

***In situ* Analytical TEMs for SOFCs' Fundamentals**

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Solid oxide fuel cells were aimed as the dynamic material systems to be studied in their fundamentals finding out their precise reaction mechanism in nano-scale and seeking the solutions for basic questions on the limitations of these devices such as the high operation temperatures and the material degradations. The two essential oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) in these systems were monitored in TEM via changes in the atmosphere of the instrument's column from a highly reductant to an exceedingly oxidant environment.

Various half and complete bulk cells were made by a pulsed laser deposition (PLD) method at diverse environments regarding to the each substance of the cells and electron transparent specimens were prepared by a micro-sampling focused ion beam (FIB) technique. A 20mol% gadolinium-doped ceria (GDC20) ionic-electronic conductor was selected as the solid electrolyte material and two Pt and FIB-deposited W electrodes were set at two sides of the GDC layer as the active electrode and inactive electrode, respectively.

Half and complete cells' microstructures were characterized by X-ray diffraction (XRD), and STEM energy dispersive X-ray spectroscopy (EDS). Elemental analyses confirmed interdiffusions between the cells' substances to be as less as 15 nm.

Oxygen ionic conduction and the redox reactions in these cells were visualized and understood by *in situ* off-axis electron holography in a conventional FE-TEM equipped with a home-made environmental system inserting gas inside the OL pole piece of the instrument [1]. The variations of electro-static inner potentials in the electrolyte layer of the cell at different environments were interpreted as the local distribution of the oxygen anions inside the solid oxide electrolyte during the OER and ORR.

It was found that the system would experience further oxidation as the oxygen released from the active electrode(s) and subsequently goes under a reduction as ORR occurs at the interfaces and oxygen diffuse into the electrolyte. However, the inner-potential behavior in these systems was reverse comparing with another conventional solid electrolyte of SOFC, i.e. yttria-stabilized zirconia, YSZ [2].

The reaction mechanisms during of the cells were investigated by *in situ* electron energy loss spectroscopy (EELS). The EEL spectra were acquired from the electrolyte and electrode interfaces as the cells were heated from R.T. to elevated temperatures. It was found that the cerium doped cations were remained stable in their *tetra-valent* state at all interfaces in every environment. However, the valence state of the gadolinium doped cations enhanced to *tetra-valent* state from the common *tri-valent* as the OER progress in the solid electrolyte.

This conclusion denote the role of the doped cations in solid oxide electrolyte not

only to introduce oxygen vacancies in the electrolyte microstructure and facilitate the ionic conduction by the host cations, but also to participate in the reactions at least in their initial states.

References

- [1] A. H. Tavabi, et al. "In-situ off-axis electron holography of hetero-interface in oxygen atmosphere", *J Electron Microsc*, 60 (5), 307-314, (2011).
 [2] A. H. Tavabi, et al. "In-situ analytical electron microscopy studies of redox reactions in an YSZ/Pt interface", *Microscopy and Microanalysis*, in print (2012).

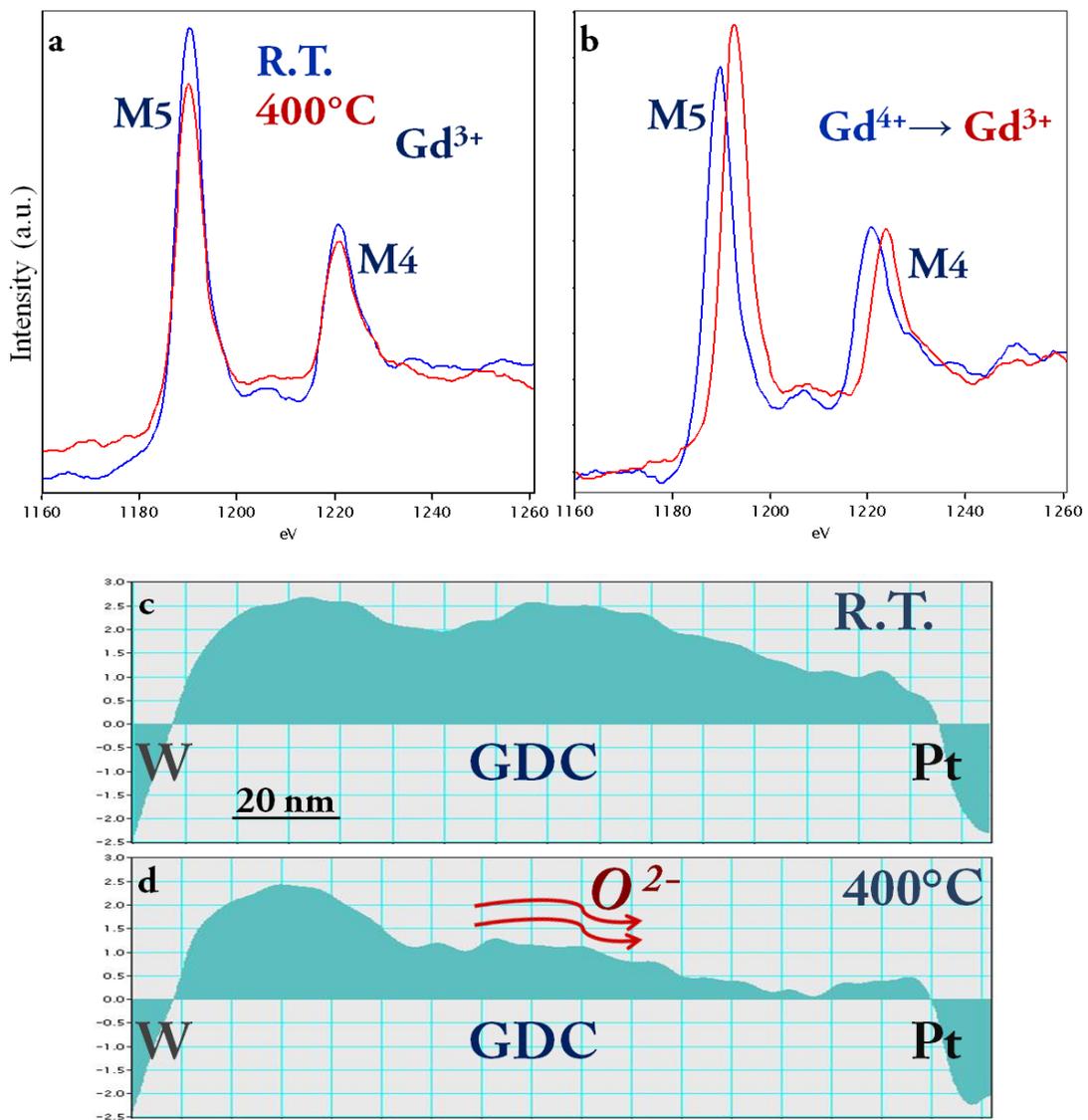


FIG. 1. EEL spectra from gadolinium M-edges at electrode-electrolyte interfaces at R.T. and 400°C, inactive W electrode (a) and active Pt electrode (b). Phase shift profiles along the cell at R.T. (c) and 400°C (d)