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In situ X-ray studies of film cathodes for solid oxide fuel cells

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ABSTRACT

Synchrotron-based X-ray techniques have been used to study *in situ* the structural and chemical changes of film cathodes during half-cell operations. The X-ray techniques used include X-ray reflectivity (XR), total-reflection X-ray fluorescence (TXRF), high-resolution diffraction (HRD), ultra-small angle X-ray scattering (USAXS). The epitaxial thin film model cathodes for XR, TXRF, and HRD measurements are made by pulse laser deposition and porous film cathodes for USAX measurements are made by screen printing technique. The experimental results reviewed here include A-site and B-site segregations, lattice expansion, oxidation-state changes during cell operations and liquid-phase infiltration and coarsening of cathode to electrolyte backbone.

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1. Introduction

The high energy conversion efficiencies of solid oxide fuel cell (SOFC) make them attractive for various applications ranging from stationary distributed power sources to auxiliary power sources for trucks and military equipment [1]. Since cathode overpotentials play a substantial role in determining the overall system performance and hence cost and efficiency [2] improved cathodes would make SOFCs even more attractive. Improving cathode efficiency is especially important in lowering the operating temperatures of SOFCs to reduce cost and increase SOFC durability. Thus, understanding the origins and mechanisms of cathode overpotential losses is important for creating SOFCs that broadly compete with established power-generating technologies.

An SOFC cathode reduces air-supplied oxygen molecules (O_2) to doubly charged oxygen ions, $2O^{2-}$, while supplying the electrons ($4e^-$) to the external circuit as shown in Fig. 1. The oxygen ions subsequently annihilate with the oxygen vacancies, $V_O^{\bullet\bullet}$ in the cathode. The vacancies are continuously supplied by electrolytes such as Yttria-stabilized zirconia (YSZ) in steady-state operating condition. However, the cathode processes suffer large overpotential losses and the detailed mechanisms and reaction pathways are not well known. In fact, a detailed examination of these active components reveals surprisingly complex and dynamic processes, at least at the elevated temperature and near atmospheric pressure SOFC operating conditions. The important processes occur on a variety of length scales from atomic (*e.g.* catalytic decomposition of oxygen) to many microns (*e.g.* the porous cathode microstructure), and on time scales that range from the very fast (*e.g.* surface segregation) to long time (*e.g.* grain growth in components). While the overall features of these processes can be deduced from *ex situ* measurements using electron-based techniques and microscopy, their potential dynamic response to changes in operating conditions makes the generalization of those results questionable without *in operando* verification.

X-ray techniques are unique in their ability to perform *in situ* and *in operando* studies of materials properties and processes. When coupled with high energy synchrotron radiation sources, X-rays can penetrate through high pressure atmospheres and microns-to-millimeters of most oxide materials. This allows atomic-level investigation of structures and properties under elevated temperature environmental conditions relevant to SOFC operation. In particular, planar samples can be used to increase the sensitivity of the X-rays to the surface of the sample. Finally, the high intensity of X-rays enables real-time and spatially-resolved measurement of critical material processes. While X-rays are generally useful for studying all of the components of an SOFC, we will focus this review on determinations of the structure and chemical state of cathodes, the time evolution of those properties, and how those properties relate to performance of an SOFC. We start with a brief introduction to the relevant X-ray techniques. This introduction is aimed at orienting the reader and providing pointers to more complete reference materials. After the introduction, we will highlight several findings derived from the application of X-ray techniques to *in situ* studies of $La_{1-x}Sr_xMnO_3$ (LSM), and $La_{1-x}Sr_xCo_{1-y}Fe_yO_3$ (LSCF) cathode materials and compare the results to previous studies of LSM, LSCF, and $La_{1-x}Sr_xCoO_3$ (LSC).

2. X-ray techniques

X-ray techniques have a long and rich history, and there are a number of excellent textbooks describing the application of

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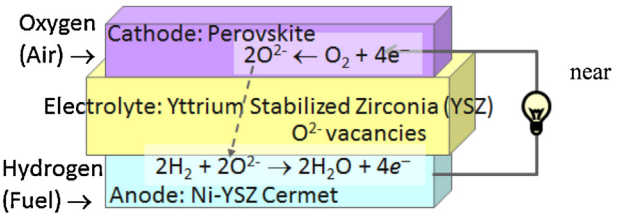

Fig. 1. A schematic view of a solid oxide fuel cell. The direction of current is indicated by an arrow and light bulb.

X-ray techniques to materials science problems [3,4]. Up until the development of broadband synchrotron radiation sources (*e.g.* the Advanced Photon Source at Argonne National Laboratory in USA), X-ray techniques were centered around X-ray diffraction. However, the capabilities of X-ray techniques have been greatly extended by the very high brightness and energy tunability of synchrotron X-ray sources based on high-energy electron storage rings, and some of these relatively new capabilities have been described by Als-Nielsen and McMorrow [5]. A key concept of modern X-ray techniques is that, to first order, X-ray scattering measures the amplitude of the Fourier transform of the electron density [6]. Thus, the X-ray scattering can be inverted to obtain detailed pictures of the electron density or, more typically, the autocorrelation of the electron density [3,7]. Our goal here is to highlight techniques that are of particular usefulness in the study of the mechanisms and operation of SOFCs.

2.1. X-ray reflectivity

The use of X-ray reflectivity (XR) to convert conventional X-ray techniques into surface sensitive probes has greatly expanded their range of use [8,9]. X-rays have an index of refraction that is slightly less than unity [10]. Thus, at grazing incidence angles X-rays can be totally reflected from a smooth surface as shown for LSM in Fig. 2. Since almost all of the X-rays are reflected, there are only evanescent fields present in the film in the angular region where the X-rays are totally reflected. The dependence of both the penetration length and the field strength of the evanescent field as a function of grazing angle are also shown in Fig. 2. It is clear that at shallow grazing angles below the critical angle for total X-ray reflectivity (the inflection point of the X-ray reflectivity curve), X-rays only penetrate a few nanometers into a smooth thin film. By changing the grazing angle by only a few tenths of a degree, X-rays can be used to probe either the surface region or the bulk properties of a thin film.

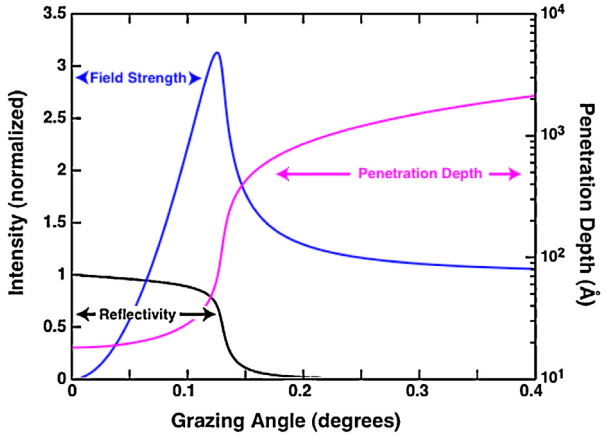

Fig. 2. The calculated effect of X-ray refraction on 24 keV X-rays incident at grazing angle on a flat La0.7Sr0.3MnO3 surface.

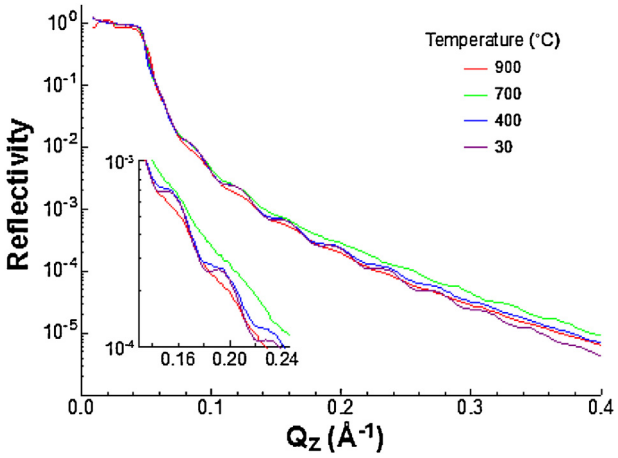

Fig. 3. The X-ray reflectivity of a 20 nm thickness film of La0.7Sr0.3MnO3 on a DyScO3 substrate in 150 Torr of O2 as a function of temperature. Note that the oscillations get weaker as the temperature is raised, indicating that the interfaces are becoming rougher or, equivalently, more diffuse.

As the incident angle is increased out of the total reflection regime, X-ray reflectivity measurements become sensitive to both long-range structures in the thin film (*e.g.* the period of a superlattice or the thickness of a thin film on a substrate), and the sharpness and roughness of both the surface and buried interfaces. For example, Fig. 3 shows the X-ray reflectivity from an LSM film grown on $DyScO_3$ (DSO) as a function of temperature. Short period oscillations are clearly present in the data at 30 °C and 400 °C that disappear by 700 °C [11]. These oscillations result from interferences between the bottom and top layers of the LSM film and their disappearance indicates that the interfaces are becoming rougher. Quantitative measures of the roughness can be determined by fitting the reflectivity data and the lateral size of the roughness can be determined by looking at the rocking dependence of the reflectivity. Using these types of measurements, X-ray reflectivity has proven to be a powerful *in situ* probe of film roughening and interdiffusion. van der Lee has written an extensive review of the use of X-ray reflectivity to study the structure of materials [12,13].

2.2. Grazing incidence X-ray scattering

The use of grazing incidence X-ray scattering (GIXS) has become a routine surface analysis technique. In the GIXS geometry (shown in Fig. 4), the incident X-ray beam strikes the sample at a small grazing angle. As just discussed, by tuning the grazing angle a slight amount, X-ray scattering measurements (*e.g.* powder diffraction) can be performed as a function of depth. The use of GIXS to study the surface structure of thin films has been employed to study surface structure [14,15] crystal growth in reactive environments [16,17] and the study of surface catalytic reactions [18,19]. There have been a number of good reviews of the technique. Fuoss and Brennan is an early review that discusses application to a variety of materials science problems [8]. Renaud et al. is a review focused on the use of GIXS to study larger surface structures such as nanoparticles [20].

2.3. Crystal truncation rod analysis

For an infinite crystal, the Bragg diffraction spots are points in reciprocal space. However, if the crystal is cut, creating a surface, streaks of intensity perpendicular to the surface are added to every Bragg reflection. Since these streaks are due to truncating the crystal, they are typically referred to as crystal truncation rods (CTRs).

The dependence of the CTR intensity with distance away from a Bragg point is very similar to that of an X-ray reflectivity