

## A “Hidden” Mesoscopic Feature Revealed By Electron Microscopy Could Facilitate Ion Transport In Solid Electrolytes

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Conventional wisdom tells us that ion transport in solids is slower than that in liquid [1,2]; however, because of the technical and safety concerns related to the nature of liquid electrolytes, future energy technologies such as batteries, fuel cells, and supercapacitors, must rely on the use of solid state ion conductors [3]. The ion transport mechanism in solids is very different from that in liquid. Rather than transport via a diffusive mechanism, ion transport in solids is based on an ion hopping mechanism whereby ions jump from one site to nearby vacancy sites in the crystal lattice. Therefore, the mechanism of ion transport can be explored by revealing the atomic arrangements within the materials. For decades, research on this subject has primarily been focused on understanding ion transport pathways based on the unit cell structure using theoretical approaches. Designing unit cell level atomic arrangements with a lower activation energy and connected sites for ionic hopping has served as the primary criteria to enable new solid state ionic conductors with fast ion transport [4]. In this presentation, we show that a mesoscopic-scale feature, previously overlooked by other characterization techniques, could play an important role in facilitating ionic conduction in solids.

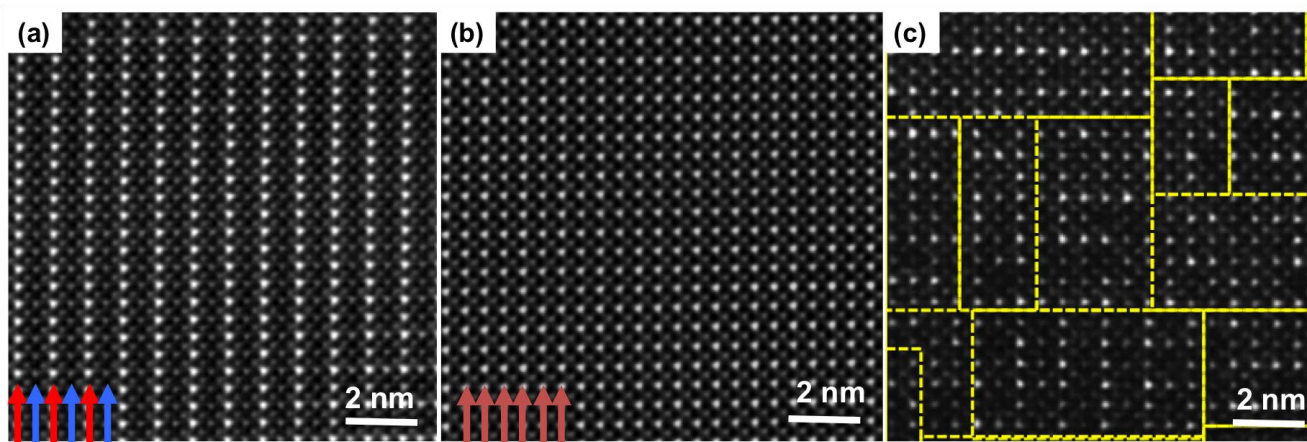
Perovskite structured  $(\text{Li}_{0.33}\text{La}_{0.56})\text{TiO}_3$  (LLTO) is considered as a Li-ion-conducting solid electrolyte for use in all-solid state batteries for many years, owing to its high ionic conductivity and desirable compatibility with conventional intercalation cathode materials [5]. This material exhibits two perovskite polymorphs depending on the synthesis conditions: an A-site cation ordering structure with alternative La-rich and La-poor (rich in Li and vacancies) atomic layers, or a structure with  $\text{La}^{3+}$ ,  $\text{Li}^+$ , and vacancies randomly distributed. Benefiting from an easier access for  $\text{Li}^+$  to the nearby vacancy sites in the La-poor layer, the ordered structure typically exhibits a higher ionic conductivity compared to its random counterpart. There is, however, an exception when the sample is quenched from 1350°C (1350LLTO). X-ray diffraction (XRD) reveals that 1350LLTO has randomly distributed A-site ions, evidenced by the absence of signature superlattice peaks corresponding to the ordered structure. It does, however, have a higher ionic conductivity than its ordered counterpart. High-resolution STEM imaging supported the results from XRD analyses. The atomic structures for a typical ordered lattice and 1350LLTO are shown in Figures 1a and 1b, respectively. Rather than alternating intensity variations in  $\langle 001 \rangle$  (arrows in Figure 1a), the A-site atomic columns shown by arrows in Figure 1b exhibit homogenous contrast, indicating a random distribution of  $\text{La}^{3+}$ ,  $\text{Li}^+$ , and vacancies at the A-sites in the perovskite structure. The controversy between the observed microstructure and ionic conductivity raises an important question: are there any microstructural features overlooked by both XRD and STEM?

Our recent microscopy research revealed the presence of a unique mesoscopic domain structure in 1350LLTO that was essentially “hidden” (Figure 1c). This domain size averages ~2-6 unit cells (u.c.)

with A-site cation ordering within each domain. The reason that the domain structure was overlooked by STEM is due to a combination of a small feature size (1-3nm) and the randomly oriented ordered domain structure in 3-D space. The typical thickness of a TEM specimen is ~20nm and since S/TEM imaging presents a projection of all the atoms comprising the specimen thickness, the image contrast resulting from cation ordering become averaged (or blurred) in the resulting image when the specimen thickness is larger than that of the domain size. The true observation of extremely small mesoscopic features involves a significant improvement of the TEM specimen preparation method and a significant reduction of surface contamination on the TEM specimen. A specimen thickness of ~5nm was finally achieved (a detailed description of the sample preparation method will be provided in the presentation). The formation of such a unique domain structure in 1350LLTO is a key factor towards achieving its high ionic conductivity. Molecular dynamics simulations confirmed that the conductivity enhancement results from maximizing ion transport pathways in 3-D that is introduced by the unique domain structure. These results reconcile the long-standing inconsistency between microstructure and conductivity in LLTO, and indicate that a delicate balance between ordered and random atomic configurations is crucial in material design for fast solid-state ionic conductors. [6]

#### References:

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**Figure 1.** High angle annular dark field (HAADF)-STEM images of a typical LLTO specimen with an ordered structure (a), a LLTO sample that was quenched from 1350°C (b), and a representative image of the 1350LLTO sample after special specimen thinning to ~5nm and surface cleaning. Arrows in the images label the A-site cation layers, and the yellow dash line in (c) delineates domain boundaries.