New insight on the failure mechanism of nano-Si based anodes for Li-Ion Batteries

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Introduction

Silicon is widely considered as one of the most promising anode materials for Li-ion batteries due to its alloying reaction with Li. The packing density of the Li atoms within the $\text{Li}_{12}\text{Si}_5$ alloy is even higher than the one exhibited by the structure of metallic Li [1]. The high density of the Li atoms in the Si structure brings about the highest theoretical capacity (4200mAhg^{-1}) [2]. Despite that, Si-based electrodes suffer from poor cyclability due to severe mechanical stress involved in the alloying and de-alloying processes. These are responsible for macro-fractures of the host electrode structure and loss of electrical contact [3]. However, using Si nano-particles to fabricate composite electrodes reduces cracking, but it does not completely solve the capacity fading. Herein further considerations on the fading mechanism are proposed.

In this work we synthesized Si nano-particles by means of a Laser assisted Chemical Vapor Pyrolysis (LaCVP) reactor. These particles were used to fabricate composite electrodes, whose structural and morphological properties were investigated before and after cycling.

Experimental

Silicon nano-particles were synthesized by LaCVP. The synthesis procedure is described elsewhere [4]. Electrodes were prepared suspending the particles in a Polyvinylidene fluoride (PVdF SOLEF 1015) solution in *N*-Methyl-2-pyrrolidone (NMP MERCK-Schuchardt) and sonicated for 1 h. The weight ratio between the polymer binder and the active material was set to 1:3. No conductive additive was added to the slurry. Electrodes were dried out 280°C in order to promote thermal activation of the PVdF [5]. Coin cells (CR2320 Hohsen) were assembled inside a He filled glove box using metallic Li as negative electrode, LiPF_6 in EC:DMC 1:1 mixture (Mitsubishi Chemical) as electrolyte and the Si/PVdF composite as the positive electrode. The cells were cycled with a galvanostatic procedure in a Maccor (S4000) battery tester in order to assess the electrode behavior in terms of capacity and cycling performance. TEM (coupled with EDS) was carried out to study morphology, size and crystallinity of the as-produced nano-particles. Their composition and crystalline structure were also studied by XRD. The morphology of the electrodes before and after cycling was further studied via SEM.

Results and discussion

The as-produced Si nano-particles are shown to be stable in air. The XRD analysis indicates that the Si nano-particles are crystalline. The characteristic peaks match with the crystallographic data of the Si lattice (i.e. JCPDS no. 75-0590). No traces of crystalline Si oxides are detected, suggesting that surface oxidation of the particles resulted most likely in an amorphous oxide layer only.

Si nano-particles show a mean diameter of 20nm, a crystalline core and an amorphous outer layer of 1-2 nm thick (see figure 1), which then is attributed to the naïve

oxide layer. The dense and homogeneous layer therefore accounts for the stability of the nano-particles in air.

Fig. 1: TEM bright field image showing the typical morphology and structure of Si nano-particles produced via LaCVP.

Figure 2 shows SEM images of the electrodes' surface before and after cycling. In particular, the microstructure and the texture of the whole electrode are not damaged by repeated cycling. No cracks were observed throughout the images. This confirms that the mechanical failure, in this case, is not the cause of the capacity fading observed after the 10th cycle (see figure 3).

Fig. 2: SEM images of Si/PVdF composite electrode before (left) and after 50 cycles (right).

Therefore, we suggest that the electrical contact is probably lost at the interface between the polymer and the active material surface. Hence, the chemical affinity between the polymer and the particle surface is of utmost importance to increase the lifetime of a nano-Si based electrode.

Fig. 3: Gravimetric capacity vs cycle number of the composite electrode based on nano Si and PVdF. A pronounced fading of the capacity is observed after the 10th cycle.

References

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