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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Adsorbed layers of iron tetrasulfonated phthalocyanine have been examined using cyclic voltammetry on the silver single crystal low index surface: (100), (110), and (111). The peak potentials and charge under the voltammetry peaks show some dependence on the crystal planes. The effects of the underpotential deposition of lead on the adsorbed macrocycle have also been examined on the silver single crystal electrode. The lead can be underpotential deposited on the silver directly through a pre-adsorbed macrocycle layer without desorbing the macrocycle. The data are explained in terms of a model for the adsorbed macrocycle which has the

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TECHNICAL REPORT NO. 58

Spectroscopic and Electrochemical Studies of Transition-Metal

Tetrasulfonated Phthalocyanines:

VI.   The Adsorption of Iron Tetrasulfonated Phthalocyanine on

Single Crystal Silver Electrodes

by

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1 November, 1985

SPECTROSCOPIC AND ELECTROCHEMICAL STUDIES

OF

TRANSITION-METAL TETRASULFONATED PHTHALOCYANINES:

VI. THE ADSORPTION OF IRON TETRASULFONATED PHTHALOCYANINE ON SINGLE CRYSTAL SILVER ELECTRODES

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INTRODUCTION

The adsorption of iron tetrasulfonated phthalocyanines (Fe-TsPc) has been studied on several electrode surfaces which include ordinary and stress-annealed highly ordered pyrolytic graphite (1-3), platinum (2) and polycrystalline silver (4). The techniques of cyclic voltammetry (1,4), reflectance spectroscopy (2) and surface enhanced Raman spectroscopy (SERS) (4-6) have revealed much information on the adsorption. However, questions concerning the state of the complexes and particularly their aggregation on the electrode surface remain not completely answered. In the present work we have studied the adsorption of Fe-TsPc on Ag single crystal electrodes with (100), (110) and (111) orientations. Because of the interaction between the adsorbed molecules and the electrode surface, some sensitivity of this adsorption to the substrate structure may be expected. This could throw some light on these questions and provide some data which may help in understanding the electrocatalytic properties of these adsorbed layers with respect to the oxygen reduction reaction (1,3). The interaction of the adsorbed Fe-TsPc with the

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underpotential deposition of lead on single crystal silver substrates has also been examined.

EXPERIMENTAL

Single crystals of Ag, 99.99% pure, were obtained from Metal Crystals Ltd., Cambridge, England. They were oriented to better than 1°, mounted in heat shrinkable Teflon tubing and mechanically polished by standard metallographic techniques with diamond paste, gradually decreasing the size of the grit to 1 um. The crystals were further polished chemically, using procedures similar to those already reported (6,7). An aqueous solution of 30 volume percent H_2O_2 and a solution of 21.5 g/l of NaCN were mixed in a 1:1 ratio for polishing the Ag (111) single crystal surface. For the Ag (100) face, a lower concentration of 20 volume percent H_2O_2 was used. The crystals were held for 5 s in these solutions, during which time vigorous gas evolution occurred. They were taken out, held in air for 3 s and transfered into a solution of 37.5 g/l NaCN, where gas evolution ceased. After washing, the procedure was repeated several times, in most instances in a fresh solution of H_2O_2 and NaCN until a highly reflecting surface was obtained. The electrode surface was then thoroughly washed in pure water. The surface obtained in this way was protected by a drop of pure water and transfered into electrochemical cell. This chemical polishing procedure yielded surfaces of high quality, such that it was possible to obtain from them characteristic LEED patterns without any additional cleaning or high temperature annealing (8).

The supporting electrolyte was 0.1 M $HClO_4$ prepared from Baker Ultrex grade $HClO_4$ and high purity water (reverse osmosis, followed by distillation). Some voltammetry measurements have been done in 0.05 M H_2SO_4 prepared from Baker Ultrex acid. Gold was used as a counter electrode. All potentials are given vs. a saturated Hg/Hg_2Cl_2, Cl^- reference electrode. The Fe-TsPc has been synthesized and purified in this laboratory according to a modified

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procedure of Weber and Busch (9).

RESULTS AND DISCUSSION

Adsorption of Fe-TsPc

Linear sweep voltammetry has been used to examine the adsorption of Fe-TsPc on silver single crystal electrodes and to see whether this technique is capable of detecting some dependence on the crystallographic orientation of the surface. Figs. 1 and 2 show voltammetry curves obtained in 0.1 M $HClO_4$ and 0.05 M H_2SO_4, respectively, containing 1×10^{-5} M Fe-TsPc for the low-index single crystal silver electrodes. The voltammograms indeed reveal some structural sensitivity of the adsorption Fe-TsPc. These data have been obtained at the sweep rate of 200 mV s^{-1}. The sweep rate dependence of the voltammetry curves has been determined in the 50-400 mV s^{-1} sweep range and is discussed later. Table 1 summarizes some data for peak 1 from Figs. 1 and 2. [The more cathodic peak has been labeled the peak 1, and the more anodic labeled peak 2, in accordance with a notation used in reference (3).] The anodic and cathodic sweep peak potentials, the mid-potentials, and the peak potentials, and the peak separations depend on the surface orientation. The charge-transfer process associated with the peak 1 is apparently more reversible on the Ag (110) surface, showing a peak separation of 25-30 mV. The least reversible appears to be the process for peak 1 on the (100) face, showing a peak separation of 50-60 mV, while the (111) face is close to it with $\Delta E_p = \sim 40$-50 mV. For a polycrystalline surface Zecević et al. (3) have found $\Delta E_p = \sim 40$ mV for a sweep rate of 0.1 V s^{-1}. These differences may be due to the way the molecule is adsorbed on the different single crystal surfaces, as has been discussed in connection with the Raman data (10). Uncertainity in the determination of the peak potentials prevents a similar comparison with the present data for peak 2.

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Stirring dependence of the voltammetry peaks was observed in the $HClO_4$ solutions but not the H_2SO_4 solutions. Over a period of the order of a minute, the peak heights almost double after introduction of stirring in the 0.1 M $HClO_4$ solution containing 1×10^{-5} M Fe-TsPc but not in the 0.05 M H_2SO_4. This difference is probably due to more than a monolayer of the Fe-TsPc being adsorbed on the Ag (hlk) surfaces in the $HClO_4$ solution under these conditions. The stirring sensitivity in $HClO_4$ solution is presently being investigated in more detail. Zecevic et al (3) have shown that the voltammetry curves are not sensitive to the oxidation and reduction of the solution phase Fe-TsPc but only the adsorbed species. The large negative charge on the adsorbed Fe-TsPc plus the negative charge on the solution phase species results in an extreme double layer effect. This, together with the low solution phase concentration results in very slow oxidation-reduction kinetics for the solution phase species.

The peak areas show also some dependence on the crystal orientation. Table 2 gives the charge under the peaks recorded in the anodic sweeps for both acids. The highest charge appears to be associated with peak 1 on the Ag (111) surface. On the other hand, for peak 2, the smallest charge is seen on this face. For the (100) face as well as the (111) face and polycrystalline surface, the charge under peak 1 is larger than that for peak 2. A surprising result has been obtained with the (110) face. The charge of the peak 2 is larger than that of the peak 1.
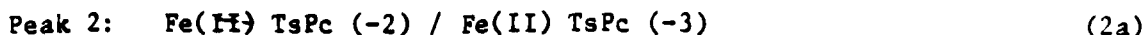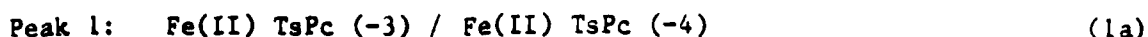
On the basis of solution phase electrochemical studies (3, 11, 12) the peaks observed in Figs. 1 and 2 can be assigned as follows:

Peak 1: Fe(I)TsPc (-2)/Fe(I)TsPc (-3) (1)

Peak 2: Fe(II)TsPc (-2)/Fe(I)TsPc (-2) (2)

In other words, the first peak is due to a charge transfer process involving the macrocycle ligand, while the second is due to a charge transfer process

involving the central metal ion. Alternatively these peaks may be assigned:

Peak 1:   Fe(II) TsPc (-3) / Fe(II) TsPc (-4)   (1a)

Peak 2:   Fe(II) TsPc (-2) / Fe(II) TsPc (-3)   (2a)

with iron in the two valent states for both peaks and the oxidation reduction processes for both peaks involving orbitals associated principally with the macrocycle ligand. The Pc ligand in its normal oxidation state carries two negative charges, not considering the charge associated with the partially ionized sulfonic acid groups. It may be oxidized to the cation radical TsPc(-1) or reduced to the anion radicals TsPc (-3, -4).

Zecević et al. (3) have shown that four charge transfer processes are found with the Fe-TsPc adsorbed on pyrolytic graphite electrode. The dissolution of Ag prevents the two peaks at more positive potentials from being observed. The ratio of the charge between peaks 1 and 2 may be affected by the way the species is adsorbed on the single crystal surfaces. We have recently observed in a thin-layer cell that at a very low coverage of Fe-TsPc on the Ag (100) and Ag (111) surfaces, only peak 1 appears (12). With increasing coverage, peak 2 grows and this affects the shape as well as charge of peak 1. This might be explained by a change in the way the macrocycle is adsorbed at low solution concentrations and low coverages (12).

The (110) surface may be envisoned as an array of parallel "rails" on the ideal surface (13,14). The atoms in "rails" may interact differently with Fe-TsPc than the atoms from a "flat" electrode surface. This could be the origin of the marked change in the ratio of the sizes of peak 1 and peak 2 for (110) face. It may also explain the more reversible behavior of the charge transfer processes on this surface (Table 1).

The Raman spectra of the adsorbed Fe-TsPc indicate differences in the relative peak intensities on the three low index surfaces of Ag single crys-

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tals without electrochemical activation of the surfaces. The peak frequencies are unchanged on the three low index surfaces and essentially the same as for the solution phase species. These Raman data including polarization measurements have been interpreted as providing evidence that the Fe-TsPc is adsorbed with the plane of the macrocycle ligand perpendicular to the surface with one or two of the sulfuric acid groups interacting with the silver surface. In earlier work (2) the in situ visible reflectance spectra were examined for the Fe-TsPc on polycrystalline platinum and the basal plane of highly order pyrolytic graphite. These spectra were essentially the same as for the solution phase. These measurements must be extended to single crystal silver surfaces but even as they stand provide further evidence that the Fe-TsPc tends to adsorb in such a configuration that the interaction of the macrocycle with the electrode surface is very weak. The perpendicular configuration is the most likely explanation for such a weak interaction (6). The parallel configuration would be expected to produce a significant change in the electron orbitals of the ligand, and hence, changes in the visible absorption spectra as well as frequencies of vibrational modes involving the macrocycle ligand.

The charge associated with the change in oxidation reduction states of the adsorbed Fe-TsPc has been estimated from the area of the peaks. The charge under the peaks on single crystal surfaces is somewhat lower than that observed with ordinary pyrolytic graphite electrodes (3). This is most likely due to a lower ratio of true to apparent area for the Ag single crystal electrodes. The charge obtained by Zagal et al. (1) for peak 2 for Fe-TsPc adsorbed on the basasl plane of highly ordered pyrolytic graphite was ~3 $\mu C/cm^2$, which compares favorably with that on the Ag(111) surface. Unfortunately these workers did not examine peak 1 on this surface.

Assuming that the surface redox couples obey the Nernst equation with an activity coefficient of unity, the peak current for the voltammetry is given

by

$$i_p = \frac{n^2 F^2 \Gamma v}{4RT} \qquad (3)$$

where Γ is the total surface concentration of the adsorbed complex in moles/cm^2, v is the potential sweep rate, and n is the number of electrons per adsorbed molecule. The charge under the peak is known and is equal to

$$Q = \Gamma n F \qquad (4)$$

The value for n can be calculated from

$$n = \frac{i_p}{Q} \cdot \frac{4RT}{Fv} \qquad (5)$$

Experimental values of Q and i_p give values from n = 0.94 for Ag(111) in HClO$_4$ (peak 1) to n = 1.2 for Ag(110) in H$_2$SO$_4$ (peak 1). Most results fall around n = 1. Therefore, one electron appears to be exchanged in both redox processes, irrespective of the surface orientation and the electrolyte. Just why the ratio of the charge under peaks 1 and 2 varies so much with the single crystal surface remains to be explained. Aggregation and μ-oxo bridging (e.g. (Fe-TsPc)$_2$O may be involved.

Coadsorption of lead adatoms. The underpotential deposition (upd) of lead on silver electrode yields voltammograms highly dependent on the crystalographic orientation of the surface (3,15,16). Sharp peaks have been observed with Ag (111), and to a certain degree with Ag (100) surface. Upd on such surfaces should be highly sensitive to the coadsorption of some other species.

Fig. 3 gives the voltammetry curves for the upd of Pb on the Ag (100) surface in the absence and in the presence of preadsorbed Fe-TsPc. A third curve shows peak 2 for Fe-TsPc, which can be seen if the cathodic potential limit is more positive than the commencement of the upd of Pb, and if a much faster sweep is used. The curve for the upd of Pb shows the same general features as the curves published earlier (15). Some of the fine structure,

including two shoulders in the anodic scan and a very sharp pair of peaks at E
= -0.353 V, has not been observed earlier. The effect of the adsorbed Fe-TsPc
is unexpectedly small. In the cathodic scan, the main peak is shifted to a
more negative potential causing it to merge with the sharp peak. In the
anodic scan, the sharp peak is clearly seen, although it is smaller and
slightly shifted to a more positive potential. It is rather surprising that
the total amount of the upd lead is not affected by the presence of Fe-TsPc on
the surface. This is seen in Fig. 4 showing the charge-potential isotherms
obtained by integration of cathodic scans in Fig. 3. A charge of 210 μC cm^{-2}
is obtained on Ag(100). A superlattice structure of Pb-c(2x2) gives 196 μC
cm^{-2} with the electrosorptive valence taken as 2. Considerably higher cover-
ages have been reported earlier; i.e., 337 $\pm$ 6, 372 $\pm$ 6, 372 $\pm$ 20 and 303
$\pm$ 10 μC cm^{-2} in refs. 7, 15 and 16. The reasons for these differences is not
clear.

Assuming a Frumkin-type isotherm for the upd of Pb, the activity of the
upd lead, a can be given by

$$a(\Gamma) = K \cdot \theta \cdot (1- \theta)^{-1} \cdot \exp(-g\theta) \tag{6}$$

where K is an equilibrium constant. From Fig. 4 the interaction parameter g
can be calculated for lead adatoms for the two surfaces. The upd of Pb on Ag
can be described by a pseudo-Nernstian equation (15),

$$E = E_{Pb/Pb^{2+}} + [(RT/zF) \ln(a_{Pb^{2+}}/a(\Gamma))] \tag{7}$$

where a_{Pb} is the activity of lead cations in the solution phase.
From eqs. 6 and 7 the underpotential shift can be expressed as follows:

$$\Delta E = E - E_{Pb/Pb^{2+}} = - (RT/zF) \left[\ln[\theta/(1-\theta)] -g\theta + \ln K \right] \tag{8}$$

The interaction parameter g can be calculated from the slope of the θ vs E
isotherm at $\theta = 0.5$ according to

$$g = 4 + (zF/RT)(\partial \Delta E/\partial \theta)_{\theta = 0.5} \tag{9}$$

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The electrosorption valence of Pb adatoms on Ag (100) is $\gamma = 2$(15). In such a case, it is possible to take Q, the charge associated with the upd of Pb, as an approximation of Γ, the surface concentration of adatoms. The similar slopes in Fig. 4 at Q corresponding to $\theta = 1/2$ indicate a similar interaction between lead adatoms in the absence and in the presence of Fe-TsPc. Equation 9 gives $g = -1.5$ in both cases. This means that the lateral interaction of Pb atoms is not strong. An alternative procedure based on the half width of the sorption peak (3) is difficult to apply because of unseparated peaks of the upd of Pb on the Ag(100) surface.

The data for the upd of Pb in the presence of preadsorbed Fe-TsPc are interesting because they may give indirect information on the orientation of Fe-TsPc on Ag (100) surface. The small effect of Fe-TsPc on the upd of Pb, and particularly the equality of charges for Pb both with and without the adsorbed Fe-TsPc, further support the proposal that the Fe-TsPc is oriented perpendicular to the surface, allowing Pb atoms to "intercalate" through them and adsorb on Ag(100). An explanation involving a desorption of Fe-TsPc from the silver surface and readsorption of Fe-TsPc on Pb adatoms is quite unlikely. In the absence of FeTsPc in the solution phase, such a process should result in an irreversible desorption of Fe-TsPc and its escape into the bulk solution. This, however, does not happen. The adsorption/desorption of Pb by "cycling" the electrode potential can be repeated over a number of cycles up to 1.5 h at 5 mV/s. Only after that time does a characteristic voltammogram for the upd of Pb alone start to reappear. This indicates a strong adsorption of Fe-TsPc on the Ag(100).

The possibility can not be ruled out, however, that the Pb would upd through the adsorbed Fe-TsPc layer, even if it were adsorbed with the ligand plane oriented parallel to the surface. Stickney et al.(17) have reported the underpotential deposition of Cu on Pt(11₁) through an adsorbed iodine layer

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without the iodide coverage influenced by the upd Cu.

The data for the coadsorption of Pb and Fe-TsPc are preliminary. They provide evidence which favors the perpendicular adsorption of the Fe-TsPc on the Ag(100) surface, as does also the Raman data (4,6,10). These upd experiments illustrate an interesting way for probing other similar adsorption processes which may not be amenable to more direct techniques.

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Table 1. The anodic and cathodic peak potentials, mid-potentials and peak separations for peak 1 for Fe-TsPc adsorbed on single crystal silver electrodes at the sweep rate of 0.2 V s^{-1} at -25°C

| Surface | 0.1 M HClO$_4$ | | | 0.05 M H$_2$SO$_4$ | | |
	E_{pa} (V)	E_{pc} (V)	E_m (V)	ΔE_p (V)	E_{pa} (V)	E_{pc} (V)	E_m (V)	ΔE_p (V)
Ag(100)	-0.335	-0.395	-0.365	0.060	-0.335	-0.385	-0.360	0.050
Ag(110)	-0.330	-0.355	-0.342	0.025	-0.330	-0.360	-0.345	0.030
Ag(111)	-0.340	-0.395	-0.367	0.050	-0.340	-0.380	-0.360	0.040

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Table 2: Charge density Q_1 and Q_2 associated with peaks 1 and 2 for the Fe-TsPc adsorption on the Ag single crystal electrodes

Surface	0.1 $\underline{M}$ HClO$_4$		0.05 $\underline{M}$ H$_2$SO$_4$	
	$Q_1/\mu C\ cm^{-2}$	$Q_2/\mu C\ cm^{-2}$	$Q_1/\mu C\ cm^{-2}$	$Q_2/\mu C\ cm^{-2}$
Ag(100)	8	4	6.0	3.5
Ag(110)	4.0	4.5	5.5	8
Ag(111)	10	3	10	3

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Figure Captions:

Fig. 1.   Voltammetry curves of single crystal silver electrodes in 0.1 $\underline{M}$
HClO$_4$ with 1x10^{-5} $\underline{M}$ Fe-TsPc. Sweep rate 0.2 V s^{-1}. The orientation
of the electrode surface is given in the graph. T = ~25°C.

Fig. 2.   Same as in Fig. 1 but for 0.05 $\underline{M}$ H$_2$SO$_4$.

Fig. 3.   Underpotential deposition of Pb on the Ag(100) surface in 0.1 $\underline{M}$
HClO$_4$ with 10^{-3} $\underline{M}$ Pb^{2+}, without (-·-) and with (——) preadsorbed
Fe-TsPc. Sweep rate 5 mV s^{-1}. Dashed line gives the curve obtained
with the sweep rate 0.2 V s^{-1} (see text).

Fig. 4.   Charge associated with the upd of Pb on the Ag(100) surface without
and with preadsorbed Fe-TsPc obtained from curve for a sweep rate of
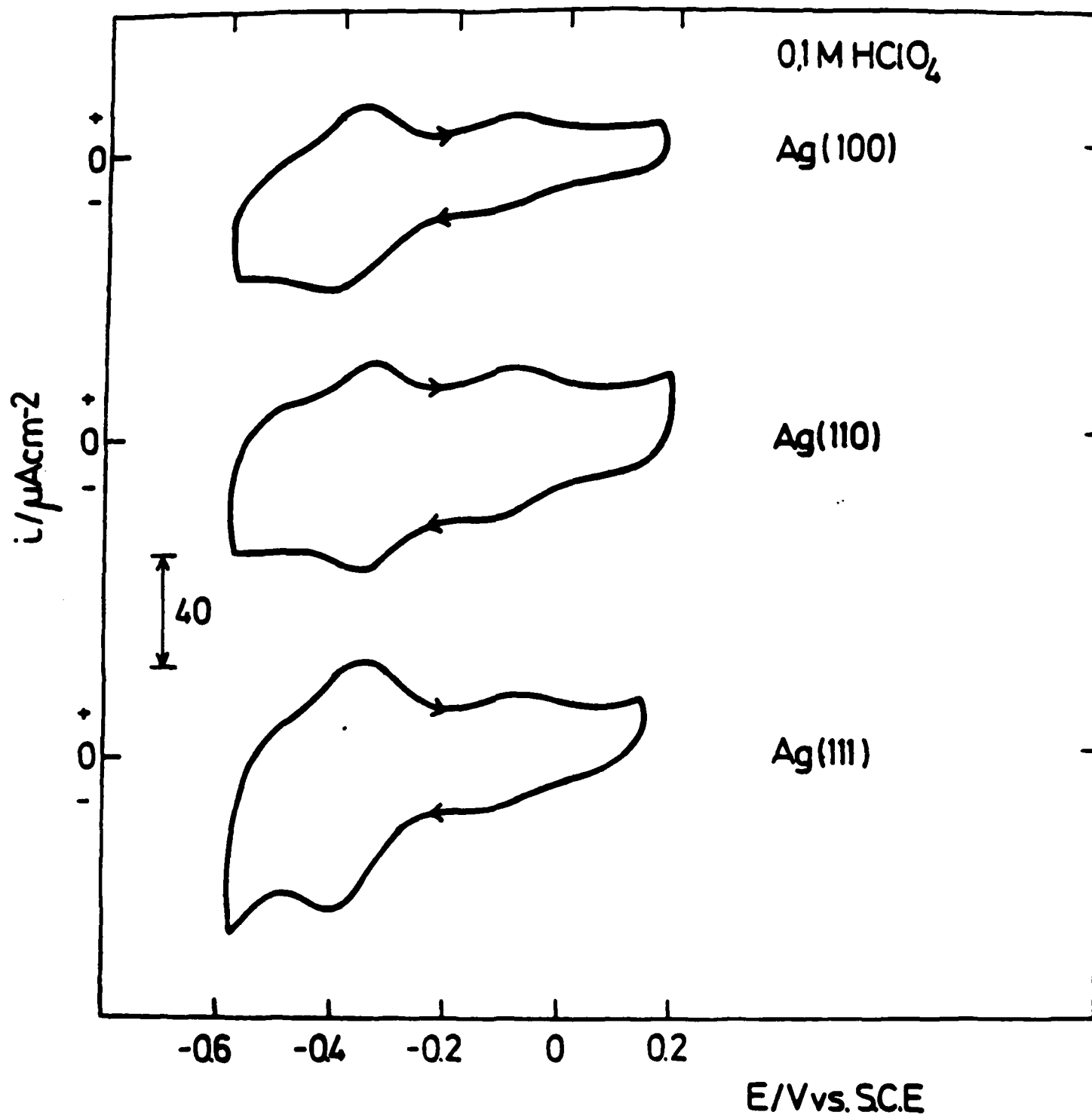0.2 Vs^{-1} in Fig. 3.

Fig. 1. Voltammetry curves of single crystal silver electrodes in 0.1 M HClO₄ with 1x10⁻⁵ M Fe-TsPc. Sweep rate 0.2 V s⁻¹. The orientation of the electrode surface is given in the graph. T = -25°C.
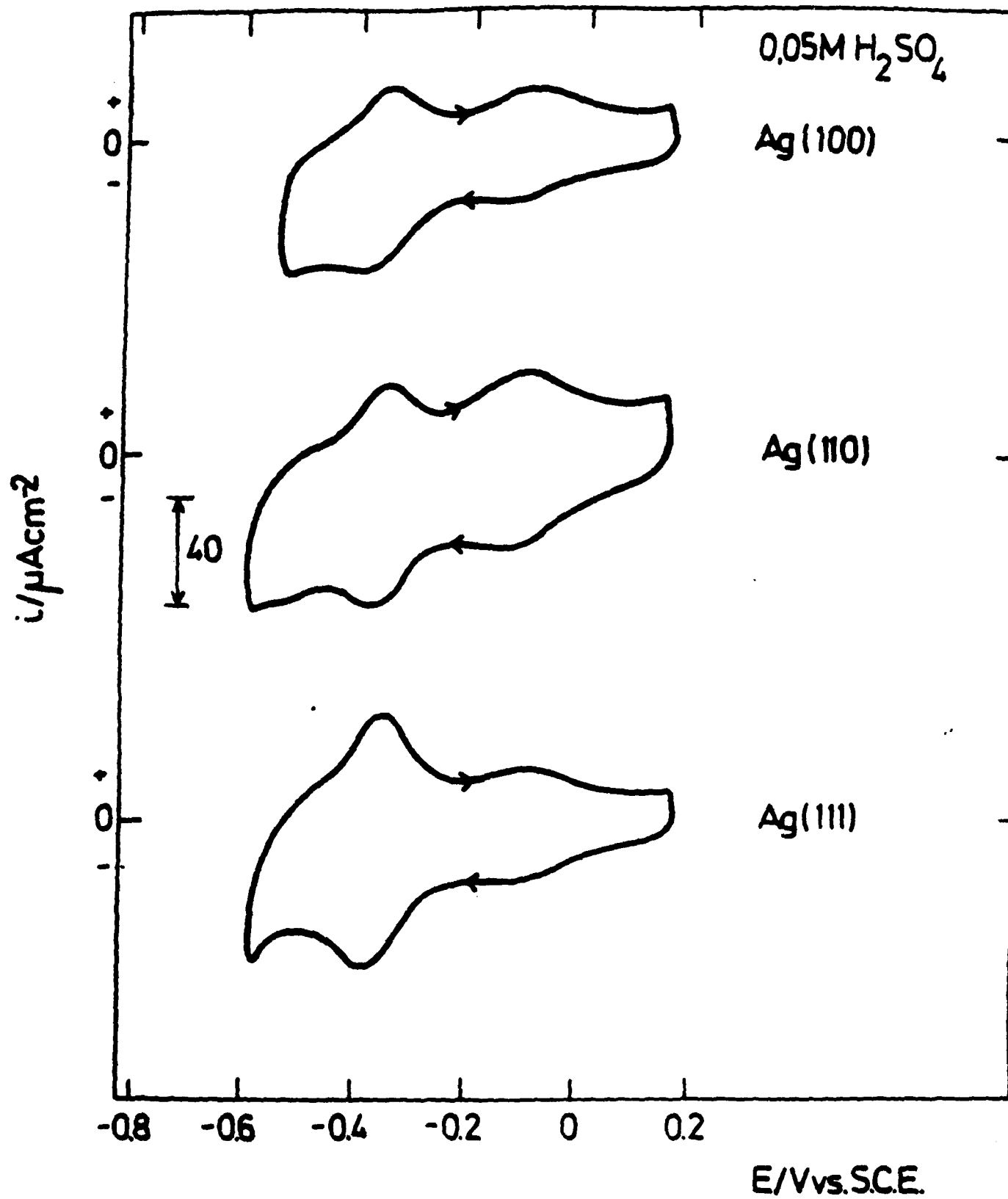
0.05M H_2SO_4

Ag(100)

Ag(110)

Ag(111)

i/μAcm^2

40

-0.8   -0.6   -0.4   -0.2   0   0.2

E/V vs. S.C.E.

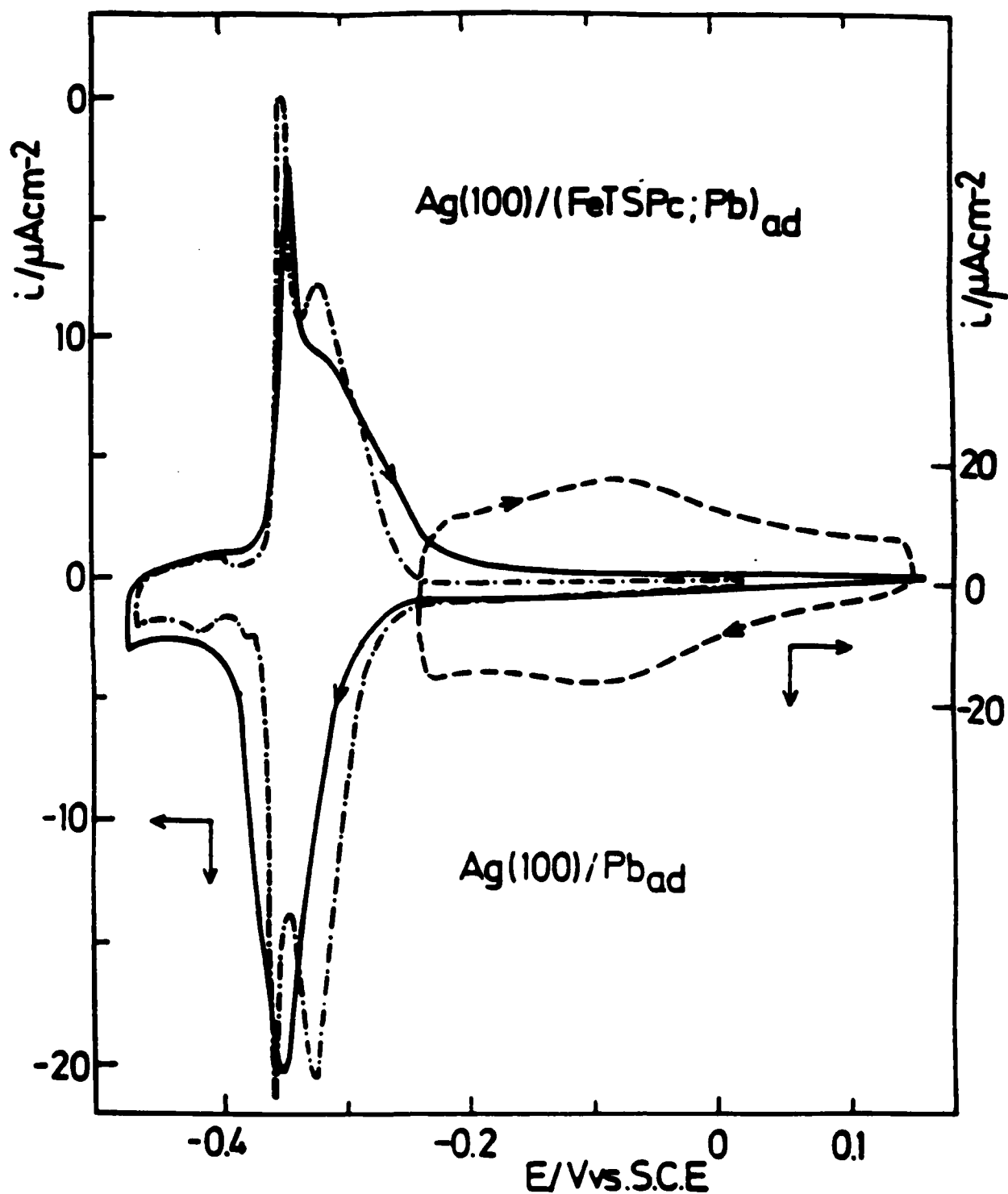Fig. 2.   Same as in Fig. 1 but for 0.05 $\underline{M}$ H_2SO_4.

Fig. 3. Underpotential deposition of Pb on the Ag(100) surface in 0.1 M HClO$_4$ with 10^{-3} M Pb^{2+}, without (-·-) and with (——) preadsorbed Fe-TsPc. Sweep rate 5 mV s^{-1}. Dashed line gives the curve obtained with the sweep rate 0.2 V s^{-1} (see text).
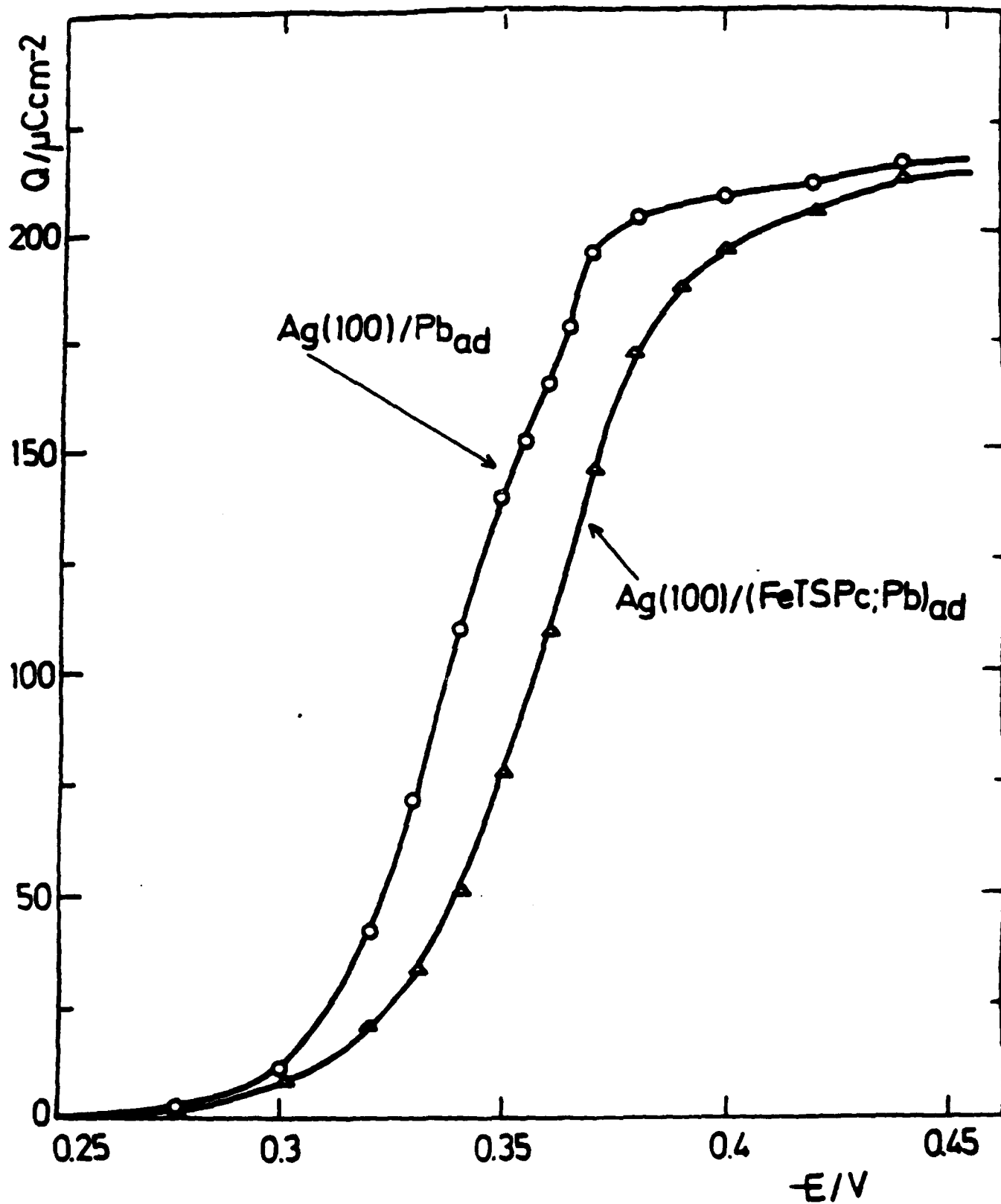
Fig. 4. Charge associated with the upd of Pb on the Ag(100) surface without and with preadsorbed Fe-TsPc obtained from curve for a sweep rate of 0.2 Vs⁻¹ in Fig. 3.

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