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Short communication

In situ transmission electron microscopy observations of lithiation of spherical silicon nanopowder produced by induced plasma atomization

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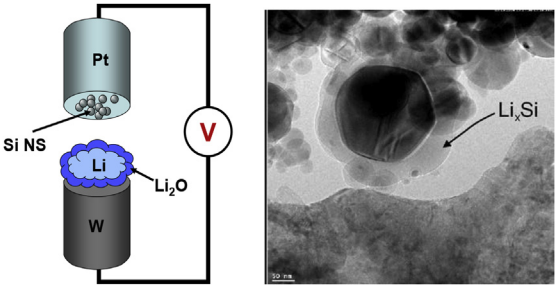
HIGHLIGHTS

- Morphological characterisation of crystalline silicon synthesized by induced plasma atomization.
- Electrochemical measurements of high gravimetric capacity nano Si (4900 mAh/g).
- *In situ* TEM of single particle volume expansion using open-cell configuration.

GRAPHICAL ABSTRACT



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ABSTRACT

Composite Li-ion anode can be fabricated using silicon nanopowders synthesized by induced plasma atomization. Properties of such nanopowder were characterized by physical and electrochemical methods. Primary particles were crystalline with spherical shape and the typical diameter ranging from 50 to 200 nm. The Si nanopowder showed a high gravimetric capacity (4900 mAh/g) at first discharge and around 12% irreversible loss of lithium. In addition, observations of a single silicon particle made by *in situ* TEM permitted to compare the volume change during lithiation with other silicon anode nanomaterials.

1. Introduction

Carbonaceous materials are typically used in the negative electrode for Li-ion batteries. Because higher energy Li-ion batteries are demanded in electric vehicles, alternative electrode materials are being sought. Silicon is an attractive alternative material due to its high theoretical gravimetric capacity density of 4200 mAh/g when the $Li_{4.4}Si$ phase is formed [1,2]. In spite of this advantage, Si-based anodes show numerous problems that prevent their use in commercial Li-ion batteries. A significant capacity fade occurs during cycling and low coulombic efficiency is obtained. The

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performance degrades during the first few cycles due to the large volume change during charge/discharge. It ultimately leads to mechanical degradation and loss of electrical contacts [1,3,4]. However, when small particles [5,6] or thin-films [7,8] containing silicon are used as the negative electrode, performance and cycle life improves markedly. It is recognized that nanoscale materials can be reversibly deformed far beyond the limit of large-grained materials; this phenomenon is called superplasticity [9]. Moreover, recent *in situ* methods based on transmission electron microscopy have provided new insights into the expansion/contraction during lithium insertion/extraction in silicon nanoparticles and nanowires [10–12].

Large-scale application of silicon as anode in Li-ion batteries will require suitable synthetic methods. An attractive method for the fabrication of silicon nanopowders, from micrometric silicon particles, is based on induced plasma atomization because of the high temperature processing capability and high quenching rates that can be achieved [13]. Nanoparticles produced by plasma have high crystalline structure, spherical morphology, narrow particle size distribution and high purity [14].

This study reports the synthesis of silicon nanopowders by induced plasma method and both their physical and electrochemical characterization. In addition, the volume change during lithiation of a single silicon particle in the presence of smaller particles is investigated by *in situ* transmission electron microscopy (TEM) to be compared with other silicon anode nanomaterials.

2. Experimental

2.1. Powder synthesis

Spherical silicon nanopowder (Si NS) was synthesized by induced plasma atomization using a 3 MHz, 60 kW RF plasma torch (Tekna Plasma Systems). The powder was prepared from a micrometric 99.999 wt% pure (5N) silicon powder in a pure evaporation-condensation manner. More specifically, the micrometric silicon powder was heated and evaporated in the plasma torch. The resultant vapors were subsequently quenched very rapidly and homogeneous nucleation led to the formation of a fine nanopowder aerosol (Fig. 1).

To prevent any surface contamination (or passivation), handling of the nanosilicon powder and its packaging in metal-plastic bags were done in an argon-filled glove box.

2.2. Powder characterization

The silicon nanopowder morphology was observed using a Hitachi S-4700 scanning electron microscope with a field emission electron gun (FE-SEM) and a FEI Titan 80-300 scanning/transmission electron microscope (S/TEM), which is fitted with a probe forming lens aberration corrector and operated at 300 kV. Phase composition and structure were analyzed by using a Rigaku Mini-Flex 600 X-ray diffractometer (XRD) with a cobalt source. The particle size was measured by laser scattering method with a Horiba LA-950V2 and by BET gas adsorption method with a Quantachrome Quadrasorb SI.

2.3. Electrode preparation and coin cell assembly

The silicon nanopowder was mixed with acetylene carbon black (Denka Black) and sodium alginate (Aldrich) with a ratio of 50:25:25 using water as solvent to a viscosity of ~8500 cP for coating. A high-energy mixer (SPEX Certiprep) was used to de-agglomerate and mix the nanopowder. The slurry was coated on a copper foil to achieve loadings of approximately 0.6 mg/cm^2. The electrode was pre-dried at 75 °C in a convection oven and then carefully dried at 110 °C under mild vacuum for 12 h.

CR2032 coin cells (Hohsen) were assembled in a He-filled glove box using a Celgard 3501 separator and 200 μm lithium foil anode (FMC Lithium). The electrolyte was composed of 1 M $LiPF_6$ in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (7:3 by volume) with the addition of 2 V% of vinylene carbonate (VC) (Ube). The cells were galvanostatically charged and discharged at 25 °C using a VMP3 cycler (Bio-Logic) with a C/24 rate for formation cycles and a C/6 rate for life cycles over the voltage range of

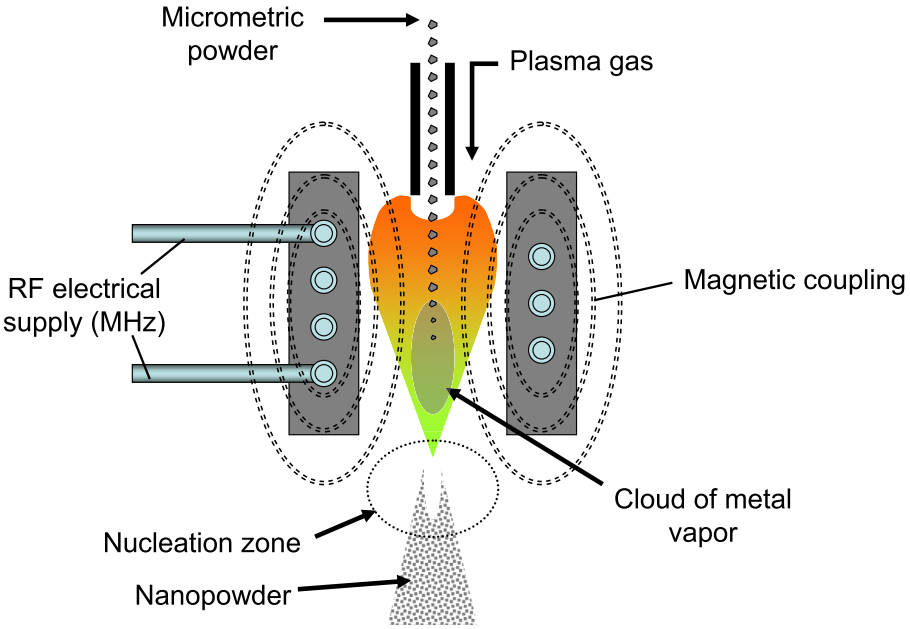

Fig. 1. Schematic of nanopowder synthesis using induction plasma torch.