in size to ~1-10 μm diameter agglomerates, whilst retaining an overall plate-like morphology (Fig 2(a)). The graphene/C65 composite agglomerations appear more angular than the rounder carbon particles present after graphene is milled individually (Fig 2(b)), with the presence of the C65 nanoparticles on the surface of the graphene agglomerates clearly visible. This suggests that the presence of C65 nanospheres coating the nanoplatelets might prevent the individual layers from aggregating in the most compact manner.

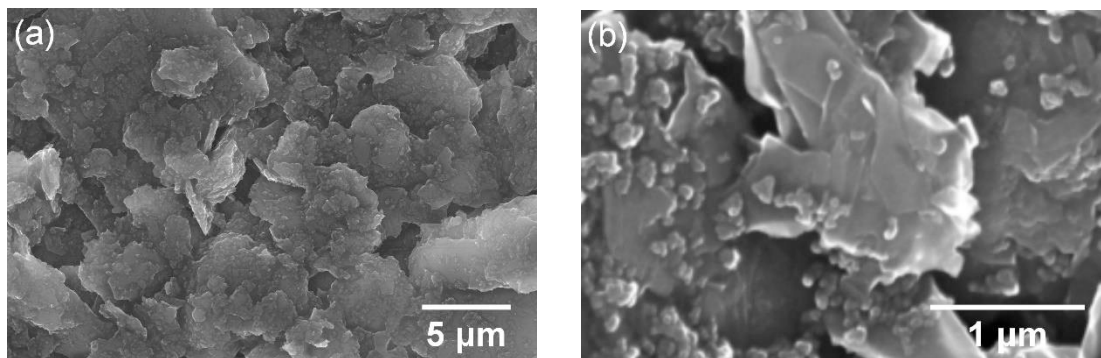


Figure 2. (a) Graphene and C65 conductive additive dry milled together for 15 min. (b) Higher magnification image showing surface decoration of graphene agglomerates with C65 carbon spheres.

3.2 Graphene-based anode fabrication

The microstructure of the two graphene-based electrodes constructed using standard centrifugal mixing of anode solutions and with/without subsequent wet ball milling for 15 minutes were examined by optical microscopy and SEM (Fig. 3). It was observed that the surface of the standard procedure unmilled electrode was rougher than the milled electrode, with significant pores present on the electrode surface (Fig. 3(a)). The change in electrode surface morphology is clearly apparent in the SEM analysis, where the milled electrode surface appears flatter/more uniform with an even distribution of smaller pores $<1\mu\text{m}$ diameter (Fig. 3(c)).

Considering the morphology of the FLG graphene after electrode construction using standard centrifugal mixing of the anode solutions (Fig 3(a, b)), the graphene platelets look comparable in morphology to the as-received graphene, and the C65 nanospheres appear as a distribution of nanoparticle clusters, preferentially located on the edges of the graphene platelets (Fig. 3(b)). For the electrode material that underwent additional wet ball milling, the graphene/C65 microstructure remains the same (Fig 3(c, d)) and the platelet size is comparable to the as-received graphene (Fig 1(a)). This implies that additional wet milling, whilst changing and improving the morphology of the electrode by reducing porosity and flattening the surface does not cause the graphene nanoplatelets to form large carbon aggregates.

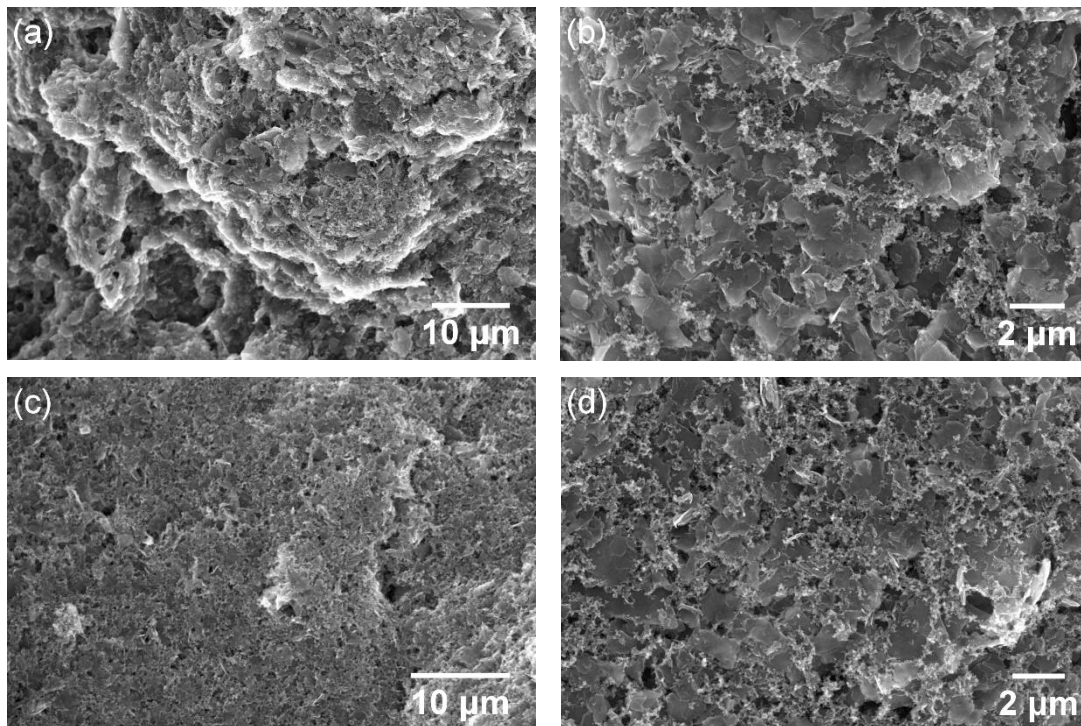


Figure 3. SEM images of Graphene/C65 electrodes prepared with and without wet milling. (a, b) No milling. (c, d) 15 min wet mill.

4. Conclusions

The impact of wet and dry ball milling on the processing of graphene anode materials has been investigated. It is found that the dry mechanical milling of graphene for 15 minutes results in the formation of large carbon aggregate particles. The inclusion of 12.5 wt% C65 carbon nanoparticles in the dry milling process results in more angular morphology graphene/C65 composite aggregates. Solution fabrication of graphene/C65 anodes with centrifugal mixing retains the platelet morphology of the graphene. An additional 15 min wet ball milling of the electrode ink containing graphene nanoplatelets results in a significantly smoother electrode surface along with a more evenly distributed and smaller pore structure, without causing the nanoplatelets to aggregate.

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