# The Effect of Pre-polarization of a Platinum Anode on the Current Obtained in the Controlled Potential Oxidation of Iron and of Arsenic

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In the course of some experiments on the electrolytic oxidation of arsenic in acid solution[1] the authors experienced difficulty in obtaining the same current values in successive electrolyses under supposedly the same conditions. A principal cause was found to be the presence of a variable amount of oxide on the surface of the smooth platinum anode employed in the electrolysis. It was then found that the pre-treatment of the electrode, particularly with regard to hydrogen or oxygen evolution, could cause at least a tenfold variation in currents obtained in the oxidation of both iron and arsenic. Although various investigators[2,3,4] have demonstrated the presence of platinum oxides on electrodes and mention has been made of the effect of prepolarization on current efficiency in certain electrolyses,[5] iron and arsenic are not among these, nor have there been any studies made at constant potential. This paper is therefore offered to present data pertaining to these two cases and to call attention to the presence of a phenomenon which the authors feel may be of more common occurrence and significance than is generally recognized.

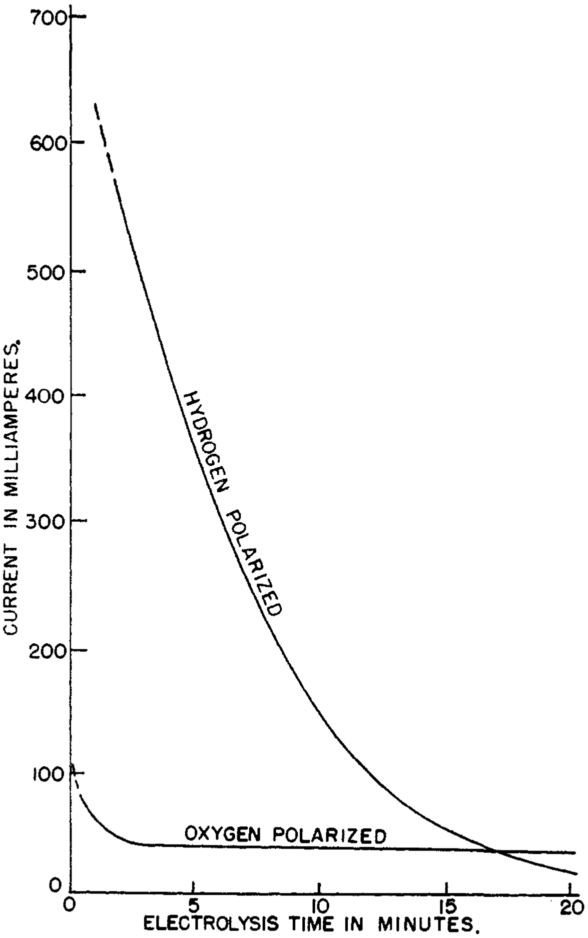

Fig. 1.—Effect of pre-polarization on current obtained in electrolytic oxidation of arsenic.

Slomin-type platinum electrodes, a divided compartment cell, an automatic potentiostat, and an automatic recorder were used. These have all been described previously.[1,6] The iron oxidations were conducted at an anode potential of $-0.7$ volt and the arsenic at $-1.0$ volt *vs.* satd. calomel electrode. The electrolyte was 1 *M* sulfuric acid approximately 0.025 *N* in iron or arsenic. Unless otherwise stated the potential was applied before the anode was lowered into the solution so that electrolysis began immediately, and before each run the resistances in the potentiostat were manually set at the position that previous runs had shown would give the desired potential at the beginning of the electrolysis. Pre-polarization was carried out in 1 *M* sulfuric acid for two minutes with a total applied potential of 4.0 volts, delivered from two cells of a 6-volt storage battery. This gave quite vigorous gas evolution, some heat, and a maximum

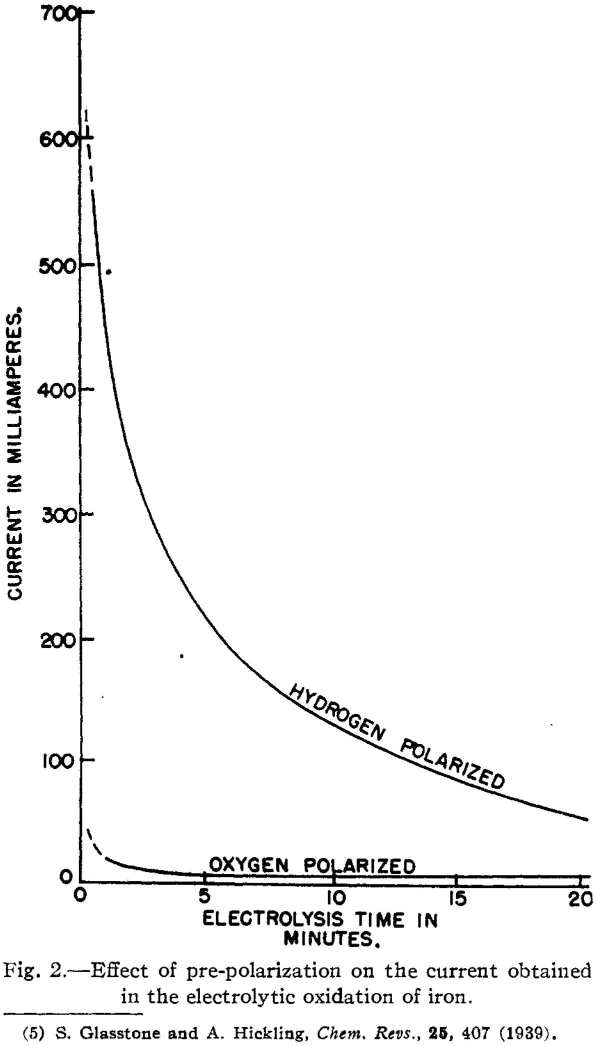

Fig. 2.—Effect of pre-polarization on the current obtained in the electrolytic oxidation of iron.

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[1] B. B. Baker and W. M. MacNevin, This Journal, **75**, 1473 (1953).

[2] J. D. Pearson and J. A. V. Butler, *Trans. Faraday Soc.*, **34**, 1163 (1938).

[3] A. Hickling, *ibid.*, **41**, 333 (1945).

[4] S. E. S. El Wakkad and S. H. Emara, *J. Chem. Soc.*, 461 (1952).

[5] S. Glasstone and A. Hickling, *Chem. Revs.*, **25**, 407 (1939).

[6] W. M. MacNevin and B. B. Baker, *Anal. Chem.*, **24**, 986 (1952).

polarization effect. It was found that an electrode either anodically or cathodically polarized in this fashion remained in its same condition after several hours of standing in 1 $M$ sulfuric acid and was not changed even by several minutes in hot concentrated nitric acid. By "remaining in its same condition" is meant that the electrode would exhibit the same behavior in a subsequent electrolysis, which was the only criterion we could apply as to the state of the surface of the electrode.

Figure 1 shows the subsequent effect in an arsenic oxidation of prior hydrogen and oxygen pre-polarization treatment of the platinum anode. Figure 2 shows similar behavior in an iron oxidation.

It was further observed (Fig. 3) that if an oxygen pre-polarized electrode was allowed to stand for one hour in the arsenic solution before beginning the electrolysis the electrode slowly reverted to a condition similar to that of a hydrogen pre-polarized electrode. The most likely explanation is that the arsenic(III) reduces the platinum oxide (probably (PtO) and gives a clean platinum surface. A similar process occurs if the electrode stands in the iron solution before the electrolysis is begun but the reaction is quite rapid, about 10 to 20 seconds sufficing for the complete removal of the oxide. The speed of this reaction probably accounts for this effect not having been observed before in iron oxidations. However, it should be noted that, as Fig. 2 indicates, if the potential is applied and maintained, then the current remains low throughout the entire electrolysis. This means that the iron solution cannot reduce the oxide while the potential is applied and oxidation is occurring at the electrode.

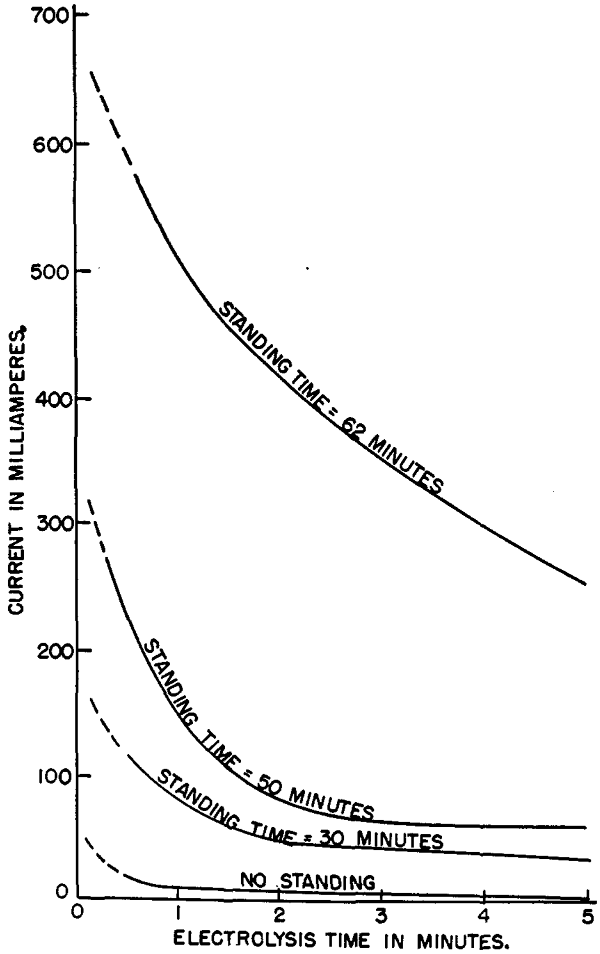

Fig. 3.—Effect of oxygen pre-polarized electrode standing in As(III) solution prior to electrolysis.

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## X-Ray Examination of Polychlorotrifluoroethylene[1]

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The X-ray investigation of the structure of polychlorotrifluoroethylene has been undertaken in order to obtain an understanding of the behavior of the polymer in terms of its structural parameters. The polymer, known commercially as KEL-F, is of interest because of its chemical inertness, low solubility, high softening point, and satisfactory electrical and mechanical properties.

The development of crystallinity at temperatures below the first order transition temperature at 211° has been investigated by X-ray methods. The data supplement those obtained by Price[2] using optical methods.

Debye–Scherrer diagrams of the polymer were obtained using crystal monochromatized CuK$\alpha$ radiation and a flat camera. The patterns of unoriented polycrystalline samples showed one strong line at about 5.5 Å. and several other relatively weak lines at smaller spacings. A high resolution Geiger counter spectrometer was used to study the fine structure that had been observed in some of the Debye–Scherrer patterns of highly crystalline samples.

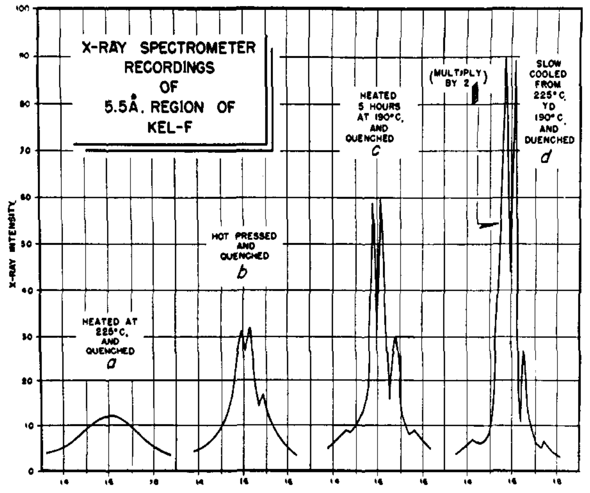

Fig. 1.

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[1] This paper was presented at the Diamond Jubilee Meeting of the American Chemical Society held in New York in September, 1951.

[2] F. P. Price, THIS JOURNAL, 74, 311 (1952).