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Effect of Experimental Parameters on Water Splitting Using a Hematite Photoanode

Olivier Vorlet*[a], Francesco Giordano[a], Thierry Chappuis[a], and Christoph Ellert[b]

Correspondence: O. Vorlet[a], E-mail: olivier.vorlet@hefr.ch; [a]HES-SO Haute Ecole Spécialisée de Suisse occidentale, Haute école d'ingénierie et d'architecture de Fribourg, Institut ChemTech, CH-1705 Fribourg; [b]HES-SO Haute Ecole Spécialisée de Suisse occidentale, HES-SO Valais-Wallis, Institut Systèmes industriels, CH-1950 Sion

Abstract: Many studies designate hematite as a promising material for direct water splitting into hydrogen and oxygen. For a real outdoor application, it is important to consider hourly and seasonal conditions like temperature and sunlight intensity. The performance of an undoped hematite thin-film photoanode was tested in a photoelectrochemical cell under varying conditions of temperature and light intensity. Both parameters show a positive effect on performance under outdoor conditions.

Keywords: Hematite · Light intensity · Photoelectrochemical cell · Temperature · Water splitting

Introduction

The production of hydrogen from renewable intermittent energy sources provides a solution for storage of clean energy. This enables the production of liquid fuels such as methanol, which can be used in existing infrastructure. Solar-induced water splitting using a hematite (α-Fe_2O_3) photoanode in a photoelectrochemical (PEC) cell is one of the most promising technologies.

α-Fe_2O_3 is an inexpensive material with high chemical stability in alkaline conditions. The band gap of about 2.0–2.2 eV provides good absorption in the visible spectrum up to 590 nm with a theoretical conversion up to 20% of incident solar energy into hydrogen. However, several factors limit the practical performance of hematite for solar water splitting, such as high rate of carrier recombination, poor charge transport and short lifetime of minority carriers. The phenomena that occur in a PEC cell are not yet fully understood, but it is clear that the semiconductor/electrolyte interface holds a great importance for the performance.[1]

For commercial application, it is important to consider hourly and seasonal conditions such as variation of sunlight intensity and temperature in outdoor conditions. Several simple models have been proposed to predict the behavior of a PEC cell as a function of temperature and light intensity. The Gartner model describes the electron/hole formation in the space-charge layer of the semiconductor:[2]

$$I_{ph} = q\phi\left(1-\frac{e^{-\alpha W}}{1+\alpha L}\right) \tag{1}$$

where, I_{ph} is the photocurrent, q is the charge of the electron, ϕ is the photon flux, α is the absorption coefficient, W is the width of the space-charge layer and L is the carrier diffusion length (2–4 nm for α-Fe_2O_3). The Gartner model assumes that every hole contributes to the photocurrent. This model predicts a linear relationship between the luminous flux and the photocurrent.

The temperature dependence can be explained in several ways. Carrier diffusion length is defined as:

$$L = \sqrt{D\tau} \tag{2}$$

where D is the diffusion coefficient and τ is the minority carrier lifetime, which are two temperature-dependent parameters. The carrier lifetime (τ) is weakly dependent on temperature.[3] Carrier diffusion coefficients D_n (for electrons) and D_p (for holes) are related to minority carrier mobility (μ) and temperature by the Einstein equation:[3,4]

$$D_i = \frac{k_B T}{q}\mu_i \tag{3}$$

Finally, the empirical Varshni equation gives the band gap variation as a function of temperature:

$$E_g(T) = E_g(0) - \frac{AT^2}{T+B} \tag{4}$$

where A and B are fitting parameters of a given semiconductor and $E_g(0)$ is the band gap at zero kelvin.[3]

Experimental Part

Photocurrent measurements were performed in a 'cappuccino' photoelectrochemical cell with a standard three-electrode configuration. The hematite photoanode[5] was used as working electrode (WE), a platinum foil electrode (Metrohm ref 6.0305.100) as counter-electrode (CE) and an Ag/AgCl KCL 3M (Metrohm ref 6.0733.100) as reference electrode. The cell was filled with about 20 ml of electrolyte aqueous solution of 1.0 M NaOH (pH = 13.6) prepared with Milli-Q water. Only 0.28 cm^2 of the photoanode was in contact with the electrolyte and was exposed to sunlight. To obtain the photocurrent density-voltage (J-V) curves, an external potential bias is applied between the working electrode and the counter electrode at a scan rate of 10 mV s^{-1} by a Bio-Logic SP-50 potentiostat. The potential (E_{we}) was measured between the working electrode and the reference electrode and reported against the reversible hydrogen electrode (RHE) according to the Nernst equation:

$$E_{RHE} = E_{we} + E^{o}_{AgCl} + 0.059pH \tag{5}$$

with E^0_{AgCl} = 0.210 V at 25 °C. The temperature dependence of about 1 mV/°C is neglected. The photoanode was illuminated with a Xenon short arc lamp (Osram XBO R 180/45C) with integrated parabolic reflector and IR short pass filter (Thorlabs

FEL0800, cutoff 800 nm). The incident illumination power was measured with a calibrated photodiode (Thorlabs S120VC) and adjusted with the lamp power supply (Lumina Power XLB-300).

The PEC cell was placed in a thermostatic box. The temperature was measured by a thermocouple immersed in the electrolyte and is controlled with a Peltier element.

Effect of Sunlight Intensity

Power density was varied from 30 to 100 mW cm^{-2} which corresponds to an illumination of 0.3 to 1.0 sun equivalent. The electrolyte temperature is kept constant at 26 °C. The J-V curve shows a characteristic curve with a saturation region between 1.4 and 1.7V$_{RHE}$ as a flat area (plateau)[5] defined by an inflection point Jpl (Fig. 1).

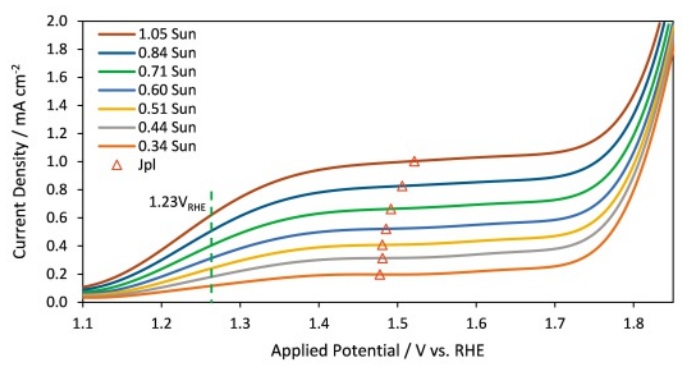

Fig. 1. Photocurrent density-voltage (J-V) diagram of the hematite photoanode at different light intensities from about 0.3 to 1.0 sun equivalent.

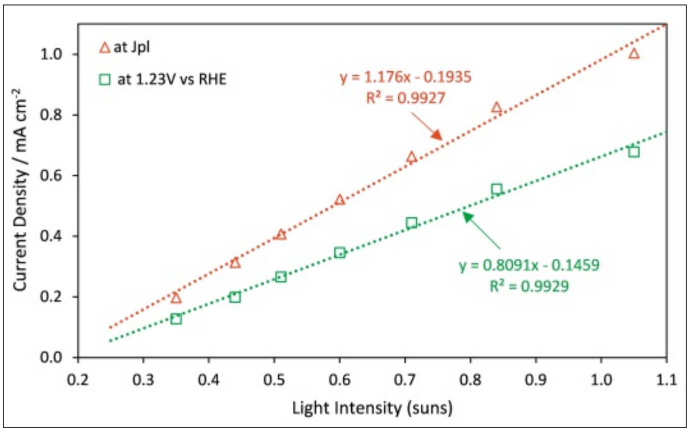

Fig. 2. Linear relationship between light intensity in sun equivalent and the generated photocurrent density.

The current density observed at 1.23VRHE or at Jpl (plateau) follows a nearly linear relationship (Fig. 2) in accordance with Eqn. (1). No saturation effect is observed with increasing illumination. The non-linearity for higher illuminations can be explained by the increased hole recombination rate observed with higher generation rate.[6]

Effect of Temperature

The temperature varied from 25 °C to maximum 50 °C to prevent evaporation of the electrolyte. The electrolyte was replaced at each experiment (Fig. 3).

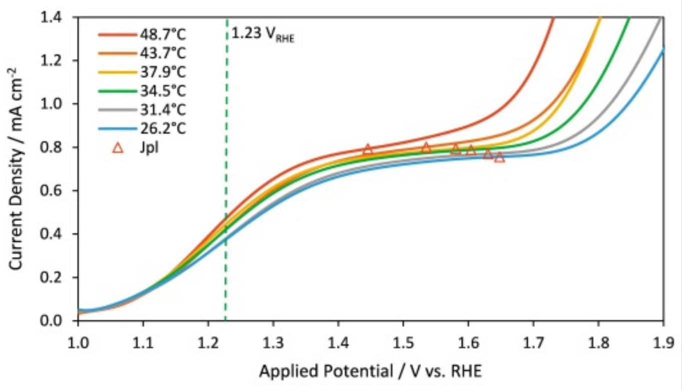

Fig. 3. Photocurrent density-voltage (J-V) diagram of the hematite photoanode at various temperatures from about 25 °C to 50 °C.

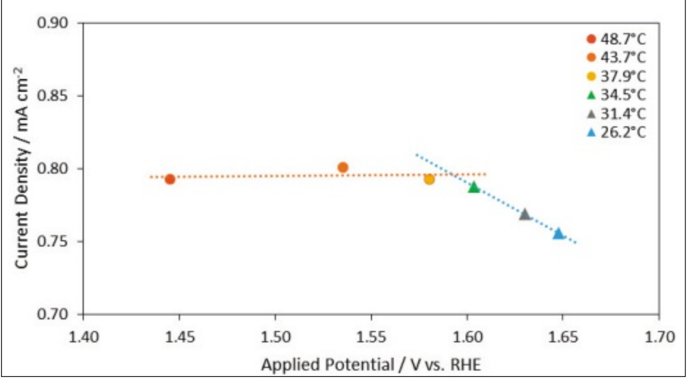

Fig. 4. Drift of inflection point (J_{pl}) as function of temperature.

The temperature has an effect on position of the inflection point defined in the photocurrent saturation region. The photovoltage show a consistent shift to lower potential. The photocurrent increases with temperature but we can see a saturation effect beyond about 35 °C (Fig. 4). The photocurrent increase is mainly due to the improved minority carrier mobility and therefore the carrier diffusion length. This fact is weakly countered by the minority carrier lifetime which typically decreases slightly with temperature.[7]

Conclusion

This study shows a positive effect of sunlight intensity and temperature on a photoelectrochemical cell for water splitting with hematite photoanode. The photocurrent increases linearly with sunlight without significant saturation effect. The advantageous temperature effect avoids the loss of efficiency due to PEC cell overheating. For a commercial application, the photoelectrochemical cell does not require a cooling system under conventional operating conditions.

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