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Free Energy of Formation of PdO by Impedance Dispersion Analysis

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The sharp increase in low-frequency impedance at a Pd/solid electrolyte interface below the thermodynamic transition temperature has been used to determine the free energy of formation for PdO. This observation has been exploited in the development of a new generation of absolute oxygen monitors.

In earlier work (*1, 2*) we observed that the interface between palladium and oxide ceramics, after they had been reaction welded, could be of two different types. This was related to the thermodynamic stability of its oxide in the ambient atmosphere. This observation is of consequence in high-temperature electrochemical cells of the type Pd/YSZ/Pd, in which the metal and the ceramic electrolyte form such bonds. Pd will then be an excellent electrode if it behaves as a noble metal. The charge transfer resistance across such an interface, which is due to the oxygen redox equilibrium, will be minimal. This can be measured by the cell's low-frequency ac impedance. However, the presence of an oxide between electrode and electrolyte will obstruct the charge transfer processes at the triple-phase contacts of metal, electrolyte, and oxygen atmosphere. The cell's faradaic impedance will then be substantially increased. The presence or absence of PdO under thermal equilibrium can therefore be observed by measuring the impedance of a cell over the frequency range in which faradaic transfers are normally observed (i.e., less than 5 kHz), and analyzing the data in complex impedance space (*3, 4*). A more convenient procedure, with negligible loss of accuracy, is to simply measure the impedance amplitude at a fixed, low, frequency as a function of temperature.

Disks of 10 *m/o* yttria-stabilized ZrO_2 (diameter 10.4 mm, 1.3 mm thick) were sputtered on both sides with 600–700 nm of Pd metal. The construction of the cell and experimental details have been described elsewhere (*5*). Experiments were carried out between 400 and 1000°C in argon/O_2 gas mixtures ($10^{-4} < P_{O_2} \leq 1$ atm), and analyzed by the variation of resistance of a cobalt oxide wire at 1000°C (*6*) and by the standard oxygen galvanic probe (Pt/YSZ/Pt) with a reference atmosphere. The gas flow rate was 3.5 liters hr^{-1}. For each atmosphere impedance spectra were obtained at temperature intervals of 20 to 50°C. The actual PdO decomposition temperatures were located by monitoring the impedance at 10 Hz over intervals of 1 to 3°C after thermal equilibrium had been reached.

In Fig. 1 the impedance amplitude at 10 Hz is plotted against the temperature for four different oxygen partial pressures. For each curve the high-impedance region at low temperature includes the bulk resistivity of the PdO in the third phase and the charge transfer resistance which has been increased

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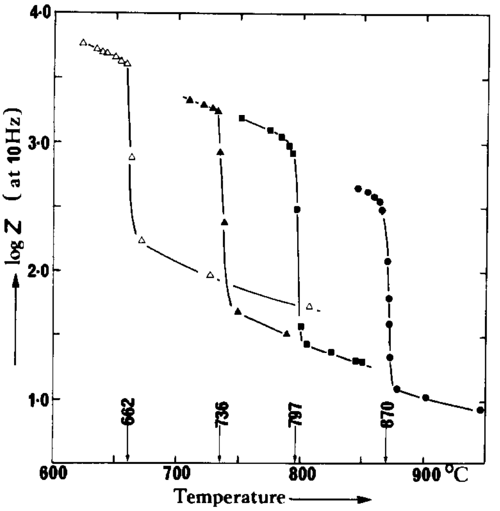

FIG. 1. The impedance–temperature relation at 10 Hz for a Pd/YSZ/Pd cell at: ●, 1 atm; ■, 0.208 atm; ▲, 0.049 atm; and △, 0.0046 atm.

by the presence of PdO. These are absent at high temperature. The transition from high to low resistivity, or vice versa, takes place reproducibly over a temperature range of 5 to 8°C, provided equilibrium has been reached. In the Pourbaix–Ellingham diagram (*7*) of Fig. 2 the decomposition temperatures at each oxygen partial pressure have been superimposed on the curves relating $RT \ln(P_{O_2})^{1/2}$ to the Kelvin temperature.

From the points of intersection the free energy equation for the formation of PdO has been analyzed to be:

$$\Delta G°_T = -(113\,900 \pm 750) + T(99.9 \pm 1.5)\ \text{J mole}^{-1}.$$

The agreement with literature data (*8–10*) over the entire temperature range is within the experimental error and virtually indistinguishable from Warner's results (*9*). Standard enthalpy and entropy for the formation of PdO at 298°K are: $\Delta H°_{298} = -121\,010 \pm 800$ J mole^{-1}, $S°_{298} = 33.5 \pm 1.5$ J K^{-1} mol^{-1} for the reaction Pd + $\frac{1}{2}O_2 = PdO$.

Using the above thermodynamic data, impedance dispersion analysis on Pd/ZrO_2–Y_2O_3/Pd cells, or simply the measurement of their ac conductivity at low frequency, can be used as an *absolute* method to determine oxygen partial pressures which are univariantly related to the decomposition temperature of PdO in such a cell (*11*). Similar probes can be designed using Pt, Ir, Ru, or Ni with or without an anodic or cathodic dc bias and an appropriate electrolyte to match the decomposition temperature ranges.

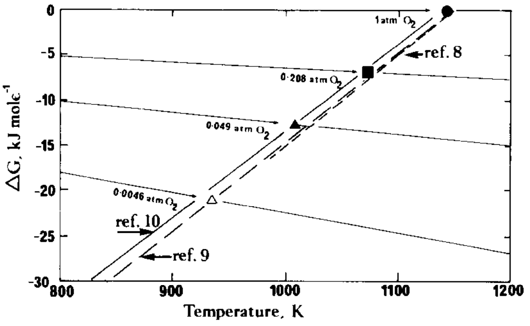

FIG. 2. Pourbaix–Ellingham diagram for the formation of PdO. →, $RT \ln(P_{O_2})^{1/2}$ versus temperature; ●, ■, ▲, and △, free energy equation, this work.

Acknowledgment

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References

1. H. J. DE BRUIN, A. F. MOODIE, AND C. E. WARBLE, *J. Mater. Sci.* **7**, 909 (1972).
2. H. J. DE BRUIN, *Nature* (*London*) **272**, 712 (1978).
3. A. D. FRANKLIN, *J. Amer. Ceram. Soc.* **58**, 465 (1975).
4. H. J. DE BRUIN AND S. P. S. BADWAL, *J. Aust. Ceram. Soc.* **14**(2), 20 (1978).
5. S. P. S. BADWAL AND H. J. DE BRUIN, *Aust. J. Chem.* **31**, 2337 (1978).
6. A. DUQUESNOY AND F. MARION, *Bull. Soc. Chim. Fr.*, 77 (1964).
7. W. L. WORRELL AND J. HLADIK, *in* "Physics of Electrolytes" (J. Hladik, Ed.), Vol. 2, p. 747, Academic Press, London/New York (1972).

8. H. Z. KLEYKAMP, *Z. Phys. Chem. Neue Folge* **71**, 142 (1970).

9. J. S. WARNER, *J. Electrochem. Soc.* **114**, 68 (1967).

10. W. E. BELL, R. E. INYARD, AND M. TAGAMI, *J. Phys. Chem.* **70**, 3735 (1966).

11. H. J. DE BRUIN AND S. P. S. BADWAL, Australian Provisional Patent Applications, PD 4563/78 (31 May 1978), PD 6823/78 (17 November 1978), and PD 7374/79 (16 January 1979), "Electrode-Active Oxygen Monitor."