KINETICS OF ANODIC REACTIONS OF MOLTEN POTASSIUM THIOCYANATE ON PLATINUM: FORMATION AND GROWTH OF ANODIC FILM*

A. J. CALANDRA, M. E. MARTINS and A. J. ARVÍA

División Electroquímica, Instituto Superior de Investigaciones, Facultad de Ciencias
Exactas, Universidad Nacional de La Plata, La Plata, Argentina

Abstract—The film-growth process occurring on platinum anodes when molten potassium thiocyanate is electrolysed at 190°C has been investigated. The kinetics of the process has been studied by the application of different relaxation techniques. The film growth controls the rate of the process, and its mechanism comprises a surface diffusion process occurring after SCN⁻-ion oxidation. The film-thickening stage approaches a parabolic growth law. The faradaic rectification of the film is discussed in terms of its physicochemical properties and the actual site where anodic and cathodic reactions take place.

Résumé—On a étudié le procès de croissance du film sur des anodes de platine pendant l'électrolyse du thiocyanate de potassium à 190°C. La cinétique du procès a été étudiée par l'application de différentes techniques de relâchement. Le croissence du film controle la vélocité du procès et son mécanisme comprend un procès de diffusion superficiel qui a lieu après l'oxydation de l'ion SCN⁻. L'étape de grossissement du film obeit à une loi de croissence parabolique. La rectification faradaïque du film est discutée du point de vue de ses propriétés physique-chimiques et les lieux réels où les réactions anodiques et cathodiques se produisent.

Zusammenfassung—Es wurde der Wachstumsprozess eines Filmes untersucht, der an Platinelektroden auftritt, wenn geschmolzenes Kaliumthiocyanat bei 190°C elektrolysiert wird. Die Kinetik dieses Prozesses wurde unter Anwendung verschiedener Relaxationstechniken bestimmt. Der geschwindigkeitsbestimmende Schritt ist der Wachstumsprozess des Filmes. Sein Mechanismus schliesst eine Oberflächendiffusion ein, die nach der Oxydation der SCN⁻-Ionen auftritt. Die Periode der Filmverdickung kann durch ein parabolisches Wachstumsgesetz angenähert werden. Die faradaische Gleichrichtung des Filmes wird diskutiert an Hand seiner physikalisch-chemischen Eigenschaften und des reellen Ortes, an dem die anodischen und kathodischen Reaktionen ablaufen.

INTRODUCTION

THE ELECTROCHEMISTRY of molten alkali thiocyanates has been the subject of several investigations. A first paper was published on a reference electrode for use in melts, including potassium thiocyanate.¹ Electrode reactions of different ionic species dissolved in molten potassium thiocyanate have also been reported.²⁻⁴ These studies mainly refer to the *E/i* characteristics of the reacting ions in potassium thiocyanate used as solvent and attempt to establish the existence of particular oxidation states of the ions in the melt. The electrochemical behaviour of the pure molten alkali thiocyanates was studied^{5,6} in the temperature range between 150 and 325°C. These studies were undertaken to develop electrolyte systems usable in high energy-density thermal batteries.⁵ A polarographic *E/i* curve from KSCN melt exhibits two definite waves in the cathodic direction, which were attributed to thiocyanate-ion reduction and potassium-ion discharge, respectively, and one anodic wave related to thiocyanate-ion oxidation. The latter process however is rather complicated because of the formation of a film on the electrode, which causes a sort of passivation effect, making it difficult to interpret the kinetic results on the basis of a probable reaction mechanism.

* Manuscript received 1 September 1970.

The present study attempts to elucidate the electrode processes related to the formation and dissolution of the insoluble material on the platinum anode, when molten potassium thiocyanate is electrolysed. This is important because molten thiocyanate has promising properties as a solvent in molten salt electrochemistry, and electrode passivation might interfere with any electrode process, particularly with those occurring at positive potentials. To tackle this problem the present paper refers to various relaxation techniques which give reproducible information that can be mechanistically interpreted.

EXPERIMENTAL TECHNIQUE

Electrolysis cell and preparation of chemicals

Two different cells made of Pyrex glass were employed. One consisted of a container of about 600 cm³ with a three-electrode arrangement, the working electrode being a platinum disk, the counter-electrode a large platinum sheet placed in a separate compartment, and a reference electrode as shown in previous publications.^{7,8} The second cell was smaller, about 300 cm³ capacity, and the working electrode was a vertical platinum wire. Two procedures were used for preparing the working-electrode surface, (i) mechanical polishing of the platinum to a mirror surface, (ii) electrolytic cleaning with cathodic current pulses. Two different reference electrodes were used. One was a bright platinum wire dipped in molten thiocyanate placed in a compartment ending in a fritted glass disk. This arrangement was placed into a glass sheath filled with the molten electrolyte and ending in a Luggin-Haber capillary tip. The second was a silver wire immersed in a 0.1 M solution of silver sulphate in molten potassium thiocyanate. The cell compartments were separated by means of fritted glass disks. The cell was housed in an air thermostat adjusted to $190 \pm 0.5^\circ\text{C}$.

The electrolyte was molten potassium thiocyanate (Riedel de Hæn and Carlo Erba). The chemicals were firstly dried in vacuum for several hours; drying was started at room temperature and ended with the salt in the molten state.

Relaxation techniques

(i) *Current/potential curves.* Non-steady current/potential curves were obtained with conventional circuitry. The curves were recorded with a Varian X-Y plotter.

(ii) *Galvanostatic build-up curves.* A conventional galvanostatic circuit, comprising a 300-V power pack and a range of resistors higher than $10^6 \Omega$, was used for these experiments. After the galvanostatic build-up curves the decay of electrode potential was recorded by switching the current off. For the purpose an electronic switch was employed, the E /time curves being either displayed and photographed from a Tektronix 545-A oscilloscope screen or recorded for longer times.

(iii) *Potentiostatic current/time response.* To obtain the electrode response to potentiostatic pulses, the circuit shown in Fig. 1, comprising a potentiostat coupled with a potential-control device, was used. The initial electrode potential was first adjusted with the F_1 potentiometric circuit. Later the selected potential to be applied to the electrode was controlled with the F_2 potentiometric circuitry. The switch L_1 was used to command the pulses. The current/time plot was displayed on a potentiometric recorder; current was measured by reading potential drops on standard resistors connected in series in the circuit.

FIG. 1. Circuitry for potentiostatic technique.

(iv) *Current-reversal techniques.* Experiments involving a sequence of anodic and cathodic galvanostatic current pulses were made. Figure 2 shows a scheme of the reverse-pulse technique. For the purpose two high-voltage power packs were used for the anodic and cathodic pulses respectively. They could be independently connected by means of a mercury relay (Polter and Brumfield 5 ML) commanded by a pulse generator. The length of the cathodic and anodic pulses as well as those of current interruption could be adequately regulated. The electronic set was manually operated.

(v) *Faradaic rectification.* Faradaic rectification was used under ac current control. Figure 3 shows a scheme of faradaic rectification circuitry. Initially a constant current of 10 mA was applied to the working electrode to form a definite amount of film. The current was interrupted when galvanostatic conditions no longer held and the potential of the working electrode was out of control. Later an ac signal was applied and simultaneously the oscilloscope was triggered. Both current and potential were displayed on a Tektronix 502 double-beam oscilloscope screen. The current was measured by means of known resistors. The ac signal was provided by a Cenco audio-oscillator. Frequencies of 10 Hz to 100 kHz and variable amplitudes were used.

RESULTS

Anodic current variation at constant potential

Current/time curves recorded at constant potentials are shown in Fig. 4. They exhibit a rapid initial current increase up to a maximum current and later decrease

FIG. 2. Circuitry for the reverse pulse experiments.

FIG. 3. Scheme of circuitry employed for faradaic rectification effect.

asymptotically approaching a small residual current. The potential region required to observe such current response within a time of about 10 s is rather small, and the larger the applied potential, the higher the corresponding current peak and the shorter the time for its appearance.

Various other interesting facts are derived from the potentiostatic transients. Thus, the transient area, which corresponds to a charge probably related to the formation of non-conducting species that passivate the electrode surface, is practically independent of the applied potential; it is between 10 and 12.5 mC/cm². This coincides fairly well with the charge involved in the galvanostatic transient, the latter being characterized by a transition time, as referred to further on.

FIG. 4. Current/time records at constant overpotential $\eta = E - E_{\text{rest}}$. Dotted lines correspond to theoretical curves calculated as indicated in the text.

FIG. 5. Semilogarithmic plots of η vs t_{max} and η vs i_s . The dotted lines correspond to the slope $2.3RT/F$.

The time related to the maximum current, t_m , decreases when the applied potential is increased. It appears that $\log(t_m)$ is directly proportional to the applied potential, as shown in Fig. 5. The absolute slope of the best straight line comprising the results is 0.090 V.

Galvanostatic transients

Typical potential/time records are shown in Fig. 6. When a first galvanostatic anodic pulse is applied to the clean electrode after a rapid potential increase related to the charge of the electrochemical double layer, a net transition time, τ , at 0.5–0.8 V (referred to the initial electrode potential) is observed. Table 1 contains values of τ at different currents and the product $I\tau$ with different electrode treatments. The product $I\tau$ is reasonable constant for a particular electrode treatment.

FIG. 6. Galvanostatic build-up of anode potential with a clean platinum electrode.

TABLE 1. TRANSITION TIME FOR THE FILM GROWTH PROCESS

A cm ²	$I \times 10^4$ A	τ s	$I\tau \times 10^3$ C/cm ²	Electrode pre-treatment
0.4	206	22.2	11.43	Mechanically polished
0.4	448	11.4	12.77	Mechanically polished
0.4	728	6.3	11.46	Mechanically polished
0.4	728	7.2	13.10	Mechanically polished
0.4	730	7.2	13.14	Mechanically polished
0.071	202	4.5	12.80	Mechanically polished
0.071	216	6.9	20.99	Cathodic cleaning
3.07	620	67.1	13.55	Cathodic cleaning
3.07	1520	34.2	16.93	Cathodic cleaning
3.07	1540	33.0	16.55	Cathodic cleaning

The length of the transition time depends on the degree of electrode surface cleanness. Thus, if after the first pulse the current is switched off after the transition time and later a second anodic pulse is applied, no transition time is observed for the second anodic pulse. Similarly, if the anodic current is interrupted for a short time during the transition time and immediately a second anodic pulse is applied at the same constant current, Fig. 7, the sum of the second transition time plus the time of the first plateau approaches the transition time read when the clean electrode is used for the first experiment.

Beyond the transition-time region the potential increases further, at an approximately constant rate. It must be stressed that due to the high resistance exhibited by the passive film beyond the transition time, galvanostatic conditions may be not actually prevailing; therefore any interpretation of the relationship between potential and time in this potential region should be regarded as only tentative.

Once high positive potentials have been reached there are two possibilities, either to apply a cathodic galvanostatic pulse and to record the potential/time curve, or to switch off and to leave the anode potential to decay spontaneously towards the initial rest potential. Both experiments are of interest since different and complementary kinetic information can be obtained from them.

Galvanostatic reverse pulses

After the first anodic pulse the electrode potential becomes highly positive, depending on the duration of the pulse. Under these circumstances, if a cathodic

FIG. 7. Galvanostatic build-up of anode potential. a, galvanostatic build-up of anode potential; b, two anodic pulses, the second one applied after current interruption for a short period.

pulse is suddenly applied without current interruption, a rather complex cathodic build-up curve is observed. Initially a very rapid potential decay occurs at a rate of about 5×10^3 V/s, depending on the anodic polarization reached and galvanostatic cathodic pulse applied. Later the cathodic potential attains its quasi-steady value.

At least three different situations should be distinguished as far as the cathodic potential build-up after the anodic pulse is concerned. One of them corresponds to the application of the first cathodic pulse covering a low range of negative potential. For this case, the potential/time curve is smooth and apparently follows a rather simple law. The second situation arises when cathodic pulses corresponding to larger currents are employed. In these circumstances the potential approaches, after the initial abrupt change, a maximum value, decreasing afterwards to attain the quasi-steady value. The following anodic pulse exhibits then at least two transition times in addition to the transition time already described, Fig. 8. These transition times are

FIG. 8. Galvanostatic build-up of anode potential after previous cathodic pulse. Different transition times mentioned in the text are also indicated.

located at less positive potentials than the latter, which is assigned to a film-growth process at the electrode surface.

The third case is observed when cathodic pulses are applied after previous anodic and cathodic pulses described for the second case. The cathodic build-up curves exhibit in this case at least two or three very poorly defined transition times, Fig. 9.

The ohmic or pseudo-ohmic contribution involved in these experiments is difficult to estimate. The ohmic drop is easily visualized in the galvanostatic anodic transients. For the cathodic transients the effect is masked by the very rapid initial potential jump, particularly when potential/time curves are recorded at low sweep rates. It is quite evident from the reverse-pulse experiments that the resistances of the anodic and cathodic electrochemical processes are significantly different, the former being much larger than the latter and definitely time dependent.

Let us now consider an experiment comprising a set of anodic and cathodic transients such as those shown in Fig. 9, involving cathodic pulses of different duration and low cathodic polarizations. It first appears that the length of the anodic transition time depends on the duration of the cathodic pulse given at a definite current to clean the electrode.

FIG. 9. Galvanostatic build-up of anode and cathode potential during the reverse pulse experiments. Cathodic pulses applied after exceeding the anodic transition time.

From experiments comprising a set of anodic and cathodic pulses it is possible to make an interesting material balance of anodic and cathodic processes. The charge, Q_1 , involved in the first galvanostatic anodic pulse, is given by $I_a\tau$, where I_a is the constant anodic current and τ the transition time. During the following cathodic pulse, the corresponding charge $Q_{1c} = I_c t_c$, where I_c is the constant cathodic current and t_c the duration of the cathodic pulse. The charge Q_{1c} is equal to the charge involved in the second anodic pulse, calculated as $I_a\tau'$, where τ' is the transition time found for the latter pulse.

If the same experiments comprise sufficiently high cathodic polarizations, the second anodic transient exhibits two shorter transition times, as already reported (Fig. 8), at less positive potentials than those corresponding to the larger ones. The charge related to the first small transition time, τ_1' , is larger than that corresponding to the second small transition time, τ_2' . For the material balance, the following equality holds,

$$I_a\tau = I_c t_c = I_a(\tau_1' + \tau_2' + \tau'). \quad (1)$$

These results indicate a cathodic dissolution of the passive film at the interface, which contributes again to passive film formation during the second anodic pulse. Furthermore, if other products are produced by reduction at higher cathodic polarizations, these products also oxidize during the following anodic pulse and contribute to the passivation of the electrode by film formation. The product $I_a(\tau_1')^{1/2}$ is a reasonable constant, but this relationship could not be tested for τ_2' , since the latter is poorly defined.

The balance involved in (1) is related to the reduction of SCN^- ion in the melt yielding S^{2-} and CN^- ions,^{1,3,5} both ions being oxidized at less positive potentials than SCN^- ion, giving as oxidation products sulphur and $(\text{CN})_2$. The latter in the presence of the former may yield the same product as during the oxidation of SCN^- ion in the melt.

Anode-potential decay

The anode-potential decays at open circuit were measured starting from positive potentials corresponding to the region of the transition time and to the region beyond the transition time (Fig. 10). There is an initial sudden drop of potential of ohmic

FIG. 10. Typical anode-potential decays when current interruption occurs at different potential.

nature and then the change of the anode potential after current interruption follows with a good approximation the potential/log(time) relationship usually found for electrode processes with rate under activation control. This relationship is satisfied over various logarithmic decades of time, as shown in Figs. 11–13 for different experimental conditions. Decay slopes obtained from those plots are assembled in Table 2. As seen, they are reasonably independent of the electrode treatment prior to the electrolysis. It is interesting to observe that when the anodic potential decay occurs from potentials related to the transition time, there is a unique decay slope for any initial potential whose value is very close to $2.3(RT/F)$ V. But for those experiments where the electrode potential at interruption is located above the one corresponding to the transition time, the decay slope b_a increases quite markedly and its value depends on the initial potential. Here, the decay slope is a linear function of potential in the region where the potential exceeds that of the transition time and is nearly constant at lower potentials (Fig. 14). Apparent electrode capacitances calculated from anode potential decay are assembled in Table 3.

FIG. 11. Semilogarithmic plot of anodic overvoltage decay.

FIG. 12. Semilogarithmic plot of anodic overvoltage decay.

The electrode differential capacitances calculated from the anodic galvanostatic build-up of potential in the potential region preceding the transition-time zone, are of the order of $50 \mu\text{F}/\text{cm}^2$ (Table 4). These figures may correspond to an electrochemical double layer of rather simple structure. On the other hand, results derived from potential regions beyond the transition time, where it might be assumed that a net passive film exists, comprise electrode capacitances far lower than those just reported, being of the order of $0.1 \mu\text{F}/\text{cm}^2$.

Faradaic rectification

By applying an ac signal to the cell and simultaneously recording both the electrode potential and current from the oscilloscope screen, as illustrated in Fig. 15, a net voltage rectification is observed. The effect has been investigated with ac in the range

FIG. 13. Semilogarithmic plot of anode overvoltage decay.

TABLE 2. DECAY SLOPES UNDER DIFFERENT EXPERIMENTAL CONDITIONS

i A/cm ²	b V	
5.05×10^{-4}	0.120	Current interruption during film growth
5.05×10^{-4}	0.094	Current interruption during film growth
5.08×10^{-4}	0.150	Current interruption during film growth
19.50×10^{-4}	0.134	Current interruption during film growth
25.90×10^{-4}	0.128	Current interruption during film growth
8.69×10^{-3}	1.75	Current interruption at 4.05 V
22.70×10^{-3}	4.30	Current interruption at 9.25 V
44.00×10^{-3}	5.70	Current interruption at 12.50 V

FIG. 14. Dependence of the decay slope on the starting potential. Dotted line indicates the region where the decay slope is potential-independent.

TABLE 3. ELECTRODE CAPACITANCES FROM ANODE-DECAY CURVES

i A/cm ²	b_d V	$t' \times 10^4$ s	$C \times 10^8$ F/cm ²
8.69	1.75	3.80	4.35
22.7	4.30	2.95	3.59
44.0	5.70	4.57	8.12

TABLE 4. ELECTRODE CAPACITANCES FROM BUILD-UP OF ANODE POTENTIAL

i mA/cm ²	C $\mu\text{F}/\text{cm}^2$	Electrode condition
0.110	0.62×10^{-1}	With film
0.112	1.21×10^{-1}	With film
0.205	1.47×10^{-1}	With film
0.205	1.00×10^{-1}	With film
0.205	0.68×10^{-1}	With film
8.60	71.5	Without film
22.7	68.0	Without film
44.9	49.5	Without film

FIG. 15. Displays of faradaic rectification experiments.

a, c and d, experiments with passivating film on the electrode at 10 and 100 Hz and different amplitude; b, passivating film at 100 Hz and low amplitude; e, response in the absence of passivating film; f, passivating film at 1000 Hz when rectification has disappeared.

of 10–10³ Hz and for different amplitudes. After repetitive cycles a steady faradaic rectification effect is observed solely when the electrode is passivated and frequencies of 10 and 100 Hz are used. Therefore it is quite reasonable to relate it to the presence of the passivating film. When there is no film on the electrode surface, the ac voltage signal is sinusoidal—lagging the current signal. The phase angle is altered when faradaic rectification occurs.

Both the duration and stability of the rectification effect depend on the ac frequency and amplitude. For small amplitudes and higher frequencies no rectification is observed, or the effect is unsteady and disappears after a few cycles (Fig. 16).

From a set of current and potential cycles it is possible to construct the current/potential relationship for the anodic and cathodic processes. These curves are shown in Figs. 17–19 and were made from results illustrated in Fig. 15 without any double-

FIG. 17. Current/potential curves derived from faradaic rectification experiments. Data taken from display d shown in Fig. 15.

layer correction. The plots show a marked resistance to current flow in the anodic direction. The anodic E/i plot exhibits a very pronounced hysteresis; the anodic polarization is much higher in the returning half-cycle. On the other hand, during the cathodic half-cycle the resistance to current flow is very low, a limiting voltage being attained as the cathodic current approaches infinity. It looks as if the resistance offered by the cathodic process becomes zero when the limiting voltage is reached. This description of the faradaic rectification suits the experiments at 10 and 100 Hz, although for the latter the hysteresis loop at constant amplitude extends over part of the cathodic region. The anodic polarization apparently decreases when the frequency increases. The limiting cathode potential however is independent of the current frequency.

FIG. 18. Current/potential curves derived from faradaic rectification experiments. Data taken from display c shown in Fig. 15.

FIG. 19. Current/potential curves derived from faradaic rectification experiments. Data taken from display a shown in Fig. 15.

FIG. 16. Display of the breakdown of passivity. Experiment started with a film formed during a 30-s electrolysis at 10 mA.

E/I curves obtained from rectification patterns, at 10 and 100 Hz with the corresponding amplitudes changing by a factor of 10 as shown in Figs. 17–19, indicate a tendency of the anodic and cathodic resistances to charge-transfer to attain the same magnitude. As far as this is concerned, a lower amplitude of current signal at higher frequencies appears to be equivalent to a higher amplitude at lower frequencies. For experiments performed at 1000 Hz no rectification was observed, but the current and voltage signals were out of phase.

Current/potential curves

If one attempts to obtain for the anodic reaction a polarization curve either at constant current or at constant potential no stability either of potential or current is attained. Therefore, no polarization curves in the conventional way can be obtained with molten potassium thiocyanate.

It is however possible to draw E/I curves for both the anodic and the cathodic processes by recording simultaneously the E/I characteristics. For the former case an initial anodic polarization is applied, the current through the working electrode reaches a maximum and immediately it decreases steadily while the voltage increases, as illustrated in Fig. 20. The E/I recording corresponds to a relaxation of the electrochemical system. This plot exhibits a linear relationship between E and I and the negative slope of the straight line implies a resistance opposed to the flow of anodic current. The resistance for a particular working electrode is independent both of the initial potential or current.

If the same kind of experiment is attempted for the cathodic process, the response of the working electrode is very peculiar, as shown in Fig. 20. First the initial resis-

FIG. 20. Current/potential curves obtained without any potential or current control.

tance is much lower than that referred to above for the anodic reaction, and it becomes smaller as the cathode potential increases up to a certain point, where the curve exhibits a loop. Then the resistance starts to increase and the cathodic current becomes zero, without any appreciable change of the cathode potential. This indicates that charge transport at the cathodic interface is much easier than at the anodic interface, and that the cathodic current flow after a certain electrolysis time is no longer controlled by the charge transport at the cathodic interface but by the process occurring at the counter-electrode. This behaviour of the platinum cathode

is consistent with preliminary observations made on the electrolysis of molten potassium thiocyanate in a U-shape cell having two equal platinum electrodes. Thus, on electrolysis the system, the electrode that acted as anode was rapidly covered by a yellowish insoluble film, which after the polarity was reversed, disappeared from this electrode, the same product being formed on the counter-electrode, which had become the anode after the change of polarity. This experiment could be repeated indefinitely.

In general, all the foregoing results depend to some extent on the treatment of the electrode surface prior to its use as anode. Thus, both galvanostatic as well as potentiostatic transients indicate that the activity of electrodes previously cathodically cleaned was higher than that exhibited by those only polished to a mirror surface by conventional methods.

DISCUSSION

The results show clearly that the anodic discharge of SCN^- ion in the molten state on platinum corresponds to an electrochemical process where the products of the anodic reaction interfere, provoking passivation of the electrode. As already reported,⁵ the anodic discharge of SCN^- ion at low anodic potentials can be represented by the over-all reaction:

Probably the initial product formed is dimeric thiocyanogen, unstable above $+2^\circ\text{C}$, which immediately undergoes polymerization to parathiocyanogen $(\text{SCN})_x$. This substance has been reported as a yellow-orange solid that is insoluble in most solvents.⁵

As deduced from non-steady experiments, two main processes should be distinguished at anodic potentials. The initial reaction extends from the beginning of the electrolysis with a clean electrode surface until the surface is uniformly covered by the reaction product. This first process is characterized by the transition time observed during the galvanostatic transient. The following process is related to the thickening of the passivating film after the uniform film has been formed. The E/I curves, as well as the transients obtained at times larger than the one corresponding to the galvanostatic transition time, give information about this second stage. These stages are usually recognized when anodic film formation takes place on the electrode surface⁹ and for a more comprehensive treatment of the results it is convenient to consider them separately.

Kinetics of film growth

The potentiostatic transients are governed by the mechanism of film growth. For platinum electrodes in molten potassium thiocyanate, the metal acts only as the initial reaction surface and therefore only two formally different types of kinetic control for film growth are left to interpret the results: either the film growth controls the rate, or the process is controlled by the resistance to current flow located in the bulk of the melt or in the external circuit. For the latter, the potentiostatic transient exhibits a constant current which drops when the electrode surface is completely covered; hence this possibility should be discarded for the present case. On the other hand, the potentiostatic response of the anode agrees with a film-growth control.

For the growth of an anodic film at constant thickness the rate equation is⁹

$$\frac{dA}{dt} = \frac{iM}{zF\rho\delta}, \quad (3)$$

where A is the covered surface area, i the current through the cell, M the molecular weight of the reacting species, z the number of electrons entering the electrode reaction per mole of reacting species, ρ the density of the growing nuclei and δ the film thickness.

When the rate of film growth is determined by the peripheral area of the growing patches at constant potential, the covered area of the reacting surface changes with time according to ¹⁰

$$A = 1 - \exp \left[-n\pi \left(\frac{i_2 M}{zF\rho} \right)^2 t^2 \right], \quad (4)$$

where n is the number of nuclei per unit area, i_2 the cd on the faces of the growing nuclei and t the time elapsed.

The expression of the cd as a function of time results from (3) and (4),

$$i = \frac{2\pi n M i_2^2 \delta}{zF\rho} t \exp \left[-n\pi \left(\frac{i_2 M}{zF\rho} \right)^2 t^2 \right]. \quad (5)$$

Equation (5) corresponds to the shape of the anodic potentiostatic transients. To give numerical values to (5) various reasonable assumptions may be made. As the reaction involves one electron per mole of reacting ion, $z = 1$ and $M = 58$. n can be taken equal to 10^9 sites/cm², a figure that according to the literature⁹ is reasonable. δ can be estimated in different ways. One of these consists in deriving its magnitude from the $I_a\tau$ product of the galvanostatic transient, after correcting it for the anodic residual current, since this quantity is directly proportional to the film thickness. The film density is taken as 2 g/cm³. The criterion followed to select the physical properties of the film takes into account that the SCN⁻ ion and SCN radical are respectively electronically similar to the halide ions and halogen atoms. Hence, the density of the polymer may be estimated by interpolation in the graphs of density *vs* molecular weight for solid halogens. The resulting δ is 3.0×10^{-6} cm. The same figure is also obtained from the potentiostatic transients. The area covered by the transients, after correction for the residual current, should be directly related to δ , as it was in the previous case for the galvanostatic transient. This coincidence reflects, furthermore, that both transients are actually related to the same electrochemical process.

The i_2 value can be obtained from the time required to attain the maximum anodic current in the potentiostatic transient. The time, $t_{\max}$, associated with the maximum current is given by the following equation, obtained by differentiating (5),

$$t_{\max} = \frac{zF\rho}{i_2 M} \sqrt{\frac{1}{2\pi n}}. \quad (6)$$

According to (6) the time for the occurrence of the maximum current, $t_{\max}$, is inversely proportional to i_2 . Values of i_2 calculated at different anode potentials are reported in Table 5. These values are comparable to the largest growth rates determined for

TABLE 5. KINETIC PARAMETERS RELATED TO FILM GROWTH

$E - E_{\text{rest}}$ V	$t_{\max}$ s	i_2 mA/cm ²	Q mC/cm ²
0.525	1.2	36.2	10.7
0.512	1.5	29.0	13.0
0.500	2.4	17.6	10.5

the anodic growth of AgCl films¹¹ although the corresponding overvoltage is, in the present case, much higher.

To facilitate the plot of (5) after considering (6), it can be written

$$i = \frac{zF\rho\delta}{t_{\max}^2 M} t \exp \left[-\frac{t^2}{2t_{\max}^2} \right]. \quad (7)$$

Equation (7) indicates that the potentiostatic transient can be traced when the value of $t_{\max}$ is known, and its shape is particularly affected by δ . In Fig. 4 the dotted lines correspond to the theoretical potentiostatic transients. In spite of some crude assumptions involved in the foregoing discussion, within the range of anode potentials investigated, there is a reasonably good agreement between the experiments and (5).

Another important kinetic result derived from the potentiostatic transients is the overpotential dependence of the cd on the faces of the growing nuclei. As shown in Fig. 5, a Tafel line is satisfied for i_2 and its slope approaches the value RT/F . This means that the kinetics of the nuclei growth for the case of the polymeric film on platinum, in terms of the i_2/E relationship, is analogous to that observed for the growth of anodic oxides.⁹ This result is valuable for indicating the likely mechanism of film growth.

The type of processes involved in nucleation and film growth at the electrode surface explains the influence of pre-treatment of the electrode surface on the kinetics, because the number of initial nucleation centres and their energetic conditions should depend on the state of the initial electrode surface.

Probable mechanism for film growth

The foregoing kinetics of film growth in terms of a film growth control, suggest the probable mechanism for the process, on the basis of the partial reactions

Step I corresponds to the charge-transfer reaction on any part of the platinum surface including the nucleation centres, yielding a SCN radical at the electrode surface. Step II corresponds to the surface migration of the radical towards a nucleation centre indicated as Pt^* . Actually, step IIa must predominate at short times before any impingement of separate nuclei has occurred, while step IIb must predominate at the end of the process. If v_I and v_{-I} are the forward and reverse reaction rates of step I and a quasi-equilibrium is assumed,

$$k_I a_s a_{\text{SCN}^-} \exp \left[\frac{\alpha FE}{RT} \right] = k_{-I} a_i \exp \left[-\frac{(1-\alpha)FE}{RT} \right], \quad (8)$$

where k_I and k_{-I} are the specific rate constants, a_s , a_{SCN^-} and a_i refer to the activities of the surface, of SCN^- ion and of the intermediate at the electrode surface, respectively; E is the applied voltage at the interface and α is the transfer coefficient assisting the reaction in the anodic direction.

If step II (IIa or IIb) is rate-determining the rate of nuclei growth, v_{II} , is

$$v_{\text{II}} = k_{\text{II}} a_{\text{Pt}^*} a_i, \quad (9)$$

where a_{Pt} refers to the activity of any kind of nucleation centres. From (8) and (9) results

$$v_{\text{II}} = K_{\text{I}} k_{\text{II}} a_{\text{Pt}} a_{\text{S}} \exp \left[\frac{FE}{RT} \right]. \quad (10)$$

Equation (10) comprises the equilibrium constant of step I and it implies a SCN^- ion activity equal to one, as is reasonable for the pure melt. The rate of nuclei growth is given in terms of i_2 , a cd that is attained after a definite time from the electrolysis initiation. Therefore, to establish if the influence of the pre-exponential factor in (10) is negligible as compared to the exponential term, one should know the values of a_{S} , and consequently those of a_{Pt} , at the instant corresponding to i_2 . As the activity of the surface can, in principle, be assumed proportional to the fraction of initial area covered, (4) is suitable for the purpose. Plots of this equation are shown in Fig. 21.

FIG. 21. Change of the degree of surface coverage with time according to (4).

As seen, at t_m , in the potential range investigated, the surface coverage is nearly constant at 0.4. Consequently a_{S} and a_{Pt} , at t_m , appear as potential-independent terms. This means that no appreciable error is introduced if the pre-experimental factor is taken as a constant in the overvoltage range covered by the potentiostatic experiments. Furthermore, if the surface coverage at t_m is constant, the contribution of any adsorption energy term depending on the degree of surface coverage, such as would be the case, for instance, if the intermediate obeyed a Slugyin-Frumkin isotherm, would appear also as a constant term in the pre-exponential factor. Therefore under the experimental conditions dealt with in the present circumstances, the slope of the $E/\log i_2$ curve should appear as independent of the type of adsorption isotherm prevailing for the reaction intermediate. Then, (10) in terms of i_2 , is

$$i_2 = FK' \exp \left[\frac{FE}{RT} \right], \quad (11)$$

where K' includes all the constant terms discussed above. Equation (11) implies a Tafel slope of RT/F which is actually approached by the experimental results. The slope RT/F is consistent with the decay slopes obtained at current interruption at potentials lower than those corresponding to the galvanostatic transition time. This means that the differential capacitance associated to the electrochemical double layer is practically constant in the potential range covered by the present work and also that

the same reaction mechanism applies to the relaxation process. Therefore, film-growth control implies the occurrence of steps I and II (IIa or IIb), where the latter controls the rate of the over-all film growth process.

Thickening of the anodic film

The galvanostatic transients show that film thickening takes place after the occurrence of the transition time, that is after the complete coverage of the electrode surface. To estimate the extent of film thickening one should refer to the experiments of anode-potential decay at current interruption, starting from anode potentials exceeding that corresponding to the galvanostatic transition time. The decay slopes, in this case, are a function of the initial potential, as seen in Fig. 14, and their interpretation can be given by assuming that a layer of total thickness δ' is present at the interface at current interruption and that only a fraction of the potential appears across the activation-energy barrier.¹² In this event, one can relate the fraction of total potential across the film, αE , to the electric field $\mathcal{E} = E/\delta'$, by

$$\alpha E = a\mathcal{E}, \quad (12)$$

where a is the distance from the minimum to the peak of the free energy barrier.

Let us assume that the rate of film thickening is given by

$$i = i_0 \left\{ \exp \left[\frac{\alpha FE}{RT} \right] - \exp \left[- \frac{(1 - \alpha)FE}{RT} \right] \right\}, \quad (13)$$

where i_0 is a constant. At large E , the second term of (13) is negligible and the differential equation of the decay transient at current interruption is

$$C \frac{dE}{dt} + i_0 \exp \left[\frac{\alpha E}{RT} \right] = 0. \quad (14)$$

Taking into account (14) and further assuming C is constant, after integration we have

$$E = \text{const} - b_a \ln(t + t'), \quad (15)$$

where t' is a constant obtained from the semilogarithmic plot. According to (12) to (15),

$$b_a = \frac{\delta' RT}{Fa}. \quad (16)$$

Hence the decay slope is directly proportional to the total film thickness. Values of δ' calculated from (16) are shown in Table 6. These figures, which are within the order

TABLE 6. APPARENT FILM THICKNESS DERIVED FROM DECAY SLOPES

a Å	z	b_a V	δ Å
3	1	1.75	56.1
3	1	4.30	139.0
3	1	5.70	184.0

of 100 Å, allow the interpretation of the low capacitance obtained at potentials corresponding to film thickening. Since capacitance is defined in general by the equation

$$C = \frac{i}{|dE/dt|}, \quad (17)$$

the system behaves as if there were a capacitive element in parallel with the normal resistance through which the current flows. Its capacitance can then be written

$$C = \frac{\epsilon}{4\pi\delta'}, \quad (18)$$

where ϵ is the dielectric constant. This equation satisfies the experimental observations that the capacitance diminishes as δ' increases, and the initial slope of the anode overpotential decay increases as the potential of interruption increases. This behaviour has similarly been observed for anodic film formation on passive iron.¹³

On the basis of (18) one can evaluate the average dielectric constant of the passivating film. Thus, if C is taken as $0.1 \mu\text{F}/\text{cm}^2$, for $\delta' = 100 \text{ \AA}$, it gives a result of the order of 2. This dielectric constant is quite reasonable if the film corresponds precisely to that of a polymer material. This polymeric film must be responsible for the electrical behaviour of the interface, and particularly for the faradaic rectification effect, which is analysed further on.

Kinetics of anodic film thickening

To obtain quantitative information about the thickening of the anodic film one should refer to potentiostatic transients and analyse how the current flowing after the film-growth process changes with time, on the assumption that the charge passed is proportional to the thickness of the film.

Within an oversimplified scheme, the time t_A required for film-growth termination can be taken as the time for the initiation of film thickening. The values of t_A are easily obtained from the plots of the time dependence of the fraction of initial area covered, since they correspond to the time to achieve full electrode coverage. Therefore data obtained from the descending branch of the potentiostatic E/time plot, starting from t_A , are useful for the purpose. As shown in Fig. 22, reasonably good

FIG. 22. Parabolic law plot for film thickening at different anode potentials.

○, $E - E_{\text{rest}} = 0.500 \text{ V}$; +, 0.512 V ; ●, 0.525 V .

straight lines are obtained by plotting Q^2 vs t . The higher the electrode potential, the larger the slopes. Therefore, the parabolic growth law, frequently observed for the formation of various insoluble substances on solid surfaces, seems to be obeyed.¹⁴

The kinetic law related to the thickening of the anodic film depends on the conducting properties of the film. If the latter is considered to be a non-conducting film, the parabolic growth law arises from two different models. One of these, deduced for films of the oxide structure,^{12,14} either for small electric fields within the film as compared to RT , or very thick films, yields

$$\delta' = \left(\frac{4AnFEt}{RT} \right)^{1/2} \exp \left(- \frac{\Delta G_0^*}{2RT} \right) + \text{const}, \quad (19)$$

where ΔG_0^* is the standard free energy of activation for the film growth.

A relationship between δ' and t of the same form as (19) but with different constants results from a simple diffusion mechanism,¹⁵ where it is assumed that the rate of thickening is proportional to the concentration gradient of the charge-transport species. The parabolic law is then

$$(\delta')^2 = \frac{2D}{H} (C_1 - C_0)t, \quad (20)$$

where D is the diffusion coefficient of the charge transport species in the film, C_1 and C_0 are its concentration at the metal/film and film/melt interfaces respectively and H is the proportionality constant relating concentration to thickness.

The fact that the slopes of the Q^2/t plots increase with increase of potential may at first sight imply that (19) better satisfies the results. This conclusion however is not definite, because with a potential dependence of $(C_1 - C_0)$, (20) would also be valid. Another difficulty arising in the Q^2/t plots is that they do not intersect the origin. This may be due to the oversimplified assumption and the accuracy in the definition of t_A . Further experimental work is certainly required to arrive at a sounder conclusion about this point.

A model for faradaic rectification in the presence of the passive film

When the film growth process is finished, film thickening follows and the electrical resistance increases simultaneously, as shown in Fig. 23. For the sake of simplicity, let us assume that the electrode is positively charged and the surface is covered with a uniform and compact layer of the passivating film, which acts as a dielectric. In this case, negative charges are induced at the face of the film attached to the electrode surface, while the film becomes positive at the film/melt interface. Consequently, either the SCN^- ion or the electron left in the process, if the discharge has occurred at the interface, has to surmount an energy barrier within the film which hinders any movement of negatively charged species towards the electrode acting as electron sink. The SCN radical formed in the reaction polymerizes on the external face of the growing film or inside it.

When the film already exists on the surface and the electrode is negatively charged, as occurred either in the reverse pulse or periodically in the faradaic rectification experiments, the situation is completely different. The inner face of the film becomes positively charged and the outer face negatively. Now there should be no appreciable

FIG. 23. Time dependence of film resistance during potentiostatic experiments. Δ , $E - E_{\text{rest}} 0.500$ V; $\times$, 0.512 V; $\circ$, 0.525 V.

resistance to charge transfer if reduction of the film occurs preferentially at the metal/film interface, since there is practically no barrier to be surmounted for the reacting species. Besides, the reduction process of the $(\text{SCN})_x$ film at low cathodic potentials can occur by various concurrent reactions, which can be represented by the general stoichiometric equations

where n and x are integers. The most likely reaction product at low cathodic polarization must be the SCN^- ion, although as intermediate species ions such as $(\text{SCN})_2^-$, $(\text{SCN})_3^-$ etc may exist. This cathodic process rapidly destroys the passivating film and also probably provokes, additionally, its mechanical detachment.

From the structural point of view electron capture by the film is reasonable. The bonding energy of SCN groups, as compared to the bond energy of the halogen molecules to which the $(\text{SCN})_2$ is electronically similar must be low and their electron affinity high. Therefore the energetics of the reaction towards SCN^- ion formation may be quite favourable. For the same reason, ions such as $(\text{SCN})_2^-$ are also probably formed as intermediates.

If the cathodic pulses cover larger voltages, then the reduction process continues further, according to

and the final products become trapped at the reaction interface if all the polymer film has not disappeared. The formation of S^{2-} and CN^- ions at the metal/film interface means that the application of a reverse pulse should first provoke the oxidation of the S^{2-} ion, later the oxidation of the CN^- ion and finally that of the SCN^- ion. These processes become characterized by typical transition times in the anodic galvanostatic pulse for the case described, and the charge required for the first transition time must be twice that for the second. The products yielded by these oxidations must all contribute to the nucleation and film-growth processes during the anodic transient. These facts have certainly been observed.

In conclusion, the faradaic rectification can be qualitatively explained with the

electrical properties assigned to the passivating film. This is certainly an oversimplified model, where no porosity effect or other disturbance has been taken into account. However a first approach to the characteristic behaviour of anodic oxidation of molten SCN^- ion on platinum, and of its kinetics and probable electrochemical mechanisms, has been envisaged. Each of the questions referred to in the foregoing description deserves further work.

Acknowledgement—The authors thank the Consejo Nacional de Investigaciones Científicas y Técnicas of Argentina for financial support.

REFERENCES

1. G. W. HARRINGTON and H. T. TIEN, *J. phys. Chem.* **66**, 173 (1962).
2. G. METZGER, *Rapp.* CEA-R-2566. Centre d'Etudes Nucléaires, Saclay, France (1964).
3. A. ELUARD and B. TRÉMILLON, *J. electroanal. Chem.* **13**, 208 (1967).
4. M. E. MARTINS, G. PAUS, A. J. CALANDRA and A. J. ARVÍA, *Anal. Asoc. Quím. Arg.* **57**, 91 (1969).
5. R. E. PANZER and M. J. SCHAEER, *J. electrochem. Soc.* **112**, 1136 (1965).
6. K. F. DENNING and K. E. JOHNSON, *Electrochim. Acta* **12**, 1391 (1967).
7. A. J. ARVÍA, A. J. CALANDRA and H. A. VIDELA, *Electrochim. Acta* **10**, 33 (1965).
8. M. E. MARTINS, A. J. CALANDRA and A. J. ARVÍA, *Electrochim. Acta* **15**, 111 (1970).
9. D. A. VERMILYEA, *Advances in Electrochemistry and Electrochemical Engineering*, ed. P. DELAHAYE and C. W. TOBIAS, Vol. 3, p. 211. Interscience, New York (1963).
10. M. AVRAMI, *J. chem. Phys.* **7**, 1103 (1939).
11. M. FLEISCHMANN and H. R. THIRSK, *Electrochim. Acta* **1**, 146 (1959).
12. N. CABRERA and N. F. MOTT, *Rep. Progr. in Phys.* **12**, 163 (1948–49).
13. J. L. ORD and J. H. BARTLETT, *J. electrochem. Soc.* **112**, 160 (1965).
14. K. HAUFFE, *Oxidation of Metals*, p. 365. Plenum Press, New York (1965).
15. M. A. GENSHAW, in *Electrosorption*, ed. E. GILEADI, p. 73. Plenum Press, New York (1967).