Unusually strong cathodic photoeffect at silver in contact with aqueous solutions containing carbon dioxide

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Abstract
Unexpectedly large photocurrents arising at polycrystalline silver electrodes, during cathodic reduction of carbon dioxide dissolved in various aqueous salt solutions, are reported. The quantum yields of the photocurrent are shown to be strongly affected by the surface roughness, reaching almost 1% at the photon energy of 3.5 eV. The sharp peak of the photocurrent observed at this photon energy suggests that surface plasmons on silver play the main role in the observed photoeffect.

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Unusually strong cathodic photoeffect at silver in contact with aqueous solutions containing carbon dioxide

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Unexpectedly large photocurrents arising at polycrystalline silver electrodes, during cathodic reduction of carbon dioxide dissolved in various aqueous salt solutions, are reported. The quantum yields of the photocurrent are shown to be strongly affected by the surface roughness, reaching almost 1% at the photon energy of 3.5 eV. The sharp peak of the photocurrent observed at this photon energy suggests that surface plasmons on silver play the main role in the observed photoeffect.

1. Introduction

The photoelectric (photogalvanic) effect, originally discovered by Becquerel [1,2], arising when a clean metal-electrolyte interface is illuminated in the range of wavelengths non-absorbed by the solution, was intensively investigated since early 1960 [3-13]. Those studies, and especially the work of Barker et al. [10-12], have permitted the assignment of the observed negative photocurrents to the emission of photoexcited electrons from the cathodically polarized metal into the electrolyte.

In order to bring about a measurable photocurrent, the electrons reaching the solution have to be captured by some species acting as scavengers (such as, for example, protons, NO₃⁻ and NO₂⁻ ions or N₂O). Except for very high concentrations of scavengers, the photoemitted electrons are considered to be thermalized and solvated before reacting with the solution species [14,15]. The resulting photocurrents are typically in the range of 10⁻⁶-10⁻⁵ A cm⁻² [10,13].

In this Letter, we report a series of observations regarding an unusually strong cathodic photoeffect arising under illumination (with visible and near-UV light) of a bulk silver electrode polarized in solutions containing dissolved carbon dioxide.

2. Experimental

The experiments were performed using a two-compartment, tight, teflon electrolysis cell equipped with a quartz window. The platinum counter-electrode was separated from the silver "working" electrode by a nafion membrane. To avoid the contamination of the solution with chloride ions, a HgO/Hg/0.1 M NaOH reference electrode was chosen instead of a calomel electrode and (after being corrected for the junction potential) all potentials are expressed relative to the normal hydrogen electrode.

The working electrode was the cross section of a 0.7 cm diameter silver rod shielded with teflon. Specpure 99.999% silver was obtained from Johnson Matthey. Standard preparation of the Ag electrode involved polishing with fine emery papers and with a suspension of 0.3 µm alumina powder. After being rinsed with distilled water, the electrode was immediately placed in the cell. Before some experiments, the surface of the silver electrode was electrochemically roughened through a series of oxidation-reduction cycles performed in 0.1 M...
aqueous NaClO₄, in the range of potentials from −0.5 to +0.61 V, at 1 V s⁻¹.

Solutions were made from reagent grade chemicals and twice distilled water and were subsequently purified by pre-electrolysis. The latter was usually conducted for 48 h between two platinum electrodes separated by a nafion membrane and the catholyte was finally employed for the experiments. 99.9998% pure carbon dioxide passed through a column with activated carbon before being introduced to the electrolysis cell. During all experiments the temperature was kept at 298 K by means of a coil-shaped glass tubing immersed in the solution and supplied with Lauda thermostat type K4R.

Two different light sources were used: a Spectra Physics model 2025-04 argon-ion laser, with 334.0, 351.1, 363.8 nm emissions lines, and a 450 W xenon lamp (Osram) set in an Oriel model 6141 housing and equipped with an ISA Inc. monochromator. The absolute intensity of the incident light from the monochromator was measured with a model 730A radiometer/photometer from Optronic Laboratories Inc. The light was mechanically modulated, in general at 7 Hz.

The electrochemical equipment consisted of an ELPAN potentiostat type EP-20 and an Elpan waveform generator type EG-20. The photocurrent was recorded at normal incidence of the light on the vertically mounted electrode, using a Stanford Research Systems lock-in amplifier type SR 530. All data acquisition was controlled by a PC XT computer employing Keithley DAS 20 hardware and software home written in the ASYST language.

3. Results and discussion

The most striking aspect of the optical effects accompanying reduction of CO₂ at a polycrystalline silver cathode is the magnitude of the photocurrent reaching ≈0.9 mA cm⁻² at −1.4 V (fig. 1). It is to be pointed out that previously reported photocurrents, associated with the process of photolysis from different electrodes into solutions containing various scavengers, did not exceed a few μA cm⁻² [10,13].

As shown in fig. 2, the illumination of the silver electrode with intermittent light in the potential range from ≈−0.7 to −1.25 V leads to the multiplication of the current by a factor of 2 or more. In this case (i.e. that of the Ag electrode immersed in CO₂ saturated sodium perchlorate solution), the appearance of the photocurrent coincides with the increase of the dark current due, to a large extent, to the cathodic reduction of CO₂ into CO.
The role of CO₂ (or of one of its reduction intermediates), acting as scavenger towards photoemitted electrons, has been confirmed through measurements made with a series of solutions containing, or not, dissolved CO₂, including solutions of sodium carbonate and bicarbonate. Absence of any significant photocurrent in a Na₂CO₃ solution as well as a substantial increase of the photocurrent after a NaHCO₃ solution was saturated with CO₂ (cf. fig. 3) exclude, in fact, carbonate and also bicarbonate ions as possible scavengers. As also shown in fig. 3, in spite of relatively high light intensities (near-UV lines originating from an argon laser) there are no signs of saturation of the photoinduced current approaching a mA cm⁻² range.

Another important feature is a very short response time of the current, recorded for the silver electrode, to the light pulse. No delay in the appearance and the decay of the photocurrent was perceptible within the opening and the closing period of the chopper, i.e. ≈ 3 ms (fig. 3b). The latter observation, together with the fact that comparable photocurrents were obtained both under continuous and intermittent illumination of the silver electrode, allow in principle to rule out the local “warming up” as playing any significant role in the photoeffect.

An insight into a possible origin of the observed phenomenon was brought about by the spectral response of the photocurrent, presented in fig. 4 as the quantum yield of the silver electrode versus incident light. In all such measurements, the photocurrent exhibited a clear-cut maximum at ≈ 360 nm, i.e. at a photon energy close to the value of 3.5 eV assigned to surface plasmons at the silver–aqueous solution interface [16–18]. In addition, as shown in table 1, the quantum yield was strongly affected by the extent of roughness of the silver surface (monitored by a standard cyclic voltammetric procedure leading to an enhancement of the surface Raman spectra [19]).

The mechanism by which optically excited surface plasmons contribute to the photoemissive yield has first been discussed by Endriz and Spicer [20] in connection with their vacuum photoemission experiments. According to these authors, the characteristic extra photoemission is the result of the energy transfer from decomposing surface plasmons to a single electron. Direct evidence for this kind of mechanism in the case of silver – a low plasma frequency metal – has been reported by Sass et al. [16]. Their experiments, involving a silver electrode cathodically polarized in 0.5 M aqueous sulphuric acid (with H₂O⁺ ions acting as scavengers), showed on the photocurrent versus photon energy curves the existence of a maximum at ≈ 3.5 eV, i.e. close to the surface plasmon energy for silver in vacuum, 3.6 eV [16].

In order to appreciate correctly the intensities of
the photoeffect described in the present Letter and of that observed by Sass et al. [16], it is useful to compare the respective quantum yields. The maximum quantum yields, expressed as photoemitted electrons per incident photon, are typically $3 \times 10^{-3}$ (up to $7 \times 10^{-3}$ for the roughened surface, cf. table 1), obtained during our experiments performed in NaClO$_4$ and NaHCO$_3$ solutions saturated with CO$_2$, as compared to $\approx 1 \times 10^{-4}$ in ref. [16]. Another significant difference is in the shape of the quantum yield-photon energy curves which, in the first case, peaks extremely sharply at $\approx 3.5$ eV (fig. 4, present work) and, in the second, shows in the same energy range as a rather flat maximum (refs. [16,17]). Importantly, the dominant contribution to the photocurrent associated with photons of an energy close to 3.5 eV (fig. 4) becomes still more prominent with increasing the silver surface roughness (table 1).

In an attempt to explain the role played by CO$_2$ in the observed photo-process at the silver electrode, the experiments were extended to gold. In fact, the latter metal exhibits an activity similar to that of silver towards electrochemical reduction of CO$_2$ leading also to the formation of CO as the main reaction product [21]. Photocurrents observed at the gold electrode were very weak in comparison with those at silver and rose with increasing photon energy without exhibiting any particular feature (fig. 4).

Inspection of figs. 1 and 2 indicates a potential range from $\approx -0.55$ to $-0.65$ V as a threshold for the appearance of a significant photocurrent at the silver electrode polarized in 0.1 M aqueous NaClO$_4$ saturated with CO$_2$. These potential values are much less negative than the reported onset of the cathodic photoemission current at mercury in a CO$_2$ saturated KCl solution ($\approx -1$ V versus NHE) [22]. As a matter of fact, at potentials anodic to $-1$ V, the CO$_2$ radical anion, considered as the primary product of the solvated electron capture by CO$_2$, apparently undergoes oxidation at the mercury electrode [23]. This makes rather improbable the involvement of CO$_2$ radicals in solution as possible intermediates of the CO$_2$ reduction at the illuminated silver electrode. We expect the forthcoming surface Raman spectroscopic measurements to throw some light on the mechanistic aspect of the latter reaction, both in the dark and under illumination.

As one possible explanation of the unusual magnitude of the photo-current observed at the silver may be a direct transfer of the photo-emitted electrons to some adsorbed species, we performed comparative experiments with a more conventional scavenger, NO$_3^-$ ion. Interestingly, the main features of the photoelectrochemical behaviour of silver in 0.1 M NaNO$_3$ solution, such as the maximum amount of the photocurrent and a sharp peak of the quantum yield placed at 3.5 eV, were closely similar to those described above for NaClO$_4$ solution saturated with CO$_2$. The NO$_3^-$ ions are not expected to undergo adsorption at the silver electrode in the range of potentials close or negative to the potential of zero.

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**Table 1**

Effect of increasing surface roughness on the quantum yield (at 360 nm) of the photocurrent for silver in contact with 0.1 M NaClO$_4$ solution saturated with CO$_2$. Electrodes were polarized at $-1.35$ V.

<table>
<thead>
<tr>
<th>No. of oxidation-reduction cycles (cf. text)</th>
<th>Quantum yield $\times 10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.2</td>
</tr>
<tr>
<td>6</td>
<td>3.75</td>
</tr>
<tr>
<td>16</td>
<td>4.35</td>
</tr>
<tr>
<td>30</td>
<td>4.35</td>
</tr>
<tr>
<td>50</td>
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<tr>
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<tr>
<td>500</td>
<td>6.6</td>
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<tr>
<td>900</td>
<td>7.0</td>
</tr>
</tbody>
</table>

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**Fig. 4.** Quantum yields of the photocurrent at silver (---) and gold (-----) electrodes as a function of the wavelength. Both electrodes were polarized at $-1.35$ V in 0.1 M NaClO$_4$ saturated with CO$_2$; light modulated at 7 Hz.
charge. Further experiments will be oriented towards evaluation of other implications of the reported, unusually strong photoeffect at silver, including its possible relation to the well known enhancement of surface Raman scattering at this metal [24].

Acknowledgement

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References