Tailoring nano-structured cathode materials for high performance Li-S batteries
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Li/S batteries exhibit a theoretical specific capacity of 1672 mAh/g and energy density of 2600 Wh/kg, which would advance beyond state-of-the-art Li-ion batteries. However, making Li/S batteries practical for energy storage device poses considerable challenges due to several performance-related issues inherent from sulfur chemistry, including the dissolution of long-chain lithium polysulfide intermediates, the insulated nature of S and Li2S, and the volume variation during cycling. To solve these issues, a possible solution is to encapsulate S in tailored conductive matrix, as shown below.1-4

![Figure 1 Schematic Illustration of the GS-MWCNT@S composite and its electrochemical performance.](image1)

A multilayered carbon nanotube/sulfur (MWCNT@S) composite with core–shell structure was successfully embedded into the interlayer galleries of graphene sheets (GS) through a facile two-step assembly process. The GS-MWCNT@S composite has a 3D hierarchical sandwich-type architecture with S loading up to 70%. The thickness of the S layer on the MWCNTs is 20 nm. The composite exhibits a high initial capacity of 1396 mAh/g at a current density of 0.2C (1C = 1672 mA/g), corresponding to 83% usage of the sulfur active material. Much improved cycling stability and rate capability are achieved. The superior electrochemical performance of the GS MWCNT@S composite is mainly attributed to the synergistic effects of GS and MWCNTs, which provide a 3D conductive network for electron transfer, open channels for ion diffusion, strong confinement of soluble polysulfides, and effective buffer for volume expansion of the S cathode during discharge.

![Figure 2 Schematic Illustration of the PPy/PEG-SA-CNTs composite and its electrochemical performance.](image2)

Polypyrrole-polyethylene glycol-modified sulfur (PPy/PEG-SA-CNTs) composite and its electrochemical performance.

Polypyrrole-polyethylene glycol-modified sulfur / aligned carbon nanotubes (PPy/PEG-SA-CNTs) were synthesized by using an in situ polymerization method. The ratio of PPy to PEG equaled 31:7:1 after polymerization, and the PEG served as a cation dopant in the polymerization and electrochemical reactions. The S, Ppy, PEG-A-CNT, and chloride content in the synthesized material was 64.6 %, 22.1 %, 0.7%, 12.1 %, and 0.5 %, respectively. The thickness of the polymer shell was about 15-25 nm. The cathode exhibited a high initial specific capacity of 1355 mAh/g, and a reversible capacity of 924 mAh/g was obtained after 100 cycles. PPy/PEG provided an effective electrolytically conductive network and a stable interface structure for the cathode. Remarkably, the battery could work at a very high current density of 8 A/g and reached an initial capacity of 542 mAh/g; it also retained a capacity of 480 mAh/g after 100 cycles. The addition of PEG as a dopant in the PPy shell contributed to this prominent rate improvement. Lithium ions and electrons were available everywhere on the surfaces of the particles, and thus could greatly improve the electrochemical reaction; PEG is a well known solvent for lithium salts and a very good lithium-ion catcher.

![Figure 3 Schematic Illustration of the PANi-S/MWCNT composite and its electrochemical performance.](image3)

A schematic illustration of the PANi-S/MWCNT composite and its electrochemical performance. Rapid in situ chemical oxidation polymerization of polyaniline was carried out to coat MWCNT core/sulfur shell structures. The S-coated-MWCNTs were obtained by ballmilling and thermal treatment. A 70.0% sulfur, 20.2% emeraldine PANi salt and 9.8% MWCNT composite gave the typical two reduction peaks and two oxidation peaks; these are due to three polysulfide species. The initial discharge capacity was 1334.4 mAh/g for the PANi-S/MWCNT electrode and the remaining capacity was 932.4 mAh/g after 80 cycles. The columbic efficiency is up to 92.4%. Because of the porous polymer, the diffusion distance of the lithium ion from the bulk liquid was reduced. The gel-like cathode composites and the higher conductivities improved the kinetics of the lithium sulfur redox reaction.

![Figure 4 Schematic Illustration of the S-PTh composite and its electrochemical performance.](image4)

A schematic illustration of the S-PTh composite and its electrochemical performance. Novel sulfur/polythiophene (S-PTh) composites with core/shell structure composites were synthesized via an in situ chemical oxidative polymerization method. A suitable ratio for the composites was found to be 71.9% sulfur and 18.1% polythiophene. Conductive polythiophene acts as a conducting additive and a porous adsorbing agent. It was uniformly coated onto the surface of the sulfur powder to form a core/shell structure, which effectively enhances the electrochemical performance and cycle life of the sulfur cells. The initial discharge capacity of the active material was 1119.3 mAh/g and the remaining capacity was 830.2 mAh/g after 80 cycles.

Reference