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TECHNICAL NOTE

The deleterious effect of high phosphoric acid concentrations on the kinetics of anodic hydrocarbon oxidation

S. B. BRUMMER,* S. KIRKLAND, AND M. J. TURNER

Tyco Laboratories, Inc., Waltham, Massachusetts 02154, USA

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Phosphoric acid has become the electrolyte of choice for the intermediate temperature hydrocarbon fuel cell following the early observations of Grubb and Niedrach [1]. For simplicity of design it has become common, in line with the normal procedures in acid H_2 fuel cells, to use very concentrated H_3PO_4 (i.e. ~95%) solutions [2]. There are reports [3] that the water content of the electrolyte does not significantly affect the kinetics of hydrocarbon oxidation, and this is somewhat unexpected since it has been shown [4] that the overall reaction for the oxidation process is

$$C_nH_{(2n+2)}+2nH_2O \longrightarrow nCO_2+(6n+2)H^+ +(6n+2)e^-,$$

i.e. H_2O is a reactant. In the course of an extended investigation of the mechanism of hydrocarbon oxidation in H_3PO_4, [5–14] we have investigated the C_3H_8 oxidation rate as a function of H_3PO_4 concentration, and we have found some very serious deleterious effects at high acid concentrations. We believe these are a major reason for the performance decays which are found in operating fuel cells [15]. The purpose of this note is to present these results.

Experimental procedures are substantially as has been reported elsewhere [11]. Studies were made with platinized Pt electrodes [10] in H_3PO_4 at 130°C. Purification of the electrolyte and humidification procedures for the gases have been described earlier [7]. A slight change in procedure involved use of a vertically-oriented, partially immersed Pt fuel cell electrode as a reference. The potential of this electrode, which was in a separate compartment of the cell, was controlled by generating H_2 electrolytically until the electrode was half immersed in the gas and half immersed in the solution. This electrode system has the advantage of having a very high exchange current, without the need to bubble pre-humidified H_2 through the solution. Potentials are referred against this reversible hydrogen electrode (RHE).

As in earlier studies the surface of the electrode was cleaned prior to taking each measurement by anodizing at 1·35 V versus the RHE for 2 min. Currents were then studied as a function of time at each potential of interest. Generally, currents decreased rapidly during the first few minutes but became substantially steady after 20 min, showing only a small decay in the following hour (~10%). The current readings reported were generally taken after 40 min at potential. We emphasize that there is no real steady state for these systems, just a continuous decay under continuous load conditions which takes hundreds or thousands of hours. There are various processes involved in this long-term current decay, but the currents measured in the first hour or two are indicative of the hydrocarbon oxidation rate on an apparently clean electrode. These can usually be reproduced by, for example, the above-mentioned anodic pretreatment.

For normalization purposes, data are expressed in terms of 'real cm^2'. This real area was

*Present address: EIC Inc., Cambridge, Mass. 02139

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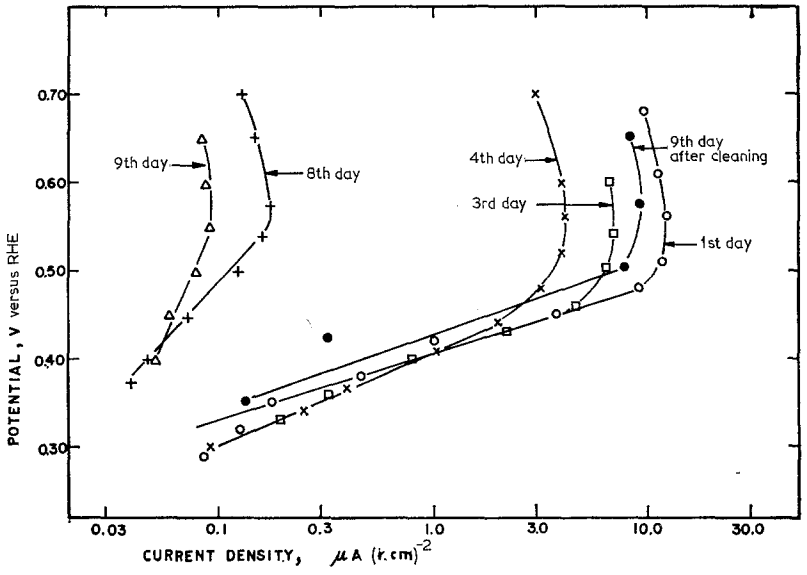

Fig. 1. C_3H_8 oxidation; day-by-day decay of potential-current curves on a platinized Pt electrode in 95% H_3PO_4.

estimated from the amount of reducible oxide present on the electrode after 2 min at 1·25 V. Previous work showed that this quantity is 400 μC (real cm)$^{-2}$ of area, the latter being determined by reference to the cathodic H-atom charging method on smooth platinum, as described earlier [16].

A long-term decay problem which was found in 95% acid is shown in Fig. 1 for the oxidation of C_3H_8. There is a steady systematic decrease in activity from day-to-day. In the region above 0·5 V, where the reaction is initially diffusionally-limited, the oxidation rate decreases by more than two orders of magnitude in the course of 9 days. This decrease in activity could not be reversed in the usual way for these reactions, i.e. by any form of anodic or cathodic treatment of the electrode. We did find that it could be substantially eliminated by removing the electrode from solution and boiling it for 10 min in saturated Na_2CO_3 solution.

We have used this Na_2CO_3 procedure in the past to clean glass cells on those occasions when they have become coated with a solid white product which is thought to be a dehydrated/polymerized form of H_3PO_4. We may point out that we have not proved that this material is polymerized H_3PO_4, but the white product which is sometimes formed on our glassware does so in those parts of the system which have lost water and, based on the general chemistry of H_3PO_4 [17], the inference that this material is a polymeric phosphate seems reasonable.

A further effect of acid concentration is shown in Fig. 2. Here we show the 40 min current-potential curve (each electrode was boiled in Na_2CO_3, as above, before taking the data sets) as a function of phosphoric acid concentration. Since H_2O is a reactant in hydrocarbon oxidation, we would expect in general a negative result from using more concentrated acid. However there is a compensating effect, since the water vapor pressure of concentrated acid is much lower and hence the hydrocarbon solubility in it should be higher. In practice, there is a serious loss of performance in proceeding from 80 to 95% acid.

In summary, then, we see that the very concentrated acid which it has been customary to use in hydrocarbon fuel cells from the viewpoint of engineering simplicity exhibits two serious disadvantages with respect to relatively dilute acid (80%):

1. Long-term performance decays are observed which can be reversed by cleaning the electrode in Na_2CO_3. This implies that the decay is caused by a dehydrated/polymerized form of H_3PO_4. Unquestionably, the bulk of the severe

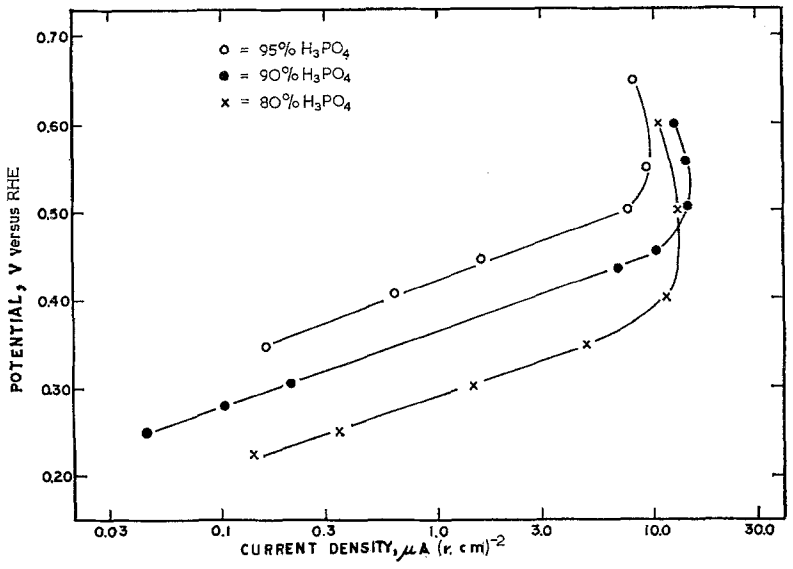

Fig. 2. C_3H_8 oxidation; potential-current curves on a platinized Pt electrode as a function of H_3PO_4 concentration.

initial performance decay found in hydrocarbon fuel cells with very concentrated electrolytes results from this process.

2. Even with a clean electrode, where care is taken to eliminate any polymeric H_3PO_4, the initial reaction rate is slower in more concentrated acids. For example in going from 80 to 95% H_3PO_4, the potential at equal currents is shifted more positive by ~140 mV, a performance loss which can be ill-afforded in the practical device.

In other studies, no deleterious day-by-day degradation of performance was found under comparable conditions for O_2 reduction. This is fortunate for H_2-O_2 fuel cells, but the C_3H_8 data seem to rule out the use of very concentrated H_3PO_4 in hydrocarbon fuel cells.

Acknowledgement

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