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Review

Nano- and bulk-silicon-based insertion anodes for lithium-ion secondary cells

Uday Kasavajjula[a], Chunsheng Wang[a,**], A. John Appleby[b,*]

[a] *Department of Chemical Engineering, Center for Manufacturing Research, Tennessee Technological University, Cookeville, TN 38505, USA*
[b] *Center for Electrochemical Systems and Hydrogen Research, Texas A&M University, College Station, TX 77843-3402, USA*

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Abstract

The increase in energy density and power density requirements for lithium-ion secondary cells for commercial applications has led to a search for higher capacity electrode materials than those available today. Silicon would seem to be a possible alternative for the graphite or carbon anode because its intercalation capacity is the highest known. However, the large capacity fade observed during initial cycling has prevented the silicon anode from being commercialized. Here we present a review of methodologies adopted for reducing the capacity fade observed in silicon-based anodes, discuss the challenges that remain in using silicon and silicon-based anodes, and propose possible approaches for overcoming them.

Keywords: Silicon anode; Lithium-ion batteries; Volume changes; Cycle life

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Contents

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[*] Corresponding author. Tel.: +1 979 845 2033; fax: +1 979 845 8281.
[**] Corresponding author. Tel: +1 931 372 3678; fax: +1 931 372 6345.
E-mail addresses: ajappleby@gmail.com (A.J. Appleby), cswang@tntech.edu (C. Wang).

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1. Introduction

Lithium-ion (Li-ion) cells are now the most widely used secondary battery systems for portable electronic devices. Compared to conventional aqueous rechargeable cells, such as nickel–cadmium and nickel metal hydride, Li-ion cells have higher energy density, higher operating voltages, lower self-discharge, and lower maintenance requirements [1]. These properties have made Li-ion cells the highest-performing available secondary battery chemistry. However, due to miniaturization and other advances presently occurring in the portable device industry, and to use their advantages for aerospace, military, and automobile applications, their mass capacities (Wh kg^{-1}), and energy densities (Wh l^{-1}) require a further increase. This can be carried out by replacing the widely-used lithium cobalt oxide cathodes and carbonaceous anodes with higher performance electrode materials. In general, the total mAh g^{-1} capacity of Li-ion cells may be expressed in terms of anode and cathode capacity as follows:

$$\text{Total cell (mAh g}^{-1}) = \frac{1}{(1/C_A) + (1/C_c) + (1/Q_M)} = \frac{C_A C_C Q_M}{C_A Q_M + C_C Q_M + C_A C_C}$$

where C_A and C_C are the theoretical specific capacities of the cathode and anode materials, respectively, and $1/Q_M$ is the specific mass of other cell components (electrolyte, separator, current collectors, case, etc.) in g mAh^{-1}. $1/Q_M$ will vary with cell geometry and dimensions, and will include any failure to obtain the theoretical capacity values and any other excess required, e.g., to provide excess cathode material for formation of the surface electrolyte interphase (SEI) film at the anode. For carbon, C_A is 372 mAh g^{-1}, and for $LiCoO_2$, C_C is 135 mAh g^{-1}. For the Sony 18650G8 cell (2550 mAh, 46 g), Q_M may be calculated to be 130.4 mAh g^{-1}. A similar calculation may be performed in terms of mAh cm^{-3}.

So far, specific capacities between 160 and 200 mAh g^{-1} may be obtained with new cathode systems such as $LiMn_{1-x}Mi_xO_2$ [2], $Li[Ni_xCo_{(1-2x)}Mn_x]O_2$ [3], defective Li–Mn–O spinels [4], olivine $LiFePO_4$ [5,6], and related materials. These correspond to a 9–18% increase in total mAh g^{-1} capacity over today's cells, which is insufficient to satisfy requirements. Since finding suitable cathode materials with higher capacities has been a difficult issue, higher performance Li-ion cells will require anode materials with considerably higher specific capacities than those of carbons or graphites.

The total cell capacity as a function of C_A is shown in Fig. 1 for C_C values of 140 and 200 mAh g^{-1} and for Q_M = 130.4 mAh g^{-1}. A slow increase in total capacity is observed until C_A reaches 1200 mAh g^{-1}, after which improvement becomes negligible. At this C_A value, total cell capacities will be 63.9 and 74.1 mAh g^{-1} for C_C equal to 140 and 200 mAh g^{-1}, respectively. However, if anode porosity can also be reduced, allowing reduction in the total amount of electrolyte (e.g., for Q_M increased by one-third to 173.9 mAh g^{-1}), the corresponding total cell capacities will be 72.9 and 86.3 mAh g^{-1}.

This makes it clear that to obtain a noticeable improvement in the specific capacity of Li-ion cells, it is essential to replace carbonaceous anodes with anodes having capacity on the order of 1000–1200 mAh g^{-1} [7]. Experimental work on anodes using chemical elements which form alloys with lithium was started in early 1960s. In 1971, Dey [8] found that lithium can be electrochemically alloyed with a number of metals at room temperature, including Sn, Pb, Al, Au, Pt, Zn, Cd, Ag, and Mg. However, the alloying process resulted in complete disintegration of the electrodes and loss of electronic contact. Similarly, Sharma and Seefurth [9] reported the formation of Li–Si alloys in high temperature cells operating in the 400–500 °C range. It was reported that the alloying process in silicon anodes results in formation of $Li_{12}Si_7$, $Li_{14}Si_6$, $Li_{13}Si_4$, and $Li_{22}Si_5$ alloys [10]. Study of the Li–Si binary system [9–11] indicated that each silicon atom can accommodate 4.4 lithium atoms leading to formation of $Li_{22}Si_5$ alloy, i.e., a specific insertion capacity of 4200 mAh g^{-1}, the highest among the above alloying elements. In addition to

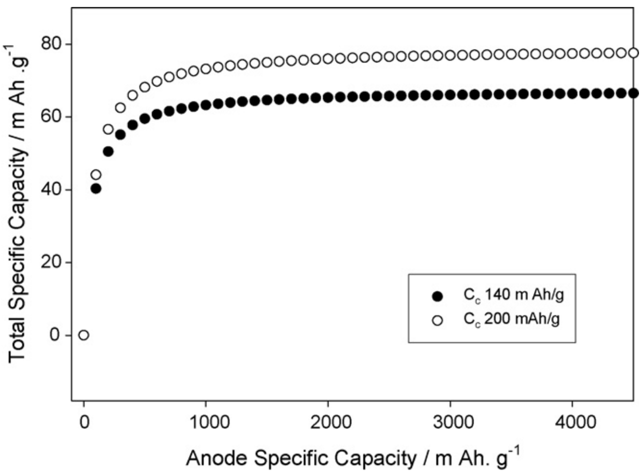

Fig. 1. Total capacity of 18650 Li-ion cell as a function of anode capacity (C_A), including masses of other required internal components and case. Capacities of cathodes considered were 140 and 200 mAh g^{-1}.