Role of cerium in activating solar fuels production in transition metal-oxides

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Earth abundant and environmentally friendly transition metal oxides are attracting broad research for thermochemical redox cycles. Despite progress, a major challenge is ensuring fast and reversible redox kinetics and large oxygen exchange capacities.
We provide insights on the role of Ce dopants in unlocking the redox capacity of manganese oxide nanoparticles, via the formation of an intermediate carbide stage [1, 2]. We perform a detailed analysis of the structural evolution and chemical composition of the material during the redox steps, as a function of the cerium content, by combining synchrotron-based spectroscopy (NEXAFS, in-depth XPS profiling) and in-house microscopy (SEM, TEM). We observe that in every cycle the cerium atoms migrate from the bulk to the surface of the 20nm-nanoparticles and back, and that the presence of cerium in 3+ oxidation state both within the lattice of the metal oxide and on its surface is essential to the formation of the carbide phase, ensuring high and stable reduction kinetics. This is optimally achieved for a cerium content of 3%. Smaller Ce content (1%) are insufficient to stabilize the redox reactions resulting in the rapid growth of the manganese oxide grains, while higher doping content (5%) cause the rapid segregation and inactivation of Ce.

References

[1] X. Gao, G. Liu, Y. Zhu, P. Kreider, A. Bayon, T. Gengenbach, T. Lu, Y. Liu, J. Hinkley, W. Lipiński, A. Tricoli, Nanoenergy, 50 (2018) 347.
[2] I. DI Bernardo, X. Gao, P. Kreider, T. Tran-Phu, Y. Zhu, X. Cai, J. Lipton-Duffin, A. Bayon, W. Lipiński, A. Tricoli, *submitted*.

Figures

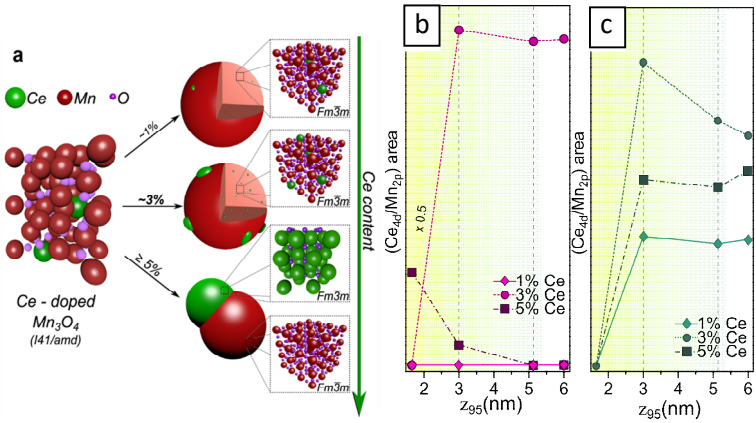

Figure 1: a) Proposed simplified schematics of the structural enhancement mechanism of the optimally doped Ce compounds as a function of the Ce content. b, c) Ce concentration in the MnO nanoparticles, in the reduced and oxidized stage respectively, as a function of the distance from the surface (z95) for different initial Ce doping concentration.