

A novel Process for Preparation of High-Energy and High-Power Composite Anodes

G-A. Nazri and M. Nazri
GM R&D Center, MC: 480-102, Warren,
Michigan 48090-9055, e-mail
g.nazri@gm.com

A novel process has been developed to prepare high energy density anodes for rechargeable lithium batteries. The process involves formation of metal and alloy clusters embedded in a conductive matrix. The metal and alloy clusters are produced within the conductive matrix through reaction of the appropriate metal halides with Si (or P), forming a volatile Si halides (or phosphorus halides). Composites of several sp metals capable of alloying with Li such as Pb, Sn, Sb, and Bi have been produced with a variety of matrices, including graphitic, carbonaceous and glassy materials. Electrochemical tests of these composite anodes in Li cells demonstrate significantly superior energy capacity compared to the LiC₆ anodes currently used in commercial lithium batteries.

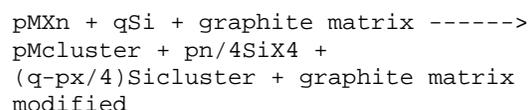
Current rechargeable lithium batteries use carbon or graphitic anodes (LiC₆) with maximum energy density of about 372 mAh/g. The use of metallic lithium, with much higher energy density, has not been successful. been used in the past. Lithium alloys have also been examined as candidate anodes for lithium batteries. However, due to degradation of the electrode during cycling, they have not been developed to a commercial product.

We report here development of a process to produce small metal and alloy clusters within conductive matrix. Preparation of composite anodes involves reaction of suitable metal halides with Si or P powders. This process will incorporate both metallic and/or nonmetallic elements and alloys in the matrix. The composite provides a unique composition and structure that allows alkali metals, such as lithium, to be reversibly inserted and extracted from the composite matrix electrode.

This process significantly, facilitates control of the shape and size of the active particles within the matrix. Therefore, energy density (related to metal concentration) and rate capability (related to cluster size) of the electrode can be tailored with this process.

The synthetic process involves reaction of metal halides and silicon powder. The silicon and metal halide are premixed with the matrix material and heat treated at a temperature close to the melting point of the metal halide. Near the melting temperature of the halide, silicon powder reacts with the metal halide to produce gaseous Si halides and metal clusters. Suitable metal halides include metals from the third, fourth, and fifth row of groups III, IV, and V of the periodic table. Silicon can be substituted

by other elements, such as P, which also generate volatile halide compounds at the temperature of the reaction zone. A typical reaction can be illustrated as



The temperature of the reaction is usually close to the melting point of the metal halide. The reaction rate is driven toward completion as the Si halides escape from the reaction zone. By adjusting the ratio of the metal halide to silicon concentration, the quantity and size of metal clusters and excess silicon can be controlled to optimize the battery electrode performance.

The lithium extraction capacity of the Pb/Si containing composite electrode was 872 mAh/g at 0.1 mA/cm², and 610 mAh/g at 3mA/cm². The energy capacity of this typ of anode is much higher than that of typical lithium battery with carbonaceous anodes.

In addition, the process developed in this work significantly reduces the initial irreversible capacity of the anode. This derives directly from selective etching and removal of bonded and trapped impurities from graphite by reactive SiCl₄, produced during the reaction. Analogously, antimony chloride can be used as the metal halide. The reversible capacity for lithium extraction of electrode containing Sb/Si was 815 mAh/g.

Use of other elements, instead of Si to form volatile and reactive halides are possible. Use of other halides of Pb, Bi, Sn, and Sb are also possible. Use of alloying elements may also produce clusters of small sizes, and alloying elements can be utilized in the same process. Several examples will be discussed.