

Catalytic Electrodes for the Anodic Oxidation of Propane

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The complete electrochemical oxidation of simple hydrocarbons such as propane to CO_2 , protons and electrons can be accomplished in aqueous electrolytes with the proper combination of catalyst and temperature (1, 2). In fuel cell applications, an acidic electrolyte is usually required to reject the CO_2 produced at the anode, and a moderate temperature in the range of 100 to 200°C is necessary for an appreciable anode reaction rate. Under these conditions of temperature and acidity, anodic and chemical corrosion of electrocatalysts can be severe.

These adverse corrosion conditions limit the choice of electrocatalysts. In this investigation, some noble metals of Group VIII as pure metals, binary chemical codeposits and chemically reduced deposits on conductive substrates are considered. The object of this study was to evaluate the contribution of the chemical and physical properties of these electrocatalysts to their activity in the direct propane anode.

Two conditions of electrolyte and temperature were chosen, namely 85% H_2PO_4 at 140°C and 3N H_2SO_4 at 95°C . Under the first of these conditions, propane has shown a level of activity almost sufficient for practical fuel cells. The second set of conditions represents an objective in terms of reduction of general corrosion, better conductivity and possibly a superior oxygen electrode for combination with the hydrocarbon anode. Unfortunately, the temperature coefficient of the propane anode current going from 150 to 95°C is so large that the maximum anode power (milliwatts cm^{-2}) rapidly drops below a practical level. Anodic measurements in 3N H_2SO_4 have been useful, however, in evaluating electrocatalysts, principally because of a very characteristic limiting current density.

Experimental

All test electrodes consisted of a polytetrafluoroethylene (PTFE) bonded catalyst layer similar to those described previously (3, 4), a porous PTFE backing and a 45 mesh platinum collector screen. These three layers were compressed into a laminate as shown in Figure 1. Propane gas was fed through the electrolyte impermeable backing to the catalyst layer. The anode reaction occurs in this layer by virtue of intimate contact of reactant gas, liquid electrolyte and solid electrocatalyst. The collector screen serves to carry the current from the electrocatalyst to the external circuit.

The test cell was a spontaneous propane/oxygen cell operating under controlled resistive load. Anode potentials were measured with respect to a hydrogen reference electrode at room temperature using the same electrolyte as in the test cell. Connection to the test cell was made through a bridge and capillary system shown in Figure 2. Potential readings were obtained after three minutes at each resistive load setting. In the region of the limiting current observed in 3N H_2SO_4 at 95°C , these potential readings were unstable. Limiting currents measured by a potentiostatic technique using the Wenking 6LR potentiostat agreed well with those measured by the controlled resistive load technique.

A careful procedure for operation of these anodes was established in order to provide meaningful and reproducible values of anode potential and limiting current density. This involved reproducible preparation of the electrodes, pretreatment of the anodes consisting of high rate anodic oxidation of propane followed by open circuit equilibration with propane to an anode potential of about +0.1 volt versus the hydrogen electrode, adjustment of the propane flow rate and careful positioning of the potential measuring capillary at the center of and touching the collector screen. The cell contained a volume of electrolyte sufficient to provide water for the anode reaction and maintain a constant electrolyte composition. The reproducibility of anode potentials was about ± 10 mv and of the limiting current densities ± 1 mA cm⁻².

Catalyst Preparation

Borohydride reduction of the chloro complexes of the noble metals was frequently used to prepare catalysts. 5 to 10% aqueous solutions of NaBH₄ were added dropwise (3 to 6 ml/min) to solutions of the noble metals. In general, the reductions were carried out with the maximum possible dilution of the aqueous reaction mixtures and maximum rate of addition consistent with the size of the samples to be prepared. For deposition of platinum onto a conductive support, the support material was first suspended in water with stirring. Then a solution of chloroplatinic acid was added and allowed to contact the suspension for about 15 to 30 minutes prior to the initial borohydride addition. All finished catalysts were washed carefully to remove residual salts.

Anode Polarization at Platinum Black

Anodic potential versus current density plots which are representative of the behavior of platinum black/propane are shown in Figure 3. In 3N H₂SO₄ at 95°C, a well defined limiting current density of 28 mA cm⁻² (geometric current density) is observed for 20 mg cm⁻² of platinum black. However, the situation is not typical in that a rapid decrease in anode current is observed when the anode potential attains values above + 0.6 volt versus H.E. In this region platinum surface oxide formation may inhibit the propane anode process (5). The limiting currents cited herein refer to the point at which the anode potential changes by more than about 0.1 volt per 1 mA cm⁻² change in current density.

The source of the limiting current in 3N H₂SO₄ is believed to be some step in the electrode surface process rather than mass transport of propane to the surface. A diffusional limitation would be approximately described by a modification of the Nernst diffusion layer equation (6),

$$i_d = \frac{nFCD}{\delta}$$

where

i_d = diffusion limited current density (A cm⁻²)

D = diffusion coefficient of propane (cm² sec⁻¹)

δ = diffusion layer thickness (cm)

n = Faradays per mole = 20.

Since the real electrode area is about 4000 times the geometric area by an electrochemical measurement of surface area (7), and estimates of C and D are 2×10^{-7} moles/cc and 4×10^{-5} cm² sec⁻¹ respectively, the estimated diffusion layer thickness for $i_d = 28$ mA cm⁻² is 2 cm. This is obviously too thick by about two orders of magnitude. The conclusion is that the limiting current is not diffusion controlled in 3N H₂SO₄ at 95°C.

In 85% H_3PO_4 at 140°C, the anode polarization curve shows no limiting current in the region of spontaneous discharge of the propane/oxygen cell ($< 200 \text{ mA cm}^{-2}$). The anode potential at 20 mA cm^{-2} provides a meaningful figure of merit for an electrocatalyst and is used as such in Tables I and II. A polarization curve for the oxygen cathode in 85% H_3PO_4 at 140°C is also shown in Figure 3.

Unsupported Noble Metal Catalysts

Several platinum group noble metal catalysts as single metals or borohydride reduced binary codeposits were subjected to anode polarization tests. The results are shown in Table I. BET surface area measurements are included to show that the source of variations in performance is generally not the gross surface area of the catalyst. It may be argued that there are large differences in the real electroactive area for propane oxidation which account for the observed differences. This reasoning is difficult to refute without further studies, especially of propane adsorption.

In Table I, platinum is the most effective of the single noble metal catalysts while a codeposit of 75% platinum, 25% rhodium is apparently more active than either of the pure metals. However, borohydride reduction does not produce a black as active as those obtained from Engelhard. For this reason, the absolute activity of the best platinum-rhodium combination is less than that of the best platinum black.

Platinum Deposited on Carbides and Graphitic Carbons

The borohydride reduction of platinum onto the conductive substrates, graphite, titanium carbide and tungsten carbide produced catalysts with moderate activity for propane as shown in Table II. These supports were chosen for their electrical conductivity ($\sigma = 10^{-1}$ to 10^{-3} ohm cm when measured on compressed powders), corrosion stability and the possibility of cocatalysis.

The general effect of the conductive support is to improve the utilization of platinum at low loadings between 2.5 and 7.5 mg cm^{-2} of platinum. If there is a specific cocatalytic effect of the substrate, it is not large enough to be obvious from the data in Table II. A conductive support is necessary at low levels of platinum, as the utilization of unsupported platinum is already severely limited at 10 mg cm^{-2} .

The surface area and conductivity of the support are no doubt very critical, but commercially available carbides do not present a wide choice of these properties. Two sets of titanium and tungsten carbides were studied, I -325 mesh TiC and WC and II, 3-4 micron TiC and 1- 1.2 micron WC. The surface areas of these materials are somewhat anomalous in that the large particle size TiC (I) has a higher specific area than the smaller sized material indicating a difference in particle structure. Nevertheless, platinum catalysts prepared from all of these supports have similar activities with the WC supported material showing poor performance in hot phosphoric acid.

Graphitic carbons appear to be promising supports providing one can be found with sufficient stability to chemical and anodic corrosion. Stackpole 219XG has shown some corrosion stability (3). Cyanamid graphite has not been tested for this property. The relatively high surface area of the graphites allows a better distribution of metal catalyst than is available with the titanium and tungsten carbides.

Discussion

Owing to the corrosion limitations imposed on electrocatalysts for propene in hot acid electrolytes, the initial phase of this research effort has been directed toward metals of the platinum group. However, there are transition metals outside of the platinum group which have good corrosion stability, and there may be a number of binary or multicomponent alloys which have much better corrosion resistance than their pure metal constituents. Beyond chemical and anodic corrosion resistance, the problem is to find a catalytic source property or properties such as the proper 1) electronic configurations and energetics, 2) lattice spacings or 3) oxide coverage and structure. Unfortunately, the simultaneous combination of an effective catalytic source property with corrosion resistance is not easy.

The electrical conductivity of an electrocatalyst for a fuel cell electrode is a very critical problem. Fuel cell electrodes should be thin and are required to carry very high current densities. Under these conditions, it is necessary to have excellent electrical conductivity from a catalytic site to a collector point in the electrode structure. It is remotely possible that a non-conductive catalyst could be useful through catalysis of a purely chemical step in the electrode process, but this requires extremely efficient and rapid migration of intermediate species between conductive and non-conductive sites, a condition which is unlikely for complex hydrocarbon anode reactions. A possible exception is the case in which a non-conductive catalyst in the electrode promotes a low temperature water shift reaction of the hydrocarbon or one of the intermediates to produce hydrogen which would then serve as the active fuel.

The future of the direct hydrocarbon anode for fuel cells depends on significant improvement in one or more of the following areas:

- 1) better utilization of platinum or platinoid metals
- 2) new non-platinoid catalysts
- 3) new invariant electrolytes

Optimization of electrode and cell design is of great importance, but the catalyst and electrolyte problems remain the fundamental problems to be solved.

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TABLE I
Unsupported Noble Metal Catalysts

| <u>Electrode</u> | <u>Surface Area (BET)</u> <u>(m²/g)</u> | <u>3N H₂SO₄ @ 95°C</u> <u>Limiting Current Density</u> <u>(mA cm⁻²)</u> | <u>85% H₃PO₄ @ 140°C</u> <u>E₀ vs. H.E. @ 20 mA cm⁻²</u> <u>(mv)</u> |
|------------------------------|---|--|--|
| <u>Engelhard Blacks</u> | | | |
| Platinum (10) ¹ | 27 | 14 | 425 |
| Platinum (20) | 27 | 28 | 375 |
| Ruthenium (20) | 46 | 2 | Current Limited |
| Rhodium (20) | 4.3 | 1.5 | Current Limited |
| Palladium (20) | 28 | ca. 1 | - |
| <u>Borohydride Reduction</u> | | | |
| Platinum (10) | 16 | 4 | 500 |
| Platinum (20) | 16 | 12 | 455 |
| Pt (10) Rh (10) | 29 | 4.5 | - |
| Pt (15) Rh (5) | 20 | 13 | 416 |
| Rhodium (20) | 26 | 2.5 | - |
| Pt (9.5) Ir (0.5) | - | 4 | 505 |

¹ - Values in parentheses are mg. of catalyst per cm² electrode area.

TABLE II

Platinum Deposited on Carbides and Graphites

| Electrode ¹ | Surface Area of Support (m ² /g) | 3N H ₂ SO ₄ at 95°C Limiting Current Density (mA cm ⁻²) | 85% H ₃ PO ₄ at 140°C E _a vs. H.E. at 20 mA cm ⁻² (mv) |
|-----------------------------------|---|---|--|
| Pt (2.5) ² TiC (7.5) I | 4 | - | 715 |
| Pt (5) Cyanamid Graphite (15) | 11.4 | 7 | 481 |
| Pt (5) Stackpole Graphite (15) | 15 | 4 | 521 |
| Pt (7.5) TiC (22.5) I | 4 | 5 | 473 |
| Pt (7.5) WC (22.5) I | 0.11 | 4 | Current Limited |
| Pt (7.5) Cyanamid Graphite (22.5) | 11.4 | 9 | 445 |
| Pt (7.5) TiC (22.5) II | 0.43 | 5 | Not Reproducible |
| Pt (7.5) WC (22.5) II | 0.39 | 8 | Current Limited |
| Pure TiC (10) I | 4 | - | ca. 700 |
| Pt (10) | None | 4 | 500 |

1-3

1 - The platinum was deposited by borohydride reduction in all cases.

2 - The values in parentheses represent the amount of material in the electrode in mg cm⁻².

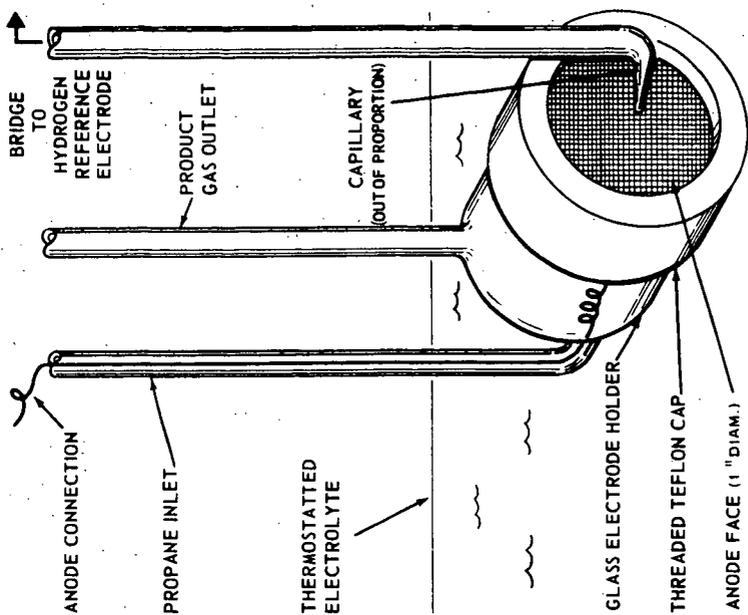


FIGURE 2 ANODE HALF CELL

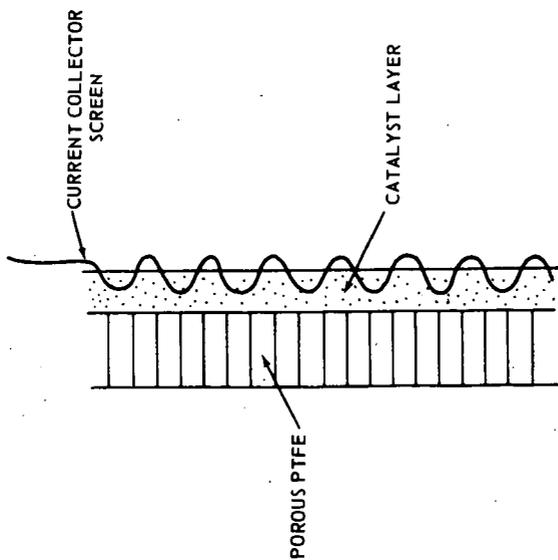


FIGURE 1 TEST ELECTRODE

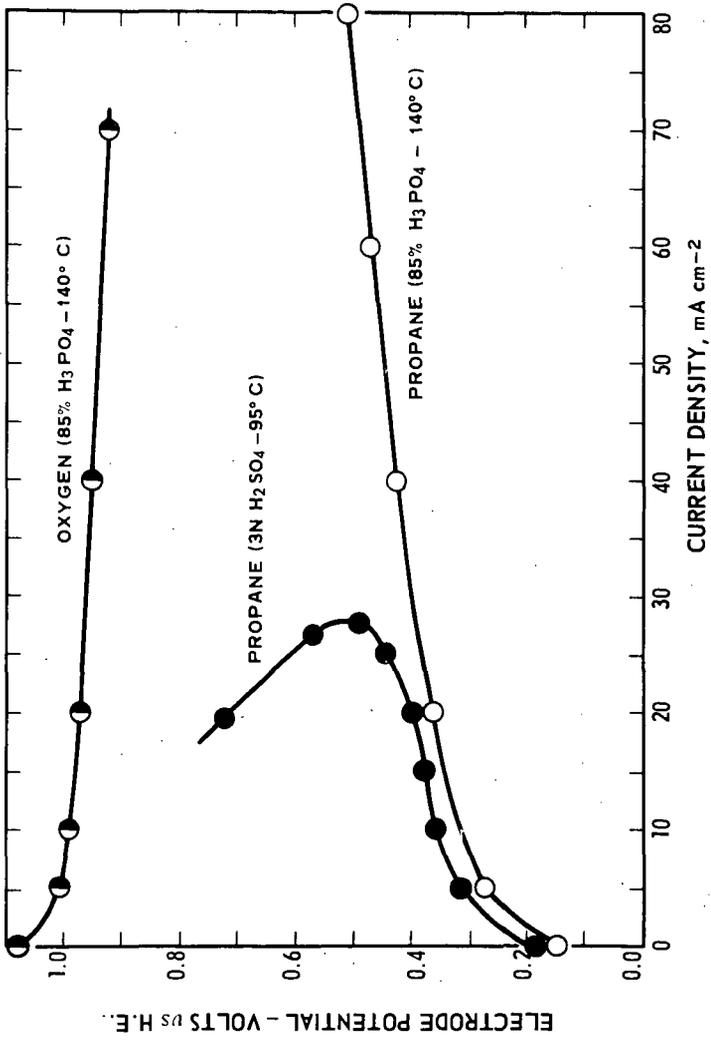


FIGURE 3 ELECTRODE POLARIZATION - CONTROLLED RESISTIVE LOAD