

High performance silicon-based negative electrodes for Li-ion batteries

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Introduction

Silicon-based electrodes are much more attractive negative electrodes for lithium-ion batteries than graphite, due to their much larger capacity [1], but their low cyclability is the main issue. Two distinct causes explain such fading: (i) decrepitation of Si grains and disintegration of the composite electrode architecture, resulting in loss of electrical contact [2,3]; and (ii) formation of an unstable solid electrolyte interphase (SEI) resulting in severe electrolyte degradation at the surface of the Si phase [4,5]. To solve these problems, several strategies have been undertaken, among which are: (i) the use of nanosized particles to better accommodate large strain without cracking; (ii) the use of capacity limitation to minimize volume changes; (iii); the use of electrolytes containing a film-forming agent; and (iv) the use of binders favoring a resilient bonding between the particles in the composite electrode.

In this communication, we review our recent strategies in order to improve the cyclability of low cost Si-based electrodes, i.e. comprehension of the failure mechanism, analysis of the SEI composition, use of nanostructured copper current collectors, and development of ball-milled nanostructured Si-based electrodes.

Results and discussion

Understanding the failure mechanism of silicon based negative electrodes for lithium ion batteries is essential for solving the problem of low coulombic efficiency and capacity fading on cycling, and to further implement this new very energetic material in commercial cells. To reach this goal, we have coupled several complementary characterization techniques [5]. ⁷Li MAS NMR analyses of the charged batteries demonstrate that the major part of the lithium lost during the charge of batteries is not trapped in Li_xSi alloys but instead at the surface of the Si particles, likely as a degradation product of the liquid electrolyte [5].

Results of ⁷Li and ¹⁹F MAS NMR quantitative analysis show that the amount of lithiated surface species accounts for a negligible part of the irreversible capacity loss, and ¹³C NMR analysis confirms that a significant part of the irreversible capacity loss is due to the degradation of the carbonate solvents with the formation of non-lithiated carbon species as oligomers or polymers [6]. The SEI formation is minimized in the presence of FEC/VC liquid electrolyte additives [7].

We will also show that the mechanical cohesion of Si electrodes and their adhesion onto the current collector may lead to cyclability failure. To overcome the adhesion issue, an electrochemically nanostructured copper foil was evaluated as a current collector for micrometric Si

powder (ball-milled) based electrodes prepared by the conventional slurry-coating method. The formation of a bunch of copper nanowires on the current collector makes a rough surface, which enhances the adhesion of the Si composite electrode. This induces a major decrease of the irreversible capacity associated with the electrical disconnection of the Si particles with cycling, which results in a great improvement of the electrode cycle life [8].

A Si-based electrode with improved performance can be achieved using high-energy ball-milling as a cheap and easy process to produce Si powders prepared from a coarse-grained material such as wafer scraps. With FEC/VC liquid electrolyte additives, a composite electrode based on ball-milled Si powders can discharge/charge 900 cycles with a coulombic efficiency above *ca.* 99% when the capacity is limited at 1200 mAh g⁻¹ of Si (Figure 1), compared to only 650 cycles for the nano-Si based electrode [9]. Ball-milled powders present all the advantages of nanometric Si powders, but not the drawbacks. Compared to non-milled micrometric or nanometric powders, the improved performance of nanostructured milled Si powders is linked to a strong lowering of particle disconnection at each charge, while the irreversibility due to SEI formation remains unchanged.

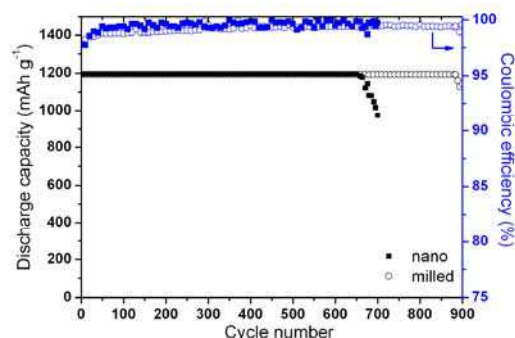


Figure 1. Discharge capacities and coulombic efficiencies with cycling in FEC/VC containing electrolyte of milled millimetric Si (○) or nanosized (■) Si-based electrodes. The discharge capacity was limited to 1200mAh g⁻¹ and the rate was 1Li/Si in 2h.

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