

Titanium dioxide electrodes for water photo-electrolysis: modelling of photoelectrochemical processes

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Solar photoelectrolysis of water is considered as a promising route towards green hydrogen production. Since its first demonstration in 1969 [1], improving the efficiency of the process remains the major challenge. Current research efforts focus on the development of improved photoelectrodes enabling higher photocurrents and larger solar-to-hydrogen conversion. Of special interest are photoactive semiconductors being used as photoanodes. Employing concepts of nanostructuring and doping combined with liquid phase technologies for constructing favorable layered configurations, metal oxides offer strategic advantages when it comes towards the use of abundant non-critical materials and sustainable fabrication of efficient large-area photoanodes. Deeper comprehension of the underlying photoelectrochemical processes provides the necessary feedback to a successful progress.

In this presentation, boron-doped nanostructured TiO₂ film electrodes are used as photoanode. We show that its photoelectrochemical performance can be successfully described by mathematical and physical models. This finding is of wider general interest to understand and improve the performance of nanostructured layered photoanode architectures.

Experimental methods

Boron-doped TiO₂ nanoparticles (TNPs) were synthesized by a sol-gel method [2]. The TNPs were dispersed in liquid media and deposited by spray-coating techniques on transparent FTO/glass substrates followed by a sintering process.

The FTO-supported TNP film was used as photoanode in a 3-electrode glass cell. Photoelectrochemical studies, namely cyclic voltammetry (CV) and transient photocurrent measurements were performed under AM1.5 illumination. Results were analyzed by mathematical and physical models.

Results and discussion

Electrochemical CV measurements in the dark are simulated according to a model summarized by Berger et al. [3]. The simulation reveals the existence of two types of trap-states contributing to charge accumulation. The density of one trap state is maximum at the conduction band minimum, and decreases exponentially towards the band gap. Another trap state is deep in the gap and monoenergetic. Fitting improvement underlines for the first time the influence of the electrode potential on the equivalent series resistance (Figure 1, left). The relevance of deep trap states, not in equilibrium with the conduction band [4], responsible for variations in the charging and discharging cycles is discussed.

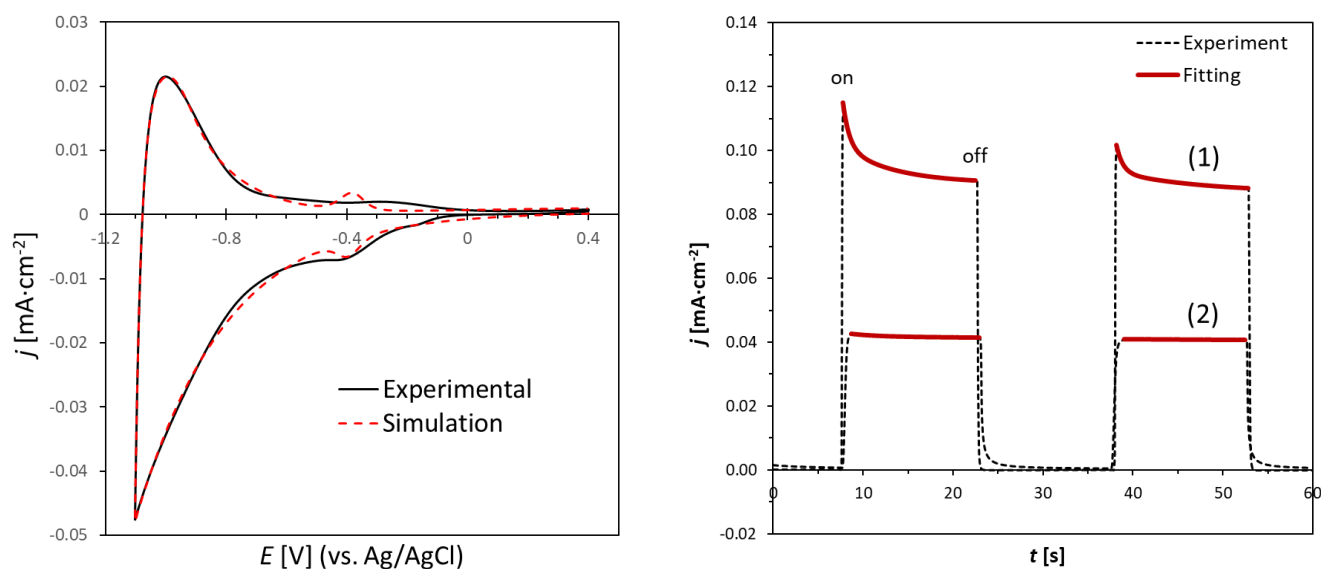


Figure 1. Experimental measurements in 0.1M Na₂SO₄, and fitting curves. Left: CV on TiO₂(1) at 20 mV·s⁻¹. Right: Transient photocurrent measurements at 0.4 V. TiO₂(1) and TiO₂(2) electrodes, which were prepared by different dispersion protocols for TNPs, are compared.

Experimental results of transient photocurrent measurements are modeled through exponential decay as suggested by [5], but considerably improved by introducing a double exponential decay, underlining the need for taking into account processes occurring at different time scales (Figure 1, right). Most likely, the first decay can be associated to the trapping of photogenerated carriers at surface centres, while the second decay can be assigned to the refilling of surface traps becoming available after charge recombination [6]. The fitting is successfully applied to two differently prepared TiO₂ photoanodes (Figure 1, right), and points out the relevance of controlling the film processing conditions to achieve improved photocurrent performance.

Acknowledgements

Financial support from Spanish MICINN/AEI under project PID2019-104272RB-C51/AEI/10.13039/501100011033 and the Diputación General de Aragón under project T03_20R (Grupo Reconocido) is acknowledged.

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