



Unique reduced graphene oxide as efficient anode material in Li ion battery

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Abstract. Unique reduced graphene oxide named solar reduced graphene oxide (SRGO) was found to be an excellent anode material in Li ion battery. SRGO exhibited first cycle discharge- and charge-capacities as high as 1480 and 880 mAh g⁻¹, respectively. Moreover, the coulombic efficiency was found to be >95% and the specific capacity retention even after 60 cycles was >500 mAh g⁻¹.

Keywords. Carbon materials; graphene oxide; energy storage; Li ion battery.

1. Introduction

Of late, reduced graphene oxide (RGO) was effectively used as an electrode material in dye-sensitized solar cell [1], supercapacitor [2] and Li ion battery (LIB) [3]. Generally, RGO is synthesized by reducing graphene oxide (GO) [4]. It was observed that the method of reducing GO to RGO has a great effect on the electrochemical behaviour of RGO. It should be noted that different reduction methods [4] render differences in porosity, specific surface area, crystallinity and surface functional groups pertaining to RGO, which then, behave accordingly. Nonetheless, excellent reduction methods were demonstrated to obtain varied RGO samples that performed excellently as anode materials in LIB [3,5–7]. In this work, photothermally reduced GO named solar reduced graphene oxide (SRGO) was explicated as anode material in LIB. It is important to note that this work does not involve any sophistication, such as the use of highly sophisticated lasers [8,9] to obtain RGO. The motivation behind testing SRGO as anode material in LIB is owing to its previously reported characteristics [1–3], like high specific surface area and presence of residual functional groups (owing to partial reduction of GO), layered, structured and mesoporosity, which might result in enhanced adsorption of Li ions at the anode, intercalation of Li ions in between the stacked graphene layers and improved activity at the anode/electrolyte interface, respectively. Really, as expected, SRGO was found to be an excellent anode material in LIB.

2. Cell fabrication and testing

Synthesis and all the relevant characteristics were already reported [2]. However, for convenience, this part was rewritten and presented in 'supplementary information'. Coin cell fabrication and testing were carried out by following the standard practices [10]. SRGO (70 wt%), Super P carbon (15 wt%) and Kynar 2801 (15 wt%) binder were mixed in N-methylpyrrolidinone and stirred for 10 h to obtain the anode slurry, which was then coated (using Doctor Blade technique) to a thickness of ~25 μm onto 10 μm thick etched-Cu foil. Then, the anode material-coated Cu foil was dried for 12 h at 80°C and was cut into circular discs of diameter 16 mm each, such that each anode had an active area of 2 cm² and ~4 mg of active anode material. All components of LIB (coin cells, size 2016) were dried before assembling in Ar-filled glove box. In each of the coin cell, Li (Hosen Metal Co., Japan), glass micro-fibre filter (GF/F, Whatman Int. Ltd., Maidstone, England) and 1 M LiPF₆ in ethylene carbonate and dimethyl carbonate (1:1 by volume, Merck Selectipur LP40) were used as counter electrode, separator and electrolyte, respectively. Room temperature cyclic voltammetry (CV) of the coin cells was performed in the voltage range of 0.005–3.0 V and at a scan rate of 58 μVs⁻¹ using MacPile II (Biologic, France) instrument. Room temperature Galvanostatic cycling (GC) of the coin cells was performed at a current density of 100 mA g⁻¹ using Bitrode battery tester (model SCN, Bitrode, USA). Room temperature electrochemical impedance

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spectroscopic (EIS) measurements were carried out (using impedance analyzer from Solartron Instruments, UK) in the voltage range of 0–3.0 V and at a scan rate of 0.01 mV s^{-1} . EIS measurements were performed on a fresh cell, after 70 charge–discharge cycles at 0.005 V and then, on the same cell at different voltages.

3. Results and discussion

Figure 1 shows the discharge–charge behaviour of SRGO. First cycle-specific capacities of SRGO are 1480 (discharge) and 880 (charge) mAh g^{-1} , respectively, which are far greater than 372 mAh g^{-1} , the theoretical capacity of graphite, and the commercial anode material in LIB. Cycling performance of SRGO is shown in figure 2, which clearly indicates that the first cycle columbic efficiencies are comparatively low ($\sim 60.6\%$). However, from the 2nd cycle onwards, the reversible capacity was found to be above 97%. The specific capacity retention even after 60 cycles was $>500 \text{ mAh g}^{-1}$, which is a good value. CV characteristics of SRGO are shown in figure 3. The nature of discharge–charge

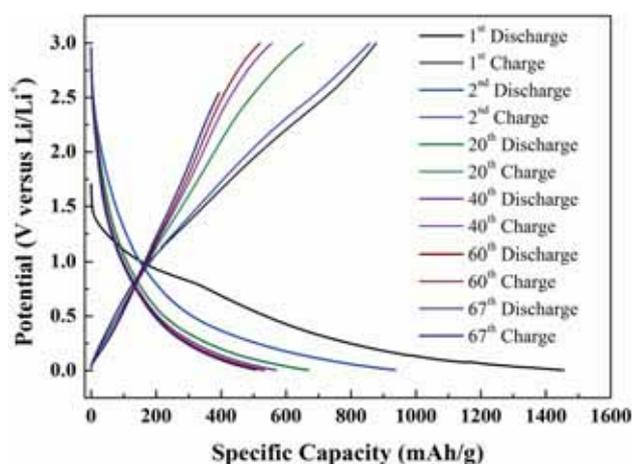


Figure 1. Discharge–charge profiles of SRGO anode.

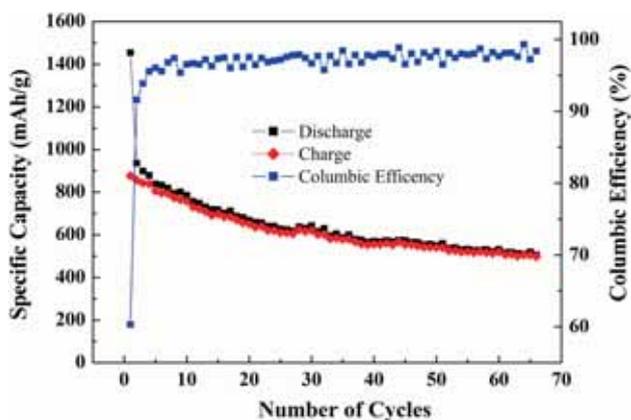


Figure 2. Performance of SRGO anode with cycling.

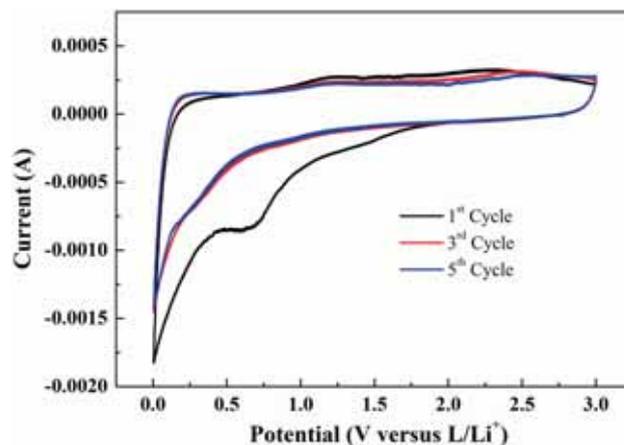


Figure 3. CV curves of SRGO.

behaviour correlates well with the shape of CV curves (figure 3) and previously reported results [3].

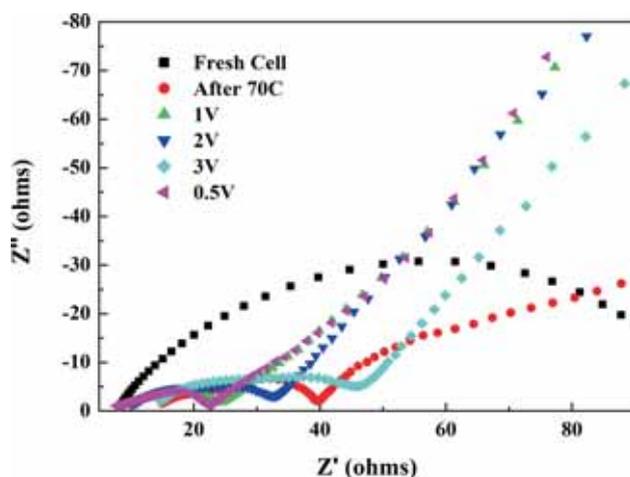
From figure 3, it can be clearly observed that the first lithiation resulted in two cathodic peaks, one in the range of 0.5–0.9 V due to the formation of solid electrolyte interphase (SEI) at anode's surface [3], and the other one below 0.2 V corresponding to Li^+ ions' insertion into SRGO. However, the first current peak was absent from the 2nd cycle onwards. From figure 3, it can also be clearly observed that the first delithiation resulted in large voltage hysteresis. It is now known that as layered materials (such as graphene) discharge, Li reacts with suitable materials' defects at low potential and as they charge, bonds between Li and the defects are broken at high potential. As a consequence, large voltage hysteresis ensues (as shown in figure 3) in the case of layered materials such as SRGO. However, as cycling progresses, the current peaks stabilize, indicating good reversibility and thereby lower voltage hysteresis is observed (as in 3rd and 5th cycles, figure 3).

Table 1 shows comparative results. In the case of few-layered graphene (FLG) [3] (one type of RGO), the specific capacity due to the Li^+ ion intercalation mechanism is less. In the case of SRGO, there is an open-pore structure, which enables Li^+ ion intercalation into the sheets, facilitates efficient intercalate kinetics and displays high-cyclic stability. In both SRGO and FLG cases, the measured specific capacity (at voltages $>0.5 \text{ V}$) is due to the combination of SEI formation and solvent's reduction in the electrolyte [3]. The observed secondary Li storage mechanism in SRGO is attributed to the presence of defects and adsorption of Li^+ ions on both sides of the graphene layers in each SRGO particle.

Figure 4 shows EIS spectra recorded during first lithiation of SRGO. At open circuit voltage (fresh cell), Nyquist plot depicted a semicircle in the high-frequency (HF) region and an inclined line in the low-frequency (LF) region. Such an observation is attributed to the non-lithiated electrode's blocking character and initial contact problems [11,12]. At 0.005 V, after 70 cycles in discharged state, Nyquist plot

Table 1. Anodic behaviour of different RGO samples.

Refs.	1 st discharge and charge capacities (mAh g ⁻¹)	Reversible capacitance (mAh g ⁻¹)	Coulombic efficiency (%)	Pros	Cons
[3]	400 and 250 (at 40 mA g ⁻¹)	376 (60 cycles)	>95	High coulombic efficiency	Multi-step synthesis; low capacity values
[5]	1233 and 672 (at 0.2 mA cm ⁻²)	502 (30 cycles)	54.5	High 1st discharge–charge capacities; good reversible capacitance	Multi-step synthesis; low coulombic efficiency
[6]	1481.5 and 601 (at 100 mA g ⁻¹)	—	85 (80 cycles)	Same as above	Multi-step synthesis
[7]	1079 (discharge capacity) (at 40 mA g ⁻¹)	1002 (50 cycles)	93	Better discharge performance; excellent capacity retention; good performance at high current rates	Multi-step synthesis
[8]	370 (discharge capacity) (at 1.86 mA g ⁻¹)	—	>96 (1000 cycles)	High coulombic efficiency; good performance at high current rates	Sophisticated synthesis; low capacity values
[Present study]	1480 and 880 (at 100 mA g ⁻¹)	505 (65 cycles)	>95	Green reduction; high 1st discharge–charge capacities; good reversible capacitance; high coulombic efficiency	Difficult to reduce uniformly

**Figure 4.** Electrochemical impedance of SRGO at different voltages.

depicted three parts, namely a semicircle (HF region), another semicircle (medium-frequency (MF) region) and a steep-sloped line (LF region) attributed to Li-ion movement through the SEI, the charge transfer step and Li-ion diffusion in the bulk active mass, respectively [13–15]. Nyquist plots in the range of 0.005–3 V are also shown in figure 4, which clearly indicates that the evolution of SEI (caused by electrolyte

decomposition due to chemical reduction) does not occur on the anode's surface at potentials >1.0 V in agreement with CV observations. At lower potentials, the inclined straight line (LF region) appears closer to the x -axis, while the plot depicts a semicircle in the MF region.

4. Conclusions

SRGO performed excellently as anode material in LIB by exhibiting first cycle discharge- and charge-capacities of 1480 and 880 mAh g⁻¹, respectively, at a high current density of 100 mA g⁻¹. SRGO exhibited coulombic efficiency >95% and specific capacity of more than ~500 mAh g⁻¹ even after 60 cycles. Both intercalation and adsorption of Li⁺ ions at anode are found to be responsible for excellent Li storage by SRGO.

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