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Suppression of Polysulfide Dissolution by Polypyrrole Modification of Sulfur-based Cathodes in Lithium Secondary Batteries

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Lithium-ion batteries (LIB) have been installed in a wide range of portable electronic devices. A demand of high-energy densifications and weight savings of LIB has increased. So far, theoretical capacity of the conventional $LiCoO_2$ cathode, about 140 mA h g^{-1}, is being achieved. As a next generation cathode, sulfur has attracted attention due to its high theoretical capacity of 1672 mA h g^{-1}. S cathode-based full batteries combing with the Si or Li metal anodes can achieve four or five times more capacity compared to the existing C–$LiCoO_2$ system. However, the S cathode has a severe problem of polysulfide dissolution into the electrolyte. This dissolution of polysulfide causes a "redox shuttle mechanism," which leads to an over charge (low in coulombic efficiency) and rapid fading of the capacity. In order to solve this problem, we propose a novel method of modifying the S cathode by coating it with a polypyrrole (PPy) film, which is prepared by oxidative electro-polymerization using a solution consisting of, 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (BMP-TFSI), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), and pyrrole. The cross sectional FE-SEM image of the PPy-S/Ketjenblack (KB) cathode indicates that the PPy film covers the S/KB cathode surface with uniform thickness as shown in Fig. 1. Since the Li^+ transport number of the PPy film was found to be close to unity, the covering PPy film demonstrates a superior ability to inhibit the polysulfide dissolution into the electrolyte. As shown in Fig. 2 (a), on the S/KB cathode without the PPy film, the charge current continued to flow at ca. 2.4 V at the 2nd cycle and never reached the upper voltage limit (3.0 V) because of the shuttle mechanism. Thus, further cycles could not continue. On the other hand, the PPy coated S/KB (PPy-S/KB) cathode achieved over 300 cycles stably with over 97% coulombic efficiency during the all cycles (See Fig. 2(b)). Thus, the strategy of coating the S cathode with PPy is successful in inhibiting the dissolution of polysulfides.

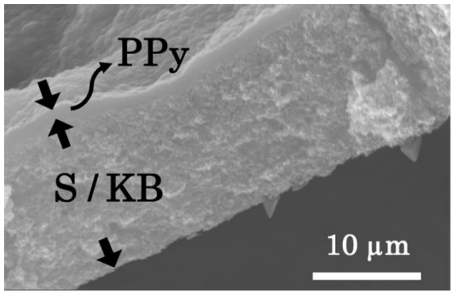

Fig. 1 Cross-sectional FE-SEM image of the PPy-S/KB composite cathode (×3.0 k).

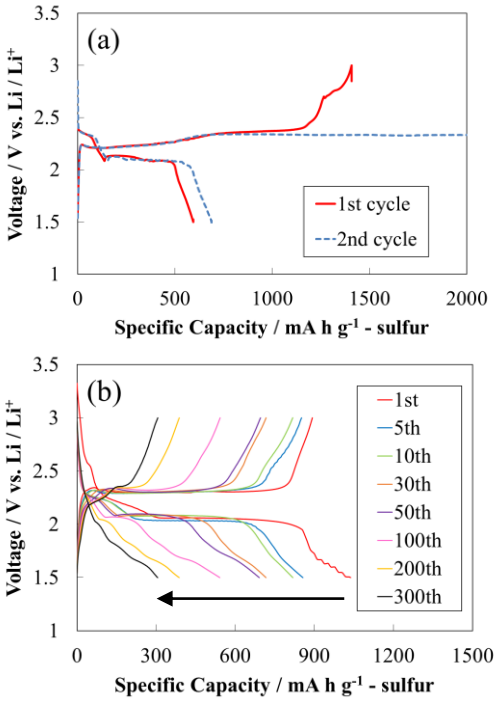

Fig. 2 Typical charge-discharge voltage profiles of (a) S/KB cathode and (b) PPy-S/KB cathode cycled at 0.03 C (25 µA cm^{-2}).

Reference:

[1] N. Nakamura, T. Yokoshima, H. Nara, T. Momma, T. Osaka, *J. Power Sources*, **274** (2015) 1263-1266.

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