Ternary-layered separator to retard the shuttle of polysulfides towards highly-stable lithium–sulfur batteries

January 4 2016

High-energy-density batteries are essential to meet the demand for future applications in portable electronics and electrical vehicles. Owing to the theoretical energy density of 2600 Wh/kg, the lithium-sulfur battery is considered one promising candidate for next-generation, high-energy battery solutions. However, shortcomings in fast capacity degradation and low cycling efficiency haven't been solved, which hinders the practical application of lithium sulfur battery system. A researcher at Tsinghua University has proposed a ternary-layered separator system for lithium-sulfur batteries with long lifespan, high coulombic efficiency, and high sulfur utilization.

"A new generation of rechargeable lithium-sulfur batteries rely on multi-electron transfer redox chemistry," said Dr. Qiang Zhang at Tsinghua University to Phys.Org. "Except for the high energy density, lithium-sulfur batteries have advantages over routine lithium-ion batteries such as cheap cathode material and low-temperature operational performance."

Despite the advantage of lithium sulfur systems, there exists an inherent shuttle effect of polysulfide intermediates in a lithium-sulfur cell. "Such shuttle effects cause the low Coulombic efficiency and induce capacity degradation via consumption of active sulfur and internal chemical reaction," said Dr. Jia-Qi Huang, an associate professor in Tsinghua University.

This research group has made great efforts toward an ion-selective separator for lithium-sulfur cells. Based on physical confinement and electrostatic repulsion, the researchers covered the surface of routine polymer separators with ultrathin graphene oxide (GO) nanosheets and then cast a thin Nafion layer onto it. "In the structure of ternary-layered separator, macroporous polypropylene separator serves as matrix layer and provides mechanical strength for the separator. GO sheets formed a layer with small channels for lithium ion transportation and served as a compact barrier layer with oxygenated functional groups to anchor Nafion. In this way, we can significantly lower the area loading of the Nafion retarding layer and maintain the permselectivity for lithium ions against polysulfide anions. Both electrostatic repulsion and size selective effect are effective with this strategy." said Ting-Zhou Zhuang, a master candidate in the research group.

In total, the functional loading layer on the routine separator is only 0.053 mg cm^{-2}. When the ternary separator is incorporated into lithium-sulfur batteries, the discharge capacity was improved from 969 to 1057 mAh g^{-1}; the Coulombic efficiency increased from 80 to 95% without the LiNO3 additive; the decay rate was decreased from 0.34% to 0.18% in 200 cycles; and the self-discharge was inhibited. The sulfur utilization reached 73% with a high sulfur loading amount of 4.0 mg cm^{-2}.

"Membrane modification has been demonstrated to be an effective method for lithium-sulfur batteries. Ternary membrane structure makes the best use of every building block, and the multilayered composite separator is more efficient than a single-layer separator. This strategy opens up new opportunities in developing multifunctional separator toward better batteries." said Qiang Zhang.

A proof-of-concept ternary separator of a layered PP/GO/Nafion was rationally designed, fabricated, and applied in Li–S batteries with improved sulfur utilization, coulombic efficiency, and long cycling life.

This work offers a concept of a ternary system, in which the rational combination of building blocks into hierarchical structures was indispensable to fully demonstrate their roles in the ternary system with multi-functions and multi-applications.

More information: Ting-Zhou Zhuang et al. Rational Integration of Polypropylene/Graphene Oxide/Nafion as Ternary-Layered Separator to Retard the Shuttle of Polysulfides for Lithium-Sulfur Batteries, *Small* (2015). DOI: 10.1002/smll.201503133

Provided by Tsinghua University