

## Anomalous Diffusion of Lanthanum from LaFeO<sub>3</sub> to CaTiO<sub>3</sub> and the Formation of Locally Ordered La<sub>x</sub>Ca<sub>1-x</sub>TiO<sub>3-δ</sub> Perovskite Phase Therein

M.B. Katz, H. Liu, G.W. Graham, and X.Q. Pan

Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109

Solid oxide fuel cells of various sorts are rapidly becoming viable power plants for mobile and field applications, and are therefore of increasing interest to the scientific community. Fuel cell anodes often comprise solid solutions of two or more perovskite oxides, both for their stability – chemical and mechanical – and for their relatively fast oxygen diffusion rate. One such solid solution under consideration is CaTiO<sub>3</sub>/LaFeO<sub>3</sub> [1], written as La<sub>x</sub>Ca<sub>1-x</sub>TiO<sub>3-δ</sub> or La<sub>2(1-x)/3</sub>Ca<sub>x</sub>TiO<sub>3-δ</sub>, depending upon the Ti formal oxidation state. Though this system has been studied in the past, primarily by x-ray diffraction, the interface of the diffusion couple and its local structure and nature have yet to be examined in great detail. In this report, we image directly the CaTiO<sub>3</sub>/LaFeO<sub>3</sub> interface using aberration-corrected scanning transmission electron microscopy (STEM) and examine the local chemistry by way of electron energy-loss spectroscopy (EELS). [2]

We first grow LaFeO<sub>3</sub>/CaTiO<sub>3</sub> perovskite bilayer thin films on SrTiO<sub>3</sub> (100) substrates by pulsed laser deposition, followed by a calcination treatment in flowing dry air at 800 °C for 1 hour. We subsequently section the thin films into cross-sectional STEM specimens for examination.

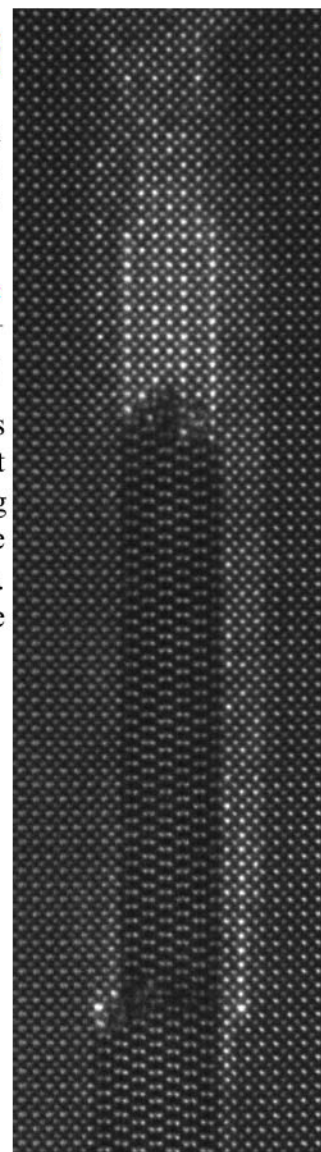
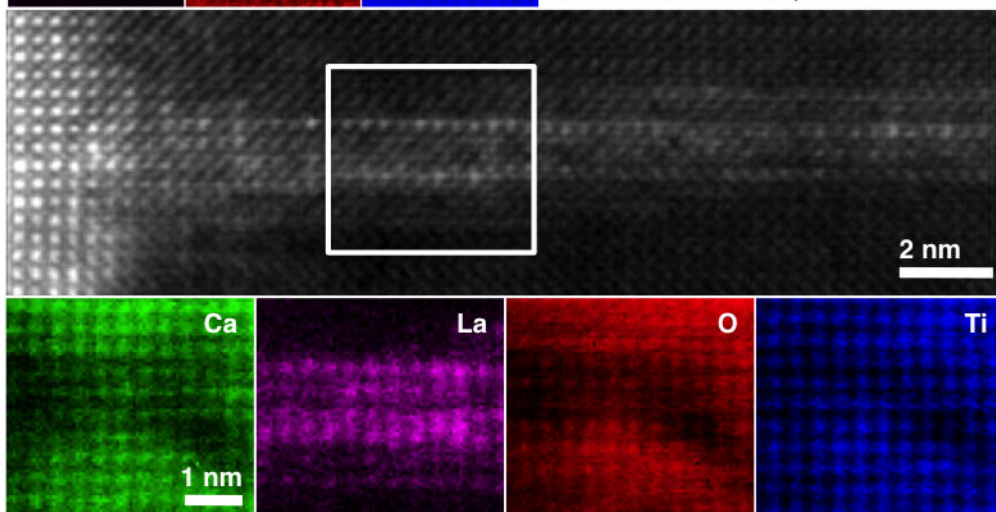
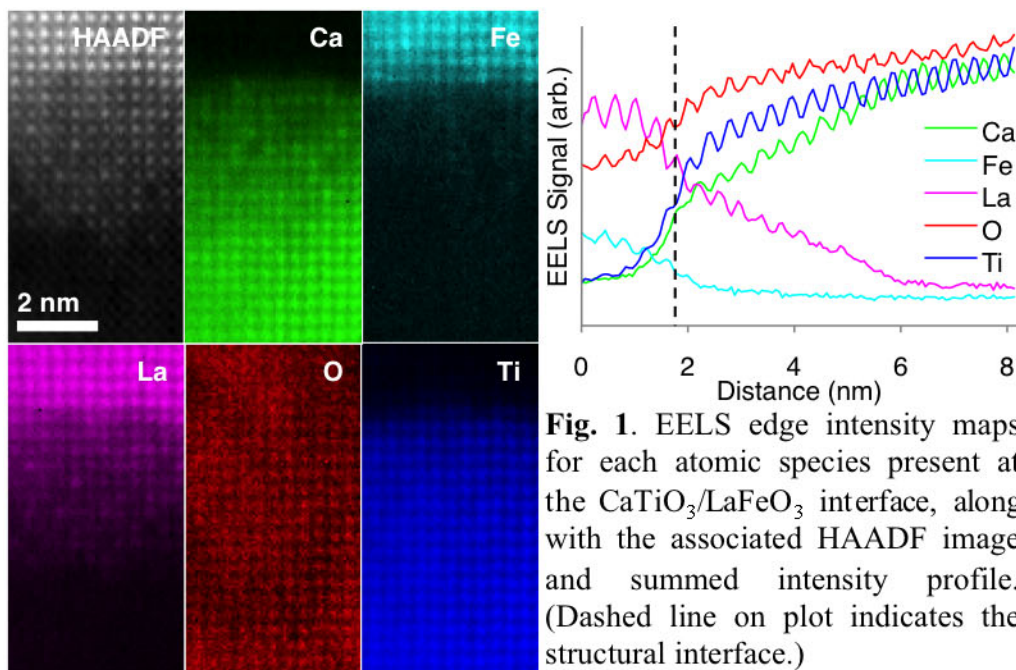
Diffusion proved to be asymmetric – La diffused significantly into the CaTiO<sub>3</sub> film with no Ti counterdiffusion into LaFeO<sub>3</sub> detected. Generally, the diffusion distance was approximately 2 to 3 nm into the CaTiO<sub>3</sub>, as shown in Figure 1, which is comparable with the bulk diffusion length of La in similar perovskites at 800 °C (no published data on La in CaTiO<sub>3</sub> could be found). The La contained within the CaTiO<sub>3</sub> film occupies exclusively the perovskite a-site, substituting for Ca. La diffusion was far more extensive along extended defects within the CaTiO<sub>3</sub>. The two predominant types of such defects were rotation domain boundaries, between sections of CaTiO<sub>3</sub> rotated by 90° in the plane from each other, and interfaces between CaTiO<sub>3</sub> and anatase TiO<sub>2</sub> inclusions grown epitaxially within the CaTiO<sub>3</sub>. Grain boundary diffusion is known to be much faster than through the bulk. In this case, La is expected to diffuse 300-500 nm with the given experimental conditions. Again, La occupied only CaTiO<sub>3</sub> a-sites within a few nanometers of these fast-diffusion channels, as shown in Figures 2 and 3.

Finally, in local regions within the CaTiO<sub>3</sub> along its interface with LaFeO<sub>3</sub>, an a-site-ordered perovskite could be observed. In fact, images reveal at least two ordered variants. In the first variant, three quarters of the Ca has been substituted by La, with alternating a-layers of LaO and La<sub>0.5</sub>Ca<sub>0.5</sub>O. Other regions present a more complex ordering scheme in which only half of the Ca atoms have been substituted. Schematics for both variants are shown in Figure 4. These ordered structures, which may form *en masse* in bulk electrodes, may greatly affect the mechanical and electrocatalytic properties of the anode.

[1] V. Vashook *et al.*, J. Alloys Comp. **354** (2003) 13.

[2] M.B. Katz *et al.*, in preparation

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**Fig. 2.** A HAADF image of a vertical fast diffusion path in the  $\text{CaTiO}_3$  film populated with anomalously high La content, along with EELS elemental maps of the region indicated.

**Fig. 3.** HAADF image showing high La content around an anatase  $\text{TiO}_2$  inclusion.

