

AN ELECTROCHEMICAL METHOD OF OXYGEN  
FUGACITY CONTROL OF FURNACE ATMOS-  
PHERE FOR MINERAL SYNTHESES<sup>1</sup>

MOTOAKI SATO, *U. S. Geological Survey, Washington D. C. 20242.*

ABSTRACT

A new method of controlling the oxygen fugacity of furnace atmosphere for mineral synthesis has been developed. The method consists of generating hydrogen gas by the electrolysis of water, mixing it with water vapor and another gas such as nitrogen, argon, or carbon dioxide, and monitoring the oxygen fugacity of the gas mixture with a solid-electrolyte oxygen probe. The oxygen fugacity of the gas mixture is adjusted by regulating the electrolysis current. Several minerals sensitive to oxygen fugacity have been successfully synthesized by this method.

Syntheses of oxides or silicates of transition elements often require a delicate control of the oxygen fugacity of the ambient atmosphere. For syntheses near 1 atm total pressure, calibrated mixtures of CO<sub>2</sub> and CO or CO<sub>2</sub> and H<sub>2</sub> are used routinely to provide appropriate atmosphere (Darken and Gurry, 1945). For hydrothermal syntheses under elevated pressures, a step-wise control is achieved by the use of oxygen "buffers" surrounding a special metal capsules permeable to hydrogen (Eugster, 1957). A more flexible control may be made by applying a given pressure of hydrogen through a metallic membrane permeable to the gas (Shaw, 1963).

The gas-mixture method requires either a very careful control of the flow rates of the component gases or the use of commercially available premixed and analyzed mixtures. The controlled-flow-rate method is more flexible in obtaining desired oxygen fugacities, but the calibration procedure is more involved. The range of uncertainty tends to be greater when the gas mixing ratio departs from unity by more than a few orders of magnitude in either method.

It was found in the present investigation that the use of a high-temperature oxygen concentration cell based on doped zirconia solid electrolyte greatly simplifies the calibration procedure. It was also shown that multicomponent mixtures, such as H<sub>2</sub>O-H<sub>2</sub>-N<sub>2</sub> can be used without additional complexity as the result of the direct monitoring of the oxygen fugacity. Even automatic regulation of the ambient oxygen fugacity of a complex assemblage was shown to be easily achievable.

The use of stabilized zirconia as the solid electrolyte for high-temperature oxygen concentration cells was first introduced by Kiukola and Wagner (1957) and has rapidly become a very popular method for the

<sup>1</sup> Publication authorized by the Director, U. S. Geological Survey.

determination of oxygen fugacities of gases, liquids, and solids at temperatures higher than about 500°C. Scores of papers have been published on this subject within the last decade. Those that specifically deal with the determination in gases include papers by Schmalzried (1962), Matsushita and Goto (1964, 1966), Möbius (1965, 1966) and Sato and Wright (1966).

Oxygen-sensing cells may be designed in several ways, but the principle is the same. When unequal oxygen fugacities exist at two sides of an oxide-ion conductor (electrolyte), an emf is developed according to the relationship

$$\begin{aligned} E &= (RT/4F) \ln [f_{O_2}^{(I)}/f_{O_2}^{(II)}] \\ &= 4.96 \times 10^{-5} T \log [f_{O_2}^{(I)}/f_{O_2}^{(II)}] \text{ Volt} \end{aligned} \quad (1)$$

where  $R$  is the gas constant,  $T$  the absolute temperature, and  $F$  the Faraday constant. The emf is picked up and read with an electrometer or a potentiometer by attaching noble metal conductors to the two surfaces of the solid electrolyte. The most suitable solid electrolytes known at present are yttria-stabilized zirconia ( $Y_2O_3$  9 mole %) and lime-stabilized zirconia ( $CaO$  15 mole %). These solid solutions have fluorite-type structures with vacancies in the oxygen positions, which give rise to high oxide-ion mobilities. They are chemically inactive and highly refractory. As indicated by equation (1), it is possible to determine an unknown oxygen fugacity value by measuring the emf and the temperature if the second oxygen fugacity value is known. Various substances have been used as the reference oxygen source including air, pure oxygen, Ni-NiO mixture, and Fe-FeO mixture. An example of the design of the cell which uses air as the reference is schematically shown in Figure 1.

The control of the oxygen fugacity of a furnace atmosphere can be made by inserting such an oxygen probe into the hot zone of the furnace and so adjusting the mixing ratio of appropriate gases that the emf reading of the probe matches the emf value calculated through equation (1) for a desired oxygen fugacity value. In the case of two-gas mixtures such as  $CO_2/CO$  and  $CO_2/H_2$ , the predominant gas is allowed to flow into the furnace at a constant rate and the minor gas is mixed into the former through a flow regulating device of some sort as in the conventional gas mixture method.

A novel method successfully tried in our laboratory, however, depends on a simpler regulating method as shown in Figure 2. Nitrogen gas is bubbled through the cathode chamber of a water electrolysis cell at a constant rate, while the rate of evolution of hydrogen gas in the cathode chamber is regulated by turning a rheostat placed in series with the electrolysis cell or adjusting the voltage of a dc source such as a battery-

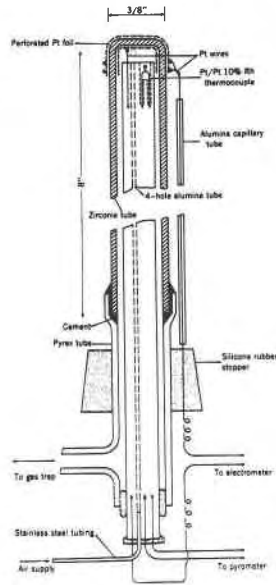


FIG. 1. Solid-electrolyte oxygen probe for measuring the oxygen fugacity of furnace atmosphere at high temperatures. A gas of known oxygen fugacity such as air is slowly circulated through the interior of the stabilized zirconia tube as the oxygen fugacity reference. The oxygen fugacity of the furnace atmosphere, which is in contact with the exterior wall of the zirconia tube, can be determined from the emf developed across the wall of the hot zone of the furnace, and the oxygen fugacity of the reference gas by using equation (1).

charger. The nitrogen gas coming out of the cathode chamber contains water vapor and hydrogen, and therefore establishes a certain oxygen fugacity value at high temperatures depending on the ratio of the partial pressures of water and hydrogen. Argon gas may be used instead of nitrogen. For relatively high oxygen fugacities at moderate temperatures, carbon dioxide may be used more advantageously than nitrogen as less delicate control of the hydrogen evolution rate is required for a given oxygen fugacity under these conditions. The construction of the electrolytic cell can be made very simple as is shown in Figure 2. A coil of platinum wire is used as the cathode and a nickel plate bent to a cylindrical form is used as the anode. The electrolyte solution is normally 10 weight percent NaOH. However, if  $\text{CO}_2$  is bubbled through the cell, sodium bicarbonate solution must be used because the reaction of the gas with NaOH tends to precipitate sodium carbonate and clog the cathode chamber. The gas mixture is then bubbled through a gas wash bottle filled with distilled water and led to the furnace. The gas wash

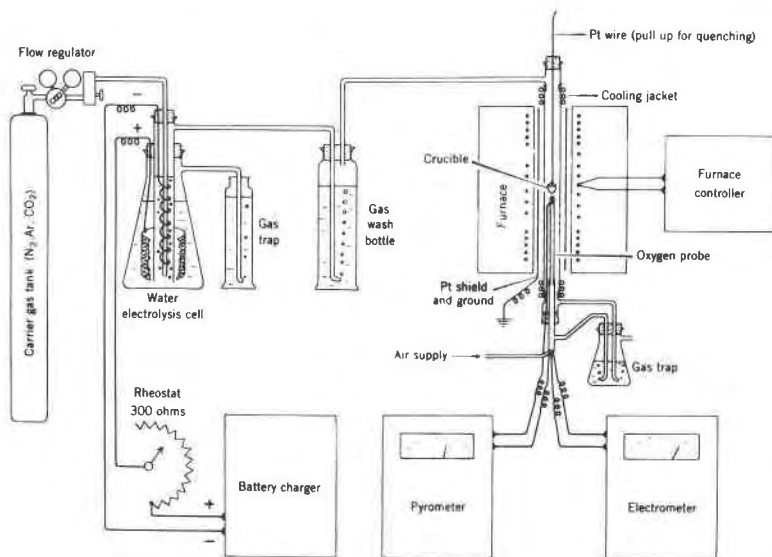


FIG. 2. Schematic instrumental arrangement of the electrochemical method for regulating oxygen fugacity of furnace atmosphere for mineral synthesis. Hydrogen gas is generated by electrolyzing water and mixed with water vapor and other gases. The oxygen fugacity of this gas mixture, which constitutes the furnace atmosphere, is monitored by the electrometer connected to the solid-electrolyte oxygen probe and adjusted to a desired value by regulating the electrolytic current.

bottle, which is kept at room temperature, eliminates excess condensation water, which is picked up when the electrolytic cell is heated as the result of a vigorous electrolysis, and thus regulates the partial pressure of water vapor.

Figures 3, 4, and 5 show typical current versus  $\log f_{O_2}$  relationships for nitrogen, argon, and carbon dioxide streams, respectively, at temperatures about 1018°C and flow rates about 0.06 cubic foot per hour. These curves all have a reversal of curvature at intermediate oxygen fugacity ranges marked by dashed lines. This phenomenon probably occurs partly because the initial bottled carrier gases contain trace oxygen and partly because the oxygen in air diffuses into the ambient chamber despite a slightly positive pressure existing inside the chamber. The overpotential hindering the hydrogen evolution is not likely the cause of this phenomenon, because the oxygen fugacities of the gas mixtures decrease with increase in current above the inflection point indicating an addition of hydrogen to the gas mixture even in the low current range.

In theory, the  $\log f_{O_2}$  value at a given temperature of a mixture of water vapor, hydrogen, and an inert gas (argon or nitrogen) should vary lin-

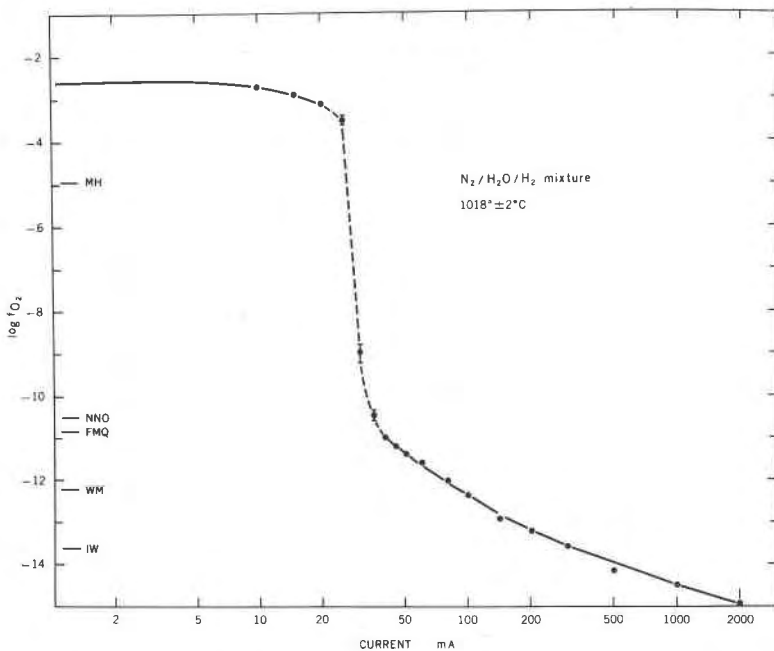


FIG. 3. Plots of  $\log f_{O_2}$  values of  $N_2/H_2O/H_2$  mixture versus the water electrolysis current (in mA) at  $1018^\circ \pm 2^\circ C$ . The nitrogen flow rate was about 0.06 cubic foot per hour and the water vapor pressure about 24 mm Hg. The oxygen fugacity values of common oxygen buffers at this temperature are shown along the  $-\log f_{O_2}$  axis for reference. The notations for these buffers are: MH (magnetite-hematite), NNO (nickel-nickel oxide), FMQ (fayalite-magnetite-quartz), WM (wustite-magnetite), and IW (iron-wustite).

early with the electrolysis current. The water vapor pressure at  $25^\circ C$  is  $3.15 \times 10^{-2}$  atm. The hydrogen partial pressure is a function of both the rate of evolution by electrolysis and the flow rate of the gas mixture. The cathodic reaction,  $2H^+ + 2e^- = H_2$ , requires 2 faradays ( $1.93 \times 10^5$  ampere-second) of electricity per mole of hydrogen. This amounts to the evolution of  $456 \text{ cm}^3$  of hydrogen per ampere per hour at  $25^\circ C$ . At the flow rate of 0.06 cubic feet per hour of the mixture, the partial pressure of hydrogen is calculated to be 0.269 atm per ampere. The logarithm of the dissociation constant of water at  $1018^\circ C$  is  $-7.134$ . By assuming ideal gas behavior for all the component gases, we obtain the theoretical oxygen fugacity of the above gas mixture at  $1018^\circ C$  as a function of the electrolysis current  $A$  as

$$\begin{aligned} \log f_{O_2} &= 2[\log Kd(H_2O) + \log f_{H_2O} - \log (f_{H_2}/A)] \\ &= -14.74 + \log A \end{aligned}$$

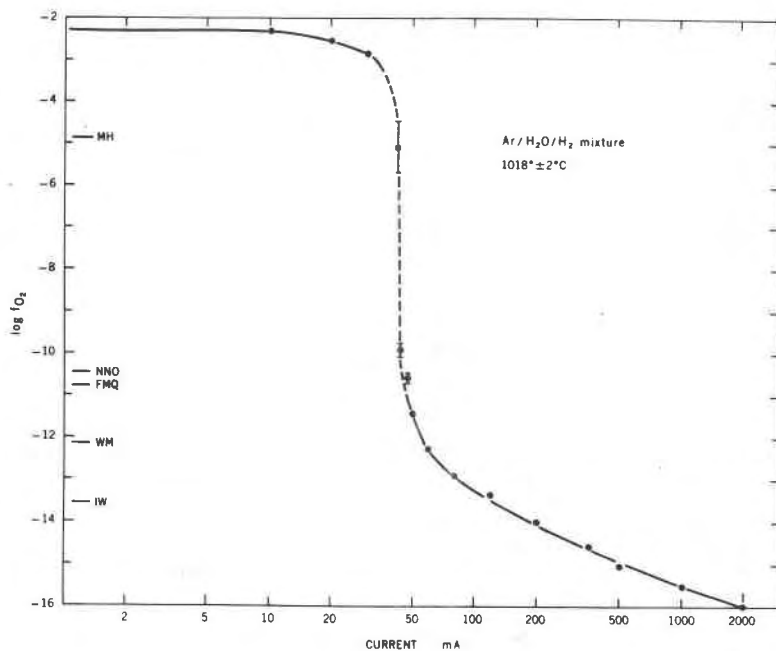


FIG. 4. Plots of  $\log f_{O_2}$  values of Ar/H<sub>2</sub>O/H<sub>2</sub> mixture versus the water electrolysis current (in mA) at 1018 ± 2°C. The argon flow rate was about 0.06 cubic foot per hour and the water vapor pressure about 24 mm Hg. The notations for the common oxygen buffers are the same as in Figure 3.

The agreement of the above equation with the measured values in Figures 3 and 4 is generally poor, particularly at the low current side. The above result suggests that it is important to directly monitor oxygen fugacity whenever possible, particularly when the mixing ratio departs from unity by more than one order of magnitude. Impurities and undetected leakages may result in erratic oxygen fugacity values even in a well-calibrated gas mixing train.

Within the above-mentioned reversal ranges a good regulation of the oxygen fugacity is difficult and the precision falls below 0.01 log unit and sometimes below 0.5 log unit at the center. Within the ranges marked with solid lines, the control of oxygen fugacity better than 0.01 log unit over a 24-hour period can easily be achieved. Using this electrochemical method of ambient oxygen fugacity control, a number of oxides and silicates including magnetite, wustite, fayalite, and manganese oxides have successfully been synthesized. The application of this method to phase equilibria studies has also been initiated on our laboratory.

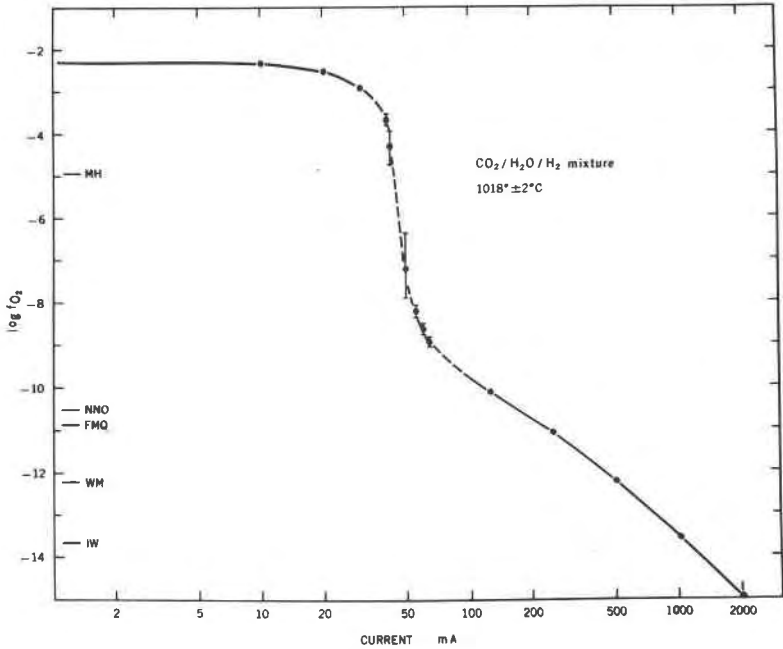


FIG. 5. Plots of  $\log f_{O_2}$  values of  $CO_2/H_2O/H_2$  mixture versus the water electrolysis current (in mA) at  $1018 \pm 2^\circ C$ . The carbon dioxide flow rate was about 0.06 cubic foot per hour and the water vapor pressure about 24 mm Hg. The notations for the common oxygen buffers are the same as in Figure 3.

## REFERENCES

- DARKEN, L. S., AND R. W. GURRY (1945) The system iron-oxygen, I. The wustite field and related equilibria. *J. Amer. Chem. Soc.* **67**, 1398-1412.
- EUGSTER, H. (1957) Heterogeneous reactions involving oxidation and reduction at high pressures and temperatures. *J. Chem. Phys.* **26**, 1760.
- KIUKOLA, K., AND C. WAGNER (1957) Measurements on galvanic cells involving solid electrolytes. *J. Electrochem. Soc.* **104**, 379-387.
- MATSUSHITA, Y., AND K. GOTO (1964) On the application of the oxygen concentration cells with the solid electrolyte,  $ZrO_2 \cdot CaO$  to the basic research work in process metallurgy. *J. Fac. Eng. Univ. Tokyo B*, **27**, 217-280.
- , AND ——— (1966) The application of oxygen concentration cells with solid  $ZrO_2 \cdot CaO$  to thermodynamic research. In *Thermodynamics, Vol. I*, International Atomic Energy Agency, Vienna, Austria, p. 111-129.
- MÖBIUS, H.-H. (1965) Sauerstoffionenleitende Festelektrolyte und ihre Anwendungsmöglichkeiten—Grundlagen der gaspotentiometrischen Sauerstoffbestimmung. *Z. Phys. Chem* **230**, 396-412
- (1966) Sauerstoffionenleitende Festelektrolyte und ihre Anwendungsmöglich-

keiten—Potentiometrische Titrationsen oxydabler Gase mit Luft in Festelektrolytzellen. *Z. Phys. Chem.* **231**, 209–214.

SATO, M., AND T. L. WRIGHT (1966) Oxygen fugacities directly measured in magmatic gases. *Science*, **153**, 1103–1105.

SCHMLAZREID, H. (1962) Über Zirkondioxyd als Elektrolyt für elektrochemische Untersuchungen bei höheren Temperaturen. *Z. Elektrochem.* **66**, 572–576.

SHAW, H. R. (1963) Hydrogen-water vapor mixtures—Control of hydrothermal atmospheres by hydrogen osmosis. *Science*, **139**, 1220–1222.

*Manuscript received, October 21, 1969; accepted for publication, March 4, 1970.*