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Complementary X-ray and neutron radiography study of the initial lithiation process in lithium-ion batteries containing silicon electrodes

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ABSTRACT

Complementary *in operando* X-ray radiography and neutron radiography measurements were conducted to investigate and visualize the initial lithiation in silicon-electrode lithium-ion batteries. By means of X-ray radiography, a significant volume expansion of Si particles and the Si electrode during the first discharge was observed. In addition, many Si particles were found that never undergo electrochemical reactions. These findings were confirmed by neutron radiography, which, for the first time, showed the process of Li alloying with the Si electrode during initial lithiation. These results demonstrate that complementary X-ray and neutron radiography is a powerful tool to investigate the lithiation mechanisms inside Si-electrode based lithium-ion batteries.

1. Introduction

In operando and nondestructive methods of investigation and visualization are valuable for the study of lithium ion batteries (LIBs), which are believed to meet the future power requirements from consumer electronics to large-scale energy storage systems [1–5]. Previous *in operando* visualizations of LIBs have been realized through several dedicated electrochemical cells with "end/point" contact architecture between the active material [6], and ionic [7] or Li_2O electrolyte [8] as well as with an open-cell configuration [9]. However, these electrochemical cells with the above mentioned features are inherently different from commercially available LIBs [10]. On the other hand, commercial available LIBs have been investigated by *in situ* X-ray diffraction (XRD) [11], nuclear magnetic resonance (NMR) [12] and Raman spectroscopy [13]. Nevertheless, these analytical tools are specialized only in revealing structural and compositional information without imaging ability and therefore do not provide effective spatially resolved information about the underlying de/lithiation mechanism. Obviously, *in operando* and nondestructive diagnostic techniques with the ability to temporally and spatially visualize de/lithiation processes inside commercially available LIBs might open up new opportunities for high-capacity and high-power electrode materials for next-generation energy storage systems.

In the present work, by using a commercial CR2032 coin cell and a self-made radiography cell (radio-cell, which can adequately simulate a commercial CR2032 coin cell), we investigated and visualized the initial lithiation inside silicon-based LIBs via *in operando* X-ray and neutron radiography measurements. By X-ray radiography, we have observed a significant volume expansion of Si particles and Si electrode during the first discharge. Moreover, we also observed that lots of Si particles never undergo electrochemical reactions. These results were further confirmed by the neutron radiography. In addition, by employing the neutron radiography, for the first time, the process of the Si particles and Si electrode alloying with Li during the first discharge were shown. The obtained results presented here, which cannot be deduced from macroscopic electrochemical characterizations and conventional structure/composition-probing techniques, expand our understanding of the underlying lithiation mechanisms in commercial LIBs and could show the way to new design principles for high-performance next-generation LIBs.

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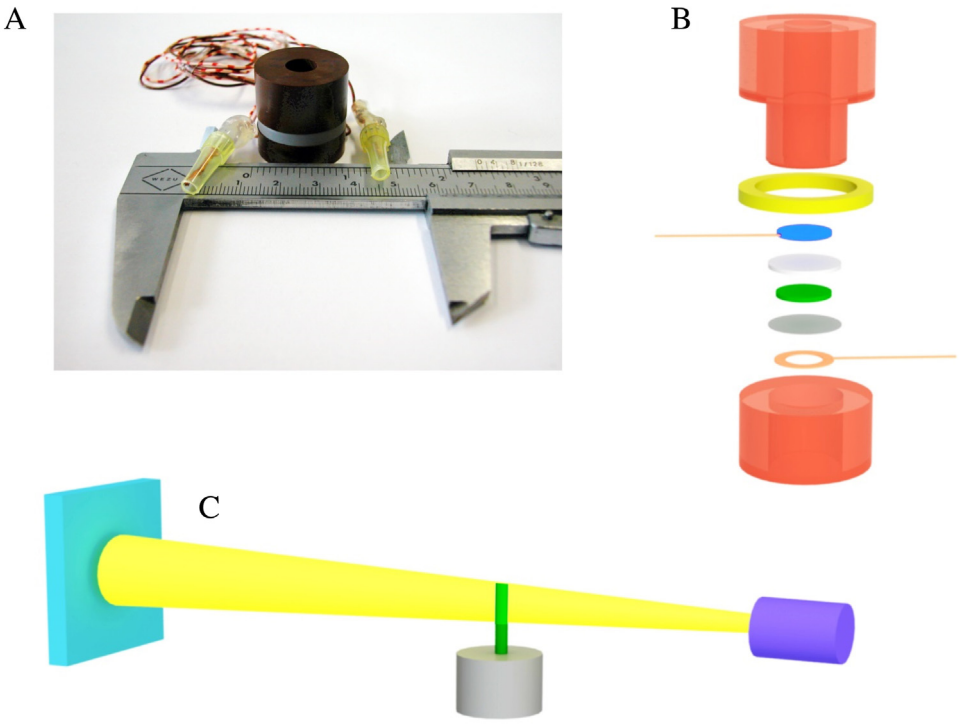

Fig. 1. A Photograph of the *in operando* X-ray radio-cell, B, Schematic illustration of the radio-cell as explained in the experimental section, C, Schematic representation of the experimental setup. From right to left: X-ray source (purple), beam (yellow), sample and sample table (green and gray), detector (blue). The neutron radiography setup is designed analogously. In both setups, the samples (X-ray radio-cell and neutron CR2032 coin cell) were penetrated by the x-rays and neutrons along their axes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

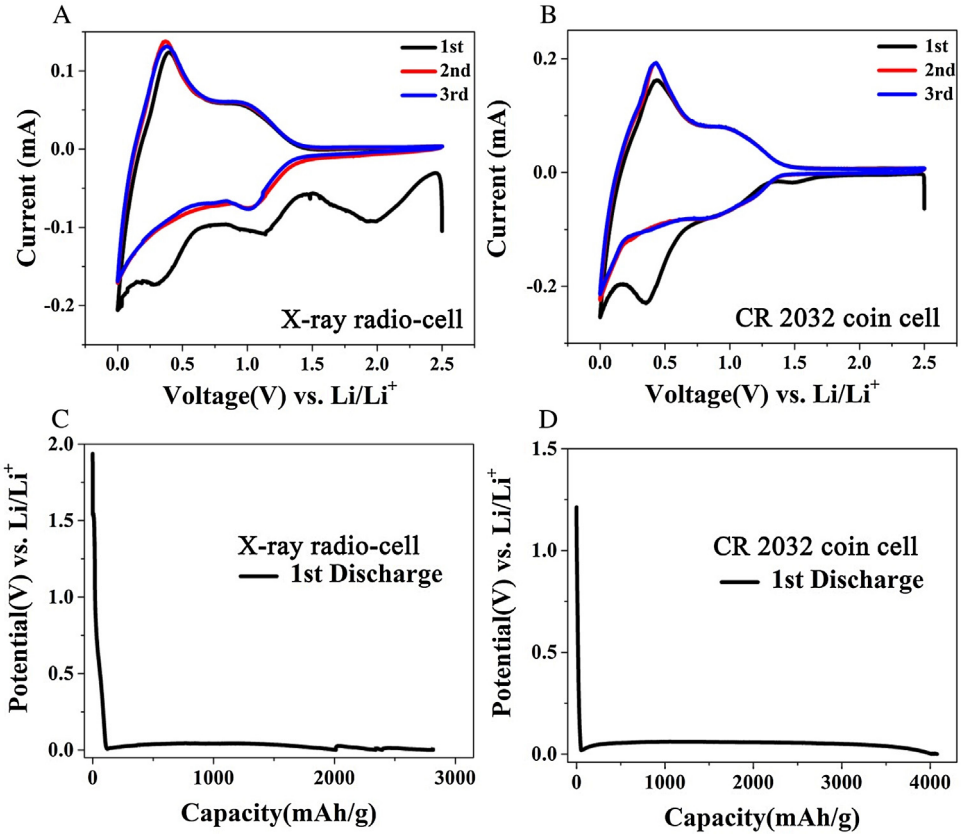

Fig. 2. Electrochemical characterizations of the two types of cells used: A and B, CV scans of the radio-cell and CR2032 cell; C and D, first discharge curves of the radio-cell and CR2032 cell. Figure A and C are revised with permission from Ref. [28].