doi:10.1017/S1431927615005024 Paper No. 0423 Microsc. Microanal. 21 (Suppl 3), 2015

Atom Probe Tomography Characterization of Engineered Oxide Multilayered Structures

M. I. Nandasiri[1], N. Madaan[1], A. Devaraj[1], J. Bao[2], Z. Xu[2], T. Varga[1], V. Shutthanandan[1], and S. Thevuthasan[3]

[1] Environmental and Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland WA, 99354
[2] Computational Material Sciences, Pacific Northwest National Laboratory, Richland WA, 99354
[3] Qatar Environment and Energy Research Institute, Qatar Foundation, Doha, Qatar

The high temperature operation of solid oxide fuel cells (SOFC) is one of the main challenges we have to overcome, especially for commercializing SOFC for portable power generating applications [1]. Solid state electrolytes with enhanced oxygen ionic conductivity at low and intermediate temperatures are needed to lower the operating temperature of SOFC [2]. Thus, there is an ongoing need to develop new electrolytes or modify existing electrolytes to enhance the ionic conductivity. Recently, oxide multilayer hetero-structures with enhanced ionic conductivity stimulated a great interest as SOFC electrolytes [3]. Here, we investigate the influence of engineered nano-scale interfaces on the ionic conductivity of doped ceria and zirconia multilayer thin film electrolytes by utilizing state-of-the-art characterization techniques including atom probe tomography (APT).

The multilayer thin films with alternative layers of samaria doped ceria (SDC) and scandia stabilized zirconia (ScSZ) were grown using oxygen plasma-assisted molecular beam epitaxy (OPA-MBE) to understand the effect of nano-scale interfaces on oxygen ionic conductivity through these films. The number of layers in the SDC/ScSZ multilayer thin films was varied from 2 to 20 by keeping the total film thickness constant at 140 nm. Oxygen ionic conductivity measurements were carried out as a function of temperature on well characterized samples using four probe surface impedance spectroscopy. Although these measurements demonstrate significantly higher ionic conductivity in multilayer thin films in comparison to a single layer thin film or bulk polycrystalline materials, the mechanisms associated with the enhanced ionic conductivity through nano-scale interfaces is not well-understood. Elemental inter-diffusion and dopant segregation across multiple interfaces could play important roles in the oxygen ionic conductivity through these hetero-structures. As such, we carefully characterized the structural and chemical properties of the materials utilizing various bulk and surface sensitive capabilities including x-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS). In particular, the interfaces in multilayer thin films were carefully characterized using APT to study the elemental distributions along with the elemental inter-diffusion and dopant segregation at the interfaces.

Laser assisted APT can provide quantitative three-dimensional chemical analysis of dielectric materials with lateral and depth resolutions in the order of 0.2-0.3 nm and chemical sensitivity up to parts-per-million levels with field-of-view on the order of 100 × 100 × 100 nm^3 [4, 5]. Although conventionally APT has been extensively used to characterize metals and alloys, it is comparatively in its infancy in characterizing oxides and insulators especially composites consisting of heterogeneous structure [6]. Oxide multilayer structures add additional

complications to the characterization of the doped ceria/zirconia multilayers. We have used APT to map the elemental distribution in these films and interfaces and Fig.1 shows 3-D reconstruction of APT experiments carried out parallel to the interfaces and perpendicular to the interfaces along with the XPS depth profiling of these multilayer thin films.

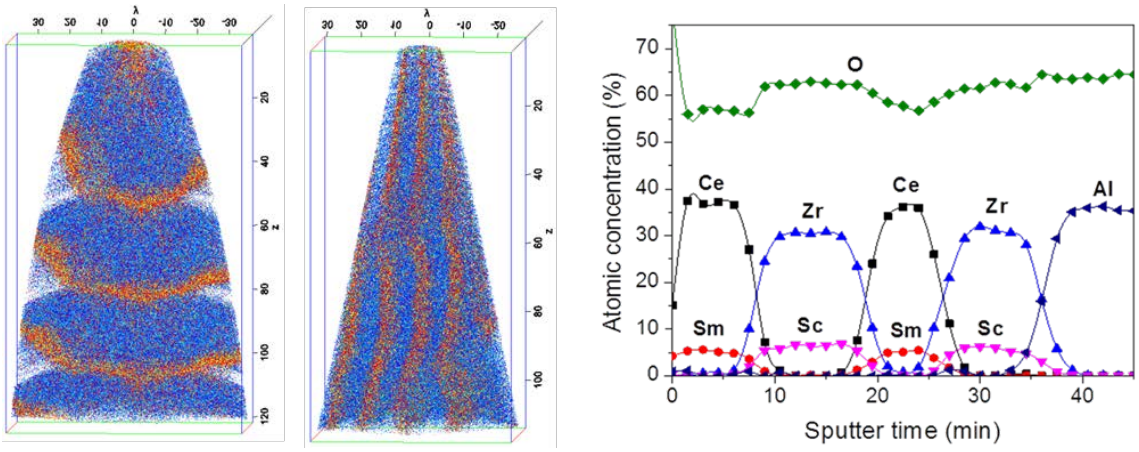

Fig. 1: Three dimensional reconstructions of APT data (Red ions correspond to CeO_2 layer and blue ions correspond to ZrO_2 layer) along with the XPS depth profiles of SDC/ScSZ multilayer thin films.

The APT reconstructions demonstrate asymmetric tip shape evolution and artifacts associated with trajectory aberrations and we carried out level set model calculations to explain these artifacts [7]. The asymmetric evolving shape predicted by the level set model will be qualitatively compared with the experimental data collected by aligning the hetero-structured interfaces perpendicular and parallel to the tip axis.

[1] Singhal, S.C., *Solid oxide fuel cells for stationary, mobile, and military applications.* Solid State Ionics, 2002. 152-153: 405-410.
[2] Wachsman, E.D. and K.T. Lee, *Lowering the Temperature of Solid Oxide Fuel Cells.* Science, 2011. 334(6058): 935-939.
[3] Emiliana, F., P. Daniele, and T. Enrico, *Ionic conductivity in oxide heterostructures: the role of interfaces.* Science and Technology of Advanced Materials, 2010. 11(5): 054503.
[4] Kelly, T. F., Larson, D. J., *The second revolution in atom probe tomography*. MRS Bulletin, 2012. 37 (2): 150-158.
[5] A. Devaraj, R. Colby, W. P. Hess, D. E. Perea, S. Thevuthasan, *The Role of Photoexcitation and Field Ionization in the Measurement of Accurate Oxide Stoichiometry by Laser Assisted Atom Probe Tomography.* Journal of Physical Chemistry Letters, 2013. 4(6): 993-998.
[6] A. Devaraj, R. Colby, F. Vurpillot, S. Thevuthasan, *Understanding Atom Probe Tomography of Oxide-Supported Metal Nanoparticles by Correlation with Atomic-Resolution Electron Microscopy and Field Evaporation Simulation*. Journal of Physical Chemistry Letters, 2014. 5: 1361-1367.
[7] Z. Xu, D. Li, W. Xu, A. Devaraj, R. Colby, S. Thevuthasan, B. P. Geiser, D. J. Larson, *Simulation of heterogeneous atom probe tip shape evolution during field evaporation using a level set method and different evaporation models.* Computer Physics Communications, 2015. 189: 106-113.

https://doi.org/10.1017/S1431927615005024 Published online by Cambridge University Press