

Probing Surface and Bulk States of Cathode Materials With Synchrotron-based Soft X-rays in a Functioning Solid Oxide Fuel Cell

Anthony H. McDaniel^{1,*}, William Chueh¹, Andrey Shavorskiy², Tolek Tyliszczak², Hendrik Bluhm³, Kevin F. McCarty¹, and Farid El Gabaly¹

¹Sandia National Laboratories, Livermore, California 94551 USA

²Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720 USA

³Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

It is a tremendous challenge to examine the surface and bulk properties of solid oxide fuel cell (SOFC) electrodes while in operation. That is, with the electrodes hot, immersed in a gaseous environment, conducting an ionic current, and supporting gradients of electric and chemical potential across a solid electrolyte membrane. As such, the vast majority of experimental investigations on SOFC electrode surfaces using photon- or electron-based techniques have been conducted through forensic analysis (i.e., ex situ). While forensic analysis does provide useful information on quenched systems far removed from the active environment, the causal links between surface composition and electronic structure to electrochemical activity remain elusive. It is well recognized that in order to gain mechanistic insight and improve material performance, these relationships must be established.

Recently, a concerted effort to probe SOFCs at high temperature and near ambient pressure by X-ray photoemission has produced several works documenting the thermodynamic and kinetic behavior of electrode surfaces. Efforts by ourselves and others, in collaboration with scientists at Lawrence Berkeley National Laboratory, have identified electrochemically active intermediates,^{1,2} the enhanced concentration of reduced active phases,³ the predominance of phase segregation,^{4,5} as well as the location of electrochemically active regions^{6,7} on the surfaces of various SOFC materials. All of these experiments were performed in a single-chamber experiment using electrolytic cells.

In order to further develop electrochemical X-ray techniques for probing advanced energy materials, we have deployed a research platform that realizes a fully functioning galvanic cell (i.e., two isolated chambers separated by an electrolyte capable of supporting a Nernst potential). This new platform incorporates both ambient pressure X-ray photoemission (APXPS) and X-ray absorption (XAS) spectroscopies, which now makes it possible to simultaneously probe surface and bulk states of electrode materials in a functioning fuel cell.

Salient features of our experimental apparatus are illustrated in figure 1 and will be described within the context of an SOFC cathode experiment. We note that this platform can and has been used to study other systems. Here a single crystal of yttria-stabilized zirconia (YSZ) is hermitically sealed to a YSZ tube. The two sides of the membrane are patterned with cathode and anode formulations and exposed to different gas environments; O₂ over the cathode and humidified H₂ over the anode. Both at 0.67 mbar total pressure and operating at 650 °C (though other conditions are certainly possible). The membrane-sealed tube is mounted onto an X-Y-Z manipulator and housed within a vacuum chamber that interfaces to an endstation on BL11.0.2 at the Advanced Light Source,

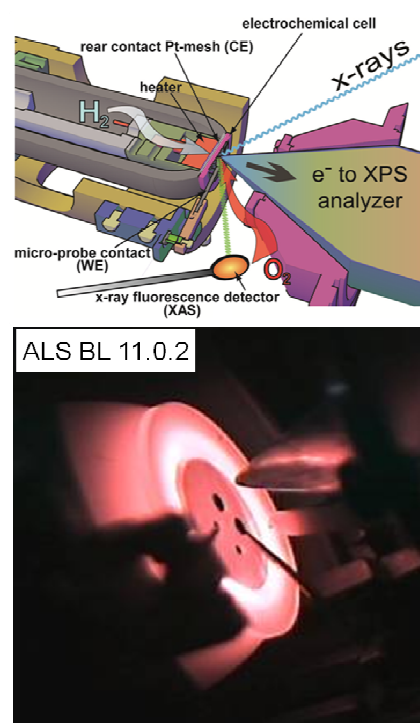


Fig. 1. (top) Cutaway view of the fuel cell in operation. Synchrotron X-rays strike the cathode surface. Ambient pressure XPS probes the composition in the near surface region. XAS probes electronic states at the surface and in the bulk. (bottom) Picture of BSCF perovskite microelectrodes positioned in front of the energy analyzer.

Lawrence Berkeley National Laboratory. This endstation is equipped with a SPECS electron energy analyzer capable of operating at 25 mbar pressure, and is used to record both XPS and partial electron yield XAS. A shielded diode is used to measure the fluorescent photon yield XAS. Thus, surface compositions, surface electronic states, and bulk electronic states can be measured while manipulating the cathode environment (i.e., O₂ pressure, temperature, and cell potential).

We will demonstrate the utility of this approach by presenting results of an experimental campaign focused on understanding what gives rise to the enhanced ORR activity observed on Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) perovskite cathodes.

References

1. F. El Gabaly, K. F. McCarty, H. Bluhm, and A. H. McDaniel, *Phys. Chem. Chem. Phys.*, **15**, 8334 (2013).
2. F. El Gabaly et al., *Chem. Commun.*, **48**, 8338 (2012).
3. W. C. Chueh et al., *Chem. Mater.*, 120507111054001 (2012).
4. E. J. Crumlin et al., *Energy Environ. Sci.*, **5**, 6081 (2012).
5. E. Mutoro et al., *J. Phys. Chem. Lett.*, **3**, 40–44 (2012).
6. C. Zhang et al., *Nat. Mater.*, **9**, 944–949 (2010).
7. F. El Gabaly et al., *Phys. Chem. Chem. Phys.*, **12**, 12138 (2010).