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METHANE CONVERSION BY

SOLID ELECTROLYTE MEMBRANES

FINAL REPORT

FOR THE PERIOD

JANUARY 1, 1989

TO

AUGUST 31, 1993

Gas Research Institute
8600 West Bryn Mawr Avenue
Chicago, Illinois 60631

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(January 1, 1989 - August 31, 1993)

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for

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16. Abstract (Limit: 200 words)

This program is focusing on solid-state fuel cells which operate in the same temperature range as molten carbonate fuel cells. One approach involves selecting new solid electrolytes with high ionic conductivity at ≅600°C. Experimentally determined activation energies for ionic transport in perovskite solid electrolytes have been found related to lattice and thermodynamic parameters. Using this approach, we have identified solid electrolytes having high ionic and low electronic conductivity. These electrolytes have been incorporated in small unoptimized laboratory fuel cells that may perform better at 600°C than zirconia based SOFC's at 1000°C, assuming that many other issues can be resolved. These issues include the chemical and physical stability of cell components, including electrocatalysts for each respective half-cell reaction and the development of multicell designs and fabrication procedures. Progress has been made in identifying anode electrocatalysis towards promoting partial and complete CH_4 oxidation. New fuel cell structures are being defined using thin-film techniques involving metalloorganic chemical vapor deposition (MOCVD) of solid electrolytes.

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RESEARCH SUMMARY

Title Methane Conversion by Solid Electrolyte Membranes

Contractor Eltron Research, Inc. GRI Contract Number: 5089-260-1824

Principal Investigators A. F. Sammells, M. Schwartz, R. L. Cook and J. H. White

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Report

Objective

1) 600°C solid-state fuel cells (SOFC) possessing new highly conductive solid electrolytes.

2) Effective, continuous oxidative coupling of methane at the lowest possible temperatures.

Technical Perspective and Approach

We are pursuing two approaches towards identifying intermediate temperature SOFC's. One approach involves identifying crystallographic parameters and ionic constituents for achieving rapid ionic mobility. This may lead to selecting solid electrolytes possessing high ionic conductivities which would provide small internal resistance losses in fuel cells. Initial focus has been on the influence of these parameters on activation energy, E_a, for ionic conduction. In future work we will additionally address the role of carrier density towards improving ionic conductivity in these materials. The second approach is involving the evaluation of metalloorganic chemical vapor deposition for depositing thin-film solid electrolytes to give SOFC's possessing intrinsically low internal resistance losses.

To provide electrocatalytic sites at the fuel cell anode compatible with either partial or complete methane oxidation, we are varying both electronic and ionic conductivity within solid-state lattice and lattice surface oxygen binding energies.

We are also exploring the use of mixed ionic and electronic conducting membranes for promoting methane oxidative dimerization at intermediate temperatures.

Results

We have:

- Shown how the activation energy, E_a, for anion conduction in perovskite electrolytes varies with thermodynamic and lattice geometric parameters. Perovskite lattices which favor low E_a for anion migration include: i) that the overall lattice possess a moderate metal-oxygen binding energy, and heats of formations ii) perovskite solid electrolytes possess large free volumes, iii) preferred $(r_{critical}/r_{O^{2-}})^2$ ratios for A-A-B saddle points $\cong 0.5$, and iv) that the lattice minimally polarizes the mobile anion by having

itself high polarizability.

- Identified perovskite-related structures possessing intrinsic anion vacancies that have high ionic conductivity.

- Incorporated new perovskite solid electrolytes into fuel cells which operate at intermediate temperatures.

- Tape-cast perovskite solid electrolytes in dense self-supporting films of 50 microns thickness.

- Designed and fabricated the hardware for a semi-internally manifolded intermediate temperature fuel cell stack.

- Identified criteria for selecting mixed ionic-electronic conducting perovskite membranes for methane oxidative dimerization.

- Found that more tightly bound O^- species present at the interfacial region give a higher probability towards promoting partial methane oxidation.

- Identified mixed-ionic-and electronic-conducting oxide candidates for SOFC electrodes and oxygen separation membranes.

- Prepared thin films of yttria stabilized zirconia (YSZ) using metalloorganic chemical vapor deposition.

Project Implications

This research sought to develop correlations underlying highly conductive solid electrolytes and employ more conductive electrolytes in laboratory fuel cells which operate at temperatures several hundreds of degrees below the 1000°C temperatures used in current solid oxide fuel cells (SOFCs). The goal of the research was to improve the reliability and cost of planar SOFCs through the use of electrolytes that could function under relatively mild temperatures. Although the research did not identify a candidate reduced-temperature SOFC device, its extensive findings provide a basis for further development. GRI does not plan to continue this contract.

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