

FLUORIDE ELECTROLYTES FOR SATURATED  
HYDROCARBON FUEL CELLS

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INTRODUCTION

The direct electrochemical oxidation of saturated hydrocarbons to carbon dioxide and water has been carried out at current densities in the vicinity of 100 ma/cm<sup>2</sup> only since 1963.<sup>1-8</sup> The most frequently investigated electrolyte in this connection has been phosphoric acid, primarily in the temperature range 150° to 200°C.<sup>1-6</sup> Although some success has been obtained with low molecular-weight hydrocarbons at about 100°C, this was at the expense of very high platinum loadings in the electrodes.<sup>7,8</sup> It has been found recently that the system CsF-HF-H<sub>2</sub>O provides electrolyte compositions with which current densities in excess of 200 ma/cm<sup>2</sup> can be obtained at 150°C, particularly with propane as the fuel.<sup>9,10</sup> Further work with fluoride electrolytes disclosed that the HF-H<sub>2</sub>O system showed good reactivity with saturated hydrocarbon fuels at temperatures in the range 80-110°C.<sup>10</sup> All normal saturated hydrocarbons in the range C<sub>1</sub> to C<sub>16</sub> have shown reactivities within a factor of 20 to 50 of one another, both with the CsF-HF-H<sub>2</sub>O and HF-H<sub>2</sub>O electrolytes.<sup>10</sup>

Because of the strong effect of electrolyte composition on propane performance at 150°C,<sup>9,10</sup> it was decided that a more thorough investigation of the effects of electrolyte composition and temperature on the kinetics of the anodic oxidation of propane was in order.

EXPERIMENTAL

In order to prevent any contamination of the electrolyte or electrodes, all portions of the apparatus which contacted the electrolyte were made of Teflon or platinum. The cell parts are shown in Figure 1. The end plates were Monel and did not contact the electrolyte. The gas compartments machined in the Teflon housing were 3 mm deep and of 11.38 cm<sup>2</sup> circular area. The electrodes used were Teflon-bonded platinum black supported by 45-mesh platinum screens, which also served as current collectors. The platinum black loading for the electrodes was usually 50 mg/cm<sup>2</sup>, and the electrodes were prepared by procedures very similar to those in Reference 11. The center Teflon piece in Figure 1 served as the electrolyte compartment, and usually a piece having a 3 mm thickness was used. The cell parts were held together tightly by bolts; no gaskets were used since the Teflon parts formed a leak-tight seal to one another.

The electrolyte was prepared from Baker and Adamson reagent grade 48% hydrofluoric acid, having less than 20 ppm impurities; from cesium fluoride, synthesized with less than 100 ppm impurities by procedures already reported;<sup>12,13</sup> and from quartz-redistilled water. To prepare electrolytes having fluoride concentrations higher than those accessible with the above reagents, pure, anhydrous HF was distilled from a tank of Matheson anhydrous HF, 99.9% min. purity. Electrolyte compositions were determined by acid-base titrations for HF, and by a gravimetric method for Cs as Cs<sub>2</sub>SO<sub>4</sub>; water was determined by difference.

The gases used were electrolytic grade oxygen, 99.6% minimum, and Matheson instrument grade propane, 99.5% minimum purity. For short experiments it was found that pre-saturation of the gases was not necessary in order to maintain the electrolyte composition constant. When necessary, presaturation could be accomplished by thermostatted water bubblers, in order to prevent possible deposition of carbon on the electrode surface.<sup>14,15</sup>

Figure 2 shows a schematic diagram of the apparatus in which the cell was operated. The fuel feed rate was controlled via a needle valve and capillary-tube flowmeter in the case of gaseous fuels, and via a constant speed syringe drive in the case of liquid fuels. The fuel cell and identical reference cell were operated in a forced-convection air thermostat. The reference cell contained two high-area reversible hydrogen reference electrodes of Teflon-bonded platinum black. The exit gas streams from the cell passed through traps (to separate any liquid leaving the cell) and then to a gas chromatograph for analysis, as desired. The electrolyte was circulated slowly (about 2 to 3 cc/min) through the cells by gravity, and then returned to the reservoir by an all-Teflon pump. The electrolyte circulation system was kept closed to minimize evaporation.

The electrical characteristics of the anode, the cathode, and the cell as a whole were measured with the aid of a modified Kordes-Marko interrupter.<sup>16,17</sup> The interrupter circuit yielded potential readings on a resistance-free basis, and all potentials of individual electrodes are so reported with respect to a reversible hydrogen reference electrode in the same electrolyte and at the same temperature. The current density-voltage data were taken at steady state (usually 2-5 minutes after a change in current) and in the order of increasing current density, starting at open circuit. Results for decreasing current densities were the same, except at current densities below about 2 ma/cm<sup>2</sup>. Cell voltages, including resistive losses can be calculated from the reported IR-free values ( $E_{a-c}$ ) using the expression

$$E = E_{a-c} - i\rho l \quad (1)$$

where  $i$  is the current density

$\rho$  is the specific resistance of the electrolyte, 1-2 Ohm-cm

$l$  is the inter-electrode distance, 0.3 cm.

Additional information concerning the experimental apparatus and techniques may be obtained from Reference 18.

The results reported below were gathered from a total of over 50 experiments using more than 20 cells, primarily with C<sub>3</sub>H<sub>8</sub> as the fuel.

## RESULTS AND DISCUSSION

**CsF-HF-H<sub>2</sub>O Electrolytes:** There are two independent composition variables in the CsF-HF-H<sub>2</sub>O system. The variables chosen to characterize the composition were the HF/(CsF + HF) molar ratio (or, alternatively, the F<sup>-</sup>/Cs<sup>+</sup> equivalent ratio), and the mole percent H<sub>2</sub>O. The effects of the two independent composition variables on the rate of anodic oxidation of propane were studied by preparing electrolytes of selected compositions and determining the current density-potential relationship for propane at various temperatures, most frequently at

150°C.

The propane performance at an electrolyte composition near the optimum for 150°C is shown in Figure 3. The maximum current density that could be supported under these conditions was 400 ma/cm<sup>2</sup>, at an anode vs H<sub>2</sub> reference potential of 0.6 volt. For all the cells operated at 150°C, the best straight-line Tafel plots yielded an  $\alpha_n$  value of 0.5 in the current density range of 40 to 250 ma/cm<sup>2</sup>. In the current density range above 250 ma/cm<sup>2</sup>, the anode performance could be improved by increasing the propane flow rate, up to a certain point, indicating a gas-phase mass transport limitation, rather than a kinetically limited current density.

The most striking relationship between electrolyte composition and propane performance at 150°C was found in a set of experiments which included electrolytes containing varying amounts of Cs<sub>2</sub>CO<sub>3</sub> as an alternative to excess HF. The results are expressed in terms of the current density at an anode vs reference potential of 0.5 volt, as a function of the F<sup>-</sup>/Cs<sup>+</sup> ratio, as shown in Figure 4. The water content was not the same for all of the experiments of Figure 4; the effect of this variable will be accounted for below. The data points in Figure 4 were obtained from several cells. Each datum point represents an average value for all cells operated at that particular F<sup>-</sup>/Cs<sup>+</sup> ratio. Note that the break in the curve in Figure 4 is located at an F<sup>-</sup>/Cs<sup>+</sup> ratio of about 1.2 rather than 1.0. At a F<sup>-</sup>/Cs<sup>+</sup> ratio of 1.0, the pH is still greater than 7. The pH does not drop below 7 until the F<sup>-</sup>/Cs<sup>+</sup> ratio exceeds about 1.2. The increase of performance with higher F<sup>-</sup>/Cs<sup>+</sup> ratios is consistent with the idea that an acidic electrolyte is required for rapid oxidation of saturated hydrocarbons. The maximum rate of propane oxidation at E<sub>a-r</sub> = 0.5 volt was 400 ma/cm<sup>2</sup>, nearly 2 orders of magnitude greater than that observed for the alkaline system Cs<sub>2</sub>CO<sub>3</sub>-H<sub>2</sub>O.<sup>19</sup>

It was found that the water content of the electrolyte also has an influence on the rate of propane oxidation, but its effect is much less than that of the HF/(CsF + HF) ratio. The separation of the effects of the two composition variables on cell performance was accomplished by an iterative data reduction procedure requiring a considerable number of data points. The value of HF/CsF = 2.0 was chosen for the point at which the effect of water content at 150°C would be determined, since this was in the vicinity of the best performance. The data in the range 1.8 < HF/CsF < 2.1 were normalized to HF/CsF = 2.0, and the effect of water content was established. The original data of Figure 4 were then normalized to an optimum water content of 12.5 mole percent and were replotted as shown by the solid line in Figure 5. The effect of water content at 150° is shown in Figure 6, for two values of the anode vs reference potential.

The results for other operating temperatures were reduced in a similar manner, using the iterative procedure. The final results for the effect of electrolyte composition on propane performance at several temperatures are shown in Figures 7 and 8. Some of the data used were not gathered at the temperature values selected for correlation. In these cases, the current densities were adjusted to correspond to the desired temperature, using the observed enthalpies of activation. These adjusted data points are indicated as extrapolated in Figures 7 and 8.

The results in Figures 7 and 8 show that for any temperature in

the range 90 to 150°C, the maximum propane performance can be obtained by using the highest HF/(CsF + HF) ratio possible, and a water content in the range 12-15 mole percent. In this way, current densities in excess of 400 ma/cm<sup>2</sup> at E<sub>a-r</sub> = 0.5 volt and 150°C can be expected, in the absence of mass transport limitations.

It has been found that the HF/CsF ratio at any selected temperature has a maximum practical limit set by the boiling point of the electrolyte under the conditions of operation. For instance, a boiling point of 160°C was obtained for an electrolyte having 10 mole percent water and a value of 2.1 for the HF/CsF ratio. This limits the operating temperature at atmospheric pressure to about 150-155°C. At lower temperatures, higher HF/CsF ratios are possible. For example, values of 3.0 and higher may be obtained at 110°C.

The main virtue of the CsF is that of suppressing the vapor pressure of the HF by forming stable complexes such as CsF·HF, CsF·2HF, etc.,<sup>20</sup> raising the boiling point of the electrolyte. Therefore, higher operating temperatures can be used with a concomitant increase in current densities for the oxidation of saturated hydrocarbons. Alkali metal fluorides other than cesium fluoride or rubidium fluoride are not suitable substitutes because they are not soluble enough and do not reduce the HF vapor pressure sufficiently<sup>21,22</sup> to allow significant performance improvements. Cesium fluoride was used in this work because of its greater abundance and therefore more favorable economics.

HF-H<sub>2</sub>O Electrolytes: The rate of electrochemical oxidation of propane in the HF-H<sub>2</sub>O system is affected by the composition of the electrolyte, and since there is only one composition variable, the optimum composition for a given temperature is easily established. The temperature range over which reasonable rates of oxidation were obtained was found to be from about 80°C to the boiling point. The HF-H<sub>2</sub>O system forms a maximum boiling azeotrope at 37 mole percent HF, with a boiling point of 112°C,<sup>23</sup> thus setting the upper operating temperature at about 110°C.

The Tafel plots for a propane cell at 105°C, using a composition near that of the azeotrope, are shown in Figure 9. The performance at 105°C is not as high as the best obtained at 150°C (see Figure 3), but only a moderate performance premium was paid for a 45°C decrease in operating temperature. The maximum current density observed (130 ma/cm<sup>2</sup>) was set by the gas-phase diffusional resistance of the Teflon film on the anode, as shown by the fact that higher maximum current densities were observed when thinner Teflon films were used. The effects of both temperature and HF-H<sub>2</sub>O electrolyte composition on cell performance are summarized in Figure 10. The dotted portions of the curves indicate those compositions which have a boiling point below the indicated temperature and hence are only accessible at pressures above atmospheric. Since the optimum composition (25-30 mole percent HF) is not far from that of the azeotrope, it has been found convenient to use the azeotrope for routine fuel cell operation.

Enthalpies of Activation and Tafel Slopes: The enthalpy of activation for the overall anode reaction was obtained from a plot of the logarithm of the current density at a fixed anode overvoltage versus the reciprocal of the absolute temperature. The enthalpy of activation was determined over the temperature range 80 to 170°C and over the composition range from no added HF to pure HF. The results

are shown in Figure 11. It was found that the temperature range had no effect on the enthalpy of activation, but that there was a sharp transition from a value of 3.7 kcal per mole to 18 kcal per mole at a  $\text{HF}/(\text{CsF}+\text{HF})$  ratio of about 0.66, which corresponds to  $\text{CsF}\cdot 2\text{HF}$ . The higher enthalpy of activation indicates that the highest operating temperature possible should be used, but only up to the point of being able to maintain a  $\text{HF}/(\text{CsF}+\text{HF})$  ratio above 0.66.

The values of  $\alpha n$  obtained from the Tafel plots over the temperature range  $80^\circ$  to  $170^\circ\text{C}$  are summarized in Figure 12. The closed points indicate those data which were normalized with respect to electrolyte composition effects. At low temperatures (below  $130^\circ\text{C}$ ), the Tafel plots usually showed two straight-line regions, a low slope (high  $\alpha n$ ) at low current densities ( $<10 \text{ ma}/\text{cm}^2$ ) and a high slope (low  $\alpha n$ ) at high current densities ( $>20 \text{ ma}/\text{cm}^2$ ). For temperatures above  $140^\circ\text{C}$ , only one Tafel slope was observed, with a value of  $\alpha n$  near 0.5.

The composition effect on Tafel slopes is shown for various temperatures in Figure 13. At  $150^\circ\text{C}$ , for electrolytes of low HF content, the Tafel curve shows two slopes, which eventually yield to a single slope of  $\alpha n \approx 0.5$  at high HF contents. For the higher  $\text{HF}/(\text{CsF}+\text{HF})$  ratios at lower temperatures, however, the two-sloped Tafel curve persists. Only slight changes of Tafel slope with water content have been observed. In general, the best propane performance is associated with compositions which show a high enthalpy of activation and  $\alpha n$  values of 0.5 and higher. By suitably adjusting electrolyte compositions and temperatures, the optimum performances shown in Figure 14 were obtained. The  $150^\circ\text{C}$  curve was obtained using an electrolyte of the composition shown in Figure 3.

## CONCLUSIONS

The relationships between the rate of the electrochemical oxidation of propane on platinum black and electrolyte composition for the systems  $\text{CsF}-\text{HF}-\text{H}_2\text{O}$  and  $\text{HF}-\text{H}_2\text{O}$  have been established. Maximum propane fuel cell performance at a given temperature in the range  $90 - 150^\circ\text{C}$  is obtained with the maximum  $\text{HF}/(\text{CsF}+\text{HF})$  ratio, at an optimum water content of 12 to 15 mole percent, for the range  $\text{HF}/\text{CsF} = 2.0$  to  $3.0$ . Operating temperatures down to  $80^\circ\text{C}$  are feasible for the  $\text{HF}-\text{H}_2\text{O}$  system, while retaining good propane performance. Power densities (on an IR-free basis) of  $80 \text{ milliwatts}/\text{cm}^2$  at  $150^\circ\text{C}$  and  $30 \text{ milliwatts}/\text{cm}^2$  at  $105^\circ\text{C}$  are possible in optimum composition fluoride electrolytes.

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Figure 1. Photograph of cell parts.

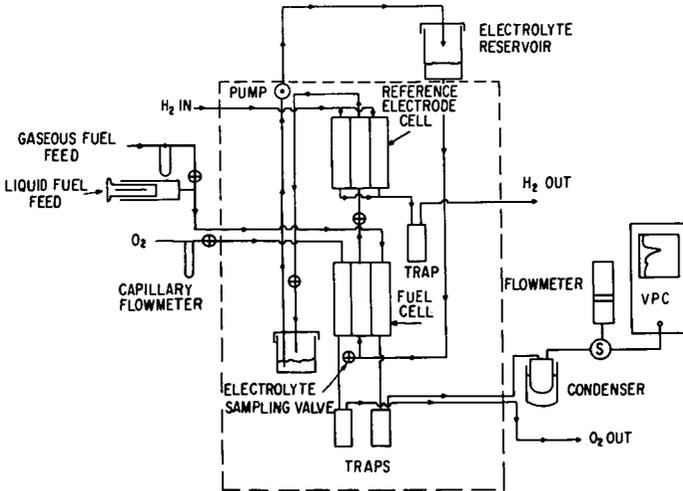


Figure 2. Schematic diagram of fuel cell apparatus.

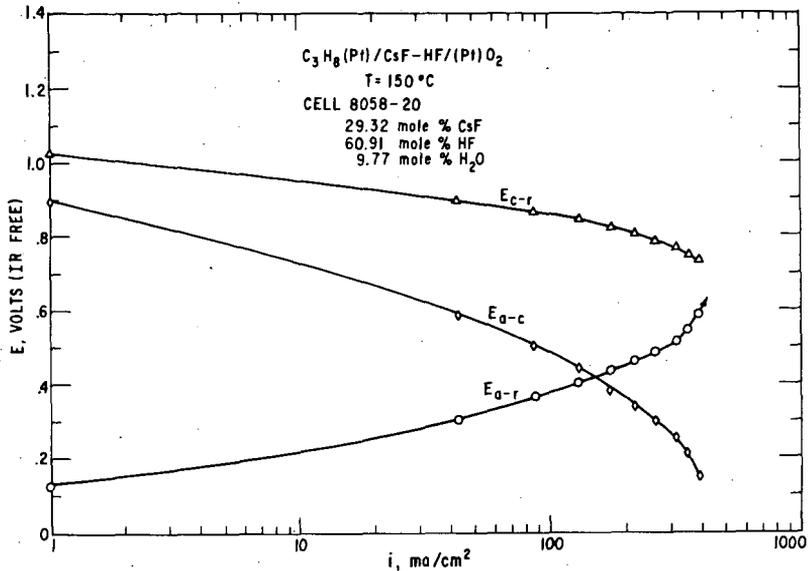


Figure 3. Propane performance at 150°C using CsF·2.1 HF + 15 mole percent water as electrolyte.

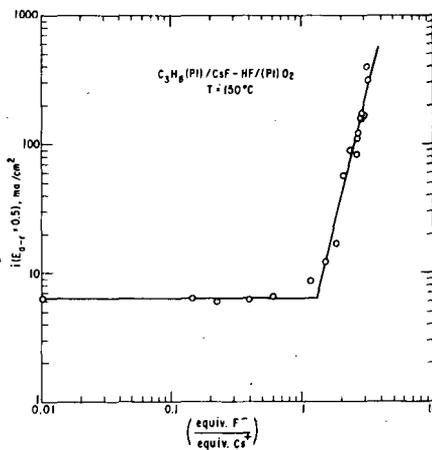


Figure 4. Effect of  $F^-/Cs^+$  ratio on propane current density at  $E_{a-r} = 0.5$  V; 150°C.

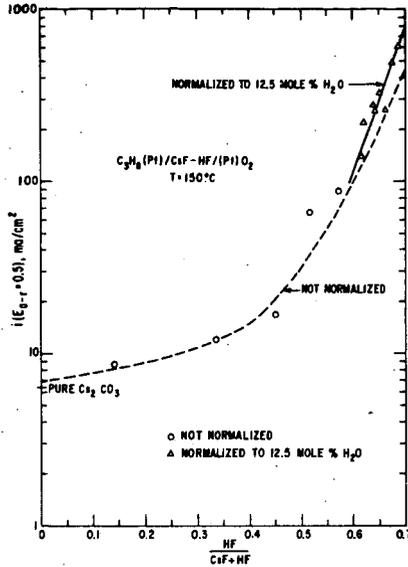


Figure 5. Effect of electrolyte HF content on propane performance for:  $\Delta$  12.5 mole %  $H_2O$ ;  $\circ$  variable water content;  $150^\circ C$ .

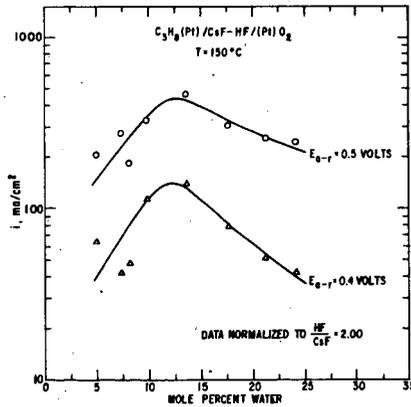


Figure 6. Effect of electrolyte water content on propane performance for:  $\circ$   $E_{a-r} = 0.5$  V;  $\Delta$   $E_{a-r} = 0.4$  V; at  $150^\circ C$  and  $HF/CsF = 2.00$ .

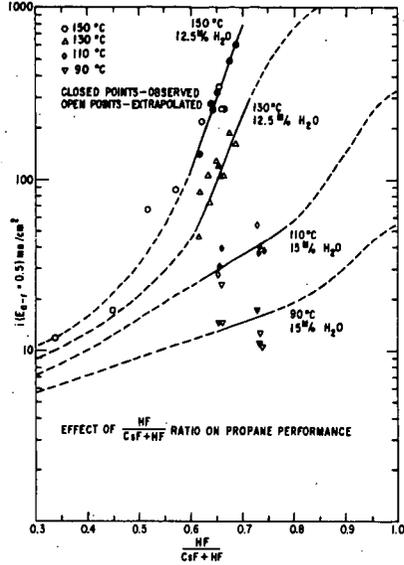


Figure 7. Effect of electrolyte HF content on propane performance for various temperatures and water contents.

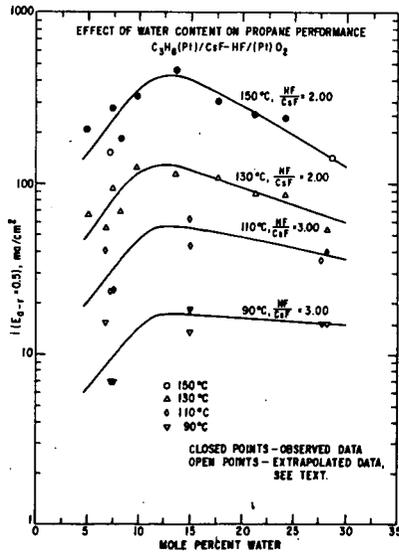


Figure 8. Effect of electrolyte water content on propane performance for various temperatures and HF contents.

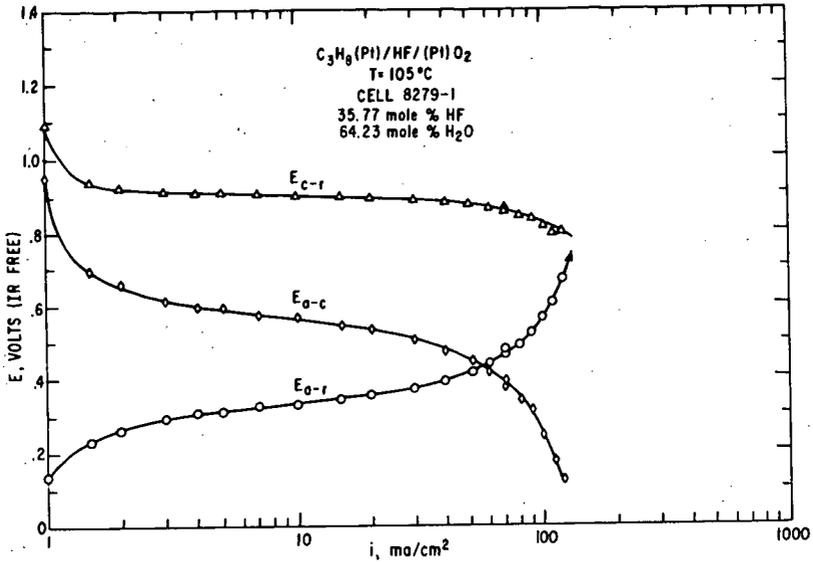


Figure 9. Propane performance at 105°C with 37 mole % HF electrolyte.

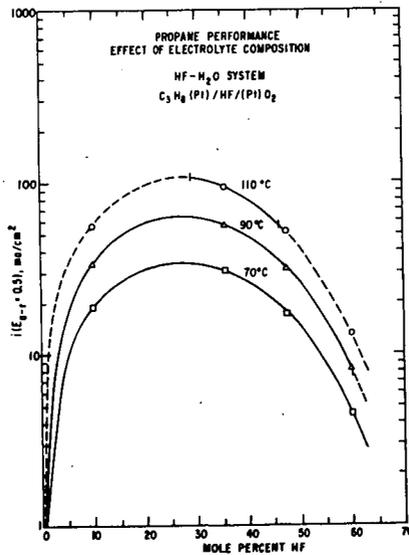


Figure 10. Effect of HF-H<sub>2</sub>O electrolyte composition on propane performance at various temperatures.

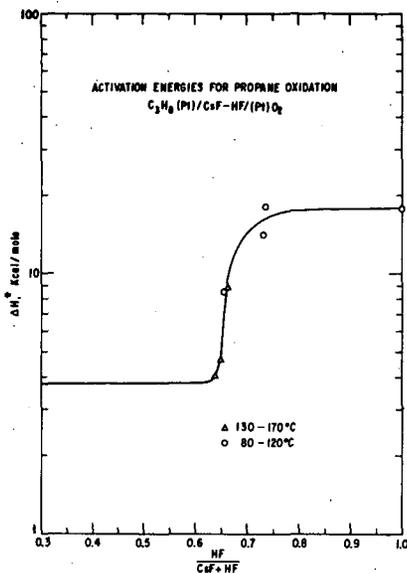


Figure 11. Effect of electrolyte composition on enthalpy of activation for propane oxidation.

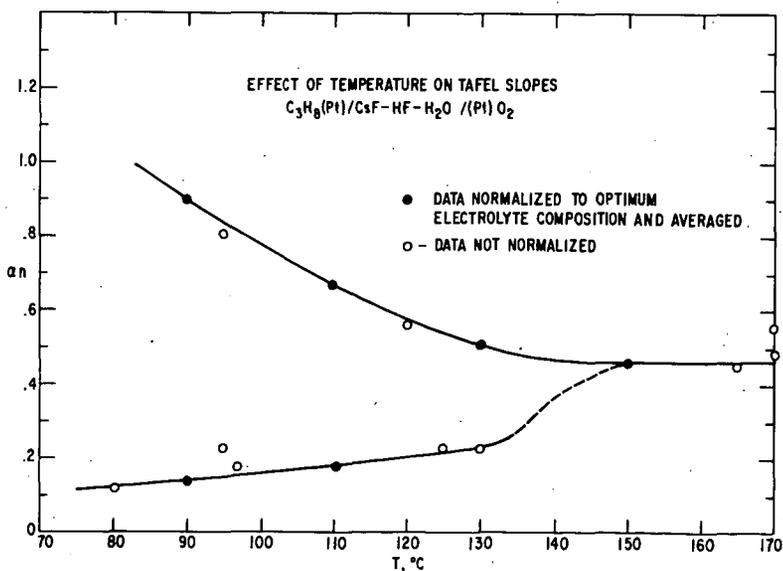


Figure 12. Effect of temperature on values of  $\alpha n$  obtained from Tafel plots of propane performance.

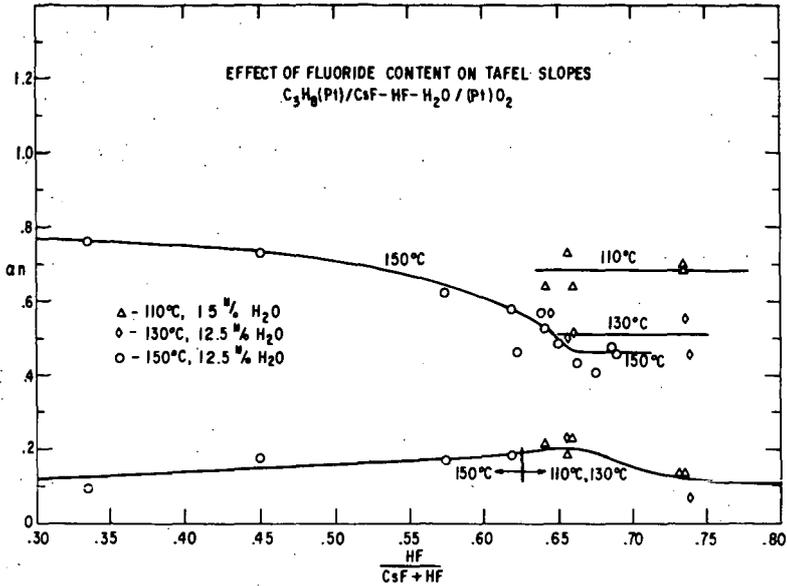


Figure 13. Effect of electrolyte composition on value of  $\alpha n$  for various temperatures.

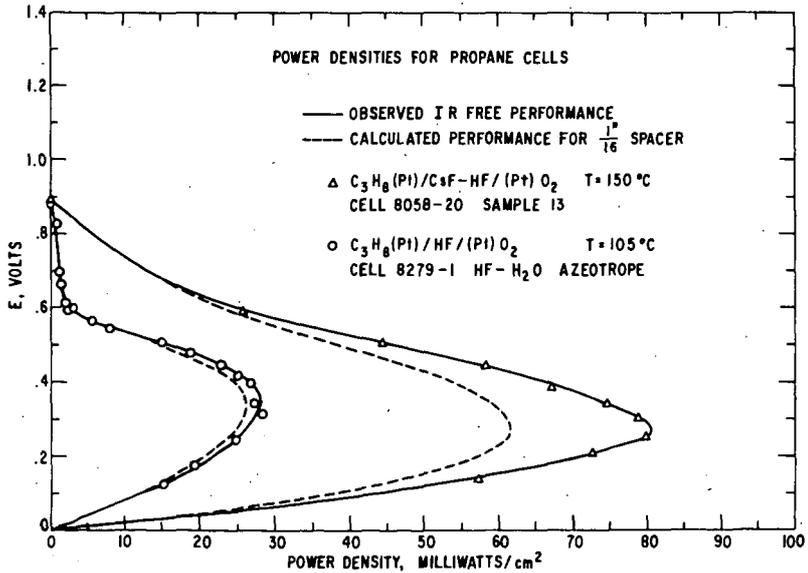


Figure 14. Propane performance at optimum electrolyte compositions for 150° and 105°C.