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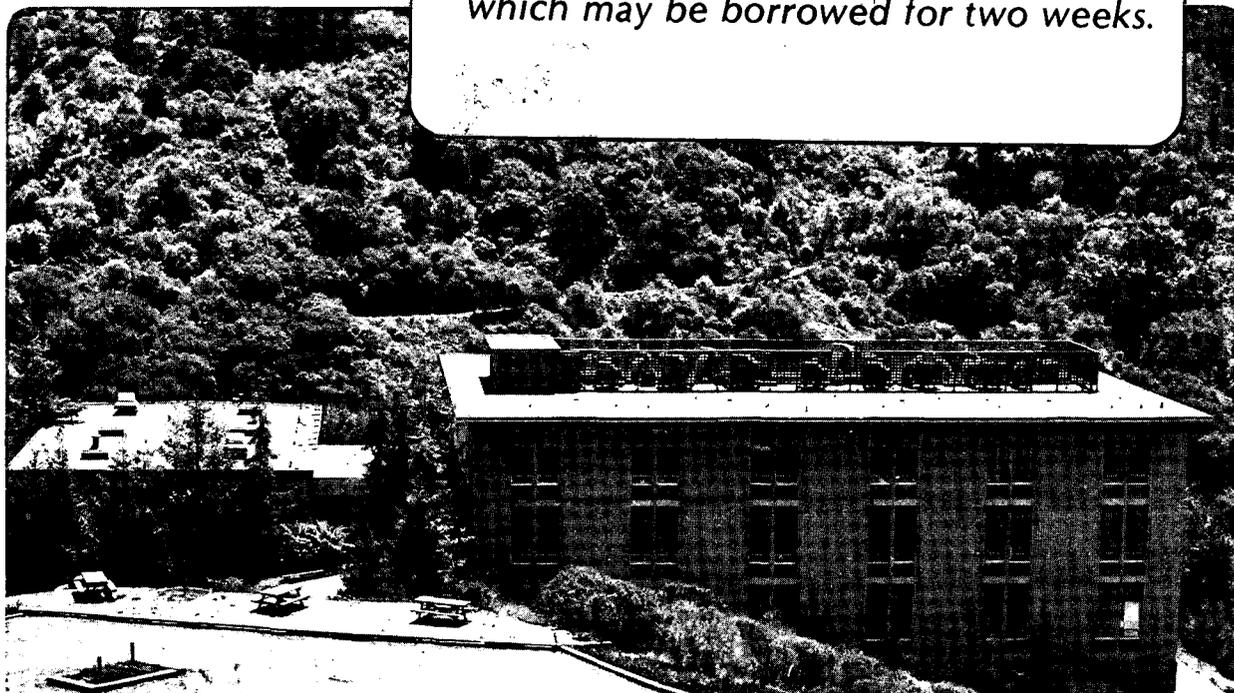
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October 1988

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METHANE OXIDATION WITH PROTON CONDUCTING CERAMIC ELECTROLYTES

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The successful conversion of methane to ethylene in an energy producing fuel cell is attractive from both a fundamental and technological (economic) viewpoint. Recent advances in solid electrolyte research and ceramic processing, as well as in the catalytic oxidative coupling of methane to ethylene should make this approach quite promising.

Ideally, the electrochemical conversion of methane to ethylene would take place at moderate temperatures (400 to 600 °C), at high current densities (50 to 100 mA/cm²), and generate electric power at reasonable energy efficiencies (as opposed to consuming it in an electrolytic process). A schematic representation of such a fuel cell is seen in fig. 1. The basic elements of this cell are the air electrode (cathode), the methane electrode (anode), and the proton conducting solid electrolyte. The air electrode presents no difficulty in that it is already an established technology, and in fact such electrodes have been routinely prepared in the context of the fuel cell effort at this laboratory. The innovations then in this effort will be in the successful combination of high conductivity protonic electrolytes with electrocatalysts known to promote the oxidative coupling of methane to ethylene.

The recent introduction of perovskite proton conductors [1 - 4] such as SrCe_{0.95}Yb_{0.05}O_{3-x} encourages the development of this approach. These compounds have high solubilities for hydrogen and have demonstrated high current densities for hydrogen extraction. Although the Sr compound demonstrates high conductivity at 900 °C, a related compound, BaCe_{0.95}Yb_{0.05}O_{3-x} has much higher conductivity at lower temperatures and a proton transference number of close to one. The conductivity of this protonic electrolyte at 600 °C is approximately 5 x 10⁻³ (Ω cm)⁻¹, and at 500 °C is approximately 2 x 10⁻³ (Ωcm)⁻¹. The ionic conductivities of these ceramics imply that the energy efficiency of systems based on them will probably be limited by the electrolyte. However, the reported relative densities of these electrolytes has been in the range of 85% of theoretical density, which is actually fairly low. Well known solid electrolytes such as the sodium beta aluminas, are routinely sintered to greater than 96 % relative density. In fact,

it is probable that significant improvements in the electrical and mechanical properties of the SrCeO_3 type electrolytes can be realized through advance ceramic processing techniques. Additionally, the processing of thin-walled ceramics (to reduce iR drop in cell) of various geometries such as extruded catalyst supports is an established technology, and does not represent a serious constraint. Further, the protonic conductivity in polycrystalline electrolytes is likely to be limited by grain boundary resistivity. Grain boundary effects can be reduced by adjusting ceramic precursor dopant concentrations [5], which can lead to order of magnitude increases in conductivity. Also, manipulation of the ceramic microstructure, such as increasing the grain size and modifying grain orientation, can affect the grain boundary conductivity favorably. These types of approaches have been pursued successfully as part of the solid electrolyte program in this laboratory.

In order for the electrochemical activation of methane as outlined above to be successful it is necessary to find effective electrocatalysts. Fortunately, a promising catalytic process for the conversion of methane to ethylene was reported in the early 1980's by George E. Keller and Madan M. Bhasin at Union Carbide [6]. Their research focussed on the oxidative coupling of methane via appropriate catalysts. In essence, the net reaction in their catalytic approach is the same as that for the fuel cell outlined in fig. 1. In examining various catalysts for the process, they found that the most successful catalysts for oxidative coupling of methane were the low temperature melting metals of group III-A, IV-A, and V-A, in addition to manganese and cadmium. The principal product of the catalytic reaction is ethylene, with lesser amounts of ethane and traces of acetylene. Inherent in this process is the need to maintain a high oxidation state of the catalyst material; in a fuel cell this would be determined by the cell potential. For the catalytic process then, the metal oxide catalyst is reoxidized by exposure to air at the reactor temperature. In order to avoid competing non-catalytic reactions in the gas phase the reactor must be operated in a cyclic fashion, by alternatively flowing methane and air between short nitrogen bursts. In the fuel cell the reactants are maintained in different compartments, eliminating the need for programmed feed of the reactants, and of course generating electric power in the process of methane to ethylene conversion.

The targeted areas for investigation can therefore be delineated as (1) electrocatalyst studies leading to the development of cermet electrodes using catalysts referenced in the work of Keller and Bhasin, (2) preparation and improvement of $\text{BaCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-x}$ proton conducting ceramics, (3) integration of

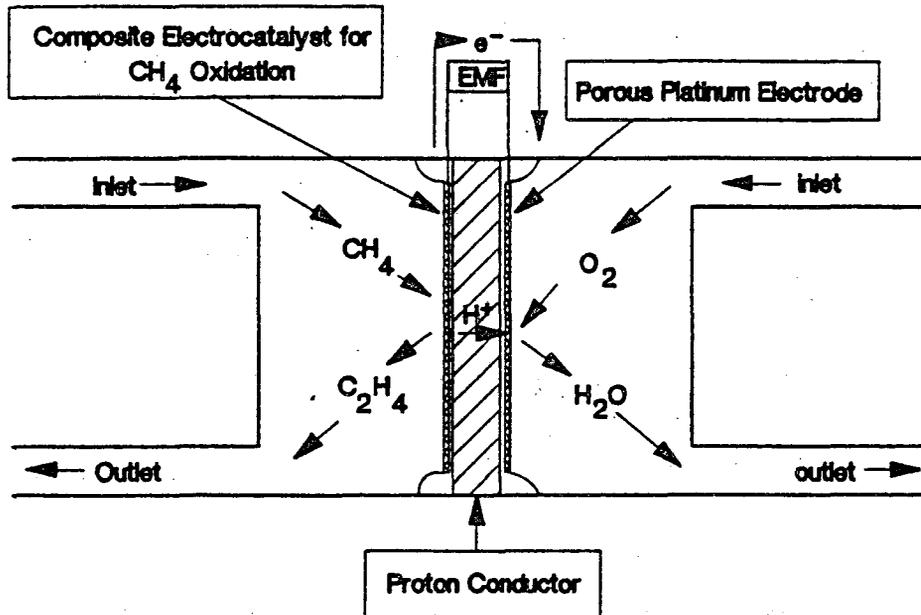
the above components into a working fuel cell, (4) characterization and optimization of fuel cell conversion of methane to ethylene. In light of the above information it seems that electrochemical conversion of methane to ethylene and higher hydrocarbons is in fact a very promising avenue for new research.

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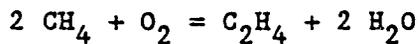
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6. J. Haggin, *Chem. & Eng. News*, p. 22-24, July 4, 1988.

Fuel Cell Schematic for Oxidation of CH₄ to C₂H₄ and C_n Species



THERMODYNAMIC DRIVING FORCE AND EMF

Using Oxygen to Drive Oxidation of Methane:



$$\Delta G_{\text{rxn}}^{298} = -287 \text{ KJ/mol} \quad E^\circ = +0.75 \text{ volts}$$

$$\Delta G_{\text{rxn}}^{673} = -299 \text{ KJ/mol} \quad E^\circ = +0.77 \text{ volts}$$

$$E_{\text{cell}}^{673} = 0.77 - \frac{RT}{2F} \ln \left(\frac{P_{\text{H}_2\text{O}}/P_{\text{CH}_4}}{P_{\text{C}_2\text{H}_4}} \right) - \frac{RT}{4F} \ln P_{\text{C}_2\text{H}_4} + \frac{RT}{4F} \ln P_{\text{O}_2}$$

Use of air electrode at 1 atm yields a loss of only 20 mV.

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