## Solid Oxide Photo-electrochemistry with Oxides "Breathing" upon UV Light and Solar Cells Operating at 400°C

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Photo-electrochemistry is largely based on aqueous electrolytes. However, the efficiency and/or materials stability in such cells is still not sufficient for widespread application. This raises the question whether solid electrolyte based systems may also be an option. Very little is known on the realizability of all solid state photo-electrochemical cells based on oxide ion conductors; UV light was shown to accelerate oxygen incorporation into  $SrTiO_3$  [1] and a theoretical model of a solid state photo-electrochemical cell including a mixed conducting electrode was described in Ref. [2]. Here, we present experiments of two novel approaches to solid oxide photo-electrochemical cells.

 $SrTiO_3$  with Pt current collector was used as an electrode on an oxide ion conductor (YSZ). Upon UV light, cell voltages in the 200 mV range result at ca. 400°C. Oxygen incorporation of the illuminated  $SrTiO_3$ , i.e. a kind of "breathing" of the electrode, modifies the voltage and an EMF remains even after switching off the light. Two effects take place: a photo-voltage develops, which is coupled to the external circuit via a solid electrolyte, and a battery-type (Nernst) voltage builds up upon illumination. The latter reflects the oxygen chemical potential difference induced by the "breathing" of the oxide and corresponds to a kind of light driven-battery charging.

A second approach makes use of a high temperature solar cell which consists of a Sr-doped LaCrO<sub>3</sub> thin film on a SrTiO<sub>3</sub> single crystal. This heterojunction leads to photo-voltages as high as 900 mV at 400°C [3]. The photon induced driving force was then used to pump oxygen from low to high oxygen partial pressures and thus to chemically store photon energy [3]. In the corresponding solid oxide photo-electrochemical cell, the bottom electrode of the oxide solar cell (Sr-doped LaFeO<sub>3</sub>) was employed as the top electrode of a zirconia based solid electrochemical cell. By short circuiting the outer electrodes of this oxide hetero-structure electrochemical oxygen pumping became possible.

[1] X. Ye, J. Melas-Kyriazi, Z. A. Feng, N. A. Melosh, W. C. Chueh, Phys. Chem. Chem. Phys. 2013, 15, 15459-15469.

[2] R. Merkle, R.A. De Souza, J. Maier, Angew. Chem. Int. Ed. 2001, 40, 2126-2129

[3] G. C. Brunauer, B. Rotter, G. Walch, A. K. Opitz, G. Ponweiser, J. Summhammer, J. Fleig, Adv. Funct. Mat. 26 (2016) 120-128