Optimizing Soft X-ray Spectroscopy for Silicon Anode Lithium Mapping

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Background incl. aims
Silicon has emerged as a promising candidate material for anodes in lithium-ion batteries due to its high theoretical capacity (about 10 times that of graphite). However, the practical use of silicon faces challenges related to its large volume expansion (~300%) upon lithiation, which leads to mechanical degradation and pulverization of the electrode over repeated charge/discharge cycles. This degradation results in loss of electrical contact, reduced cyclability, and capacity fading.

To address these issues and optimize silicon-based anodes, extensive research efforts are underway. One critical area of investigation involves understanding the distribution and behavior of lithium within silicon structures during battery operation. The distribution of lithium impacts the electrochemical performance and stability of the battery.
Various techniques are employed to study silicon-based anodes, including microscopy (e.g., scanning electron microscopy, transmission electron microscopy) for structural analysis, spectroscopy (e.g., X-ray diffraction, X-ray photoelectron spectroscopy) for chemical characterization, and electrochemical methods for performance evaluation. But the lithium distribution in the anodes cannot be found by these techniques.

However, soft X-ray emission spectroscopy (SXES) is a powerful technique that can provide detailed insights into the lithium distribution within silicon anodes with high sensitivity and spatial resolution. SXES allows researchers to map the chemical states of lithium in different states of charge (SOC) and investigate phenomena such as lithium trapping, where lithium becomes immobilized within the silicon structure, contributing to capacity loss and reduced battery efficiency over time.

By studying these fundamental processes, we aim to develop strategies to mitigate silicon degradation, enhance lithium utilization, improve battery cyclability, and ultimately advance the performance and lifespan of lithium-ion batteries. Furthermore, this study aims to establish optimal measurement conditions for SXES when analysing silicon-based anodes in lithium-ion batteries. By identifying and demonstrating the most effective measurement parameters and techniques, our goal is to streamline SXES procedures for battery research, facilitating broader adoption and use by other researchers in the field.

Methods
This research focuses on investigating silicon-based anodes derived from lithium-ion batteries fabricated in our laboratory using micrometer-sized silicon particles as the anode material. The batteries are assembled in coin cell half-cell format, featuring electrodes with a diameter of 18 mm. Assembly and subsequent disassembly for post-mortem analysis are meticulously conducted within an argon atmosphere glovebox to ensure controlled environmental conditions and prevent exposure to moisture and oxygen.

After disassembly, the electrodes undergo a thorough cleaning process using dimethyl carbonate (DMC) and are then dried under vacuum to eliminate any residual contaminants. For SXES analysis, a plane surface is essential. Therefore, a small portion of the electrode is extracted and a cross-section is meticulously prepared using the IB-19520CCP cross-section

polisher from Jeol under a cooled atmosphere at -120°C. The transfer from the glovebox to the ion polisher and subsequently to the scanning electron microscope (SEM) is carried out in an inert transfer vessel to ensure that the sample remains shielded from air or moisture throughout the process.

SXES investigations are performed using a JSM-IT800 SEM equipped with the JS50XL SXES detector from Jeol. This advanced setup enables high-resolution analysis of lithium distribution and chemical states within the silicon-based anodes.

Results

Our investigation revealed significant influences of probe current, excitation voltage, and exposure time on the spectroscopy results. Identifying optimal settings for these parameters is crucial, balancing high signal intensity with minimal sample degradation during measurements. Additionally, variations in lithium (Li) distribution within the analysed particles were observed. By employing mapping techniques, we were able to spatially resolve and identify regions enriched with lithium, providing valuable insights into its distribution within the silicon-based anodes. This detailed elemental mapping enhances our understanding of lithium behavior in battery materials and underscores the importance of precise measurement conditions in SXES for comprehensive battery research.

Conclusion

In conclusion, our study underscores the significance of SXES in elucidating the complex interplay between lithium distribution and silicon-based anode performance in lithium-ion batteries. The challenges associated with silicon's volume expansion upon lithiation and subsequent mechanical degradation highlight the critical need for advanced characterization techniques to optimize battery materials.

Through our investigation, we have demonstrated the pivotal role of SXES in mapping lithium distribution with exceptional sensitivity and spatial resolution. Our findings emphasize the impact of probe current, excitation voltage, and exposure time on spectroscopy results, emphasizing the importance of optimizing measurement parameters to balance signal intensity and sample integrity.

The observed variations in lithium distribution within the anode particles provide valuable insights for developing strategies to mitigate lithium trapping and enhance battery cyclability. By enhancing our understanding of lithium behavior at different states of charge, we aim to contribute to the development of more efficient and durable lithium-ion batteries.

Keywords:

SXES, Silicon-based Anodes, Lithium-Ion Battery

Reference:

[1] Y. Domi, H. Usui, A. Ando, K. Nishikawa, and H. Sakaguchi, "Analysis of the Li Distribution in Si-Based Negative Electrodes for Lithium-Ion Batteries by Soft X-ray Emission Spectroscopy," ACS Applied Energy Materials, vol. 3, no. 9, pp. 8619–8626, 2020, doi: 10.1021/acsaem.0c01238.

[2] X. Zhou, S. Qiao, N. Yue, W. Zhang, and W. Zheng, "Soft X-ray emission spectroscopy finds plenty of room in exploring lithium-ion batteries," Materials Research Letters, vol. 11, no. 4, pp. 239–249, 2023, doi: 10.1080/21663831.2022.2141586.