

# Photochemical oxidation of water and electrochemistry of silver chloride complexes occluded in zeolite A

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## Abstract

Appropriately prepared  $\text{Ag}^+$ -A zeolites evolve oxygen on illumination in the presence of water.  $\text{Cl}^-$  occluded in the cavities of zeolite A forms silver chloride complexes which are essential for the photochemical behaviour of the system. At approximately neutral pH,  $\text{Cl}^-$  leads to enhanced  $\text{O}_2$  evolution up to a critical concentration above which the oxygen evolution drops abruptly. Cyclic voltammograms of zeolite A monograin layers on glassy carbon electrodes containing occluded silver chloride complexes in the dark and on irradiation are reported.

*Keywords:* Oxidation of water; Silver chloride complexes; Zeolite A; Silver zeolite A; Cyclic voltammograms

## 1. Introduction

The photochemical oxidation of water in the presence of silver chloride and silver zeolites on irradiation with near-UV light has been reported [1,2]. By measuring the pH dependence of  $\text{O}_2$  evolution during irradiation of  $\text{Ag}^+$ -A zeolite samples, we have found a maximum sensitivity in approximately neutral aqueous suspensions [3]. However, after adding  $\text{Cl}^-$  to aqueous  $\text{Ag}^+$ -A zeolite suspensions, oxygen evolution is only observed above pH 9; below pH 4,  $\text{Cl}_2$  is measured and in the region in between the photoproduct hypochlorite is obtained [4]. During an investigation of the spectral sensitivity of the water oxidation ability of  $\text{Ag}^+$ -A zeolites, we found that self-sensitization takes place: as the reaction proceeds, the sensitivity is extended from the near-UV-visible wavelengths towards the red range [5]. A similar self-sensitization was observed for photochemical chloride evolution [6]. The self-sensitization effect was also observed on monograin  $\text{Ag}^+$ -A zeolite layers on quartz windows [7]. These monograin layers were used to develop electrodes to study the electrochemical properties of redox species inside zeolite cavities [7–9] and, eventually, to achieve electrochemical oxidation of the  $\text{Ag}^+$  reduced during the photochemical oxidation of water. During these investigations, it was

observed that the addition of  $\text{Cl}^-$  up to a certain amount is important for the oxidation of water to oxygen at approximately neutral pH. After exceeding a certain  $\text{Cl}^-$  concentration, the oxygen evolution stops abruptly under these conditions.  $\text{Cl}^-$  inside the zeolite cavities influences the voltammograms of silver zeolite-modified electrodes and experiments are reported in the dark and on illumination.

## 2. Experimental details

### 2.1. Incorporation of chloride into zeolite A

Saturated aqueous solutions of  $\text{CaCl}_2$  or  $\text{NaCl}$  containing suspended  $\text{Na}^+$ -A zeolite (Linde 4A, Baylith T, Bayer) were refluxed for 15 h [10]. The zeolites were washed with cold bidistilled water until the washing water was free of  $\text{Cl}^-$ , as demonstrated by adding 0.01 M  $\text{AgNO}_3$ . Thus all the  $\text{Cl}^-$  ions were occluded in the zeolite cage at room temperature. To make sure that no traces of these anions remained on the surface of the zeolite, the samples were treated twice for 1 h with boiling bidistilled water. During this treatment, the zeolite samples lost a small portion of the occluded  $\text{Cl}^-$ . For comparison, a zeolite A sample was stirred in a saturated  $\text{CaCl}_2$  solution at room temperature overnight. The chloride content of the zeolite samples

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was analysed by suspending 50 mg in 2 ml bidistilled water and adding 0.5 ml concentrated sulphuric acid to destroy the zeolite framework. The samples so obtained were covered with 5 ml heptane and the chloride was oxidized to chlorine by adding 0.5 ml of a 0.5 M  $\text{KMnO}_4$  solution. After 30 min of reaction, the two phases were mixed by intense shaking. The chlorine in the organic phase was analysed photometrically. Calibration data were obtained by treating known amounts of NaCl in the same way. The  $\text{Cl}^-$  content was  $0.93 \pm 0.04$  ions and  $1.90 \pm 0.02$  ions per unit cell after treatment with NaCl and  $\text{CaCl}_2$  respectively. Only traces of  $\text{Cl}^-$  were found in the samples treated at room temperature. Samples of zeolite A containing  $\text{Br}^-$  and  $\text{I}^-$  were prepared in a similar way. Anion contents of  $1.3 \pm 0.1$  per unit cell were observed. These samples were also treated twice for 1 h with boiling bidistilled water. They lost only traces of halide ions during this treatment, which means that the larger  $\text{Br}^-$  and  $\text{I}^-$  anions are occluded even at 100 °C.

## 2.2. Ion exchange

$\text{Ca}^{2+}$ -A zeolite containing chloride (1 g) was exchanged with  $\text{Ag}^+$  by treating samples prepared as described above four times for 1 h with 10 ml 1 M aqueous silver nitrate solutions. These samples are denoted as  $(\text{Ag}^+)_n(\text{Cl}^-)_x$ -A zeolites, where  $n$  and  $x$  refer to one unit cell. Only part of the incorporated  $\text{Ag}^+$  remains exchangeable, the rest is trapped within the zeolite cavities. To determine the stoichiometry of the occluded silver chloride complexes, the exchangeable silver ions were replaced by sodium ions. The samples were then carefully washed with bidistilled water and dissolved in 10% HF solution. After adding portions of 1 M NaOH until the pH was greater than 12, the silver ions were complexed with  $\text{CN}^-$  and determined quantitatively by atomic absorption spectroscopy (AAS). The result of this analysis was that  $6 \pm 0.5$   $\text{Ag}^+$  ions per unit cell are occluded, which means that the  $\text{Ag}^+/\text{Cl}^-$  ratio is approximately three.

## 2.3. Photochemical experiments

Photochemical experiments were performed in an apparatus similar to that described in Ref. [5] at room temperature with a similar type of Clark sensor and the same calibration procedure. Zeolite samples (500 mg) were suspended in 130 ml water and illuminated with white light from a 1000 W xenon lamp (total radiant power, approximately  $20 \text{ mW cm}^{-2}$ ). The irradiated surface area was  $35 \text{ cm}^2$ . Only part of the light was absorbed by the suspension.

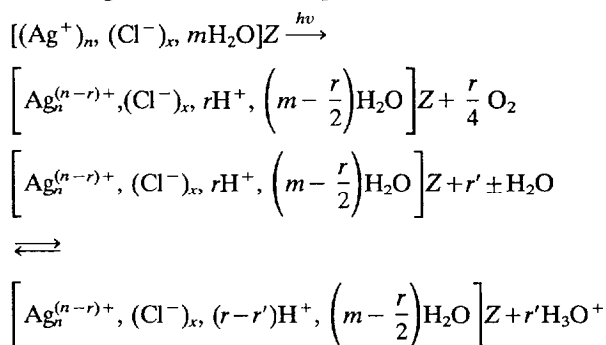
## 2.4. Electrochemical experiments

Monograin zeolite layers were prepared on glassy carbon (Victor Kyburz AG, Switzerland,  $1 \text{ cm}^2$ ) as described in Ref. [8]. Electrochemical experiments were carried out in a standard one-component, three-electrode cell that allows illumination of the working electrode. The counter-electrode was a Pt sheet electrode and the reference electrode was a saturated  $\text{Ag}/\text{AgCl}$  electrode. The potentials were referred to this electrode and not corrected for iR drop and liquid junction potentials. Voltammetric experiments were performed with a Schlumberger electrochemical interface SI 1286. A 1 M KCl solution was used as electrolyte.

## 3. Results

### 3.1. Photochemical oxygen evolution

Aqueous suspensions and monograins layers of  $(\text{Ag}^+)_n(\text{Cl}^-)_x$ -A zeolite are photoactive. In pure water they evolve oxygen on illumination, while silver ions are reduced and protons are set free according to the following stoichiometric equations



where Z represents the negatively charged zeolite lattice. This is illustrated in Fig. 1 where we show the result of a test carried out as described in Section 2. The first three peaks are the calibration peaks of the Clark sensor and correspond to the injection of 9.3, 13.9 and  $18.6 \mu\text{g}$  of  $\text{O}_2$  (dissolved in water) respectively. The pH drop during the illumination was similar to that described in Ref. [5].

Samples of  $(\text{Ag}^+)_n(\text{Cl}^-)_x$ -A zeolite containing no exchangeable silver ions are also photoactive, but evolve less oxygen.  $\text{Ag}^+$ -A zeolite containing no  $\text{Cl}^-$  and without chloride in the surrounding solution does not evolve oxygen on illumination and remains white under the applied conditions. However, oxygen signals appear immediately after the addition of small amounts of sodium chloride on illumination due to the formation of silver chloride on the surface of the zeolite crystals which was also shown to be photoactive. If the  $\text{Cl}^-$  concentration exceeds a critical value, the oxygen evolution stops between pH 8 and pH 6. This is illustrated

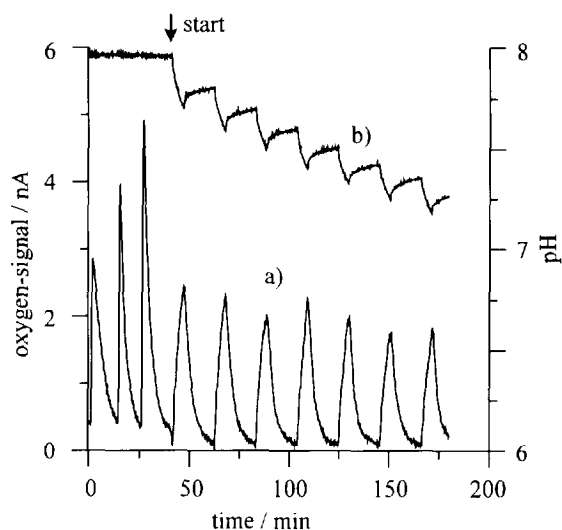


Fig. 1. Photochemical oxygen evolution (a) and pH change (b) of an  $(\text{Ag}^+)_n(\text{Cl}^-)_x$ -A zeolite suspension. The first three peaks are due to the calibration of the Clark sensor.

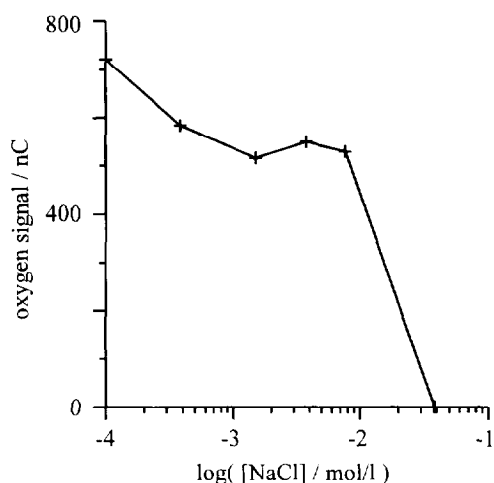


Fig. 2. Photochemical oxygen evolution of an  $(\text{Ag}^+)_n(\text{Cl}^-)_x$ -A zeolite suspension at pH 7. The integrated Clark sensor signals are plotted vs. the concentration of the subsequently added NaCl in the solution.

in Fig. 2 where we show the results of an experiment which was carried out in the same way as that reported in Fig. 1, but with the addition of portions of a 1 M NaCl solution. At the beginning, the added sodium chloride has little influence on the oxygen signal, but when the NaCl concentration of the zeolite suspension exceeds  $10^{-2}$  M the oxygen signal drops to zero.

These observations clarify the experimental problems encountered in the photochemical experiments when we tried to obtain quantitative results. They are in full agreement with previous results [4,6], where the photoproducts in chloride-containing solutions were found to be chlorine in acidic media, oxygen in alkaline media and probably hypochloride in neutral solutions. However, at that time we did not know that  $\text{Cl}^-$  up to a critical value had such a large influence on the photochemical oxygen evolution ability of  $\text{Ag}^+$ -A zeolite.

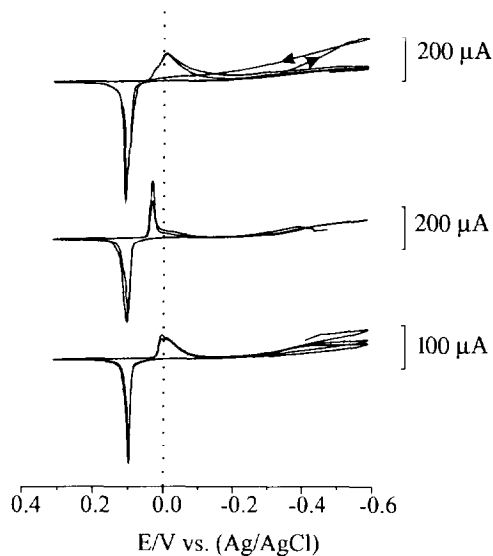


Fig. 3. Cyclic voltammograms of an  $(\text{Ag}^+)_n(\text{Cl}^-)_x$ -A zeolite-modified electrode in the dark (top and bottom) and on illumination (middle) in 1 M KCl (scan rate,  $2 \text{ mV s}^{-1}$ ). The cyclic voltammograms shown at the top were measured first, then those in the middle and finally those at the bottom.

### 3.2. Electrochemistry

A new method for preparing mechanically stable, dense,  $1 \mu\text{m}$  zeolite monograin layers on substrate electrodes allows detailed information to be obtained on the electrochemical behaviour of zeolite-modified electrodes containing redox species, and it is possible to distinguish between an intrazeolite ion transport mechanism and an intrazeolite electron transport mechanism [8,9]. We have applied the same technique to study the voltammetric behaviour of a monograin  $(\text{Ag}^+)_n(\text{Cl}^-)_x$ -A zeolite-modified glassy carbon electrode. The voltammograms shown at the top of Fig. 3 were measured first in the dark. The cathodic response of the first cycle (indicated by arrows) is broad and ranges from  $-350$  to  $-600 \text{ mV}$  vs.  $\text{Ag}/\text{AgCl}$ . In the subsequent scans, the cathodic peak becomes narrow and appears at  $0 \text{ V}$ . On illumination (middle), it becomes sharper and shifts to a more positive potential, whereas the anodic peak remains nearly unchanged. After switching the light off (bottom), the same qualitative voltammetric behaviour as in the second and later scans before illumination is observed, but the current is smaller.

### 4. Discussion

It has been shown that  $\text{Cl}^-$  inside the zeolite cavities and in the surrounding solution plays a complex role. Up to a critical concentration, which is probably in the region of an  $\text{Ag}^+/\text{Cl}^-$  ratio of unity,  $\text{Cl}^-$  enhances the photochemical oxidation of water under the conditions reported here. As soon as the critical concentration of

free  $\text{Cl}^-$  is exceeded, photochemical oxygen evolution stops. Up to this limit, the  $(\text{Ag}^+)_n(\text{Cl}^-)_x$ -A zeolite samples show the same type of self-sensitization as reported previously [5,7].

The voltammograms of the  $(\text{Ag}^+)_n(\text{Cl}^-)_x$ -A zeolite-modified glassy carbon electrodes are significantly different from those observed for  $\text{Ag}^+$ -A zeolite-modified glassy carbon electrodes where eight distinct silver species are obtained [8]. The silver chloride complexes trapped in the zeolite cavities show a more uniform and quasi-reversible voltammetric behaviour. In the voltammograms performed on illumination, we assume that the photochemically reduced silver species serve as seeds for the electrochemical reduction of the remaining silver ions occluded in the zeolite cavities which causes a positive shift of the cathodic cycle. To quantify our observations, experiments are necessary, in which pH,  $\text{Cl}^-$  concentration, type and concentration of the cocations, wavelength, light intensity and electrode potential are scanned in a systematic way. These experiments will provide a detailed understanding of the mechanism of the photochemical oxidation of water and of the self-sensitization of the  $(\text{Ag}^+)_n(\text{Cl}^-)_x$ -A zeolites.

Interesting aspects of silver chloride-containing zeolites have been discussed recently by Ozin and coworkers [11]. They synthesized and characterized silver halide clusters inside a sodalite lattice and found that the sodalite framework is involved in the electronic transitions and significant orbital overlap exists between the  $\text{Ag}^+$  ions and the framework constituents. Band formation is assumed for an extended silver halide cluster lattice at increasing  $\text{Ag}^+$  loadings.

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