Understanding The Response Behavior of Potentiometric Sensors For Non-Equilibrium Gas Mixtures

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Many applications of gas sensors require concentration measurements of reactive gases in mixtures that are out of thermodynamic equilibrium. These applications include: hydrogen and hydrocarbon fuel gas sensors operating in ambient air for explosion hazard detection, carbon monoxide detection in ambient air for health protection, combustion efficiency sensors for stoichiometry control, and nitric oxide sensors for air pollution monitoring. Many potentiometric and amperometric electrochemical sensor technologies have been developed for these applications. A class of potentiometric sensors developed for gas mixtures are the non-Nernstian sensors (1). This presentation defines a categorization and theoretical analysis of three distinct electrochemical processes that can produce a non-Nernstian sensor response.

The non-Nernstian sensors types may be grouped into three subcategories:

a. Catalytic/non-catalytic electrode sensing mechanism
b. Adsorption poisoning sensing mechanism
c. Mixed potential sensing mechanism

The first type of sensing mechanism uses a porous electrode that catalyzes thermodynamic equilibrium between the gases in a mixture, a solid electrolyte that conducts one of the gas species and a second electrode that does not catalyze thermodynamic equilibrium. The second electrode response is not directly affected by the presence of the second gas; the second gas acts only as an inert diluent gas.

The type b sensors operate on the principle that the strong chemisorption of one of the gas species alters the electrode kinetics for a second gas species. The adsorbed species is not directly involved in a redox process.

The type c sensor mechanism exploits the property that multiple gas/electrode/solid electrolyte redox reactions occurring at a triple phase boundary surface with differing kinetic rates determine the electrode potential. At low analyte gas concentrations the kinetics of each redox process are independent of each other. At high gas concentrations competition for reactions by the adsorbed gases causes this approximation to become invalid. Heterogeneous catalysis away from the triple phase boundary also alters the gas response by changing the reacting gas concentrations near the triple phase boundary (2).

A variation of the type c sensor uses a dense thin film of a metal oxide deposited on a solid electrolyte surface. The metal oxide surface selectively catalyzes a desired redox reaction between the analyte gas and oxygen from the metal oxide lattice. The chemical potential of oxygen in the film is thus controlled by the catalytic reaction and sensed by an oxide solid electrolyte/reference electrode combination (3,4).

REFERENCES

1. P.T. Moseley, Non-Nernstian, Potential generating Gas Sensors, P.T. Moseley and B.C. Tofield, Editors, Adam Hilger, Bristol U. K. (1987)

2. F. H. Garzon, R. Mukundan and E. L. Brosha Solid State Ionic Devices, E. D. Wachsman *et al*, Editors, **PV 2000-32**, p. 305, The Electrochemical Society Proceedings Series, Pennington, NJ (2000)

3. F. H. Garzon and E. L. Brosha, US patent application S-84,906

4. J. Mizusaki, K. Yashiro, T. Kawada, and H. Ohama, abstract no. 0759, The 202 Meeting of the Electrochemical Society, Salt Lake City UT (2002)