doi:10.1017/S1431927622007541
Microsc. Microanal. 28 (Suppl 1), 2022

Dynamic Observation of Nanovoid Formation in Lithium- Manganese-rich Cathode Materials with Solid Electrolyte

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Lithium-ion batteries (LIB) are becoming a dominant technology to power a wide range of applications such as small portable devices and electric vehicles. Despite a great success of LIBs, there are continuous request for improving the performance of LIBs to fulfill the needs from the customers: longer use per charge, fast charging, safe operation, etc. Cathode material is of importance to increase the capacity and energy density of LIBs since limited capacity from cathodes limit the capacity of overall LIBs. Among various cathode materials, lithium- and manganese-rich (LMR) layered oxide materials have been attracting much attention as it can deliver high capacity (~ 300 $mAhg^{-1}$) [1]. Conventional lithium transition metal oxide cathode materials deliver the capacity based on the redox from the transition metal. In case of LMR, additional redox from the oxygen occurs during electrochemical reactions, resulting in high capacity. Implementing solid-state electrolyte is a promising solution to address safety issue of current LIBs by replacing flammable liquid electrolyte with solid material [2]. In addition, solid-state electrolyte may enable us to increase energy density by using lithium-metal as anode. Thus, all-solid-state-batteries are actively being explored.

Microstructure of layered oxide cathode materials is a crucial factor for determining the performance of the material. Well-defined layered structure can provide lithium ions 2-dimentional diffusion path while structural deformation to cubic structures (spinel and rock-salt) may result in limiting Li diffusion. Therefore, structural evolutions of cathode materials have been studied with liquid electrolyte so far. However, how the structure of cathode evolves inside all-solid-state batteries during operation has not been probed yet. Also, understanding the interface between electrolyte and electrode are of importance as lithium ions' transfer across the boundary is essential for electrochemical reactions. Interfacial reactions between liquid electrolyte and cathode have been actively investigated and indeed, prior research demonstrated that microstructural changes at the interface strongly affect the performance degradation of the battery cells [3, 4]. However, the microstructure between cathode and solid electrolyte have not been thoroughly explored yet.

Here, we investigate the interfacial structure between $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ (LNMO, a typical LMR material) cathode and LiPON solid electrolyte. In addition, structural changes in cathode are tracked upon delithiation by applying bias on a cross-sectional solid-state cell using a Nanofactory sample holder. We find an inherent surface modification at the LNMO facing with LiPON, featuring the oxygen loss, Mn reduction, phase transition and the formation of nanopores. Intrinsic chemical reactions between LiPON and LNMO may be responsible for the changes in the surface of cathode even before starting electrochemical reaction. With applying voltage, lithium ions are extracted from LNMO. As a result, nanovoids starts appearing initially near the interface with LiPON and further lithium removal promotes growth of nanovoids toward the inside of the LNMO particle. Nanopores and nanovoids are different: nanopores exist at pristine state while nanovoids are formed during lithium removal. It is noteworthy that phase transition from layered structure to spinel or rocksalt structure is not found near the nanovoids. This work demonstrates the intrinsic surface reconstruction and dynamical structural changes of LNMO during charge in a solid battery with LiPON, which help to reveal the origin of performance fading in Li- and Mn-rich cathode inside ASSLB [5].

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[5] This research was supported by the Center for Functional Nanomaterials (CFN), which is a U.S. Department of Energy Office of Science User Facility, at Brookhaven National Laboratory under Contract No. DE-SC0012704.