Chronoamperometric study of membrane electrode assembly operation in unbiased continuous flow photoelectrochemical water splitting

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Water splitting was performed in a photoelectrochemical cell with water oxidation and hydrogen formation reactions in two separate compartments. A photoanode consisting of carbon paper loaded with TiO_2 and a cathode made of Pt dispersed on carbon black spread also on carbon paper were fixed on both sides of a Nafion[®] membrane and electrically coupled via an external circuit. Anode and cathode compartments with serpentine flow field were operated either in liquid or vapor phase. Electrical current was monitored with chronoamperometry and D_2 formation from deuterated water using mass spectrometry. Mapping the photocurrent under a variety of reaction conditions enabled identification of the limiting factors related to proton and photocarrier transport and product evacuation. This comprehensive research approach to the operation of a PEC will assist future optimization of cell design and development of membrane electrode assemblies.

1 Introduction

The production of solar fuels *via* artificial photosynthesis currently is one of the most appealing scientific challenges¹. Especially the solar generation of hydrogen using semiconductor materials is attracting the interest of the scientific community². The pioneering work of Honda and Fujishima on solar water splitting using titanium dioxide electrodes already dates over 40 years back³. Today, a variety of advanced semiconductor materials are under investigation^{4,5}. Suspended TaON and WO_3 semiconductor nanoparticles coated with cocatalysts and a ZrO_2 shell to reduce surface defects⁶ is one of the most powerful systems for solar water splitting. Grätzel and co-workers greatly improved the performance of Fe_2O_3 photoanodes by Si doping and Cu_2O photocathodes by applying a protective coating^{7–9}. The Nocera team developed a cobalt electrocatalyst¹⁰ and combined it with a triple junction silicon semiconductor to achieve high overall water splitting efficiency in a wireless system under neutral pH conditions¹¹.

Besides the semiconductor and co-catalyst materials, the design of the photoelectrochemical cell (PEC) in which the solar water splitting is performed is critical. In a conventional photoelectrochemical experimental setup, the two electrodes are immersed in aqueous solution and connected

via wiring^{11–15}. Such approach has been used in the seminal work by Fujishima and Honda³ and in Khaselev and Turner's tandem cell¹⁶. In a more advanced wireless design a semiconductor layer sandwiched between the two electrodes serves as electrical connection^{2,11,17}. Separation of the produced hydrogen from the oxygen can be envisioned by separating anode and cathode in two compartments. The intercompartment proton transfer in such device can be achieved by a proton conducting membrane or a frit^{15,18–20}. In such configuration protons generated at the anode diffuse through the aqueous electrolyte and the membrane barrier to the cathode. Some researchers circumvented the need for a liquid electrolyte by attaching the anode and cathode at either side of a proton exchange membrane^{21–24}. This design resembles a fuel cell, which commonly comprises a Nafion[®] membrane between the electrodes.

Physical separation of cathode and anode allows to optimize the reaction conditions in each compartment separately. At the cathode liquid water impedes hydrogen gas evolution from the electrode surface²² while at the anode, the presence of liquid water is favorable²⁵. In such solid electrolyte photoelectrochemical cell the design of the interface is critical. Spurgeon *et al.* designed an electrically conducting interface with embedded p-Si micropillars which could be used in such a set-up²⁶. Gray suggested a tandem cell in which a photoanode absorbs the blue part of the solar spectrum and is transparent to the red part, which is absorbed by a photocathode²⁷. These encouraging developments demonstrate

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Fig. 1: The home-made PEC. Left: photograph of assembled PEC; Right: scheme of the components.

the potential of a solid electrolyte photoelectrochemical cell with separate anode and cathode compartments. Compared with single compartment systems, photocurrents of such two-compartment PECs are currently insufficient for practical application and processes affecting performance are poorly understood. In order to assess the influence of a solid electrolyte in photoelectrochemical cells, we built a basic continuous flow two-compartment PEC. Separated anode and cathode serpentine flow compartments can be operated independently either in liquid or vapor phase. By operating the cell with a minimum of external interfering factors and mapping photocurrent under various reaction conditions the parameters influencing the performance of the PEC could be disentangled. To cope with very low hydrogen formation rates, deuterated water was fed to the cell and D_2 formation monitored by mass spectrometry at the cathode outlet. The results of PEC chronoamperometry will aid the development of improved PEC designs.

2 Experimental

2.1 Materials

MilliQ water with resistivity of $18.2 \text{ M}\Omega\text{-cm}$ was used. Nitrogen gas (99.999 %, Air Liquide, Brussels, Belgium) was purified (Varian CP17970 filter, Agilent, Santa Clara, CA) to remove all traces of oxygen before usage. Oxygen gas (99.995 %, Air Liquide, Brussels, Belgium) was used without further purification. A stream of purified N_2 was bubbled through a vessel with MilliQ water at 20°C to generate a gas stream with a water content of 0.017 mg/ml . Hydrogen peroxide (50 wt.%) was purchased from Acros Organics (Fair Lawn, NJ). Sulphuric acid (95-97 %), deuterium oxide (99.9 atom%) and Nafion[®] solution (20% in ethanol) were obtained from Sigma Aldrich (St. Louis, MO). Toray carbon paper 030 was obtained from Fuel Cell Earth (Stoneham, MA). E-Tek 60% platinum/carbon black (Pt/CB) powder was from Umicore (Brussels, Belgium). Degussa P25 powder was obtained

from Evonik (Essen, Germany). Nafion[®] 117 proton exchange membrane was obtained from Quintech (Göppingen, Germany) and will be referred to as Nafion[®].

2.2 Electrode preparation

The electrodes consisted of conducting and chemically inert Toray paper loaded with a catalyst. The cathode was prepared by depositing platinum-loaded carbon black (CB) on Toray paper (1 cm diameter) *via* drop-casting of a suspension of Pt/CB/Nafion[®] solution in ethanol, followed by air drying at 60°C . A Pt loading of 0.09 mg/cm^2 and a Nafion[®] coating of 0.015 mg/cm^2 was achieved. The anode was made by electrophoretic deposition of P25 TiO_2 on Toray paper according to the method of Boccacini *et al.*²⁸. A home-made electrophoresis cell was used consisting of inox sheets (AISI 321) held 1.0 cm apart by a Teflon[®] liner. A circular hole in a Teflon[®] mask with a diameter of 1 cm ensured that an area of 0.78 cm^2 of the Toray paper was coated. The potential was controlled by a potentiostat (Versastat 4, Princeton Research Systems). An electric field of 10 V/cm was applied for 60 s. After deposition, the electrodes were dried in air for 24 h and subsequently annealed in air for 2 h at 450°C , attained at a ramping rate of 10°C/min . The deposited amount of TiO_2 was 0.5 mg/cm^2 in all cases.

2.3 Membrane electrode assembly (MEA)

Nafion[®] membranes were preconditioned according to an established procedure. The membrane was boiled in 5% hydrogen peroxide for 1 h and then treated in alternating baths of boiling $1 \text{ M H}_2\text{SO}_4$ and boiling water for 2 h and 3 h, respectively. After the last treatment in boiling water, the membrane was kept in MilliQ water in the dark at room temperature. Prior to using a membrane, it was removed from the water, quickly blotted to remove bulk water and then kept in an inox holder at room temperature for 24 h. Membrane electrode assemblies (MEA) were prepared by fixing the anode and cathode sheets on opposite sides of a pretreated Nafion[®] membrane, and hot-pressing between teflon liners at 5 MPa and 130°C for 2.5 min to obtain the MEA. After hot-pressing, the assembly was carefully removed from between the liners and allowed to cool in an inox holder. In some experiments, the MEA was modified by embedding the anode in Nafion[®]. To achieve this, a few droplets of Nafion[®] solution were cast on the anode and an additional layer of Nafion[®] membrane was added on top of the anode, prior to hot-pressing.

2.4 Photo-electrochemical cell (PEC)

The pressed MEA was inserted in a home-made photo-electrochemical cell (PEC) consisting of a graphite flow-field

plate at the cathode compartment and a home-made fused silica plate at the photoanode side (Fig. 1). Both the fused-silica plate and the graphite plate contained serpentine flows providing an optimal contact of the fluid with the electrode surface. After insertion of the MEA in the PEC, a cleaning protocol was performed. The anode compartment was fed with nitrogen-purged MilliQ water (peristaltic pump, Watson Marlow, Wilmington, MA) and the cathode with purified nitrogen gas flow. The system was purged overnight (at least 15 h) before making electrical contact. After this pretreatment, the cell was short circuited and the dark current monitored. The dark current quickly evolved towards values between 10 and 500 nA. Equilibrium was defined when only minor variations in dark current were observed for at least 5 minutes. In a standard experiment, a continuous flow of nitrogen-purged MilliQ water was pumped through the anode compartment at a rate of 0.75 ml/min. At the cathode side the nitrogen gas flow was 25 ml/min. The cell was illuminated by means of a broad spectrum Xe lamp with IR filter (200-750 nm; Oriel 66984, Newport, Irvine, CA) adjusted such that the incident intensity equalled 100 mW/cm². The photocurrents were recorded at 100 ms intervals using a potentiostat (Versastat 4, Princeton Applied Research, Oak Ridge, TN) and Versastudio electrochemical analysis software. Note that periodic oscillation of the photocurrent was observed, due to the operation of the peristaltic pump feeding liquid water to the anode compartment. The outlet of the cathode compartment was analyzed with a Quantitative Gas Analyzer (Hidden Analytical, Warrington, UK).

3 Results

3.1 Photocurrent and hydrogen formation under standard conditions

The photocurrent profile under standard conditions (liquid water at the anode compartment and nitrogen gas at the cathode compartment) has some particular features (Fig. 2). Upon illumination, the photocurrent rapidly increases and then falls to about half the peak value (anodic overshoot, AO). After a subsequent steady current increase (CI), a current decay (CD) sets in that persists until the end of the illumination. Finally, after the light is shut off, a cathodic undershoot (CU) is sometimes observed, depending on experimental conditions. Under standard conditions, the maximum photocurrent observed after the AO was around 50 μ A (Fig. 2). Based on the electrode surface area, this photocurrent corresponds with 64 μ A/cm² and an overall photoconversion efficiency of *ca.* 0.1 %. This is a low value, because we intentionally built a system with a minimum amount of components to investigate the influence of the proton conducting membrane. Nonetheless, it is comparable to the efficiency of similar

Fig. 2: Typical photocurrent profile under standard conditions during the first illumination run (anode: liquid water; cathode: N₂; illumination in the period 20-715 s). AO: anodic overshoot; CI: current increase; CD: current decay; CU: cathodic undershoot (not present here).

set-ups employing oxide semiconductors^{17,21,22}.

In the experiment of Figure 3 the influence of the duration of the dark period on the photocurrent was investigated. When the illumination is briefly interrupted, the AO does not return. After longer dark periods, however, an AO is observed. The height of the anodic overshoot is related to the length of the dark period.

The photocurrent profile during an experiment under standard conditions with 59 h continuous illumination is shown in Figure 4. The current decay persists over a long period. At the end of the illumination period the photocurrent is 8 μ A and not yet stabilized. However, when after a 45 min dark period the cell is illuminated again, the current is partly restored to a value of 20 μ A (Fig. 4), which corresponds to the level originally reached after 8 h of illumination. This suggests that long-term performance could be improved by alternating periods of illumination with short dark periods. The membrane-electrode assembly could several times be mounted and dismantled in the cell without deterioration of the performance under standard reaction conditions.

The hydrogen concentration in the cathode outlet was below the detection limit of the mass spectrometer due to interfering signals. In order to monitor product formation under continuous flow operation, deuterated water was used at the anode compartment and D₂ formation was measured at the cathode outlet (Fig. 5). The light was switched on and off again several times to probe the development of photocurrent

Fig. 3: Photocurrent under standard conditions with interruption of illumination for 5, 30, 210 and 1000 s in the periods indicated with arrows.

and D_2 formation. In the first 2500 s the formation of D_2 is lagging behind the generation of photocurrent. A likely explanation is that initially the Nafion[®] membrane is still in protonated form and (undetected) H_2 is formed, rather than D_2 . Later D_2 formation and photocurrent respond in parallel to illumination. In dark periods, although there is no photocurrent some D_2 is still detected at the cathode outlet, indicating retarded D_2 release by the platinum cathode. Delayed D_2 release could also partly explain the slow D_2 response at the beginning of the experiment. The Faradaic efficiency over the entire experiment of Figure 5 was estimated at *ca.* 94 %. Considering some photocurrent may have served H_2 production and the D_2 concentration did not return to zero at the end of the experiment, the Faradaic efficiency could even be close to 100 %.

3.2 Influence of reaction conditions in anode and cathode compartment on photocurrent

To gain insight into the photocurrent profiles the reaction conditions in the anode and cathode compartment of the PEC were varied. In a typical experiment, illumination periods of 500 s were interrupted with dark periods of 200 s. The observations are summarized in Table 1. Experimental conditions Nr. 1 correspond to the standard conditions.

Under Experimental conditions Nr. 2 the cathode was fed with liquid water instead of nitrogen gas (Fig. 6, Table 1). The anodic overshoot was limited. Significant cathodic undershoot was observed when the lamp was switched off. In a next experiment, under Experimental conditions Nr. 3 both

Fig. 4: Photocurrent decay during a long experiment under standard conditions. A 45 min dark period after 59 h of illumination gives rise to an anodic overshoot and partial restoration of the photocurrent.

compartments were run in vapor phase (Fig. 7). A high anodic overshoot peaking at 250 μA was obtained, and no cathodic undershoot. The photocurrent showed a continuous decay and evolved to *ca.* 2 μA after 2 h of illumination (not shown). A current increase as observed under standard conditions (Fig. 2) was absent. Under Experimental conditions Nr. 4, the water flow at the anode was saturated with oxygen gas (Fig. 8). Feeding water with dissolved oxygen to the anode suppressed the photocurrent. When the cathode compartment was purged with an oxygen gas stream instead of nitrogen, an enhanced photocurrent was obtained (Fig. 9). No anodic overshoot was observed, and a current increase followed by a decay, similar to the standard run (Fig. 2). Cathodic undershoot was not observed.

Feeding 0.5 M H_2SO_4 solution (nitrogen-purged) to the anode did not enhance the photocurrent (experimental conditions Nr. 6, Fig. 10). A beneficial effect on photocurrent was obtained when an acidic solution was fed to both compartments (experimental conditions Nr. 7, Fig. 11). To avoid introduction of a chemical bias, the same acid concentration was used on both sides. There was no anodic overshoot, no current increase nor cathodic undershoot. By feeding 0.5 M hydrogen peroxide solution to the anode, photocurrents were more than doubled compared to standard conditions (experimental conditions Nr. 8, Fig. 12). Such enhanced photocurrent tentatively is explained by a current doubling effect caused by electron injection into the conduction band of TiO_2 ^{14,21,29,30}. There was no overshoot and no current decay. The dark currents were negative, as reported by others before¹⁴. The photocurrent profile obtained does not resemble

Fig. 5: Photocurrent (expressed as rate of electron transfer) and rate of D_2 formation (as detected at the outlet of the cathode compartment) in a deuterated water splitting experiment under standard conditions. Illumination periods are indicated.

Fig. 7: Photocurrent in 500 s illumination period of an experiment with anode and cathode operated in vapor phase conditions (H_2O -saturated N_2 ; Experimental conditions Nr. 3).

Fig. 6: Photocurrent in 500 s illumination period of an experiment with anode and cathode operated under continuous liquid water flow (Experimental conditions Nr. 2).

Fig. 8: Photocurrent in 500 s illumination period of an experiment with anode fed with O_2 -saturated water and cathode flushed with N_2 (Experimental conditions Nr. 4).

the square-shaped profiles seen in literature^{14,29,31} but instead a steady-state photocurrent is preceded by a current increase.

3.3 Membrane electrode assembly with Nafion embedded anode

Inspired by the beneficial effect of Nafion[®] coating of electrodes in fuel cells^{32,33} and of TiO_2 in photocatalytic applications³⁴, the standard MEA was modified by treating the photoanode with Nafion[®] solution and fitting an additional layer of Nafion[®] on top of it. In such configuration the carbon paper with TiO_2 nanoparticles was sandwiched between

two Nafion[®] membranes. With this configuration, a new type of photocurrent profile was obtained (Fig. 13). Upon illumination an AO occurred, and subsequently the photocurrent quickly rose to steady-state values exceeding the AO peak. A relatively stable photocurrent of $108 \mu A$ was obtained, corresponding to an overall photoconversion efficiency of 0.22 %. During dark interruption the current decrease was less sharp compared to the standard MEA (Fig. 2). A second interruption of the light confirmed this behavior and showed the dark current to be persistent over longer time.

Table 1: Overview of water splitting experiments under different reaction conditions using a standard MEA. Photocurrent values refer to the values obtained at the end of the 500 s illumination period. AO: anodic overshoot; CI: current increase; CD: current decay; CU: cathodic undershoot; Y: yes; N: no.

Exp. Cond.	Anode conditions	Cathode conditions	Photocurrent (μA)	AO	CI	CD	CU	Figure
1 (standard)	Liquid water	Nitrogen gas	50	Y	Y	Y	N ^a	2
2	Liquid water	Liquid water	35	Y	Y	Y	Y	6
3	Water vapor	Water vapor	40 ^b	Y	N	N	N	7
4	Oxygen-saturated liquid water	Nitrogen gas	17	Y	Y	Y	Y	8
5	Liquid water	Oxygen gas	74	N	Y	Y	N	9
6	0.5 M sulphuric acid	Nitrogen gas	54	Y	N	Y	Y	10
7	0.5 M sulphuric acid	0.5 M sulphuric acid	158	N	N	Y	N	11
8	0.5 M hydrogen peroxide	Nitrogen gas	116	N	Y	N	Y	12

a: undershoots did occur after long illumination times (> 1000 s);

b: after 2 h of illumination, this value dropped to $2 \mu\text{A}$.

Fig. 9: Photocurrent in 500 s illumination period of an experiment with anode fed with N_2 -flushed water and cathode flushed with O_2 (Experimental conditions Nr. 5).

Fig. 10: Photocurrent in 500 s illumination period of an experiment with anode fed with N_2 -flushed 0.5 M H_2SO_4 and cathode flushed with N_2 (Experimental conditions Nr. 6).

3.4 Influence of illumination intensity

The photon conversion capability of the PEC was further assessed by modulating the irradiation intensity under standard conditions to lower and higher values and using the standard MEA as well as the MEA with Nafion[®] embedded anode (Figs. 14 and 15, respectively). After a few illumination and dark periods (not shown), the light intensity was increased stepwise from 40 to 150 mW/cm^2 . After each light interruption an AO occurred and photocurrent stabilized at a level depending on light intensity. The AO peak values and the steady state photocurrents are plotted against illumination intensity in Figure 16. For the standard MEA, the AOs increase proportionally with light intensity while the steady-state photocurrents show saturation behavior (Figs. 14 and 16). In the experiment with the modified MEA, the steady-state photocurrents

are much higher and exceed the AO peaks. Both the AO and steady-state values show proportionality with light intensity and no saturation (Figs. 15 and 16).

4 Discussion

4.1 Anodic overshoot (AO)

Anodic overshoot (AO) in a PEC frequently has been reported^{15,18,19,22,29–31,35–42}. Often, an AO can be explained by photocorrosion⁹ but this is unlikely in our case, as TiO_2 is a very robust material⁴³ and the overshoot is reproduced after a dark period (Fig. 3). The membrane electrode assembly was robust and could be dismantled and mounted again in the PEC without deterioration of performance. Bulk recombination processes are known to eliminate many of the

Fig. 11: Photocurrent in 500 s illumination period of an experiment with anode and cathode fed with N_2 -flushed 0.5 M H_2SO_4 (Experimental conditions Nr. 7).

Fig. 12: Photocurrent in 500 s illumination period of an experiment with anode fed with 0.5 M H_2O_2 and cathode flushed with N_2 (Experimental conditions Nr. 8).

photogenerated charge carriers in TiO_2 ⁴⁴. Since recombination in the bulk occurs on much shorter time scales compared to AO, recombination as a cause of AO can be discarded^{45,46}. In literature, capacitive charging of surface states has been identified as another possible origin of AO^{14,29,38,40–42,47}. Initially, surface states present on TiO_2 function as traps for photoholes from the bulk, while the photogenerated electrons flow to the counter electrode. After these hole traps are saturated, newly photogenerated holes will tend to accumulate because their consumption in the water oxidation reaction is a slow, four-hole process. Enhanced recombination after saturation of surface states can then explain why the initially high photocurrent drops to a lower steady-state value^{38,48}.

Fig. 13: Photocurrent obtained under standard conditions with two dark periods using a MEA with Nafion[®] embedded anode. Illumination periods are indicated.

Elimination of hole traps occurs in a time scale of minutes⁴⁹, matching with the duration of the observed AO.

Some authors identified photoelectrons instead of holes to accumulate in the semiconductor leading to enhanced recombination and reduced photocurrent⁵⁰. The nature of the accumulating charge carrier was clarified through experimental conditions Nr. 8 (Fig. 12), in which H_2O_2 was added to the anode compartment as a hole scavenger^{14,29–31}. The absence of an AO in presence of H_2O_2 can be ascribed to efficient removal of photogenerated holes through the facile oxidation reaction of H_2O_2 to water. If electron transport were limiting, the presence of a hole scavenger would have no influence on the development of AO peaks, which was not the case.

Investigation of cathode phenomena under different reaction conditions revealed an additional contribution to AO peaks. Reduction of traces of molecular oxygen initially adsorbed on the cathode, to water is a facile reaction, and the rapid depletion of the initial molecular oxygen impurity may cause a temporary electrical current excess²². Indeed, when oxygen gas continuously is supplied to the cathode compartment, AO is absent (Fig. 9, Conditions Nr. 5).

Anodic overshoot occurred not only using a fresh MEA, but also after a period in the dark (Fig. 3). The duration of a dark period has a strong influence on the intensity of the AO. Interruption of the illumination for less than 5 s does not generate an AO, while longer interruption times cause AO. This points at a slow underlying process occurring in the dark. After a first illumination period, all traces of residual oxygen are reduced to water so oxygen depletion can not

Fig. 14: Photocurrent obtained under standard conditions at varying illumination intensities. The light intensity is indicated in mW/cm^2 .

Fig. 15: Photocurrent obtained under standard conditions using a MEA with an additional layer of Nafion[®] on top of the anode, at varying illumination intensities. The light intensity is indicated in mW/cm^2 .

account for this AO. While regeneration of surface states at the TiO_2 particles of the anode can contribute⁴², proton accumulation at the cathode is suggested to contribute in the following way. When the illumination is interrupted, protons continue to diffuse from the anode to the cathode, because of the photoelectrochemically generated proton concentration gradient between anode and cathode. Since in absence of photocurrent protons are not electrochemically reduced, the proton concentration at the cathode rises above the steady-state value under illumination. When the light is turned on again, temporarily the current is high because of enhanced electron consumption for proton reduction at the cathode, and then drops again to the steady-state value. After a short dark period AO is absent, as in this case the proton concentration at the cathode has not yet sufficiently increased. The influence of proton concentration at the cathode on AO was further evidenced as follows. When sulfuric acid is provided at the anode only, AO is present after a dark period (Fig. 10, Conditions Nr. 6). The observation is readily explained by the proton accumulation mechanism. When both compartments are fed with sulfuric acid, there is no AO (Fig. 11; Conditions Nr. 7). An infinite supply of protons is provided all the time, and high photocurrent is reached all the time. Summarizing, three potential causes of AO can be proposed for a PEC that is operated under standard conditions with water fed at the anode and nitrogen purging at the cathode, viz. (i) hole trapping at the photanode, (ii) reduction of oxygen impurities at the cathode, and (iii) enhanced proton concentration at the cathode after a dark period.

4.2 Current increase (CI)

Increasing photocurrents in a PEC rarely have been observed^{21,39,50,51} and the origin of this CI phenomenon has not been addressed. In the present experiments under different experimental conditions at anode and cathode (Table 1), a CI after the AO is absent in presence of acid, suggesting the CI should be related to proton transfer. It is to be expected that some time is needed to generate a sufficient proton concentration at the anode to drive proton diffusion through the Nafion[®] membrane. According to this interpretation the CI corresponds to the reaching of a given steady-state proton concentration at the cathode. When mineral acid at high concentration is provided at the anode (Fig. 10) or both anode and cathode (Fig. 11), the proton supply at the cathode is no longer dependent on the water splitting process and CI is absent.

In the experiment under standard conditions (Fig. 2), the CI is ended at about 260 s. In the period of illumination (20–260 s), in total 9.8 mC of charge was transferred. Assuming absence of side reactions, this corresponds with *ca.* 102 nmol of protons produced. Using a 1D Fickian diffusion model, the proton flux to the cathode at the maximum photocurrent can be estimated. Using a diffusion constant according to a Grotthuss proton transport mechanism of $2.4 \cdot 10^{-5} \text{ cm}^2/\text{s}$ ⁵² and a membrane thickness of *ca.* 200 μm ⁵², the proton flux corresponds to 660 pmol/s at 50 μA photocurrent. It necessitates a concentration difference of 55 $\mu\text{mol}/\text{cm}^3$. Based on the volume of the anode compartment of 91 mm^3 , *ca.* 50 nmol protons are present at the anode.

Fig. 16: AO peak (a) and maximum photocurrent obtained in subsequent period (b) under standard conditions at different illumination intensities, using a standard MEA configuration and MEA configuration with Nafion[®] embedded anode. (experiments of Figs. 14 and 15).

Assuming an average proton flux of 330 pmol/s in the period 20–260 s, *ca.* 79 nmol protons have been transferred to the cathode. Summing up both contributions, *ca.* 129 nmol protons are to be generated, which is in reasonable agreement with the measured amount of 102 nmol.

The observation of enhanced and quickly increasing photocurrents in the experiment with Nafion[®] embedded anode is remarkable (Fig. 13). We ascribe this to two possible effects. When the photocatalyst is in close contact with Nafion[®], proton conductivity is enhanced^{32,33} which facilitates proton transport to the cathode compartment. In addition, Nafion[®] adsorption is known to change the surface charge of TiO₂ such that it is negatively charged even in acidic solution³⁴. The electrostatic field caused by a negative surface charge on TiO₂ can improve charge separation⁵³ which reduces charge carrier recombination²⁹.

With the MEA with Nafion[®] embedded anode the stable photocurrent scales linearly with illumination intensity, without saturation effects (Figs. 15 and 16). In previous intensity-modulated experiments the behavior of a PEC has been explained in terms of charge carrier recombination and water splitting kinetics^{29,42,46,50}. Recombination of charge carriers is expected to increase linearly with light intensity, since the concentration of majority carriers can be approached as being constant^{46,54}. The water splitting reaction appears to be pseudo-first order in hole concentration⁵⁵. In the experiment using the standard MEA (Figs. 14 and 16), saturation behavior is observed. The difference between the two MEA's can be interpreted in terms of a difference in proton conduction efficiency. These results confirm that proton transport can be a very important factor in unbiased systems at neutral pH.

4.3 Current decay (CD)

Current decay was observed under different experimental conditions (Table 1). CD could be due to a loss of catalyst from the electrodes⁷ but this explanation seems unlikely as currents can be restored after dark periods (Fig. 4). During operation in vapor phase (Fig. 7), the current decay is most probably caused by dehydration of the MEA^{25,56}. The present experimental conditions with permanent illumination of the MEA with Nafion[®] membrane seem to be more critical with respect to membrane dehydration than in electrolysis experiments⁵⁷.

In liquid phase it is generally accepted that molecular oxygen serves as a mediator for recombination processes, which is detrimental for performance^{22,38,39,42}. The absence of significant band bending in nanosized semiconductors⁵⁸ allows electron transfer from the conduction band to molecular oxygen in the electrolyte^{38,42}. Molecular oxygen produced at the photoanode can act as an electron scavenger and capture electrons from the conduction band or from electron trapping sites in TiO₂, after which it can in turn act as a hole scavenger, thus completing the recombination cycle⁵⁹.

Under standard conditions, as an experiment proceeds and more oxygen is being produced, recombination rates increase and the photocurrent drops. As such, the observed photocurrent is a result of the competition between the oxidation of water and of oxygen anions, regulated by the oxygen concentration⁶⁰. The influence of molecular oxygen was evaluated by saturating the anode compartment with oxygen (Fig. 8). In this measurement, the photocurrent was 17 μA compared to 50 μA under standard conditions. In the long-term experiment the photocurrent dropped even deeper

to 8 μA (Fig. 4). Clearly, recombination *via* oxygen is not the only process that determines the current decay.

Processes occurring at the cathode could also play a role in CD. Seger and Kamat²¹ measured a 40 % lower photocurrent in absence of a convective flow through the cathodic compartment and suggested this was due to insufficient evacuation of hydrogen bubbles. Ampelli *et al.*²² mentioned the detrimental effect of gas cap formation on the electrode surface. Here, we propose that hydrogen build-up at the cathode is partly responsible for a CD. When the cathode compartment is operated in liquid phase, the current is lower compared to gas phase (Table 1). Hydrogen gas removal at the cathode side is impeded during our experiments because a water film is formed on the cathode surface. Water at the anode reaches the cathode through the Nafion[®] membrane⁵⁶, which was visually confirmed since some water droplets are present in the cathode flow channel when opening the cell after use. Due to its limited solubility in water, hydrogen removal is slow and leads to either a concentration overpotential (diffusional transport) or a bubble overpotential (gas evolution). In the presence of oxygen at the cathode, the photocurrent is higher and the current decay is slower (Fig. 9). Oxygen can reach the cathode surface and react with protons to form water as the reaction product⁵⁷. It is clear that a cathodic compartment should preferably be operated in the gas phase and water accumulation should be avoided as much as possible. To accomplish this, it will be necessary to adapt the membrane in order to reduce water transport. Alternatively, the anode compartment could be operated under vapor phase conditions, which could lead to higher currents but may complicate moisture management (Fig. 7).

4.4 Cathodic undershoot (CU)

Cathodic undershoots are a common feature in many photoelectrochemical experiments and a straightforward explanation can be given^{14,29,30,38,40,47,48}. Undershoots happen when the current is reversed, *i.e.* electrons flow from reductants at the platinum electrode to the TiO_2 electrode, where they reduce oxidant species. This is in essence what happens in a fuel cell. It occurs when illumination is turned off and the driving force to push the reaction to the right is eliminated. At the platinum side, hydrogen gas is then oxidized into protons. At the titanium dioxide side, accumulated oxygen can be the oxidant, but trapped holes may accept electrons as well. We only observed undershoots in certain cases. After very long measurements, a lot of product has accumulated at either side so undershoots occur. The same holds for experiments in which water flows through the cathodic compartment, as hydrogen builds up more easily. In this respect, the presence of undershoots can be used as an indicator for the amount of product

accumulation. This would mean the absence of an undershoot indicates adequate mass transport and an efficient reaction.

5 Conclusion

This study has shown that PEC chronoamperometry is a valuable tool to identify limiting factors in a photoelectrochemical water splitting cell. Water splitting was performed in a photoelectrochemical cell with Nafion[®] membrane sandwiched between two carbon papers with photoactive TiO_2 nanoparticles on the anode side and Pt/carbon black particles on the cathode side. An advantage of such PEC with separated electrodes is that the produced hydrogen gas can be collected separately from the oxygen. Reproducible photocurrents were generated and a Faradaic efficiency close to 100 % was achieved. For the first time pure water splitting without bias was performed in a two-compartment PEC. Complex photocurrent profiles were registered, starting upon illumination with an anodic overshoot, followed by a current increase, a current decay and a cathodic undershoot when the light is switched off. Insight into the origin of these phenomena was gained by varying the reaction conditions in the two compartments and adding gases, hole scavengers and acid. The anodic overshoot was ascribed to the saturation of surface states at the TiO_2 particles, oxygen impurities at the cathode, and proton accumulation at the cathode after an intermittent dark period. The current increase period is due to the progressive build-up of the proton concentration gradient over the Nafion[®] membrane. A current decay is due to membrane dehydration when the PEC is operated in vapor phase. Under liquid conditions, recombination *via* oxygen is deteriorating the photoefficiency at the anode and hydrogen evolution is problematic at the cathode. Cathodic undershoot typically observed after long illumination times is due to the reverse reaction in dark conditions. The obtained experimental data can serve the validation of theoretical models currently being developed^{20,61,62}. The gained insight will guide further improvement of PEC components and reactors. The influence of a solid electrolyte separator was investigated. Using pure water at neutral pH, proton conduction was identified as a major efficiency limiting factor. In an improved design of the membrane electrode assembly, the photoanode was embedded in additional Nafion[®] and a doubling of photocurrent was achieved. The improvement was ascribed to the negative surface charge of Nafion[®] coated TiO_2 particles and improved proton conductivity. Additional improvements are expected when including a water oxidation catalyst at the anode. By implementing more advanced materials, combined with smart interface engineering, efficiencies of two-compartment PECs could be raised to a practical level.

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