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Electrocatalytic oxidation of hydrocarbons on a stabilized-zirconia electrolyte employing gold or platinum electrodes

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The electro-oxidation of those hydrocarbon fuels commonly derived from coal (e.g. CO, CH_4 and H_2) was studied using a disc of scandia-stabilized zirconia $(ZrO_2)_{0.92}(Sc_2O_3)_{0.08}$, the anodic face of which was coated with *either* porous platinum *or* gold as the electrode material. The cathode face of the disc was coated with porous platinum and exposed to air which provided the source of oxygen. The stabilized-zirconia reactor disc was operated at 700° C and 1 atmosphere in both the self-generated-power (fuel-cell) mode and the applied-power mode. From the experimentally observed behaviour of the current–overpotential curves the electrocatalytic oxidation of hydrocarbons is found qualitatively to be independent of whether porous gold or platinum is used at the anode. This behaviour indicates that the solid electrolyte itself is playing the major role in the electrocatalytic processes since platinum would be expected to be much more catalytic than gold in the electro-oxidation of these fuels. The fuel species investigated showed the following trend in the current drawn, and thus reactivity, at a given overpotential: $H_2 > CO > CH_4$.

1. Introduction

Solid-oxide electrolytes of the oxygen-ion type, operating at the elevated temperatures (around 1000° C) used in fuel-cells, offer a very efficient means of directly converting the chemical energy of hydrocarbons into electrical energy. An excellent treatise on the theoretical and experimental studies that have been made on the electrochemistry of solid-oxide systems is presented by Kroger [1], who has pioneered much of the work in the field. Another good review on the subject is that by Kofstad [2]. One major drawback of these systems has prevented their full commercial exploitation in fuel cells: the limited lifetimes of constituent materials at operating temperatures around 1000° C. These temperatures are used because electrolyte conductivity and reaction rates are high at 1000° C. In the present investigation, more hospitable temperatures for materials (around 700°C) are employed, but electrochemical kinetics must be taken into account at these lower temperatures.

With the advent of the replacement of petroleum as a source of energy by the generation of hydrocarbons from coal, wood, oil shale, etc., interest has arisen in solid-electrolyte fuel cells. Wen and Mason [3] have made some initial observations on the electrocatalytic oxidation of hydrocarbons, where there is evidence that the scandia-stabilized zirconia electrolyte was itself implicated in the electrocatalysis with platinum electrodes. Similar behaviour was observed in a few early measurements employing gold electrodes [4]. Work by Pancharatnam *et al.* [5] on the kinetics of cathodic dissociation of nitric oxide to its elements has indicated that the solid electrolyte plays a major role in the electrocatalysis. It is thought that F-centres (trapped electrons or coloured centres) [1, 2] present in the electrolyte at the cathode may act as catalytic sites. In later discussions of hydrocarbon anodic oxidation, F- or

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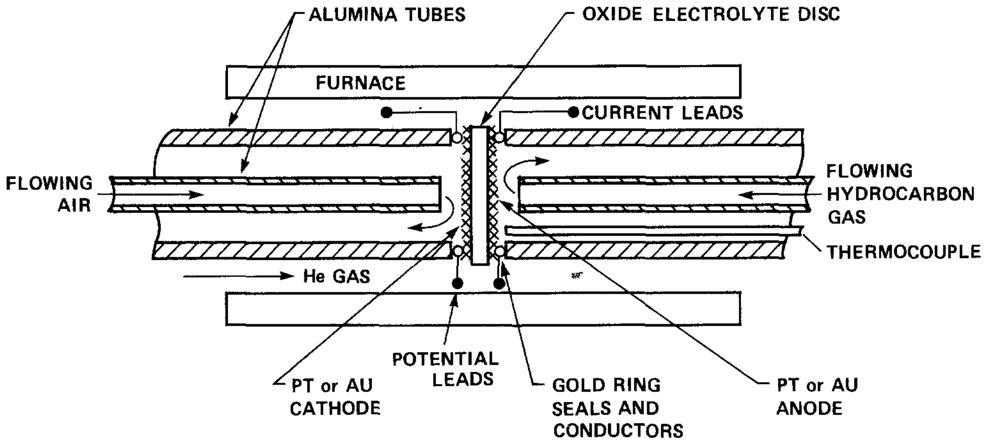

Fig. 1. Schematic diagram of the solid-electrolyte fuel-cell system with platinum or gold electrodes.

V-centres (or holes) in the electrolyte at the anode are suggested as possibly acting as catalytic sites for the fuel species.

In this current work, the rate of electrocatalytic oxidation of hydrocarbons on stabilized zirconia was measured systematically with either porous platinum or gold electrodes. The catalytic role of the solid electrolyte will be seen to predominate over either metal electrode, platinum or gold.

2. Experimental

The apparatus used in these studies is shown in Fig. 1. The electrochemical reactor consists of a disc of scandia-stabilized zirconia 2.5 cm in diameter and 2 mm thick; gold rings are used to provide a seal between each face of the disc and the adjacent alumina tubes and also to act as electrical contacts for measurement of electrical potential and current. The fuel gas and air are introduced through the inlet tubes and each gas strikes the face of the disc normally in a stagnation–flow regime. The rate of mass transfer and concentration of reactant next to the face of the disc may be calculated from a knowledge of the fluid flow rate by using fluid mechanics theory.

Colloidal metal pastes supplied by Englhard Industries, New Jersey, were used in preparing the electrodes. The pastes employed were platinum #6926 (unfluxed) and gold #A-3156 (unfluxed). The platinum paste was always used as recommended by the manufacturer in the preparation of the reference air cathode. Two coatings of the paste were applied to the stabilized-zirconia discs and these were then fired in air in a furnace at about 750–850° C. Pretreatment of the electrode–electrolyte system was carried out at 850° C by passing a current of 550 mA for one hour with air at each electrode. This pretreatment was found to give reproducibility in the ensuing electrochemical measurements.

After pretreatment, the system's alternating current resistance R_{ac} was measured with an a.c. bridge at a high enough frequency (1 kHz) to avoid electrode polarization. Values of R_{ac} were measured at regular intervals during the course of the electrochemical measurements. The value of $R_{ac} = 7.8\ \Omega$ and was found to be invariant with time. A temperature of 700° C was employed in the measurements and in all cases dry air at 1 atmosphere continually flowed at a rate of 80–100 $cm^3 min^{-1}$ normal to the face of the platinum–air electrode. Pure fuel gases at 1 atmosphere were fed to the anode at a flow rate in the range 30 to 100 $cm^3 min^{-1}$. The gases were dried by passing them through a liquid-nitrogen cold-trap. However, in some cases the fuel gases were saturated with water vapour by bubbling the gas through a container of distilled water at 50° C; this resulted in a gas mixture containing 12.2 mol% water at 1 atmosphere. Dry helium was used to flush out the fuel compartment between runs and current–overpotential curves obtained with helium in the fuel compartment indicated, as would be expected, that the system behaves as a simple oxygen pump under these physical con-

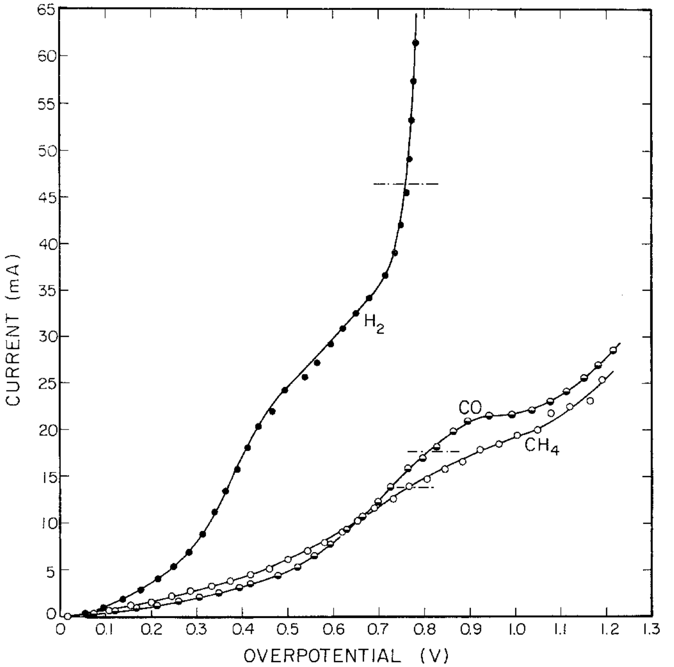

Fig. 2. Electrochemical behaviour of dry hydrocarbons versus air for a porous Pt electrode at 700° C and 1 atmosphere. (—·—·—· Maximum overpotential attainable in fuel-cell mode of operation.)

ditions, as demonstrated by Yuan and Kroger [6].

3. Results and discussion

A general summary of the electrocatalytic behaviour of H_2, CO and CH_4 (both dry and containing 12.2 mol% H_2O) at either a porous Pt or Au anode is presented in Figs. 2 to 5. As also shown in an earlier study [3], and as might be expected, H_2 is much more electrochemically active than the more complex molecules CO and CH_4. In the present study the electrochemical behaviour of CO and CH_4 has been more clearly defined, with CO tending to be the more reactive of the pair. A comparison of Figs. 2 and 3 for dry gases reacting at 1 atmosphere on porous Pt and Au anodes respectively, indicates qualitatively similar electrocatalytic behaviour for these two metals. If the metal electrodes were playing a major role in the electrocatalysis one would expect Pt to be much more active than Au. Pt is known to adsorb oxygen atoms strongly and to be a good hydrocarbon oxidation catalyst, whereas Au is known to be a very poor adsorber and a poor hydrocarbon oxidation catalyst. An excellent review of this subject is

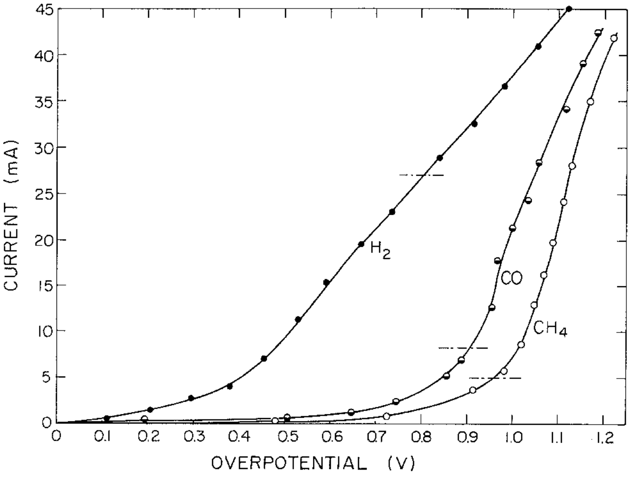

Fig. 3. Electrochemical behaviour of dry hydrocarbons versus air for a porous Au electrode at 700° C and 1 atmosphere. (—·—·—· Maximum overpotential attainable in fuel-cell mode of operation.)

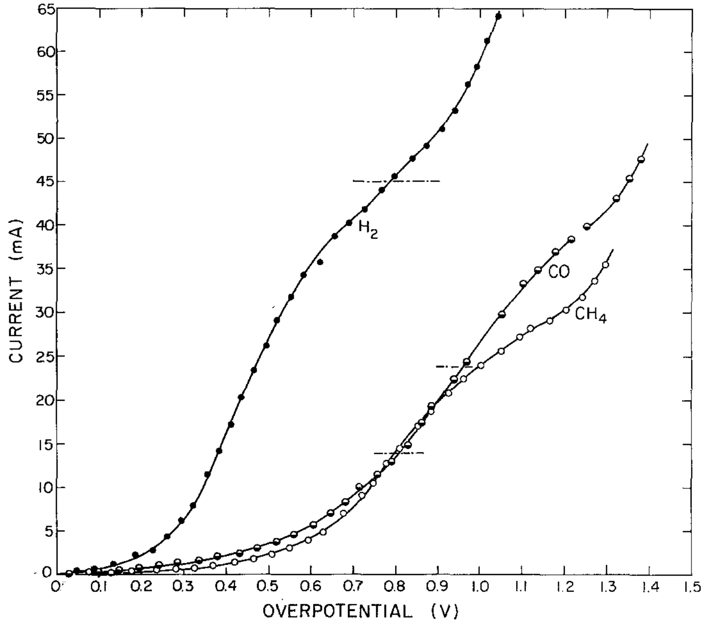

Fig. 4. Electrochemical behaviour of hydrocarbons containing 12.2 mol% H_2O versus air for a porous Pt electrode at 700° C and 1 atmosphere. (— · — · — · Maximum overpotential attainable in fuel-cell mode of operation.)

given by Wedler [7]. The data presented in Figs. 4 and 5 are also for porous Pt and Au electrodes except that, in these cases, the fuel gases contained 12.2 mol% H_2O. H_2O was added to see if the electrochemical reactivity of CO and CH_4 could be enhanced by the introduction of the water–gas shift reaction to form H_2. From the qualitative similarity of the 'wet' and 'dry' data it can be concluded that under the present experimental conditions the water–gas reaction did not play a significant role.

3.1. *Oxidation of dry hydrocarbons on a solid electrolyte with either porous platinum or gold anodes*

The electrocatalytic oxidation of H_2, CO and CH_4 was studied at 700° C and 1 atmosphere on the solid electrolyte with either a porous platinum or gold anode. The relative reactivity of these gases is indicated in the current–overpotential curves shown in Figs. 2 and 3. The results confirm earlier observations [3] that hydrogen is the most electro-

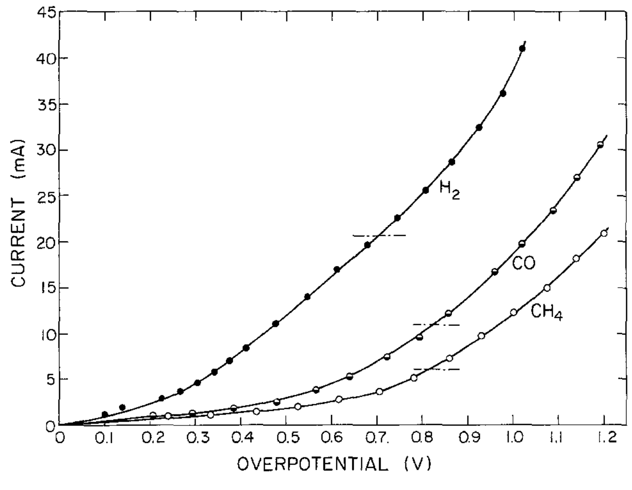

Fig. 5. Electrochemical behaviour of hydrocarbons containing 12.2 mol% H_2O versus air for a porous Au electrode at 700° C and 1 atmosphere. (— · — · — · Maximum overpotential attainable in fuel-cell mode of operation.)

chemically active species; however, in the present study the differences in the catalytic behaviour of CO and CH_4 has been more clearly delineated. In the ensuing discussion of the behaviour of the electro-oxidation of fuel gases on porous platinum and gold electrodes, it should be borne in mind that the morphology of platinum and gold electrodes deposited in the manner described above is dissimilar. The platinum electrode consists of many more dispersed metal particles than does the gold electrode. Thus the electrocatalytic behaviour for the two metals can at best be compared semiquantitatively.

As might be expected CO and CH_4 are relatively inactive compared to the simple molecule, H_2. Inspection of Figs. 2 and 3 shows the presence of inflection points in the current–overpotential curves, which suggests that the same diffusion-controlling process occurs at intermediate overpotentials, but that this is overcome at higher overpotentials with the onset of higher chemical reactivity. Simple stagnation–flow, fluid-mechanical calculations indicate that gas-phase diffusion control is not playing a role in this observed behaviour. It is suspected that surface diffusion of species along the electrolyte surface is causing this diffusion-controlled behaviour. That the platinum curves (Fig. 2) display more pronounced diffusion-controlled behaviour than the gold curves (Fig. 3) is most likely due, as just stated, to the differences in morphology of the surfaces. However, in spite of this difference in morphology, a comparison of Figs. 2 and 3 shows that neither the platinum or gold appears to be playing a major electrocatalytic role, for aside from the shapes of the curves, the magnitude of the electro-reactivity of both systems is not too dissimilar. This behaviour would not be expected if the metals were the electrocatalysts, for platinum is much more electrocatalytic for these anodic oxidations than gold. Thus it is speculated that active sites in the electrolyte, perhaps F- or V-centres (or holes) [1, 2], predominate in anodic electrocatalytic processes.

In the progression of the current–overpotential curves, the low-overpotential system generates its own power (in the fuel-cell mode) until the *iR* drop and polarization potentials become so large that an external power source must be applied to proceed to higher values of currents (and overpotential). This demarcation is designated by the horizontal lines in Figs. 2 and 3. It is significant that because of higher activation polarization in the case of CH_4 and CO the range of operation in the fuel-cell mode is much more restricted than for the active species, H_2.

3.2. *Oxidation of hydrocarbons containing 12.2 mol% water on a solid electrolyte with either porous platinum or gold anodes*

The rate of electrocatalytic oxidation of H_2, CO and CH_4 containing 12.2 mol% H_2O was measured at 700° C and 1 atmosphere using both porous platinum and gold electrodes. The purpose of the inclusion of water vapour was to see if the water-shift reaction might enhance the anodic reactivity of CO and CH_4. The results are summarized in Figs. 4 and 5. By comparing these figures with Figs. 2 and 3 respectively it is seen that the water-shift reaction does not play a measurable role at 700° C and 1 atmosphere. Inspection of Figs. 3 and 5 for dry and moist gases on gold anodes shows somewhat lower activity and no points of inflection in the latter case for all three gases. This behaviour reflects a tendency for a slow change in surface morphology resulting in less porosity of the electrode with passage of time. Again the demarcation between the fuel-cell and driven modes is indicated by the horizontal lines. As was the case with the dry gases, the platinum and gold electrodes do not appear to be playing the important role that the electrolyte does in the anodic electrocatalysis.

4. Conclusion

The work presented in this paper surveys the general reactivity of H_2, CO and CH_4 at a solid-electrolyte anode, and the data strongly suggest that the solid electrolyte is playing the major electrocatalytic role. Beyond this observation it is premature to conjecture on the exact mechanism actually occuring in this complex system. The electrochemical behaviour is consistent with the scheme proposed by Weisbart and Ruka [8] where it is proposed that the fuel could be oxidized by reacting directly with the oxygen ion (O_0^x) near the three-phase interface. Such a mechanism is one of several currently being tested by systematic experimentation.

In the continuing investigation, reference electrodes have been installed so as to permit the anodic and cathodic current–overpotential behaviour to be independently measured. To obtain reaction rate and mass action expressions the concentrations of reactant fuels are being varied between 0.01 and 1 mol fraction with helium as a diluent. To obtain valuable information on the activation enthalpies of the anodic and cathodic processes, the operating temperature is being varied between 700 and 850° C. Effluent fuel-gas composition is being monitored by means of gas-phase chromatography since there is evidence that the complex molecules CO and CH_4 were not always completely electro-oxidized to CO_2 or CO_2 and H_2O. The possibility of side reactions suggests the interesting prospects of obtaining both electrical energy and useful products from the solid electrolyte fuel cell. Finally, the morphology of the surface is being carefully controlled and stabilized by sputtering electrode metals on the rough electrolyte surface instead of using pastes. Inexpensive metals such as Ni and Co can be used because of the highly catalytic electrolyte.

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