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FINAL REPORT

**SIMULTANEOUS PARTICULATES, NOx, SOx REMOVAL FROM FLUE
GAS BY ALL SOLID-STATE ELECTROCHEMICAL TECHNOLOGY**

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prepared for

**DIANE R. MADDEN
U.S. DEPARTMENT OF ENERGY
PITTSBURGH ENERGY TECHNOLOGY CENTER
P.O. BOX 1940
PITTSBURGH, PA 15236**

by

**W. JEFFREY COOK
LINDA P. CORNELL
MAJID KEYVANI
MARINA NEYMAN
HELIPUMP CORPORATION
8435 BRECKSVILLE ROAD
CLEVELAND, OHIO 44141**

and

**DENNIS J. HELFRITCH
RESEARCH COTTRELL ENVIRONMENTAL SERVICES AND TECHNOLOGIES
P.O. BOX 1990
SOMERVILLE, NEW JERSEY 08876**

APRIL 17, 1990

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ABSTRACT

This contract pursued development of an electrochemical process to control the level of sulfur and nitrogen oxides in coal combustion flue gases. The process uses a solid-state oxygen ion conducting electrochemical reactor which reduces NO_x and SO_2 to nitrogen, sulfur, and oxygen. The solid electrolyte is a ceramic oxide-ion conductor such as a yttria stabilized ceria or zirconia. The reactor has no moving parts and requires no material reagents; electric power is the only consumable. Sulfur, the only by-product, is condensed downstream of the electrochemical reactor.

Experimental NO and SO_2 reduction rates were determined on yttria stabilized ceria and zirconia solid electrolyte with gold electrodes. Variable experimental parameters included gas composition, applied voltage and electrocatalyst. Simulated flue gases containing up to 2700 ppm of SO_2 , 500 ppm of NO and 2% oxygen were tested at temperatures of 450°C to 500°C . A series of transition metal oxide electrocatalysts were applied to the cathode in order to improve the reactivity of NO and SO_2 over that of oxygen. The best electrocatalysts were based on ruthenium, either as the simple oxide or as the perovskite strontium ruthenate. Results suggest that acceptable rates of SO_2 and NO reduction can be obtained in flue gases containing up to 1% oxygen.

The solid electrolyte electrical characteristics were examined in the presence of flyash in a high temperature particulate control apparatus. The presence of flyash caused no significant decrease in current through the solid electrolyte. Also, SO₂ and NO reduction performance was determined before and after exposure to flyash. Reduction rates in the presence of oxygen were unchanged after exposure. Both metal and ceramic high temperature filters were tested for particulate removal efficiency and pressure drop; metal filters gave the best results.

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1. INTRODUCTION

This report summarizes the research performed on the project "Simultaneous Particles, NO_x and SO_x Removal from Flue Gas by All-Solid State Electrochemical Technology" under contract number DE-AC22-87PC79855.

The process controls SO_x , NO_x , and particulate emission from coal combustion flue gases. It is based on a solid-state, electrochemical reactor which converts NO_x and SO_2 to nitrogen, sulfur, and oxygen. Sulfur is condensed downstream at a lower temperature. Particulates are removed with a filter or electrostatic precipitator. The process utilizes no other material input (flue gas is the only fluid), has no moving parts, and produces no sludge(s).

The reactor consists of an electrochemical cell where the electrolyte is a solid oxygen ion conducting ceramic such as stabilized ceria or zirconia and the electrodes are electronically conductive material(s). Porous metal such as silver or gold were used as electrodes in the experimental work.

A simplified electrochemical cell schematic is shown in Figure 1. Flue gas contacts the cathode. The voltage applied to the cell supplies electrons to the cathode and removes them from the anode. At the cathode, SO_2 is reduced to sulfur vapor and oxygen ions and NO_x is reduced to nitrogen and oxide ions. Sulfur and nitrogen remain with the flue gas; oxygen ions dissolve in the solid electrolyte. At the anode an equivalent number of oxide ions are converted to oxygen gas. The cathodic electrode reactions are:

Figure 1
Simplified Cell Schematic

The anodic electrode reaction is:

The overall process is:

Figure 2 shows the oxygen ion conductivity in reciprocal ohm-cm of the three solid electrolytes [1,2,3] used in the experimental work as a function of temperature. The temperature range of 450 to 500°C was used in most experimental work. For comparison typical aqueous electrolytes are in the range of 0.1 to 1. The YSZ is zirconia stabilized with 8 mole percent yttria and is commonly used in solid oxide fuel cells. However, its conductivity is much lower than the bismuth and ceria electrolytes. The tungsten stabilized bismuth has the highest conductivity but the samples tested were quite fragile. In addition, the stabilized bismuth ceramics cannot be used at high applied potential because they have a decomposition voltage of about 0.5 volts [4]. The stabilized ceria is nearly as conductive as the stabilized bismuth and it is stable at higher voltages and mechanically more rugged. For these reasons the ceria electrolytes was used in most of the experiments.

Figure 3 shows the thermodynamic decomposition voltage for various species found in coal flue gas as a function of temperature. The nitrogen oxides will decompose at any positive

FIGURE 3
REDUCTION POTENTIALS vs TEMPERATURE

applied potential. Sulfur dioxide begins to decompose at about 0.7 volts. Carbon dioxide and water vapor require an applied potential greater than one volt. Another reaction which occurs is the reduction of oxygen gas to oxide ions on the cathode. This causes pumping of oxygen gas from the cathode to the anode. The thermodynamically required voltage for this process is zero. This oxygen pumping is the main parasitic reaction that occurs. The actual applied voltage must be greater than the thermodynamic voltage in order to provide a driving force for the reactions at the electrodes (kinetic overpotential) and the conduction of oxygen ions through the solid electrolyte (ohmic overpotential).

In order to selectively reduce NO and SO₂ in the presence of oxygen, electrocatalysts must be used to enhance the NO and SO₂ reduction kinetics over the oxygen kinetics. The major experimental effort was directed at finding such electrocatalysts. Various transition metal oxides were placed on the cathode surface of the electrochemical cell and NO and SO₂ reductions were measured with and without oxygen present.

Other experiments looked into the effect of flyash on the electrolytic cell. Electrical measurements were made on electrochemical cells while flyash passed by them and NO and SO₂ reduction measurements were made on cells which had been exposed to flyash. Also high temperature filters were tested to remove flyash upstream of the electrochemical reactor.

Other groups have also studied the reduction of NO and SO₂ on stabilized zirconia. Professor Mason and others at Stanford University have investigated the decomposition of NO on scandia stabilized zirconia and other stabilized zirconias[5,6,7]. Ceramatech has studied the decomposition of SO₂ on yttria stabilized zirconia[8]. Ceramatech's work used only electrical measurements and did not include any gas composition measurements. Therefore, the effect of oxygen on the reduction of SO₂ could not be measured. These studies were performed at temperatures from 600° to 900°C.

2. ELECTROCHEMICAL REACTOR FABRICATION PROCEDURE AND EXPERIMENTAL APPARATUS

Most experiments were done on 1 in. diameter solid electrolyte disks. Some later tests were done on larger electrolyte sheets.

2.1 Experimental Apparatus

The experimental setup is shown in Figure 4. Gas cylinders containing mixtures of 500 ppm NO in nitrogen or helium and 2700 ppm SO₂ in nitrogen or helium were purchased from Matheson. Some higher concentration gas mixtures were also used. These gases along with air or oxygen are metered through a manifold containing three Matheson rotameters Model 7642, with 150 mm number 610A tubes. The gas flows through the reactor and across the solid electrolyte disk. The reactor is heated in a 2" Linberg Model 55322-3 tube furnace with a model 59344 programmable controller. A Pine Instruments model RDE4 potentiostat supplies current to the cell at a constant voltage. The voltage can be controlled to within a few millivolts. The experiments conducted early on in this contract used a power supply instead of a potentiostat.

The NO gas concentration was measured with a Horiba model VIA-300 non-dispersive infrared analyzer (NDIR). It has a range of 0 to 1000 ppm and can measure composition changes down to a few ppm. The unit is equipped with a reducing catalyst bed which converts all the NO₂ in the gas stream to NO. Therefore, the unit measures total NO_x. Sulfur dioxide concentration measurements were made with a Hewlett Packard (HP) Model 5880 gas chromatograph (GC) and later with a Horiba VIA-300 NDIR. Porapak

Figure 4
Schematic of Experimental Set-Up

Q and R packings were used in the GC. The NDIR has a range of 0 to 10,000 ppm SO₂ and can measure composition changes down to a few ppm. The GC is less accurate and can measure changes of 100 ppm.

Both NDIR's are equipped with a voltage output as well as an LCD display. These voltages along with the applied voltage and current from the potentiostat are measured with a HP 3497 data acquisition system. The output from the data acquisition is sent to an HP 9836 computer where the applied voltage and current are displayed and the NO and SO₂ concentrations are plotted as a function of time. The AC resistance of the cell was measured at 1 kHz with an HP 4265B universal bridge.

2.2 Reactor

Two different reactors were used for testing the disks. One half of the first reactor is shown in Figure 5. The other half is the mirror image of the half shown in the figure. The disk was held between two 1" diameter mullite tubes. Four threaded stainless steel tie rods pass through holes in a stainless steel collar at the end of each mullite tube. The ends of the tie rods were spring loaded to hold the disk and tubes in place. The gas passed down a 1/4" mullite center tube, across the face of the disk and back through the annulus between the 1/4" and 1" tubes. Electrical contact with the disk was made with silver wires connected to pieces of silver or gold foil. The foil was placed between the disk and the mullite tube and made contact with the anode or cathode of the disk. The disk was sealed to the tube with ceramic cement. Ceramabond and Sauereisen ceramic cements

Figure 5 First Reactor

Experimental Reactor Assbly	Dr. Byi Asnien
Full Scale	AUG. 19, 1987
PETC/NO _x	Miss M. G. G. 1411
Helpump	Helpump

HELIPUMP

were used.

The ceramic cements could not form a gas tight seal. The ceramic seal which was located in the hot zone of the furnace cracked when the temperature was raised. To remove the disk from the reactor usually required breaking the disk. The reactor was useful for taking electrical data but the gas leaks caused us to abandon this reactor.

The new quartz reactor, shown in Figure 6, was designed and built using a cold zone seal. The reactor consists of two pieces connected by a ground glass joint. The joint extends out of the furnace in the cold zone and was sealed with silicone cement. The outer piece is a quartz tube with a standard hemispherical cap with a standard female taper joint. The outer tube seals the disk from the atmosphere. The inner piece contains a holder for the ceramic disk and two concentric quartz tubes (1" and 1/4" diameter) for gas flow. Gas flows through the inner tube, across the disk and back out through the annulus between the inner and outer tubes. The larger tube has a slot near the end to hold the solid electrolyte disk. The disk is held in the slot with Interam gasketing. Gold foil attached to silver wires was used to make electrical contact to the disk. The gold foil was placed between the Interam and the disk electrode. The Interam expands when heated and provides electrical contact between the foil and the disk. The silver wires pass out of the reactor through holes in the cold zone section of the inner piece and are sealed with silicone cement.

A second quartz reactor was constructed using a similar

Figure 6 Quartz Reactor

Quartz Electrode Disc Carrier Assembly

Quartz Electrode Disc Carrier Assembly	
Designed By: Cook	5/5/1988
Measurements in mm.	Project: FLU

Female Quartz Unit

Female Quartz Unit	
Designed By: Cook	Project: FLU
Measurements in mm.	5/5/1988
HELIPUMP	

design. However, the disk slot in the inner piece is made of stainless steel. It is joined to the quartz portion of the reactor with a graded glass seal.

A stainless steel reactor, shown in Figure 7, was constructed to hold the larger electrolyte plates. Gas enters at the the center of the cathode, flows by the cathode, around the edge of the plate, passes by the anode and leaves at the center of the anode. The gas inlet tube is part of the outer cylinder. The gas outlet tube, anode and cathode wire lead tubes and a thermocouple are part of the inner cylinder. The inner and outer cylinder pieces are bolted together and sealed with a gasket in the cool zone outside the furnace. The silver wire leads are attached to the electrolyte plate with Sauereisen ceramic cement. A conductive silver organometallic paste is painted on top of the cement to make electrical contact between the leads and the electrode. The electrolyte plate is held in an insulating ceramic holder and other insulating material is placed around the plate to prevent shorting to the stainless steel.

2.3 Solid Electrolytes

Ceramic electrolyte disks and plates made of tungsten stabilized bismuth, yttria stabilized ceria (YSC), and yttria stabilized zirconia (YSZ) were tested in the reactor. The compositions, dimensions and suppliers of the electrolytes are shown in Table 1.

Figure 7
Plate Testing Reactor

Table 1
Solid Electrolytes Tested for NO_x and SO₂ Reduction

	Solid Electrolyte	thickness	size	Supplier*
Disks	(Bi ₂ O ₃).78(WO ₃).22	1.5 mm	1" dia.	HT
	(ZrO ₂).92(Y ₂ O ₃).08	1.0 mm	1" dia.	TT
	Ce.8Y.15O _{1.925}	.8 mm	1" dia.	TT
	Ce.8Y.15O _{1.925}	.4 mm	1" dia.	TT
Plates	Ce.8Y.15O _{1.925}	.8 mm	2.4"x2.4"	TT
	(ZrO ₂).92(Y ₂ O ₃).08	4 mm foam	2.5"x1.6"	HT

* HT - Hi-Tech Ceramics, Alfred NY.
TT - Transtech, Adamstown MD.

The plates along with 1.5" diameter yttria stabilized ceria disks were also tested in the particulate apparatus. Most of the ceramic electrolytes were made by calcining, grinding and pressing the powders together. The powder used to make the thicker stabilized ceria disks was made by coprecipitation.

The conductivity of the electrolytes was measured with an AC resistance bridge at 1 KHz. The high frequency AC measurement eliminates the kinetic and mass transfer resistance of oxygen transfer at the electrodes. Typical resistance measurements for the electrolyte disks are given in Table 2. Conductivities of the electrolytes are calculated from the resistance and dimensions of the disks and are shown in Table 3.

Table 2
Resistance of Solid Electrolyte Disks in Ohms

Temperature °C	Zirconia	Ceria .8mm	Ceria .4mm	Bismuth
600	3			
550				3
500		5-6	10-12	16
450	55	13-17		16-38
400				80
350				200
300				360
250				960

Table 3
Conductivity of Solid Electrolyte Disks in (Ohm-cm)⁻¹

Temperature °C	Zirconia	Ceria .8mm	Ceria .4mm	Bismuth
600	6.6x10 ⁻³			
550				9.9x10 ⁻³
500		2.9x10 ⁻³	7x10 ⁻⁴	1.9x10 ⁻³
450	3.6x10 ⁻⁴	1.1x10 ⁻³		1.1x10 ⁻³
400				3.7x10 ⁻⁴
350				1.4x10 ⁻⁴
300				8.2x10 ⁻⁵
250				3.1x10 ⁻⁵

The conductivity of the stabilized zirconia and the coprecipitated stabilized ceria agreed with the literature data plotted in Figure 2. The calcined stabilized ceria and the stabilized bismuth have somewhat lower conductivities than the literature values. The lower conductivities may have been caused by increased grain boundary resistance in the disk. Some resistances were higher when electrocatalysts were placed on the disk surface.

2.4 Electrolyte Coating

A coating of yttria stabilized zirconia was applied to the yttria stabilized ceria disks. Use of this coating on ceria fuel cells has been described previously[2]. The coating prevented degradation of the anode. Anode degradation occurred when the ceria disk was exposed to 1.5 volts for more than an hour. The coating was also used on the cathode in order to increase the surface area. The coating was prepared from a solution of yttrium and zirconium salts mixed in the proper proportion. The solution was painted on the disk and fired at 1300°C. Other proprietary solid electrolyte coatings were supplied by IGR

Enterprises.

2.5 Electrocatalyst Application

The purpose of the electrocatalyst is to promote the selective reduction of NO and SO₂ over the reduction of oxygen on the cathode. Transition metal oxides, mixtures of transition metal oxides and perovskites were tested as electrocatalysts. Perovskites are transition metal oxide mixtures of definite chemical composition and crystal structure. Their properties, preparation methods and application are discussed in the next section. The transition metal oxide electrocatalysts came from two sources, commercially available resinate materials from Engelhard and proprietary formulations from IGR Enterprises.

The electrocatalyst materials from Engelhard are listed in Table 4.

Table 4
Organometallic and Resinate Solutions from Engelhard

Metal	Form	Metal %
Ruthenium	Met. Organic	
Chromium	Resinate	9.6
Molybdenum	Resinate	13.3
Vanadium	Metallo. Organic	
Cobalt	Resinate	12.0
Tungsten	Resinate	22.2

The Engelhard solutions are painted on the cathode side of the electrolyte and fired in air. The firing causes the oxide to form. Gold electrodes are applied after the electrocatalyst is fired. The ruthenium material is in the form of a thick paste. It is thinned with toluene to make it spreadable with a brush. The other materials can be applied directly. In some cases more than one coat was applied. The disk was dried at about 90°C

after each coat and then fired at 550°C to 1100°C. Direct application of the Engelhard chromium did not produce an adherent layer. However, A slurry of chromium (III) hydroxide in ammonia water fired on the disk at temperatures up to 1100°C did produced an adherent layer.

The transition metals were selected based on literature data showing that they were either catalytic for NO reduction or absorbed NO (Ru[9],Cr[10],Mo[11],Co[12],W[13]).

2.6 Perovskites

The methods of preparation and some properties of perovskite oxides as electrocatalysts for NO_x and SO₂ reduction were studied.

2.6.1 Perovskite Structure

Perovskite-type oxides constitute a group of compounds with a cubic structure and unit formula ABO₃. The structure is shown in Figure 8. The larger cation, A, situated at the center of the cube, is 12-coordinated with the oxide anions. The B cations occupy the corners of the cube and are in six-fold coordination with the anions. The oxygen atoms situated at the midpoints of the edges are each surrounded by two cations in position B and four cations in position A.

The position A in the structure is most frequently filled by alkaline, alkaline earth or rare earth (Ln) ions, although other cations may have the proper size for occupation of these sites [14]. A transition metal is the most usual B component in perovskite oxides.

The orbitals of the rare earth ions are so small that they

Figure 8
Perovskites Structure
and Composition

Unit formula ABO_3

The structure of perovskite. The mineral perovskite ($CuTiO_3$) has this cubic structure at high temperature. The A ion is in dodecahedral oxygen coordination, the B ion is in an octahedral oxygen cage.

A ions may be alkaline, alkaline earth or rare earth.

B ions - transition metals.

have very little interaction with each other or with electrons of the transition metal cations in position B. Therefore, the influence of the rare earth ions is derived mainly from the effect of ionic size on the unit cell parameters. These changes in the crystal dimensions may be expected to produce variations in the A-O and B-O interactions and in the physical and chemical properties of the compounds.

The properties of perovskites that are important in catalysis are primarily the stability of mixed valence states of transition metals, such as Co, Mn, Ru, in the perovskite structure, the stabilization of unusual valence states, the mobility of oxygen ions, and the stabilization of noble metal in high dispersion.

2.6.2 Perovskite Properties as Electrocatalysts for NO_x and SO₂ Reduction

Current catalytic NO reduction devices use Pt and Pt-Pd alloys which are costly and depend heavily on the continued availability of noble metals. Substitute catalysts include primarily non-noble metal oxides, but these suffer from relatively low catalytic activity, low thermal stability and often a lack of chemical stability in the exhaust environment [15].

The use of perovskite-type oxides avoids several of these objections, and these oxides have been widely investigated for this purpose.

Ru-based catalysts are the main candidates for NO reduction in automotive exhaust. But, ruthenium catalysts suffer from the high volatility of ruthenium oxides which leads to significant

losses of Ru [16,17]. The primary approach to that problem has been the stabilization of Ru in perovskite-related structure [18-22]. Useful ruthenates are the perovskites SrRuO_3 and LaRuO_3 .

The effect of SO_2 on the activity and selectivity of Ru-containing catalysts for the reduction of NO has been studied [23]. It shows that in the presence of SO_2 , the perovskites have appreciably better selectivity than Ru metal. Perovskites of transition metals have been shown to be catalysts for the reduction of SO_2 to elemental sulfur [24-27]. Catalysts such as LaTiO_3 , LaCoO_3 and $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ were used for this reaction. Carbon monoxide was used as the reducing agent.

The earliest application of perovskite oxides was as electrodes in fuel cells. For example, LaCoO_3 as a cathode material [28] in a cell operating at 1100°C has electronic conductivity of $800 \text{ ohm}^{-1} \text{ cm}^{-1}$.

Thus, the purpose of our study was to identify perovskite oxides which would not only be electronically conductive to substitute for the Au electrodes but also be catalytically active for NO_x and SO_2 reduction. Based on literature information, ruthenates and cobaltates were selected as possible candidates.

2.6.3 Perovskite Preparation Methods

Several methods have been described for the preparation of perovskites [29]. They can be classified as physical and chemical methods.

Physical Methods

- o spray-drying
- o freeze-drying

Chemical Methods

- o coprecipitation
- o complexation
- o thermal decomposition.

However, chemical methods are most frequently employed. The thermal decomposition method was selected to minimize the exposure of the YSC electrolyte to mechanical or thermal shock. The SrRuO_3 was synthesized from a stoichiometric solution of $\text{Sr}(\text{NO}_3)_2$ and RuCl_3 and $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ was formed from a stoichiometric solution of $\text{Sr}(\text{NO}_3)_2$, $\text{La}(\text{NO}_3)_3$, and $\text{Co}(\text{CH}_3\text{COO})_2$. These solutions were painted on the ceramic electrolyte surface and fired at low temperature to decompose the nitrates and acetates and then at high temperature for the removal of chloride and to sinter the powder. A thin perovskite layer was formed.

Atomic composition of perovskites was analyzed with a scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDS) and is shown in Figure 9. Cubic structure of perovskites was confirmed by x-ray diffraction. The X-ray diffraction pattern is shown in Figure 10. For x-ray diffraction analysis, a Philips Automated PW1710 Micro Processor Powder Diffractometry system was employed.

Data obtained from the diffractometer indicated that a high degree of polycrystalline material was present in both the SrRuO_3 and $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ samples. Since these samples were deposited on a ceramic substrate, a separate diffraction analysis was performed to check for possible data interference caused by the ceramic. All of the x-ray data was compared to A.S.T.M. powder diffraction files.

Some substrate interference is present; however, both

Figure 9
EDS of Strontium Ruthenate

NOSTD: STANDARDLESS ANALYSIS OF BULK SAMPLE

SPECTRUM: SRRU51

ELEMENT	RELATIVE K	WT%	ATOMIC %
S	0.0054	0.58	1.95
SR	0.1782	21.36	26.14
Y	0.1054	12.00	14.46
RU	0.1977	23.39	24.80
CE	0.3945	42.67	32.65
TOTAL		100.00	100.00

Figure 10
X-Ray Diffraction Analysis
of Strontium Ruthenate

SrRuO₃ Powder on Substrate

Substrate

compounds are present in a crystalline state. The degree of peak intensity on the attached charts is the result of sample concentration and crystal imperfection. Since a very small amount of compound was on the substrate surface, lower detection would be expected.

2.7 Electrode Application

Electrodes are applied to both sides of the ceramic electrolyte using organo-metallic inks, paints or paste. The paints and pastes are suspensions of the metal in an organic solvent similar to toluene with some binding material which provides adherence to the ceramic. The electrodes were applied to the ceramic electrolyte either by painting with a small brush or printing. The electrodes were dried at 90°C, and fired. Most tests had a single anode on one side of the electrolyte and a single cathode on the other side. Some tests were done with a reference electrode also present. The electrodes were tested for conductivity using an ohmmeter. If the resistance was greater than a few ohms, an additional coat of paint was applied and the piece was fired again. The piece was also tested for shorting between the anode and cathode. If the room temperature resistance between the anode and cathode was not infinite, the piece could usually be sanded around the edges to eliminate the electrical short. If the electrical short could not be removed the electrolyte would not be further tested.

Many types of electrode materials were tested. They include silver paste, gold paint, nickel ink and paste, stainless steel paste, titanium nitride paste, molybdenum disulfide, and iron

disulfide. These materials were selected as electrode candidates because of their electrical properties and corrosion resistance at operating temperatures. Besides being electrically conductive, the electrodes must be porous enough to allow the gases to reach the interface of the electrode and the electrolyte.

Silver paste 3353 with 64% by weight silver from Metech was painted on the disk. The disk was fired in air at 500°C for 10 minutes. A conductive coat of silver was obtained. Ceramic electrolyte pieces with silver electrodes had high currents and measurable NO reduction in the electrochemical reactor. However, when SO₂ was reduced, the current dropped toward zero. This may have been caused by the reaction of sulfur with the silver to give nonconductive silver sulfide. A silver palladium mixture from O. Hommel was also tested and gave similar results.

Nickel ink A-3207 from Engelhard was painted on stabilized zirconia and bismuth disks and fired in air at 850°C for 10 min. On some materials the coating turned green and was non-conductive. This may be due to the formation of nickel oxide. The dark green coating formed on the zirconia disk was conductive but did not have good adhesion properties. The nickel layer had many bubbles. Nickel paste number 5575 from Ferro was applied to the disk by painting and printing. The disks were fired in N₂ at 600°C for ten minutes. The painted samples had a high resistance even after many coats. The printed samples had a thick layer of nickel which was conductive. However, when the printed disk was tested in the reactor, hardly any current could be drawn from the

disk. The nickel layer may have been non-porous and too thick preventing gas from reaching the electrode electrolyte interface.

A stainless steel coating, Duralco 230 by Cotronics Corporation was tried. The material came in two parts, a liquid and a powder which were mixed together and applied to the disk. The disk was fired at 350°F for one hour. The resulting layer was non-conductive (resistance greater than a megaohm).

A titanium nitride, TiN, coating from ZYP Coatings was tried. The product is a suspension of TiN formulated to give a coating with good adherence to ceramics and metals. A cured coating has 75% TiN. TiN has a resistivity of 21.7 microhm-cm at room temperature. Samples were fired in air and in nitrogen at 400°C to 600°C. The resulting golden brown electrodes had resistances in the kilo-ohm range even after several coats.

Other nonmetals such as molybdenum disulfide (MoS_2), iron disulfide and perovskites were also tested as electrodes. A conductive MoS_2 layer was obtained when the sample was fired in nitrogen, but when this disk was exposed to oxygen at high temperature it oxidized and became nonconductive. The iron disulfide sample was nonconductive. Perovskites, such as $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ are known to be electronic and ionic conductors [30]. However, only one lanthanum cobaltate perovskite prepared by Helipump had a measurable conductivity at room temperature. More experimentation is needed in the synthesis, application and sintering of perovskites to ceria disks.

A gold paint from Engelhard (Hanovia), called liquid bright gold, was tested. It is a solution of 10% organometallic gold in an organic liquid. The disk was painted and fired at 500°C. One

to 2 coats produced a conductive layer with a resistance of less than an ohm. These disks were subsequently tested in the reactor and gave excellent results. The gold was not effected by the reduction of SO_2 . Most of the electrochemical experiments were done with gold electrodes.

The gold electrode did not need to be very thick. Gold is one of the three most conductive metals, having a resistivity of 6.6×10^{-6} ohm-cm at 450°C (conductivity $150,000 \text{ (ohm-cm)}^{-1}$) and making it 100 million times more conductive than the solid electrolyte. The thickness of the gold layer was estimated by weighing the disk before and after painting and firing. The resulting layer thickness is about 1 to 2 thousand angstroms.

3. EXPERIMENTAL NO AND SO₂ REDUCTION DATA

Most experiments were run at 450°C to 500°C at applied voltages of up to 1.5 volts and a feed gas flow rate of 0.1 liters/min. Gas mixtures of 500 ppm NO and 2700 ppm SO₂ with 0 to 2% oxygen in nitrogen or helium were fed to the electrochemical reactor. The NO or SO₂ concentration in the outlet gas stream were measured as a function of time with and without an applied voltage. The electrochemical NO or SO₂ reduction was determined from the steady state gas stream concentrations.

The current passing through the cell was also measured. Current or coulombic efficiencies were calculated from the gas flow, reduction and current. The current efficiency measures the fraction of the current that actually reduces NO or SO₂. The electrical power costs of the electrochemical reactor are inversely proportional to the current efficiency. It is defined as the current calculated from Faraday's law and divided by the measured current (equation 1). The Faraday's law current, equation 2, is proportional to the gas flow and the measured reduction.

$$\text{current efficiency} = 100\% * i_F / i \quad (1)$$

$$i_F = G * (C * 10^{-6}) * N * F / (22.4 * 60) \quad (2)$$

where:

- i = measured current in amps.
- i_F = Faraday's Law current in amps.
- G = gas flow in standard liters/minute
- C = concentration change in ppm
- N = electrons per molecule reacted (equivalents/gmole)
 - 2 for NO
 - 4 for SO₂
- F = Faraday's Constant
 - 96,487 coulombs/ equivalent

The constants 22.4 and 60 convert the gas flow from liters/min. to gmoles/sec.

Current efficiency's are less than 100% due to two factors, electronic conduction and oxygen reduction. Solid electrolytes conduct electrons as well as oxygen ions although their electronic conductivity is approximately 100 times smaller than their ionic conductivity. The electronic conductivity will increase if the electrolyte is partially reduced to a lower valence state or to the elemental metal by application of voltages above the decomposition potential of the electrolyte. Electronic conduction has no kinetic or mass transfer resistance at the electrode surface as does oxygen ion conduction. This effect increases the ratio of electronic to ionic current and decreases the current efficiency.

Oxygen reduction is the main factor that reduces current efficiency. The oxygen concentration in the gas can be 10 to 100 times that of the NO or SO₂ and the thermodynamic potential needed for oxygen pumping is zero. In experiments where no oxygen is fed to the cell the oxygen concentration is still on the order of 10 ppm due to impurities in the gas cylinder and the formation of oxygen due to the reduction of NO or SO₂ (the anode and cathode are not separated).

3.1 Reduction Without Electrocatalysts

A NO reduction of 8 ppm was measurable at 1.2 volts on a yttria stabilized zirconia disk with 100 cc/min. of 500 ppm NO at 450°C. The NO reduction increased to 20 ppm at 1.5 volts. When the flow was reduced to 20 cc/min., the reduction increased

further to 100 ppm at 1.5 volts. Current efficiencies of about 30% were obtained. A reduction of 7% to 12% of SO_2 was measured with the GC at 1.5 volts with a flow rate of 20 cc/min. of 2700 ppm SO_2 . The current efficiency was greater than 70%. The SO_2 reduction was too small to measure at 100 cc/min. due to the inaccuracy of the GC. The NO reduction in the presence of oxygen was 10 ppm at 1.5 volts and 100 cc/min with a current efficiency of about 2%. Currents were about 1 mA without oxygen and 4 mA with oxygen at 1.5 volts.

A reduction of 2 to 5 ppm NO was measured on a bismuth disk at 450°C , 500 ppm NO, 100 cc/min. and 0.8 volts. The current was 13 mA and the current efficiency was 0.4%. When one volt was applied at an NO flow of 20 cc/min. for about an hour the current rose from 13 to 160 mA but the NO concentration only dropped 8 ppm. When bismuth disks were exposed to voltages above 0.5 volts the electrode and electrolyte degraded. The electrode became pitted and parts of the electrolyte changed color. Early measurements at 0.4 volts on tungsten stabilized bismuth with gas streams of NO_2 indicated that NO_2 was being reduced but it was not known if it was reduced to nitrogen or NO. These measurements were done with an FT-IR using the absorbance at 1600 cm^{-1} as a measure of the NO_2 concentration. The NDIR used in later experiments measures total NOx reduction (NO and NO_2).

Table 5 shows the measured NO reduction in ppm and percent, measured current in milliamps, and calculated current efficiency on yttria stabilized ceria disks as a function of applied voltage, temperature, gas flow rate and oxygen content of the

gas. The measured currents are also plotted in Figure 11. The currents for the YSZ disk at 450°C in NO with and without 2% oxygen are also plotted for comparison.

Table 5
NO Reduction on Yttria Stabilized Ceria

Temperature °C	Voltage	Gas Flow cc/min	NO Reduction ppm %		Current mA	Current Efficiency %	
<hr/>							
0% Oxygen 450°C	1.0	100	5	1%	1.0	7	
	1.0	20	25	6%	1.0	7	
	500°C	0.8	50	6	1%	.5	7
	.95	100	11	2%	1.0	16	
	1.0	100	36	7%	1.7	30	
	1.2	100	137	28%	7.0	28	
	1.2	50	203	42%	6.4	23	
	2% Oxygen 450°C	1.0	100	3	1%	12	0.4
1.0		50	6	2%	12	0.4	
500°C		1.0	100	2	1%	11	0.3

The 0% oxygen runs were made with a feed gas concentration of about 450 ppm NO and the 2% oxygen runs were made at about 350 ppm NO. At 450°C NO reduction was observed at lower voltage on ceria than on zirconia. The NO reduction and current increases sharply with an increase in applied voltage. The NO reduction also increases rapidly with temperature. The reduction is roughly inversely proportional to the feed gas flow. The NO reduction and current efficiencies are much lower and the currents are much higher in the presence of oxygen.

The SO₂ reduction on yttria stabilized ceria at 450°C was also measured with the GC. With a feed gas of 100 cc/min of 2700 ppm SO₂ a reduction of 0% to 1% was measured at 1.0 volts and 4% to 6% at 1.2 volts. Current efficiencies were near 100%.

Reductions of a few percent were also measured in 1800 ppm SO₂ and 2% oxygen. At 500°C and a feed gas of 100 cc/min of 2700 ppm SO₂, reductions of 2% to 4% were measured at 1.0 volts and 3% to 5% were measured at 1.2 volts. Current efficiencies were near 100%. The accuracy of the SO₂ concentration measurements with the GC was much less than the NO concentration measurements.

3.2 Solid Electrolyte Coatings

Solid electrolyte coatings were applied to the ceria disks to prevent anode degradation and to enhance surface area. The preparation methods are described in section 2.4. Table 6 shows the measured NO reduction at 500°C and 500 ppm NO on a yttria stabilized ceria disk with a solid electrolyte coating on the cathode for various coating firing temperatures and feed gas flow rates.

Table 6
NO Reduction on Yttria Stabilized Ceria with a Solid
Electrolyte Coating on the Cathode as a Function of
Coating Preparation Temperature

Temperature 500°C, 500 ppm NO, no oxygen

Firing Temperature	Gas Flow cc/min	NO Removal (%)
Low	100	45
Low	30	70
Medium	100	28
High	100	20
no treatment	100	8-25

The lower firing temperature gave the best results. Less sintering probably occurred at the lower temperature producing a larger surface area. Placing the coating on the anode instead of the cathode gave an NO reduction of 10% at the same conditions

(100 cc/min).

3.3 Electrocatalyst Coatings (IGR)

The first electrocatalysts tested on yttria stabilized ceria disks were supplied by IGR Enterprises. The NO reduction in the absence of oxygen on these electrocatalysts is shown in Table 7. As seen, electrocatalyst A showed a better performance in terms of the percentage of NO removal. At 30 cc/min of 500 ppm NO (balanced with N₂), a 75% NO removal was achieved. Current efficiencies ranged from a few percent to 37%.

Table 7
NO Reduction on IGR Electrocatalysts at Different
Firing Temperatures

Conditions: 500°C, 100 cc/min of 500 ppm NO, 0% O₂

Electrocatalyst	Firing Temperature	NO Removal (%)
A0	LOW	60
A0	MEDIUM	54
A0	HIGH	55
B	LOW	30
B	MEDIUM	27
B	HIGH	9
C	LOW	15
C	HIGH	18
D	LOW	56

All the experiments were repeated with a gas stream of 2% O₂ and 500 ppm NO. Among all the electrocatalysts, only electrocatalyst A showed some NO reduction. For 100 cc/min of 0.3% O₂ and 500 ppm NO, 45% removal of NO was achieved.

Other formulations of electrocatalyst A were made which had measurable NO reductions in the presence of 1% and 2% oxygen.

The NO reductions are shown in Table 8 as a function of catalyst formulation and firing temperature in 0%, 1% and 2% oxygen.

Table 8
NO Reduction as a Function of IGR Electrocatalyst
and Oxygen Concentration

Conditions: 100 cc/min of 500 ppm NO at 1.5 volts and 500°C

Electro Catalyst	Firing Temp.	% NO Reduction		
		0% O ₂	1% O ₂	2% O ₂
A1*	T1	61	4	-
A1	T4	46	15	3
A1	T5	57	2.5	0
A2*	T0	58	-	-
A2	T1	47	4	0
A2	T2	45	8	0
A2	T3	35	12	2.5

500°C < T0 < T1 < T2 < T3 < T4 < T5

* Different formulations of electrocatalyst A

The current efficiencies for the NO reductions are shown in Table 9.

Table 9
Current Efficiency for NO Reduction as a Function
of IGR Electrocatalyst and Oxygen Concentration

Conditions: 100 cc/min of 500 ppm NO at 1.5 volts and 500°C

Electro Catalyst	Firing Temp.	Current Efficiency %		
		0% O ₂	1% O ₂	2% O ₂
A1*	T1	4.1	0.2	-
A1	T4	3.2	1.0	0.18
A1	T5	11.5	0.15	0
A2*	T0	17.7	-	-
A2	T1	5.7	0.4	0
A2	T2	6.7	0.9	0
A2	T3	3.6	1.2	0.2

500°C < T0 < T1 < T2 < T3 < T4 < T5

* Different formulations of electrocatalyst A

Sulfur dioxide reductions were also measured on electrocatalysts A and B. The percent reduction as measured on

the GC and current efficiency are shown in Table 10.

Table 10
SO₂ Reduction and Current Efficiency
as a Function of IGR Electrocatalyst

Conditions: 100 cc/min of 2700 ppm SO₂ and 0% O₂
at 1.5 volts and 500°C

Electro Catalyst	% SO ₂ Reduction	Current Efficiency %
A3	6	23
B1	6	22
B2	6	27

3.4 Single Transition Metal Electrocatalyst Coatings

A series of Engelhard electrocatalysts were applied to the yttria stabilized ceria disks and were tested for NO and SO₂ reduction. The catalysts and coating procedures are described in section 2.5. The measured NO reductions in 0%, 1% and 2% oxygen for different electrocatalyst coatings and preparation procedures are shown in Table 11.

The measured NO reductions decrease as the oxygen content of the gas increases. The best results in 1% and 2% oxygen were obtained on the ruthenium electrocatalyst.

The current efficiency for NO reduction for the same conditions as Table 11 are given in Table 12.

Table 11
NO Reduction as a Function of Electrocatalyst
and Oxygen Concentration

Conditions: 100 cc/min of 500 ppm NO at 1.5 volts and 500°C

Electro Catalyst	# of Coats	Firing Temp.	0% O ₂	% NO Reduction 1% O ₂	2% O ₂
W	1	550°C	14	2.5	1.5
W	3	550°C	8	1	0
W	3	700°C	9	0	-
<hr/>					
Ru	1	550°C	47	5	0
Ru	3	550°C	(15% at 1.2V)	7	5
Ru	3	550°C		11	4
Ru	3	650°C		3	-
Ru (S*)	3	550°C	12	10	4.5
Ru	6	600°C	32	1	0
Ru	6	700°C	15	2	2
<hr/>					
Cr	1	500°C	17	0	-
Cr	1	550°C	6	0	-
Cr	1	1100°C	1	0	-
V	1	1100°C	2	1	-
V	1	1100°C	4	0	-
Co	1	550°C	37	1	1

* Sulfided in 1% H₂S at 300°C

Table 12
Current Efficiency for NO Reduction as a Function
of Electrocatalyst and Oxygen Concentration

Conditions: 100 cc/min of 500 ppm NO at 1.5 volts and 500°C

Electro Catalyst	# of Coats	Firing Temp.	Current Efficiency %		
			0% O ₂	1% O ₂	2% O ₂
W	1	550°C	1.0	0.2	0.15
W	3	550°C	3.6	0.8	0
W	3	700°C	0.4	0	-
<hr/>					
Ru	1	550°C	2.8	0.2	0
Ru	3	550°C	(5.9 at 1.2V)	0.9	1.1
Ru	3	550°C	2.3	0.4	0.1
Ru	3	650°C	1.8	0.3	-
Ru (S*)	3	550°C	0.8	0.6	0.2
Ru	6	600°C	3.0	0.01	0
Ru	6	700°C	2.0	0.1	0.02
<hr/>					
Cr	1	500°C	0.04	0	-
Cr	1	550°C	0.04	0	-
Cr	1	1100°C	0.2	0	-
V	1	1100°C	0.2	0.07	-
V	1	1100°C	0.1	0	-
Co	1	550°C	9.0	0.3	0.3

* Sulfided in 1% H₂S at 300°C

Again the ruthenium electrocatalyst shows the best current efficiency in 2% oxygen. The sulfided ruthenium electrocatalyst was also tested in 4% oxygen where a 2.5% NO removal and 0.07% current efficiency were obtained. Higher current efficiencies were obtained in the absence of oxygen at 1.2 volts. The 6 coat Ru disk fired at 600°C gave a 15% reduction and 10% current efficiency and the Co disk gave a 30% reduction and 15% current efficiency at 1.2 volts.

Sulfur dioxide removal was measured on tungsten, ruthenium, cobalt and vanadium electrocatalyst. The results are given in Table 13.

Table 13
SO₂ Reduction and Current Efficiency
as a Function of Electrocatalyst

Conditions: 100 cc/min of 2700 ppm SO₂ and 0% O₂
at 1.5 volts and 500°C

Electro Catalyst	# of Coats	Firing Temp.	Gas Flow cc/min	% O ₂	% SO ₂ Reduction	Current Efficiency %
W	1	550°C	100	0	4-6	19
Ru	3	550°C	100	0	7-11	4
Ru	6	600°C	100	1	18-23	2
Ru	6	700°C	100	1	10-13	18
Co	1	550°C	33	0	2-5	58
V	1	1100°C	30	1	8-9	1

3.5 Mixed Transition Metal Oxide Electrocatalysts

Mixtures of the electrocatalysts used in the single electrocatalyst tests were applied to the yttria stabilized ceria disks. The measured NO and SO₂ reductions in 0%, 1% and 2% oxygen for different electrocatalyst mixtures are summarized in Table 14.

Table 14
NO_x and SO₂ Reduction as a Function of Mixed Oxide
Electrocatalyst and Oxygen Concentration
(measured as % NO and SO₂ reduction)

Electrocatalyst	Percent NO Removal Per Cent Oxygen			Percent SO ₂ Removal	
	0%	1%	2%	0%	1%
Ru + Co	5-44	0-6	0-4	6-14	11-13
Ru + V	1-35	0-1	0-1	14-17	-
Ru + Cr	0-10	4	2	-	-
Co + Mo	2-7	0	-	6	-

(Ru + Co) Electrocatalysts: Three (Ru + Co) disks were tested. Two different procedures were used to prepare the disks. The Ru and Co electrocatalysts were coated and fired separately on one of the disks (Co was fired at 1100°C, and Ru at 600°C). In applying the electrocatalysts on other two disks, a mixture solution of Ru and Co was prepared and coated on the disks. The disks were fired at 600°C. The latter procedure, overall, has shown better results for removing NO and SO₂ from the gas. A typical SO₂ reduction of 12%, in 1% O₂, with a current efficiency of 12-16%, was achieved with the (Ru + Co) disks, fired at 600°C. The current efficiencies in NO were up to 4.4% without oxygen and 1% in 1% oxygen.

(Ru + V) Electrocatalysts: Two (Ru + V) disks were tested. The (Ru + V) disks were fired at 600°C. One disk did not show any selectivity in removing the NO, however, a second disk showed a 35% reduction in the absence of oxygen and a 1% reduction in 2% oxygen. The current efficiencies were 2.5% without oxygen and 0.02% with oxygen. Tests with a mixture of 500 ppm NO and 2700 ppm SO₂ resulted in 17% SO₂ removal with a current efficiency of 18%.

(Co + Mo) Electrocatalysts: The (Co + Mo) disk was fired at 800°C. This disk did not show any selectivity for removing NO, and only 6% SO₂ removal and 5% current efficiency was measured by the GC. No further tests were carried out with the disk.

(Ru + Cr) Electrocatalysts: The (Ru + Cr) disk was prepared by first applying Cr and firing at 1100°C, and then coating Ru on the disk and firing at 600°C. A 2% NO removal was obtained with this disk in 2% oxygen. Current efficiencies were less than 1% with and without oxygen.

3.6 Perovskite Electrocatalysts

Three different perovskites were tested as electrocatalyst on yttria stabilized ceria disks. These included lanthanum strontium cuprate (La_{.9}Sr_{.1}CuO₃), lanthanum strontium cobaltate (La_{.9}Sr_{.1}CoO₃ and La_{.5}Sr_{.5}CoO₃) and strontium ruthenate (SrRuO₃). The properties and preparation methods for the perovskites are presented in section 2.6. The measured NO reductions and current efficiencies in 0%, 1% and 2% oxygen on the perovskite electrocatalysts are shown in Table 15. A La_{.5}Sr_{.5}CoO₃ perovskite was also tested but there was no reduction in the absence of oxygen. Strontium ruthenate disk number two gave the best NO reductions and current efficiencies in the presence of oxygen. The current efficiency of this disk is plotted as a function of oxygen concentration and voltage in Figure 12. The current efficiency in 1% oxygen and 1.2 volts is higher than any other electrocatalysts measured.

FIGURE 12
 NO CURRENT EFFICIENCY WITH A SrRuO_3 ELECTROCATALYST
 ON A YTTRIA STABILIZED CERIA ELECTROLYTE DISK

Table 15
NO Reduction and Current Efficiency as a
Function of Perovskite Electrocatalyst

Conditions: 100 cc/min of 500 ppm NO

	NO reduction %			Current Efficiency %		
	0% O ₂	1% O ₂	2% O ₂	0% O ₂	1% O ₂	2% O ₂
1.5 Volts						
La _{0.9} Sr _{0.1} CuO ₃	2	2	1	.09	0.06	0.04
Ru + La _{0.9} Sr _{0.1} CuO ₃	23-28	1-2	1-2	.9	0.03	0.1
La _{0.9} Sr _{0.1} CoO ₃	28	1	1	3.2	0.2	0.2
SrRuO ₃ (1)	16	6-7	4-5	1.7	1.5	0.9
SrRuO ₃ (2)	25	11	2	5.2	4.7	0.7
SrRuO ₃ (3)	25	-	-	4.6	-	-
1.2 Volts						
SrRuO ₃ (2)	17	8	1	22.	6.6	0.8
SrRuO ₃ (3)	13	-	1	1.4	-	0.7

(1) Disk fired at 800°C

(2) Disk fired at 900°C

(3) Two coats of perovskite

3.7 NO and SO₂ Reduction on Ceria and Zirconia Plates

NO and SO₂ reductions were measured on yttria stabilized ceria and zirconia plates coated with ruthenium and strontium ruthenate electrocatalysts as a function of temperature, applied voltage and oxygen content of the gas. The plate dimensions are given in Table 1 of section 2.3. The ceria plate has about 7 times the area of the ceria disks.

The ceria and zirconia plates were tested in the stainless steel reactor described in section 2.2. When SO₂ and oxygen both flowed through the reactor at the operating temperature, the outlet SO₂ concentration was lower than the inlet. This occurred even when the reactor was empty (no solid electrolyte present). The change in SO₂ concentration was temperature and oxygen

concentration dependent. As the temperature or oxygen concentration was decreased the outlet SO_2 concentration would rise to the inlet concentration. This phenomenon may be due to catalytic oxidation of some of the SO_2 to SO_3 on the walls of the stainless steel reactor. The electrochemical SO_2 reductions in oxygen reported below do not include this catalytic reaction. All SO_2 reductions on the ceria and zirconia plates were done with the NDIR. The NDIR does not measure the presence of SO_3 .

Table 16 shows measured individual and simultaneous NO and SO_2 reductions and current efficiencies, in parentheses, for a ceria plate coated with ruthenium on the cathode. The temperature and NO or SO_2 feed composition in ppm are shown at the top of each box. The current efficiencies listed for the combined NO and SO_2 reductions are the sum of the NO and SO_2 current efficiencies and are due mostly to the SO_2 .

Both the NO and SO_2 reductions are highly temperature dependent. The amount of NO reduced at 459°C is about 12 times higher than at 387°C in both 0% and 1% oxygen at the same voltage. The SO_2 reductions are 4 to 7 times higher at 487°C than at 387°C . Based on this data the NO activation energy is approximately 30 Kcals/mole and the SO_2 activation energy is about 17 Kcals/mole.

The NO reductions and current efficiencies are strongly dependent on oxygen concentration while the SO_2 reductions and efficiency are less dependent. Although the reductions increase with increasing applied voltage the current efficiencies tend to decrease.

Table 16
NOx and SO₂ Reduction on a Ruthenium Electrocatalyst
Ceria Plate (2.4"x2.4") as a Function of Oxygen
Concentration, Temperature and Voltage

(measured as % NO and SO₂ reduction)

Gas flow = 100 cc/min NO runs

= 155 cc/min SO₂ runs

Volts	NO reduction % (cur. eff.)			SO ₂ reduction % (cur. eff.)		
	0% O ₂	1% O ₂	2% O ₂	0% O ₂	1% O ₂	
<u>387°C</u>				<u>387°C</u>		
				2700 ppm		
1.2 V	8% (15%)	>.5%		1.9% (77%)		
1.5 V	13% (13%)	.5% (.5%)		2.4% (26%)		
<u>459°C</u>				<u>487°C</u>		
				2400 ppm	1540ppm	
1.0 V	68% (49%)	6% (.5%)	6% (.5%)	7% (63%)	7.9% (48%)	
1.2 V	84% (6%)	6% (.3%)	6% (.3%)	8.9% (47%)	11% (46%)	
1.5 V				19% (52%)	14% (36%)	

Simultaneous NO and SO₂ Reduction at 474°C
Gas Flow = 100 cc/min

Volts	0% Oxygen			1% Oxygen		
	NO % 230 ppm	SO ₂ % 1160 ppm	cur. eff. NO+SO ₂	NO % 220 ppm	SO ₂ % 580 ppm	cur. eff. NO+SO ₂
0.8	9.6%	8.6%	77%	1%	13%	45%
1.0	26%	10.8%	71%	1%	18%	44%
1.2	22%	13.4%	51%	1%	22%	40%
1.5	74%	24.9%	64%	1%	27%	33%

The amount of NO reduction decreases in the presence of SO₂. However, the SO₂ reduction is not effected by the presence of NO. The total current efficiency is higher than the individual efficiencies when both NO and SO₂ are present and oxygen is absent and about the same as the SO₂ current efficiency when oxygen is present.

NO (450 ppm) and SO₂ (2700 ppm) reductions were also measured in 0%, 1% and 2% oxygen at 500°C on 1.6" by 2.5" by 3 mm 8% yttria stabilized zirconia (YSZ) foam coated with gold electrodes. The high surface area foam cathode was coated with a strontium ruthenate (SrRuO₃) perovskite electrocatalyst. The NO and SO₂ reductions and current efficiencies at applied voltages of 0.5 to 1.8 volts and a gas flow of 100 cc/min are given in Table 17.

Table 17
NOx and SO₂ Reduction on YSZ with a Strontium
Ruthenate Electrocatalyst as a Function of Oxygen
Concentration and Voltage

Conditions: 500°C, 100 cc/min

NO feed conc. 430 to 530 ppm

SO₂ feed conc. 1650 to 2500 ppm

Volts	NO reduction %			Current Efficiency %		
	0% O ₂	1% O ₂	2% O ₂	0% O ₂	1% O ₂	2% O ₂
	530 ppm NO	480 ppm NO	430 ppm NO			
0.5	.8			4		
0.8	1.7		1.4	5		2
1.0	3.0-4.7	3.5		7-11	5	
1.2	4.4-8.0	4.6	1.6	8-13	6	2
1.5	6.6-17	5.0		10-20	5	

Volts	SO ₂ reduction %			Current Efficiency %		
	0% O ₂	1% O ₂	2% O ₂	0% O ₂	1% O ₂	2% O ₂
	2500 ppm	1890 ppm	1650 ppm			
1.0	1.8		1.6	51		25
1.2	2.6	2.3	2.2	64	31	26
1.5	3.9	2.9	2.4	74	29	21
1.8	5.1	3.5	3.0	79	28	20

The reductions are lower on YSZ than on ceria but some of the current efficiencies are higher. The current efficiency improves with increasing voltage in the absence of oxygen which is the opposite of what happens on ceria. The efficiency remains nearly constant in the presence of oxygen. The current efficiency for NO in 1% oxygen is nearly the same as measured on one of the ceria disks coated with SrRuO_3 .

A ceria plate coated with SrRuO_3 was electrochemically tested, exposed to flyash and then electrochemically retested. The plate was exposed to flyash in the particulate testing apparatus at Cottrell Environmental Sciences. The flyash testing apparatus and testing procedure are described in section 4. The plate was exposed to flyash for 20 hours at 800°F. A dust of flyash particles was left on the plate during electrochemical retesting in order to simulate conditions in a coal fired power plant. The electrode resistances increased from 1.3 ohms before testing to 2.4 ohms after flyash exposure. The NO and SO₂ reductions and current efficiencies, in parentheses, before and after exposure at applied voltages of 0.5 to 1.5 volts and at a gas flow of 100 cc/min are given in Table 18.

Table 18
NO_x and SO₂ Reduction at 500°C on a SrRuO₃ Electrocatalyst
Ceria Plate (2.4"x2.4") Before and After Exposure to Flyash

Before Exposure

Volts	NO reduction % (cur. eff. %)	
	0% O ₂ 453ppm NO	2% O ₂ 373ppm NO
0.8	20.5% (7.8)	4.0% (.9%)
1.0	49.2% (10.0)	4.0% (.6%)
1.2	67.3% (10.1)	-
1.5	82.3% (8.6)	4.0% (.3%)

After Exposure to Flyash for 20 hrs. at 800°F

Volts	NO reduction % (cur. eff. %)		SO ₂ reduction % (c.f.%)	
	0% O ₂ 447 ppm NO	2% O ₂ 382 ppm NO	0% O ₂ 2410 ppm SO ₂	2% O ₂ 1300 ppm
0.5	5.1% (10%)	1.3% (1.6%)		
0.8	7.8-20.1% (12-29%)	5.2% (3.3%)		
1.0	8.5-29.3% (11-25%)	5.2% (2.0%)	2.4% (35%)	
1.2	11.5-32.4% (7-20%)	5.2% (1.3%)	2.7% (25%)	
1.5	13.9-44.7% (6-12%)	5.2% (0.8%)	5.0% (27%)	3% (6%)

The NO reduction in the absence of oxygen was less after exposure to flyash but the reduction in the presence of oxygen was slightly improved. The SO₂ reduction was also lower after exposure than the unexposed ruthenium ceria plate in Table 16. However, since the electrode and electrolyte were not damage by the flyash and the NO and SO₂ reduction were not severely effected, the electrochemical process can be used in a flyash laden stream. More testing would be needed to see if there is degradation due to flyash exposure over weeks and months.

The plate reactor has as shorter gas residence time than the disk reactor. This shorter residence time along with the quick response of the NDIR's, permits observation of the dynamics of the NO and SO₂ reactions over time intervals as small as a minute. When voltage is applied to the electrodes, the initial SO₂ and NO reductions in the presence of oxygen are greater than

their steady state values. Also when the applied voltage removed the NO and SO₂ concentrations do not immediately return to the values they had before voltage was applied but rise above these values for a few minutes. This phenomenon has been observed on both the ruthenium and SrRuO₃ electrocatalysts on ceria and the SrRuO₃ electrocatalyst on zirconia. Also, if a negative voltage is applied to the plate the NO or SO₂ concentration will increase line value for a few minutes and then begin to drop. This data is consistent with a voltage dependent absorption of NO and SO₂ on the electrocatalyst cathode surface.

4. PARTICULATE CONTROL EXPERIMENTS

4.1 Objectives and Approach

The use of solid state ceramic electrolytes for SO_2 and NO_x reduction requires operation at temperatures exceeding 800°F , in order for the ionic conductivity of the electrolyte to be high enough for efficient operation. For a coal fired boiler, this means that an electrolytic SO_2/NO_x removal system must be placed between the economizer and the air heater. The concern over the effects of flyash deposition on the electrode surfaces led to the initiation of the research reported here.

The first objective of this work was to determine the degree of degradation of ionic conduction caused by the deposition of flyash on the electrode surface. The second objective was to demonstrate an effective means to restore electrical performance by removing the deposition or by demonstrating a method by which to prevent the deposition from occurring in the first place.

The experiment was designed to satisfy both objectives within the context of a single test procedure. A test apparatus was designed to produce flyash laden flue gas and to simultaneously expose as many as nine, energized electrolytic cells to this flow. The flue gas was high in oxygen and contained no sulfur dioxide, so the ability of the cells to pump molecular oxygen was used to monitor their performance. It was assumed that flyash deposition would degrade molecular oxygen pumping in the same way as oxygen obtained from SO_2 .

Provisions were made such that some of the electrolytic cells were periodically cleaned of flyash by means of jets of compressed air, simulating soot blowing. Also some of the cells

were preceded by filters which would simulate an upstream baghouse and would serve to prevent flyash from reaching the cells.

The experiment was designed for long term operation, since dust deposition on surfaces and filters requires long times to fully develop. A pulse jet filter system was provided for each filter to periodically dislodge accumulated filter cake in order to allow continuous operation.

Several filter media were tested, since filters capable of operation at temperatures higher than 500°C are not yet well characterized with respect to pressure drop and particulate penetration. Metallic filters are available for temperatures up to 1000°F, and ceramic filters are available for temperatures up to 2000°F. Two metal and two ceramic filters were chosen for this test program.

Testing began on March 24, 1989, and the last operation of the apparatus was on December 12, 1989. During this period, a cumulative test time of over 180 hours was achieved.

4.2 Experimental Apparatus

4.2.1 Flow System

A nine-element apparatus used for the testing described by this report is shown schematically by Figure 13. This apparatus was designed to simultaneously operate nine, 1' x 1' filter panels, followed by nine, 1" x 2" electrolyte-electrode cells. Each filter-cell module was assembled as shown in Figure 14. The filter modules were then mounted on the common housing such that the filter planes were vertical as shown in Figure 13.

Figure 13

High Temperature Filtration Test Stand

SIDE VIEW

FRONT VIEW

The hot process gas was produced by a 60,000 Btu/hr. natural gas burner. Flyash was mixed with the hot gas upstream of the filter modules. An Acrison feeder was used to meter the ash, such that the desired particulate loading was achieved. The gas flow was evenly distributed over the width of the common housing by means of vanes and perforated plates with the flow expansion inlet. The gas subsequently made a 90° turn into the individual filter modules, and immediately passed through the filter panels. The gas then flowed past electrolytic cells which were mounted within the modules as shown in Figure 14. Downstream orifice plates were used to measure the flow passing through each filter cell module. The flow rates were adjusted by means of in-line ball valves.

The nine individual flows were subsequently recombined within a common manifold. A fan was used to draw the gas through the system. Ambient dilution air was mixed with the high temperature process gas just upstream of the fan inlet in order to protect the fan from excessive temperature.

A pulse jet type cleaning system was utilized to allow continuous operation over long time periods. Each filter module contained four, 1/4", compressed air nozzles, directed at the back face of the filter panel. The filter modules were cleaned in sequence by pressurizing the nozzles with a 200 millisecond pulse of 100 psi air. It was found that this yielded an instantaneous reverse air flow rate of 18 cfm per square foot of filter surface and a total reverse air volume of .06 ft³ per square foot of surface. These values are similar to those found

Figure 14
Individual Filter Cell

for commercial pulse-jet filters.

The electrolytic cells were cleaned in a similar fashion. Two compressed air nozzles were supplied for each cell, one nozzle directed at each electrode face. These nozzles were pressurized in the same manner as the filter cleaning nozzles.

The ash used for testing was obtained from the precipitator hoppers of Public Service Electric and Gas Company's Mercer Station. The ash was generated from the combustion of coal with average as received properties:

6.53%	Moisture
5.45%	Ash
.84%	Sulfur
13,661	Btu/lb

A mineral analysis of the flyash is given in Table 19. The ash particle size is given by Figure 15. The mass mean diameter is 7.8 microns and the standard deviation is 3.43, values typical for PC fired boilers.

Table 19
Ash Mineral Analysis

<u>Mineral</u>	<u>Wt. Percent</u>
SiO ₂	38.71
Al ₂ O ₃	26.61
TiO ₂	1.33
Fe ₂ O ₃	15.13
CaO	5.56
MgO	1.68
Na ₂ O	1.40
K ₂ O	2.21
SO ₃	2.98
P ₂ O ₅	0.34
L.O.I.	3.22
Undet.	0.87

Figure 15

Fly Ash Particle Size Distribution

4.2.2 Measurement Methods

Temperatures, flow rates, particulate loading, pressure drops and electrolyte currents are parameters that define system performance, and as such were routinely monitored. Gas temperatures were measured by means of thermocouples at the gas burner exit, within the common housing, and within each filter module. Gas flow rates were measured by means of the orifice plates installed downstream of each filter module. The pressure drops across each filter were measured by means of U-tube manometers.

Particulate loading was measured by the insertion of an Alundum thimble filter downstream of the orifice plate. This pre-weighed thimble was allowed to filter the full flow of one filter module for several hours and was subsequently weighed.

The electrolyte performance was determined by applying one volt across the electrodes and measuring the resulting ionic oxygen current across the electrolyte. The electrical schematic of this system is shown in Figure 16.

4.2.3 System Operation

The system was brought up to temperature with the ash feed and filter cleaning system off. Once the operating temperature was achieved, the ash feed and compressed air pulse cleaning systems were turned on. The gas flow through each cell was generally maintained at 4.5 ACFM, which yields a filter air cloth ratio of 4.5 ACFM/ft² at the typical temperature of 850°. Each filter was jet pulse cleaned, or back flushed, once every five minutes.

Data recording was done during business hours, and consisted

Figure 16
Cell Circuit Diagram

of hourly gas temperature, gas flow rate, filter pressure drop, and electrolyte current for each cell. The data sheet used for this purpose is shown in Figure 17.

Overnight, the ash feed and pulse jet cleaning system were turned off, but the gas burner and fan were left on to keep the system hot. The entire system was turned off on weekends. In addition to recording the filter pressure drops, the filtration efficiencies were periodically measured by means of drawing the entire flow of a filter through a pre-weighed alundum thimble-type filter, which was subsequently weighed again.

4.3 Filters and Cells

4.3.1 Filter Media

Four high temperature filter media were selected for testing. They were:

- o Bekipor ST25GFX - a tridimensional web of randomly laid Inconel fibers, forming a solid porous plate by means of sintering. Maximum recommended temperature = 1020°F. Supplier: N.V. Beraert, S.A., Zwevegen, Belgium.
- o Dynapore 405705 Laminated Filter Plate - Layers of stainless steel wire cloth and perforated plate sintered into a monolithic porous structure. Supplier: Michigan Dynamics, Inc., Garden City, Michigan.
- o Nextel Woven Ceramic Fabric - A woven fabric of Alumina-Boria-Silica fibers, weighing 13 oz/sq. yd. Maximum recommended temperature: 2100°F. Supplier: 3M Co., St. Paul, Minnesota.
- o KE85 Felt - a self-supporting, thick, felt-like material made of refractory fibers held together with an organic binder. Maximum recommended temperature = 1650°F. Supplier: BWF KG, Offingen, West Germany.

4.3.2 Electrolytic Cells

The electrolyte elements supplied by Helipump (yttria

ENGINEERING DEPT

CLIENT—JOB NO. _____

SUBJECT ELECTR

Figure 17

Typical Data Sheet

DATE _____

DATE _____

DATE _____

APPVD. _____

DATE _____

DATE	5/25									5/26					
TIME	0800	0900	1000	1100	1200	1300	1400	1500	1600	0800	0900	0930	1030	1130	1230
SYSTEM PRESS "H ₂ O	+1.2	-1.3	-1.3	-1.2	-1.2	-1.2	-1.2	-1.2	-1.2	-1.5	-1.1	-1.6	-1.4	-1.4	-1.4
FLY ASH LB / HR	0	1	1	1	1	1	1	1	1	0	0	1	1	1	1
FLY ASH FEED SET	0	13	13	13	13	13	13	13	13	0	0	13	13	13	13
INLET TEMP °F	1427	1512	1503	1498	1500	1501	1497	1496	1495	1484	1470	1611	1589	1581	578
CONTROL TEMP °F	973	1008	1002	1025	1035	1045	1039	1027	1033	964	1022	1021	1009	1021	1010
CONTROL SET °F	1200	1200	1200	1200	1200	1200	1200	1200	1200	1200	1200	1200	1200	1200	1200
AIR PRESS. PSIG	0	98	96	98	97	98	98	96	98	0	0	95	96	98	97
D.C. VOLTS	.5	.5	.5	.5	.5	.5	.5	.5	.5	.5	.5	.5	.5	.5	.5
C CRIFILE ΔP	13.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	13.4	13.7	5.0	5.0	5.0	5.0
E MEDIA ΔP	N.A.	-	-	-	-	-	-	-	-	-	-	-	-	-	-
L TEMP. °F	710	698	684	663	673	683	680	692	728	722	746	756	729	724	726
L CURRENT MA	.39	.43	.42	.65 FLUE	.70 FLUE	.78 FLUE	17	26	.32	20 FLUE	16 FLUE	23	24	41	69
# CELL CLEAN.	OFF	-	-	-	-	-	-	-	30 OFF 120N	OFF	OFF	OFF	-	-	-
1 MEDIA CLEAN	N.A.	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C CRIFILE ΔP	4.0	3.0	3.0	2.0	1.5	1.1	1.1	1.0	1.0	.8	.8	.8	.8	.8	.8
E MEDIA ΔP	10.7	11.1	14.0	13.0	12.3	12.1	12.5	13.1	13.7	12.0	12.6	12.0	12.0	12.1	12.5
L TEMP. °F	744	763	773	780	779	777	773	767	763	712	725	735	739	737	738
L CURRENT MA	N.A.	-	-	-	-	-	-	-	-	-	-	-	-	-	-
# CELL CLEAN.	N.A.	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2 MEDIA CLEAN.	OFF	30 OFF 120N	-	-	-	-	-	-	-	OFF	OFF	30 OFF 120N	-	-	-

stabilized zirconia with silver electrodes) were mounted in stainless steel brackets, designed to be held within the 2" x 2" channel of the test modules. The mounting arrangement is shown in Figure 18. The silver electrode wires were sandwiched between the insulation and the electrode surfaces and thus made electrical contact at these points. The wires were passed out of the test cell through a cylindrical ceramic bushing with separate channels for each wire. Approximately two square inches of electrode surface (one side) were exposed when the electrolyte was mounted as shown in Figure 18.

4.3.3 Filter/Cell Arrangement

The filter/cell element positions are numbered as shown in Figure 19. The arrangement of filters and electrolytic cells are given in Table 20. The table indicates which of the electrolytic cells were cleaned with compressed air and which were not cleaned. Jet pulse cleaning was utilized for all the filters.

Figure 18
Electrolyte Assembly

Figure 19

Test Cell Identification

1	2	3
4	5	6
7	8	9

Table 20
Filter/Cell Arrangement

<u>Test Element</u>	<u>Contents</u>
1	No filter Electrolyte - no cleaning
2	BWF KE 85 filter Electrolyte - no cleaning
3	No filter Electrolyte with cleaning
4	Bekipor ST 25 GFX filter Electrolyte - no cleaning
5	3M Nextel filter Electrolyte - no cleaning
6	Dynapore 405 705 filter Electrolyte - no cleaning
7 - 9	Not used

4.4 Results

4.4.1 Electrolytic Cells

The yttria stabilized zirconia electrolyte cells began failing soon after the testing commenced. Each cell exhibited a similar mode of failure, which began with a rapidly fluctuating current and eventually resulted in a complete short circuit. Within three weeks, five of the six cells had short circuited in this fashion.

The short circuits appeared to be caused by the silver electrode material migrating through pores in the electrolyte under high temperature conditions. A cell could sometimes be reconditioned by slowly increasing its temperature to 1100°F, holding for a few hours and then slowly reducing temperature.

The yttria stabilized ceria cells with gold electrodes were installed in positions #1 and #4 on 5/24. These cells shorted

out after several days of operation. It was found that the shorting out of these cells occurred when the gold electrode material migrated across the edge of the electrolyte. This could sometimes be corrected by heating to 1100°F in an oven, but a simpler method was found to be using sandpaper to scrape away the bridge across the electrodes.

The yttria stabilized zirconia cell in position #3 operated well for over 100 hours. During this time period its current versus temperature characteristic was measured on three occasions. These measurements are shown in Figure 20. The electrodes were clean when the 4/4/89 data was taken. The system had been operated with flyash for one day prior to the data of 4/18/89, and the cell had been exposed to flyash for 56 hours when the 5/1/89 data was taken. It is seen that the presence of flyash on the electrodes does not alter the temperature-current characteristic, since all data points lie along the same curve. This behavior was also observed for the yttria stabilized ceria cells.

4.4.2 Filters

The four filters identified in Section 4.3 were operated intermittently over the period from 4/17/89 to 12/8/89. During this period, a cumulative time of 180 hours was achieved. Each filter was jet pulse cleaned every five minutes. The flyash loading was held at approximately 2.3 gr./scf. The air cloth ratios were generally held at 4.5 ACFM/sq. ft., and the gas temperature varied between 600°F and 850°F.

The pressure drop versus time histories of each filter is

Cell #3 Current vs. Temperature

shown in Figure 21. The vertical lines represent breaks in system operation, such as evenings and weekends. The KE85 filter ruptured due to high pressure drop (9 inches water) after seven hours of operation, and no data is shown for this filter. The structural integrity of the remaining three filters was good through the entire program. The figure shows that the pressure drops differ substantially, the Nextel filter often exceeding 8 inches of water, with the Bekipor under 2. The positions of these two filters were switched at 140 hours, in order to determine whether relative position within the test apparatus would influence the results. It is seen that the filter performances were unchanged as a result of the switch.

Figure 22 shows how the pressure drop of each filter varied as a function of air cloth ratio. The curves can be described by the equation $P = K(ACR)^x$, where x is between 1.2 and 1.6, which is typical for fabric filtration.

The results of filter collection efficiency testing are given in Table 21. It is seen that the metal mesh filters (Bekipor and Dynapore) are much more efficient than the woven ceramic fiber (Nextel). All of the filters were tested at an air/cloth ratio of 4.5 ACFM/sq. ft., a cleaning pulse pressure of 100 psig, and a cleaning pulse every five minutes. In an effort to improve the Nextel efficiency, tests were performed on this filter using 60 psig cleaning pressure, and no pulse cleaning at all. The resulting outlet particle loadings were .021 gr./scf and .004 gr./scf, respectively, indicating that the act of pulse jet cleaning causes much of the ash penetration through the

Figure 21

Filter Pressure Drops vs. Time On Stream

TIME ON STREAM, HOURS

PRESSURE DROP, INCHES WATER

Figure 22

Filter Pressure Drops vs. Air Cloth Ratio

filter.

Table 21
Filter Efficiencies

<u>Filter</u>	<u>Test #</u>	<u>Gr/SCF*</u>	<u>Efficiency**</u>
No filter (Inlet loading)	1	2.16	---
	2	2.46	---
	3	2.30	---
	Ave	2.3	---
Bekipor	1	.0001	99.99
	2	.00048	99.98
	3	.00075	99.97
	Ave	.0062	99.97
Nextel	1	.041	98.22
	2	.064	97.22
	3	.047	97.96
	4	.033	98.57
	5	.0731	96.83
	Ave	.052	97.74
Dynapore	1	.00039	99.98
	2	.00061	99.97
	3	.00057	99.98
	Ave	.00052	99.98

* 1 Gr/SCF = 1 grain per standard cubic ft. = 2.29 gm/m³

** Based on an average inlet loading of 2.3 Gr/SCF

4.5 Conclusions

The project objectives were to determine how the deposition of flyash affects electrolytic cell performance, and how deleterious effects may be resolved by means of electrode soot blowing or by upstream flyash filters. It was found that performance of the electrolytic cells is negligibly changed as a result of flyash deposition on the electrode surfaces. Because of this conclusion, the objectives relating to the effectiveness of corrective action (i.e., soot blowing or flyash filters)

become academic.

It was seen that cells with electrode cleaning or cells preceded by filters behaved no differently than cells exposed to the full flyash deposition with no electrode cleaning. Nevertheless, the experiment was designed to simultaneously address each objective, and hence data was generated and conclusions can be drawn with respect to filter performance. The filtration parameters of greatest importance are particle collection efficiency and pressure drop. Extensive data on each of these parameters was obtained for three filter media. This data is summarized in Table 22. It can be concluded from the table that considering both collection efficiency and pressure drop, the overall performance of the filters is Bekipor, Dynapore, Nextel.

Table 22
Filter Performance Summary

Filter	Efficiency (Percent)	ΔP @ 4 ACFM/Sq. Ft. (Inches water)
Bekipor	99.97	1.3
Nextel	97.74	4.9
Dynapore	99.98	2.2

5. ECONOMICS AND DESIGN

5.1 Design Basis

A design and economic analysis of the electrochemical process was done for a 500 megawatt power plant burning high sulfur coal. The flue gas conditions were taken from the report "Economic Evaluation of FGD Systems", EPRI-CF-3342 [31]. The EPRI economic analysis excludes particulate removal equipment (section 1.1 and 2.1.6.1 of the report [31]). Since high temperature particulate removal is not required and a conventional electrostatic precipitator can be used for particulate collection, particulate removal costs are also excluded from the analysis of the electrochemical FGD process. The coal is a 4% sulfur deep mined Illinois bituminous coal. The gas flow rate of sulfur dioxide is 39,200 lb/hr. and the concentration is 3020 ppm. The total gas flow rate is 1,279,000 SCFM (60°F). The NO_x concentration or flow rate was not specified in the report. It is assumed to be 500 ppm of NO or 3,040 lb/hr. Ninety percent removal of SO₂ and NO_x is required.

5.2 Sulfur Condensation

The flow diagram of the process is shown in Figure 23. The electrochemical reactor operates at temperatures near the operating temperature of the economizer. The sulfur removal step, which condenses liquid sulfur from the flue gas operates from the sulfur dew point down to near the freezing point of sulfur. The sulfur dew point for 90% conversion of the 3020 ppm of SO₂ to sulfur is 154°C (310°F) and the freezing point is 119°C (247°F). At a final condenser temperature of 121°C (250°F), 89%

Figure 23
Process Flow Diagram

of the sulfur is condensed. The liquid sulfur flow rate is 7.0 long tons/hr. The sulfur condenser is placed downstream of the electrostatic precipitator or bag house to prevent flyash from contaminating the sulfur.

The condensation of sulfur is practiced commercially in the Claus process. The Claus process converts hydrogen sulfide to sulfur. The process consists of a thermal oxidation reactor plus two or three catalytic reactor stages with sulfur condensation occurring between each stage. The outlet of the final and coolest condenser stage typically operates at temperatures from 265°F to 300°F [32]. This is close to the sulfur condenser temperature in the electrochemical process. The Claus sulfur condensers operate at gas velocities of from 37 to 110 ft/sec. Velocities below 20 ft/sec have problems with sulfur fog formation. The condensers are designed with a 1% slope in the gas flow direction to collect the liquid sulfur. The condensers are made of carbon steel. Sulfur separators are used to retain sulfur droplets greater than 100 microns. The separators are designed for a gas velocity of 10 ft/sec to prevent entrainment.

A sulfur condenser area of 50,000 ft² is required to cool the flue gas and condense sulfur. The furnace feed air is used as coolant. A sulfur separator with a diameter of 60 feet is required.

5.3 Electrochemical Reactor

The reaction rates used for design are based on the experimentally measured NO reduction rate on a YSC disk with a SrRuO₃ electrocatalyst (Table 15, disk 2) and the SO₂ reduction

rate on a YSC plate with Ru electrocatalyst (Table 16). The applied voltage was 1.2 volts and the oxygen concentration was 1%. The SO_2 measurements were made at 486°C with an SO_2 concentration of 1540 ppm. This is close to the average SO_2 concentration in the reactor design $((3020+302)/2=1660 \text{ ppm})$. The NO data was at 500°C and 500 ppm. The reduction rate per unit area is the product of the gas flow in cc/min times the ppm reduction times 10^{-6} divided by 22400 cc/gmole divided by the surface area in square inches.

NO rate: 33 ppm reduction
 100 cc/min gas flow
 .785 in^2 electrode area
 1.876×10^{-7} gmole NO/ in^2 /min

SO_2 rate: 175 ppm reduction
 155 cc/min gas flow
 5.76 in^2 electrode area (2.4"x2.4")
 2.10×10^{-7} gmole SO_2 / in^2 /min

The current efficiencies were 6.6% for NO and 46% for SO_2 .

The reactor would be constructed of rectangular ceria honeycomb with a spacing of 1/8 inch between plates and a plate thickness of 1/32 inch (0.8 mm). The plate thickness is the same as used in the experimental reactor. The cross pieces holding the honeycomb together could be more widely spaced. The cells would be electrically wired in series so that higher voltages could be used. The honeycomb has a surface area of 8 in^2 per cubic inch so the NO and SO_2 reduction rates per unit volume are:

NO : 1.50×10^{-6} gmole/min/ in^3
 SO_2 : 1.68×10^{-6} gmole/min/ in^3

The amount of NO and SO_2 to be reduced in the reactor is:

NO : 90% of 3,040 lb/hr. or 689 gmole/min
 SO_2 : 90% of 39,200 lb/hr. or 4167 gmole/min

The required reactor size is:

NO size: $4.58 \cdot 10^8 \text{ in}^3$ or $2.65 \cdot 10^5 \text{ ft}^3$
SO₂ size: $2.48 \cdot 10^9 \text{ in}^3$ or $1.43 \cdot 10^6 \text{ ft}^3$
total size: $2.93 \cdot 10^9 \text{ in}^3$ or $1.70 \cdot 10^6 \text{ ft}^3$

The reactor volume is quite large and is about 5 times the volume of a wet lime scrubber system [31]. The reactor residence time is about 30 seconds. The reactor mass is 95,000 tons. If the reactor were rectangular in shape it would be 75'x150'x150' and have a pressure drop of 2.9 inches of water.

The electrochemical reactor power requirements are proportional to the amount of NO and SO₂ to be reduced and the applied cell voltage. The power required is the product of the Faraday's law current times the cell voltage divided by the current efficiency. The power requirements are:

NO : 40,200 Kw
SO₂: 69,900 Kw
Total: 110,100 Kw

This is 22% of the plant power.

A typical oxygen concentration at the economizer of a coal power plant is 3% [33] with the concentration rising to 4.5% at the stack due to air leakage in the air preheaters. The oxygen content of the flue gas can be reduced to 1.4% by co-firing with natural gas. The NO reduction and current efficiency are more sensitive than SO₂ to higher oxygen concentrations as can be seen from the data in Table 18.

5.4 Process Economics

The electrochemical reactor cost is estimated on a cost per cubic inch basis. The cost of the electrolyte, electrocatalyst

and electrode plus a fabrication cost are summed. The electrolyte is 90% by weight ceria but for cost estimating purposes it is considered 100% ceria. Ceria has a density of 7.1 g/cm³. Since the reactor is 75% voids (3/32"/1/8") the electrolyte effective density is .065 lb/in³. The cost of optical grade ceria is 1.90 \$/lb (50 lb bags, delivered)[34]. The cost in larger quantities would probably be less. This gives an electrolyte cost of .12\$/in³.

The gold electrode material can be made very thin. The gold layer used in experiments was one to two thousand angstroms thick. A layer 250 angstroms thick would have a resistance of 2.6 ohms/square and at the experimentally measured current densities of about 1 mA/cm² would cause a negligibly small voltage drop. The cost for 1 in² of 250 angstrom thick gold is 0.005\$ (at \$500 per troy ounce). Since there are 16 square inches of anode and cathode area per cubic inch the electrode cost is 0.08\$/in³. The ruthenium electrocatalyst is assumed to have the same thickness as the gold. Ruthenium costs about one fifth as much as gold [35] and is used only on the cathode. Its cost is therefore 0.008\$/in³. Strontium ruthenate of the same thickness would probably cost less. The total materials cost is 0.21\$/in³. Adding a fabrication and installation cost of 0.14\$/in³ gives a total cost of 0.35\$/in³. This cost is of the same magnitude as platinum coated automotive catalytic converters.

The total process capital is given in Table 23.

Table 23
Process Capital Cost

	Cost in Millions of Dollars
Electrochemical Reactor	1026.0
Reactor Shell	5.8
Power Supply	5.5
Sulfur Condenser	.2
Sulfur Separator	.6
Sulfur Pit	.4
	<hr/>
Total	1038.5
	2078 \$/kW

The major cost is the electrochemical reactor. Its cost is calculated by multiplying the $0.35\$/\text{in}^3$ by the reactor volume of $2.93 \times 10^9 \text{ in}^3$. The other process capital costs are based on Guthrie[36] except the sulfur pit which is from the EPRI report[31]. The power supply is assumed to have twice the cost of an equivalent rated high voltage transformer. The calculation of the 30-year levelized busbar cost of power based on the EPRI guidelines is given in Table 24 [31] (Volume 3, Appendix B, Table 1). The design capacity factor is 65% for base load. Capital and maintenance items are estimated using the percentages of process capital suggested in the EPRI guidelines. The electric power cost is 45 mills/kw-hr and sulfur cost is 90\$/long ton [33]. Levelization factors are taken from the EPRI guidelines. The 30-Year Levelized Busbar Cost of Power at Levelized-Capacity Factor of 65% is 146 mills/kWh.

5.5 Process Improvements

Improvements in the electrolyte and electrode can be made to decrease the cost of the process. The electrolyte can be made thinner and the electrolyte surface area and therefore electrode

Table 24
CAPITAL INVESTMENT AND REVENUE REQUIREMENT
SUMMARY TABLE

Capital Investment	\$/kW
Process Capital	2078
General Facilities	104
Engineering and Home Office Fees	208
Project Contingency	623
Process Contingency	623
Total Plant Cost	3637
Total Plant Investment	3844
Preproduction Costs	77
Total Capital Requirement	3921

Operating and Maintenance Costs	\$/kW-yr
Operating Labor	0.32
Maintenance Labor	16.62
Maintenance Materials	24.94
Administrative and Support Labor	5.08
Total O&M First Year	46.96
Fixed O&M First Year	30.53
Variable O&M First Year	2.89 mills/kWh
Consumables (power)	9.9 mills/kWh
By-product Credit (sulfur)	1.26 mills/kWh

30 Year Levelized O&M Costs	mills/kWh
Variable	6.68
Consumables (power)	24.16
By-product Credit (sulfur)	2.91
Fixed	70.64 \$/kW-yr
30 Year Levelized Carrying Charges (Capital)	599.86 \$/kW-yr

30 Year Levelized Busbar Cost of Power	145.68 mills/kWh
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surface area can be increased. Yttria stabilized zirconia solid electrolytes used in solid oxide fuel cells have thicknesses of 0.25 mm for planar fuel cells and 0.04 mm for monolithic and tubular fuel cells [37]. The surface area can be increased with improved solid electrolyte coatings. A five fold increase in area should be possible. An increase in surface area causes a proportional increase in reaction rate and current per unit volume of reactor for the same overvoltage on the anode and cathode. The reactor volume is therefore decreased by a factor of 5. An increase in current density of a factor of 5 in the bulk electrolyte would cause a proportionally higher ohmic overvoltage of oxygen ion conduction. This ohmic overvoltage was less than one tenth of a volt in most of the experiments. A reduction of the electrolyte thickness to 0.25 mm would decrease the ohmic overvoltage by a factor of 3 so the net effect would be a negligible change in the required applied voltage.

The cost per unit volume is increased by the need for more electrode material and decreased due to the decrease in the amount of electrolyte. The estimated cost with gold electrodes is \$0.62/in³. If a conductive perovskite like those used in solid oxide fuel cells could be used, the cost would be reduced to 0.25\$/in³. The reactor volume, capital cost and levelized busbar cost for an electrolyte with a five fold increase in surface area and a thickness of 0.25mm with gold and perovskite electrodes is shown in Table 25.

Table 25
Electrochemical Reactor Size, Capital Cost and Levelized Cost
with Improved Electrolytes and Electrodes

	Improved Electrolyte with Gold Electrodes	Improved Electrolyte with Perovskite Electrodes
Reactor Volume in ³	5.86×10^8	5.86×10^8
Reactor Cost	$\$372 \times 10^6$	$\$154 \times 10^6$
Process Capital \$/kW	744	308
Total Capital \$/kW	1404	581
Levelized Busbar Cost in mills/kW-hr	65.9	39.8

The electrical power requirements, sulfur by-product and sulfur removal and power supply capital costs are unchanged. The same percentages of process capital are used for calculating the non-process capital and maintenance costs. The reactor pressure drop would be 5.0 inches of water. The above improvements can be done with known technology.

Further improvements in the costs can be achieved by increasing the temperature and improving the efficiency of the electrocatalyst. Using the activation energies of the NO and SO₂ reactions estimated in Section 3.7, the NO reduction rate would increase by 5.3 times and the SO₂ reduction rate would increase 2.4 times if the temperature were raised to the economizer inlet temperature of 565°C[33]. If the current efficiency for NO reduction could be raised by a factor of 3 for 6.6% to 20% and the current efficiency for SO₂ reduction could be raised from 46% to 75% by improving the electrocatalyst performance then the electrical power requirements would be cut in half. The reactor volume, electrical power requirements, capital cost and levelized busbar cost for the higher operating temperature reactor with and

without current efficiency improvements are shown in Table 26.

Table 26
Electrochemical Reactor Size, Power, Capital Cost and
Levelized Cost at 565°C with Improved Electrocatalysts

	Experimental Electrocatalysts	Improved Electrocatalysts
Reactor Volume in ³	2.27×10^8	2.27×10^8
Power Requirements kW	110,100	56,190
Reactor Cost	$\$56.6 \times 10^6$	$\$56.6 \times 10^6$
Process Capital \$/kW	129	129
Total Capital \$/kW	243	243
Levelized Busbar Cost in mills/kW-hr	29.1	17.3

The costs are based on an electrochemical reactor with perovskite electrodes and an improved surface area electrolyte. The reactor pressure drop for these cases is about 6.9 inches of water. The levelized cost of 17.3 mills/kW-hr for NO_x and SO₂ removal with the improved electrocatalysts is comparable to the cost of other FGD processes without NO_x removal.

6. CONCLUSION

The reduction of NO and SO₂ has been demonstrated on yttria stabilized ceria and zirconia electrolytes at 450° to 500°C in the presence of oxygen. Acceptable reduction rates and electric power requirements for sulfur dioxide and nitrogen oxide removal were obtained in up to 1% oxygen with ruthenium and strontium ruthenate electrocatalysts. Electrocatalytic improvements are needed for higher oxygen concentrations, with the NO reduction rates and efficiencies being most sensitive to oxygen concentration. The best electrocatalysts were ruthenium and the perovskite strontium ruthenate. Further work is needed with ruthenium perovskites as electrocatalysts and conductive perovskites as electrodes.

Exposure to flyash over a few days did not damage the electrochemical reactor. Therefore, high temperature filters most likely will not be needed. Of the high temperature filters tested, the stainless steel filters performed better than the ceramic filters.

The economics show that with some small improvements in surface area, electrode cost and oxygen selectivity the electrochemical process in one percent oxygen is an economically competitive process which does not generate environmentally hazardous by-products.

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