

Solid State NMR Study of Lithium Iron Polysulfide Li_8FeS_5 During Charge–Discharge Cycle

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Lithium sulfide (Li_2S) is one of the promising positive electrode materials for the next-generation lithium ion rechargeable batteries because of its high theoretical capacity of 1167 mAh/g. However, Li_2S is electronically and ionically resistive, giving rise to relatively low electrochemical performance during the cycles. Among the several attempts that have been made to enhance the conductivities, we successfully prepared a Fe-containing Li_2S -based positive electrode material Li_8FeS_5 , which gave an excellent discharge capacity of ca. 730 mAh/g [1]. The structural changes of Li_8FeS_5 during the charge–discharge cycles were investigated based on X-ray scattering and X-ray absorption spectroscopy techniques [2]. In the present study, we report the structural and dynamic behaviors of Li_8FeS_5 during the initial cycle in details by using solid state NMR spectroscopy.

A powder mixture of Li_2S and FeS (molar ratio of 4 : 1) was sintered by the spark-plasma-sintering (SPS) method and then mechanically milled with acetylene black to yield Li_8FeS_5 -carbon composite active material. Coin-type cells were assembled with Li foil as a counter electrode and 1M LiPF_6 electrolyte solution (EC : DMC = 1 : 1 in volume ratio) for the electrochemical measurements. The electrochemical measurements were galvanostatically performed with a current density of 46.7 mA/g and a potential window of 1.0–2.6 V vs. Li/Li^+ . The cells were disassembled in the Ar-filled glovebox for *ex-situ* ^7Li MAS NMR measurements. The *ex-situ* and *operando* ^7Li NMR measurements were performed at 14.1 T. Spin-lattice relaxation times (T_1) were acquired with the saturation-recovery technique at the temperature range from -40 °C to 60 °C.

Operando ^7Li NMR measurement indicated that the ^7Li signal of Li_8FeS_5 reversibly decreased and increased in intensity with a continuous peak shift on the Li extraction and insertion processes, respectively. High-resolution ^7Li MAS spectra showed the different Li environments between the states of charge and discharge at similar Li contents, suggesting that the delithiation and lithiation processes were different from each other. Also, it was confirmed that the charge compensation was mainly achieved by S at the potential range of 1.5–2.6 V and by Fe at the range of 1.0–1.5 V, respectively. The activation energy for the local hopping of Li ions in the pristine structure was estimated to be 18 kJ/mol (ca. 0.2 eV). Interestingly, it decreased during the delithiation, suggesting the possibility of the improved ionic conductivity during the charge-discharge process.

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References:

- [1] T. Takeuchi, H. Kageyama, K. Nakanishi, M. Ogawa, T. Ohta, A. Sakuda, H. Sakaebe, H. Kobayashi, Z. Ogumi, J. Electrochem. Soc. 162 (2015) A1745–1750.
- [2] T. Takeuchi, H. Kageyama, K. Nakanishi, M. Ogawa, T. Kawaguchi, K. Ohara, K. Fukuda, A. Sakuda, T. Ohta, T. Fukunaga, H. Sakaebe, H. Kobayashi, E. Matsubara, PRiME 2016 Conference Proceedings, #154.