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A novel ionic host solid electrolyte interface formation on reduced graphene oxide of lithium ion battery

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ABSTRACT

Challenges to developing lithium-ion batteries include achieving high-energy density, low irreversibility, and lithium-ion transportation at electrode material interfaces. Numerous studies have used ameliorative electrode surfaces, composite materials, or modified electrolytes to improve battery performance. This study creates an ionic host solid-electrolyte interface (SEI) material using electrochemical self-polymerization. This ionic host SEI is fabricated with carbon oxide-containing functional groups —C—O— and —O—C(O)— on a reduced graphene oxide (rGO) anode surface to improve the performance of lithium-ion battery, including reversible capacity and *c*-rate ability. The results show that the ionic host SEIs on rGO material provides additional 84% of energy density increment. Compared to the graphite material, the energy density can only be increased 3.7% because of the lack of functional groups on the graphite surface. By using this technique to fabricate functional groups on electrode surfaces and prepare suitable electrolyte additives, lithium-ion batteries perform better and exceed previous manufacturing processes.

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1. Introduction

With electrical equipment demands, the high energy and power density performance of lithium ion batteries are important. However, the poor electric conductivity of the electrode materials and the slow ionic transportation of the interface between electrode and electrolyte prevent lithium-ion battery improvements. Since Geim and Novoselov won the Nobel Prize in 2010, graphene has attracted considerable scientific attention for various energy-related applications because of its incredible physicochemical properties, including superior specific capacity, high surface behavior, chemical tolerance, and a wide electrochemical window [1–3]. However, using graphene has numerous disadvantages, which are caused by incremental interface interaction and expansion of the interlayer space because of unique active sites on the edges and surface defects [4]. Amelioration of electrode materials, such as surface modifications [5,6] and composite methods [7–9], has been used to overcome these disadvantages. For example, Wang et al. used nitrogen-doped graphene nanosheets (GNSs) as a lithium-storage material that exhibited 900 mAh g^{-1} (1/20 C) reversible capacity and 250 mAh g^{-1} (2.5 C) rate capability to enhance the performance of pristine graphene [3]. Galinski and Acznik used pyrrolidinium-based ionic liquid to replace the conventional electrolyte on graphene material, achieving good cycle stability because of irregular solid electrolyte interface (SEI) formation [10]. Pan et al. studied the effect of reduction process on electrochemical behavior of reduced graphene oxide (rGO) nanosheets. They pointed out that the enhanced capacity was not fully determined by the *d*-spacing of graphene-based materials, nor affected by structure integrity. The surface structure defects could result in a SEI formation and the extra Li ion trapping, while the inner and edge structure defects could lead to reversible capacity [11].

This study proposes an anode material with core–shell infrastructure, which consists of rGO and a specific ionic host material. This ionic host material is a type of artificial SEI fabricated by using electrolyte additives and the functional groups on the rGO surface. Previously, Devi et al. has stated that water can be used as a polyurea catalyst to trigger polymerized reactions [12]. Last year, we published that maleimide (MI) and water (H_2O) were used as a binary additive to increase battery performance at high temperatures by using novel 3D SEI formation on graphite anode material [13]. However, the MCMB can only provide nearly 330 mAh g^{-1} of energy density. In order to reinforce the rate-ability and energy density of the battery, the rGO has been choice to the next candidate of anode material in lithium ion battery.

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Table 1
The functional group desorption amounts and the first discharge capacities of Li/GNS-300 and Li/MCMB half cell.

Properties	GNS-300		MCMB	
(—C—O—) desorption (mmol g^{-1})	7.68		0.06	
(—O—C=O) desorption (mmol g^{-1})	2.61		0.01	
Classification	1st discharge capacity (mAh g^{-1})	Augmented ratio (%)	1st discharge capacity (mAh g^{-1})	Augmented ratio (%)
E	618	–	374	–
E/MI	722	16.8	380	1.6
E/MI/100 ppm H_2O	1138	84.1	388	3.7

In this study, the rGO has synthesized with functional groups on its surface, which is anticipated to react with the MI-based chemicals and H_2O as the electrolyte additives. This technique produces an electrochemically self-polymerized ionic host material on the rGO surface which provides high reversible capacity and excellent rate capabilities. This research also examines the qualities and quantities of functional groups on the rGO anode surfaces on active sites and identifies the characteristics of the novel ionic host SEI.

2. Experiment

In this study, GNSs were synthesized using a modified Hummer method [14]. This method required placing 8 g graphite powder (SFG44 flake graphite, TIMCAL®) and 4 g $NaNO_3$ into 560 mL concentrated H_2SO_4 solution and stirring for 2 h. Thirty-two grams $KMnO_4$ was then slowly added to the flask in an ice bath for 2 h. The mixture was then diluted using 800 mL de-ionized (DI) water. Approximately 5% H_2O_2 was added to the solution until the color of the mixture changed to brown, indicating fully oxidized graphite. The as-prepared graphene oxide slurry was re-dispersed into DI water. The mixture was then washed using 0.1 M HCl solution to remove SO_4^{2-} ions. The graphene oxide (GO) solution was washed with DI water to remove the residual acid until the pH was neutral. After drying in an oven at 80 °C overnight, a brown GO powder was obtained. The GO powder was placed in a furnace at 300 °C for 2 h in a reducing atmosphere of 15% H_2 and 85% N_2 for thermal exfoliation. The GO has become rGO material (GNS-300) and all of the characteristics have been identified by Liu's previously works [15,16].

GNS-300 was used for electrochemical tests. The composite electrode consisted of 89 wt% GNS-300, 1 wt% Super-P (40 nm, TIMCAL®) as a conductive additive, and 10 wt% styrene-butadiene rubber (SBR) and sodium carboxymethyl cellulose (CMC) binders. The electrolyte is a commercial product that contains 1 M lithium hexafluorophoshate ($LiPF_6$) in an ethylene carbonate (EC), propylene carbonate (PC), and diethyl carbonate (DEC) mixture (3:2:5 by volume ratio, electrochemical grade and from Ferro) with 2 wt% vinylene carbonate (VC). Above electrolyte was confirmed less than 20 ppm water by Karl Fischer moisture titrator. N′N-1, 4-phenylenedimaleimide [0.1 wt% (MI)] and additional H_2O (100 ppm) were completely dissolved in the electrolyte at room temperature. The following abbreviations are used: electrolyte (E), electrolyte with additional water (E/100 ppm H_2O), electrolyte with MI (E/MI) additive, and electrolyte with MI and H_2O (E/MI/100 ppm H_2O) additives. All of the electrolytes are prepared in the dry room (dew point <−50 °C; relative humidity <6%) to guarantee that there is no other moisture was absorbed. The electrochemical characteristics of the electrolytes were measured by incremental capacity analysis using a Biologic VMP3 from 3 to 0.1 V at a scan rate of 0.1 mV s^{-1} with a two-electrode anode half coin cell 2032, consisting of a GNS-300 working electrode and a lithium foil counter electrode.

The morphology and the surface composition of the GNS-300 electrodes were observed by scanning electron microscopy (SEM) after a Pt coating had been sputtered and at an accelerating voltage of 5 and 15 kV using an energy dispersive spectrometer (EDS) on a LEO-1530 microscope. Furthermore, the Pt coater is also in the dry box. Before any observations were made, the specimens were disassembled and washed with dimethyl carbonate (DMC) in dry room, and dried in a vacuum for overnight. The samples put into a special built high vacuum stainless steel holder for transfer of anode electrodes from dry room to the SEM instruments. The SEI will not be influenced by the treatment of the graphite before cell assembly and drying for the prepared program. Transmission electron microscopy (TEM) analysis was conducted with a field-emission transmission electron microscope (JEOL JEM-2100F). Temperature programmed desorption-gas chromatography (TPD-GC) with He as a carrier gas was used to define the surface functionalities of anode materials. Electrochemical performance tests were conducted using constant current constant voltage (CC–CV) mode in a voltage range of 0.005–3.5 V at 0.1 C/0.1 C on a Maccor battery tester series 4000. The standard drain rates of batteries were charged (lithium-ion intercalation) and discharged (lithium-ion de-intercalation) at 0.1, 0.5, 1, 1.5, and 2 C between 0.005 and 3.5 V.

Electrochemical impedance spectroscopy (EIS) was performed using a Biologic VMP3 in the frequency range 100 M to 0.01 Hz with an AC amplitude of 5 mV at 25 °C. All EIS measurements employed a half cell (CR2032) consisting of carbon anode electrodes and lithium metal (area 1.0 cm^2) under 100% state of discharge (SOD).

3. Results and discussion

Table 1 shows the correlation between functional groups and battery capacity from temperature programmed desorption-gas chromatography (TPD-GC) analysis. It shows a reaction difference between rGO (GNS-300) and graphite (mesocarbon microbeads; MCMB). This result reflects the existence of several types of carbon oxide containing functional groups, including —C—O— desorption from hydroxyl —C—OH—, epoxide —C—O—C—, phenol, carbonyl —C—O—O—H—, ether, and —O—C(O)— desorption corresponds to carboxylic and lactone [17,18]. The amount of —C—O— (7.68 mmol g^{-1}) and —O—C(O)— (2.61 mmol g^{-1}) desorption contained in GNS-300 is higher than that of MCMB. This implies that the sensitive combination reaction of functional groups and electrolyte additives increases battery capacity. Previously works introduced a restriction of Li_2O results in thinner SEI formation on the MCMB surface with MI additives and provided 4.9% capacity increment and 16.7% capacity retention better than the electrolyte without any additives [19,20]. In addition, a binary electrolyte additive (MI/H_2O) has been discovered its mutual combination reaction to form a particular SEI on the MCMB surface. This particular SEI enhances the battery capacity and cycle performance at high temperature (55 °C) testing. In this study, Table 1 shows that the MI and H_2O are synthesized with an abundance of —C—O— and —O—C(O)— functional groups on the rGO surface by electrochemical reaction. This synthesis of the lithium ionic host SEI layer results in additional 84%

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