Spatially Resolved Ionic Diffusion and Electrochemical Reactions in Solids: A Biased View at Lithium Ion Batteries

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I. Introduction

Processes on different length scales determine battery performance.

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II. Concept

A majority of battery materials exhibit a volume change upon lithium intercalation or extraction. Measurement of local strains can help to distinguish between ionic and electronic transport which is difficult with current measurements.

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III. Operational regimes

Based on the operational regime, ESM can be used to investigate the ionic transport in electrode materials, the transport across the electrode/electrolyte interface, or the transport through the full battery.

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IV. Understanding the ESM signal for LiCoO₂

The local Li-ion concentration can be changed by the application of a local bias.

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V. The role of grain orientation and surface morphology

From analytical modeling above for high frequency regime:

Anisotropic ionic transport in LiCoO₂
- position-dependent τ and β determined by crystallographic orientation and surface morphology
- anisotropic volume expansion
- effective driving force acting on Li-ions depend on angle between field direction and direction of easy ionic transport

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VI. Describing ionic transport in LiCoO₂ thin film cathodes

Local activation energy mapping: temperature-dependent ESM

The temperature-dependent ESM signal for each individual pixel show linear curves in Arrhenius-type plot. From the slope, we can extract spatially resolved maps of the activation energy (after image alignment and Gaussian filter application to reduce pixel-to-pixel noise).

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VII. Future development: In-situ ESM in liquid

Technical challenge
- Application of electrical signals to tip surrounded by conductive medium.
- LiF(x) and LiF(x):mixed model for electromechanical probing in liquid.
- EFM shows stripping ferroelectric domain pattern in in-plane piezoresonance force microscopy (PFM) image.
- PFM has comparable estimation and detection principles to ESM.

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