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Journal Name

COMMUNICATION

## Reduction of graphene oxide in Li-ion batteries

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Graphene or graphene based composites are widely used in various fields. Reducing graphene oxide is a simple and common method to preparing graphene for energy storage field such as Li-ion batteries. However, thermal reduction needs a high temperature in vacuum or inert gas condition and chemical reduction needs hazardous reduction agent. Accordingly, we report an electrochemical method to reduce graphene oxide in Li-ion batteries. By this method, we could assemble graphene oxide based composites electrodes into cells and directly reduce the graphene oxide in-situ. Compared to the conventional method to reduce graphene oxide, our work is simple and effective. Especially when the reduced graphene oxide is used in Li-ion batteries, our method could greatly simplify the electrodes fabrication process.

Graphene and graphene composite materials have attracted great attention in many fields such as electronic devices, energy storage and sensors due to their excellent physical and chemical parameters such as high surface area, high electronic conductivity, great mechanical properties and many others.<sup>1-6</sup> For different applications, scientists have developed respective way to producing graphene with desirable properties.<sup>1</sup> Among the methods, reducing graphene oxide (GO) is a main and scalable way to synthesize graphene used in energy storage and conversation fields.<sup>7-10</sup> In Li-ion batteries, using graphene/active materials composites as electrodes is an effective way to improve electrochemical performance.<sup>11-13</sup> Graphene serves as the conductive filler or structure support. The graphene/active materials composites electrodes are usually prepared by reducing GO/active materials composites.<sup>11,12</sup> Chemical, thermal and electrochemical reduction pathways are the common methods to reduce graphene oxide.<sup>14,15</sup> Chemical reduction is the most common method to reduce GO, but the reducing agent such as hydrazine are dangerous.<sup>7,16</sup> Heat-treating in vacuum or inert gases is an effective

method to reduce the GO, while the high temperature and gases condition are not conventional to fabricate electrodes.<sup>11, 14, 17</sup> Compared to the chemical reduction and thermal reduction of GO, electrochemical reduction method is green and easy to reduce GO.<sup>18, 19</sup> As we know, many graphene based composites are widely used in Li-ion batteries.<sup>5,20,21</sup> According, we report a simple electrochemical way to reduce GO in Li-ion batteries. By this method, we could prepare graphene based electrodes without pre-treating such as heat-treating. The GO/active materials composites electrodes could be directly assembled into the batteries. During the first several cycling processes, the GO would be reduced to reduced graphene oxide (RGO) in-situ with improved conductivity. This is a novel electrochemical reducing method which is in favour of the graphene based electrodes fabrication.

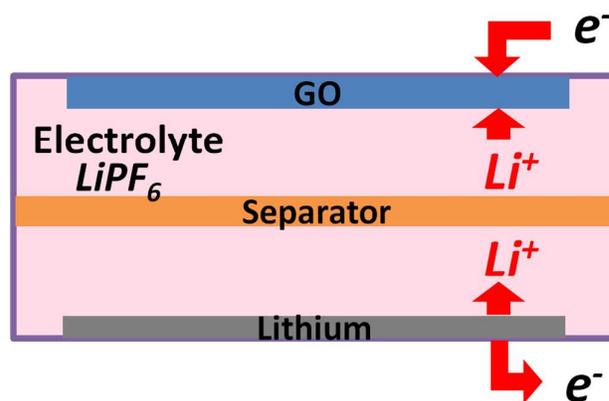


Fig. 1. The lithiation process of GO in the half cell. And during lithiation, the GO was reduced to RGO.

The GO used was synthesized by a modified Hummers method.<sup>22</sup> GO aqueous solution was dropped onto the copper foil. We dried this copper foil in air at 80 °C in an oven and got graphene oxide electrodes. The thickness of our GO electrodes was about 10 μm and the mass loading was around 0.6 mg. The areal density is about 0.6 mg/cm<sup>2</sup>. The electrodes were assembled into half-cells (LIR2032 Coin-type) as working electrode and Li metal (MTI) as counter electrode in Ar filled glove box. We applied a 25 μm thick

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micron porous polypropylene membranes as the separator (Asashi Kasei). 1 M LiPF<sub>6</sub> in ethylene carbonate/diethyl carbonate (1:1 vol/vol, Ferro Corporation) was used as the electrolyte. We cycled cells between 0 and 3V versus Li<sup>+</sup>/Li (BS- 9300R/10V2A MTI 8 channels battery analyser) at room temperature. During the electrochemical test, the GO in the batteries was reduced. After electrochemical cycling, we opened the batteries and got the cycled electrodes. The cycled electrodes were dipped in acetonitrile and diluted hydrochloric acid respectively to wash out the electrolyte and SEI. After that, we transferred the reduced graphene oxide film from the electrode to silicon chip. As comparison, we prepared GO samples by dropping the GO aqueous solution onto the silicon chip and drying in the air at 80 °C without cycling.

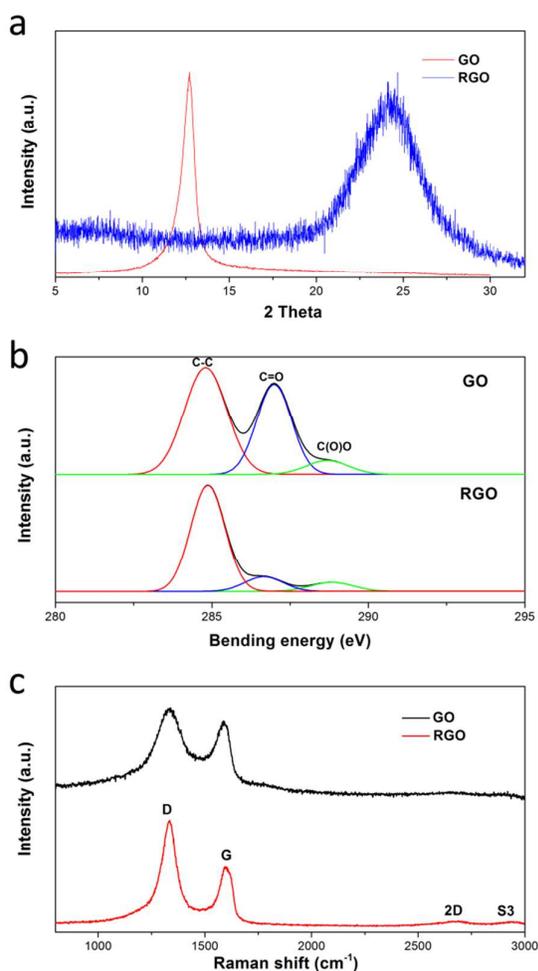


Fig. 2. Characterizations of graphene oxide (GO) and reduced graphene oxide (RGO). (a) XRD patterns of GO (red) and RGO (blue). (b) The C<sub>1s</sub> XPS spectra of GO and RGO. (c) Raman spectra of GO (black) and RGO (red).

Table 1 XRD, Raman and XPS results of GO and RGO

XRD	Raman	XPS	Square resistivity
d-spacing (nm)	I <sub>D</sub> /I <sub>G</sub> (%)	O <sub>1s</sub> /C <sub>1s</sub> atomic ratio	

GO	0.696	1.19	0.58	~700MΩ/square
RGO	0.360	1.74	0.18	~50Ω/square

The GO before and after cycling (current density 0.1A/g) was characterized with X-ray diffraction (XRD) and X-ray photoelectron spectra (XPS) as shown in Figure 2. A typical broad peak near 12.70° (d-spacing ~0.70 nm) was observed for the GO before reduction. After the electrochemical cycling, the peak position of RGO appeared at 2θ = 24.58° (d-spacing ~0.36 nm). And as we know, the high resistance of GO is due to the large amount of oxygen-containing groups. Accordingly, removing these groups could effectively recover the electric conductivity of GO. Figure 2b shows the XPS C<sub>1s</sub> spectra of GO and RGO samples. C-C (284.5 eV) for sp<sup>2</sup> carbon in graphite, C-O (286.5 eV) and C(O)O (289.1 eV) were detected in the GO sample. After the electrochemical process, the intensities of oxygen-containing groups are far diminished compared to those GO. Atomic ratios (O<sub>1s</sub> / C<sub>1s</sub>) largely decreased from 0.58 of GO to 0.18 of RGO. This result suggested the electrochemical process in Li-ion batteries could decrease the major of oxygen-containing groups. As a consequence, it would recover the conductivity to some extent. Raman spectrum is a common method to verify the reduction of GO by observing D and G bands. In the Raman spectrum of our GO sample, D-band at 1339 cm<sup>-1</sup> indicates the edge planes and disordered structures and G-band at 1586 cm<sup>-1</sup> corresponds to the first-order scattering of the E<sub>2g</sub> mode observed for sp<sup>2</sup> domains. After the GO was reduced by lithiation/delithiation in Li-ion batteries, the ratio I<sub>D</sub>/I<sub>G</sub> of RGO increased due to the increase in the number of carbon edge-atoms during reduction and the decrease of the size of the in-plane sp<sup>2</sup> domains.<sup>23, 24</sup> All results such as XRD, Raman spectrum and XPS suggested that a major of oxygen functional groups of GO would be removed during the lithiation/delithiation process in Li-ion batteries. Hence, the RGO would exhibit an improved electric conductivity. The GO films (~10μm) after cycles between 0 and 3V versus Li<sup>+</sup>/Li at rate of 0.1 A/g showed sheet resistivity of around 50 Ω/square range which was much lower than the GO films of about 700 MΩ/square range. The electric conductivity of RGO is high enough as conductive fillers for Li-ion batteries.

Figure 3a shows the electrochemical performance of GO electrodes during the lithiation/delithiation process between 0-3 V at a rate of 0.5 A/g. The GO electrode get an initial lithiation capacity of 341 mAh/g, however the delithiation capacity was only about 47 mAh/g. During the second cycle, the coulombic efficiency increased to 48%. Then, the coulombic efficiency gradually increased and finally reached a stable level after 30 cycles. The capacity of GO electrode was stable at around 50 mAh/g. For explaining the extremely low coulombic efficiency at the first cycle, we tested the cyclic voltammetry profiles of GO electrodes in half cells with Li metal as counter electrode at a scan rate of 0.1 mV/s. (Figure 3b) An obvious reduction peak at 0.5 V-2 V was observed in the first cycle, and in the following cycles the peak disappeared. We suggested this disappeared peak was due to the reduction of GO with the following reaction during the electrochemical process:



$\text{Li}^+$  was from the electrolyte and the anodes could inject  $e^-$  during lithiation. This process is similar to the lithiation process of transition metal oxides such as Co, Fe and Ni, but the reaction of GO is irreversible.<sup>23, 25, 26</sup> We used XRD and TEM to characterize the RGO and found the formation of  $\text{LiOH}\cdot\text{H}_2\text{O}$  (Figure S1). The  $\text{LiOH}$  is probably from the following 3 ways. 1. The formation of solid electrolyte interface (SEI) which is consisted of  $\text{LiOH}$ ,  $\text{Li}_2\text{O}$ . 2. The  $\text{Li}^+$  reacts with the hydroxyl of the GO and form  $\text{LiOH}$ . 3.  $\text{Li}_2\text{O}$  is easy hydrolyzing. The  $\text{Li}_2\text{O}$  from the SEI and the reduction of GO was easily hydrolyzed to  $\text{LiOH}$  in the environment after we took the GO electrodes from the cells.

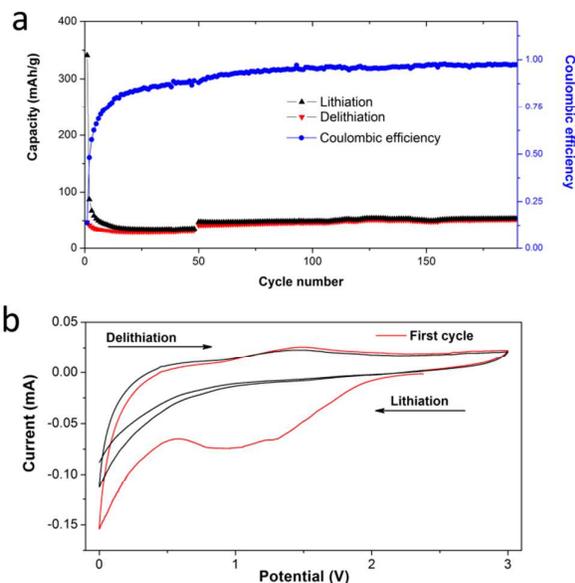
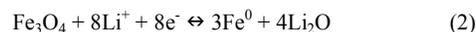


Fig. 3. The electrochemical characteristics of GO electrodes. (a) Electrochemical performance of GO electrode during fully lithiation and delithiation. (b) Cyclic voltammetry profiles of the GO electrodes.

We fabricated GO/  $\text{Fe}_3\text{O}_4$  and GO/ Si composites electrodes to prove that the GO based composites electrodes directly assembled in cells could work well. For the GO/  $\text{Fe}_3\text{O}_4$  electrodes, the  $\text{Fe}_3\text{O}_4$  nanoparticles aqueous solution was prepared with a procedure following Bartosz *et al.*<sup>27</sup> We simply mixed  $\text{Fe}_3\text{O}_4$  and GO aqueous solution together, and dropped the mixed solution onto a copper foil. The copper foil with GO/  $\text{Fe}_3\text{O}_4$  aqueous solution is dried in air and subsequently calcendered. We used thermogravimetric analysis (TGA) to determine the chemical composition of the GO/  $\text{Fe}_3\text{O}_4$  composites. The GO/  $\text{Fe}_3\text{O}_4$  sample was heated in air at a heating rate of 10  $^\circ\text{C}/\text{min}$  to 900  $^\circ\text{C}$ . During the heating process, the GO was firstly reduced to RGO, finally oxidized to  $\text{CO}_2$ , and  $\text{Fe}_3\text{O}_4$  was oxidized to  $\text{Fe}_2\text{O}_3$ . Accordingly to the remaining weight ( $\text{Fe}_2\text{O}_3$ ), the original fraction of  $\text{Fe}_3\text{O}_4$  is calculated to be 67.7% by weight (Figure 4a).

The copper foil with GO/  $\text{Fe}_3\text{O}_4$  sample as the work electrodes was assembled into the cell directly with Li metal (MTI) as counter electrode. We applied a 25  $\mu\text{m}$  thick micron porous polypropylene membranes as the separator (Asashi Kasei). 1 M  $\text{LiPF}_6$  in ethylene carbonate/diethyl carbonate (1:1 vol/vol, Ferro Corporation) was used as the electrolyte. The GO/  $\text{Fe}_3\text{O}_4$  electrode gets an initial

delithiation capacity of 903 mAh/g and maintain the delithiation capacity of 496 mAh/g after 300 cycles (Figure 4b, the mass loading including 32.3% GO and 67.7%  $\text{Fe}_3\text{O}_4$ ). We noticed that the GO/  $\text{Fe}_3\text{O}_4$  electrode show a much higher coulombic efficiency (76.2%) than the pure GO electrodes (2.1%) at the first cycle. We believe the  $\text{Li}_2\text{O}$  which is produced during the reduction of GO is irreversible for the pure GO electrode. However, for the GO/  $\text{Fe}_3\text{O}_4$  electrodes, the  $\text{Li}_2\text{O}$  could be reduced with the following reaction:



Accordingly, for the GO/  $\text{Fe}_3\text{O}_4$  electrodes, part of the  $\text{Li}_2\text{O}$  from the reduction of GO could be decomposed, leading to a higher coulombic efficiency than the pure GO electrodes during the first cycle.<sup>28</sup>

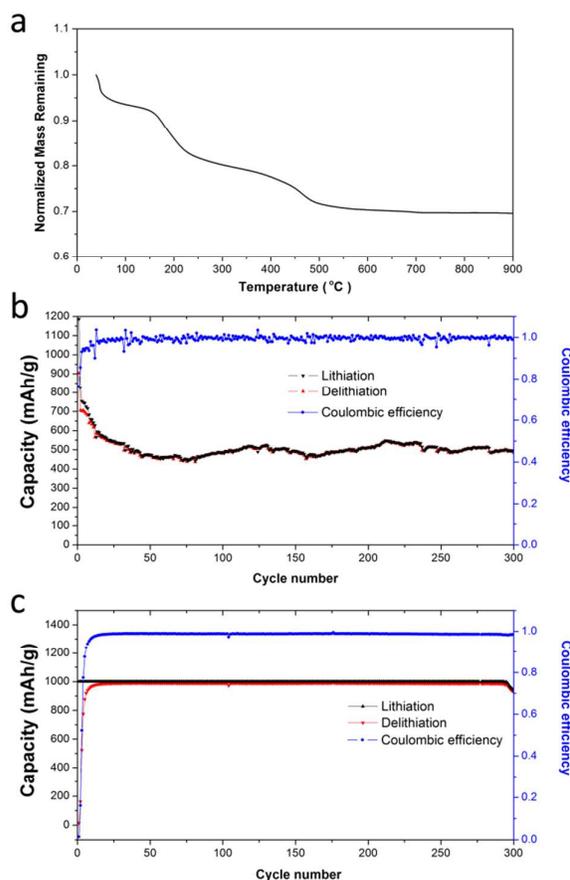


Fig. 4. The characteristics of GO based composites electrodes. (a) Thermogravimetric analysis of GO/  $\text{Fe}_3\text{O}_4$  composites. (b) Electrochemical performance of GO/  $\text{Fe}_3\text{O}_4$  composites electrode during fully lithiation/delithiation between 0-3 V at a rate of 0.1 A/g. (c) Electrochemical performance of GO/ Si composites electrode during lithiation/ delithiation at a constant capacity of 1000 mAh/g between 0-1 V at a rate of 0.5 A/g.

We prepared GO/Si composites electrodes by coating the GO layers upon silicon micron particles on the copper foil. The fabrication process is simple. Silicon particles were dispersed in ethyl alcohol with concentration of 20 mg/ml. We dropped silicon suspensions on the copper foil and dry the copper foil in air. The GO

aqueous solution is dropped upon the silicon particles and dried in air. Then the GO/Si composites electrodes were assembled into the cell directly with Li metal (MTI) as counter electrode. We applied a 25  $\mu\text{m}$  thick micron porous polypropylene membranes as the separator (Asashi Kasei). 1 M LiPF<sub>6</sub> in ethylene carbonate/diethyl carbonate/fluoroethylene carbonate (1:1:0.04 vol/vol/vol, Ferro Corporation) was used as the electrolyte. During the lithiation/delithiation electrochemical test at a constant capacity of 1000 mAh/g, the GO/Si electrodes get an initial delithiation capacity of 14 mAh/g. This irreversible capacity loss is due to the reduction of GO and the formation of SEI. Silicon reacts with Li via a different mechanism from some metal oxides such as Fe<sub>3</sub>O<sub>4</sub>: Li forms alloys with silicon.<sup>29</sup> Accordingly, the Li<sub>2</sub>O from the reduction of GO cannot be decomposed, causing the irreversible loss of capacity. This result is consisted to the low coulombic efficiency of the pure GO electrodes. And after 6 and 14 cycles, the coulombic efficiency increased to more than 90% and 98% respectively. The GO/Si composites electrodes stably cycled 293 times without capacity decay at a constant capacity of 1000 mAh/g. The galvanostatic charge/discharge curves in the 2<sup>nd</sup>, 5<sup>th</sup>, 50<sup>th</sup>, 100<sup>th</sup>, 200<sup>th</sup> confirmed that the capacity was from the lithiation of silicon and the electrochemical performance was stable. (Figure S2) As a consequence, the electrochemical performances of abovementioned GO/ Fe<sub>3</sub>O<sub>4</sub> and GO/ Si composites electrodes proved: (1) using electrochemical method to reduce GO in Li-ion battery is feasible; (2) the composites electrodes fabricated by directly reducing GO in Li-ion battery could work well.

## Conclusions

To conclude, we extended an electrochemical method to reduce graphene oxide by lithiation/delithiation in Li-ion batteries. The RGO exhibited an improved electrical conductivity. This method is simple and green compared to the conventional method. Without extra steps to reduce GO before, in-situ reducing GO in cells could simplify the fabrication process of graphene based composite electrodes for Li-ion batteries by directly assembling GO composites electrodes into cells.

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## Notes and references

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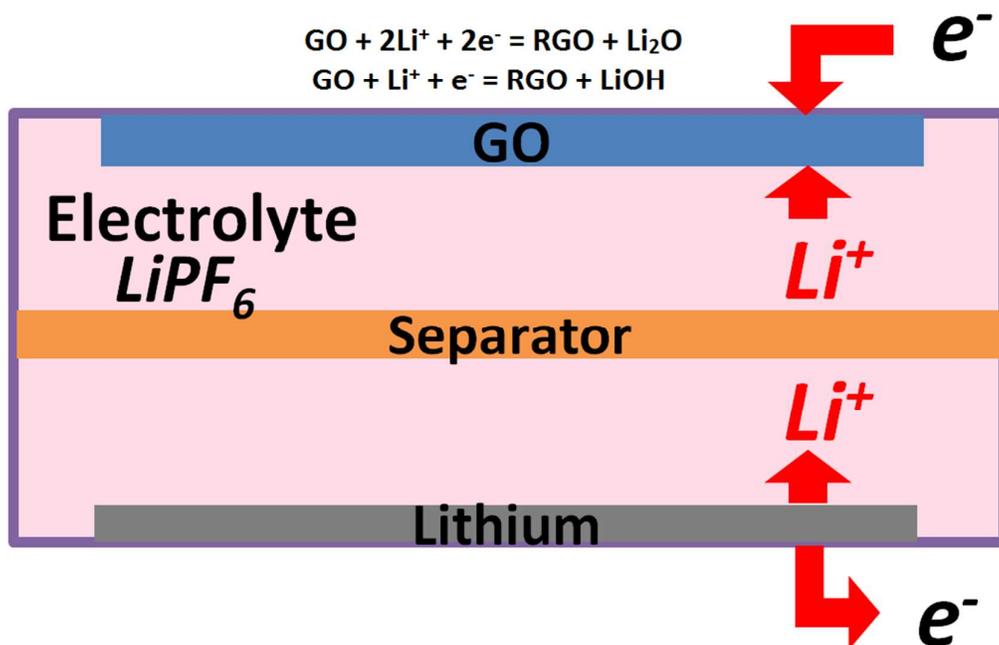
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## Table of contents entry



We report a simple in-situ approach to reduce graphene oxide in Li-ion batteries. This electrochemical method to reduce graphene oxide could be used in graphene-based electrodes fabrications.