Carbon Coated Silicon Anode in Lithium-ion Battery: Structure Analysis during Charge-discharge via In-situ XRD Measurements

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Among new anode materials, silicon is a very attractive candidate due to its potentially very large capacity, over 3000 mAh/g. Nevertheless, information for the charge-discharge (C-D) cycling properties of Si particle electrode is scarce. This is partly because it has been very difficult to achieve long enough cycle life for detailed characterization. In addition, great enthusiasm has also been shown to coat the Si particles with secondary materials, which may serve either to increase the conductivity of the electrode or to be a buffer that can partially accommodate the volumetric variation. Among these secondary materials, including C, oxides and nitrides, only coating with graphite/C has so far shown promising effect, but the role of C has not been elucidated.

We have shown that in our previous studies that the amount of conductive graphitic/carbonaceous additives and the type of binder material have very significant effects on the stability of the Si particle anode. By optimizing these electrode architecture factors, significant enhancement in the cycling stability of Si particle anode has been made. This has made it possible for us to carry out electrochemical characterizations on this type of Si electrode to a greater extent than before.

Figure 1 shows synchrotron data of NiSi/Si electrode at the first cycle with strategy of CCCV mode. During discharge (lithium insertion) process, the reflection peaks of silicon, Si(111) and Si(220), for instance, become broadening and diminishing. It indicates that the lithiation process of Si to $LiSi_x$ is a transformation from crystalline Si to amorphous $LiSi_x$. In order words, no new reflection peaks corresponding to Li-Si alloys with a new crystal structure can be observed. For charging process, no crystalline Si is formed indicating the structure of silicon after lithium extraction is amorphous or nano-sized. Apart from silicon, the reflection peaks of graphite (002) and (004) shift to low angle during discharging and high angle while charging indicating an expansion of d-spacing as lithium intercalation (from 3.350 Å to 3.699 Å) and contraction of d-spacing as lithium de-intercalation (almost reversibly from 3.699 Å to 3.357 Å). The ratio of volume change for graphite is about 10 %. Moreover, we also observed a short plateau located at ~3.5 Å while discharge to ~700 mAh/g. The plateau represents the transition state related Li insertion to graphite. The reason why we observed only one stage rather four stages may be due to larger discharging current (0.3 mA/mg).

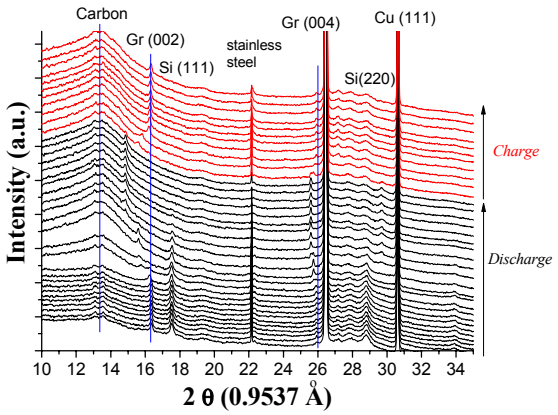

Figure 1. In situ XRD patterns of NiSi/Si composite during the first cycle at 0.3 mA/mg.

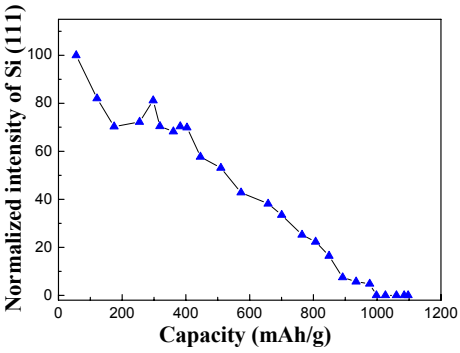

Figure 2. Integrated intensities of Si (111) during the 1st discharge process.

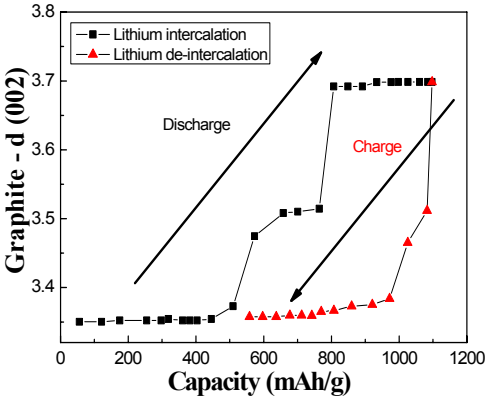

Figure 3. Calculated *d*(002) of graphite during discharge and charge processes