A study on the architecture of defects in co-doped ceria electrolytes using synchrotron light

Massardo S.[1]*, Artini C.[1, 2], Carnasciali M.M.[1, 3], Martinelli A.[4], D'Acapito F.[5], Pani M.[4].
*lead presenter: sara.massardo@edu.unige.it
1 DCCI, University of Genoa, Via Dodecaneso 31, 16146 Genova, Italy
2 CNR-ICMATE, Via De Marini 6, 16149 Genova, Italy
3 INSTM, Via Dodecaneso 31, 16146 Genova, Italy
4 SPIN-CNR, Corso Perrone 24, 16152 Genova, Italy
5 IOM-CNR, c/o European Synchrotron Radiation Facility (ESRF), Grenoble, France

Doped ceria systems, crystallizing with a fluorite-type structure, form a family of widely studied electrolytes for IT-SOCs (Intermediate Temperatures - Solid Oxides Cells). In particular, in $Ce_{1-x}RE_xO_{2-x/2}$ compounds (RE= trivalent Rare Earth), the partial substitution of Ce^{4+} by RE leads to the formation of not-associated oxygen vacancies, allowing the conduction of O^{2-} ions through the structure, thanks to a vacancy-hopping mechanism. However, the factors ruling the ionic conductivity in such compounds are quite complex and strictly related to the structure of the electrolyte and, in particular, to the different families of defects occurring in it.

In the last years, our research group extensively explored the structural and micro-structural properties of RE-doped ceria, through different techniques [1], both at ambient and non-ambient conditions, thus gaining a deep knowledge on the structure of such compounds. Moreover, we recently undertook a study on the defects architecture in co-doped ceria systems [2, 3], in which two RE doping ions with different dimensions are simultaneously used.

To deepen the knowledge on the local structure in such compounds, X-ray absorption spectroscopy and pair distribution function studies (figure 1a and 1b, respectively) were performed at the ESRF synchrotron on $Ce_{1-x}(Nd_{0.74}Tm_{0.26})_xO_{2-x/2}$ and $Ce_{1-x}(Nd_{0.63}Dy_{0.37})_xO_{2-x/2}$ samples with $x \leq 0.6$, obtained through a well-established co-precipitation synthetic protocol. The analysis of the collected data provided information on the deformations taking place in the oxide with the increasing RE amount: with the present contribution, an overview on the acquired data and their implications on the electrolyte performances will be given.

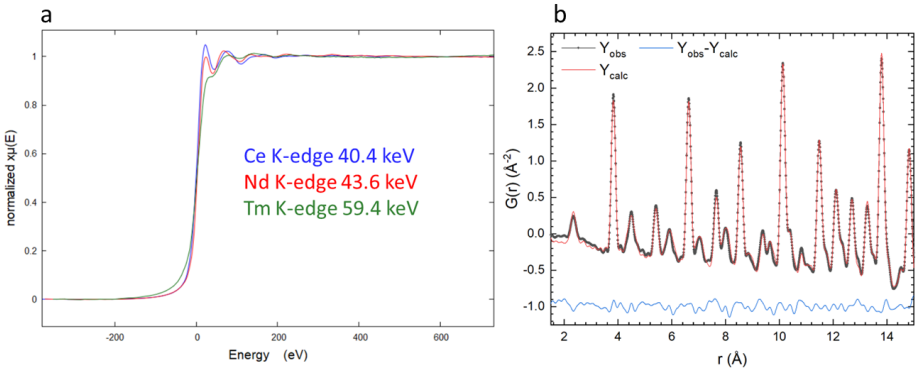

Figure 1 (a) aligned EXAFS spectra collected on the sample with x_{NdTm}= 0.6; (b) fit of the G(r) profile for a pure ceria sample.

[1] C. Artini et al. Lu-, Sm-, and Gd-doped ceria: A comparative approach to their structural properties. Inorg. Chem. 2016; 55: 10567 – 10579.
[2] C. Artini et al. The role of defects association in structural and transport properties of the $Ce_{1-x}(Nd_{0.74}Tm_{0.26})_xO_{2-x/2}$ system. J. Energy Chem. 2021; 60: 494-502.
[3] C. Artini et al. Effect of the (Nd,Dy)-Double Doping on the Structural Properties of Ceria. Inorganics 2019; 7(8): 94.