

On Direct Observation of Diffusion by Aberration-Corrected HREM

J.T. McKeown^{*}, Y.-W. Kim^{**}, W.T. Petuskey^{***}, M. O’Keeffe^{***}, U. Weierstall^{*},
and J.C.H. Spence^{*}

^{*} Department of Physics, Arizona State University, Tempe, AZ 85287

^{**} School of Materials Science, Seoul National University, Seoul 151-742, Korea

^{***} Department of Chemistry, Arizona State University, Tempe, AZ 85287

Renewable energy sources such as wind and solar energy, despite their abundance and availability, are variable and uncontrolled [1]. A continuous supply of clean energy therefore requires a significant expansion in energy storage and conversion technologies. Solid electrolytes enable technologies that can both convert (fuel cells) and store (batteries) electrical energy. The ability of a solid electrolyte to conduct ions will depend largely on microstructural defects in the material. Line and planar defects can scatter ions or build up a space-charge layer to affect ionic conductivity. More fundamentally, the diffusion of ions will be closely correlated to point-defect diffusion. Our aim is to conduct dynamic *in-situ* experiments to study the role of defects in a solid electrolyte by direct observation of atomic motion at and along defects using aberration-corrected HREM. Since conductivity (σ) is proportional to jump frequency (Γ), experiments that directly observe jump frequency will provide fundamental insight into charge-transport processes in these materials.

In order to directly observe diffusion, 1) the atomic jump frequency must be sufficiently low, and 2) there must be a discernible contrast change in the high-resolution image when atoms move between adjacent atomic columns. The jump frequency (for vacancy mechanisms) is given by:

$$\sigma \propto \Gamma = \nu z X_v \exp\left[\frac{-E_a}{kT}\right]$$

where ν is an attempt frequency, zX_v is a concentration of vacant nearest-neighbor sites, and E_a is an activation energy. Jump frequencies are typically 10^3 s^{-1} at liquid-nitrogen temperatures to 10^{10} s^{-1} at room temperature for Na β -alumina [2]). It is well known [3-5] that the sodium ion content in Na β -alumina can be replaced with divalent cations such as Ca^{2+} , Sr^{2+} , Ba^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} , yielding higher activation energies and lower diffusion rates (Fig. 1). If only a partial ion exchange is performed, the larger atomic specie will provide a contrast difference in high-resolution images, which will allow the *in-situ* observation of cation diffusion in these solid electrolytes. The application of HRTEM and HR-STEM (Fig. 2) will be discussed, as well as complications that arise from radiation damage [6]. We are particularly interested in the possibility of correlated motion among the Pb^{2+} ions in their “liquid” sheets within the conduction planes [7,8].

References

- [1] X. Lu et al. *J. Power Sources* 195 2010 2431.
- [2] A.R. West in *Solid State Electrochemistry*, P.G. Bruce (ed.), Cambridge University Press, Cambridge, 1995.

- [3] Y.-F. Yu Yao, and J.T. Kummer. *J. Inorg. Nucl. Chem.* 29 1967 2453.
 [4] B. Dunn et al. *Solid State Ionics* 5 1981 203.
 [5] R. Seevers et al. *J. Solid State Chem.* 50 1983 146.
 [6] R. Hull et al. *Solid State Ionics* 9&10 1983 181.
 [7] S. Jacobsen et al. *J. Chem. Phys.* 78 1983 4154.
 [8] This work was supported by DOE Contract No. DE-FG03-02ER45996.

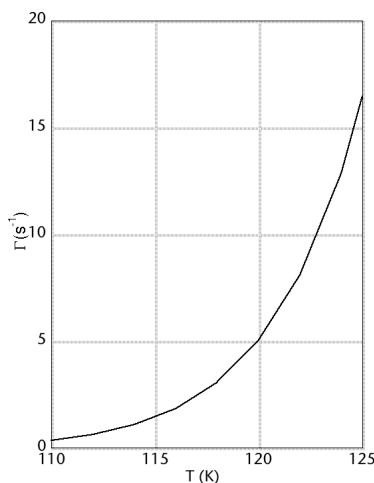


FIG. 1. Plot of the jump frequency, Γ , as a function of temperature for Pb^{2+} in β'' -alumina. An attempt frequency, ν , of 10^{13} s^{-1} and an activation energy of 0.3 eV [1] have been used. A jump frequency of $\approx 1 \text{ s}^{-1}$ is achieved at ≈ 110 – 115 K . At liquid nitrogen temperatures, the jump frequency is $\approx 10^{-7} \text{ s}^{-1}$.

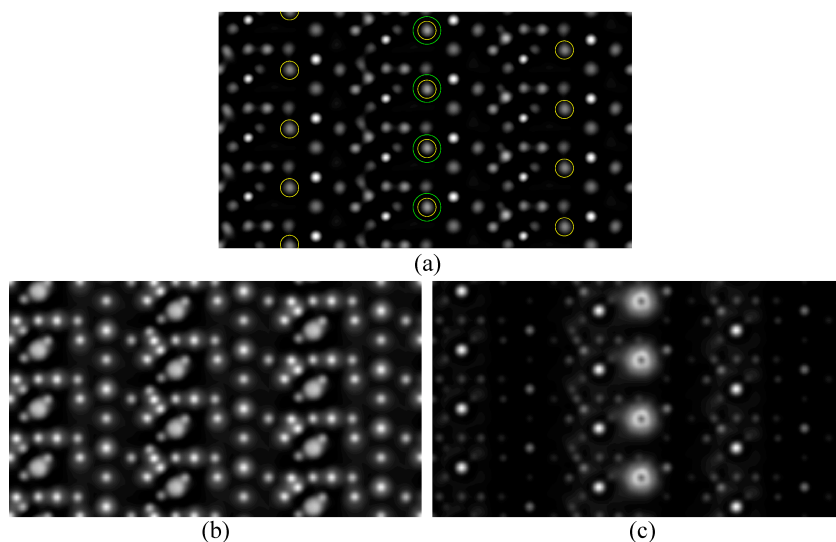


FIG. 2. (a) HRTEM, (b) bright-field HR-STEM, and (c) HAADF HR-STEM multislice image simulations for the $[10\bar{1}0]$ zone axis of β'' -alumina using an aberration-corrected microscope operating at 200 keV. The conduction planes in the structure are indicated in (a), where yellow circles show the positions of Na^+ ions and green circles show columns in which a single Pb^{2+} ion has been substituted at $\approx 65 \text{ \AA}$ through the thickness of $\approx 120 \text{ \AA}$. The Pb^{2+} ions are evident in the HAADF HR-STEM image.