CNMS Staff Science Highlight

Nanometer-Scale Mapping of Irreversible Processes on Solid Li-Ion Electrolytes

Scientific Achievement

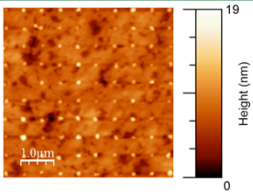
A new method to study electrochemical nucleation at the scale of less than 30 nm, which is about 1.5 orders of magnitude higher resolution than previously possible was demonstrated.

Significance

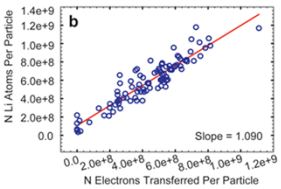
Nanoscale probing and manipulation of matter through electrical currents is a key step towards development of techniques for probing local ionic transport behavior as well as local electrochemical reactions.

Research Details

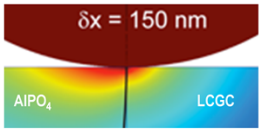
- Feedback-controlled atomic force microscopy (AFM) mapping modes employing current or height-displacement cutoffs were developed and demonstrated to study Li nucleation on a Li-ion conductive glass-ceramics with sub-30 nm resolution.
- Current control was demonstrated to study spatially resolved nucleation on nanometer scale.
- An increased nucleation rate at the boundaries between the crystalline $AlPO_4$ phase and amorphous matrix was observed and attributed to Li segregation at the interfaces .



AFM topology scan of current-compliance nucleated 100 Li particles on Li-ion conducting glass



Correlation between the number of Li atoms plated and electrons transferred during the reduction



Numerical modeling of the electric field distribution under the tip at the interface between the Li-ion conducting glass (LiCGC) with a hemispherical $AlPO_4$ inclusion

A. Kumar, T. M. Arruda, A. Tselev, I. N. Ivanov, J. S. Lawton, T. A. Zawodzinski, O. Butyaev, S. Zayats, S. Jesse, and S. V. Kalinin *Nature Scientific Reports.* (2013) DOI: 10.1038/srep01621.

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Highlight Narrative Text

Electrochemical processes associated with significant changes in material structure, lattice connectivity or composition typically proceed through the stage of new phase nucleation with subsequent growth of nuclei. A first step towards understanding and controlling reactions by currents is the elucidation and eventual control of the nucleation mechanism. Despite some recent progress, factors controlling nucleation kinetics, including the interplay between local mechanical conditions, microstructure and local ionic profile remained inaccessible. Furthermore, the tendency of the current probing techniques to interfere with the original microstructure prevents a systematic evaluation of the correlation between the microstructure and local electrochemical reactivity. In this work, spatial variability of the irreversible nucleation process of Li on a Li-ion conductive glass-ceramics surface, studied with sub-30 nm resolution, has been demonstrated. An increased nucleation rate at the boundaries between the crystalline $AlPO^4$ phase and amorphous matrix is observed and attributed to Li segregation at the interfaces. These studies open a pathway for probing mechanisms of electrochemical reactions in solids at the level of single structural defects and direct elucidation of electrochemical activities in nanoscale volumes.

Fig. 1 Current compliance approach principle for controlling nanoparticle formation was used. The image represents AFM topology map of nucleated 100 Li particles on Li-ion conducting glass (LiCGC) with general composition of (Li_2O-Al_2O_3-SiO_2-P_2O_5-TiO_2-GeO_2).

Each white dot is Li nanoparticle (20nm) size

Fig. 2 Correlation between the number of Li atoms plated and electrons transferred during the reduction

Fig. 3 Numerical modeling of electric field distribution in xz-plane under the tip apex δx = 150 nm at the interface between Li-ion conducting glass (LiCGC) with a hemispherical $AlPO_4$ inclusion. The presence of the inclusion with a lower dielectric constant(AlPO4) has no effect on the electric field in LiCGC at distances δx > 30 nm away from the inclusion.

Reference

Nanometer-scale mapping of irreversible electrochemical nucleation processes on solid Li-ion electrolytes

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