

# Catalytic and inhibitory effects of dissolved $Cd^{2+}$ on $C_3H_8$ electro-oxidation

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Studies have been made of the effect of  $Cd^{2+}$  on the oxidation rate of  $C_3H_8$  in 80%  $H_3PO_4$  at 130°C on platinized Pt electrodes.

Dissolved  $Cd^{2+}$  discharges, probably as  $Cd^0$ , and forms a stable sub-monolayer on a Pt electrode at potentials as high as 0.5 V versus RHE. Although this  $Cd^0$  layer is apparently substantially desorbed in favor of adsorbed hydrocarbon,  $C_3H_8$  adsorption is inhibited in its presence.  $C_3H_8$  oxidation is also inhibited. However, the  $C_3H_8$  oxidation rate is observed to increase under some circumstances, and this appears to be because Cd is absorbed into the Pt lattice. Co-plating of Cd and Pt leads to an electrode which, once the excess Cd has been removed, appears to be stable, and which catalyses  $C_3H_8$  oxidation by about a factor of three at 0.25 V. Above 0.3 V, this absorbed Cd somewhat inhibits  $C_3H_8$  oxidation.

## 1. Introduction

This work is a continuation of earlier studies [1-8] on the mechanism of hydrocarbon oxidation and of the catalytic effects of certain added cations on hydrocarbon oxidation [9, 10]. This latter type of investigation was initiated in an effort to use adsorbed monolayers of non-noble metals as corrosion-resistant promoters of Pt catalysis for anodic hydrocarbon oxidation. The present paper concerns the effects of  $Cd^{2+}$  dissolved in concentrated  $H_3PO_4$ .

Electrode areas of smooth Pt electrodes were estimated using H-atom deposition [12], the assumption being that one 'real'  $cm^2$  corresponds to 210  $\mu C$  of H atoms. The real area of platinized Pt electrodes was estimated by reducing the oxide present on the electrode after 2 min at 1.2 V versus RHE. The reduction was carried out at about 10 mA per geometric  $cm^2$  and, based on our observations with smooth Pt electrodes, the amount of oxide on the electrode under these conditions is 400  $\mu C$  per real  $cm^2$ .

The reference electrode comprised an auto-geneous  $H_2$  electrode, as described elsewhere [13]. Potentials are referred to this electrode, the reversible hydrogen electrode (RHE) in  $H_3PO_4$  at 130°C.

## 2. Results and discussion

Dissolved  $Cd^{2+}$  in solution generally inhibits the oxidation of  $C_3H_8$ . Studying the relationship between  $i_{C_3H_8}$  current and  $\theta_{Cd}$  coverage, we noted an ageing effect of platinized Pt in the presence of dissolved  $Cd^{2+}$ ; currents were observed to increase during the course of these experiments without change of the  $Cd^{2+}$  concentration. This effect, and the adsorption on Pt from  $Cd^{2+}$ -containing solutions, were then further investigated.

### 2.1 Adsorption studies

Studies were made of the adsorption of cadmium on the surface of the electrode with the aim of determining the  $i_{C_3H_8} - \theta_{Cd}$  relationship. Results are shown in Figs. 1-3.

In Fig. 1, we show anode chronopotentiograms at 246 mA per real  $cm^2$  on smooth Pt electrodes under  $N_2$ . Fig. 1a shows the standard background measurement, i.e., a pre-treatment at 1.35 V followed by oxide reduction at 0.1 V and adsorption at 0.3 V, either for 1 or 300 s with stirring (the longer curve in Fig. 1a). The small difference between the curves indicates the basic cleanliness of the system. Fig. 1b shows a similar chronopotentiogram taken after 1 s in the presence of 1.0

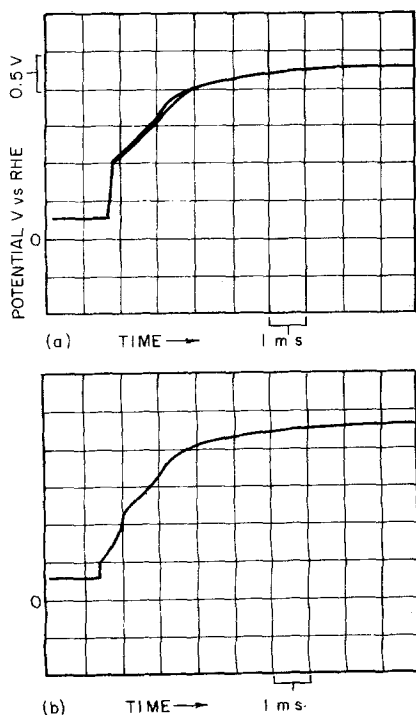


Fig. 1. Electrode oxidation chronopotentiograms from 0.30 V in 80%  $\text{H}_3\text{PO}_4$  and  $\text{N}_2$ : (a) for 1 and 300 s; (b) + 1 mM  $\text{Cd}^{2+}$  for 1 s.

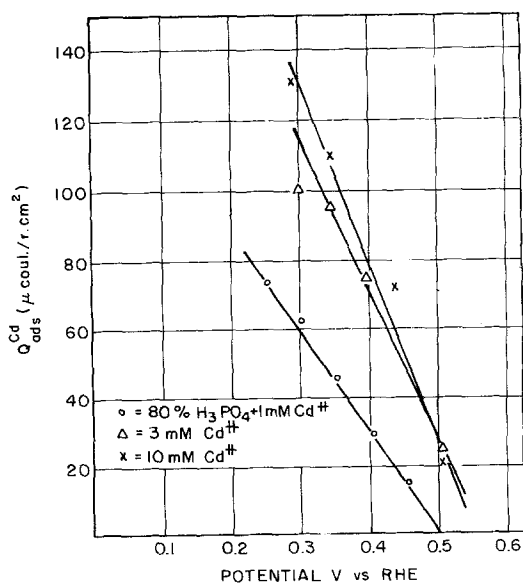


Fig. 2. Cadmium adsorption in the presence of  $\text{N}_2$ ; charge-potential curves on a smooth Pt electrode in 80%  $\text{H}_3\text{PO}_4$  + various  $\text{Cd}^{2+}$  concentrations.

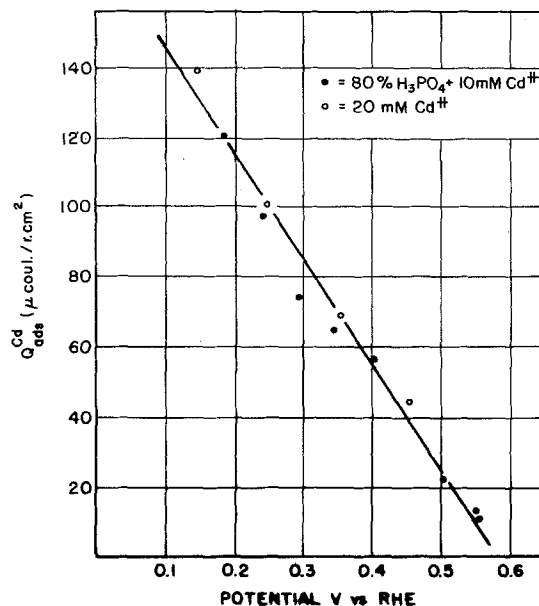


Fig. 3. Cadmium adsorption; charge-potential curves on a platinized Pt electrode in 80%  $\text{H}_3\text{PO}_4$  + various  $\text{Cd}^{2+}$  concentrations.

mM  $\text{Cd}^{2+}$ . We see a new oxidation wave starting at  $\sim 0.6$  V which is substantially complete prior to the onset of electrode oxidation. This wave corresponds to the oxidation of an adsorbed cadmium species. Calculations (only approximate because accurate diffusion coefficients are not available) on the relationship between the oxidizable adsorbed charge and the time of adsorption indicate that the surface species is probably  $\text{Cd}^0$ ; for simplicity, we will refer to the adsorbed discharged  $\text{Cd}^{2+}$  as  $\text{Cd}^0$ .

We found virtually complete formation of the  $\text{Cd}^0$  layer during the first second of adsorption. In Fig. 2 we show the 1 s adsorption charge for  $\text{Cd}^0$  as a function of potential and  $\text{Cd}^{2+}$  concentration. The amount of adsorption is very high, considering the extent by which the potential exceeds the reversible  $\text{Cd}/\text{Cd}^{2+}$  potential, i.e.,  $-0.34$  V with 10 mM  $\text{Cd}^{2+}$  at  $25^\circ\text{C}$ . [14]. In this case at 0.3 V, assuming a  $\text{Cd}^0$  layer 1:1 with respect to Pt surface sites, we have about 0.6 of a monolayer, and even at 0.5 V there is appreciable  $\text{Cd}^0$  coverage.

On platinized Pt (Fig. 3) there is also appreciable coverage over the whole range of interest for  $\text{C}_3\text{H}_8$  oxidation. These particular measurements were made in the presence of  $\text{C}_3\text{H}_8$ . For this reason, and because  $\text{C}_3\text{H}_8$  adsorption displaces the  $\text{Cd}^0$  adsorbate, measurements of  $Q_{\text{ads}}^{\text{Cd}}$  were also

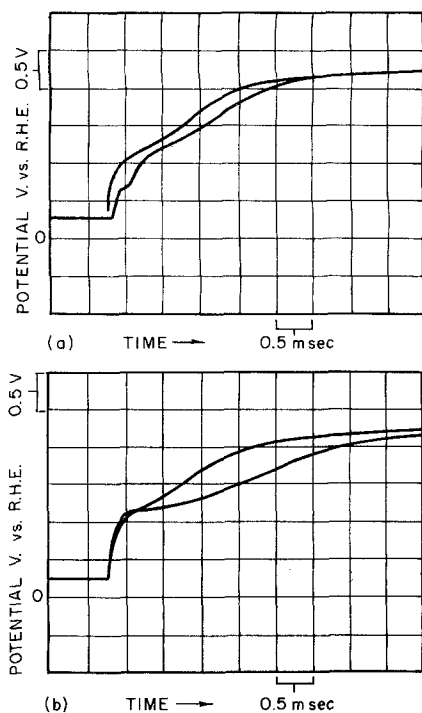


Fig. 4. C<sub>3</sub>H<sub>8</sub> oxidation, chronopotentiograms from 0.30 V in 80% H<sub>3</sub>PO<sub>4</sub> + 1 mM Cd<sup>2+</sup>; (a) adsorption for 0.01 and 1 s; (b) adsorption for 0.01 and 300 s.

made after 1 s. The data do not then refer to the steady state. The significant point, however, is that with both types of electrodes there is substantial Cd<sup>0</sup> adsorption in the potential range of interest.

Figs. 4 and 5 show the effect of adsorbed Cd<sup>0</sup> on C<sub>3</sub>H<sub>8</sub> adsorption on smooth Pt. In Fig. 4a we show chronopotentiograms taken from 0.3 V in the presence of both C<sub>3</sub>H<sub>8</sub> and 1 mM Cd<sup>2+</sup>. These curves show: at 0.01 s, there is neither Cd<sup>0</sup> nor C<sub>3</sub>H<sub>8</sub> adsorption; at 1 s, Cd is adsorbed but insignificant C<sub>3</sub>H<sub>8</sub>; at 300 s, the Cd<sup>0</sup> wave has disappeared and we see a typical C<sub>3</sub>H<sub>8</sub> adsorbate oxidation wave. The implication is that a fully formed C<sub>3</sub>H<sub>8</sub> layer virtually displaces all the Cd<sup>0</sup>, as Gilman reported, for example, with C<sub>2</sub>H<sub>6</sub> and Cl<sup>-</sup> [18]. The effect of whatever Cd<sup>0</sup> then remains on the electrode, however, is considerable (Fig. 5). We see, that below ~0.45 V C<sub>3</sub>H<sub>8</sub> adsorption is diminished. Above this potential, there is an enhancement of organic adsorption.

## 2.2 Current potential studies

The small amounts of Cd<sup>0</sup> which may be co-

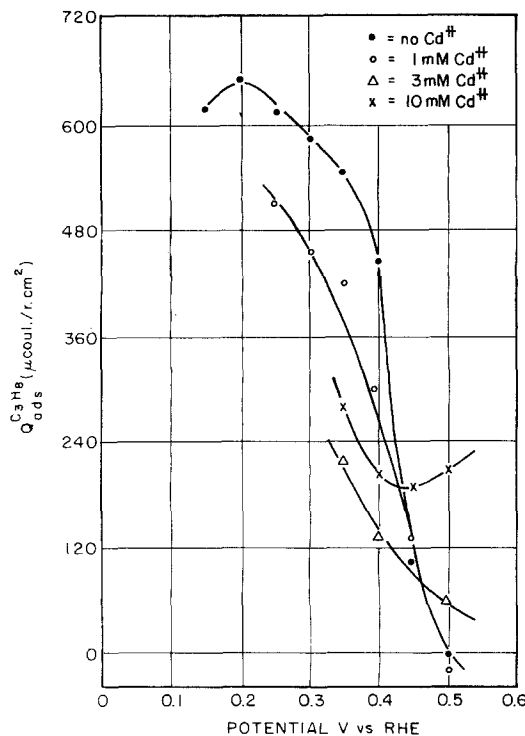


Fig. 5. C<sub>3</sub>H<sub>8</sub> adsorption; steady state charge-potential curves on a smooth Pt electrode in 80% H<sub>3</sub>PO<sub>4</sub> + various Cd<sup>2+</sup> concentrations.

adsorbed with the organic material have a substantial effect on the oxidation rate of C<sub>3</sub>H<sub>8</sub> (Fig. 6). This type of inhibition probably results because deposits of Cd<sup>0</sup> have lower catalytic activity for the reaction than have Pt. The most serious inhibition was found at the lowest potentials where, we believe [8], the rate limiting step is oxidation of adsorbed  $\geq\text{C-OH}$  by adsorbed H<sub>2</sub>O. Because the organic coverage at 0.3 V only decreases by ~50% (Fig. 5) while the current diminishes by an order of magnitude (Fig. 6), the predominant effect of Cd<sup>0</sup> must be on the kinetics of the water addition step rather than on the initial hydrocarbon adsorption step. The effect of deposited Cd<sup>0</sup> is similar to that reported earlier for Cu<sup>0</sup> [9]. It is appropriate to point out that inhibition of C<sub>3</sub>H<sub>8</sub> oxidation by dissolved cations could be the result of a double-layer effect [10] since we find no Cd<sup>0</sup> on the electrode in the presence of the C<sub>3</sub>H<sub>8</sub> layer.

In the course of taking the data of Fig. 6, we observed the above mentioned ageing effect, i.e., the tendency of the current to increase with time in the course of the experiment. In the experiment of Fig. 6, Cd<sup>2+</sup> was added incrementally to achieve

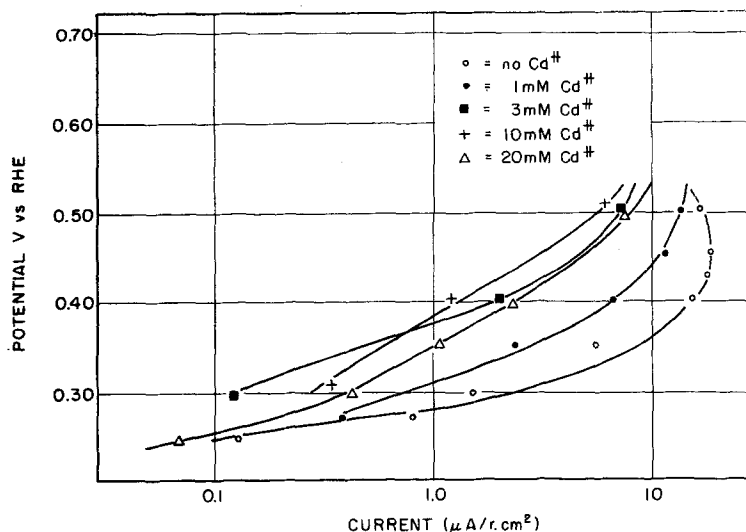


Fig. 6.  $C_3H_8$  oxidation; current-potential curves on a platinumized Pt electrode in 80%  $H_3PO_4$  + various  $Cd^{2+}$  concentrations.

total concentrations of 1, 3 and then 10 mM. The steady state currents were observed to decrease with each  $Cd^{2+}$  addition, as indicated. In the course of the 10 mM experiment, a part of the above adsorption study was carried out and, during these measurements, both the electrode area and its intrinsic catalytic activity (i.e., per unit of area) were observed to increase.

Figs. 7 and 8 summarize the experiments which were carried out to investigate this effect *in situ*. Fig. 7 shows the area-normalized current-potential curves carried out in the course of this experiment.

Initially the electrode area was  $43\text{ cm}^2$ , corresponding to a roughness of 24 (Run No. 1). While making the adsorption measurements, the area was observed to increase and, even after cleaning with  $Na_2CO_3$ , it was still  $50\text{ cm}^2$  (Run No. 2). Under these circumstances the normalized current was about a factor of 2 higher than that for the original platinumized Pt. In Runs No. 3 and 4, the area was deliberately increased to 60 and  $83\text{ cm}^2$ , respectively. This was achieved by cycling 85 times between 1.25 V for 5 s, down to 0.35 V for 1 s, and oxidizing with 200 mA to 1.5 V and returning

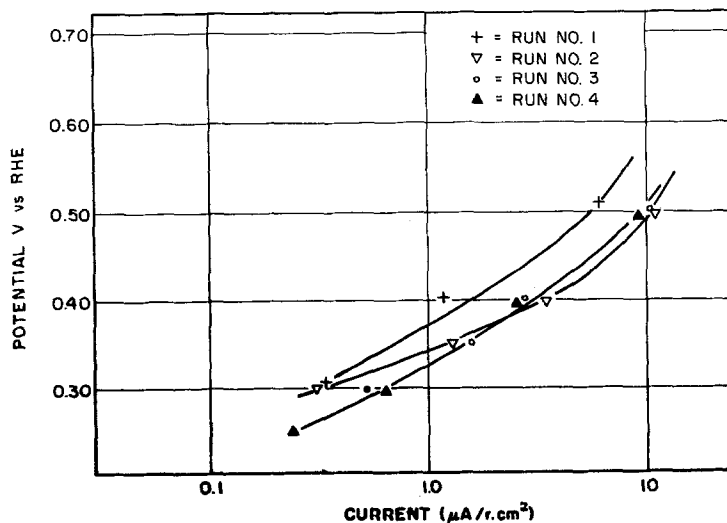


Fig. 7.  $C_3H_8$  oxidation; current-potential curves on a platinumized Pt electrode in 80%  $H_3PO_4$  + 10 mM  $Cd^{2+}$  after adsorption studies.

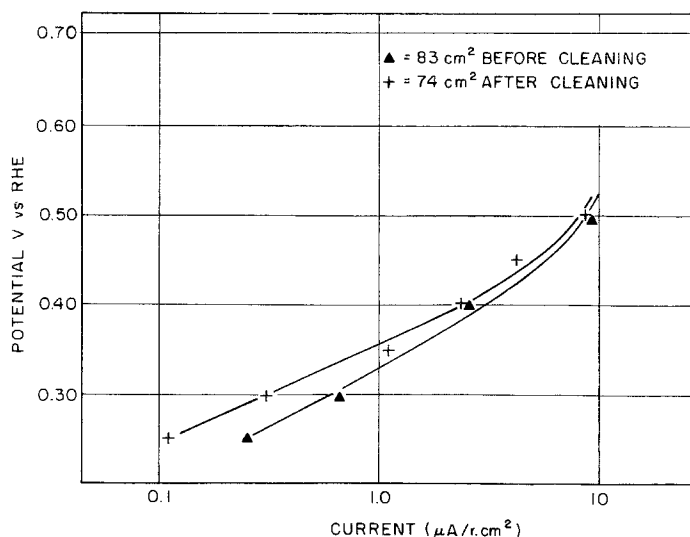


Fig. 8. C<sub>3</sub>H<sub>8</sub> oxidation; current-potential curves on a platinized Pt electrode in 80% H<sub>3</sub>PO<sub>4</sub> + 10 mM Cd<sup>2+</sup> before and after acid cleaning.

to repeat the cycle. Some further improvement in the C<sub>3</sub>H<sub>8</sub> oxidation rate was noted at the lower potentials and the previously gained 'enhancement' at the higher potentials was retained.\*

The results suggested to us the possibility that Cd was being incorporated into the Pt lattice during the potential cycling sequence. The phase diagram of the Pt-Cd system indeed shows solid state solubility of about 10 atm % Cd in Pt [15] (extrapolated to 100° C), so that this idea seemed rather reasonable. In order to confirm it, the electrode, whose area had been increased to 83 cm<sup>2</sup> in the presence of 10 mM Cd<sup>2+</sup> (Run No. 4), was removed from solution and washed in dilute HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. This would have the effect of removing a large part of any Cd dissolved in the platinized Pt. The results are shown in Fig. 8, and we see that particularly at the lower potentials this acid rinse does have the effect of reducing the previously gained 'enhancement'. This result emphasizes the possibility that Cd is being incorporated into the platinized Pt electrode.

\* Comparison of these curves with Fig. 6 shows that no net catalytic effect versus the pure Cd<sup>2+</sup>-free electrolyte was observed with this concentration of Cd<sup>2+</sup>. However, the substantial initial effect of Cd<sup>2+</sup>, i.e., to adsorb as Cd<sup>0</sup> on the surface of the Pt, would certainly mask any attempt to obtain an overall enhancement compared with the absence of Cd<sup>2+</sup> in solution. Further experiments, as reported, were carried out to incorporate Cd into the electrode, but without any Cd<sup>2+</sup> in the test solution.

Efforts were then made to co-plate Cd and Pt. For this purpose H<sub>2</sub>PtCl<sub>6</sub> plating solution was used in the presence of various amounts of dissolved CdCl<sub>2</sub>. The electrodes were plated at 50 mA cm<sup>-2</sup> for 2 min, followed by 2 min of anodization and 2 more min of cathodization. They they were washed in hot water and anodized for 1 min at 50 mA cm<sup>-2</sup> three times in dilute H<sub>2</sub>SO<sub>4</sub>. Finally, they were heated overnight in concentrated H<sub>3</sub>PO<sub>4</sub> at ~110° C to help age them. For one set of electrodes (numbers 7, 9, and 10—see below), this last step was carried out in the presence of 1 mM Cd<sup>2+</sup>, the aim being to try to prevent possible Cd loss from the plated electrode during aging. Table 1 summarizes the preparation of the electrodes used in the experiments described below.

Table 1. Electrode preparation

Electrode number	Preparation procedure
1	Plated in absence of Cd <sup>2+</sup> and used in experiment of Figs. 7–10.
2	Plated in the absence of Cd <sup>2+</sup> .
3	Plated in the presence of 1 mM Cd <sup>2+</sup> .
4,9	Plated in the presence of 3 mM Cd <sup>2+</sup> .
5,7,10	Plated in the presence of 100 mM Cd <sup>2+</sup> .

Some results in 80% H<sub>3</sub>PO<sub>4</sub> are shown in Fig. 9. Here the C<sub>3</sub>H<sub>8</sub> current was taken after 15 min at each potential after cleaning the electrode as usual

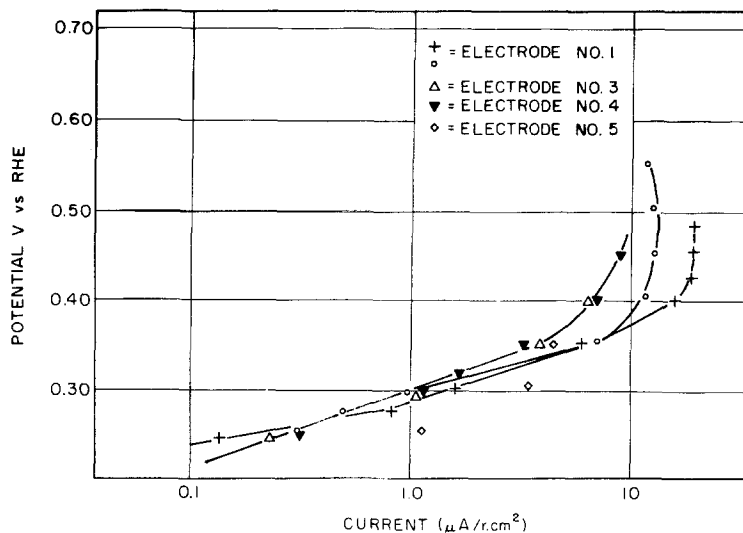


Fig. 9.  $C_3H_8$  oxidation; current-potential curves on co-plated Cd, platinumized Pt electrodes in 80%  $H_3PO_4$ .

at 1.35 V. Two curves are shown for electrode No. 1: the +’s are similar to the data shown in Fig. 6, and the 0’s were the points determined with the electrode after the end of the previous experiment. We see that the performance is somewhat degraded by the previous work in  $Cd^{2+}$  solution except perhaps at the lowest potential. Comparison is then made with the original data (+’s).

With electrodes 3 and 4 there may be some catalysis of  $C_3H_8$  oxidation at the lowest potential, but under all other conditions we clearly have net

inhibition. With electrode 5, which was plated in the presence of 100 mM  $Cd^{2+}$ , there appears to be a large catalytic effect at the lower potentials. This experiment was only carried out briefly because it was feared that a good part of the current corresponded to the dissolution of Cd from the electrode. The  $C_3H_8$  flow was then substituted by  $N_2$  and the current was found to be 0.5  $\mu A$  per real  $cm^2$ , independent of potential from 0.25–0.35 V. Thus a good part of the behavior in Fig. 9 does indeed correspond to Cd dissolution, but not all of it. For

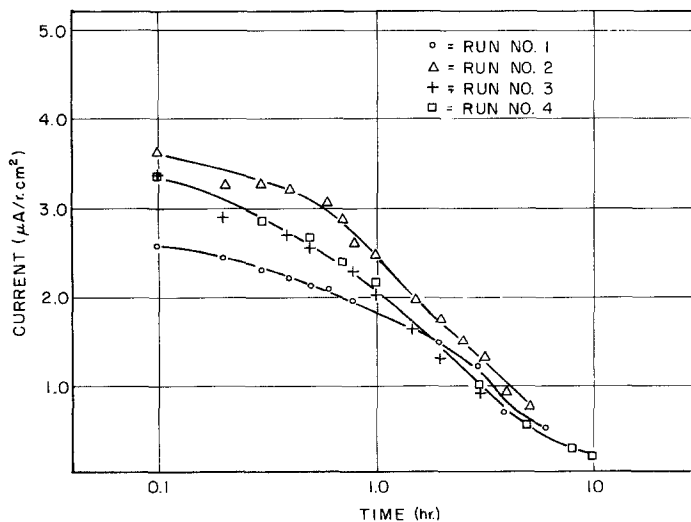


Fig. 10.  $C_3H_8$  oxidation; current-time curves at 0.32 V on a 100 mM  $Cd^{2+}$  co-plated, platinumized Pt electrode in 80%  $H_3PO_4$ .

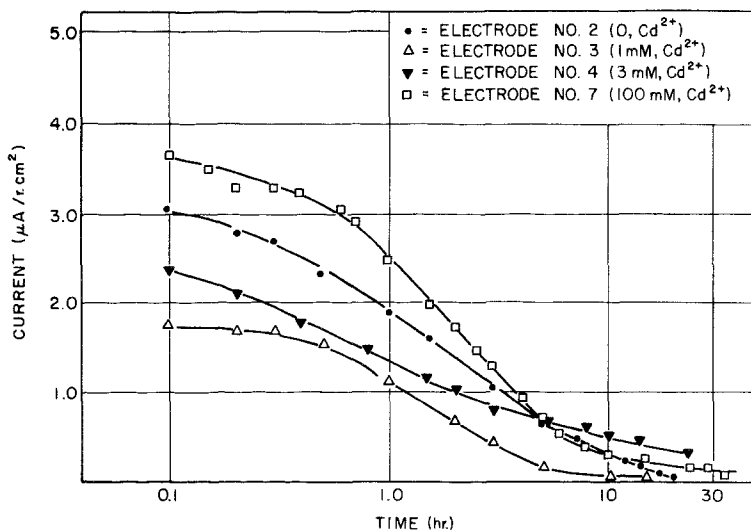


Fig. 11. C<sub>3</sub>H<sub>8</sub> oxidation; current-time curves at 0.32 V on various co-plated Cd, platinumized Pt electrodes in 80% H<sub>3</sub>PO<sub>4</sub>.

example, at 0.25 V the C<sub>3</sub>H<sub>8</sub> oxidation rate is at least 0.6 μA per real cm<sup>2</sup> implying a considerable catalytic effect. Overnight, the current with N<sub>2</sub> fell to ~0.15 μA per real cm<sup>2</sup> at 0.3 V, and the subsequent C<sub>3</sub>H<sub>8</sub> oxidation currents were more typical of the normal expectation, indeed with a small amount of inhibition. These results do show that co-plated Cd can catalyse hydrocarbon oxidation but that the layer tends not to be very stable, and the Cd-denuded electrode is inferior in performance to pure platinumized Pt.

Some overnight life tests with the above electrodes showed some surprising results in that the

electrodes' performance tended to increase. Fig. 10 shows the result of experiments carried out with electrode No. 7 (plated in the presence of 100 mM Cd<sup>2+</sup>). We see that tests after ageing at 0.32 V lead to an improvement of behaviour, and the tendency is generally to achieve a C<sub>3</sub>H<sub>8</sub> oxidation current slightly larger than in the absence of co-plated Cd. Presumably this increase corresponds to the progressive leaching out of excess Cd from the electrode, and these results suggest that the presence of too much co-plated Cd is undesirable.

A systematic investigation of the above ageing phenomenon was carried out and some results are

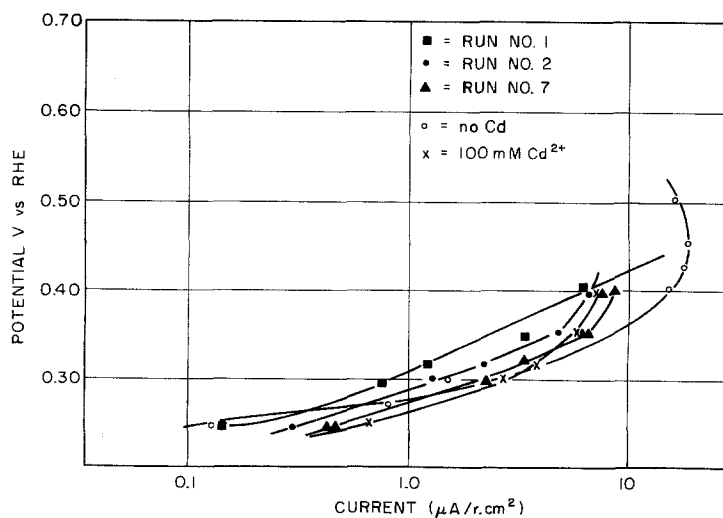


Fig. 12. C<sub>3</sub>H<sub>8</sub> oxidation; current-potential curves on a 3 mM Cd<sup>2+</sup> co-plated, platinumized Pt electrode in 80% H<sub>3</sub>PO<sub>4</sub>.

summarized in Fig. 11. Here we compare the effects of different amounts of co-plated Cd, and the current-time curves at 0.32 V represent the finally-achieved 'aged' behaviour. This was typically obtained after about the fourth cycle (cf. Figs. 10 and 11). Focussing on the behaviour after 1 h at potential, for example, we observe that the addition of small quantities of plated Cd, e.g., from 1 mM Cd<sup>2+</sup>, leads to a sharp decrease in the electrode catalytic activity. Behaviour with 3 mM plated Cd<sup>2+</sup> is slightly better but still inferior to pure platinized Pt. With 100 mM plated electrodes, the behaviour is 25% better than for pure platinized Pt. These results suggest quite definitively that after leaching of excess Cd from the platinized Pt, co-plated Cd improves the catalytic behaviour of Pt for C<sub>3</sub>H<sub>8</sub> oxidation. This behaviour is maintained for longer times of performance, and co-plated Cd does appear to retard self-poisoning of the C<sub>3</sub>H<sub>8</sub> reaction. The present results are in contrast to the previous report of Thacker [16], who concluded that the effect on Pt activity of co-plated Pb was mainly on the electrode's area; with co-plated Cd, area is a factor, but there is a significant enhancement of catalytic activity.

The current-potential curves for electrodes No. 2 (no Cd<sup>2+</sup>), 9 (3 mM Cd<sup>2+</sup> in plating solution) and 10 (100 mM Cd<sup>2+</sup>) are compared in Fig. 12. Electrodes No. 9 and 10 were used after ageing overnight at 0.32 V a sufficient number of times that no further improvement was found. The general observation is that co-plated Cd increases the C<sub>3</sub>H<sub>8</sub> oxidation rate at low potentials but inhibits it above 0.30 V. For example, at 0.25 V, the oxidation current on pure Pt is 0.13 μA per real cm<sup>2</sup>. With electrode No. 9, *i*<sub>0.25 V</sub> was 0.49 μA per real cm<sup>2</sup>; with electrode No. 10 it was 0.62 μA per real cm<sup>2</sup>.

We see that while *adsorbed* Cd substantially *inhibits* C<sub>3</sub>H<sub>8</sub> oxidation on Pt, *adsorbed Cd catalyses* the reaction at low potentials. There are also some indications that adsorbed Cd inhibits the self-poisoning of the C<sub>3</sub>H<sub>8</sub> reaction, thus improving the long-life behaviour of the electrode. This indicated inhibition of self-poisoning is probably the reason for the catalytic effect, even at short times of study at the lowest potentials, since the main inhibitor of the hydrocarbon reaction at these low potentials is the presence on the electrode of partially oxidized hydrocarbon species [8], and Cd<sup>2+</sup>

in solution (i.e. Cd<sup>0</sup> on the surface) evidently does diminish C<sub>3</sub>H<sub>8</sub> adsorption (Fig. 5). Above 0.3 V, adsorbed Cd inhibits C<sub>3</sub>H<sub>8</sub> oxidation. This is probably because the reaction under these circumstances is becoming more controlled by the initial adsorption of the hydrocarbon [8], and it is not surprising that surface Cd, a poor H-abstraction catalyst [17], is not advantageous in this respect.

### Acknowledgement

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### References

- [1] S. B. Brummer, J. I. Ford and M. J. Turner, *J. Phys. Chem.* **69** (1965) 3424.
- [2] S. B. Brummer and M. J. Turner, in *Hydrocarbon Fuel Cell Technology*, (Ed. B. S. Baker), Academic Press, Inc., New York, (1965) p. 409.
- [3] *Idem*, *J. Phys. Chem.* **71** (1967) 2825.
- [4] *Idem*, *ibid*, 3494.
- [5] *Idem*, *ibid*, 3902.
- [6] A. H. Taylor and S. B. Brummer, *J. Phys. Chem.* **72** (1968) 2856.
- [7] *Idem*, *ibid*, 73 (1969) 2397.
- [8] S. B. Brummer, *Advances in Chemistry Series*, Number 90, 'Fuel Cell Systems-II', p. 223 (1969).
- [9] S. B. Brummer and M. J. Turner, *Proceedings of 23rd Annual Power Sources Conference*, May 1969, p. 26.
- [10] S. B. Brummer, M. J. Turner, S. D. Kirkland and H. Feng, *Proc. of the Symposium on Electrocatalysis*, San Francisco, May 1974, p. 128.
- [11] S. B. Brummer, S. D. Kirkland and M. J. Turner, *J. Appl. Electrochem.* **3** (1973) 337.
- [12] S. B. Brummer, *J. Phys. Chem.* **69** (1965) 562.
- [13] S. B. Brummer, M. J. Turner and H. Feng, *Tyco Laboratories, Inc., First Semi-Annual Report on Contract DAAK02-71-C-0117*, June 1971, p. 44.
- [14] W. M. Latimer, *Oxidation Potentials*, Prentice-Hall, Inc., Englewood Cliffs, N. J. (1952) second edition.
- [15] M. Hansen, *Constitutions of Binary Alloys*, McGraw-Hill, New York, (1958).
- [16] R. Thacker, *Hydrocarbon Fuel Cell Technology*, (B. S. Baker, Ed.), Academic Press, New York, (1965) p. 525.
- [17] G. C. Bond, *Catalysis by Metals*, Academic Press, Inc., New York (1962).
- [18] S. Gilman, *J. Phys. Chem.* **71** (1967) 2424.