Cold gas sprayed semiconductor-based electrodes for the photo-induced water oxidation

I. Herrmann-Geppert [a,b], H. Gutzmann [b], P. Bogdanoff [c], T. Emmler [a], P. Hillebrand [c], M. Schieda [a], F. Gärtner [b], T. Klassen [a,b]

[a] Helmholtz-Zentrum Geesthacht, Institute for Materials Research
Max-Planck-Str. 1, 21502 Geesthacht, Germany

[b] Helmut-Schmidt-University (University of Armed Forces), Institute for Materials Technology
Holstenhofweg 85, 22043 Hamburg, Germany

[c] Helmholtz-Zentrum Berlin, Institute for Solar Fuels
Hahn-Meitner-Platz 1, 14109 Berlin, Germany

One of the most challenging tasks in photo assisted water splitting for hydrogen generation is the development of low cost, but highly efficient photoelectrodes. Identifying suitable catalysts and processes opens up the way to build photoelectrochemical cells for large-scale hydrogen production.

In this contribution the potential of cold gas spraying for the production of photoelectrodes employing semiconductors for the water oxidation reaction (OER) is presented. Conventional methods of coating usually employ wet chemical methods with subsequent calcination steps to obtain strong binding between the catalyst particles and the substrate. In the cold gas spraying process particles are accelerated to high velocities by a pressurized gas. The nitrogen used as process gas is preheated and then expanded in a De Laval type nozzle. By impact on the substrate the particles deform and break up and thus can build an efficient interface to the back contact (analyzed by cross-section SEM). In Fig. 1 a scheme of the cold spray technique is shown.

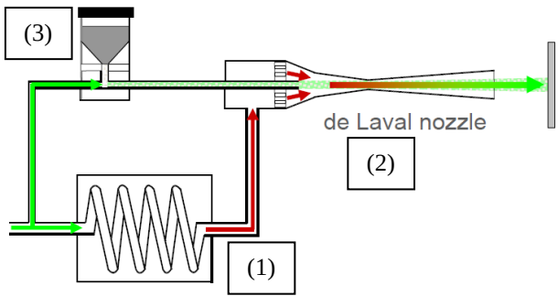

Figure 1. Scheme of the cold gas spraying technique. The pressurized carrier gas is heated (1) and accelerated in a converging/diverging nozzle (2). The powder particles are fed to the gas stream (3). The TiO_2 particles are accelerated in the process up to 800 m/s.

Cold gas spraying is a method for the direct coating of surfaces and does not require additives that have to be removed afterwards e.g. by a calcination step but allows the direct formation of a working electrode ensemble.

Firstly, cold gas spraying of titanium dioxide was probed whose films show 0.28 mA/cm^2 at 1.23 V(NHE) and a pronounced photovoltage in photoelectrochemical experiments. In Fig. 2 the chopped CV measurement on TiO_2 cold gas sprayed film under AM1.5 in 0.5 M H_2SO_4 is presented.

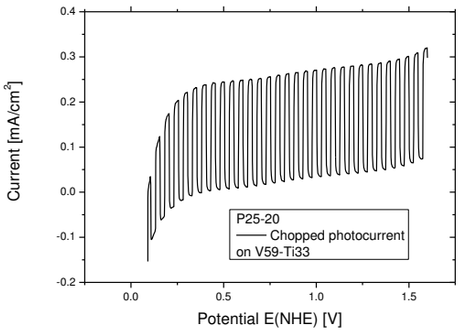

Figure 2. Chopped photocurrent measurement under AM 1.5 on cold gas sprayed TiO_2 films (4 MPa, 800 °C, using nitrogen as process gas) in 0.5 M H_2SO_4 (25 mV/s, A =2.5 cm^2)).

For the coating process only particles in the µm-range can be utilized. Therefore, P25 TiO_2 was agglomerated to particles with a size of approximately 20 µm. Due to the impact on the substrate during the cold gas spraying the particles break up which form a porous film. Furthermore the substrate is deformed so that a caldera-type substrate structure is formed which enables an embedment of the TiO_2 particles in the substrate.

Interestingly, in the physical-chemical analysis (Raman, XRD, UPS, XPS) indications were found that the catalyst surface is changed due to the cold gas spray process. Spray parameters and the film thickness on the substrate were varied in order to investigate the influence of the operation properties on the photoelectrocatalytic properties of the TiO_2 coatings. These findings are compared to films obtained from the established wet-chemical deposition methods.

Finally, the perspective for the photoelectrode production by preliminary results is given for promising visible light photoelectrocatalyst (e.g. tungsten oxide and hematite).