Chemical Kinetic Processes in Oxides Studied by Relaxation Experiments of Optical Absorption and Electrical Conductivity

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Chemical kinetics of gas-solid reactions plays an important role in the operation of fuel cells, metal-air batteries, chemical sensors, and many industrial catalytic processes. Kinetics of gas-oxide reactions can be studied by using chemical relaxation experiments, in which a sudden change in oxygen activity, aO_2, of the surrounding atmosphere of an oxide is introduced and the time-dependent change in physical properties of the sample, *e.g.*, mass, electrical conductivity, or optical absorption, is monitored. The kinetic data can be analyzed using appreciate kinetic models to derive reaction and diffusion parameters, *i.e.*, the surface exchange coefficient, k_{chem}, and the chemical diffusion coefficient, D_{chem}. These chemical reaction parameters and transport properties are essentially determined, among other factors, by defect chemistry of oxides due to the coupling of electronic and ionic defects in the kinetic processes. In the present work, chemical relaxation experiments on selected oxides will be reported and chemical relaxation processes dominated by surface exchange reaction and/or chemical diffusion will be discussed. In the case of Ce-containing yttria stabilized zirconia (Ce-YSZ) it will be shown that the combined results from relaxation experiments of optical absorption (of electronic species, $V_{\mathrm{O}}^{\cdot\cdot}$) and electrochemical impedance (related to ionic species, $\mathrm{Ce}_{\mathrm{Zr}}^{'}$) can provide experimental evidence for defect interactions in Ce-YSZ.

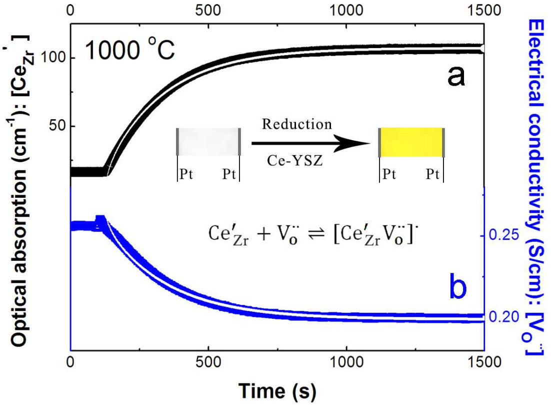

Figure 1: Relaxation experiments on $\mathrm{Ce_{0.08}Y_{0.2}Zr_{0.72}O_{1.9}}$ upon aO_2-jump from O_2 to ArH_2 at 1000 °C, (a) optical absorption and (b) electrical conductivity, monitored by optical spectroscopy and electrochemical impedance spectroscopy under in-situ conditions, respectively, showing the evidence for defect interactions in Ce-YSZ upon reduction. The white solid lines are fits to a kinetic model involving k_{chem} and D_{chem}.