Highlights

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Role of Associated Defects in Oxygen Ion Conduction and Surface Exchange Reaction for Epitaxial Samaria-Doped Ceria Thin Films as Catalytic Coatings

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Samaria-doped ceria (SDC) thin films are particularly important for a wide range of applications, such as catalysts, gas sensors, memristors, solar-to-fuel convertors, oxygen storage devices, and microsolid oxide fuel cells. In this paper, we report a comparative study investigating ionic conductivity and surface reactions for well-grown epitaxial SDC films varying the samaria doping concentration. With increasing doping an enhancement in the defect association is observed by Raman spectroscopy. By using complementary techniques, such as electrochemical impedance spectroscopy and electrochemical strain microscopy (ESM), we show for the heavily doped films the detrimental effects of associated defects on the "bulk" ion conduction properties and the beneficial effects on the "surface" oxygen exchange activity. In a model experiment, through a solid solution series of samaria doped ceria epitaxial films, we reveal that the occurrence of associated defects in the bulk affects the surface charging state of the SDC films to increase the exchange rates. The implication of these findings is the design of coatings with tuned oxygen surface exchange by controlling the bulk associated clusters for future electrocatalytic applications

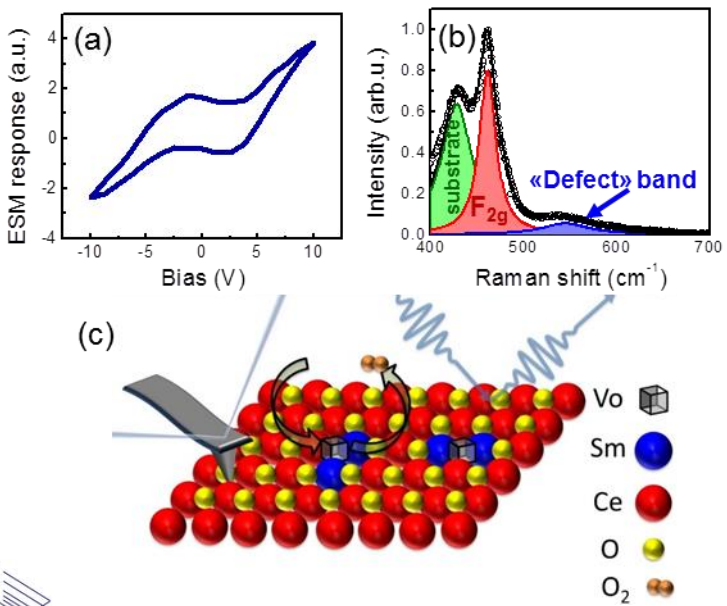

Figure 1. (a) ESM hysteresis loop related to the needed finite voltages to activate the forward and reversed redox-processes in the SDC films. (b) Raman spectra normalized to the maximum peak intensity showing the peak corresponding to the $NdGaO_3$ substrate, while the F_{2g} and "Defect" (D) band are ascribed to the film: F_{2g} is the oxygen anionic–cationic stretching Raman band of the ceria cubic fluorite structure and D is the second order phonon scattering on oxygen vacancies. (c) Schematics of the ESM tip scan and Raman laser radiation interaction on the SDC surface during the oxygen exchange reaction.