

Effective Activation and Stabilization of Si Negative Electrode by Using a Li Pre-doping Technique

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In recent years, new-generation energy storage systems such as Li-S and Li-air batteries have been attracted much attention because of the high energy densities over 500 Wh kg⁻¹ [1]. The high energy storage systems do not basically have Li⁺ ion in the positive electrodes and need Li metal negative electrode (NE), whose theoretical capacity is ca 3860 mAh g⁻¹. However, Li metal NE has a risk of short circuit by Li dendrite deposition and the poor rate capability by the small surface area due to the flat morphology, i.e. foil or thin film. On the contrary, Si is one of the good candidates for the NEs because of the high theoretical capacity of ca. 4200 mAh g⁻¹, and the suppression of Li dendrite deposition due to the Li alloying/de-alloying reactions. In addition, morphology of Si active materials, e.g. nanoparticles, nano-wires, nano-flakes, not only suppresses the capacity fading due to the crack and pulverization but also accelerates the rate capability of Si NEs by increasing the surface area. However, for applying the Si NEs to next-generation batteries, it is necessary to Li pre-dope into the Si NEs. Namely, the easier and more convenient Li pre-doping technique must be developed in the practical use. In this study, we prepared two types of Li pre-doped Si NEs by direct Li pre-doping (DP) [2] and electrochemical Li charging (EC) methods without and with fluoroethylene carbonate (FEC) as an additive, and investigated the charge/discharge properties by a half-cell operation at limiting capacity of 2000 mAh g (Si)⁻¹.

To investigate the Li pre-doping state of Si NEs, the photo and SEM images of Li pre-doped Si NEs were compared (Fig. 1). In the case of no FEC addition, the Li pre-doping was inhomogeneous for both EC and DP treated Si NEs and partially cracked by mechanical stress due to the inhomogeneous Li alloying. In contrast, for the both FEC added ones exhibited clearly homogeneous Li pre-doping. Especially for the DP method, Si nanoparticles became larger, indicating a deeper Li pre-doping. This indicates that the FEC addition formed proper and homogeneous SEI films on the surface and promoted the fast Li alloying even in shorter time (3 h). As a result, the capacity fading was suppressed up to 50 cycles (Fig. 2). Moreover, the cycleability was drastically improved by a further addition of 10 wt% FEC into the electrolyte. The high capacity of 2000 mAh g⁻¹ was kept up to over 230 cycles.

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[1] P. G. Bruce et al., Nature materials, 11 (2012) 19-29.

[2] M. Saito et al., Electrochemistry, 85(10) (2017) 656-659.

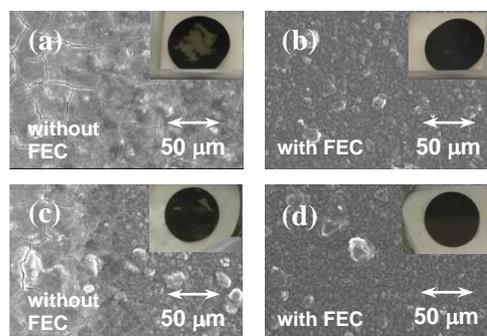


Fig. 1. Photo and SEM images for the Li pre-doped Si NEs by (a,b) EC and (c,d) DP methods.

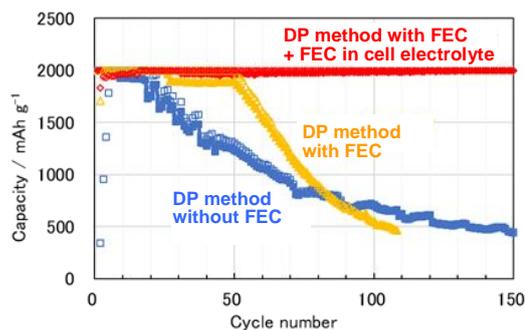


Fig. 2. Cycleability of the DP treated Si NEs at limiting capacity of 2000 mAh g⁻¹ at the rate of 700 mA g⁻¹ at 30°C.