Synthesis of Si-Ni composites by plasma spray PVD for negative electrode of lithium-ion batteries

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Abstract: The present work describes synthesis of the nanostructured Si-Ni composites for LiB anodes by plasma spray physical vapor deposition method. The X-ray diffraction analysis and X-ray photoelectron spectroscopy measurement of the resultant composites revealed that the formation of high electrical conductivity of NiSi2. Moreover, anodes prepared from the Si-Ni composites exhibited a discharge capacity as high as 1286 mAh/g with ~96% columbic efficiency after 50 cycles.

Keywords: Plasma spray, nanostructured Si-Ni composites, anode material, lithium ion battery.

1. Introduction

Si is one of the most promising candidate materials for lithium ion battery (LiB) anodes owing to the high theoretical capacity of 4200 mAh/g, more than 10 times higher than that of graphite which is now commonly used as an anode material in commercial LiB. However, presently, practical applications of Si as an anode material have two major limitations [1]. First, Si has poor cyclability because of the large volume change (~400%) that occurs during lithiation and delithiation. This large volume change can cause mechanical fracture and loss of electrical contact with the current collector, leading to a rapid capacity fade of the cell. Second, the low electrical conductivity of Si-based materials impedes fast lithiation [2].

To address the above issues, substantial effort has been focused on synthesizing nanostructured alloys and dispersing the active material in an inactive matrix to form composites. In this case, the inactive component plays a structural buffering role to minimize the mechanical stress induced by the large volume change of active silicon [3]. For instance, the nanostructured alloys such as Li-Si, Co-Si, Cu-Si, and Ti-Si, and composites such as Si/C, Si/TiN, Si-Ni, and Si/TiB2 were widely synthesized and characterized [2-6]. However, many studies on the electrochemical behavior of alloys and composites have reported just a slightly improvement in cycling performance [2-5].

The present work describes the use of plasma spray physical vapour deposition (PVD) to prepare nanostructured Si-Ni composites for LiB anodes. Herein, nickel silicides in the composites are expected to accommodate the volume changes and to insure good electronic and ionic conductivities of the electrode material. The morphology of the resultant composites was characterized using X-ray powder diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy, and transmission electron microscopy. Moreover, we tested the electrochemical performance of anodes prepared from Si-Ni composites by plasma spraying.
the raw materials after being homogeneously mixed using a pot mill rotator (Asone, PM-001). The molar content of nickel in the feed powders has been adjusted to 5 at.%.

The precursors were introduced at a feed rate of 1 g/min with argon as the carrier gas. The high enthalpy of the plasma enables the precursors to instantaneously evaporate. The vapours of the injected Si and Ni powders are transported with the plasma flow to the reaction chamber and become supersaturated because of the rapid temperature decrease in the tail flame which leads to homogeneous nucleation. Moreover, the supersaturated vapour easily condenses on the nuclei by heterogeneous condensation [8-10]. Thus, this technique provides an efficient and one-step synthesis of nanocomposite anodic materials for LiB.

The morphology of the composites was observed using transmission electron microscope microscopy (H-9000NAR Hitachi Japan) operated at 300 kV and scanning electron microscopy (SEM-4200 Hitachi Japan). The phase compositions of the composites were determined by X-ray Photoelectron Spectroscopy (ESCA-850 Shimadzu Japan) and powder X-ray diffraction (Bruker D2 Phaser) using monochromatic CuKα radiation.

### Table 1: Experimental conditions

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC power</td>
<td>9 kW</td>
</tr>
<tr>
<td>RF power</td>
<td>100 kW</td>
</tr>
<tr>
<td>Radial Ar</td>
<td>140 sclm</td>
</tr>
<tr>
<td>Tangential Ar</td>
<td>30 sclm</td>
</tr>
<tr>
<td>Radial H₂</td>
<td>50 sclm</td>
</tr>
<tr>
<td>Deposition time</td>
<td>10 min</td>
</tr>
<tr>
<td>Chamber pressure</td>
<td>500 Torr</td>
</tr>
</tbody>
</table>

2.2. Electrochemical measurement

The prepared composites were directly used as active materials after passing them through a 45-μm sieve. For electrochemical studies, electrodes were prepared from a mixture of 65 wt.% active material, 15 wt.% conductive carbon, and 25 wt.% binder in N-methyl-2-pyrrolidone (NMP). The slurry was applied by doctor blade onto an etched copper foil current collector, and oven-dried at 110 °C for 60 min.

The electrochemical performance of the composite anode was investigated with a 2016 cell assembled in an argon-filled glove box. Lithium metal foil was used as the cathode, and the electrolyte was a 1-M solution of LiPF₆ in ethylene carbonate/diethyl carbonate (EC/DEC, 1:1 v/v), with a polypropylene-based membrane as the separator. The charge-discharge cycles were performed at 0.1 C-rate for 1–3 cycles and 0.5 C-rate for 4–50 cycles at room temperature using an ACD01 charge-discharge battery test system.

3. Results and discussion

3.1. Characterization of the composites

The XRD patterns of composites prepared with 5 at.% Ni in the feed powders is shown in Fig. 2. For comparison, the standard XRD patterns of Ni₅Si₂, Ni₅Si, and Ni₂Si are also shown in Fig. 2, which were derived from Ref [11]. The XRD patterns of the prepared composites indicate that all the diffraction peaks can be ascribed to Si and/or Ni₅Si₂. However, the diffraction peaks of Ni powder and nickel silicide of Ni₂Si and NiSi were not observed from Table 1 Experimental conditions.

![Fig. 2 XRD patterns of the prepared composites.](image)

![Fig. 3 Normalized XPS spectra of Ni 2p₃/2 peaks (a) standard Ni and (b) the prepared composites.](image)

![Fig. 4 Normalized XPS spectra of Si 2p peaks of the prepared composites.](image)
the prepared composites. As shown in Fig. 2, the diffraction peaks of Si and NiSi\(_2\) are very close together, and are difficult to distinguish from each other at low NiSi\(_2\) content. Therefore, we further analyzed the existence of NiSi\(_2\) in the prepared composites using XPS, as shown in Figs. 3 and 4. The high-resolution Ni 2p3/2 spectrum obtained from both of the pure Ni (Fig. 3a) and the prepared composites (Fig. 3b). The position of the Ni 2p3/2 peak of elemental Ni was set at 851.7 eV. Compared with the peak of the pure Ni in Fig. 3a, the Ni 2p3/2 peak is moved to higher binding energy position of 853.2 eV, as shown in Fig. 3(b), which is correspond to the NiSi\(_2\) [12]. It is known from equilibrium phase diagram that NiSi\(_2\) is the incongruent phase that forms through peritectic reaction [13]. This is contrast to the common observation that congruent phases are formed preferentially by rapid quenching of high-temperature metal vapor mixture during plasma spraying PVD [7-10]. This fact indicates that NiSi\(_2\) phase form not via homogenous nucleation but via heterogeneous nucleation directly on the Si nanoparticles that form in advance. This could make these composites powders unique as evidenced later in electrochemical test. In Fig. 4 the Si 2p spectra present the peaks associated with bulk silicon, silicide, and silicon dioxide, indicating the interface Si was infinitesimally oxidized in the air.

Figures 5(a) and (b) display SEM images of the processors and the composites prepared with 5 at.% Ni content in the feed powders, respectively. In comparison with the precursors, shown in Fig. 5(a), the composites in Fig. 5(b) exhibit a higher fraction of large, irregular, and spherical particles. This indicates that complete evaporation of raw powder in plasmas and aggregation occurred during plasma treatment. The structures of the prepared composites were observed further by TEM, as shown in Figs. 5(c) and (d). Fig. 5(d) is a magnification TEM image of the large particles. The particles exhibit a dense internal structure, containing many smaller grains in Fig. 5(c). Such structures have a large grain boundary surface area and a short diffusion path, useful for improving their performance in LiB [2,5]. The magnification TEM image in Fig. 5(d) shows that the composite products were a many nanoparticle aggregation in diameter of ~50 nm.

3.2. Electrochemical investigation

Cycle performance of anode prepared from the Si-Ni composites is shown in Fig. 6. For comparison, Si aggregates anode prepared using plasma spray PVD with only silicon (0 at.% Ni) as the raw material was also tested. As can be seen, the cyclic performance of composite anodes prepared with 5 at.% Ni concentration provides direct evidence of the excellent lithium storage capabilities of these materials; the rechargeable capacity 1286 mA\(\cdot\)h/g after 50 cycles, which is approximately 400 mA\(\cdot\)h/g higher than that of Si aggregates anode. Moreover, the obtained results in this study were more than 4 times higher than
that of conventional graphite anode. The improvement in electrical performance of the Si-Ni composite anodes is attributed not only to the nanoscale structure of the composites but also to their high electrical conductivity.

The columbic efficiency of the Si-Ni composites anode is shown in Fig. 7. In the case of 1-5 cycles, the columbic efficiency was increased significantly. The low columbic efficiencies for the few first cycles can be attributed to irreversible trapping of inserted Li ions by host materials, formation of the solid electrolyte interface (SEI) layer, or the loss of electrical contact between the electrode material and the current collector [4,5]. For the subsequent cycles (6-50), the composite anode exhibits very stable capacity retention behavior and high columbic efficiency of >96%.

Figure 8 displays voltage profile and corresponding differential capacity plot (DCP) of the prepared electrode when discharged and charged for first, third, fifth and tenth cycles. Only one broad peak at 0.07 V for Si-Ni composites was observed during the first discharge (lithium alloy), which was due to the phase transition of amorphous Li, Si to crystalline Li, Li, 15. At the end of the first lithiation, all of the material has been transformed into amorphous Li, Si. In contrast to the first discharge, three peaks were observed at 0.25, 0.08, and 0.01 V in the third cycle and subsequent cycles. The peaks at 0.25 and 0.08 V may be due to the phase transitions between amorphous Li, Si. Herein, the intensities of the peaks of the Si-Ni-silicide composites remained almost the same, showing the great enhancement of the cycling stability.

4. Conclusions

We prepared nanostructured Si-Ni composites using plasma spray PVD. Moreover, anodes prepared from these composites are able to deliver as much as 1286 mAh/g with >96% columbic efficiency after 50 cycles. This observation indicates the potential of the development of nano-sized alloy composite electrode materials with high capacity at low cost using plasma spraying.

5. References