Effect of Lithiation Process on Active Materials of Lithium Ion Secondary Battery using Sulfur / Ketjen Black Cathode and Graphite Anode

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Introduction To realize high capacity of lithium ion battery (LIB), sulfur is much attractive cathode materials because of its high theoretical capacity (1672 mAh/g). However, to apply sulfur to cathode active materials of LIB, there are several problems such as low electrical conductivity of elemental sulfur, large volume change during charge - discharge cycling, and high solubility of polysulfide ion into electrolyte. To solve these problems, we investigated preparation of Sulfur / Ketjen Black (S/KB) composite materials and of organic solvent- ionic liquid mixed electrolyte. "No lithium source" in the cell components is another serious problem to develop the "full cell" with sulfur as cathode and conventional anode such as graphite. In this work, preparation of full cell by using S/KB cathode and Graphite anode was investigated focused on initiation process.

Experimental S/KB cathode (S) was prepared by mixed in the ratio of Sulfur:KB:PVdF = 45: 45: 10, wt%. Graphite:AB:PVdF=90:5:5,wt% was used as Graphite anode (G). Li(G3)TFSI + $Li(G1)_2TFSI$ electrolyte was prepared by mixed triglyme-Li equimolar complex: monoglyme-Li (1: 2, mol) in the ratio of tryglyme : monoglyme = 1:1,vol.

Results and Discussion First, lithiation process of S/KB and/or G was investigated. Fig.1 shows the rate performances of full cells with various conditions of anode and cathode. S(Li)-G full cell shows very low capacity of less than 100 mAh / g at over 10 cycles. On the other hand, S-G(Li) full cell show high capacity compared with that of S(Li)-G full cell. It is thought that irreversible capacity was large cause of this capacity decay, and that formation of surface electrode interphase (SEI) was formed on the surface of anode.

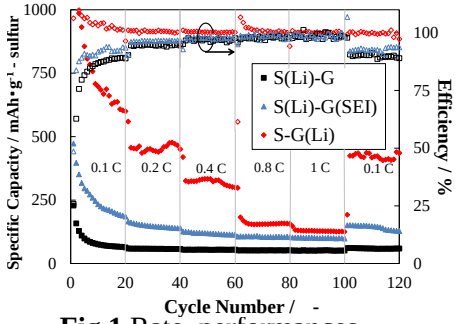

Fig.1 Rate performances of each full cells

Second, decrease in the irreversible capacity for the active materials was investigated. SEI pre-formed G anode (G(SEI)) was prepared, and S(Li)-G(SEI) full-cell was prepared. Blue plots in Fig.1 shows the performance of S(Li)-G(SEI). The performance was improved compared with that of S(Li)-G, however, it was still low value than S-G(Li). To reduce irreversible capacity on S cathode, preparation of S with initiation process was carried out by pre-cycling at 10 times. Unfortunately, this initiated S was easily peeled off when assembling. Thus, decrease in the irreversible capacity for S anode was not easy. The S-G(Li) full cell was best structure from these results.

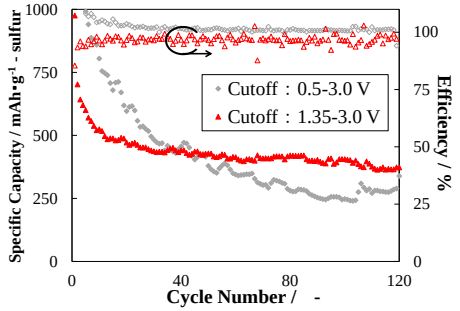

Fig.2 Cycle performances of S-G(Li) (cut-off voltage was changed)

Final, improvement of preparation conditions and operating condition for S-G(Li) was carried out. Cycle performance of S-G(Li) prepared by improved conditions was shown in Fig.2. The discharge side cut-off voltage was changed from 0.5 V to 1.35 V that was modified for S cathode. The capacity was successfully maintained 400 mAh/g at over 10 cycles. Detail of this full-cell will be discussed at presentations.

Reference:

[1] M. Watanabe et al., J. Am. Chem. Soc., 2011, 133 (33), 13121–13129

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