Mixed Conductors under Light: On the Way to Solid Oxide Photo-Electrochemical Cells

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Photon driven electrochemical reactions may contribute significantly to future sustainable energy supply. Many different oxides (e.g. TiO2 or Fe2O3) have been used so far to run the most prominent photon driven reaction, namely photo-(electro-)chemical water splitting. However, despite strong efforts still efficiency and/or materials stability are not sufficient for widespread application. In the vast majority of studies the photo-electrochemical reaction takes place in aqueous solution close to room temperature. Photo-electrochemistry based on solid oxide electrolytes, on the other hand, is an almost unexplored field. In such cells, operation temperatures of several hundred °C are required to enable sufficient oxide ion conduction. Very little knowledge is available on the experimental realizability of such cells and on their problems. UV light was shown to accelerate oxygen incorporation into SrTiO3 [1] and a theoretical model of a solid state photo-electrochemical cell including a mixed conducting electrode was described in Ref. [2].

In this contributions, experimental results are presented which introduce two approaches to solid oxide photo-electrochemical cells.

i) In one approach, first an oxide based high temperature solar cell was developed. A thin film of Sr-doped LaCrO3 on an undoped SrTiO3 single crystal leads to a heterojunction with large space charge potential. Upon UV illumination this can be used to gain photo-voltages as high as 900 mV at 400°C. Operation at 500°C still leads to 600 mV and short circuit currents in the several mA/cm2 range [3]. Interestingly, the entire SrTiO3 single crystal (0.5 mm thickness) becomes conducting upon illumination. 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 LaFeO3) 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.

ii) In the second approach, a mixed conducting oxide (TiO2 or SrTiO3) with Pt current collector was deposited directly on an oxide ion conductor (YSZ). Upon UV light, voltages in the 200 mV range result at ca. 400°C. Oxygen exchange of the illuminated mixed conductor upon UV light modified this voltage such that even after switching off the light a voltage remained. Thus, two effects come into play: a photo-voltage that is coupled to the external circuit via a solid electrolyte and a voltage due to the oxygen chemical potential difference which is built up upon illumination. The latter can be considered as the result of a kind of light driven battery charging.

[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. DOI: 10.1002/adfm.201503597