

Novel composite cathode for Li-sulfur batteries

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Li-sulfur batteries represent an attractive alternative to Li-ion batteries due to their high theoretical capacity (1675 mAh/g), low cost, and eco-friendliness of elemental sulfur. Nevertheless, the electrochemical stability and commercial application of Li-S batteries are inhibited by the insulative sulfur and Li₂S/Li₂S₂, the shuttling effect in the electrolyte, and significant volume changes on the cathode during discharge. The main problems are related to the dissolution of lithium polysulfides (PS) in the electrolyte and their parasitic reactions with electrolyte solvents and Li anode. PS diffusion to the anode compartment of the Li-S battery causes severe redox shuttle between the cathode and Li anode. Hence, effective PS immobilization in the cathode compartment of the battery is essential for the optimum performance and cycling stability of the system. PS can be physically trapped on the surface of carbon and/or immobilized in the pores of carbonaceous additive. Since the PS are bound to the carbon surface by weak van der Waals interactions, the incorporation of oxidic materials, providing a strong polar surface for efficient PS trapping, further helps to suppress the shuttle effect and subsequently the decay rate per cycle^{1,2}. Titanium dioxide³⁻⁵ Magnéli phases⁶, and ternary oxides^{7,8} belong to the most frequently used inorganic additives improving the electrochemical performance of Li-sulfur batteries. We evaluated the performance of TiO₂ and high-entropy oxychlorides as alternative additives to carbon/sulfur composite cathodes. The TiO₂ top layer and TiO₂-modified separator increased substantially the initial charge capacities of sulfur composite cathodes with different kinds of porous carbon. Charge capacities calculated from cyclic voltammetry are 1427 mAh g⁻¹, 1349 mAh g⁻¹, and 952 mAh g⁻¹ for TOB carbon, graphene nanoplatelets, and Penta carbon, respectively⁹. This represents a relative enhancement by 75%, 83%, and 44%, respectively, as referenced to the cells with titania-free materials⁹. Galvanostatic chronopotentiometry confirmed the beneficial effect of inorganic additives. The addition of novel lithiated high-entropy oxychloride LiHFeOFeCl with spinel structure (synthesized by a mechanochemical–thermal route) to the carbon/sulfur composite cathode resulted in improved long-term electrochemical cycling stability and increased charge capacity¹⁰. The carbon/LiHFeOFeCl/sulfur cathode provided a charge capacity of 530 mAh g⁻¹ after 100 galvanostatic cycles, which represents ca. 33% increase as compared to the charge capacity of a blank carbon/sulfur composite cathode (398 mAh g⁻¹)¹⁰. This considerable effect of the LiHFeOFeCl material is assigned to its excellent structural and electrochemical stability within the potential window of 1.7 V/2.9 V vs. Li⁺/Li. In this potential region, our LiHFeOFeCl exhibits no inherent electrochemical activity and acts solely as an electrocatalyst accelerating the redox reactions of PS¹⁰.

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