

RADIOCHEMICAL STUDY OF THE ANODIC CORROSION OF IRIIDIUM

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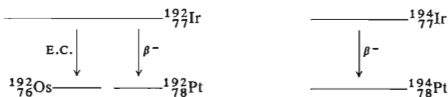
Received June 17th, 1970

^{192}Ir and ^{194}Ir isotopes with half lives of 74.4 d and 19 h, respectively, are obtained by irradiation of natural Ir with thermal neutrons. Radiochemical measurements of corrosion can be performed with the ^{192}Ir isotope. The sensitivity of the method allows to carry out studies on the electrochemical corrosion of this metal even under conditions of passivation. When this corrosion is stronger, spectrophotometric analyses of the solutions show that, with 6N or higher concentrations of HCl, $[\text{IrCl}_6]^{3-}$ and $[\text{IrCl}_6]^{2-}$ complexes are obtained. However, for concentrations lower than 1N, the formation of aquo-chloro-complexes of Ir(III) and Ir(IV) takes place, with a higher proportion of water molecules in the coordination shell as the concentration of HCl decreases.

Iridium is the most resistant of the platinum group metals to chemical and electrochemical corrosion. Earlier papers by Llopis and Jorge^{1,2} dealt with anodic corrosion and passivation of this metal in HCl solutions. Under these conditions, corrosion increased markedly by superimposing an alternating current, the effect being more pronounced at low frequencies; this corrosion leads to formation of Ir(III) and Ir(IV) complexes. The relative proportion of Ir(III) decreased as the potential became more positive and it was enhanced as the i_c -direct current density- and/or the i_a/i_c ratio increased³. In this paper that work is continued, using radioactive tracer techniques similar to that described⁴ for measuring extremely small anodic corrosion rates.

THEORETICAL

Natural iridium is built up by two isotopes ^{191}Ir and ^{193}Ir ; isotopic composition is 38.5% and 61.5% and the cross section for thermal neutron capture 750 and 110 barns⁵, respectively. Neutron irradiation of Ir in a nuclear reactor produces ^{192}Ir and ^{194}Ir isotopes. The half lives of these isotopes are respectively 74 days and 17 hours, decaying to stable osmium and platinum isotopes, according to the following simplified schemes:



The large cross section of both isotopes allows to reach the required activity in a short time of irradiation (hours). Owing to the difference between their half lives, ^{192}Ir is the only isotope remaining in the sample 10 days after the irradiation.

EXPERIMENTAL

Two electrodes arranged as reported in¹ were used in these experiments: a 3.5 cm² geometrical surface sheet, 0.2 mm thick for radiochemical experiments, and a 9 cm² sheet, 1 mm thick for other tests.

The electrochemical cell was described elsewhere⁴, graphite bars being used as counter electrodes. The dc and ac are given in⁶. The anodic corrosion tests were carried out by means of a Wenking potentiostat. Spectra of solutions were recorded with a Beckman DU spectrophotometer. The radioactivity was measured in a NaI(Tl) scintillation counter by an integral method; 1 ml samples were taken from the solution in plastic stoppered containers.

Standard solutions were prepared by dissolving 5.09 mg of the electrode by 50 Hz ac in 6M-HCl and adequate dilutions.

In experiments with alternating and superimposed currents, the electrode undergoes a deep attack, and corrosion rates are evaluated by weight loss of the metal against time.

Determination of the valence state of dissolved iridium in corrosion tests was performed on two liquid samples. In one of them, Ir(IV) is titrated by a iodometric method⁷, after bubbling nitrogen through the solution to expel the chlorine. The total iridium is titrated by the same method on the other sample, after oxidation of Ir(III) with chlorine and subsequent boiling to remove the excess.

RESULTS AND DISCUSSION

Corrosion of Iridium by 50 Hz Alternating Current

The corrosion of iridium by low frequency ac has been used for the preparation of metallographic specimens⁸. In order to enlarge the results given in¹, a series of experiments, summarized in Table I, were performed.

It becomes apparent from these results, that the Ir(III)/Ir(IV) ratio increases as the acid concentration decreases. On the other hand, the surface state of the electrode also plays a role as shown in the experiments with 1M-HCl solutions. The nature of the ionic species existing in the solutions was studied by UV and visible absorption spectra. The spectra of a number of chloro and aquochlorocomplexes of tri and tetravalent iridium are given in Table II. Spectra of some geometrical isomers have been reported by El-Awady, Boumsall and Garner¹⁴. The positions of their bands and extinction coefficients are very close.

The spectra of the solutions in 6M-HCl show only the absorption bands of the $[\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$ complex. The bands of the Ir(III) complexes do not appear in the spec-

TABLE I
Corrosion of Iridium by Low Frequency
Temperature 25°C, $i_a = 50 \text{ mA/cm}^2$, $i_c = 0$.

HCl conc.	Corrosion $\mu\text{g/cm}^2 \text{ h}$	% Ir(IV)	% Ir(III)
6M	270	33	67
1M	244	20	80
1M ^a	275	2	98
0.5M	237	5	95
0.25M	242	8	92

^a The last experiment of those quoted in the Table.

trum in spite of the high relative proportion of this valence state in the solution, since the extinction coefficients of Ir(III) complexes are one order of magnitude less than those of Ir(IV) (Fig. 1).

In 1M-HCl solutions the bands appear at different positions, according to the Ir(III)/Ir(IV) ratio.

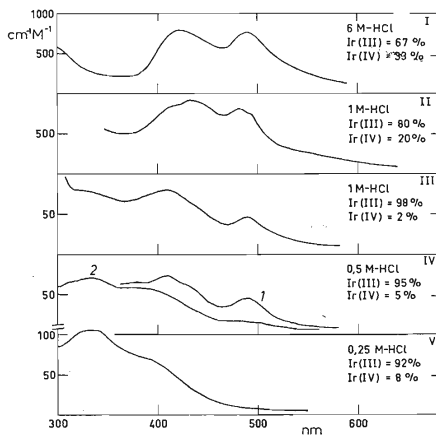


FIG. 1
Absorption Spectra

The diffuse band at 410–450 nm (spectrum II, Fig. 1) can be related basically to the aquo and diaquo Ir(IV) complexes; the hexachlorocomplex is detected by the very intense band at 490 nm.

In spectrum III, (Fig. 1) the absorption band shifts towards 410 nm and shows a slight shoulder around 390 nm, facts that can be interpreted in terms of aquo and diaquo Ir(III) complexes. The band at 490 nm is that of the hexachloro Ir(IV) complex, very intense and detectable, even at very low concentration.

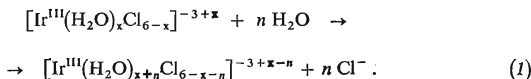
The spectra of the 0.5M-HCl solutions (Fig. 1, IV) are very similar to III, if they are recorded, as the others, immediately after the corrosion experiment (spectrum 1); some days later a fading out of the colour occurs due to the spontaneous reduction

TABLE II

The Spectra of Chloro- and Aquochlorocomplexes of Tri- and Tetravalent Iridium

Complexes	Absorption bands nm	Extinction coefficients $\text{mol}^{-1} \text{cm}^{-1}$	References
$[\text{Ir}^{\text{IV}}\text{Cl}_6]^{2-}$	414	2 480	9
	431	2 540	
	489	3 200	
	575	460	
$[\text{Ir}^{\text{III}}\text{Cl}_6]^{3-}$	356	64	10
	415	76	
	560	10	
	615	7.5	
$[\text{Ir}^{\text{IV}}(\text{H}_2\text{O})\text{Cl}_5]^{-}$	450	3 320	11
$[\text{Ir}^{\text{III}}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$	347	110	12
	405	110	
	550	12	
$[\text{Ir}^{\text{IV}}(\text{H}_2\text{O})_2\text{Cl}_4]$	350	1 090	13
	445	2 920	
	535	1 210	
$[\text{Ir}^{\text{III}}(\text{H}_2\text{O})_2\text{Cl}_4]^{-}$	333	113	13
	392	100	
	530	13.1	
$[\text{Ir}^{\text{IV}}(\text{H}_2\text{O})_3\text{Cl}_3]^{+}$	373	1 700	13
	510	1 400	
$[\text{Ir}^{\text{III}}(\text{H}_2\text{O})_3\text{Cl}_3]$	378	95.0	13

of Ir(IV) in aqueous solutions of low acidity^{15,16}. The spectrum taken after 22 days (spectrum 2) one shows no visible bands but a diffuse in the ultraviolet region around 330 nm, assigned to the diaquo Ir(III) complex. That is, the complexes produced during the corrosion of the metal, undergo an "aquation" process, which is favoured by the low concentration of chloride ions in the solution. The process can be described as



As the HCl concentration decreases to 0,25M, this "aquation" process becomes faster as shown by the similarity of the spectra V and IV 2.

Corrosion by direct and alternating currents has been further investigated. The depolarizing effect of an alternating current, at intensities higher than those of the direct current, has been pointed out by Llopis and Jorge¹, in their experiments with 6M-HCl solutions. In order to gain some information about the role of the electrolyte concentration on this effect, a set of corrosion tests in 2M-HCl with several ac and dc current densities was performed (Table III). It can be seen that at constant i_c values, the corrosion of iridium increases at higher ac current density.

On the other hand, the absorption spectra of those solutions are rather different from those obtained by corrosion with ac only. At $5 \mu\text{A}/\text{cm}^2$ dc, the spectrum shows absorption bands around 350 and 400 nm, which are related to the aquo and diaquo Ir(III) complexes. If the dc increases up to $10 \mu\text{A}/\text{cm}^2$ only a diffuse band appears around 440 nm, which can be assigned to the aquopentachloro iridium(IV) complex. Owing to the large dilution, light absorption is low and it becomes difficult to obtain and discuss these last spectra.

TABLE III
Corrosion by Direct and Alternating Currents
2M-HCl, t 25°C, 50 Hz alternating current.

i_a mA/cm^2	i_c $\mu\text{A}/\text{cm}^2$	Corrosion $\mu\text{g}/\text{cm}^2 \text{ h}$
5	5	1.8
10	5	2.8
10	10	—
15	5	4.0
15	10	1.4
15	30	—

Anodic corrosion of iridium has been studied by a radiochemical method, similar to that described in⁴. The radioactive measurements are performed on the ¹⁹²Ir isotope, $t_{1/2} = 74.4$ days. Data in Table IV are the average values of two experiments with potentials referred to the S.C.E.

TABLE IV
Corrosion by Direct Current, 50°C

Electrolyte	ε_c , mV	Corrosion $\mu\text{g cm}^{-2} \text{h}^{-1}$
12M-HCl	650	0.080
12M-HCl	700	0.164
12M-HCl	800	0.251
6M-HCl	800	0.078
6M-HCl	900	0.285
4M-HCl	1 200	—
2M-HCl	1 400	—
sat. NaCl	1 400	0.024

From these results it is clear that in Cl^- containing solutions anodic corrosion of iridium by direct current is very small but not null, if the Cl^- ion concentration is high enough. That is, the metal passivates very easily but some corrosion may remain, its rate depending upon potential, H_3O^+ and Cl^- ion concentration. On the other hand, owing to the large dilution of the solutions obtained under these conditions, it has not been possible to discuss the nature of the complexes formed.

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