

Light-induced stoichiometry changes in oxides at high temperatures

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In oxides that are stable within a certain oxygen stoichiometry range oxygen exchange with the surrounding atmosphere can be brought about by different means, e.g. changing the oxygen partial pressure in the atmosphere or the temperature [1], or applying a voltage [2]. The scarce studies on the effect of light on the oxygen exchange reaction include work on Fe-doped SrTiO₃ single crystals and anodic TiO₂ thin films, for which the kinetics of oxygen exchange following an O₂ partial pressure jump was reported to change under irradiation with UV light [3, 4].

In the present work we study the effect of UV light on the stoichiometry of the model oxides SrTiO₃ and TiO₂ in equilibrium with the surrounding atmosphere, without any other driving force. This photon-driven “oxygen pumping” process could be interesting for devices harvesting light energy as well as sensors. The material under investigation was used as an electrode in a high temperature (~400°C) electrochemical cell (oxide|yttria-stabilized zirconia|porous Pt) on which current and voltage measurements were performed with and without light in atmospheres with different oxygen partial pressure.

A time-dependent voltage up to a few hundred mV results upon light. Partly, this voltage originates from a photovoltaic effect in the cell. The time-dependent voltage contribution, on the other hand, is caused by light-driven incorporation of oxygen into the crystal. This stoichiometry change leads to a cell voltage also after switching off UV irradiation and may be considered as a kind of electrode changing by light.

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[3] R. Merkle, R.A. De Souza, J. Maier, *Angewandte Chemie International Edition*, 40 (2001) 2126-2129.

[4] H.W. Gundlach, K.E. Heusler, *Zeitschrift für Physikalische Chemie*, 119 (1980) 213-224.