Sublattice Melting in Confined Solid Electrolytes

Robert Grayson, Konstantinos Giapis (PI) Department of Chemical Engineering | rgrayson@caltech.edu

Caltech

Overview

Sublattice melts show exceptionally high ionic ("superionic") conductivity, but applications are limited by high operating temperatures and material specific chemical instabilities.



We aim to determine how nanoscale confinement can be used to tune the transport properties and thermodynamic stability of superionic sublattice melts. We use an anodic aluminum oxide platform to study confinement effects in a precisely controlled geometry.

Motivation

Sublattice melts exhibit high ionic conductivity and negligible electronic conductivity, making them ideal electrolytes for fuel cells and other electrochemical devices. Unfortunately, high operating temepratures are required to access the SLM phase. Lowering the SLM transition temperatures would facilitate their application in devices.







Cesium dihydrogen phosphate (CDP), for example, is used as a proton conducting membrane in solid-acid fuel cells. In CDP and other solid acids, the onset of chemical dehydration occurs near the SLM transition, and superionic conductivity is lost if dehydration is not checked. Lowering operating temperatures would hinder dehydration but the operating temperature is limited by the SLM transition temperature.

Sublattice Melting

for AgI).

SEM image of empty AAO

cylindrical nanopores (top:

birdseye, bot: crossection)

showing non-merging

Above the sublattice melting (SLM) transition in the solid acids (MHnXO4, with M = Cs, Rb and X = P, S) such as CDP, the tetrahedral oxyanions begin to rotationally librate almost as freely as in the melt. Consequently, the oxygens become dynamically disordered among crystallographically identical positions (a). The combination of rotation and proton hopping between minima of the symmetrical double-well hydrogen bond potential enables Grotthuss type H+ conduction (b).

Anodic Alumina Confinement Platform

electrolyte confinement because of the relative ease of

membranes, such as the one shown below, by anodization.

Pore size can be controlled through growth conditions and

surface chemistry. The solid electrolyte can be introduced to

wet etching. Atomic layer deposition enables control of

producing large area, highly uniform nanoporous

Anodic aluminum oxide (AAO) makes an ideal matrix for solid



Confined Solid Electrolyte

The bulk phase behavior of some solid electrolytes is nicely captured by a free energy function of the form [2]

$$G_{bulk} = G_{perf} + c\Delta G_{def}^0 - J c^{4/3} - TS_{config}$$

The equilibrium concentration of defects is found by minimizing G with respect to c. Depending on the magnitude of the defectdefect interaction energy J, two minima can appear in G, resulting in a first-order transition in the number of defects. In some cases, as in AgI, one sublattice remains stable across the transition and a sublattice melt forms.



Phenomenological free energy model capturing bulk behavior of the silver halides and PbF₂ [2]

In nanoscale confinement, free energy contributions from interfaces become appreciable

$G = G_{hulk} + [\gamma(c) + \Delta G_{DL}(c)]A/V$

where $\Delta G_{DL}(c)$ is the free energy of double layer formation and $\gamma(c)$ subsumes other surface contributions to the free energy. Both surface terms are expected to be a decreasing function of defect concentration and thus promote a transition in defect density at lower temperature.

New Superionics?

The surface terms in the energy balance play a role similar to the bulk defect-defect interaction energy, J, so that by tuning the confinement effect (namely, the magnitude and functional dependence on C), it may be possible to induce a superionic transition where none exists in the bulk. Promising materials for confinement induced sublattice melting include PbF₂ and CDP analogues KH₂PO₄ and NH₄H₂PO₄.

References:

[1] Boysen, D. A. Superprotonic Solid Acids: Structure. Properties, and Applications. (California Institute of Technology, 2004). [2] Hainovsky, N. & Maier, J. Phys. Rev. B 51, 15789–15797 (1995)

the pores as an aqueous solution (as for CDP) or as a melt (as Introduction of CDP solution from one side of the membrane results in crystallization CDP on the dry side, confirming pore filling.



SEM image of CDP crystallites grown through the membrane