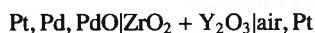E. PAWLAS-FORYST *, L. A. ZABDYR*

THE OXIDATION OF PALLADIUM

UTLENIANIE PALLADU

Thermodynamic properties of palladium oxide, PdO, were determined by means of emf technique, using solid electrolyte galvanic cells:

$$Pt, Pd, PdO | ZrO_2 + Y_2O_3 | air, Pt$$

with air reference electrode. The main experimental problem was to obtain both palladium and palladium oxide, as well in the form of powders, which was attained by complicated chemical procedure. Gibbs energy of oxidation reaction was derived from emf values measured within temperature range: 843 – 1100 K, and standard thermodynamic functions were then calculated at room temperature, using the most recent C_p data. Comparison of quantities obtained in this study with other recent experimental values from literature and data from thermochemical compilations displays very good agreement.

Własności termodynamiczne tlenku palladu wyznaczono metodą pomiaru siły elektromotorycznej odpowiednich ogniw galwanicznym ze stałym elektrolitem:

$$Pt, Pd, PdO | ZrO_2 + Y_2O_3 | air, Pt$$
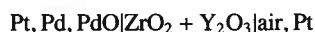
z powietrzną elektrodą odniesienia. Poważnym problemem było uzyskanie metalicznego palladu jak i jego tlenku w postaci proszku, co osiągnięto z pomocą skomplikowanej procedury chemicznej. Energię swobodną reakcji utleniania palladu wyznaczono ze zmierzonych sił elektromotorycznych w przedziale temperatur: 843 - 1100 K. Wartości standardowych funkcji termodynamicznych w temperaturze pokojowej obliczono przy pomocy najnowszych danych Cp. Porównanie wyników niniejszej pracy z rezultatami najnowszych badań innych autorów a także z wartościami z kompilacji danych termochemicznych wskazuje na bardzo dobrą zgodność.

1. Introduction

The reliability of electronic circuits is one of the crucial features when used in high risk applications such as automotive, aerospatial and medical/biomedical devices. The oxidation behaviour of palladium is of interest, due to its applications as a substrate in the high- performance electronic circuits mentioned above.

The Gibbs energy of formation of palladium oxide was measured several times; a detailed comparison of all the published $\Delta G^0_{f,PdO}$ values is given by Jacob [1]; it consists of twelve independent data sets, most of them considerably scattered. Only the results of Kleykamp [2] and Jacob [1] agree each other, therefore the aim of this study was to clear the situation and to enrich the knowledge of this problem.

2. Sample preparation

Special care was taken to obtain palladium oxide, PdO, and the palladium metal in the powder form. The fine powder of palladium is called *black palladium* and is obtained as described below: initial material – small pieces of Pd foil 0.2 mm thick, 99.99% purity, were dezoxidized in the hydrochloric acid, and then dissolved in the nitrohydrochloric acid. The solution was then evaporated to dryness and dissolved in water again several times to release the nitrogen oxides. Then solution was slightly heated and crystallization was initiated; brown crystals of $PdCl_2$ were obtained. The water solution of palladium chloride was slightly heated and reduced to metallic palladium by the sodium formate. The metal

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was precipitaded in the form of black deposit – *black palladium*.

Another portion of Pd foil was dissolved in hot nitrohydrochloric acid, until dissolution was completed. Sodium nitrate was then added in the excess to the stoichiometry of reaction: $PdCl_2 + 2\ NaNO_3 = PdO + 2\ NaCl + N_2O_3 + O_2$, to produce the semi-liquid pulp. After about half hour of heating (brown fumes of nitrogen oxides were observed, the dense pulp was cooled, and dissolved in the hot distilled water; dark powder of PdO was deposited. Both *black palladium* and PdO were checked by XRD and EDX analysis confirming their identity.

3. Experimental

EMF technique was employed to measure Gibbs energy of formation of palladium oxide, PdO, according to the reaction:

$$Pd_{(s)} +{}^1/_2O_{2(g)} = PdO_{(s)} \qquad (1)$$

using solid electrolyte galvanic cell with air reference electrode, as shown schematically below:

$$Pt, Pd, PdO|ZrO_2 + Y_2O_3|air, Pt \qquad (2)$$
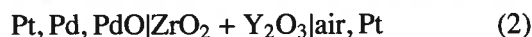
Measurements were made within temperature interval: 843 – 1100 K during both heating and cooling mode.

Closed-one-end yttria-stabilized zirconia (YSZ) tubes 5/8 mm I/O.D., and 300 mm long (Yamari, Japan) were used as the electrolyte and dry air ($Po_2 = 0.21$ atm) was employed as the reference electrode. The equimolar mixture of Pd and PdO powders was put into the electrolyte tube, and the cell itself was located in the constant temperature zone of the vertical resistance furnace. The inert atmosphere was maintained inside the cell by passing 5 ml/min argon flow of quality 5.0, dezoxidized additionally by copper column. Platinum wire 0.5 mm served as the current lead for reference electrode, and Pt wire with the palladium tip was used for working electrode. The temperature was controlled by the thermocouple (Pt-PtRh10) located at the bottom of the quartz tube, and connected to the temperature controller Omega CN 4800. The emf was measured using Keithley 2000 multimeter, linked to automatic data aquisition system. There was no need to introduce the correction for Pt/Pd thermoelectric power, because the Pt- end and Pd/Pt joint were placed within the constant temperature zone of the furnace.

The scheme of the cell cross-section is shown in Figure 1, and the sketch of the whole experimental assembly is presented in Figure 2.
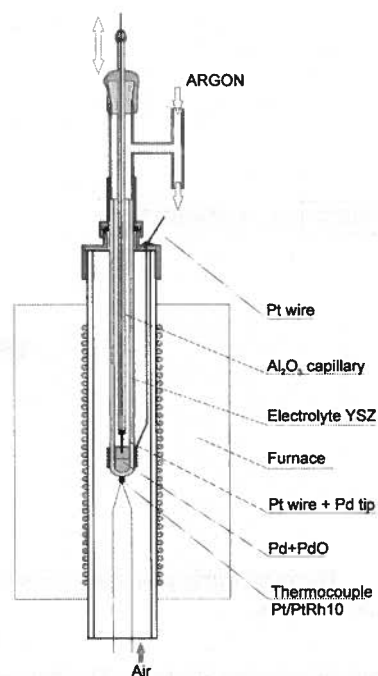

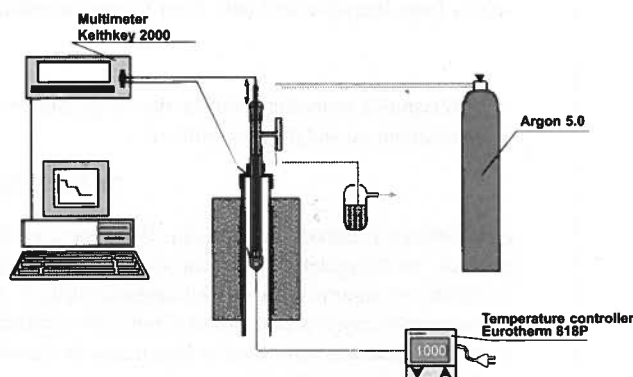Fig. 1. The cross-section through the cell (1) assembly with air reference electrode

Fig. 2. The sketch of the whole experimental equipment

4. Results

Since the linear dependence of electromotive force on temperature was observed during both heating and cooling cycles, experimental results were approximated by straight-line equation:

$$E[mv](\pm 2) = 575.11(\pm 5.55) - 0.5244(\pm 0.0057)T. \qquad (3)$$

Gibbs energy of formation of palladium oxide, $\Delta G^0_{f,PdO}$, was then derived from the measured emf values using well-known relation (4):

$$\Delta G^0_{f,PdO} = -2FE + RTln0.21 \qquad (4)$$

where: F = 96.508 J/mV – Faraday constant; R = 8.314 J/K universal gas constant; E – measured emf [mV]; T – absolute temperature [K]; 0.21 – partial oxygen pressure in the air [atm] (on the reference electrode). Combination of (3) and (4) gives:

$$\Delta G^0_{f,PdO}(\pm 0.075) = -111.0(\pm 1.1) + 0.088(\pm 0.0011) \cdot T \quad kJ/mol \tag{5}$$

The plot of measured emf versus temperature is shown in Fig. 3.

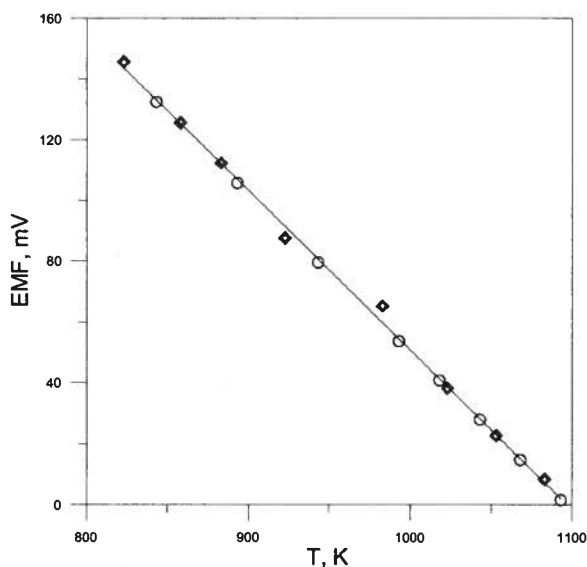Fig. 3. Plot of emf versus temperature of the cell (1) taken during heating (circles) and cooling (squares), respectively

Values of the thermodynamic formation functions

were then derived at room temperature, using the most recent C_p data by Jacob et. al. [1], as follows:

$$\Delta H^0_{298} = -115.45(\pm 1.1) kJ/mol \tag{6}$$

$$\Delta S^0_{298} = -100.6(\pm 1.1) J/mol * K \tag{7}$$

and

$$S^0_{298} = 39.83(\pm 1.1) J/mol * K \tag{8}$$

5. Concluding remarks

Thermodynamic properties of palladium oxide, PdO, were determined by means of emf technique. The main experimental problem was to obtain metallic palladium as well as palladium oxide in the form of powders; both were produced by complicated chemical procedure. Values of standard thermodynamic functions at room temperature were then derive using most recent C_p data of [1]. Agreement of our results with recent experimental values and thermochemical data from compilations is very good, as can be seen on table below:

TABLE

Comparsion of results of this work with the recent literature data

$-\Delta H^0_{298} kJ/mol$	$S^0_{298} J/mol * K$	Reference
117.99(±2.1)	36.82(±2.1)	[2]
115.51(±0.13)	37.25(±0.4)	[1]
115.48	38.91	[3]
114.09	37.62	[4]
115.45(±1.1)	39.83(±1.1)	this work

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