PROJECT facts

Advanced Research

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U.S. Department of Energy
Office of Fossil Energy
National Energy Technology Laboratory

NETL

Low-Cost Miniature Multifunctional Solid-State Gas Sensors

Description

Research sponsored by the U.S. Department of Energy (DOE) Office of Fossil Energy (FE) through the National Energy Technology Laboratory (NETL), and performed by the University of Florida, has resulted in successful development of solid-state sensor technology that can provide an inexpensive, rugged device that is capable of measuring the concentration of multiple pollutants in lean-burn coal combustion exhaust streams. This technology has been adapted to create a type of sensor that is sensitive to multiple gases including nitrogen oxides (NO_x), carbon monoxide (CO), and oxygen (O_2). The sensors work through differential electrode equilibria (DEE), a scientific approach by which a difference in the electrochemical potential (a measure of energy change) between two electrodes exposed to the same environment will occur if one or both of the electrodes does not achieve thermodynamic equilibrium. Such a sensor can be used to improve combustion control, resulting in both improved fuel utilization and reduced emissions.

There are compelling environmental and regulatory needs for the monitoring and control of NO_x and CO emissions from coal combustion sources in power plants. While the environmental performance of the Nation's coal-fired plants has steadily improved over the years since passage of the 1970 Clean Air Act (CAA) and subsequent amendments, further restrictions on emissions have been proposed in response to issues such as mercury, acid rain, ground-level ozone, nitrification of aquatic ecosystems, ambient fine particulate matter, and visibility impairment (regional haze). In March 2005, for example, the U.S. Environmental Protection Agency (EPA) issued the Clean Air Interstate Rule (CAIR) permanently capping emissions of sulfur dioxide (SO_2) and NO_x in the eastern United States, where pollution is the most pronounced and population is concentrated. When fully implemented, CAIR will reduce SO_2 emissions across 28 eastern states and the District of Columbia by over 70 percent, and NO_x emissions by over 60 percent from 2003 levels. This will result in $85–100 billion in health benefits, and nearly $2 billion in visibility benefits per year by 2015. These reductions also will substantially reduce premature mortality in the eastern United States. The benefits will continue to grow each year with further implementation.

Objectives and Technical Approach

The objectives of this research are to: advance the fundamental understanding of the DEE mechanism by applying it to the development and performance optimization of select NO_x and CO electrode elements; fabricate and test a multifunctional (NO_x, CO, O_2) sensor; and develop a miniature, low-cost, multifunctional sensor prototype for evaluation by commercial/industrial companies.

The sensor being developed is based on the same technology as that used in conventional automotive O_2 sensors, which can be used directly in high-temperature

CONTACTS

Robert R. Romanosky
Technology Manager
Advanced Research
National Energy Technology Laboratory
3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880
304-285-4721
robert.romanosky@netl.doe.gov

Richard J. Dunst
Project Manager
National Energy Technology Laboratory
626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940
412-386-6694
richard.dunst@netl.doe.gov

Eric D. Wachsman
Principal Investigator
University of Florida
339 Weil Hall
Gainesville, FL 32611-4025
352-846-2991
ewach@mse.ufl.edu

PROJECT DURATION

05/30/03 to 12/31/06

COST

Total Project Value
$550,000

DOE/Non-DOE Share
$400,000 / $150,000

ADDRESS

National Energy Technology Laboratory

1450 Queen Avenue SW
Albany, OR 97321-2198
541-967-5892

2175 University Avenue South
Suite 201
Fairbanks, AK 99709
907-452-2559

3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880
304-285-4764

626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940
412-386-4687

One West Third Street,
Suite 1400
Tulsa, OK 74103-3519
918-699-2000

CUSTOMER SERVICE

1-800-553-7681

WEBSITE

www.netl.doe.gov

exhaust streams. In this design, to reduce cost, all electrodes are included in a single sensor in the same gas stream. To attain the necessary gas selectivity, the sensor must exhibit a highly selective response to parts-per-million (ppm) levels of NO_X and CO in the presence of percentage levels of O_2. This is accomplished by synthesizing n-type and p-type semiconducting metal oxides and mixed metal oxides (e.g., perovskites); and characterizing them for phase purity by X-ray diffraction (XRD), and for particle size and distribution by means of Brunauer Emmett Teller (BET) particle surface area measurements and transmission electron microscopy (TEM). Temperature programmed reaction (TPR) of these candidate electrode materials with NO_X, CO, and O_2 then is used to determine their oxidation/reduction catalytic activity and selectivity. Temperature programmed desorption (TPD) is used to determine the species that adsorb, and the conditions (temperature and gas composition) under which they adsorb/desorb on/from the candidate electrode materials.

In the TPR and TPD experiments, stable isotope-labeled gases are used to determine whether the surface mechanism involved oxygen exchange. Experiments then determine the semiconducting response of the candidate electrode materials: n-type/p-type, sensitivity, and selectivity as a function of temperature and gas composition. These electrode materials are tested in potentiometric sensors and compared to a platinum (Pt) reference electrode in order to clarify how each of these mechanisms influenced the sensor response (sensitivity, selectivity, response time, repeatability, and drift).

Accomplishments

The multifunctional sensor has been fabricated and its performance tested in stoichiometric reaction measurements involving exposure to lean-burn combustion exhaust gas. To date, investigations of the effect of electrode microstructures on sensor sensitivity have shown that electrodes with small particle sizes and high surface areas increased sensitivity. Sensors fabricated and tested with both n type and p type metal oxide electrodes showed high sensitivity and selectivity toward NO, CO, and NO_2. Consistent with the DEE mechanism, the voltage response of the n type electrode was opposite to that of the sensor with the p type electrode. Similarly, and as expected according to this mechanism, the reducing gas (NO) and the oxidizing gas (NO_2) also exhibited opposite voltage responses.

TPD and TPR test results showed that co-adsorption of gases resulted in a complex surface species and, in addition, that the minimum sensor operating temperature was due to the saturation of the electrode surface with adsorbed gases, further confirming the DEE mechanism.

Based on these electrode studies, a prototype miniaturized sensor has been developed in conjunction with one of the university's industrial partners, Emissions Detection Technologies, Inc., for evaluation by commercial companies, and the sensors are to be field tested in actual coal-fired furnaces at sites selected by another industrial partner, General Electric Reuter-Stokes (GERS). Following extended service under operating conditions, the devices will be subjected to rigorous inspection for durability, through careful metallographic sectioning and analysis as well as measurements of changes in thermo-mechanical properties.

Benefits

Successful development and commercialization of this solid-state multifunctional sensor technology will result in availability of an inexpensive, rugged device that is capable of measuring the concentration of multiple pollutants in lean-burn coal combustion exhaust streams. Such a sensor can be used to improve combustion control in present and future coal-fired power plants, resulting in both improved fuel utilization and reduced emissions.