Anodic Oxidation and Molecular Structure: Influence on Performance of Normal Saturated Hydrocarbons in Fuel Cells

Abstract. *Variation in the rate of anodic oxidation of normal saturated hydrocarbons (at current densities of half the maximum value or higher) with the carbon number parallels the variation in the rate of diffusion (in electrochemical equivalents) of the hydrocarbon through the electrolyte. This parallelism, not previously recognized, is consistent with the concept of diffusion-influenced anode reactions. The conditions under which this behavior is expected are presented.*

Several investigators, using various electrolytes over a temperature range of 90° to 200°C and high-area platinum electrocatalysts prepared in various ways, have independently found similar relative performances for normal saturated hydrocarbons in fuel cells (*1–7*).

The conclusion might be drawn that the relative performances of the normal saturated hydrocarbons are a reflection of their relative electrochemical reactivities. However, there are other possible contributions to the characteristic variation of current density with carbon number at a constant anode potential, which is shown in Fig. 1 for an anode potential of 0.5 volt versus the reversible hydrogen electrode. These data have been normalized to a propane current density of unity, and in every case represent current densities of about half the maximum (or limiting) value and higher.

For an explanation of the shape of the curves (Fig. 1) the rate processes necessary for the maintenance of a steady state at the anode may be considered as follows: (i) mass transport through the electrolyte (such as, film or meniscus) to the electrode surface; (ii) adsorption on the electrode surface; (iii) chemical reactions forming electroactive species on the surface; and (iv) electrochemical reaction, producing CO_2 and H_2O.

The rates of these steps can be symbolized as follows, the subscripts referring to the processes mentioned above, expressed as currents:

$$\text{Rate } 1 = nFD(C_\infty - C_0)/\delta \qquad (1)$$

$$\text{Rate } 2 = k_2 C_0 \theta_F{}^m \qquad (2)$$

$$\text{Rate } 3 = k_3 \theta_{HC} \qquad (3)$$

$$\text{Rate } 4 = k_4 \theta_A \exp\left(\frac{\alpha n' F}{RT}\eta\right) \qquad (4)$$

where D is the diffusion coefficient of the hydrocarbon in the electrolyte, n is the number of equivalents per molecule, C_∞ is the solubility of hydrocarbon in the electrolyte (saturation assumed at the gas-liquid interface), C_0 is the concentration of dissolved hydrocarbon adjacent to the electrode surface, δ is the thickness of the electrolyte layer through which diffusion takes place, θ_F is the fraction of the electrode surface free of adsorbed hydrocarbon (or other) species, θ_{HC} is the fractional coverage of hydrocarbon on the surface, θ_A is the fractional coverage of the species responsible for supplying most of the current at the overvoltage η in question, and m is the order of the absorption rate. The k's are rate constants in appropriate units; α is the fraction of the overvoltage aiding the forward reaction; n' is the number of electrons in the electrochemical reaction; T is the temperature; and R is the gas constant.

The steady-state series of events which are in balance is indicated as follows:

$$C_\infty \xrightarrow{nD(C_\infty - C_0)} C_0 \xrightarrow[\text{fast}]{k_2 C_0 \theta_F{}^m} \theta_{HC} \xrightarrow[\text{fast}]{k_3 \theta_{HC}}$$

$$\theta_A \xrightarrow[\text{constant}]{k_4 \theta_A, \eta} CO_2 + H_2O \qquad (5)$$

The absolute overall rate of reaction for the process in Eq. 5 is a complex function of the reaction rate constants and the mass transport properties, D and $(C_\infty - C_0)$. However, η is set at a constant value such that $i/i_{max} > 0.5$, and if the dynamic equilibria among C_0, θ_{HC}, and θ_A are rapidly established, then the relative overall rate will be directly influenced by the relative value of nDC_∞ from hydrocarbon to hydrocarbon (assuming $C_0 << C_\infty$). Inherent in the above statement is the necessary condition that the electroactive species A (coverage, θ_A) is either the same or has similar reactivity from hydrocarbon to hydrocarbon (*8, 9*). Furthermore, the overvoltage has been set at 0.5 volt, where θ_F is known to be large (*9*).

The statements in the foregoing paragraph do not require that the overall anode reaction be diffusion-limited, but merely require that it be diffusion-influenced, that is, $i/i_{max} > 0.5$. It is not required that $C_0 = 0$, or $\theta_{HC} = 0$, but it is merely required that $C_0 << C_\infty$ and $\theta_{HC} << 1$. Furthermore, the activation energy for the overall anodic process is not expected to be that characteristic of diffusion, but a complex function of the activation energies for all of the processes involved; and

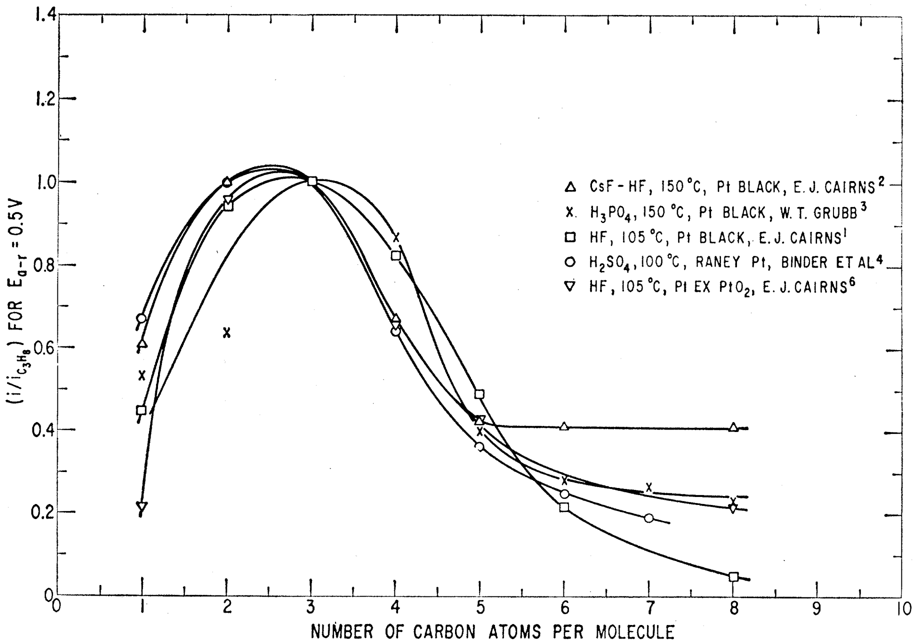

Fig. 1. Relative current densities for hydrocarbons in fuel cells. E_{a-r} is the difference in potential between the anode and a reversible hydrogen reference electrode.

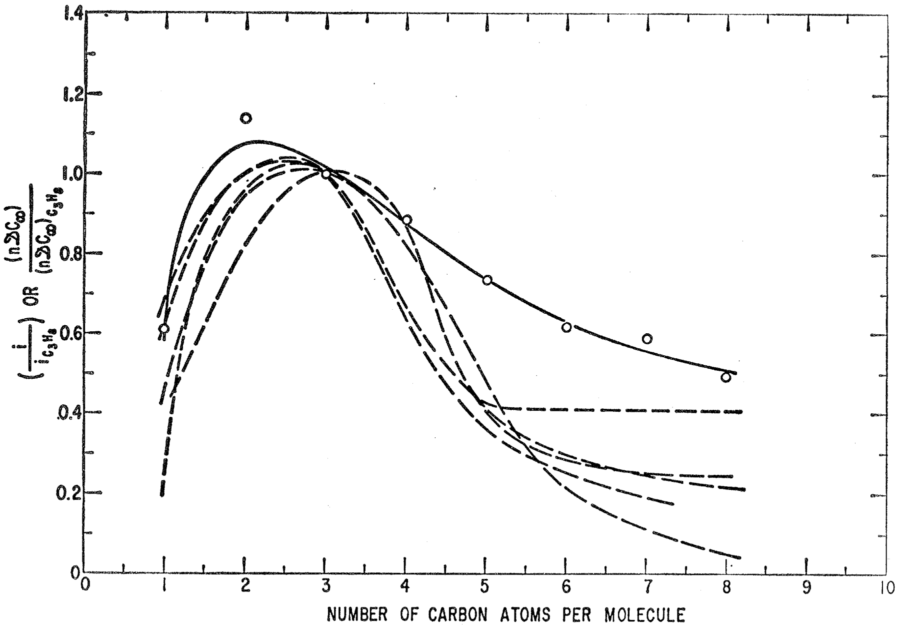

Fig. 2. Relative current densities compared to relative nDC_∞ values for saturated hydrocarbons.

therefore, it probably would have a value characteristic of a chemical or electrochemical reaction, except under the special conditions of $C_0 = 0$, $\theta_{HC} = 0$.

The diffusion coefficients (*10*) and solubilities (*11*) for normal saturated hydrocarbons in water have been reported for temperatures near 25°C. If consequences of salting-out for the various electrolytes affect the individual members of the homologous series of normal saturated hydrocarbons in the same way, it is reasonable to expect that the ratios of $(D_{HC}C_{\infty HC}/D_{C_3H_8}C_{\infty C_3H_8})$ will take on the same values from one electrolyte to another and one temperature to another. This is to be expected when the fugacities in the gas phase are made equal for all the members of the series. This, indeed, is the case for nearly all of the fuel cells reported. For octane at 100°C, it is necessary to adjust the solubility values in the manner used by McAuliffe (*11*).

The results for the various fuel cells, expressed as the ratio of current densities at an anode potential of 0.5 volt versus the reversible hydrogen electrode, are shown in Fig. 2, together with the curve for $(nD_{CH}C_{\infty HC}/nD_{C_3H_8}C_{\infty C_3H_8})$ values. The agreement in the curve shapes is clear. For the lower temperature fuel cells in particular, the deviation from the nDC_∞ curve is greatest for the fuels of higher molecular weight. The reason for this may be that the assumption of fast rates 2, 3, and 4 is not rigorous at these lower temperatures.

The agreement in curve shapes does not show that the product of the solubility and diffusion coefficient limits or determines the overall rate of the anode reaction, but simply indicates that this nDC_∞ product has an important influence upon the relative reaction rates for the conditions $i/i_{max} > 0.5$ under otherwise essentially identical experimental conditions. At lower overvoltages (and lower current densities) the curves for current density plotted against carbon number do not generally conform to the shape of those in Figs. 1 and 2 (*2*); other processes are of overriding importance (*3*).

ELTON J. CAIRNS*
General Electric Research and Development Center, Schenectady, New York

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* Present address: Argonne National Laboratory, Argonne, Illinois.

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Fossilization of an Ancient (Devonian) Soft-Bodied Worm

Abstract. *A shell-boring polychaete worm was found replaced by the mineral limonite-goethite; this fossil is probably a limonite-goethite pseudomorph after pyrite, suggesting that the soft-bodied worm was originally replaced by pyrite. External structures such as a prostomium, anterior tentacle-like palps, peristomial cirri, parapodia, setae bundles of the parapodia, and dorsal cirri of the parapodia are preserved. This worm resembles living members of the family Spionidae in form and habit. This discovery extends the known range of this family (Cretaceous?, Miocene to Recent) back about 365 million years to the Devonian period.*

In a very fossiliferous layer in the Marcellus Formation (middle Devonian) of central New York, a small, limonitic, rodlike structure resembling a worm within a worm boring in a shell of the bivalve *Cornellites flabellum* (Hall) was discovered (Fig. 1) (*1*). The similarity of this structure to some modern shell-boring polychaetes suggests that this is a mineral replacement of the soft body of a shell-boring worm entombed in its tube-lined boring (*2*). The stratigraphic record has revealed many concretionary objects that superficially resemble organic remains, but this rod has too many structures analogous to those of polychaete worms to be considered merely an object of inorganic origin accidentally resembling a worm.

This fossilized worm was found in a small hillside quarry 2.2 miles (3½ km) north of Morrisville, New York, where the middle (?) part of the Cardiff shale member of the marine Marcellus Formation is exposed. The fossil was