

PV-Hybrid Electrolysers For The Photoelectrochemical Conversion Of Sunlight Into Hydrogen: Materials, Structures and Architectures

Sebastian Fiechter, Peter Bogdanoff, Diana Stellmach, Stephan Brunken, Alejandra Ramirez

Helmholtz-Zentrum Berlin für Materialien und Energie

To replace fossil fuels solar radiation can be used as a nearly inexhaustible energy source to convert light into chemical energy for a sustainable society. Solar hydrogen as chemical energy can be produced by photochemical and photoelectrochemical processes. Up to now the efficiencies of photochemical systems remained limited while photoelectrochemical systems have proven efficiencies above 10%.

In principle photoelectrochemical/catalytic devices can be realized combining

- (a) a photocathode with a suited photoanode or
- (b) a photoelectrode with a dark electrode.

Since at room temperature a voltage of at least $U = 1.229\text{V}$ is needed to split water a sufficiently high photovoltage of the photoelectrode has to be obtained under illumination. Whenever the semiconductor surface is in contact with the electrolyte the energetic position of the valence band has to be below the redox potential for the oxygen evolution reaction (OER) ($\text{H}_2\text{O}/\text{O}_2$ ($\leq - 6.0$ eV, related to the vacuum scale) and the position of the conduction band above the potential for hydrogen evolution reaction (HER) ($> - 4.7\text{eV}$). Taking into account overvoltages to drive HER and OER a gap of of at least 2.2eV is necessary using a single semiconducting electrode.

Recently, Reece et al. [1] described a triple-junction thin film silicon solar cell equipped with non-precious metal catalysts deposited on front and back contact of the thin film device to demonstrate water splitting under illumination after immersing it into an aqueous solution. As a possible disadvantage of this structure shadowing effects of the incident light by the catalyst deposited on top of the front layer of the solar cell could occur. Therefore in our approach we have tested triple-junction silicon solar cells in superstrate configuration as an alternative [2]. Here the solar cell will be illuminated via the transparent glass substrate side of the thin film a-Si/ μc -Si solar cell while the back contact in contact with the electrolyte has been functionalized by a novel cathode catalyst layer evolving hydrogen. The catalyst used in our case consisted of carbon supported nano-scaled MoS_2 particles embedded in a conductive polymer matrix.

As a cheap anode catalyst films of manganese oxides (Mn_2O_3 , Mn_3O_4 and $\text{MnO}_2 \cdot n\text{H}_2\text{O}$) were prepared by anodic deposition from a manganese containing solution onto SnO_2 :F- glass. Electrochemical measurements in 0.1M KH_2PO_4 at pH 7 revealed that all films displayed anodic currents. Mn_2O_3 , Mn_3O_4 and $\text{MnO}_2 \cdot n\text{H}_2\text{O}$ evolved oxygen at overpotentials of 0.32, 0.36 and 0.54 V vs. RHE, respectively. In the case of screen-printed calcium manganates, most films were found to generate oxygen above 0.53 V vs. RHE.

References:

- [1] Steven Y. Reece, Jonathan A. Hamel, Kimberly Sung, Thomas D. Jarvi, Arthur J. Esswein, Joep J. H. Pijpers, Daniel G. Nocera, *SCIENCE*, 2011, **334**, 645-648.
- [2] Bernd Kaiser, Wolfram Jaegermann, Sebastian Fiechter, Hans Joachim Lewerenz, *Bunsen-Magazin*, 2011, **13**, 104-111.