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Preliminary note

Photocatalytic oxidation of water to O_2 on AgCl-coated electrodes

Martin Lanz, Gion Calzaferri *

Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, CH-3000 Bern 9, Switzerland

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Abstract

The photocatalytic oxidation of water to O_2 on thin AgCl-coated electrodes is reported. Silver produced during the photochemical oxidation of water to O_2 on AgCl can be electrochemically re-oxidized. © 1997 Elsevier Science S.A.

Keywords: Photocatalysis; Photocatalytic water oxidation; Water oxidation to oxygen; Silver chloride; Silver chloride electrodes

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We have recently reported that silver chloride layers on SnO_2-coated glass plates produce O_2 from water with a high quantum yield when irradiated under appropriate conditions. The system shows self-sensitization of photochemical O_2 evolution, which means that new photoactive colour centres are formed on near-UV illumination (340–390 nm) composed of reduced or partially reduced silver species [1]. The reaction is favoured in the presence of a small excess of Ag^+ ions, with a maximum O_2 evolution rate at pH 4–5. The Ag^+ ions act as electron acceptors, according to

$$[n\mathrm{Ag}^+, m\mathrm{AgCl}] + \frac{r}{2}\mathrm{H_2O} \xrightarrow{h\nu} [(n-r)\mathrm{Ag}^+, m\mathrm{AgCl}, r\mathrm{Ag}^0] + r\mathrm{H}^+ + \frac{r}{4}\mathrm{O_2} \qquad (1)$$

The reduced silver species must be re-oxidized to realize photocatalytic water oxidation

$$[(n-r)\mathrm{Ag}^+, m\mathrm{AgCl}, r\mathrm{Ag}^0] \rightarrow [n\mathrm{Ag}^+, m\mathrm{AgCl}] + re^- \qquad (2)$$

Realizing Eq. (2) by electrochemical means as illustrated in Scheme 1 is challenging, because this allows the spatial separation of the oxidative and reductive half-reactions of water photolysis [2,3]. Therefore we investigated the combined photochemical and electrochemical properties of AgCl layers on electrode substrates with regard to reactions (1) and (2) and made interesting and encouraging observations.

The apparatus used to study the photochemical and electrochemical properties of thin substrate layers on illumination has been described in Refs. [1,4]. Its main part is a photocell, with a volume of approximately 1 ml, connected to an N_2-purged electrolyte reservoir (volume, 130 ml). A peristaltic pump transports the electrolyte solution from the reservoir, via a capillary system, through the cell and back to the reservoir at a rate of about 1 ml min^{-1}. The AgCl layer is coated on an electrode disc which is placed in the photocell and can be illuminated through a quartz window. The AgCl-coated electrode is the working electrode of a three-electrode system for electrochemical experiments. The photocell also contains a Clark O_2 sensor (WTW Instruments, Germany) which is calibrated by injecting air-saturated water. The O_2 evolution and photocurrent can be measured simultaneously. The AgCl-coated electrode is illuminated with white light from a 450 W Xe arc lamp. The light is passed through a water filter and a Pyrex lens to remove the IR and far-UV light respectively. The light intensity at the electrode is approximately 150 mW cm^{-2} in the experiments reported here. Only part of the incoming light is absorbed by the sample, consisting of about 0.5 μmol AgCl cm^{-2}.

The AgCl layers on the electrodes were produced by precipitation. Electrically conducting SnO_2/F-coated glass and platinum were used as electrode substrates. The electrode disc was placed in a small beaker (bottom diameter, 23 mm) and covered with 2 ml of bidistilled water. First, 20 μl of 0.1 M $AgNO_3$(aq.) was added, followed by 20 μl of 0.1 M NaCl(aq.); after stirring, sedimentation of the precipitated AgCl was allowed overnight in the dark. The AgCl-coated electrode was dried at 50 °C for a few minutes and the coating was fixed with 20 μl of poly(vinyl chloride) (PVC) dissolved in tetrahydrofuran (THF) (0.5 mg ml^{-1}). The small amount of PVC was used to provide sufficient mechanical stability. However, it played no role in the photochemistry or

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* Corresponding author. Tel.: +41 31 631 42 36; fax: +41 31 631 39 94; e-mail: calza@solar.iac.unibe.ch

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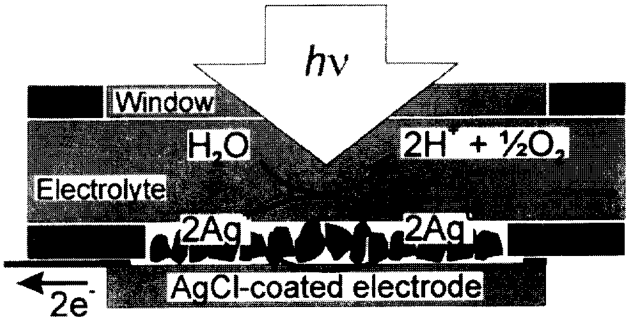

Scheme 1.

electrochemistry taking place. The electrode area exposed to the light was about 1 cm^2 and the amount of AgCl was 65 μg (460 nmol, corresponding to an equivalent charge of 44 mC). As an electrolyte, 0.1 M $NaNO_3$ aqueous solution with 1 mM $AgNO_3$ was used. The pH was maintained at pH 4–5 throughout the experiments described. If necessary, it was adjusted with 0.1 M $HClO_4$ or 0.1 M NaOH.

In the chronoamperometric experiments, the AgCl-coated electrode was polarized at 0.0 V vs. Hg/Hg_2SO_4 (0.64 V vs. NHE). Some samples were analysed by scanning electron microscopy (SEM) before and after the photoelectrochemical experiments, showing that about 50% of the electrode surface was covered by AgCl microcrystals.

Fig. 1 shows the result of a chronoamperometric experiment with an AgCl-coated SnO_2 electrode. Illumination periods of 100 min duration alternate with dark periods of 25 min duration. It is remarkable that the O_2 signal and the photocurrent coincide when the light is switched on and off and that this is observed in all the experiments. Interestingly, the photocurrent is cathodic (reductive) during the first 12 min of the first illumination period and turns anodic (oxidative) afterwards. It reaches a steady anodic value of about 2.5 μA after a few hours. The O_2 production also reaches a steady state value. During the whole experiment shown in Fig. 1, a total of 670 nmol of O_2 is produced. This means that 2680 nmol of reduced silver is produced according to reaction (1). This corresponds to almost six turnovers with respect to the total amount of AgCl coated on the electrode. The integrated photocurrent is 69 mC; hence we deduce that 27% of the reduced silver is electrochemically re-oxidized in this experiment. The remaining 73% of the reduced silver is not accessible and is probably lost somewhere in the large electrolyte reservoir. We conclude that the AgCl layer is catalytically active in the photoreduction of silver ions continuously provided by the electrolyte.

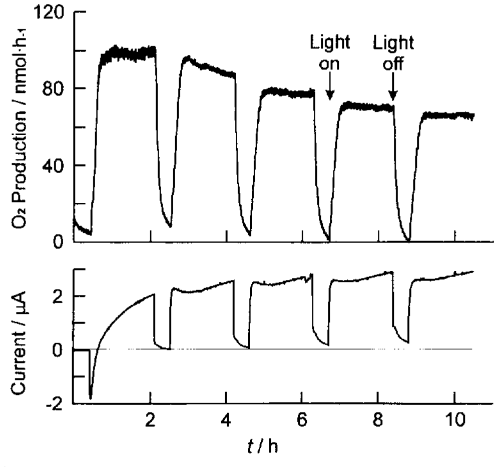

Fig. 1. Chronoamperometry of an AgCl-coated SnO_2 electrode at 0.0 V vs. Hg/Hg_2SO_4, with illumination and dark periods. The O_2 production rate (nmol h^{-1}) and the photocurrent (μA; anodic current is drawn upwards) are plotted vs. time.

We observed a similar behaviour in an analogous experiment, but this time with platinum as the electrode substrate (Fig. 2); 360 nmol of O_2 is produced until the experiment is stopped after 10.5 h, corresponding to more than three turnovers of the AgCl layer coated on the electrode. The integrated photocurrent is 43 mC. This means that 31% of the reduced silver is re-oxidized. It is remarkable that the photocurrent increases from one illumination period to the next. If only the last two illumination periods in Fig. 2 are considered, 67% of the silver produced during these two periods is simultaneously re-oxidized. If the AgCl-coated platinum electrode is illuminated for a longer time, the current reaches a steady value. This is shown in Fig. 3. In this experiment, the same AgCl-coated platinum electrode is subjected to illumination periods of 10 h alternating with dark periods of 2.5 h duration. The total charge passed in this experiment is 640 mC, which corresponds to 14.5 turnovers of the AgCl layer. The real turnover number is larger since not all of the produced silver is re-oxidized. We checked that the O_2 production did not decrease during this experiment.

We observed in the experiments shown in Figs. 1–3 that the anodic current does not usually drop completely to zero during the dark period applied. Therefore it seems to be possible to oxidize at least part of the reduced silver deposited

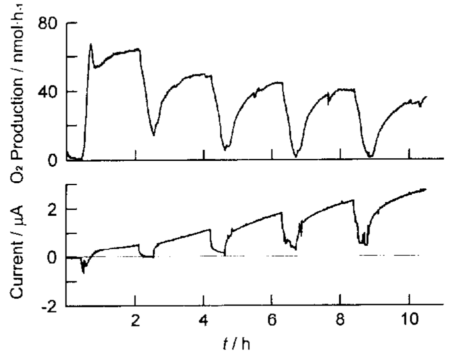

Fig. 2. Same experiment as in Fig. 1, but with an AgCl-coated platinum electrode.

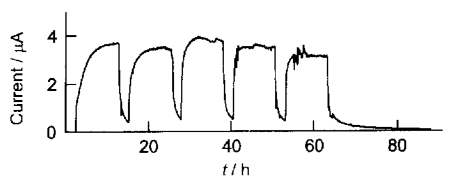

Fig. 3. Chronoamperometry of an AgCl-coated platinum electrode at 0.0 V vs. Hg/Hg_2SO_4, with illumination periods of 10 h each. The photocurrent (μA; anodic current is drawn upwards) is plotted vs. time.

on the photoelectrode during reaction (1) after illumination. To verify this hypothesis, an AgCl-coated SnO_2 electrode was illuminated in the same way for the same time as in the experiments shown in Figs. 1 and 2, but at zero current, i.e. without an applied potential. The amount of O_2 evolved was 730 nmol, close to the value in the experiment of Fig. 1. At the end of illumination, a potential of 0.0 V vs. Hg/Hg_2SO_4 was applied to the electrode, which led to an anodic dark current which was 30 μA at the beginning and decreased to zero within 150 min. Integration of the current yielded a charge of 61 mC, which means that 22% of the reduced silver was re-oxidized. This amount is somewhat smaller than that in the experiments of Figs. 1 and 2, but readily shows that part of the silver is deposited on the electrode during illumination and can be re-oxidized electrochemically.

The photocurrent is reductive during the first 10–15 min of illumination of an AgCl-coated electrode and oxidative afterwards (see Figs. 1 and 2). We assume that the cathodic (reductive) current is due to the reduction of reaction intermediates arising during the photo-oxidation of water as described in Ref. [1]. As the photoexperiment is continued, an increasing amount of reduced silver species is produced at the photoelectrode. The electrode is set at a potential at which silver oxidation takes place under the applied electrochemical conditions. This leads to the observed anodic (oxidative) current. Anodic photocurrents have been reported previously for AgCl-coated silver electrodes immersed in halide solutions [5]. However, under the conditions of Ref. [5], no O_2 evolution occurs [1], and the interpretation given for the anodic photocurrent at the electrodes differs from the explanation which holds for our experiments.

Although the photochemical oxidation of water with AgCl on UV illumination was first reported by Baur and Rebmann [6] and later investigated by Metzner [7] and others (see Refs. [1,8]), this is the first report on the photocatalytic oxidation of water on AgCl-coated electrodes. Our experiments clearly show that the AgCl layer is catalytically active in the photochemical oxidation of water to O_2 under the applied conditions. This is supported by the observation that no change is observed in the SEM images of the electrodes taken before and after the photoelectrochemical experiments. The re-oxidation of the silver produced is efficient, but not complete. The major part of the losses appears to be due to the experimental set-up used, in particular the very large ratio of the electrolyte volume of the reservoir to the volume of the electrode chamber.

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