A Polydopamine-coated Sulfur/CMK-3 Composite as a Cathode Material for Lithium-Sulfur Batteries

By

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Abstract

Rechargeable Li-S batteries are one of the promising energy storage systems as sulfur offers a high theoretical capacity of 1675 mAh·g⁻¹ at a safe operating voltage range of ~ 2.1 V and low cost. However, the Li-S batteries are plagued with some problems inherent in sulfur cathode materials such as the low sulfur utilization, low rate capacity and fast capacity fading, owing to its electronically and ionically insulating nature and the dissolution of polysulfides in the electrolyte solvent. The mainstream Li-S battery adopts 1,3-dioxolane (DOL) and 1,2-dimethoxy ethane (DME) as the electrolyte solvents which both possess high polysulfides solubility. When polysulfides dissolve in the electrolyte and migrate out of the cathode region, they might not be re-utilizable, resulting in capacity fade during the cycling.

In this research, polydopamine-coated sulfur/CMK-3 composites (PDA@S/CMK) were prepared via two facile processes including melt-diffusion method and post-thermal treatment of a highly ordered mesoporous carbon, namely CMK-3, and sublimed sulfur, followed by a self-polymerization of dopamine on the surface of the S/CMK-3 composite. Several aspects related to the materials were investigated: the selection of template for CMK-3, the optimization of temperature for post-thermal treatment and the effects of the coating ratio and coating time on the performance of the cathode material. Different characteristics of PDA@S/CMK samples were examined by various approaches, including the physical characterization methods, such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and the electrochemical methods including cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), cycle performance and rate capability at different current rates.

It is found that the short-rod-like SBA-15 is a better template for CMK-3, because the sub-micron-sized CMK-3 can provide more accessible points for guest molecules, shorter distances for Li⁺ diffusion and larger contact area between electrode and electrolyte. 250°C was selected in the post-thermal treatment to remove the sulfur from external surface and retain the sulfur confined in the channels of CMK. The ratio of 1:2 and coating time of 8 h were selected to get a uniform, stable and moderately rigid coating. It is demonstrated that the polydopamine, with a thickness of 10-20 nm, has been coated uniformly onto the surface of the S/CMK-3 composite which forms a core/shell structure. The cycling performance of the PDA@S/CMK-3 composite is very good because of a synergistic effect on the high electronic conductivity from CMK-3 and surface modification by polydopamine. The PDA@S/CMK sample delivers an initial discharge capacity of 1185.17 mAh·g⁻¹, and maintains 751 mAh·g⁻¹ after 300 cycles, indicating a capacity retention of 63.4% and a capacity decay rate of 0.12% per cycle during the 300 cycles. This good performance could be attributed to its uniform coating layer and moderate coating thickness, which can prevent the polysulfide from dissolving into the electrolyte solvent and accommodate the volume expansion during the charge/discharge process. This study shows that the PDA@S/CMK composite is a promising cathode material for Li-S batteries.

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Examination Committee:
Prof. Minhua SHAO, Chairman
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Prof. Jang Kyo KIM, co-supervisor
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Date: 25 July 2014 (Friday)
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