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Composite cathodes containing γ-sulfur and reduced graphene oxide for lithium–sulfur batteries

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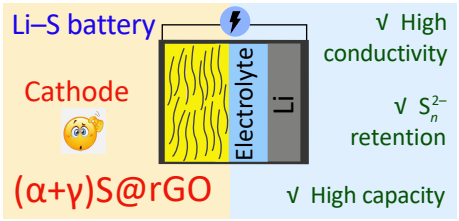
A sulfur–reduced graphene oxide (rGO) composite was investigated as a cathode material for lithium–sulfur batteries. The cathode material containing both monoclinic (γ-S) and orthorhombic (α-S) sulfur and rGO exhibits excellent electrochemical performance. The discharge capacity of (α+γ)S@rGO in Li–S battery at C/8 is 950 and 620 mAh g^{-1} for cycles 1 and 20, respectively.



Keywords: lithium–sulfur battery, cathode material, orthorhombic sulfur, monoclinic sulfur, reduced graphene oxide.

Lithium–sulfur batteries are considered as promising 'post-Li-ion' energy storage devices due to their high specific energy capacity and low cost of sulfur-containing cathodes.[1–3] Their practical application is limited by a number of factors, such as the unsafe nature of the metallic lithium anode, the low conductivity of sulfur and discharge products (Li_2S_2 and Li_2S),[4–6] a significant change in the cathode volume during charge/discharge, the formation of polysulfides (Li_2S_n, n = 4–8) soluble in the electrolyte during charge/discharge and their migration to the anode with subsequent irreversible reactions leading to the loss of active material.[2,7–9]

A promising approach to address these issues is the production of composites containing sulfur and various carbon matrices, such as meso- and microporous carbons, which are electronically conductive and capable of both transporting and encapsulating sulfur, suppressing the dissolution and migration of polysulfides.[1,2,7,10–16] Carbon materials doped with N, O and P atoms contain polar species that promote better retention of polysulfide anions in the cathode space,[17,18] thereby improving the electrochemical performance of Li–S batteries. Doped carbon materials are reported to chemically interact with sulfur, with adsorption occurring mainly through P–S or O–S bonding.[17–19] Among the carbon materials studied, reduced graphene oxide (rGO) is one of the most promising due to its high electronic conductivity, large surface area, good mechanical properties and the presence of oxygen functional groups.

The presence of monoclinic sulfur (γ-S) in composites with carbon is reported to improve the electrochemical performance of cathodes.[20–22] However, γ-S is metastable[23,24] and only orthorhombic sulfur (α-S) is present in most S/C cathodes.[25–27] The stabilization of γ-sulfur in a composite with rGO reported in this work was observed for the first time.

The S@rGO composite was prepared by melt infiltration at 155 °C.[28] The IR spectrum of rGO shows the bending vibration ν(C–H) at 800 cm^{-1}, stretching vibrations ν(C–O) at 1080 and 1198 cm^{-1}, ν(C=C) at 1550 cm^{-1}, ν(C=O) at 1730 cm^{-1}, δ(C–H) at 2850–2925 cm^{-1} and a broad peak at 3400 cm^{-1} corresponding to ν(O–H) (Figure S1, see Online Supplementary Materials). These data indicate that the oxygen-containing groups and, accordingly, the polar species in rGO are retained, which may contribute to better retention of polysulfide anions in the cathode space. At the same time, the content of such species is not too high, and both rGO and the S@rGO composite are characterized by relatively high electrical conductivity values (Table 1).

The sharp decrease in the surface area of rGO after loading sulfur indicates that sulfur occupies almost the entire surface of rGO (see Table 1). According to the scanning electron microscopy and SEM-EDX analysis, the S@rGO composite has a sponge-like structure with uniform distribution of sulfur, carbon and oxygen.

The XRD pattern of the S@rGO composite is a combination of diffraction peaks of orthorhombic α-S (ICDD PDF-2 card no. 08-0247) with metastable monoclinic γ-S (ICDD PDF-2 card no. 53-1109) in a ratio of ~1 : 1 and a broad rGO peak in the 2θ region of 15–35° (Figure 1).

In published works describing the preparation of sulfur composites with rGO,[25–27,29–31] no detection of metastable γ-sulfur modification is reported. The reason for its formation may be the stabilization of γ-S during melting/cooling in the limited space between rGO layers.

In the first cycle, the discharge capacity of the S@rGO composite at C/8 was 950 mAh per 1 g of sulfur. During

Table 1 Electrical conductivity (σ) and specific surface area (S) of rGO and the S@rGO composite.

Sample	σ/S m^{-1}		S/m^2 g^{-1}
	Measurement direction *vs.* pressing axis		
	Parallel	Perpendicular	
rGO	72	452	320
S@rGO	45	400	5

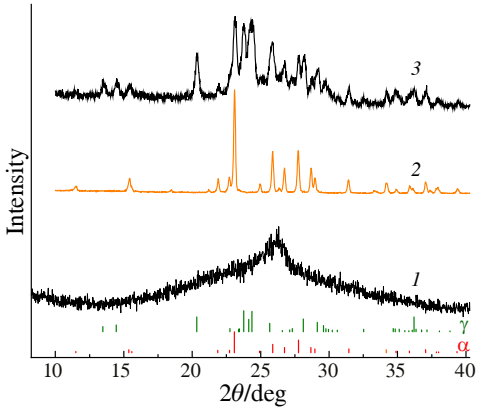


Figure 1 XRD patterns of (*1*) rGO, (*2*) initial S and (*3*) S@rGO composite, as well as bar diagrams of orthorhombic α-S (ICDD PDF-2 card no. 08-0247) and monoclinic γ-S (ICDD PDF-2 card no. 53-1109).

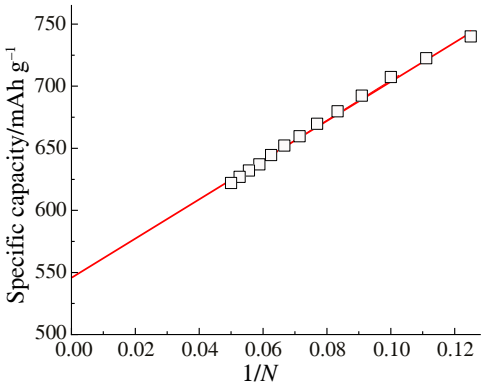


Figure 3 Dependence of the discharge capacity of the S@rGO composite on the value of 1/*N*.

subsequent cycling, a gradual decrease in the discharge capacity was observed, and by the 20th cycle, the discharge capacity was about 620 mAh per 1 g of sulfur (Figure 2). The discharge capacities of S@rGO significantly exceed those of cathodes obtained by mechanically mixing sulfur with carbon material.[32]

The capacity loss gradually decreases with increasing number of cycles (*N*) (Figure 2). During the first few cycles, the average degradation is rather high (about 2.3% per cycle), largely due to the formation of a solid electrolyte interphase (SEI) at the electrode/electrolyte boundary. Then, the dependence of the discharge capacity on 1/*N* becomes linear. Therefore, extrapolation of this dependence to zero can be used to estimate the capacity at an infinite number of cycles. Estimation by this method yields a discharge capacity of 549 ± 2 mAh g^{-1} (Figure 3).

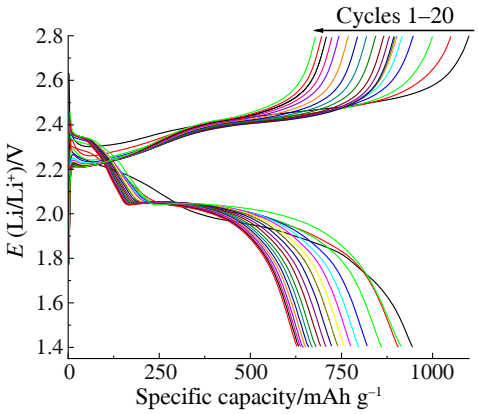


Figure 2 Charge–discharge curves of the S@rGO composite at a current density of 208 mA g^{-1} (C/8).

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7767.

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