The mixed ionic-electronic conductors studied by advanced transmission electron microscopy

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A successful oxygen transport membrane (OTM) requires not only an outstanding permeation performance, but also chemical, electrical, thermal and mechanical stabilities under practical conditions. Among promising candidates, dual-phase OTMs (DP-OTMs) are attracting continuous attention, in which two ceramic phases are coupled to provide mixed ionic-electronic conductivity. In particularly, a fluorite-spinel composite CexGd1-xO2-δ-FeyCo3-yO4 (CGO-FCO) was reported to possess both a significant oxygen permeability as well as a high tolerance under exhaust gas conditions.[1] Thus, considerable efforts have been made to further push the overall performance of CGO-FCO. However, the bottleneck still lies in the inevitable phase interation and the complex grain boundary (GB) structures. In turn, modulating the phase interaction and GB properties offers the possibility of materials engineering, which requires however a precise understanding of the emerging phase and the GBs behaviors down to atomic scale.

In our work, dense pellets of CGO-FCO with different nominal compositions were prepared by solid state reactive sintering.[2] As a result of the phase interaction, an emerging phase with the structure of GdFeO3 (GFO) was often located between CGO phases. Further energy-dispersive X-ray spectroscopy (EDXS) and electron energy loss spectroscopy (EELS) studies revealed varying compositions of the GFO phase, and its formation reduces the Fe and Co segregation at the CGO GBs significantly.[3] Besides, both crystal and chemical structure at the CGO GBs were quantified down to the sub-nm scale, as they are directly related to the ionic conductivity of the membranes.[4] CGO GBs with different coherences were compared. For the Σ3[101] GB in Fig. 1 with a high coherence, only a single layer of Gd segregation can be noticed at the edge of each grain, while the non-solute segregations from Fe and Co are restricted between the two grains. Any variation of the Ce valence state is also largely limited. In contrast, for CGO GBs with a lower coherence, all the atomic-site specific lattice distortions, elemental distributions, and valence state variations were found to be much more significant.

In summary, GFO was identified as the emerging phase within CGO-FCO. Its tunable electronic properties further broaden the opportunity for membrane optimization through phase engineering. Besides, Simultaneous Gd enrichment and Ce depletion within the ending atomic layers of the adjacent CGO grains are generally observed, while Fe and Co are segregated into the CGO GBs with varying amounts and phases. The comparison between GBs with different coherencies indicates that the valence states of Ce, and the enriched Gd, Fe and Co are all sensitive to the local structural defects at the GB. A more coherent GB would thus be beneficial for an improved GB conductivity. Our findings constitute a crucial piece for the complete picture of structure-property relationship of CGO-FCO, which may also shed light on the understanding towards other oxide heterointerface phenomena.

Graphic:

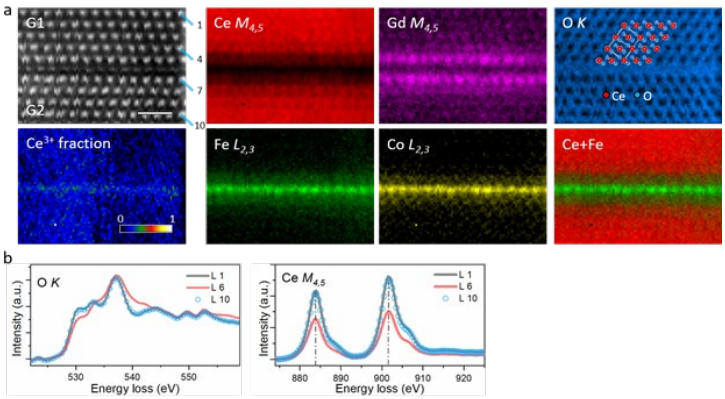

Figure 1. The Σ3[101] CGO GB. (a) EELS SI results: simultaneously acquired ADF image and elemental maps plotting the intensity from the Ce $M_{4,5}$, Gd $M_{4,5}$, O K, Fe $L_{2,3}$, and Co $L_{2,3}$ edges, together with a composite map of Ce and Fe and a Ce^{3+} fraction map. (b) Fine structures of the O K and Ce $M_{4,5}$ edge corresponding to Layer 1, 6 and 10, as labeled in (a).

Keywords:

ceramic membranes, GB-segregation, aberration-corrected TEM

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