Transient performance modeling of photoelectrochemical hydrogen generation systems

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Photoelectrochemical processes constitute a viable route for renewable hydrogen production. These processes synthesize hydrogen via the electrolysis of water induced by a light generated current on photoactive component. Several practical systems that provide separated product streams of hydrogen and oxygen follow the design guidelines established in the fuel cell community and have been demonstrated [1,2]. Of particular interest is the transient performance of such systems as they are exposed to intermittent radiation source.

We developed a transient 0D numerical model based on models proposed by Andrade *et al.* [3] and Zhang *et al.* [4] of a TiO_2-based photoelectrochemical system constructed in accordance with current fuel cell designs. The model accounted for species and photogenerated charge carriers conservation, fluid flow and electrokinetics in a simple and comprehensive equation set. The modeled system was composed of photoanodic and cathodic compartments which were separated by a proton conducting Nafion® membrane. The numerical model was compared to and validated by experimental studies of our previously developed prototype [2]. We investigated the transient performance under different transient conditions of light illumination, species mix and species phases in the channels, i.e. the anode is fed with liquid water and cathode with an inert gas, or the anode and cathode are fed with oxygen, acid or water vapor. Our results showed the experimentally observed four regimes of the transient photocurrent: anodic overshoot when the illumination starts, current increase, current decrease and cathodic undershoot when illumination is set off. Dependent on the operational conditions, these regimes appeared or weren't present.

The numerical results additionally showed that the transient behavior of the photocurrent at start up was very dependent on the initial concentration of chemical species at the electrodes and on the diffusion properties of the separator. The electrochemical reaction was driven by the concentration ratios of reactant and products, which were very large at start up since the initial ratios were close to zero, hence the overshoot current at initial time. Results also showed that the band energy level of the semiconductor play an important role in the presence of anode overshoots when illumination was switched on, which confirms the modeling results obtained by Zhang *et al.* [4].

The validated model developed provides a useful tool for system design and operational guidelines and optimization possibilities.

References

[1] B. Seger, P.V Kamat, J. Phys. Chem., 2009, 113, 18946-18952.
[2] J. Rongé, D. Nijs, S. Kerkhofs, K. Masschaele, J. Martens, Phys. Chem. Chem. Phys., 2013, doi:10.1039/C3CP50890K.
[3] L. Andrade, T. Lopes, H. Aguilar Ribeiro, A. Mendes, Int. J. Hydrogen Energy, 2011, 36, 175-188.
[4] S. Zhang, L. Jia, T. Yu, Electrochim. Acta, 2013, 89, 253-261.