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Low surface area graphene/cellulose composite as a host matrix for lithium sulphur batteries

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HIGHLIGHTS

- Low surface area graphene/cellulose composite as a host matrix for Li-S batteries.
- Graphene serves as electron conductive additive and cellulose as a spacer.
- Cellulose–graphene ratio 1:1 showed the best electrochemical performance.
- Composite enables accommodation of expansion due to formation of Li_2S.

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ABSTRACT

Graphene/cellulose composites were prepared and studied as potential host matrixes for sulphur impregnation and use in Li-S batteries. We demonstrate that with the proper design of a relatively low surface area graphene/cellulose composite, a high electrochemical performance along with good cyclability can be achieved. Graphene cellulose composites are built from two constituents: a two-dimensional electronic conductive graphene and cellulose fibres as a structural frame; together they form a laminar type of pore. The graphene sheets that uniformly anchor sulphur molecules provide confinement ability for polysulphides, sufficient space to accommodate sulphur volumetric expansion, a large contact area with the sulphur and a short transport pathway for both electrons and lithium ions. Nano-cellulose prevents the opening of graphene sheets due to the volume expansion caused by dissolved polysulphides during battery operation. This, in turn, prevents the diffusion of lithium polysulphides into the electrolyte, enabling a long cycle life.

1. Introduction

Recently, there has been a steady increase in demand for clean, efficient and safe energy due to the increasing diversity of energy applications. One of the important solutions found to meet the energy demand was lithium ion battery system. Due to their high energy density, rechargeable lithium ion batteries have become the dominant power source for portable electronics. Their energy density is limited by cell chemistry, and they do not completely meet the requirements on the field of electromobility [1].

Lithium sulphur (Li-S) batteries are one of the most promising energy conversion alternatives that can meet the demands for the suitable driving range of battery electric vehicles (BEVs). A Li-S battery system has a theoretical capacity of 1675 mAh g^{-1} and an energy density of 2500 Wh kg^{-1}. The abundance of sulphur in nature makes it a cheap raw material, which also reduces the cost of Li-S battery systems [2–5]. However, there are several problems or challenges that have to be solved or addressed in order to reach the expected goal of obtaining a high performance, safe, long life, eco-friendly and inexpensive Li-S battery. As the Li-S system is plagued by the problems of the low electrical conductivity of sulphur, the dissolution and diffusion of polysulphides into the electrolyte, and the volume expansion of sulphur intermediates during battery operation. These problems result in poor life cycle, low specific capacity, and low energy efficiency [6,7]. Recently, a great deal of effort has been made to find a suitable host matrix for sulphur impregnation, which would enhance electrochemical reaction and render polysulphide diffusion [8,9]. Different types of carbon/

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sulphur composites utilizing active carbon, carbon nanotubes [10,11], carbon fibres [12,13], mesoporous/porous carbon [14–18], graphene and modified graphene [19–28] have been proposed. These types of composites have helped to overcome the problems, which focus on enhancing the electrical conductivity of the cathode and suppressing the diffusion of soluble polysulphide intermediates during cycling. Nevertheless, it remains a challenging task to retain a high and stable capacity of sulphur cathodes for more than 100 cycles.

Graphene has been considered as one of the most important conductive carbon matrixes for Li-S batteries. It has many advantages such as very high electrical conductivity, large surface area, and tuneable surface properties, which are beneficial for energy storage devices [3]. It is a two-dimensional electronic conductor exhibiting high chemical stability, excellent mechanical strength and flexibility [19–28]. Graphene oxide (GO), prepared by several different oxidation processes, is probably the most promising way of the synthesis of graphene [29]. A number of studies have been conducted on combination of graphene and sulphur to fabricate Li-S batteries' cathodes and it was found that the batteries' performances are improved. For example, when GO was used as matrix to immobilize sulphur, uniform and thin coating of sulphur on GO sheets has been successfully obtained [20]. Developed Li-S cells using this GO-S composite demonstrate reversible capacity of 850–1400 mA h g^{-1}. In another approach using reduced GO, Zhou et al. [30] used hydrothermally reduced graphene oxide and Wang et al. used thermally expanded graphite oxide to combine with sulphur in cathodes [31]. It is revealed that the oxygen-containing groups on GO have strong binding with polysulphides through S–O bonding, which prevent them from dissolution into the electrolyte [30]. As the result, the GO-S composite cathodes show good specific capacity and stable cyclability over 100 cycles.

Nanofibrillated cellulose (NFC) consists of nano-sized cellulose fibrils that entangle into three-dimensional network with high aspect ratio [32]. The term nanofibrillated cellulose is often named as nanocellulose for simplicity. NFC is known as the biodegradable polymer which is non-toxic to human and environment friendly. We have reported that the combination of amine-functionalized NFC and chemically reduced GO (RGO) resulted in graphene nanocomposite paper with high mechanical properties and excellent electrical conductivity [33]. In this study, we combined the nanocellulose and RGO in a well-controlled manner to make porous and conductive NFC/RGO composite for sulphur deposition. The obtained NFC/RGO/S composite material was used to fabricate positive electrode for Li-S battery. The nanocellulose network acts as a structural frame [34] for the graphene-sulphur composite and prevents the opening of graphene sheets due to volume expansion caused by formation of Li_2S during sulphur reduction.

In this work, we report on the electrochemical behaviour of three different mixtures of graphene/cellulose as a host matrix in Li-S batteries. We demonstrate the effect of the ratio of graphene/cellulose, the role of electrode morphology, and we give possible explanations regarding the capacity fading observed in this system.

2. Experimental part

2.1. Materials

Graphite flake (particle size <200 μm), sulphuric acid (95–98%), hydrochloric acid (36 wt.%), potassium permanganate (99+%), sodium nitrate (99.5%), and hydrazine hydrate were purchased from Sigma–Aldrich Co.; ammonia solution (28%) was obtained from VWR Co., and hydrogen peroxide (30%) was obtained from Merck. Nanofibrillated cellulose (NFC) was received from the UPM Corporation (Finland). The material was produced by mechanical disintegration of bleached birch pulp, which was pre-treated with a Voith refiner prior to fibrillation with an M7115 fluidizer from Microfluidics Corp (Newton, MA, USA) [35]. The suspension has a solid content of 1.37 wt.%. The NFC fibrils in the suspensions are mostly 20–30 nm in diameter and several micrometres in length. The NFC was amine-functionalized according to the previous report [32].

2.2. Method

2.2.1. Preparation of graphene oxide

Graphite was oxidized to produce graphite oxide according to a modified Hummers' method [36]. Natural graphite (10 g) was added in a flask containing 250 mL concentrated sulphuric acid. The flask was immersed in an ice bath. An amount of 5 g sodium nitrate was supplied to the mixture while stirring with a magnetic bar. Subsequently, 30 g of potassium permanganate was slowly added to the flask, and the temperature of the reaction was kept below 20 °C. After being mixed for an hour, the mixture was heated to 35 °C and kept at this condition for 1.5 h. The mixture was then cooled down to room temperature and left over night. Then, 200 mL of deionized (DI) water was added slowly in 0.5 h. Next, 50 mL of hydrogen peroxide was injected to the mixture for 0.5 h. In the next step, 500 mL of DI water was poured into the flask. The mixture was washed with 1.5 L of 5 wt% HCl solution. The mixture was then washed with DI water and dried. The obtained graphite oxide (GO) in this stage was exfoliated in DI water by ultrasonic equipment (solid content 1 g of GO in 400 mL). The sonicated mixture was centrifuged at 4000 rpm for 20 min to remove the precipitate, and the dispersion was graphene oxide. Solid content of exfoliated GO sheets in the dispersion was measured to be around 2 mg mL^{-1}.

2.2.2. Preparation of NFC/RGO composite powder

NFC suspension was added to the GO dispersion while stirring with a magnetic bar. The solid content of GO/NFC was controlled to be 30/70, 50/50, and 70/30 wt/wt. The pH of the mixture was adjusted to around 10 with the ammonia solution. Hydrazine was added to the mixture as the reducing agent for GO to produce reduced graphene oxide (RGO). The amount of hydrazine was 100 μL per 100 mg of solid GO. The mixture was then heated to 95 °C and kept at this condition for 2 h for reaction completion. The mixture was cooled down to room temperature and solidified in liquid nitrogen, after which it was freeze-dried for 72 h to eliminate water, ammonia and excess hydrazine. Samples are denoted in the text as GC37 for 30/70 mixture, GC55 for 50/50 mixture and GC73 for 70/30 mixture.

2.2.3. Preparation of graphene/cellulose-sulphur (GCS) composite

A graphene/cellulose carbon matrix with three different ratios of graphene and cellulose (30:70, 50:50, 70:30) was dispersed in dichloromethane by an ultra-speed rotor for 5 min; next, sulphur dissolved in dichloromethane was added to dispersed graphene/cellulose carbon matrix and sonicated for 5 min, before removing the solvent by using rotor vapour at 40 °C. The obtained mixture was dried at 50 °C overnight and then heated at 155 °C for 6 h in an argon atmosphere to encapsulate sulphur in the graphene/cellulose composite. The content of sulphur was checked via elemental analysis (CHNS) to estimate the amount of sulphur in the composite. All the samples showed 50 wt.% sulphur in the composite. A sample with 30:70 graphene:cellulose was termed GCS37; a sample with 50:50 graphene:cellulose was termed GCS55, and a sample with 70:30 graphene:cellulose was termed GCS73.

Nitrogen adsorption–desorption isotherms were measured at −196 °C using a Tristar 3000 (Micromeritics, Norcross, GA, USA). Before the measurement, the template-free sample was outgassed for 12 h at 105 °C and for 1 h at 150 °C in the degas port of the