

High Throughput Production of Si Nanocomposite Particles by PS-PVD for Negative Electrode of Lithium Ion Batteries

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Abstract

Silicon nanoparticles (Si-NPs) have been produced at a maximum feeding rate of 17 g/min (1 kg/hr) by plasma spraying physical vapor deposition. The effect of production throughput on the composite particle structure as well as battery performance using these particles as anode active material has been investigated. The cycle capacity of the cells using high throughputs Si-NPs is improved slightly. For the co-condensation process, the guideline to configure the optimal structure favorable for battery properties is suggested.

1. Introduction

Si is one of the promising materials for the negative electrode of lithium-ion batteries (LiB) that could respond to the demand of the ever-increasing capacity in electric vehicles and smart grid. Yet, a drastic capacity decay occurs as a tremendous volume expansion up to 400% during battery charge/discharge cycle causes the fracture of active material and the loss of electrical contact [1]. To overcome this issue, the nanostructuring of the materials has been reported to be effective, such as nanosizing less than 150 nm [1,2], porous [3] and composite with other materials [4-6]. Among the current processes employed in the production of nanocomposite materials, plasma spraying physical vapor deposition (PS-PVD) seems to be advantageous in instantaneous to nanosized composite particle formation and also because of its industry-compatible high throughput production.

In fact, for LiB application, Si nanoparticles (Si-NPs) have been synthesized by PS-PVD using metallurgical-grade Si (mg-Si) as raw material at rates of >6 g/min, and the batteries using these Si-NPs have exhibited the improved cycle capacity [2]. Moreover, when Ni is added to Si feedstock, Si nanocomposite particles with directly attached Ni particles can be fabricated through the co-condensation during PS-PVD, and the battery performance of Si:Ni particles demonstrates further improvement [7].

Upon considering the high throughput production for industry technology, therefore, the structure of Si-NPs could be altered as a result of the change in co-condensation process. In this research, therefore, we have identified the nanostructured change in the Si and Si-Ni nanoparticles at fast rate production and its effect on battery performance.

2. Experimental

Si-NPs are synthesized by PS-PVD using the hybrid

plasma spray system that is equipped with DC and RF torch. This system is advantageous in that the raw powders can be injected directly into the highest temperature zone and heated efficiently. The detail of this system can be found elsewhere [8]. Raw mg-Si and Ni powders are injected into the plasma jet at different feeding rates of 1 and 17 g/min that corresponds to approximately 1 kg/hr. The Si vapor is quenched in a water-cooled powder collection vessel. Si-NPs without Ni produced at 1 and 17 g/min are denoted hereafter as [S-1] and [S-17], respectively. Likewise, the particles with 5 at.% Ni addition at 1 and 17 g/min are denoted as [N-1] and [N-17], respectively.

The Si-NPs collected from the walls of the vessel are mixed with conducting reagents and binder to form slurry. This slurry is applied onto Cu foil. After being dried and pressed, the electrode is used as anode in a 2016 half-coin cells using Li metal as a counter electrode. The cells are cycled at a constant current of 0.1 mA (0.02C) for 1-3 cycles and 0.5 mA (0.1C) for the following cycles with cut-off potentials of 0-1.5 V.

3. Results and discussion

The crystallite Si size and the relative molar fraction of the Si, Ni and Ni silicide phases are evaluated using Rietveld analysis of XRD patterns of these plasma-sprayed particles. The results are listed in Table I. The crystallite Si size is nearly doubled as the feed-rate increases to 17 g/min. In the meantime, the relative amount of the Ni silicide, especially NiSi₂, increases for [N-17] particles. This indicates that the reaction between Si and Ni is accelerated at higher powder feeding rates. The particle size distribution of PS-PVD particles is measured by static laser light scattering. Irrespective of the Ni addition, the PS-PVD particles produced at 17 g/min seem to be less agglomerated, while the particles produced at 1 g/min have several μm large agglomerates.

Fig.1 shows the cooling curve in the vessel as solid line

Table I Relative molar fraction of Si, ni and Ni silicide in the PS-PVD particles, and the Si crystallite size, estimated by Rietveld analysis.

Samples	Si (at.%)	NiSi ₂ (at.%)	NiSi (at.%)	Ni ₂ Si (at.%)	Ni (at.%)	c-Si (nm)
[S-1]	100	-	-	-	-	22.3
[S-17]	100	-	-	-	-	54.8
[N-1]	96.45	0.90	0.70	0.88	1.06	21.6
[N-17]	94.12	3.65	1.01	0.74	0.86	41.5

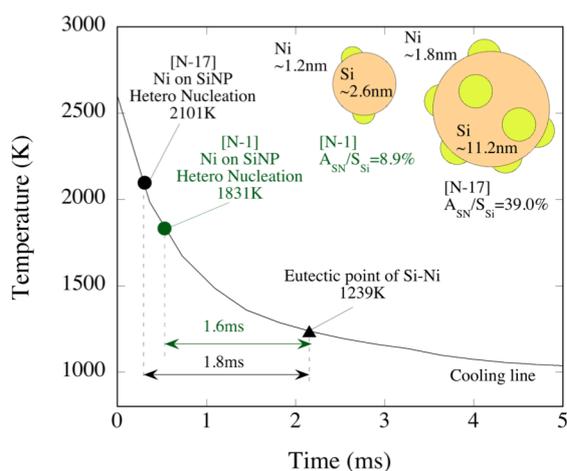


Fig. 1 Cooling curve in the vessel and schematics of Si-Ni nanoparticles at the heterogeneous nucleation temperature of Ni onto Si nanoparticle. A_{SN} represents the relative total area of the Si-Ni interface, and S_{Si} represents the surface area of Si nanoparticle.

and heterogeneous nucleation temperature of Ni on Si-NP, T_{Ni}^{Hetero} , as solid circles. T_{Ni}^{Hetero} is estimated to be 1831 K for [N-1] and 2101 K for [N-17]. From these nucleation temperatures, at 17 g/min, Ni is expected to attach onto Si-NP earlier and at higher temperature during cooling. This suggests that [N-17] particles can be exposed at higher temperature for longer time until the eutectic temperature in the Si-Ni system, compared with the case of [N-1]. Moreover, the ideal structure of Si:Ni nanoparticle at T_{Ni}^{Hetero} is also drawn in Fig.1. The relative total area of Si-Ni interface with respect to the surface area of Si-NP is increased at 17 g/min. These suggest that the reaction between Si and Ni can be enhanced further for [N-17].

Fig. 2 shows the cycle capacity of the coin cells assembling with plasma-sprayed particles as anodes. When the capacities of [S-1] and [S-17] compare, the cell containing [S-17] particles exhibits slightly improved capacity. Although the capacity of [S-17] decays a little faster due to the larger particle size, the less-agglomerated structures suppress the capacity drop in first several cycles, and this results in improved cycle performance.

In contrast, with Ni addition, the cell with [N-1] particles shows slightly higher cycle capacity than the cell using [S-1] particles. This capacity improvement is considered to be associated with directly attached Ni particle with epitaxial $NiSi_2/Si$ interface that helps to reinforce Si-NPs and retain capacity as reported in [7]. However, the capacity of [N-17] particles decays significantly, despite the including $NiSi_2$ phase as confirmed by Rietveld analysis. For [N-17] particles, nucleation temperature of Si and Ni rises, and larger amounts of Si are consumed to form Ni silicide resulting in the capacity decay. Therefore, the excess formation of Ni silicide needs to be suppressed to use the best of $NiSi_2$ phase.

4. Conclusion

The effect of high throughput production by PS-PVD on

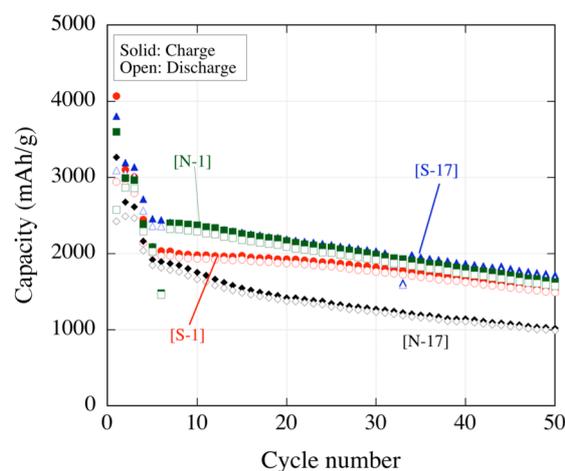


Fig. 2 Cycle capacity of plasma-sprayed particles.

formation of Si nanocomposite particles and the battery performance is investigated. In the case of Si feedstock processed, the size of nanoparticle increases to 50 nm. At 17 g/min, however, these particles become less agglomerated, and the capacity drop in the initial several cycles is suppressed. When Ni is added to Si feedstock, the cycle capacity is improved at 1 g/min due to the unique epitaxially attached Ni particle structure. However, at high powder feeding rate, the amount of Si consumed for Si-Ni reaction is increased as a result of elevated nucleation temperature. This eventually results in the reduced active Si material volume and thus significant capacity drop.

Therefore, for the simultaneous achievement of high throughputs and enhanced battery performance, vapor mixtures have to be quenched more rapidly to suppress the excess particle growth and Ni silicide formation.

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