Journal of Power Sources 299 (2015) 529–536

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Silicon as anode for high-energy lithium ion batteries: From molten ingot to nanoparticles

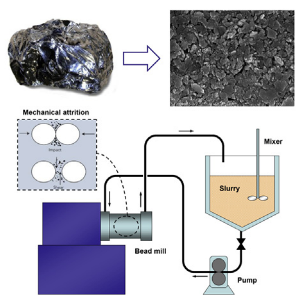
Dominic Leblanc [a, b], Pierre Hovington [a], Chisu Kim [a], Abdelbast Guerfi [a], Daniel Bélanger [b], Karim Zaghib [a, *]

[a] Hydro-Quebec Research Center (IREQ), 1800, Boul. Lionel-Boulet, Varennes, QC J3X 1S1, Canada
[b] Université du Québec à Montréal (UQÀM), Case Postale 8888, Succursale Centre-Ville, Montréal, QC H3C 3P8, Canada

HIGHLIGHTS

- Nanosilicon powder produced from mechanical attrition using bead mill.
- High gravimetric initial capacity of 2400 mAh/g at C/24.
- Improved cycle stability over micro-size silicon with sodium alginate binder.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 25 June 2015
Received in revised form
7 September 2015
Accepted 9 September 2015
Available online xxx

Keywords:
Silicon nanopowder
Anode
Li-ion battery
Mechanical attrition

ABSTRACT

In this work, we demonstrate that a new mechanical attrition process can be used to prepare nanosilicon powder from metallurgical grade silicon lumps. Composite Li-ion anode made from this nanometer-size powder was found to have a high reversible capacity of 2400 mAh g^{-1} and an improved cycling stability compared to micrometer-sized powder. It is proposed that improved battery cycling performance is ascribed to the nanoscale silicon particles which supresses the volume expansion owing to its superplasticity.

1. Introduction

Carbonaceous materials with a typical capacity of 370 mAh g^{-1} are used as anode material for conventional Li-ion batteries (LIB). Because higher energy-density LIBs are needed in longer range electric vehicles, alternative electrode materials with higher capacity are in demand. It has been known for a long time that silicon negative electrode provides higher energy density. Silicon is an attractive alternative material due to its high theoretical capacity of 4200 mAh g^{-1} when the $Li_{22}Si_5$ phase is formed [1]. In spite of this advantage, Si-based anodes show numerous problems that prevent the material from being commercially used in Li-ion batteries. When micrometer-size particles are used, a significant capacity fade occurs during cycling due to the large volume change (~300%) from alloying/de-alloying that induces cracks and a failure

* Corresponding author.
E-mail address: zaghib.karim@ireq.ca (K. Zaghib).

http://dx.doi.org/10.1016/j.jpowsour.2015.09.040
0378-7753/

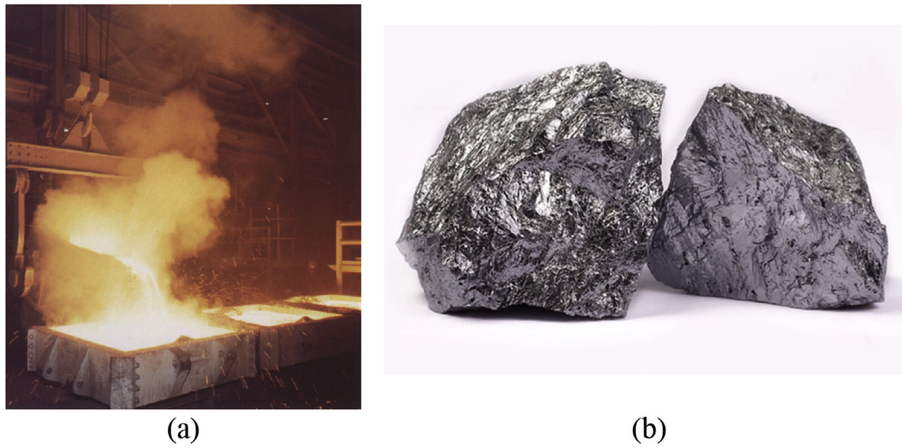


Fig. 1. (a) A typical liquid silicon casting operation and (b) MG-Si lumps from smelter.

of electrical contacts. However, when small particles [2,3] or thin-films [4,5] containing silicon are used, performance and cycle life are improved markedly. It is recognized that nanoscale materials are reversibly deformed far beyond the limit of large-grained materials; this phenomenon is called superplasticity [6].

Most of nano-Si techniques in the literature rely on processes which are neither economically viable for the commercial products nor easily scalable for the volume production. Large-scale application of nanosilicon in LIBs requires suitable synthetic methods. The objective of this work is to develop an easy-to-launch source of nanosilicon from an abundant and low-cost material: metallurgical grade silicon (MG-Si). In this manuscript, we report on the synthesis and use of silicon nanopowder made by a conventional mechanical milling process to produce cost-effective, high-energy density LIB anode.

2. Theory of MG-Si production

2.1. MG-Si an abundant and low-cost feedstock

Silicon composes more than 25 wt% of the Earth's crust and is the second most abundant element, exceeded only by oxygen [7]. MG-Si is produced in an AC submerged electric arc furnace from the carbothermal reduction of silicon dioxide [8] by a reaction that, in an idealized form, can be written as:

$$SiO_2 + 2C \rightarrow Si + 2CO$$

The carbonaceous reductants consist of a mixture of coal, charcoal, petroleum coke, and wood chips. Silica is added to the furnace in the form of quartz, quartzite, or gravel. United States has an abundance of silica and coal deposits for the production of silicon metal.

MG-Si is used primarily as an alloying element in the aluminum industry and, in the chemical industry as a precursor for polydimethylsiloxane polymers (commonly referred to as silicones). The semiconductor and solar energy industries, which manufacture semiconductor chips for computers and photovoltaic cells from high purity silicon, respectively, account for only a small percentage of silicon demand. For the year 2014, the U.S. Geological Survey (USGS) estimated U.S. silicon production was 359,000 mt [9] and the world total silicon production was 7,680,000 mt, with an average price of 1.40 US$ per pound in 2010 [10].

2.2. Molten ingot production

The elemental composition of metallurgical silicon is controlled by a careful selection of raw materials. A typical analysis of tapped

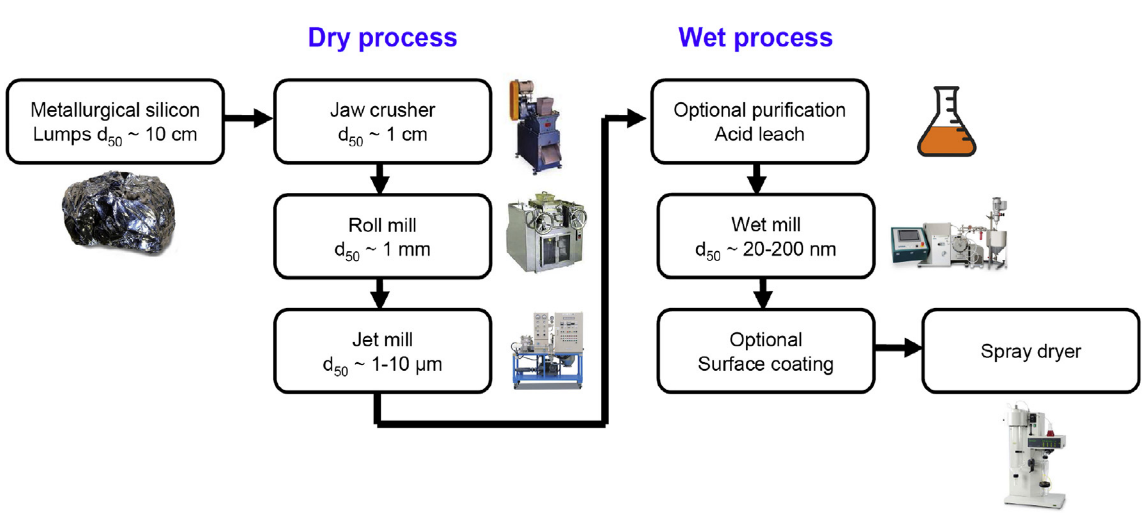


Fig. 2. Flowchart for preparation of MG-Si nanopowder from lumps by mechanical attrition.