

## Increase of TiO<sub>2</sub> Photoanodes Efficiency as a Consequence of Surface Modification with Catalyst for Dark Oxidation Reaction of Water

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Dark water oxidation reaction have been studied by recording the anode current density dependences from potential in the 3-electrode cell with Ni cathode and silver chloride comparison electrode in a solution of 1 M KOH. The electrode potential was changed using a stabilized voltage source B5-44. The current was measured with microammeter. Photoanodes for research were produced through TiO<sub>2</sub> deposition on a Ti substrate in the CVD process.

Catalyst films of Mn that accelerate the dark reaction of the water oxidation were formed by thermal deposition in vacuum over 10<sup>-4</sup> Torr. In the case of thin layers of manganese (deposition time < 20s), there was only unstable effect of accelerating of water oxidation compared to the unmodified electrode (Fig. 1). The same effect caused a mechanical wiping of thick (the deposition time 450s)

layer of manganese catalyst. However, in the case of electrochemically passivated Ti-anode (Fig. 2), which is a model of TiO<sub>2</sub> photoanode, a significant and sustained effect in reducing the potential of O<sub>2</sub> release was registered. Study of modified anode surface by X-ray photoelectron spectroscopy (Fig. 3)

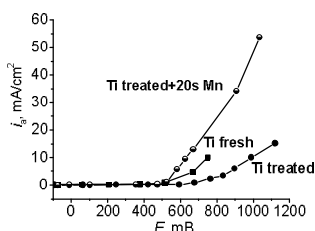


Fig. 2 Current density dependencies of O<sub>2</sub> release on Ti-anode potential in the initial state (fresh), passivated (treated) and modified (Mn)

revealed the presence of a Mn oxides (IV/III) mixture. At optimal thickness of MnO<sub>2</sub> layer (the deposition time 20s) an uniform oxygen evolution was observed over the entire surface of the modified electrode. When a thick layer of Mn oxide was obtained (deposition time > 300s), the energetic oxygen evolution was observed only at the ends of the modified electrode. This means that the active places for the passage of the water oxidation reaction are situated exactly on the border of MnO<sub>2</sub>/TiO<sub>2</sub>. Thus, thin layers of Mn oxides on the surface of TiO<sub>2</sub> photoanodes accelerate the dark water oxidation reaction.

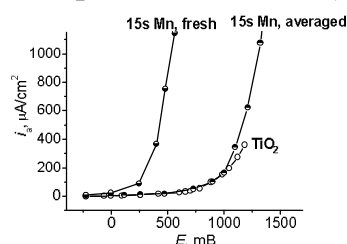


Fig. 1 Current density dependencies of O<sub>2</sub> release on potential of TiO<sub>2</sub> photoanodes modified by Mn

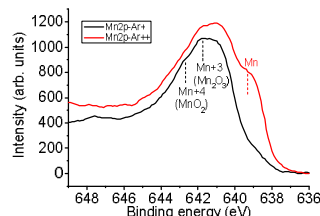


Fig. 3 XPS spectra of Ti anode modified by Mn