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How much does size really matter? Exploring the limits of graphene as Li ion battery anode material

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ABSTRACT

We unravel the role of flake dimensionality on the lithiation/de-lithiation processes and electrochemical performance of anodes based on few-(FLG) and multi-layer graphene (MLG) flakes prepared by liquid phase exfoliation (LPE) of pristine graphite. The flakes are sorted by lateral size (from 380 to 75 nm) and thickness from 20 (MLG) to 2 nm (FLG) exploiting a sedimentation-based separation in centrifugal field and, finally, deposited onto Cu disks for the realization of four binder-free anodes. The electrochemical results show that decreasing lateral size and thickness leads to an increase of the initial specific capacity from ≈590 to ≈1270mAhg^{-1}. However, an increasing irreversible capacity is also associated to the reduction of flakes' size. We find, in addition, that the preferential Li ions storage by adsorption rather than intercalation in small lateral size (< 100 nm) FLG flakes has a detrimental effect on the average de-lithiation voltage, resulting on low voltage efficiency of these anodes. We believe that the results reported in this work, provide the guidelines for the practical exploitation of graphene-based electrodes.

1. Introduction

Graphene, [1] thanks to its unique physical [2–6] and chemical properties, [3,7] including chemical stability [8] and electrochemical activity, [9] has drawn growing attention for manifold potential applications, ranging from composites, [3] to (opto)electronic. [4,5] In particular, graphene and its derivatives, such as graphene oxide (GO) [10] and reduced graphene oxide (RGO), [11] are considered promising materials in energy-storage applications. [12,13].

In the field of lithium-ion batteries (LIBs), graphene and its derivatives are being extensively explored for the realization of both anodes [14,15] and cathodes. [16,17] So far, RGO has been the most investigated material both for the realization of hybrid anodes, i.e., in combination with electrochemically active materials [12,13,18–23] and as stand-alone material. [24,25] Though, RGO is anything but the ideal anode material. In fact, although it may provide large Li storage capability, it also shows features that would discourage most battery producers. Amongst these, the commonly large irreversible capacity and the voltage hysteresis between lithiation and delithiation are the most serious ones. [12] Being the content of heteroatoms (e.g., O- and H- containing surface groups) and the amount of defects (e.g., micropores, vacancies, etc.) considered possible causes of such behaviour, graphene flakes produced by pristine graphite, i.e. without disrupting its original carbon backbone with aggressive chemical treatments, have recently come into play as possible advanced Li host [26,27].

Graphene nanoplatelets (GNPs) have demonstrated some appealing features for niche applications (e.g., low temperature and high power), [15,18] but no considerable gain in maximum specific capacity with respect to graphite. For what concern graphene, both theoretical and experimental studies have evidenced that Li storage is not thermodynamically favoured in single-layer graphene (SLG), where only low Li occupancy levels can be achieved. [24,26,28,29] This raises a natural question. What about what lies in between? Is there a critical flakes size where both beneficial properties of graphite (e.g. low operating voltage) and graphene (high conductivity and short diffusion paths) are found? Is few-layer graphene (FLG) a good active material for next-generation Li-ion batteries? Despite the fact that it is well accepted that lateral size

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and thickness (i.e. dimensions from now on) of the flakes, [26] as well as their edges, [30] are expected to play key roles on the Li^+ ion storage mechanisms [26,30–33] the link between these morphological properties, and electrochemical performances has not been established yet, neither for RGO, [12,13,19,21–23,25,34–36] nor with the less investigated un-functionalized flakes. [12,13,26,27].

With this work we aim at filling this gap. We exploit an "ad hoc" designed liquid phase exfoliation (LPE) procedure to prepare graphene-based flakes having variable dimensions in terms of dimensions. By means of sedimentation-based separation (SBS) in centrifugal field we obtain a set of FLG and multi-layer graphene (MLG) flake (i.e., FLG < 8 layers and MLG≥8 layers, respectively) [3] dispersions, which are then used to prepare binder-free anodes. The obtained data unravel the influence of the interplay of lateral size (ranging from 75 to 380 nm) and thickness (from 2 to 20 nm, e.g. with the higher end being a thickness comparable with the one of GNPs) of the flakes on the electrochemical performance upon lithiation/de-lithiation. The results indicate that the interplay between increased specific capacity voltage efficiency and irreversible effects make pristine graphene flakes not a promising anode active material in Li-ion batteries.

2. Experimental

The experimental details concerning the samples preparation and spectroscopic/microscopic characterization, as well as electrodes preparation and electrochemical characterization are reported in the supplementary information (S.I.).

3. Results and discussion

3.1. Physical-chemical characterization

We used LPE [37–39] to disperse graphite flakes in N-Methyl-2-Pirrolidone, having a surface tension (41.2 mN m^{-1}) [37–39] close to the graphene surface energy (62 mJ m^{-2}), [40,41] using ultrasonication to exfoliate graphite, see S.I. for details.

The obtained dispersion contains a heterogeneous distribution of thin/thick and small/large lateral size graphitic flakes, [37,39] which are subsequently ultracentrifuged exploiting the SBS process, [26,40,42,43] for the sorting of flakes by dimensions. In order to meet the requirements of fast deposition and non-toxicity, [37,41] the sediment is collected and dispersed in ethanol, allowing the simple one-step fabrication of binder-free electrodes. [27] The electrodes do not contain any additional conductive carbon, largely used in literature, [44] which might interfere with the electrochemical response of the graphene (e.g., by contributing to the Li storage capacity).

The morphology of the samples is characterized by transmission electron microscopy (TEM) and atomic force microscopy (AFM) analyses. The TEM images in Fig. 1a and b show that the average lateral size of the graphitic flakes decreases with the increase of the centrifugal speed, passing from 380 nm to 75 nm, see Table 1. The AFM results shown in Fig. 1c and d, demonstrate that both sample#3 and #4 have a much narrower, with respect to sample#1 and #2, thickness distributions, i.e., centred at 5 nm and 2 nm, respectively (see Table 1). Accordingly, Sample#1 and #2 are mostly formed of thick (20–50 layers) MLG flakes, while Sample#3 is composed of thinner MLG (10–15 layers) and Sample#4 comprised of FLG flakes. As also presented in Table 1, both the surface area (SA) data obtained from Brunauer–Emmett–Teller (BET) measurement and the O/C ratio calculated from XPS analysis (see Fig. S5) clearly demonstrate an increment of their values (SA from 114 ± 11 to 414 ± 41 m^2g^{-1} and O/C ratio from 0.045 to 0.110) passing from Sample#1 to Sample#4, respectively.

The comparison of the Raman spectra of the four as-prepared samples (Fig. 1e) illustrates the evolution of the G, D and 2D peaks, see S.I. about the peaks assignment. The reduction of FWHM(2D) from Sample#1 to Sample#4 indicates a decrease in the thickness of the flakes with the increase of the centrifugal speed. Statistical analysis, see section S2.2, shows that Samples#1, #2 and #3 are composed by MLG, while Sample#4 mostly contains FLGs, in agreement with AFM data. The Raman spectra also show an increase of both D and D′ peaks intensity when passing from Sample #1 to Sample #4, which could be explained assuming an increase of defects. The analysis of I(D)/I(G) as a function both FWHM(G) and Disp(G), see section S2.2, shows that there is no in-plane defect caused during the exfoliation process, and the major contribution to the D peak comes from the sample edges, [45] see S.I. for details.

The graphene dispersions deposited on the Cu substrates are characterized by SEM, see Fig. 1f. The micrographs recorded at low magnification (Fig. S6), and representative for the whole area, testify the homogeneity of the binder-free electrodes, independently from the flake size. Higher magnification images (Fig. 1f) reveal that, as the flake dimension decreases, the electrodes surface becomes more flat and compact, which from one hand could improve the electronic transport amongst the flakes, but, on the other hand, may not be beneficial for the lithium storage capacity and transport.

3.2. Electrochemical investigation

The dimensions of the graphene flakes are expected to play a crucial role on their Li^+ storage characteristics. The voltage profiles of Fig. 2a show that upon the first lithiation process the specific capacity of the electrode increases from 591 mAh g^{-1} to 1267 mAh g^{-1} as the average dimensions of the flake decreases from Sample#1 to Sample#4. However, in the de-lithiation process, Li^+ ions are released only to a certain extent, revealing a significant irreversible capacity, e.g., 40% for Sample#1. As the flakes get smaller in dimensions, more charge is irreversibly consumed in the first cycle, resulting in only 35% coulombic efficiency for Sample#4, see Fig. 2a. This loss may be ascribed to the irreversible electrolyte decomposition process leading to the formation of a solid electrolyte interphase (SEI) on the electrode surface. Variations of flake morphology lead to changes in SA (see Table 1) and edge defect, and thus in turn, of electrode reactivity. [46] In fact, as confirmed by the evident plateau evolving in all samples below 0.9 V, the charge associated to such irreversible process increases with decreasing flake dimensions, and, interestingly, the onset for SEI formation is morphology-dependent too. As the dimension of flakes reduces, the electrolyte decomposition occurs earlier, as testified by an upshift of ~100 mV of the associated plateau (see Fig. S7). Such reduced polarization suggests a catalytic effect of small/thin flakes towards the electrolyte reduction.

From the 2nd cycle onward, the specific capacity of Sample#1 and Sample#2 rapidly stabilizes without considerable fade, setting on values of 341 and 366 mAh g^{-1}, respectively, at the 20th cycle. The higher capacity provided by the smaller/thinner flakes appears to be partially lost upon cycling (see Fig. S8). The flake size has a noticeable influence on the potential window in which the capacity is delivered. During lithiation (Fig. S8a) and de-lithiation (Fig. S8b), Samples#1 and #2 provide stable capacities, mainly delivered at low potentials (i.e., in the 0.005–0.2 V and 0.005–0.25 V range for lithiation and de-lithiation, respectively). As the flakes dimension decreases, larger contributions arise from the more positive potential range instead (0.2–3 V and 0.25–3 V for lithiation and de-lithiation). Such behaviour suggests that adsorption of Li^+ is the mechanism primarily responsible for charge storage in small lateral size FLG flakes, [26,47] whereas, intercalation of Li^+ is the main process occurring in MLG flakes.

In order to get further insights in the Li^+ storage process in FLG- and MLG-based electrodes, a differential capacity analysis (Fig. 2b) is carried out in the 0.005–0.3 V potential range. For Samples#1 and #2 the Li^+ storage process evolves with a series of very sharp peaks, demonstrating fast kinetics and high reversibility. As extensively reported in literature, [32] the voltage peak sequence may here be