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Use of High-Temperature Gas-Tight Electrochemical Cells to
Measure Electronic Transport and Thermodynamics in Metal Oxides*

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ABSTRACT

By using a gas-tight electrochemical cell, we can perform high-temperature
coulometric titration and measure electronic transport properties to determine the
electronic defect structure of metal oxides. This technique reduces the time and expense
required for conventional thermogravimetric measurements. The components of the gas-
tight coulometric titration cell are an oxygen sensor, Pt/yttria stabilized zirconia (YSZ)/Pt,
and an encapsulated metal oxide sample. Based on cell design, both transport and
thermodynamic measurements can be performed over a wide range of oxygen partial
pressures ($pO_2 = 10^{-35}$ to 1 atm). This paper describes the high-temperature gas-tight
electrochemical cells used to determine electronic defect structures and transport
properties for pure and doped-oxide systems, such as YSZ, doped and pure ceria (Ca-
CeO$_2$ and CeO$_2$), copper oxides, and copper-oxide-based ceramic superconductors,
transition metal oxides, SrFeCo$_{0.5}$O$_x$, and BaTiO$_3$.

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1 INTRODUCTION

The value of directly obtaining partial molar thermodynamic quantities in the investigation of nonstoichiometric oxides is that it allows thermodynamic characterization without assuming a particular defect model. These quantities, which consist mainly of variations in oxygen chemical potential with changing temperature and composition, can best be used in support of, and in conjunction with, a proposed defect model. Together, they provide insight, understanding, and a concise description of the nonstoichiometric behavior to develop various sensors and membranes for the application of gas separation or synthesis for industry.

Of the many different measurement systems that have been used in high-temperature thermodynamic studies of metal oxides, electrochemical titration cells, which incorporate solid electrolytes, offer the greatest versatility. In previous studies of metal oxides (e.g., CeO$_{2-x}$), electron mobility ($\mu$) was determined by combining separate experimental measurements of deviation from stoichiometry ($x$) and electrical conductivity ($\sigma$). A coulometric titration technique, which extends the utility of the titration cell to include the direct and simultaneous measurements of thermodynamic quantities and electronic conductivity, is presented. To perform the high-temperature coulometric titration technique, we must understand the nonstoichiometric defect behavior in yttria stabilized zirconia (YSZ). Therefore YSZ and nonstoichiometric cerium dioxide were chosen for the purpose of demonstration.

When a metal oxide (binary, ternary, or even quaternary oxides, in which M, N, L are different nonvolatile metals), designated as M(NL)O$_2$, is in equilibrium with the surrounding oxygen atmosphere at elevated temperatures, we may write the overall reaction as (only "M" is denoted for convenience)
where $x$ indicates the deviation from stoichiometry. According to the Gibbs phase rule, two intrinsic parameters are needed to describe the $x$ values, i.e., temperature and $pO_2$; thus, $x = x(T, pO_2)$.

1.1 Defects in Yttria-Stabilized Zirconia (YSZ)

YSZ has a stable fluorite cubic structure consisting of $Zr^{4+}$ at outer face centered-cubic positions and $O^{2-}$ at inner simple-cubic positions. Because the proposed defect model in metal oxide systems is similar, YSZ was chosen for the demonstration.

When $ZrO_2$ is doped with $Y_2O_3$, a doubly ionized oxygen vacancy ($V_0^{**}$) is produced. The defect reaction can be represented as

$$\text{YO}_{1.5} \rightarrow \text{Y}^\text{Zr} + \frac{1}{2} \text{V}_0^{**} + \frac{3}{2} \text{O}_0^\text{x},$$

where $\text{Y}^\text{Zr}$ indicates yttrium on the zirconium site with a formal charge of -1, and $\text{O}_0^\text{x}$ indicates normal oxygen on an oxygen site.

The formula for YSZ containing $y$ moles of yttria is $Zr_{1-y}Y_yO_{2-y/2}$. The electroneutrality condition is

$$[\text{Y}^\text{Zr}] = 4[\text{V}_0^{**}]$$

where the bracket indicates the site fraction of each species. When the YSZ is in equilibrium with the surrounding oxygen, the overall solid/gas reaction is

$$Zr_{1-y}Y_yO_{2-y} = Zr_{1-y}Y_yO_{2-y-x} + \frac{x}{2}O_2(g)$$
The nonstoichiometric defect reactions proposed by several authors\textsuperscript{1-4} for an n-type region, i.e., at low oxygen pressure, with an enthalpy of $\Delta H^o$ are

\[ 2Zr_{\text{Zr}}^x + O_{\text{O}}^y = 2Zr_{\text{Zr}}' + V_{\text{O}}'' + \frac{1}{2}O_2(g) \]  

(5a)

or simply,

\[ O_{\text{O}}^y \rightarrow V_{\text{O}}'' + 2e' + \frac{1}{2}O_2(g), \]

(5b)

where $Zr_{\text{Zr}}'$ indicates a localized electron on a zirconium site. Because of the nonstoichiometric defect reaction, the electroneutrality equation (Eq. 3) becomes

\[ 4[V_{\text{O}}''] = [Zr_{\text{Zr}}'] + [Y_{\text{Zr}}]. \]  

(6)

The site fractions of localized electrons and yttrium atoms on zirconium sites may be expressed in terms of $x$ and $y$ as

\[ [Zr_{\text{Zr}}'] = 2x \]

and

\[ [V_{\text{O}}''] = \frac{(x + y)}{2}. \]  

(7)

The mass action constant, $K_{\text{ma}}$, associated with the defect reaction, (Eq. 5a) is

\[ K_{\text{ma}} = \frac{[Zr_{\text{Zr}}'][V_{\text{O}}'']}{[Zr_{\text{Zr}}]O_{\text{O}}'} pO_2^{1/2}. \]  

(8)

On the basis of Eq. 7 and the assumption that $[Zr_{\text{Zr}}'] = 1 - y$ and $[O_{\text{O}}'] = 1 - (y/2)$, $K_{\text{ma}}$ can be written as
By differentiating and rearranging Eq. 9, we obtain

$$\frac{\partial \log(pO_2)}{\partial \log(x)} = -4 - \frac{2x}{x+y}. \quad (10)$$

When \(y = 0.148\) (8 mole \% YSZ) and \(y \gg x\), the slope is essentially -4. For pure oxide (no doping), i.e., \(y = 0\), Eq. 10 becomes \(\frac{\partial \log(pO_2)}{\partial \log(x)} = -6\). For \(\text{ZrO}_2\) doped with 8 mole \% YSZ, the deviation from stoichiometry, \(x\), is

$$x = KpO_2^{-1/4}, \quad (11)$$

where the proportionality constant \(K = 1.61\sqrt{K_{\text{ma}}}\). Using the thermodynamic relation \(\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ\), we may also write

$$K_{\text{ma}} \propto \exp\left(-\frac{\Delta G^\circ}{kT}\right) = \exp\left(\frac{\Delta S^\circ}{kT}\right) \exp\left(-\frac{\Delta H^\circ}{kT}\right). \quad (12)$$

The reaction for the formation of oxygen is

$$\text{O}_2(1 \text{ atm, g}) + 4\text{Zr}_2^+ + 2\text{V}_0^{**} = 4\text{Zr}_2^+ + 2\text{O}_0^* \quad (13)$$

with an enthalpy of \(\Delta H_{\text{O}_2}\). From Eqs. 5 and 13, it is apparent that

$$\Delta H_{\text{O}_2} = -2\Delta H^\circ. \quad (14)$$
When we plot the log K vs. 1/T or log x (fixed pO₂) vs. 1/T, \( -\Delta H^o = 2 \) times the slope, and therefore, \( \Delta H_{O_2} \) can be obtained from 4 times the slope.

### 1.2 Solid-State Coulometric Titration

High-temperature solid-state coulometric titration of oxide systems involves the removal or addition of oxygen by means of an oxygen pump. During pumping, the solid-gas reaction is represented as

\[
\text{MO}_2(s) \xrightarrow{\text{pump-out}} \text{MO}_{2-x}(s) + \frac{x}{2} O_2(g). \quad (15)
\]

As oxygen is pumped out of the cell (and therefore out of the specimen), one can measure the EMF, which corresponds to the equilibrium pO₂ for the sample and gas. The gastight chamber incorporates an electrochemical sensor that also serves as an oxygen pump and allows for the simultaneous control of oxygen flux and measurement of oxygen potential. When pumping oxygen, two primary sources of oxygen are considered: (a) the gas phase in the cell and (b) the sample phase, which is described by Eq. 15. The total moles of oxygen pumped are denoted by \( \Delta n_{O_2} \), which can be evaluated by Faraday's law:

\[
\Delta n_{O_2} = \frac{i\Delta t}{4F} = \Delta n_{O_2(gas)} + \Delta n_{O_2(specimen)} 
\]

where \( \Delta n_{O_2(gas)} \) and \( \Delta n_{O_2(specimen)} \) are the moles of oxygen pumped from the gas and specimen, respectively. To calculate the net amount of oxygen removed from the specimen, we must subtract the gas-phase contribution from the total amount of oxygen. When the gas phase is treated as an ideal gas,
\[ \Delta n_{O_2(\text{gas})} = \frac{V}{RT} \Delta pO_2, \] (17)

where \( V \) is the free volume of the gas-tight chamber, \( \Delta pO_2 = pO_{2,f} - pO_{2,i} \), and the subscripts \( f \) and \( i \) are the final and initial equilibrium \( pO_2 \). For the specimen,

\[ \Delta n_{O_2(\text{specimen})} = \frac{W}{2M} [x_f - x_i] \] (18)

where \( W \) is the weight of the specimen, \( M \) is the molecular weight, and \( x_f \) and \( x_i \) are the equilibrium \( x \) values for a given \( pO_2 \). However, when \( \Delta n_{O_2(\text{gas})} \) is small enough in comparison to \( \Delta n_{O_2(\text{specimen})} \), the thermodynamic behavior of the system is essentially due to the solid sample.\(^3\) If we can choose by analogy with Eq. 11,

\[ x_f = K pO_{2,f}^{1/4} \]

and

\[ x_i = K pO_{2,i}^{-1/4}, \] (19)

where the proportionality constant \( K \) is the value at \( pO_2 = 1.0 \text{ atm} \). The difference between these two states is

\[ \Delta x = x_f - x_i = K[pO_{2,f} - pO_{2,i}]^{1/4} \]

\[ = K \Delta pO_2^{-1/4} \] (20)

and the proportionality constant \( K \) can be determined from Eq. 20.\(^{20}\)

### 1.3 Constant-Composition Measurement

In a gas-tight cell at low oxygen pressures, the thermodynamics of the system are essentially determined by the solid sample.\(^3\) In this condition, we can apply the Gibbs-
The Helmholtz equation, \[ \Delta H_{O_2} = \Delta G_{O_2} + T \Delta S_{O_2}, \] \hspace{1cm} (21)

where \( \Delta G_{O_2} = -4FE \), and \( \Delta S_{O_2} = -(\partial \Delta G_{O_2} / \partial T)_{x = \text{const}} = 4F(\partial E / \partial T)_{x = \text{const}} \). Therefore,

\[ \Delta H_{O_2} = -4FE + 4FT(\partial E / \partial T)_{x = \text{const}} \]
\[ = -4F[E - T(\partial E / \partial T)_{x = \text{const}}] \hspace{1cm} (22) \]

Thus, the relative partial molar enthalpy \( \Delta H_{O_2} \) and the relative partial molar entropy \( \Delta S_{O_2} \) can be determined from the changes in EMF with temperature at constant \( x \); or from, respectively, the slope of \( \log pO_2 \) vs. \( 1/T \), i.e.,

\[ \Delta H_{O_2} = R[\partial \ln pO_2 / \partial (1/T)]_{x = \text{const}}, \hspace{1cm} (23) \]

and \( \Delta S_{O_2} \), the intercept at \( 1/T = 0 \).

1.4 Electronic Transport Properties

The electronic conductivity \( (\sigma) \)

\[ \sigma = nq\mu, \hspace{1cm} (24) \]

where \( n \) is the electron concentration, and \( \mu \) the electron mobility. The mobility is expressed as

\[ \mu = \mu_0 \exp \left(-\frac{E_m}{kT}\right), \hspace{1cm} (25) \]
where \( \mu_o \) is a pre-exponential constant, and \( E_m \) is the migration energy of electrons. In fluorite structures, such as ceria, the concentration of electrons \( n \) can be denoted as

\[
n = \frac{8x}{a_o^3}
\]  

(26)

where \( a_o \) is the X-ray lattice parameter. By combining Eqs. 24-26, we obtain

\[
\sigma = \frac{8x}{a_o^3} q \mu_o \exp\left(-\frac{E_m}{kT}\right).
\]  

(27)

1.5 Electrochemical Transport

Heyne\(^6\) derived the electrochemical transport equation for ambipolar transport in metal oxides under a chemical potential gradient

\[
-j_e = j_i = (\sigma / 4q)t_t(t_e(\partial \mu_{O_2} / \partial x)).
\]  

(28)

For ionic conductors, \( t_i \gg t_e \), i.e., \( t_i \sim 1 \), it gives

\[
j_i = (\sigma / 4q)(\partial \mu_{O_2} / \partial x).
\]  

(29)

For electronic conductors, \( t_e \gg t_i \), i.e., \( t_e \sim 1 \), it gives

\[
j_e = (\sigma / 4q)(\partial \mu_{O_2} / \partial x).
\]  

(30)

2 EXPERIMENTAL APPROACH

2.1 Experimental Equipment
Electrochemical Cell Construction

Various designs of gas tight electrochemical cells are shown in Fig. 1. In Fig. 1a, two identical YSZ disks are used. The top disk of the cell serves as a permeation specimen and as an oxygen sensor. The bottom disk is primarily used as an oxygen pump. The walls of the cell consist of three 0.5-in.-diameter high-purity alumina (#998A, McDanel) rings that are separated from each other and the disks by thin Pyrex glass (#7740, Corning) rings. The alumina rings also provide high-temperature electrical insulation. Both YSZ disks were painted with platinum paste (code #6926 unfluxed, Engelhard) on the entire outer face and on that part of the inner face that would be within the enclosure. These electrodes were further prepared in air by several heating step, finally being fired at ≈980°C overnight. Platinum wires of 5 mil-diameter were used as electric leads in the Pyrex-sealed cell. The entire stack was placed in the measuring furnace along a vertical axis and a spring force was applied to the stack. A 3% O₂/Ar gas mixture was passed through the system while firing up to 1000°C. During heating, the Pyrex g (softening temperature 820°C) rings melted and provided a gas-tight seal. The limitation of mechanical pressure difference in the Pyrex seal was 0.35 atm at 920°C. This was determined by the continuous pumping in of oxygen through the electrolyte until failure. However, when the oxygen was pumped out from the inside cell, the maximum pressure obtainable was 0.03 atm because the initial gas mixture was 3% O₂-Ar. No problem in sealing was experienced when pumping oxygen out.

Four-Probe Conductivity Cell

The various conductivity specimens were prepared by sintering. The final step was to cut the bar into a four-probe conductivity specimen and load it into the coulometric titration chamber shown in Fig. 1b. Both DC and AC conductivity can be measured; the AC conductivity was measured at a constant frequency of 1592 Hz.
Measuring Assembly

The electrochemical cell was placed an alumina tube of 3.8 cm outer diameter (OD) and 35 cm length, with a flat disc end. An open window measuring 2.5 x 5 cm was cut in the bottom of the alumina tube for installation of the electrochemical cell. This portion was sealed to the brass head with water-soluble high-temperature ceramic cement (Paste #1, Sauereisen Cement Co.) and then inserted into a quartz tube. The quartz (outer) tube was 36 cm in length and 4.5 cm in OD. It was connected to the brass head by an O-ring to form a gas-tight system. A spring-loaded alumina rod was loaded onto the cell stack to facilitate sealing. A thermocouple made of 16 mil Pt–13% Rh/Pt in a 6 mm OD thermocouple tube was inserted into the 0.5-in. diameter alumina tube. A heat resistant alloy (Inconel) tube was placed in the furnace outside the measuring system. To protect it from electrical pickup, the alloy tube was grounded; serving as a heat sink, it also acts to provide a more uniform temperature.

2.2 Cell Performance Tests

To perform electrochemical transport measurements utilizing a Pyrex-glass-sealed gas-tight cell, the following preliminary tests were necessary.

Leak Test by Switching Gas

After sealing the cell, the Pyrex seals by switching the gas outside of the cell from 3% O\(_2\)-Ar (original atmosphere) to O\(_2\) (or air). If the seals are gas-tight the EMF should correlate with the oxygen potential difference within experimental error. If there are open pores or leakage is present, the indicating EMF will drop rapidly to zero after switching gas. The leak test was performed \(\approx 900^\circ C\). The successful seals showed no significant change in EMF with time.

Cell Volume Measurement by Coulometric Titration
The free volume of the electrochemical cell can be determined by coulometric titration. With the ideal gas law, $PV = nRT$, or $\Delta pO_2V = -n_{O_2}RT$ when supplying current, $n_{O_2} = i \cdot t / 4F$ and or, from the plot of $pO_2$ vs. time, $t$, the slope gives

$$\text{slope} = \frac{\partial pO_2}{\partial t} = \frac{iRT}{4F} / V.$$  \hspace{1cm} (31)

To determine the $pO_2$ range for which the above expressions are valid, a gas coulometric titration experiment was performed. The continuous pumping profile of $pO_2$ ranges from $\approx 0.2$ atm to $\approx 10^{-6}$ atm at 982°C. Also from the plot, one can see that the calculated volumes at various points are relatively constant until the $pO_2$ is $\approx 10^{-3}$ atm at 982°C. Focusing on the $pO_2$ region of air (0.21 atm), we attempted several runs to determine volume by two approaches. For these experiments, an additional monitor (Fig. 1c) was added to the cell. The first approach utilized only one disc as an oxygen pump. From a plot of $pO_2$ vs. time for this case one obtains a volume of 2.15 cm$^3$. In each case the average volume was within 0.5% of the individual runs.

**Pumping Performance Tests**

The above coulometric titration test can be used to accurately determine ionic transference numbers near 1. EMF or conductivity methods do not provide the accuracy obtainable by coulometric titration. The following experiments were carried out to determine the relative ionic transference number of various samples.

Using a three monitor cell (Fig. 1c), we evaluated the pumping performance of YSZ by supplying identical current to each of the two discs. A continuous pumping system was used, with one side pumping oxygen out and the other side pumping oxygen in. Tests were also conducted in the reverse direction. No change in EMF was noted when identical composition ZDY-2(YSZ) discs were used. However, when other YSZ discs were used (ZDY-4 [YSZ] and ZDY-2[YSZ]), changes in EMF were noted which