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The correlation between carbon structures and electrochemical properties of sulfur/carbon composites for Li-S batteries

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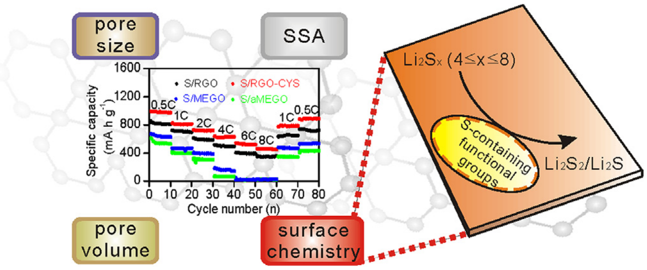
HIGHLIGHTS

- S/RGO-CYS cathode exhibits high rate capability and low capacity decay rate.
- How the carbon structure affects the sulfur/carbon cathode property is elucidated.
- Sulfur-containing groups' role in immobilizing lithium polysulfides is elucidated.
- Surface chemistry of the carbon host is more important for excellent Li-S battery.

GRAPHICAL ABSTRACT



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ABSTRACT

The structures of carbon materials greatly affect the electrochemical properties of sulfur/carbon composites for lithium-sulfur (Li-S) batteries. Understanding the effect of carbon structure factors on the electrochemical properties of sulfur/carbon composites helps in rational designing of the cathode material for optimized battery performance. We prepare reduced graphene oxide (RGO), cysteine-modified RGO (RGO-CYS), microwave-expanded graphite oxide (MEGO) and activated-MEGO (aMEGO) with specific surface areas (SSA) of 58–3010 $m^2 g^{-1}$, C/O atomic ratios of 2.41–10.81, pore sizes of 0.9–5.6 nm and pore volumes of 0.14–2.03 $cm^3 g^{-1}$. The electrochemical performance researches S/RGO-CYS > S/RGO > S/MEGO > S/aMEGO when it is listed in the order of their specific capacity, rate capability and cyclic life. And the S/RGO-CYS delivers a high reversible capacity of 455 mA h g^{-1} at 8 C. The excellent performance of S/RGO-CYS composite is ascribed to the sulfur-containing functional groups of the RGO-CYS, which helps the sulfur dispersion and stabilizes the dissoluble lithium polysulfides. Our results demonstrate that the surface chemistry of carbon materials plays a more important role than the SSA, pore size and pore volume for the electrochemical properties of sulfur/carbon composites for Li-S batteries.

1. Introduction

Lithium-sulfur (Li-S) batteries offer a high theoretical energy density of 2567 W h kg^{-1} by the multi-electron-transfer cathode reaction between elemental sulfur and lithium ions, and are a focus

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of post lithium-ion batteries technology [1–6]. Yet, there are challenging obstacles standing in the way of the large-scale application of the Li-S technology in the market, which include the potential safety risky of Li-dendrite formation, the low cyclic life as a result of the dissolution of the lithium polysulfides (Li_2S_x, $4 \le x \le 8$) in the electrolyte and the volume change (~80%) of the sulfur during lithiation/delithiation, and the poor rate capability due to the low electrical conductivity of sulfur (5×10^{-30} S cm^{-1} at 25 °C) [7–9].

Carbon materials are commonly used as the host to accommodate sulfur to address these issues relevant to the sulfur-cathode owning to their diversity, conductivity, robust stability and chemistry, and their ready abundance and cost [10–12]. The carbon structure features including the porosity, specific surface area (SSA) and surface chemistry are the keys to optimized sulfur/carbon cathode [10,13,14]. Pioneering studies have focused on tailoring the carbon pore structure to obtain pores with diameter in the range of one half to hundreds of nanometers which contain elemental sulfur at the charged state and restrain the dissolution of lithium polysulfides formed during discharge process [15–25]. A larger SSA of the carbon host that is usually accompanied with a higher porosity provides more sitting sites for sulfur, thus reduces the particle size of sulfur and increases the interface area between the electrolyte and sulfur, hence the charge/discharge reaction of the battery favors [26,27]. Carbon has a weak interaction with dissolvable lithium polysulfides, which is unsatisfactory to limit the shuttle effect and self-discharge when operating a Li-S battery. Therefore, decorating the carbon surface with functional groups or inorganic nanoparticles has been becoming an active direction in recent research to stabilize the sulfur cathode [28–31].

The electrochemical performance of the sulfur/carbon composite depends on a complex synergy between the above structural factors of carbon, yet should be more closely related to the major ones. Understanding the effect of carbon structure on the electrochemical properties of sulfur/carbon composites is of great importance to guide future rational design of the sulfur/carbon composite for optimized cathode of Li-S batteries. However, it is a challenging task due to the complexity and diversity of the carbon structures. Graphene, a sp^2-hybridized carbon, has a tunable SSA of tens to thousands square meters per gram, and is ready for functional groups decoration and micropores creation. Therefore, it is a promising model material for studying the relevant of the carbon structure to the electrochemical performance of the sulfur/carbon composite as a cathode of Li-S batteries.

Here, we prepared four types of graphene-based carbon materials. The reduced graphene oxide (RGO) has a relatively low SSA of 58 m^2 g^{-1}, a high concentration of oxygen-containing functional groups (C/O atomic ratio of 2.41) with an average pore diameter of 2.9 nm and pore volume of 0.14 cm^3 g^{-1}. The microwave-expanded graphite oxide (MEGO) has a moderate SSA of 440 m^2 g^{-1} yet an increased C/O atomic ratio of 3.57, an average pore size of 5.6 nm and pore volume of 1.43 cm^3 g^{-1}. The activated-MEGO (aMEGO) possesses a high SSA of 3010 m^2 g^{-1}, a low concentration of functional groups of C/O atomic ratio of 10.81, the lowest average pore diameter of 0.9 nm and the highest pore volume of 2.03 cm^3 g^{-1}. We further decorated the RGO with cysteine (RGO-CYS) to obtain sulfur-containing groups with a SSA (60 m^2 g^{-1}), C/O atomic ratio (2.50) and pore structure (average diameter of 2.8 nm and volume of 0.21 cm^3 g^{-1}) similar to those of the RGO. The electrochemical test of the sulfur/carbon composites with a sulfur content of 70 wt% researched S/RGO-CYS > S/RGO > S/MEGO > S/aMEGO when listed in order of their specific capacity, rate capability and cyclic life. The excellent electrochemical performance of the S/RGO-CYS comparing to the other sulfur/carbon composites in this study is ascribable to the sulfur-containing species of the S/RGO-CYS that is able to help the distribution of sulfur and to stabilize the dissoluble lithium polysulfides, and suggests that the surface chemistry of graphene-based carbon materials plays a more important role than the SSA, pore diameter, and pore volume for the sulfur/carbon cathode.

2. Experimental section

2.1. Synthesis of RGO, RGO-CYS, MEGO and aMEGO

The GO was made from the modified Hummers method [32]. The RGO was synthesized by heating GO under Ar flow at 155 °C

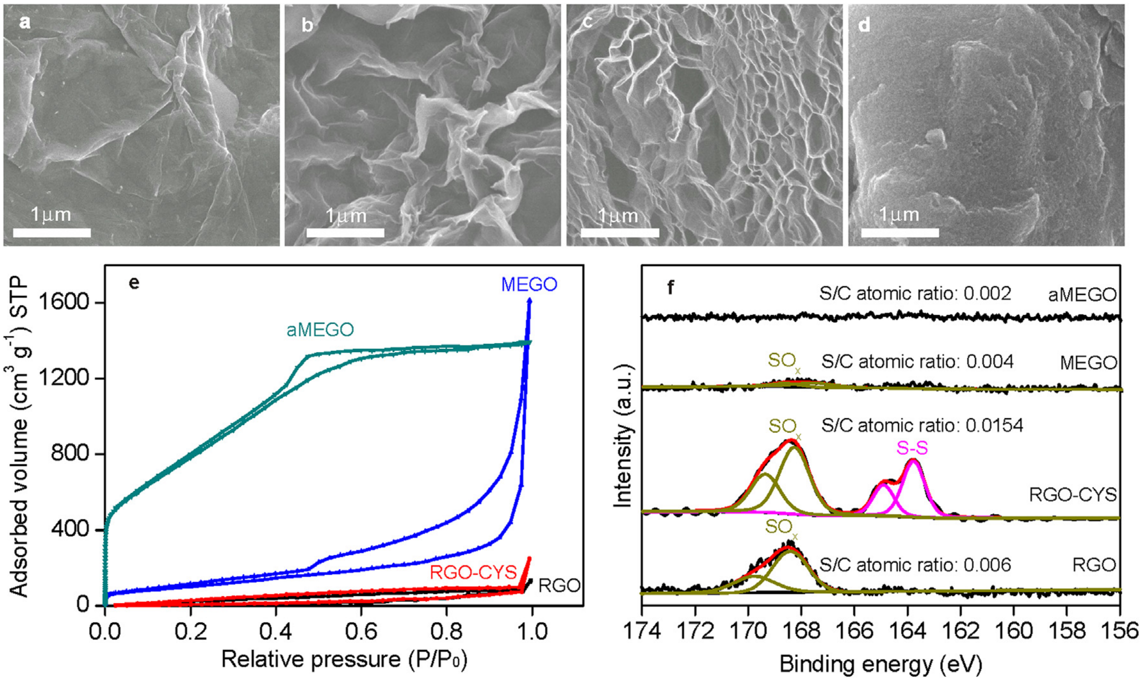

Fig. 1. SEM images of (a) RGO, (b) RGO-CYS, (c) MEGO and (d) aMEGO. (e) N_2 adsorption/desorption isotherms and (f) XPS S 2p of RGO, RGO-CYS, MEGO and aMEGO.