JOURNAL OF APPLIED ELECTROCHEMISTRY **23** (1993) 567–572

Photon-driven reduction reactions on silver*

R. KOSTECKI, J. AUGUSTYNSKI

Département de Chimie Minérale Analytique et Appliquée, Université de Genève, CH-1211 Genève 4, Switzerland

Received 9 July 1992; revised 21 December 1992

Irradiation of a polycrystalline silver electrode with near-u.v./visible light in solutions containing either dissolved carbon dioxide or nitrate ions produces strong enhancement of the cathodic current. Maximum photocurrent efficiency is observed for the photon energies of about 3.5 eV characteristic of surface plasmons on silver. In the presence of carbon dioxide in solution, the electrode illumination not only increases the rate of CO_2 to CO reduction but also shifts the onset of the CO production by about 0.5 V to less cathodic potentials.

1. Introduction

Silver, like two other group IB metals, gold and copper, exhibits a very peculiar behaviour towards the cathodic reduction of carbon dioxide in aqueous solutions leading to the formation of carbon monoxide as the main electrolysis product [1]. For a long time CO was considered to be produced only in aprotic solvents through a reaction pathway involving the formation of $^{\cdot}CO_2^-$ anion radical followed by oxygen–carbon coupling of $^{\cdot}CO_2^-$ with CO_2 [2–4].

Under the most favourable conditions, CO_2 reduction at a silver cathode in neutral or slightly acidic aqueous solutions yields CO with faradaic efficiencies exceeding 90%, the efficiency tends to decrease during prolonged electrolysis runs due to a progressive poisoning of the electrode. The latter behaviour is analogous to that observed with copper cathodes [5, 6], although in the case of silver the poisoning appears to be less severe than for copper.

In the present study a very strong photoeffect, observed during the reduction at a polycrystalline silver cathode of carbon dioxide dissolved in various aqueous solutions, is reported. The initial aim of experiments with the illuminated silver electrodes was to examine the possibility of photoactivating the process of CO_2 reduction by modifying the binding energy and/or the nature of the adsorbed reaction intermediates. Silver appeared particularly well suited for such an attempt since the excitation of surface plasmons at this metal becomes possible in the presence of near-u.v. radiation (the energy of a surface plasmon at the silver–vacuum interface is close to 3.6 eV [7, 8]).

There has been considerable recent interest in photon-driven processes at metal surfaces involving adsorbates originating from the gas phase [9]. The existence of this kind of effect at metal electrode-solution interfaces is known principally from early photoelectrochemical studies regarding the hydrogen evolution reaction [10–13].

Preliminary photoelectrochemical measurements, performed with polycrystalline silver cathodes immersed in sodium perchlorate or hydrogen carbonate solutions containing dissolved CO_2, showed very large photocurrents accompanying, over a wide range of potentials the 'dark', reduction of carbon dioxide [14]. The present paper contains a more detailed description of the photoeffects occurring at silver during reduction of both CO_2 and a typical scavanger of solvated electrons, the NO_3^- ion.

2. Experimental details

The silver electrode used for all experiments was the cross section of a 0.7 cm diameter rod shielded with Teflon. Specpure 99.999% silver was obtained from Johnson Matthey. Usual preparation of the silver electrode involved polishing with fine emery papers and with a suspension of 0.3 μm alumina powder. After being carefully washed with distilled water in an ultrasonic bath, the electrode was immediately placed in the cell. Before some experiments, the surface of the silver electrode was roughened through a series of oxidation–reduction cycles performed in 0.1 M $NaClO_4$, at $1\,V\,s^{-1}$, in the range of potentials from −0.5 to +0.61 V vs NHE.

The experiments were performed using a two compartment, tight, Teflon electrolysis cell equipped with a quartz window. A large platinum counterelectrode was separated from the silver working electrode by a Nafion® membrane. In order 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 (NHE).

Solutions were made from reagent grade chemicals and twice distilled water and were subsequently purified by pre-electrolysis. The latter was normally conducted for 48 h between two platinum electrodes

---

* This paper is dedicated to Professor Brian E. Conway on the occasion of his 65th birthday and in recognition of his outstanding contribution to electrochemistry.

separated by a Nafion membrane and the catholyte was finally employed for the experiments. 99.99% pure carbon dioxide was passed through a column with activated carbon before being introduced to the electrolysis cell. During all experiments the temperature was kept constant by means of a coil shaped glass tubing immersed in the solution and supplied from a Lauda thermostat type K4R.

Two different light sources were used for the photoelectrochemical experiments: a Spectra Physics model 2025-04 argon ion laser, with 334.0, 351.1, 363.8 nm emission 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 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.

The electrochemical equipment consisted of an Elpan potentiostat type EP-20 and an Elpan waveform generator type EG-20. All data acquisition was controlled by a PC XT computer employing Keithley DAS 20 hardware. Gaseous products in the effluent gas from the cell and the products in solution were analyzed on a Hewlett Packard 5890 Series II gas chromatograph equipped with a FID and a TCD detector. For qualitative and quantitative determination of CH_4, C_2H_4, C_2H_6, C_3H_4, C_3H_6, C_3H_8, C_3H_{10} and EtOH the FID detector and a Porapak Q column were employed, and for CO, the TCD detector and a Carbosieve SII column were used.

3. Results and discussion

3.1. *Reduction of* CO_2

As shown in Fig. 1, the potential required for the onset of CO formation on silver at 300 K is close to −1.2 V vs NHE and the efficiency reaches a maximum (about 90%) at −1.7 V. The appearance of carbon monoxide in cell effluent coincides with the transition of the current–potential curves (Fig. 2) from the diffusion controlled region (corresponding essentially to the proton discharge) to the kinetically controlled region. The experiments employing the rotating disc electrode were monitored through a special computer program. The potential was changed by a sequence of steps of constant amplitude (10 mV). For each potential value the rotation speed (ω) was modulated and the current was recorded as a function of ω. In order to avoid distortions caused by bubbles of gaseous products (especially at low rotation rates), the rotation speed of the electrode was first increased up to 20 Hz for 5 s and subsequently decreased to the chosen value. The current was recorded after another 3 s, when hydrodynamic steady-state conditions close to the surface of the electrode were attained. Characteristically, along the kinetically controlled region of the *i–E* curves, the current densities recorded in the presence of CO_2 in the solution become significantly smaller than those associated with hydrogen evolution from an acidified 0.1 M $NaClO_4$ solution of the same pH. Neither CO_2 nor CO are likely causes of the observed depression of the hydrogen evolution, since both these gases are known to interact with silver very weakly [15, 16].

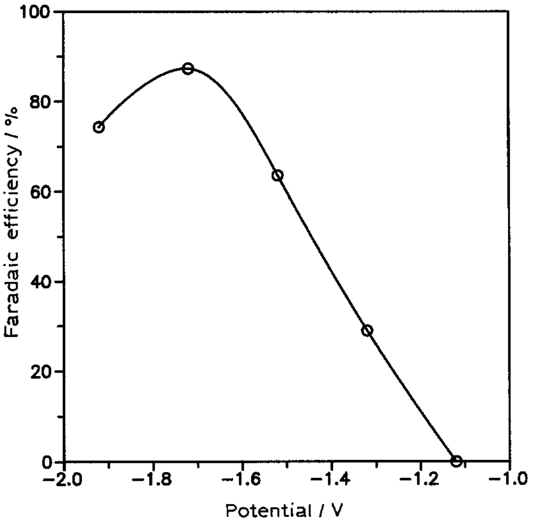

Fig. 1. Current efficiency of carbon monoxide versus potential for CO_2 electrolysis at a silver electrode (0.4 cm^2) in 0.1 M $NaClO_4$ at 300 K; CO_2 flow rate 15 ml min^{-1}. The data represent optimum efficiencies reached after about 30 min of electrolysis.

The situation depicted in Figs 1 and 2 corresponds to relatively short timescale experiments, in the course of which carbon monoxide was produced with high current efficiency. Monitoring, under potentiostatic conditions, the current and the CO concentration in cell effluent as a function of time, revealed a progressive increase of the current density accompanied by a decrease in faradaic efficiency for CO (cf. Fig. 3(a)). Interestingly, when a similar experiment was con-

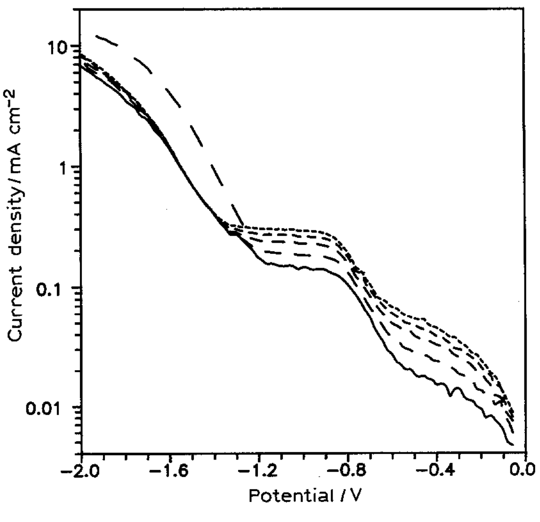

Fig. 2. Steady-state *i–E* polarization curves recorded for a silver rotating disc electrode in 0.1 M $NaClO_4$/sat. with CO_2 (pH 3.8) at 298 K. The upper, broken-line curve was obtained in 0.1 M $NaClO_4$/sat. with N_2, pH 3.8. Rot. frequency/H$_z$: (——) 2; (— —) 5; (·— —) 10; (· — — —) 15; (·----) 20; (·—) 20.

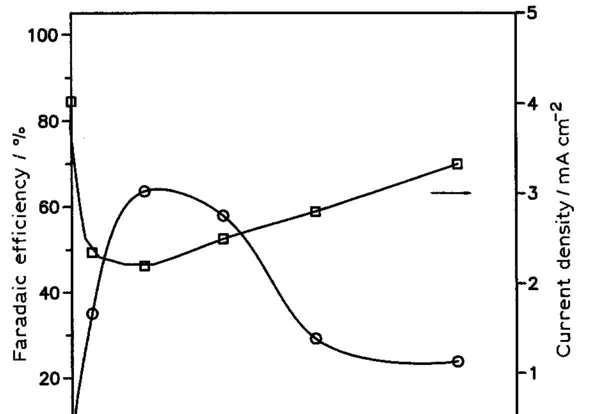

Fig. 3. Faradaic efficiency of carbon monoxide and current density against time (expressed as a total charge) for the electrolysis of a 0.1 M $NaClO_4$ solution sat. with CO_2 (CO_2 flow rate 15 ml min^{-1}) at a silver electrode (0.4 cm^2) polarized at −1.52 V. Electrolyses conducted at 300 K (a) and 285 (b).

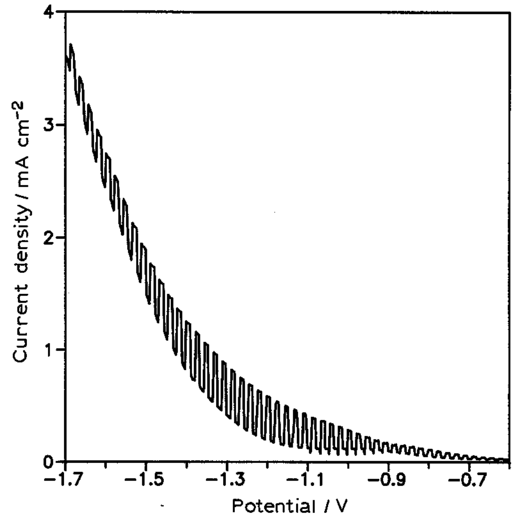

Fig. 4. Potential dependence of the photocurrent appearing during intermittent illumination (0.25 Hz) of a silver electrode polarized cathodically at 5 mV s^{-1} in 0.1 M $NaClO_4$ saturated with CO_2 and illuminated with 334, 351.1 and 363.8 nm lines of an argon ion laser (at 200 mW). $T = 300$ K. The photocurrent is shown as a difference between the upper limit (light on) and the lower one (light off) on the current–potential plot.

ducted at 285 K, the faradaic efficiency for the formation of CO remained close to 100% after the passage of 10 C while the current slowly decreased during the electrolysis (Fig. 3(b)).

3.2. *Photoelectrochemistry of silver in solutions containing CO_2*

Illumination of the silver electrode with intermittent near-u.v. light, in the potential range from about −0.7 V to −1.25 V, resulted in the multiplication of the dark current by a factor of two or more (Fig. 4). Thus, for the silver electrode immersed in CO_2 saturated sodium perchlorate solution, the appearance of a significant photocurrent coincides with the diffusion controlled plateau on the polarization curves recorded in the dark (cf. Fig. 2).

The direct implication of CO_2 in the photoelectrochemical processes occurring on silver has been confirmed through measurements made with a series of solutions containing or without dissolved CO_2, including solutions of sodium carbonate and bicarbonate. The absence of any significant photocurrent in a Na_2CO_3 solution as well as a substantial increase in the photocurrent after a $NaHCO_3$ solution was saturated with CO_2 exclude carbonate and also bicarbonate ions as possible scavengers [14]. Also, negligibly small photocurrents were recorded in nitrogen saturated 0.1 M $NaClO_4$ solution acidified to the same pH (~ 3.8) as the solution saturated with CO_2 [14].

Although carbon dioxide is known to act as a scavenger of photoemitted solvated electrons, photocurrents previously observed on mercury [12, 17] tin, indium, bismuth or lead [18] remained in the range of μA cm^{-2}. In the latter cases, the ${}^{\cdot}CO_2^-$ radical anion was considered as a primary product of the capture of a hydrated electron by a CO_2 molecule in the solution [17, 18]:

$$CO_2 + e^-_{aq} \longrightarrow {}^{\cdot}CO_2^- \qquad (1)$$

In aqueous solutions, the radical anion is supposed to undergo a subsequent reduction (at the electrode surface) to the formate anion:

$${}^{\cdot}CO_2^- + H_2O + e^-_M \longrightarrow HCOO^- + OH^- \qquad (2)$$

The latter reaction apparently requires potentials more negative than about −1.0 V vs NHE (possibly something less negative on indium and tin [18]), corresponding to the observed onset of the stationary photocurrent. Thus, the potential of about −1.0 V is generally set as a limit above which the radical anion is rapidly oxidized at the electrode [17, 19]:

$${}^{\cdot}CO_2^- \longrightarrow CO_2 + e^-_M \qquad (3)$$

leading to the virtual suppression of the photocurrent.

In many regards, the photoeffect observed on silver in solutions containing dissolved CO_2 appears different from those previously reported for other metals [17, 18]. The first important difference is in the amount of the photocurrent which in the case of silver reaches about 1 mA cm^{-1}, remaining proportional (over a large range) to the light intensity. The latter feature, along with the fact that no delay in the appearance and the decay of the photocurrent was perceptible within the opening, respectively, closing period of the chopper, i.e., about 3 ms, rule out the local warming up as playing any significant role in the described photoeffect on silver [14]. Interestingly, the photocurrent on silver becomes visible at –0.7 V (Fig. 4) with the onset being close to –0.6 V, i.e., a potential more positive by 0.4 V than those observed in the case of mercury, bismuth or lead. In the above range of potentials, the $^{\cdot}CO_2^-$ radical anions, if present in the solution, should normally be oxidized at the silver electrode. This suggests that either the $^{\cdot}CO_2^-$ anions are strongly adsorbed on silver, or a different intermediate is formed as a result of the capture of the photoemitted electron by dissolved CO_2. It must be recalled in this connection that the main final product of the CO_2 reduction on both illuminated and nonilluminated silver electrodes is carbon monoxide and not formate ion, as formed at mercury, indium or lead.

Prolonged electrolysis experiments carried out with an illuminated silver cathode showed that the onset potential for the CO formation was shifted by about 0.5 V with respect to dark conditions. Thus, for example an electrolysis performed under illumination at –0.8 V yielded 23% of carbon monoxide and significant amount of this product was still observed during similar experiment performed at –0.7 V. In the range of potentials more negative than the onset of CO production under dark conditions, the role of the near-u.v. illumination was to increase substantially (especially for not too negative potentials) the faradaic efficiency of carbon monoxide in expense of hydrogen evolution.

Another unusual feature of the photoeffect on silver is a particularly large range of potentials over which the photocurrent extends. This is in contrast with the typical evolution of the photoemission current, which tends to decay rapidly with the onset of the 'dark' reduction process, due to a depletion of the reactant (scavenger) close to the electrode surface [17, 18] (the capture of a hydrated electron is considered to occur at a distance of 1–3 nm from the surface of the cathode [20]). In the case of the reduction of CO_2 at silver, the observed photocurrent persists (and even continues to increase) on going to potentials negative with respect to the onset of the formation of carbon monoxide in the 'dark' (–1.2 V) and remains large at potentials close to the maximum faradaic efficiency for the production of CO (–1.7 V). As the process of CO_2 reduction on silver apparently becomes independent of the diffusion rate of the reactants at potentials more negative than about –1.3 V (cf. Fig. 2), the effect of illumination must be to enhance the rate determining step of the reaction.

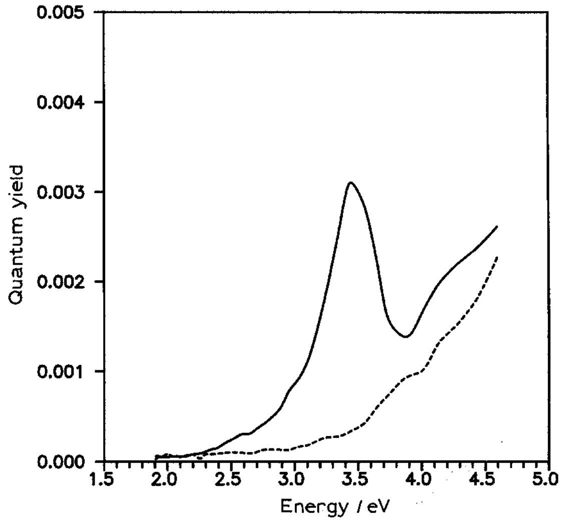

Fig. 5. Quantum yields of the photocurrent at silver (——) and gold (– – –) electrodes against photon energy. Both electrodes were polarized at –1.35 V in 0.1 M $NaClO_4$ sat. with CO_2 and light was modulated at 7 Hz.

The most characteristic aspect of the photoelectrochemical behaviour of silver in solutions containing dissolved CO_2 (such as $NaClO_4$, $NaHCO_3$ or $CsHCO_3$) was the shape of the spectral dependence of the photocurrent exhibiting a sharp maximum near the photon energy of 3.4–3.5 eV assigned to surface plasmons at the silver-aqueous solution interface [8, 20, 21] (cf. Fig. 5). In addition, as shown in Fig. 6, the quantum yield of the photocurrent 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 [22]).

Previous experiments reported by Sass *et al.* [8], involving a silver electrode cathodically polarized in 0.5 M aq. sulphuric acid (with H_3O^+ ions acting as scavengers), showed on the photocurrent against photon energy curves the existence of a maximum at about 3.5 eV, i.e. close to the surface plasmon energy

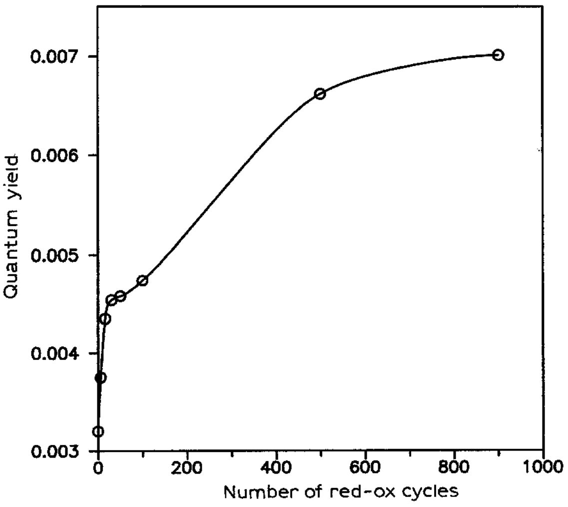

Fig. 6. Effect of increasing the surface roughness (see text) on the quantum yield (at 360 nm) of the photocurrent for silver in contact with 0.1 M $NaClO_4$ saturated with CO_2. $E = -1.35$V.

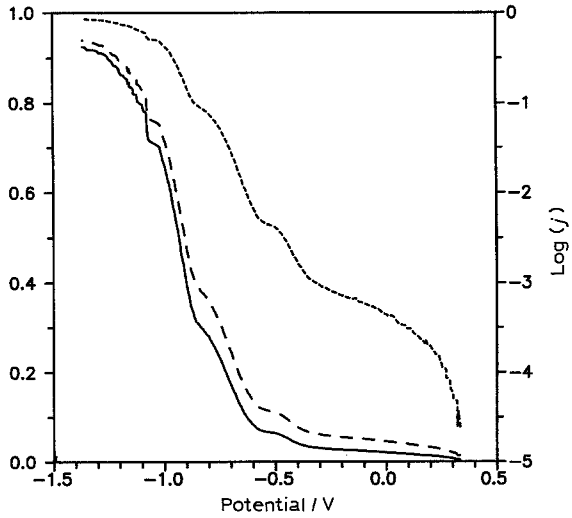

Fig. 7. Photocurrents, recorded (using a lock-in amplifier) for a silver electrode, represented as a function of potential, according to different theoretical relations (see text). Light was modulated at 7 Hz (other conditions as in Fig. 4). Key: (——) $j^{0.5}$; (– – –) $j^{0.4}$; (- - - - -) log j.

for silver in vacuum, 3.6 eV. However in the present experiments, performed in $NaClO_4$ and $NaHCO_3$ solutions saturated with CO_2, the maximum quantum yields, expressed as photoemitted electrons per incident photons, were typically 3×10^{-3} (and 7×10^{-3} for the roughened surface), as compared to 1×10^{-4} reported in [8] for protons acting as electron acceptors. The unusual intensity of the photoeffect occurring on silver, in the presence of CO_2 in solution, appears clearly through the comparison with gold (Fig. 5). The latter metal exhibits practically the same activity as silver towards electrochemical reduction of CO_2, also leading to the formation of CO as the main reaction product [1, 23]. Photocurrents observed in the near-u.v. range on the gold electrode were very weak in comparison with those on the silver and increased monotonically with increasing photon energy.

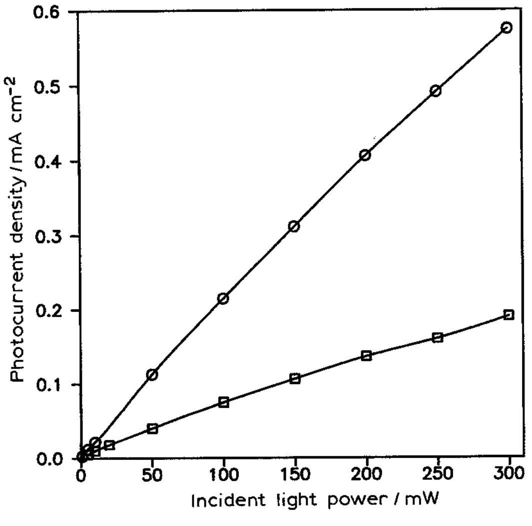

Fig. 8. Effect of light intensity on photocurrents recorded (using a lock-in amplifier) for silver polarized at −1.35 V in 0.1 M $NaClO_4$ saturated with CO_2 (upper line) and at −1.42 V in 0.1 M $NaClO_4$ + 0.001 M $NaNO_3$ (lower line). The light from argon ion laser was modulated at 5 Hz. $T = 300$ K.

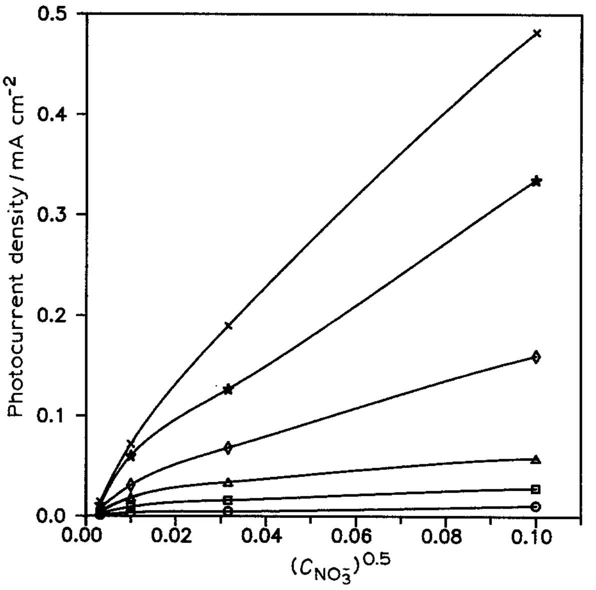

Fig. 9. Dependence of the photocurrent of a silver electrode on the square root of NO_3^- concentration. Solutions: 0.1 M $NaClO_4$ + xM $NaNO_3$. The light from argon ion laser (at 200 mW) modulated at 7 Hz; photocurrents recorded employing a lock-in amplifier. $T = 300$ K. Key: (○) −0.3, (□) −0.5, (△) −0.7, (◇) −0.9, (☆) −1.1, and (×) −1.3 V.

Most of the earlier reported experimental results regarding typical photoemission processes involving N_2O, NO_3^- ion or CO_2 as scavengers [13, 24, 25] are consistent with the so-called '$\frac{5}{2}$ power law' describing the dependence of the photocurrent (j) on the potential (ϕ) and photon energy ($h\nu$) [13, 26]:

$$j = A(h\nu - h\nu_0 - e\phi)^{5/2} \qquad (4)$$

$h\nu_0$ being the work function for emission into solution at $\phi = 0$.

An attempt to represent the photocurrent values, measured for silver illuminated with light of energy close to the maximum quantum efficiency in Fig. 5, according to Equation 4 is shown in Fig. 7. The behaviour is visibly complex, with two quasilinear portions, the first from −0.6 to −0.8 V and the second one from −0.85 to −1.0 V. No better fit was obtained using either Fowler's square law, describing principally photoemission at the metal–vacuum interface, or Heyrovsky's exponential relation proposed for the case of photodecomposition of a surface complex [13].

3.3. *Photoelectrochemical measurements in nitrate solutions*

In order to evaluate to what extent the photoelectrochemical behaviour of silver in solutions containing CO_2 is typical of the metal or of the scavenger, similar experiments were performed in the presence in the solution of another acceptor, NO_3^- ions.

The onset of the photocurrent in the nitrate solutions occurred at significantly less negative potentials than in the presence of CO_2 alone, the shift towards more anodic potentials becoming larger with increasing concentration of NO_3^- ions. In many respects, such as the spectral dependence of the photocurrent, its rapid response to the light signal or its linear dependence on light intensity (cf. Fig. 8), the photoelectrochemical behaviour of silver in the presence of NO_3^- ions resembles closely that described above for the solutions containing dissolved CO_2. In addition, the photocurrents observed in more concentrated nitrate solutions (> 0.001 M) reach a maximum at about −1.45 V (i.e. very close to that in 0.1 M $NaClO_4$/sat.CO_2) in the region of potentials corresponding to an intense 'dark' reduction of NO_3^- into NO_2^- and NH_4^+.

Attempts to express the photocurrents measured for a silver electrode at various potentials and NO_3^- concentrations as a function of the square root of $c_{NO_3^-}$ gave the result shown in Fig. 9. Clearly, in no range of NO_3^- concentrations does the silver cathode follow the linear j against $c_A^{0.5}$ relation typical of a photoemission process [13, 27]. The latter behaviour may be due, at least in part, to the adsorption of nitrate anions on silver [28].

4. Conclusions

The particularly intense photoeffect occurring on polycrystalline silver in contact with solutions containing CO_2 or NO_3^- ions, has been shown not to obey the typical relations characteristic of a photoemission process on metallic cathodes. The persistence of a strong photocurrent in the region of potentials where the 'dark' reduction reactions take place at a significant rate is indicative of the direct influence of the near-u.v. and visible light on the kinetics of electrochemical reactions on silver.

Acknowledgement

This work was supported by the Swiss Federal Office of Energy.

References

[1] Y. Hori, K. Kikuchi and S. Suzuki, *Chem. Lett.* (1985) 1695.
[2] L. V. Haynes and D. T. Sawyer, *Anal. Chem.* **39** (1967) 332.
[3] E. Lamy, L. Nadjo and J.-M. Savéant, *J. Electroanal. Chem.* **78** (1977) 403.
[4] C. Amatore and J.-M. Savéant, *J. Am. Chem. Soc.* **103** (1981) 5021.
[5] D. W. De Wulf, T. Jin and A. J. Bard, *J. Electrochem. Soc.* **136** (1989) 1686.
[6] G. Kyriacou and A. Anagnostopoulos, *J. Electroanal. Chem.* **322** (1992) 233.
[7] J. Hoffmann and N. Steinmann, *Phys. Status Solidi* **30** (1968) K53.
[8] J. K. Sass, R. K. Sen, E. Meyer and H. Gerischer, *Surf. Sci.* **44** (1974) 515.
[9] X.-L. Zhou, X.-Y. Zhu and J. M. White, *Acc. Chem. Res.* **23** (1990) 327.
[10] F. P. Bowden, *Trans. Faraday Soc.* **27** (1931) 505.
[11] P. J. Hillson and E. K. Rideal, *Proc. Roy. Soc. (London) Ser. A* **199** (1949) 295.
[12] M. Heyrovsky, *ibid.* **301** (1967) 411.
[13] Yu. Ya. Gurevich, Yu. V. Pleskov and Z. A. Rotenberg, *in* 'Photoelectrochemistry' (Consultants Bureau, New York, 1980) and references therein.
[14] R. Kostecki and J. Augustynski, *Chem. Phys. Lett.* **194** (1992) 386.
[15] P. Herrera-Fierro, K. Wang, F. T. Wagner, T. E. Moylan, G. S. Chottiner and D. A. Scherson, *J. Phys. Chem.* **96** (1992) 3788.
[16] M. Canepa, L. Mattera, M. Polese and S. Terreni, *Chem. Phys. Lett.* **177** (1991) 123.
[17] D. J. Schiffrin, *Faraday Disc. Chem. Soc.* **56** (1974) 75.
[18] Yu. B. Vassiliev, V. S. Bagotzky, N. V. Osetrowa, O. A. Khazowa and N. A. Mayorowa, *J. Electroanal. Chem.* **189** (1985) 271.
[19] G. C. Barker, *Electrochim. Acta* **13** (1968) 1221.
[20] H. Neff, J. K. Sass, H. J. Lewerenz and H. Ibach, *J. Phys. Chem.* **84** (1980) 1135.
[21] H. Neff, J. K. Sass and H. J. Lewerenz, *Surf. Sci.* **143** (1984) L356.
[22] R. P. Cooney, E. S. Reid, M. Fleischmann and P. J. Hendra, *J. Chem. Soc. Faraday I* **73** (1977) 1691.
[23] Y. Hori, A. Murata, K. Kikuchi and S. Suzuki, *J. Chem. Soc., Chem. Commun.* (1987) 728.
[24] Z. A. Rotenberg and Yu. V. Pleskow, *Elektrokhimiya* **4** (1968) 826.
[25] R. De Levie and J. C. Kreuser, *J. Electroanal. Chem.* **21** (1969) 221.
[26] Yu. Ya. Gurevich, A. M. Brodskii and V. G. Levich, *Elektrokhimiya* **3** (1967) 1302.
[27] G. C. Barker, A. W. Gardner and D. C. Sammon, *J. Electrochem. Soc.* **113** (1966) 1182.
[28] I. C. G. Thanos, *J. Electroanal. Chem.* **200** (1986) 231.