In situ Imaging and Spectroscopy of the Carbon Deposition Mechanism on Ni/CeO$_2$ Solid Oxide Fuel Cell Anode Catalyst

Ethan L. Lawrence and Peter A. Crozier

Arizona State University, School for Engineering of Matter, Transport, and Energy, Tempe, Arizona 85287, USA

Ceria is a promising anode material for intermediate temperature (350-550°C) solid oxide fuel cells (SOFCs) due to its relatively high oxygen ion conductivity at these temperatures. Long-term stability of SOFCs may be limited by carbon deposition from the fuels onto the active anode (fuel oxidation) catalyst, causing deactivation or destruction of the ceramic-metal composite structure. Ceria has been shown to inhibit carbon deposition by quickly exchanging oxygen from its lattice to oxidize carbon on the surface of the electrode [1]. We are interested in understanding how ceria can affect carbon deposition at the gas-solid interface by observing structural and chemical changes at the nanoscale. Environmental transmission electron microscopy (ETEM) provides the ability to observe nano-level structural changes under simulated reaction conditions which can be correlated with nanomaterials’ performance through in situ and operando techniques [2]. In situ electron energy-loss spectroscopy (EELS) has also allowed dynamic changes in the local oxidation state of nanomaterials to be determined during catalysis [3]. A fundamental study of the local structural and chemical changes in a Ni/CeO$_2$ catalyst occurring under reaction conditions will provide information on the carbon deposition and may suggest mitigation strategies.

An FEI Titan ETEM was used to study gas-solid interactions of a model Ni/CeO$_2$ catalyst with two carbon source gases, ethane (C$_2$H$_6$) and ethylene (C$_2$H$_4$), to gain insight into carbon deposition processes relevant to SOFC applications. NiO was loaded onto CeO$_2$ cubes which were then reduced in situ in 1 Torr H$_2$ at 400°C. The hydrocarbon gas (C$_2$H$_6$ or C$_2$H$_4$) was introduced and samples were heated to 550°C. Figure 1 shows the structural changes that occurred during hydrocarbon exposure. When exposed to C$_2$H$_4$, carbon was deposited in the form of graphite layers whereas Ni surfaces remained free of graphite during C$_2$H$_6$ exposure. In situ EELS was used to monitor the valence state of Ce$^{3+/4+}$, which varies with the oxygen content of the ceria according to Ce$_{x}^{3+}$Ce$_{1-x}^{4+}$O$_{2-x/2}$. Ce valence can thus be used to interpret carbon deposition behaviors in terms of oxygen deficiency of the ceria support. Figure 2 a) and b) show high-angular angle dark-field (HAADF) images where EELS lines scans were acquired in each source gas. Typical EELS spectra of the O K and Ce M_{4,5} edges are shown as insets. The integrated intensity ratio of the M_{4}/M_{5} peaks was used to correlate the EELS spectra to Ce valence. The table in Figure 2 c) indicates that no changes in local Ce valence states were observed during C$_2$H$_6$ exposure when compared to Ce valence state in H$_2$. During C$_2$H$_6$ exposure under identical conditions, however, localized reduction zones were observed in the ceria support near Ni particles. Therefore, ceria inhibited carbon deposition during C$_2$H$_6$ exposure through localized oxygen exchange but was unable to do so during C$_2$H$_4$ exposure [4]. These results will be discussed in terms of a Mars van Krevelen carbon oxidation mechanism.

References:
Figure 1. a) & c) Ni/CeO$_2$ at 400°C in 4 Torr H$_2$ b) Ni/CeO$_2$ in 0.5 Torr C$_2$H$_4$ at 550°C with several graphite layers covering the Ni particle. d) Ni/CeO$_2$ in 1 Torr C$_2$H$_6$ at 550°C. The Ni particle surface remains clear of graphite and the crystalline ceria becomes amorphous.

Figure 2. HAADF images of Ni/CeO$_2$ in a) 0.5 Torr C$_2$H$_4$ at 550°C and b) 1 Torr C$_2$H$_6$ at 550°C. Dotted lines indicate EELS line scan directions with position markers 1-4. The insets are typical EELS spectra of the O K and Ce M$_{45}$ edges near Ni particles. The table in c) shows the oxidation state of Ce along the line scans of a) and b) compared to a typical line scan in H$_2$. The highlighted values indicate that localized reduction zones of the ceria cube were observed near the Ni particle in C$_2$H$_6$ but no reduction zones were seen in C$_2$H$_4$.