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ELECTROCHEMICAL ABATEMENT OF POLLUTANTS NO_x AND SO_x IN COMBUSTION EXHAUST GASES EMPLOYING A SOLID-OXIDE ELECTROLYTE

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1. CONTRACT NUMBER: DE-FG22-88PC88914

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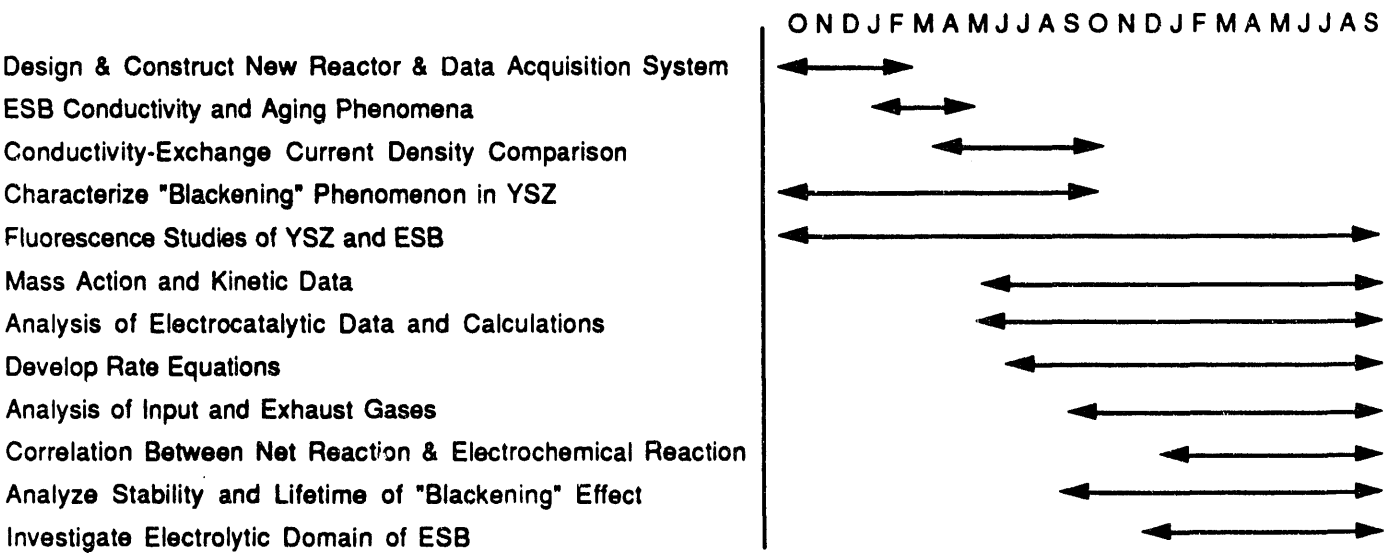
CONTRACT PERIOD OF PERFORMANCE: October 1, 1988 through September 30, 1990

2. SCHEDULE/MILESTONES:

1988-90 Program Schedule



3. OBJECTIVES:

As stated previously (Wachsman, et al.), the objective of this contract is to test the feasibility of eliminating the pollutant species NO_x and SO_x in combustion exhaust gases by pumping off oxygen employing a dry solid-oxide, oxygen-ion electrolyte system.

4. BACKGROUND STATEMENT:

In previous work, the feasibility of eliminating the pollutants NO_x and SO_x in combustion exhaust gases employing a solid-oxide pollution abatement reactor has been described (Wachsman, et al.). In such a system, NO_x (NO and NO_2) and SO_x (SO_2 and SO_3) are electrolytically dissociated on the cathodic side of a solid-oxide electrolyte, under an applied potential, forming N_2 and gaseous sulfur (which can be readily condensed downstream), with oxygen being pumped through the electrolyte. Numerous pollution abatement reactions were performed using both yttria-stabilized zirconia (YSZ) and erbia-stabilized bismuth oxide (ESB) electrolytes. These reactions indicate that such a pollution abatement reactor is feasible. These results also indicate that the solid-oxide electrolyte plays a preeminent role in the electrocatalytic mechanism, hence the bulk and surface properties of these electrolytes are receiving a significant research effort.

5. PROJECT DESCRIPTION:

While the scientific feasibility of a solid-oxide pollution abatement reactor has been demonstrated (Wachsman, et al.), many of the results of that investigation are based on preliminary data. Furthermore, the derivation of rate equations based on the mass action effect has yet to be accomplished. It is the goal of the initial phase of this research to further investigate the role of oxygen vacancies in electrocatalysis and then address the mass action effect.

6. RESULTS/ACCOMPLISHMENTS:

During the fourth quarter of this grant, the major accomplishment concerns the spectroscopic investigation of oxygen vacancies in YSZ and ESB(Wachsman, E. D., Jiang, N., Frank, C. W., Mason, D. M. and Stevenson, D. A.). The nature of electrolytic "blackening" was studied. It was found that the same reduction processes that turn polycrystalline YSZ black turn single crystals orange. Two absorption bands attributable to this orange coloration, 328 and 470 nm, were observed. The 328 nm absorption band agrees with theoretical calculations for an F-center in YSZ. Several fluorescence bands were also observed. An excitation band at 302 nm was found to increase in intensity upon reduction of YSZ and the resulting emission at 580 nm was found to have a temperature dependence typical of F-centers. These results are in agreement with the hypothesis of the formation of color-centers upon reduction of YSZ as being responsible for "blackening" and the resulting enhancement of electrocatalytic reactivity.

An excitation peak at 489 nm that results in an emission doublet at 545 and 558 nm was found in both YSZ and ESB, even though they are chemically dissimilar. We believe the common chromophore is a lanthanide (Y^{3+} and Er^{3+}, respectively) associated oxygen vacancy. This assignment explains the similar decay in 545 nm emission intensity and conductivity of ESB upon aging (Wachsman, E. D., et al.). The aging phenomenon is attributable to ordering of the oxygen vacancies in <111> directions and concomitant cation ordering (Wachsman, E. D., Jiang, N., Mason, D. M. and Stevenson, D. A.). The cation ordering in ESB can be described in terms of association of Er with O, thus decreasing the population of Er associated oxygen vacancies with time resulting in the observed decay in emission intensity.

Background research and equipment development for the mass action and kinetic data studies have been persued during this quarter as well. Literature searches have been conducted to gather information to help determine the most effective method for using gas chromotography to quantitatively analyze the input and exhaust gases. This includes the design of a new two-chamber quartz reactor, necessary to prevent the mixing of the input and exhaust gases. Fabrication of apparatus for stability studies of electrolytes has also begun.

7. FUTURE WORK:

The relationship between solid-state ionic diffusion and the heterogeneous reaction rate (conductivity vs. current exchange density) previously described (Wachsman, et al.; Wachsman, Naixiong & Mason) will be repeated for ESB in the more carefully controlled environment of a new quartz reactor tube. In addition, this relationship will be investigated for different crystallographic orientations of single crystal YSZ, also in the new reactorpresently in the design and construction stage.

Using gas chromotography and a new quartz reactor, input and exhaust gases will be quantitatively analyzed to determine reaction rates. The gas-phase mass action effect will then be investigated and a rate equation developed which includes both the electrolyte and gas phase compositions. The stability of ESB at low oxygen partial pressures will be investigated with the new apparatus.

8. REFERENCES:

Wachsman, E. D., et al., Abatement of Gaseous Pollutants in Coal-Combustion Exhaust Gases Employing a Solid-Oxide Electrolyte, DOE/PETC, 1989, in press.

Wachsman, E. D., Jiang, N., Frank, C. W., Mason, D. M. and Stevenson, D. A., Spectroscopic Investigation of Oxygen Vacancies in Solid Oxide Electrolytes, Applied Physics, submitted.

Wachsman, E. D., Jiang, N., Mason, D. M. and Stevenson, D. A., Solid State Oxygen Kinetics in Er_2O_3 Stabilized-Bi_2O_3, Journal of the Electrochemical Society, Proceedings of the First International Symposium on Solid Oxide Fuel Cells, Volume 89-11, 15-29.

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