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Is single layer graphene a promising anode for sodium-ion batteries?

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A B S T R A C T

In an attempt to find an adequate carbon material to achieve a successful reversible adsorption of Na$^+$ ions, single layer graphene, is experimentally investigated in this work, for the first time, as anode for sodium-ion batteries. To this end, single layer graphene that was grown on copper foil by chemical vapor deposition was subjected to extended galvanostatic cycling and to cyclic voltammetry in the potential range of 0-2.8 V *versus* Na/Na$^+$. Regardless of the current density and electrolyte formulation used, the amount of Na$^+$ ions adsorbed/desorbed reversibly per surface area (specific reversible cell capacity) was very modest and comparable to that obtained with bare copper electrodes of reference, thus suggesting that the reversible capacity of the single layer graphene electrode is mostly due to the electrochemical response of the copper substrate. These experimental results clearly agree with recent theoretical calculations showing that the adsorption of Na$^+$ ions on the surface of single layer graphene is energetically unfavourable unless that surface includes significant defects density.

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1. Introduction

Sodium-ion batteries (SIBs) are currently considered an attractive alternative to lithium-ion batteries (LIBs) particularly for application in stationary large-scale electric energy storage systems (EES) owing to the abundant resources, low cost and safety of sodium as compared with lithium [1,2]. In these systems, the cost is the overriding issue as they are made up of a great number of batteries, whereas the energy density at the battery unit level is not a critical factor, thus being a realistic option for the application of the SIBs since they usually have lower energy density than their counterparts LIBs. However, as it has been stressed in a recent publication [3], the cost reduction that could be achieved by using SIBs may not be significant in terms of the final energy cost ($/Wh). Therefore, the energy density of the SIBs should be improved to allow their development and subsequent implementation as EES. To this end, a variety of electrode materials [1–4], cathode and anode, and electrolytes [1,2,5,6] for SIBs have been investigated, mainly, in the last two years. The results of the research in the field of cathode materials, several of them obtained by the simple replacement of lithium by sodium in the analogue compound, appear promising with a number of layered transition metal oxides, phosphates and fluorophosphates showing acceptable

reversible capacity, stability and relatively high operating potentials [1,4].

In contrast, up to now the progress in the development of anode materials with high specific capacities and low working potential to improve the energy density of the sodium-ion battery is very limited, mainly because of the inability of the graphite and/or graphitic carbons - the anodic choice par excellence in LIBs - to reversibly intercalate sodium ions between the carbon layers to any appreciable extent. As an example, compounds with a formulation of NaC$_{186}$ were calculated after electrochemical intercalation of Na$^+$ in graphite [7] against the typical LiC$_6$ graphite intercalation compound that is formed in LIBs. Based on theoretical calculations, this difference has been assigned to the extremely weak attractive interactions forces between the graphite layers and the intercalated Na$^+$ ions [8]; as a result, sodium is deposited as metal on the electrode surface rather than intercalated. Moreover, the sodium graphite intercalation compounds (NaC$_x$ with x = 36, 16, 12, 8, 6) are unstable [9]. In fact, they do not exist under moderate conditions, which was reported to be a consequence of the clash between the graphite structure (graphite is stressed when some Na$^+$ ions intercalate into it) and the size of the Na$^+$ ion (its ionic radius is approximately 0.3 Å larger than that of Li$^+$ ion, this difference leading to changes in thermodynamic and kinetic properties) [9,10]. Therefore, efforts have been focused on the identification of other host carbon materials to achieve a successful reversible intercalation/insertion of the larger Na$^+$ anions. Thus, a variety of carbons having a certain degree of porosity, a low-ordered structure consisting of few-layers graphite nanocrystallites (graphite domains) and different morphologies, including hard and

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soft carbons [5,7,11–15], carbon fibers and nanofibers [16–20], spherical carbons [21], hollow carbon nanowires [22] and nanospheres [23], reduced graphene oxide, [24] pyrolytic carbons from graphite oxide [25], as well as highly disordered carbon composites [26,27] have been investigated as anodes for SIBs. Good results as regards capacity and cycling stability were achieved with some of these carbons, the rate capability and particularly, the low coulombic efficiency during the first charge/discharge cycle due to the relatively large surface area (as compared with graphitic carbons) being the main drawbacks to overcome. In these porous disordered carbons, the electrochemical storage of Na$^+$ ions occurs through two predominant mechanisms, insertion between the graphene layers of the small graphitic clusters in the higher potential region ($\sim$1.5–0.1 V vs Na/Na$^+$) resulting in a sloping voltage profile, and/or adsorption by filling the porous structure as showed by the plateau at the lowest potentials ($<$0.1 V vs Na/Na$^+$) [7,11,19,23]. Thus, no voltage plateaux were observed in the electrochemical profiles of electrospun carbon nanofibers [19] and reduced graphene oxide [24], indicating that the capacity was mainly due to the sodium insertion into the graphene layers. A common feature for these carbons is the large interlayer spacing [19,23,24], all of them having values $\geq$0.37 nm, which has been determined from theoretical calculations to be the critical minimum value required to allow good reversible Na$^+$ ion insertion [22]. On the contrary, a large proportion of the capacity provided by other carbons was ascribed to the adsorption of sodium into the pores [7]. In any event, the former mechanism should be preferred since the Na$^+$ ion pore-filling potential is close to that of the metal itself which may cause sodium plating. Moreover, a large fraction of the sodium storage between the graphene layers was generally accompanied by a superior anodic rate performance of the material [19,22–24]. In conclusion from these studies, it seems that graphite-like materials with large interlayer distance and low porosity are potentially the most suitable anodes to allow the development of the SIBs. In this context, expanded graphite with a large interlayer distance (0.43 nm) and a low surface area ($\sim$30 m^2 g^{-1}) have been successfully used for the first time as anode material for SIBs [28]. Therefore, the diffusion of the Na$^+$ ions in carbon materials during the electrochemical process will not be a problem if an adequate structure is designed or selected.

In an attempt to find the above mentioned ideal carbon structure, graphene monolayer or single layer graphene (SLG), a novel 2D material with very high electronic mobility is experimentally investigated in this work, for the first time, as anode for sodium-ion batteries. To this end, single layer graphene that was grown on copper foil by chemical vapor deposition (CVD) was subjected to galvanostatic cycling versus Na/Na$^+$ using constant current intensity. CVD-grown SLG on copper foil has been already applied as anode for the LIBs counterparts [29,30]. Despite this, the exact mechanism of Li$^+$ ions storage in the SLG is still a subject of controversy. It has been recently suggested and even experimentally demonstrated that they are surface adsorbed in both sides of the Cu-deposited SLG [29,31]. Because of the high surface area (2675 m^2 g^{-1} counting the two sides) and the very low mass/surface ratio of this material, huge specific capacities were measured in LIBs (i.e. 13,263 mA h g^{-1} in ref. [27]. However, the capacity values expressed in terms of surface unit were modest ($<$0.05 mA h cm^{-2}) [29,30] and lower than that of graphite anode [32]. On the basis of these results, it is evident that for the implementation of SLG as anode in LIBs, novel battery architectures of reduced dimensions and lighter should be designed in parallel. However, recent studies have concluded as regards the electrochemical adsorption of Li$^+$ ions on the surface of SLG that (i) it does not occur unless that surface showed defects [33] and the amount is smaller than that previously predicted [32]. With these

precedents in mind, in this work, emphasis was placed on the nature of the interaction of the Na$^+$ ions with the SLG.

2. Experimental section

Two-electrode (working + counter) Swagelok-type laboratory cells were used for the electrochemical characterization. The working electrodes were single layer graphene CVD-grown on copper discs of 12 mm of diameter and 18 μm of thickness of commercial origin (SLG/Cu electrode), with a surface coverage >95% and a grain size up to 10 μm (see Fig. S1 in ESI for a Raman spectrum and SEM and TEM images of the SLG provided by the supplier). For comparative purposes, bare copper discs of the same diameter (Cu electrode) of high purity (>99.99%) were also used as working electrodes. In all cases, metallic sodium disc of 12 mm of diameter and $\sim$1 mm of thickness were the counter electrodes. The electrodes in the cell were separated by two micro-fiber glass discs impregnated with one of the following electrolyte solutions: 1 M
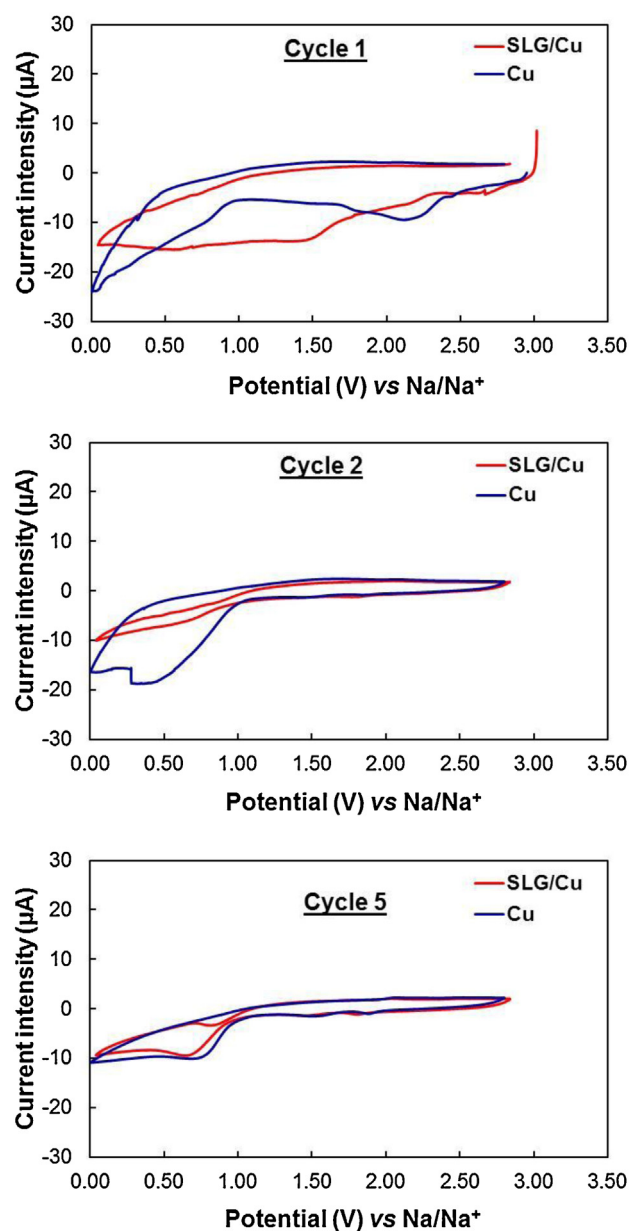

Fig. 1. Voltammograms of cycles 1, 2 and 5 of SLG/Cu and bare Cu electrodes using 1 M NaPF$_6$ (EC:DEC, 1:1, w:w) as electrolyte solution.