

***In situ* TEM Observations of Carbon Deposition on Solid Oxide Fuel Cell Anode Materials**

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Direct internal reforming solid oxide fuel cells (SOFCs) are fuel flexible electrochemical devices capable of achieving high energy conversion efficiencies. Fuel flexibility allows the devices to use carbonaceous fuels such as natural gas. However, using carbonaceous fuels directly may result in coking in which carbonaceous material deposits on the active anode reforming catalyst. Carbon deposition blocks catalytic sites and degrades cell performance. Ni-Gd co-doped ceria (GDC) anode materials have shown promise for inhibiting carbon deposition for intermediate temperature SOFCs [1]. The metal-support interaction of the anode catalyst support may play an important factor in carbon formation [2]. *Ex situ* experiments using Ni-GDC were performed using CH₄ and C₂H₆ as natural gas models. *In situ* transmission electron microscopy (TEM) and electron energy-loss spectroscopy (EELS) were also used to study effects of this metal-support interaction during early stages of carbon deposition.

NiO was loaded onto CeO₂ cubes and SiO₂ spheres to give model systems with two different metal-support interactions. Using cubes and spheres provided well-defined surfaces to study the metal-support interaction. CeO₂ cubes were initially chosen instead of GDC cubes in order to simplify the metal-support interaction. The two samples were loaded onto the same TEM grid so that both were exposed to identical conditions. An FEI Titan ETEM was used for *in situ* experiments. Samples were first reduced in 1 Torr H₂ at 400°C. C₂H₆ was introduced and samples were heated to 550°C.

Many layers of graphite developed during *ex situ* experiments using CH₄ and C₂H₆ as seen in Figure 1a-b. Ni oxidation on exposure to air was also observed in Figure 1a-b. *Ex situ* experiments were unable to provide details about the early stages of carbon deposition under reaction conditions. The *in situ* image in Figure 2 shows graphite layers on Ni particles supported on SiO₂ spheres and a corresponding energy-loss spectrum. The C-K ionization edge is visible in the energy-loss spectrum allowing the form of carbon deposited to be determined. Figure 3a shows a typical CeO₂ cube loaded with Ni particles. Figure 3b shows two particles forming graphite layers at 450°C in 1 Torr H₂ + 1Torr C₂H₆. In Figure 3c, it is seen that graphite layers continued to grow as the temperature was increased to 550°C and H₂ flow was reduced to 0.1 Torr. The image in Figure 2 was obtained under identical conditions as Figure 3c and both show comparable amounts of graphite. However, not all Ni particles on CeO₂ cubes showed graphite layers under these conditions (see Figure 4) while all Ni particles on SiO₂ spheres did show graphite layers. This is believed to be a direct effect of the metal-support interaction between Ni and ceria. Further *in situ* experiments will be performed and a detailed explanation of the metal-support interaction during deposition will be presented [3].

References:

- [1] Zhou, Y. *et al*, Physical Chemistry Letters **9** (2010), p. 1447-1453.
- [2] Shindo, T. *et al*, ECS Trans. **57** (2013), p. 1571-1576.

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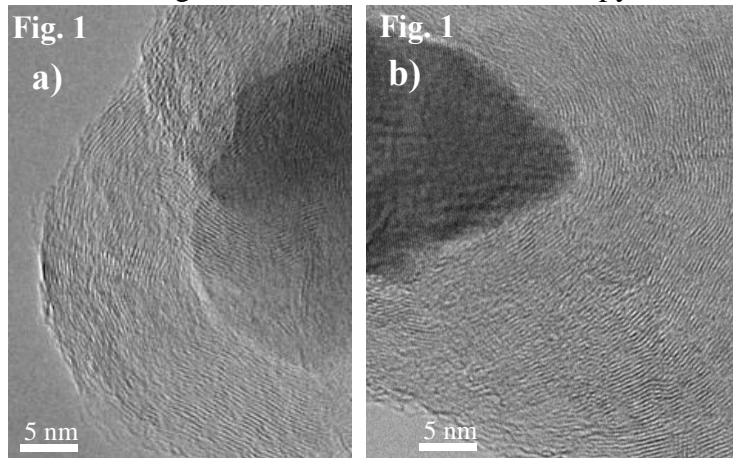


Figure 1. a) A NiO particle covered with graphite from CH₄. b) A NiO particle covered with graphite from C₂H₆.

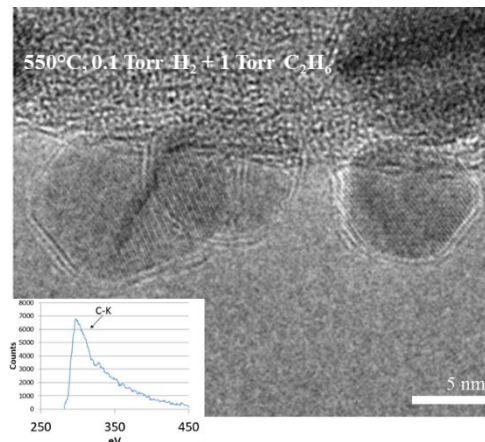


Figure 2. Graphite encapsulated Ni particles on a SiO₂ sphere. The EELS spectrum (insert) from the particles shows the C-K edge signal from the graphite.

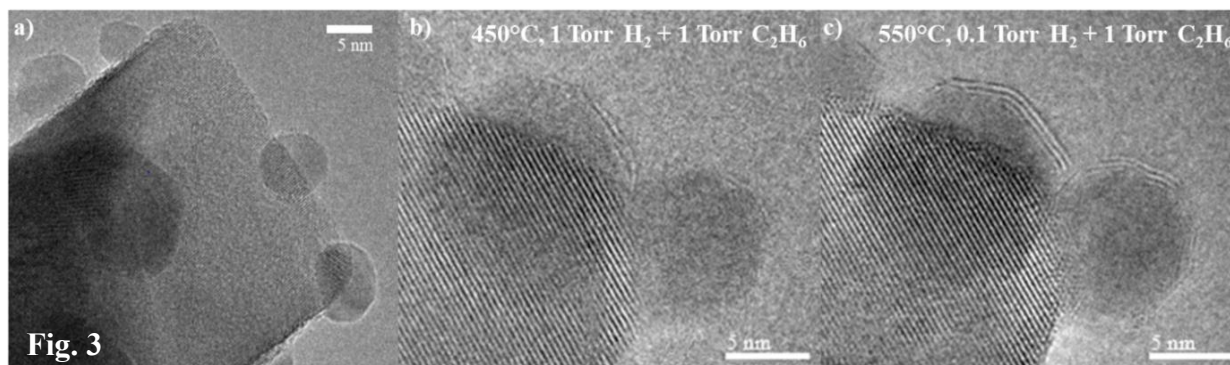


Figure 3. a) Typical Ni particles on a CeO₂ cube. b) Ni particles on a CeO₂ cube with graphite beginning to form on several facets. c) Several layers of graphite have grown on Ni particles.

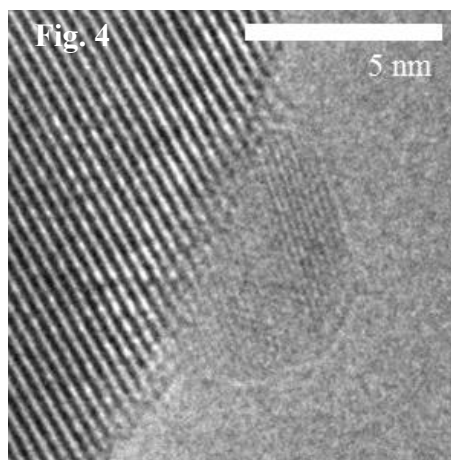


Figure 4. Ni particle on CeO₂ cube with no graphite acquired at same time and conditions as Figure 3c and Figure 2.