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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-FG22-88PC914

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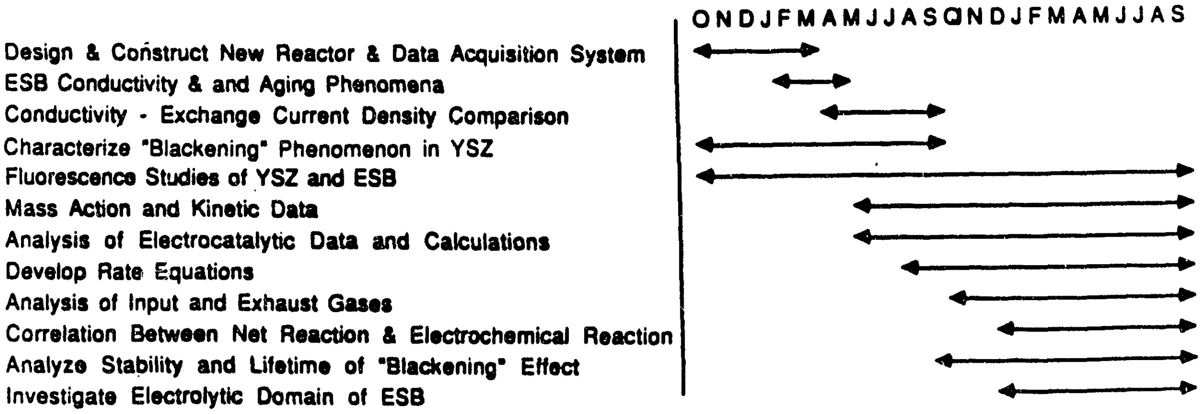
CONTRACT PERIOD OF PERFORMANCE: October 1, 1988 through September 30, 1990

2. **SCHEDULE/MILESTONES:**

1988-90 Program Schedule



3. **OBJECTIVES:**

The objective of this contract is to test the feasibility of eliminating the pollutant species NO and SO_2 in combustion exhaust gases by pumping off oxygen employing a dry solid-oxide, oxygen-ion type electrolyte system. At the same time to conserve electrical power for pumping it is desirable not to have to pump off any unreacted O_2 that may remain in the exhaust gases. The applications in mind are treating exhaust gases from such devices as internal combustion engines, gas turbines and

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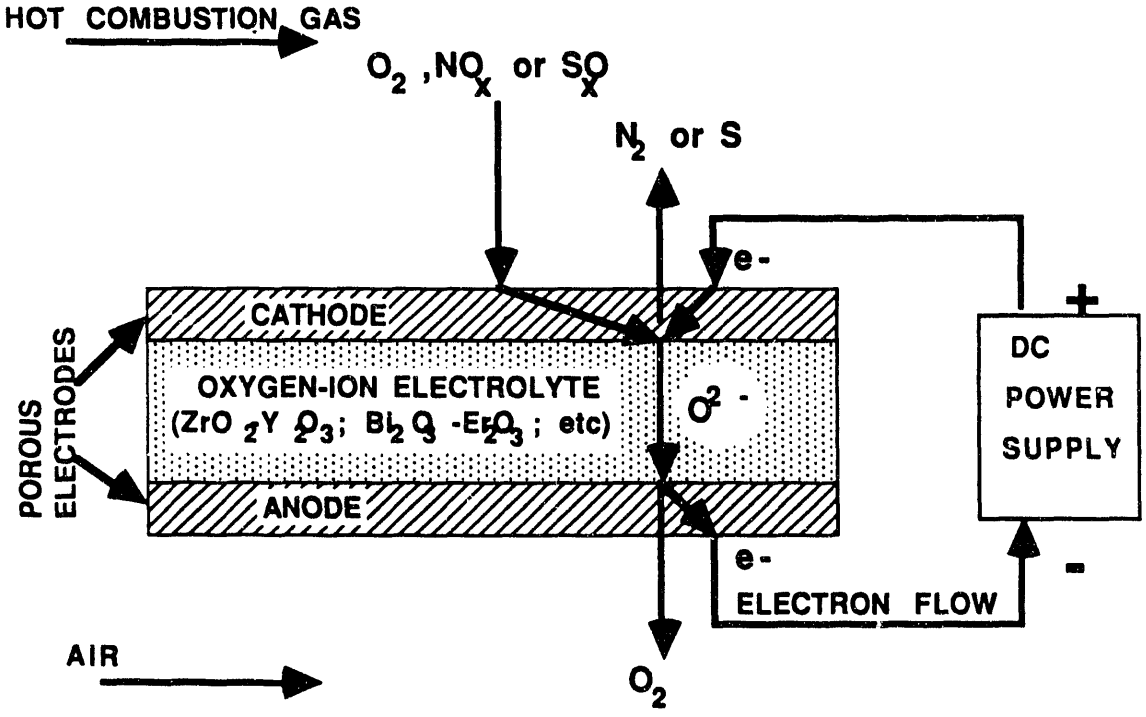
power-plant flue gases in the 400-700°C temperature range (employing stabilized-bismuth oxide electrolytes) as well as the cleanup of high pressure, combustion gas prior to entering a gas turbine in the 700-1000°C temperature range (employing stabilized-zirconia electrolytes). In optimizing the design of an electrochemical pollution-abatement reactor it is necessary to have a quantitative understanding of the basic chemical processes ocurring in the system. To this end, a study of the effect that ionic defect population as well as electrolyte composition has on electrocatalytic reaction rates is being undertaken. The precise nature of the electrocatalytic role played by ionic defects, such as F-centers, is being elucidated.

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. The advantages of such a system, as compared to other forms of pollution abatement, are numerous since the basic system is clean, dry and employs no moving parts. The concept for employing solid-oxide electrolytes for a pollution abatement reactor, operating in the oxygen-pumping mode, is shown schematically below:



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, as described above, is at least scientifically feasible. In addition, the heterogeneous reactivity of O_2 and its conductivity through the electrolyte were carefully studied in order to shed light on the fundamental kinetic mechanism of cathodic dissociation of these gaseous polyatomic oxygen compounds. The Arrhenius behavior of these two phenomna indicate a common mechanism between the rate controlling step of the heterogeneous reaction and conduction through the electrolyte. The common species to these two phenomena are oxygen vacancies. These vacancies are empty oxygen lattice sites and are the conducting species in solid-oxide electrolytes. Furthermore, we believe that the catalytic sites for the cathodic dissociation reactions are these same oxygen vacancies. Evidence for this conclusion includes the one to three orders of magnitude increase in the electrocatalytic reactivity of YSZ upon "blackening". Blackening is a term used to describe the reduction of zirconia electrolytes and the resulting darkening (blackening) observed in polycrystalline samples. We believe that reduction of zirconia electrolytes results in the formation of neutral (electron occupied) oxygen vacancies and it is these neutral vacancies that are responsible for "blackening" and the resulting increase in reactivity.

The role of oxygen vacancies in the conductivity of ESB was studied using such solid-state techniques as differential thermal analysis and x-ray diffraction. A change in the slope of conductivity vs. reciprocal temperature, at ~600°C, indicates two different conductivity regions. The above techniques were used to show that the change in slope is due to an order-disorder transition of the oxygen sublattice. At high temperatures, the oxygen sublattice is disordered resulting in a high mobility of oxygen vacancies and a low apparent activation energy. At low temperatures the oxygen sublattice tends to order, with the vacancies aligning in (111) planes. The higher activation energy in this temperature regime is then due to the extra energy required to free a vacancy from the ordered state. Furthermore, a reversible aging phenomenon in the conductivity of ESB was observed. For ESB annealed in this lower temperature region, the conductivity was observed to decay with time as the oxygen sublattice ordered. Heating above the transition point will completely reverse this process by disordering the oxygen sublattice, and returning the conductivity to its initial value.

The role of oxygen vacancies in both the conductivity of ESB and the "blackening" of YSZ was studied using fluorescence spectroscopy. Common light absorbing and fluorescing species were found in these two chemically dissimilar compounds. The only possible common fluorescing species to these oxides are the oxygen vacancies. Changes in the emision intensity of this common fluorescing species are shown to follow both the aging process in ESB and the blackening process in YSZ.

A model was proposed for the incorporation of oxygen species into the oxygen sublattice of the electrolyte, at the cathode. This model and an equilibrium relationship, between oxygen species in the gas phase and neutral oxygen vacancies in the electrolyte, are consistent with all of the observed data.

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 second quarter of this grant, the major accomplishment has been the near completion of the DTA, XRD and conductivity data for publication of the order-disorder and aging phenomena in ESB. Samples were aged at 500 °C for up to 500 hours and the DTA and XRD data confirms our thesis of an order-disorder transition of the oxygen sublattice in this material. While the as-received sample shows a change in slope and hence heat capacity at the conductivity mechanism transition point (as previously reported in Wachsman, et.al.), the samples aged for an extended period of time not only show this change in heat capacity but also exhibit a strong endotherm upon heating through this transition point. This endotherm is exhibited only on the first heating cycle as the ordered state is relaxed. Subsequent heating and cooling cycles only exhibit the change in heat capacity observed in the as-received sample and is consistent with the observed reversibility of the conductivity aging phenomenon. XRD of the aged samples is currently being done and we expect similarly consistent results with what we previously reported (Wachsman, et.al.).

The conductivity data is being obtained in the new quartz-tube reactor utilizing an HP 4284-A Precision LCR Meter. This instrument just arrived this quarter and a considerable amount of effort was expended in order to calibrate and verify the readings of this high precision instrument, using known electrical circuits as references. Initial conductivity measurements and complex impedance plots of ESB have been obtained and are consistent with our previously reported results (Wachsman, et.al.). In order to utilize the full potential of this instrument some fine tuning of the high frequency response is still necessary at which time the conductivity results will be completed and the results published.

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 pristine environment of the new reactor. In addition, this relationship will be investigated for different crystalographic orientations of single crystal YSZ, also in the new reactor.

The nature of electrolytic "blackening" will be studied using single crystal YSZ, where the process turns the crystal orange. This orange coloration confirms the hypothesis of the formation of color-centers as being responsible for "blackening" and the resulting enhancement of electrocatalytic reactivity. Fluorescence spectroscopy will be employed to obtain a better understanding of the nature of the ionic defects formed by "blackening" and to quantify their population. Identification of the specific chromophores responsible for each of the excitation and emission peaks will be attempted . An in-situ fluorescence technique for determining the color-center population and subsequent reactivity of the electrolyte is being developed. By implanting quartz optical fibers in the new reactor, adjacent to the disk, real-time fluorescence data can be obtained during the course of electrochemical reactions.

The two research directions described above will quantify the electrocatalysis oxygen-vacancy dependence, which at this time appears to be first order. The gas-phase mass action effect will then be investigated and a rate equation developed which includes both the electrolyte and gas phase compositions.

8. REFERENCES:

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

Wachsman, E. D., Naixiong, J., and Mason, D. M., Rates of Electrocatalytic Reactions Employing a Stabilized-Bi_2O_3 Electrolyte Operating at Moderate Temperatures. 1988 Fuel Cell Seminar. Long Beach, California: 1988. 65-68.

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