学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Study on the Nanomechanical Properties of All-solid-state Li-ion Battery Electrodes during Charge and Discharge Processes

（全固体リチウムイオン電池電極の充放電過程におけるナノメカニクス特性に関する研究）

All-solid-state Li-ion batteries (ASSLIBs) are considered as the next generation of rechargeable batteries because of their high chemical safety, low flammability, and wide electrochemical potential window due to the adoption of solid electrolytes. The electrochemical performance of the electrodes in both conventional liquid-type Li-ion batteries (LIBs) and ASSLIBs is severely influenced by the nanomechanical durability of the electrodes and other battery components. However, the study on the quantification of nanomechanical property changes of battery electrodes during charge/discharge process, especially for ASSLIB systems, is very limited, apparently because of the unavailability of nanomechanical characterization techniques for *operando* measurements. Therefore, the work presented in this dissertation aims to clarify the nanomechanical phenomena in various LIB electrodes assembled in ASSLIB configurations during electrode charge-discharge process.

In this study, an *operando* bimodal atomic force microscopy (AFM) and *in situ* nanoindentation set-ups were developed to track the changes in the nanomechanical properties of electrodes during charge/discharge process performed under Ar atmosphere (O_2 < 0.1 ppm, H_2O < 0.1 ppm). Combined with other surface chemical and microstructural characterization tools, the nanomechanical phenomena in the battery electrodes assembled in ASSLIB configurations were successfully elucidated.

In **Chapter 2**, real-time nanomechanical mapping and topography imaging of amorphous silicon electrode in an ASSLIB configuration were carried out during the first electrochemical lithiation and delithiation using the developed *operando* bimodal AFM system. The electrochemical measurements were performed within a potential window of 0.01 — 1.20 V vs. Li^+/Li. The use of solid electrolyte with known mechanical properties as an internal standard was introduced for the first time in *operando* nanomechanical mapping of batteries to calculate the reliable Young's modulus value of the material after correction with the actual AFM tip—sample radius *R*. During the first lithiation, the formation of lithium silicide Li_xSi from pristine Si led to a significant decrease in the Young's modulus of the Si electrode, followed by a moderate decrease in the elastic modulus up to a capacity density of 3300 mAh g^{-1} (Li content x = 3.46 in Li_xSi). Subsequent delithiation resulted in a gradual increase in the elastic modulus, which stopped at a capacity density of 1467 mAh g^{-1} (Li content x = 1.54) possibly due to a considerable volume change caused by Li_xSi phase transition. The average Young's modulus values of the Li_xSi species with different Li content x obtained from

the *operando* bimodal AFM measurements are in good agreement with theoretical calculations using first-principles studies in the literature and with the *in situ* nanoindentation technique performed on electrochemically lithiated Si electrodes with different Li content *x*, demonstrating the accuracy and reliability of the technique.

In **Chapter 3**, anisotropic electrochemical lithiation/delithiation of Si single-crystal electrodes were studied using three different single-crystal electrodes with different surface orientations of (110), (100), and (111) assembled in an ASSLIB configuration. The electrochemical lithiation of Si (110) led to the formation of amorphous Li_xSi, which is simultaneously followed by a drastic elastic modulus reduction as the transformation from *c*-Si to *a*-Li_xSi proceeded. Meanwhile, the following delithiation did not seem to fully reverse the conversion of *a*-LixSi into *c*-Si. Characterization using X-ray photoelectron spectroscopy, time-of-flight secondary ion mass spectroscopy and scanning electron microscopy with energy dispersive X-ray spectrometry acquired on the electrode cross-sections revealed the formation of Li_xSi with identical Li content *x* for both lithiated Si (110) and (100) surfaces. On the other hand, two different Li_xSi layers with lower and higher Li contents *x* were detected on the electrochemically lithiated Si (111) electrode. Interestingly, a prolonged storage of cross-sectionally exposed lithiated Si electrodes inside an Ar-filled glove box suggested the formation of Li-diffused layers from the migration of Li-ions in the *a*-Li_xSi phase into the intact *c*-Si lattices. These phenomena imply that the lithiation of *c*-Si is not kinetically controlled by the diffusion of Li-ions into *c*-Si lattices.

In **Chapter 4**, *operando* nanomechanical mapping of $LiCoO_2$ (LCO) electrode in an ASSLIB configuration was conducted by the bimodal AFM, simultaneously with topography imaging, over four charge-discharge cycles. The measurements were performed within two different potential windows: 3.00 — 4.20 V vs. Li^+/Li for the first and second cycles, and 3.00 — 4.70 V vs. Li^+/Li for the third and fourth cycles. In general, the Young's modulus of the LCO electrode increased during the charge process, and decreased during the discharge process. Correlating with the dQ/dV curves, it was found that the transformation from the hexagonal—I/II (H1/H2) bi-phase to a single phase caused a dramatic elastic modulus increase/decrease during the charge/discharge process. However, the trend in the elastic modulus increase/decrease is opposite to the theoretical studies using the first-principles in the literature for layered-LCO materials. Although the exact cause of these phenomena is still under discussion, some possibilities are proposed such as the presence of surface contamination species on the electrode cross-section, a concomitant change in the elastic modulus of the material used as the internal standard, and/or a possible phase transformation of the layered-LCO particles to other phases because of intensive heat exposure during battery fabrication/cross-section polishing by focused ion beam.

Finally, the author expects that the work presented in this dissertation will shed light on various nanomechanical and physicochemical phenomena occurring in ASSLIB electrodes during charge/discharge process. Furthermore, the obtained nanomechanical property data can enrich the literature towards the realization of high-performance and mechanically durable electrodes for ASSLIBs. Future research outlook and directions were proposed according to the obtained results to gain comprehensive understanding of nanomechanical phenomena in battery electrodes and to optimize the electrochemical performance of various battery materials.