

In Situ Measurements of Overpotentials and Surface Species with XPS on Ni/GDC Electrode in Solid Oxide Electrochemical Cells

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Ni/gadolinia-doped ceria (GDC) anodes have shown promising performance in intermediate temperature solid oxide fuel cells (SOFCs) for both H₂ and carbonaceous fuels [1-3]. In typical porous SOFC electrodes, it is not feasible to measure local overpotentials between the phase interfaces where charged transfer reactions occur. Because of the dynamic nature of the GDC surface under elevated temperatures and electrochemical biasing, it is very beneficial for SOFC model development to measure local potentials. GDC undergoes significant surface reduction under electrochemical activity with H₂ oxidation, and H₂O electrolysis potentially due to high surface reduction. Extensive studies have quantified oxygen non-stoichiometry in ceria-based electrodes [4-6]. However, behavior of Ni and GDC surface species during electrochemical activity are not well understood. To fill this gap, our team studied active thin-film GDC electrodes with interconnected porous Ni overlayers with ambient pressure XPS at the Advanced Light Source at Lawrence Berkeley National Lab.

Single-chamber cells with 300 nm thick GDC electrodes with Ni overlayers supported on a 1 mm YSZ support with a back-side Pt electrode were tested with ambient pressure XPS to monitor various cations (Ni2p, Gd4d, Ce3d and Ce4d) as well as the O1s spectra. Shifts in the O1s on both the Ni and GDC surface provided information during H₂ oxidation and H₂O electrolysis as well as CO oxidation and CO₂ splitting. Shifts in the main O1s peak binding energy as a function of cell bias and location across the thin-film Ni/GDC electrode provide a basis for measuring local electric potentials of the surfaces. The shifts in the main O1s peak associated with O²⁻ surface species provide a basis for estimating charge-transfer overpotentials as a function of electrical bias as illustrated in Figure 1 for an operating conditions at $T = 650\text{ }^{\circ}\text{C}$, $P_{\text{H}_2} = 0.25\text{ torr}$, $P_{\text{H}_2\text{O}} = 0.25\text{ torr}$. Figure 1 shows that for the test conditions, overpotentials between GDC electrode and Ni overlayer for H₂O electrolysis are smaller than for H₂ oxidation at same current. This suggests that the highly reduced GDC has improved activity for H₂O electrolysis.

In addition to the potentials measurements, fitting of the O1s spectra to the O²⁻ and OH⁻ peaks as a function of surface location and cell bias provides insight into how surface species change with bias. Figure 2 shows an analysis of O²⁻ binding energy and surface-active species through line-shapes peaks fitting. The significant amounts of OH⁻ on active Ni surfaces in 1:1 H₂/H₂O environments are not observed on the neighboring GDC surface. This suggests that H spillover may not be the dominant reaction at the Ni/GDC interface. This study will present numerous other ambient pressure XPS measurements and interpretations to show new insight into surface mechanisms on Ni and GDC in intermediate temperature SOECs.

References

I. S. Baron, N. Brandon, A. Atkinson, B. Steele and R. Rudkin, *J. Power Sources*, **126**:58, 2004.

- K. Kammer and M. Mogensen, *Electrochem. Solid St.*, **8**:A108, 2005.
- K. T. Lee, C. M. Gore and E. D. Wachsman, *J. Mater. Chem.*, **22**:22405, 2012).
- C. J. Zhang, M. E. Grass, A. H. McDaniel, S. C. DeCaluwe, F. El Gabaly, Z. Liu, K. F. McCarty, R. L. Farrow, M. A. Linne, Z. Hussain, G. S. Jackson, H. Bluhm and B. W. Eichhorn, *Nature Mater.*, **9**:944, 2010.
- S. C. DeCaluwe, M. E. Grass, C. J. Zhang, F. El Gabaly, H. Bluhm, Z. Liu, G. S. Jackson, A. H. McDaniel, K. F. McCarty, R. L. Farrow, M. A. Linne, Z. Hussain and B. W. Eichhorn, *J. Phys. Chem. C*, **114**:19853, 2010.
- W. C. Chueh, A. H. McDaniel, M. E. Grass, Y. Hao, N. Jabeen, Z. Liu, S. M. Haile, K. F. McCarty, H. Bluhm and F. El Gabaly, *Chem. Mater.*, **24**:1876, 2012.

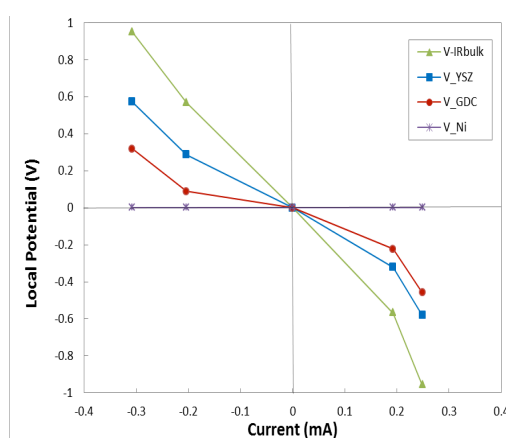


Figure 1 – Potential distribution between the interfaces of YSZ/GDC/Ni edge at $T = 650\text{ }^{\circ}\text{C}$, $P_{\text{H}_2} = 0.25\text{ torr}$, $P_{\text{H}_2\text{O}} = 0.25\text{ torr}$. Ni is grounded in the single-chamber cell, and the total cell corrected voltage ($V_{\text{cell}} - IR_{\text{bulk}}$) vs. cell current is plotted.

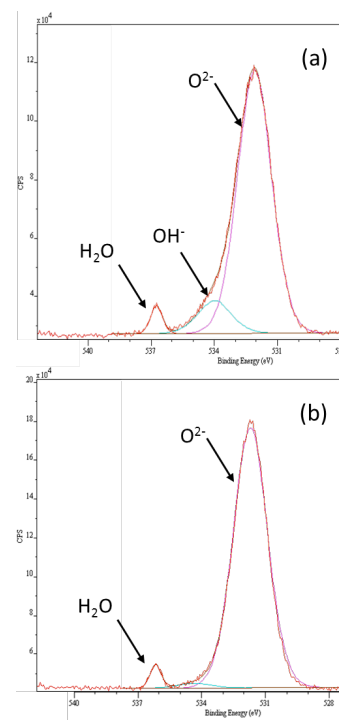


Figure 2 – Fitted O1s spectra at open circuit voltage at $T = 650\text{ }^{\circ}\text{C}$, $P_{\text{H}_2} = 0.25\text{ torr}$, $P_{\text{H}_2\text{O}} = 0.25\text{ torr}$ showing on (a) Ni showing significant OH⁻ and (b) GDC with minimal OH⁻.