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First-principles studies of lithium storage in reduced graphite oxide

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ABSTRACT

The present work performs a first-principles study of the lithiation of graphite oxides with low oxygen content, which resemble reduced graphite oxide materials. The chemical nature of the Li structure formed is analysed, leading to the conclusion that the nature of lithium binding in these materials is completely different from that observed in pristine graphite. The stability of the lithium structures formed under different loadings is studied, with the finding that the lithiation potentials predicted are within the ranges of the values observed experimentally.

1. Introduction

Rechargeable Li-ion batteries (LIBs) appear nowadays as promissory energy storage media for many applications, ranging from portable electronic devices up to electric vehicles (EV). However, for the more demanding applications uses such as EV and load-levelling applications, the challenge that remains is to improve the energy and power densities without increasing weight [1–5]. Therefore, a large amount of effort is being undertaken in the scientific and engineering community in the development of new electrode materials for this type of batteries.

Carbonaceous materials present a lot of advantages due to their excellent properties such as good thermal and electronic conductivity and great surface area, among others. In summary, these properties make them attractive materials for innumerable applications, particularly in the field of energy carriers, like hydrogen storage and electrochemical systems. Among the latter, the commercial anodes of Li-ion batteries are a typical example. In fact, graphite is the most commonly used carbon material in the manufacture of the anodes of Li-ion batteries, allowing Li ions to be stored up to a LiC_6 stoichiometry, which implies a maximum theoretical capacity of 372 mAh g^{-1} [6]. Recently, materials based on carbon nanostructures such as nanotubes [7–9] and oxidized graphene nanoribbons [10] obtained by unzipping of the carbon nanotubes [11], have been shown to outperform the Li-ion storage capacity of ordinary graphitic materials. Similarly, graphene nanosheets have been found to yield a capacity of 460 mAh g^{-1} for 100 cycles work [12] and in the case of disordered graphene nanosheets the reported reversible capacity has been even larger, ranging between 794 and 1054 mAh g^{-1} [13]. Oxidized graphene nanoribbons have shown an initial capacity of 1400 mAh g^{-1} and a reversible capacity of 800 mAh g^{-1} [10]. Something similar happens with graphite oxide with different degrees of oxidation [14] and reduced graphite oxide [15]. However, up to date storage in oxidized graphitic systems has received relatively little attention in the theoretical field [16] in comparison with studies of pristine graphitic materials [17–21]. On the other hand, highly porous structures composed of carbon nanotubes or graphite oxide can be decorated with different metals (Ti, Ni, Co, Mn, V) to promote the intercalation of lithium. These experiments also indicate that it would be possible to increase the maximum ratio of 1:6 (Li:C) found for graphite. Thus, theoretical advances in the understanding of the absorption/desorption mechanism of Li^+ ions for the new carbon materials are critical to increase the actual performance and to acquire knowledge in the experimental limitations of the carbonaceous anode materials.

In the present work we investigate lithiation of mildly oxidized graphitic nanostructures, sometimes referred as reduced graphite oxide (RGO) [16], by means of first-principles calculations. We analyse the chemical nature of the modified carbonaceous-Li structures and consider the stability of them under different Li-loadings.

1.1. Methodology

1.1.1. Calculation details

All DFT calculations were performed using the Quantum Espresso package [22] with Van der Waals interactions. The

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