

In Situ Study of Anode Reaction in Intermediate Temperature Solid Oxide Fuel Cells

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Solid oxide fuel cells (SOFC) are attracting increasing attention as a new and clean source of energy from large-scale stationary to power supply for autos applications. However, high temperatures operation regime of these devices is considered as the main limitation in SOFCs industry, which leads to serious restrictions such as short lifetime, material degradation, and high sealing cost for widespread commercialisation. Oxygen evolution reaction (OER) at SOFCs' anode is a critical section in the cell operation to reduce the working temperatures. Ceria-based cermets are of most promising candidates as the high performance anode materials for intermediate temperature SOFC (IT-SOFC).

Bulk half cells as anodes for SOFCs with a Ni electrode and a 20 molar % gadolinia doped ceria (GDC20) electrolyte were prepared by a pulsed laser deposition (PLD) method at different levels of crystallinity and the number of oxygen vacancies in the electrolyte material on a Si (100) substrate at appropriate environments for the electrolyte and electrode materials. Subsequently, TEM specimens were prepared from the half cells by a micro-sampling focused ion beam (FIB) technique and mounted on Mo FIB grids. The microstructural features of the electrolytes were characterized by X-ray diffraction (XRD) and nano electron beam diffraction (NBD). The reaction mechanism and the microstructural evolution of the cells during the anode reaction, OER, were studied applying analytical TEM approaches. In situ electron energy loss spectra (EELS) were acquired by a JEM2100 at different temperatures. Ex situ EDS elemental maps and HRTEM images of the raw and operated cells were obtained by an ARM200F [JEOL]. Electron holography observations were conducted using a modified field emission HF-2000 [Hitachi].

Modelled half cells were heated from R.T. to elevated temperatures in the microscope column and EELS spectra were measured from the electrode-electrolyte interfaces. It was found that Ni electrode would start to be oxidised to NiO at intermediate temperatures as low as 200°C confirmed by a distinct change in Ni-L edges at the interface areas. However, the electronic structure of ceria in both GDC electrolytes remained stable at all environments (Fig. 1). Nevertheless, the doped gadolinium cations appeared in a novel oxidation state at the elevated temperatures as the Gd tetra-valent cations (Fig. 1). These measurements suggested a new reaction mechanism for OER so as i) the oxygen anions released from GDC electrolyte and ii) led to NiO formation, iii) the carried charges would be also transferred to the grounded electrode and iv) the solid oxide electrolyte would be more oxidised. Similar measurements from the substrate-electrolyte interface showed the Si oxidation during the heating process that implies on the possible application of simple Si as an electrode material.

Ex situ EDS analyses from raw and heated specimens showed perfect stability of the microstructure in the operated half cells without any secondary phase formation that contradicts previous reports on such anode materials prepared and operated by other methods. Indeed, while the occurrence of OER was

detected by in situ measurements, no interdiffusion was observed between electrode and electrolyte substances (Fig. 2). It is believed that the reported [1], deleterious microstructural evolutions at GDC-Ni anode cermet are not an inherent effect of anion transfer at the oxide-metal interface, OER, and might be due to the processing method and/or anode operation environment; and could be prevented by modifications in design and fabrication anode materials.

References:

[1] Li *et al*, Phys Chem Chem Phys 13(2011). p. 9685.

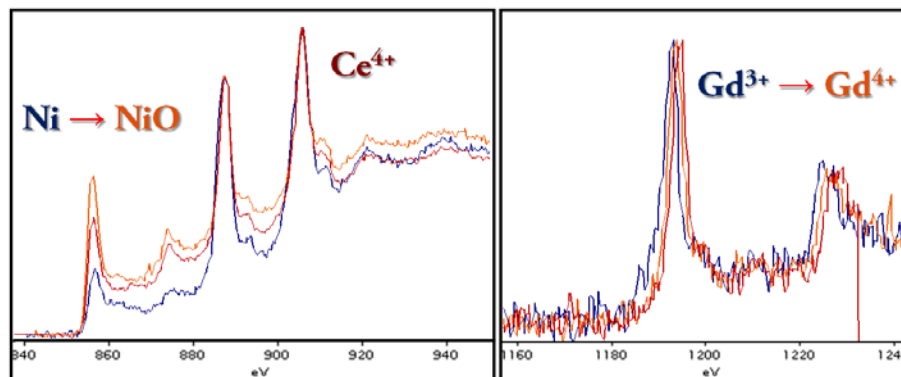


Figure 1. Electron energy loss spectra from GDC-Ni interface from Ni-L, Ce-M, and Gd-M edges at R.T. (blue), 200 (orange), and 400°C (red).

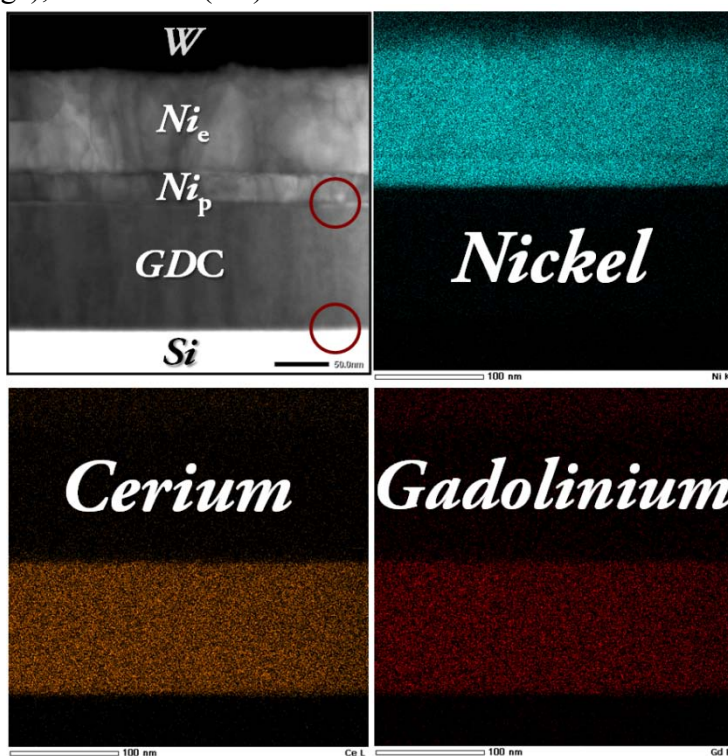


Figure 2. BF-STEM image of the raw half cell microstructure (top-right) on the Si substrate, the red circles approximately show the area from where EELS measurements has been acquired. EDS elemental map of electrolyte's cations and the electrode in the operated half cell, no interdiffusion was founded between the substances.