EXCESS HEAT IN MOLTEN SALTS OF (LiCl − KCl) + (LiD + LiF) AT THE TITANIUM ANODE DURING ELECTROLYSIS

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The electrochemical cell and a technique for precision calorimetric measurements has been developed. Experiments with molten salts containing lithium deuteride were carried out. Calorimetric measurements made on the titanium anode during experiments. Measurements were made in an inert atmosphere of helium and in an atmosphere of deuterium at various density of an electrolysis current. Excess heat was obtained on the titanium anode in a deuterium atmosphere deuterium during electrolysis. An x-ray diffraction analysis was made on the used titanium anode. The analysis of the results obtained is discussed.

1. Introduction

Measurements of thermal effects on palladium electrodes in molten salts (LiCl − KCl) + LiD and (LiCl − KCl) + LiH were reported in Ref. [1] These measurements were stimulated by the results reported by Liaw *et al.*[2] More excess heat was obtained in experiments with deuterium than with hydrogen. The equality of the input and output power on the palladium electrode in process of electrolysis was determined.[1] The factor of an output on a current should be in experiment less than unity, and in calculations the accepted value is equal to unity. In this case, it is possible to speak about excess heat.

The present paper is a continuation of these experiments.[1] Titanium iodide is used as an electrode material, and measurements were made in atmospheres of helium, and of deuterium. The goals of this paper were to report on the calibration of the electrochemical cell for calorimetric measurements during electrolysis, and on a technique for the improvement of measurements.

2. Experimental

The electrochemical cell was constructed for measurements as shown in Fig. 1. The mixture LiD + LiF was loaded into an electrochemical cell. The fluorine content of this mixture did not exceed 5 wt.%. The weight of the loaded mixture LiD + LiF was 2.6 g. A porous ceramic partition was placed from above the mixture. The partition was pressed down by the titanium electrode which surrounded by a LiCl–KCl eutectic. The composition of this eutectic was: 58 mol% LiCl and 42 mol%
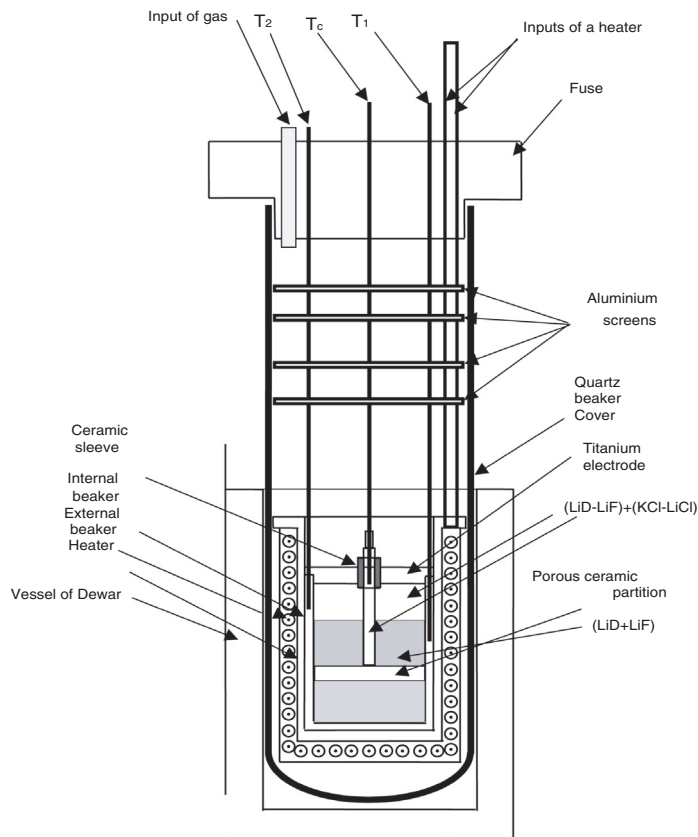
Figure 1.   Schematic of the electrochemical cell.

KCl, or 43.99 wt.% LiCl and 56.01 wt.% KCl. The LiCl–KCl eutectic and mixture LiD + LiF were heated up into a deuterium atmosphere a temperature of 360 °C for the production of molten salts. When the molten salts cooled to a temperature of 80 °C, deuterium gas was pumped out, and the electrochemical cell was filled with helium. We then opened the cell. The size of the titanium cathode shipped in molten salts was measured, and eutectic was added. The size of the cylindrical titanium electrode were: 3.4 mm diameter, 50 mm height. A chromel–alumel thermocouple in the corrosion-proof jacket was inserted into the titanium electrode to a depth of 20 mm. The weight of the titanium electrode was measured to be 1.95 g. The area of the titanium electrode covered with molten salt has been calculated to be $S = 1.372 \, \text{cm}^2$ during the experiment. The quantity of deuterium in the molten salt was calculated to be 0.13 g.

The cell was then filled with helium gas. The calibration of thermocouple data by heater power was measured. Electrolysis was run at different current densities in a helium atmosphere: $j_1 = 80.15 \, \text{mA/cm}^2$ and $j_2 = 298.74 \, \text{mA/cm}^2$. The develop-

ment of heat was measured during electrolysis. In this case the average temperature was 670 K. Electrolysis was disconnected at the end of this experiment. The energy from a heater was measured and data were compared with the calibration.

Helium gas was pumped out, and the electrochemical cell was filled with deuterium gas to a pressure hardly more than an atmosphere. The eutectic heated up to the temperature of experiment. The calibration of the electrochemical cell was determined using a heater in an atmosphere of deuterium. Electrolysis was done at current densities of $j_1 = 49.21 \, \text{mA/cm}^2$, $j_2 = 153.59 \, \text{mA/cm}^2$, $j_3 = 120.85 \, \text{mA/cm}^2$, and $j_4 = 246.57 \, \text{mA/cm}^2$. The energy from a heater was measured and data were compared with the calibration. The average value of the temperature in this experiment was 657 K.

The titanium electrode was taken from the molten salts, and taken from a cell after cooling to room temperature. The titanium electrode was washed in distilled water, and we carried out the x-ray diffraction analysis. The titanium electrode was cut and an optical analysis was carried out.

3. Heat Calculations

The equation of a calibrating straight line was calculated by the method of the least squares

$$T_{\text{c}} = 0.22078 W_{\text{heater}} + 3.65383 \, \text{mV}, \tag{1}$$

where T_{c} is the measurement of the central thermocouple in mV, and where $W_{\text{heater}} = U_{\text{heater}} I_{\text{heater}}$ is the heater power in W. Calibration data for the heater in an atmosphere of helium, a calibrating straight line, and points for checking the calibration in an atmosphere of helium after electrolysis, and in an atmosphere of deuterium before and after electrolysis, are shown in Fig. 2. The calculation of the measured power during electrolysis was made using the formula

$$W_{\text{obt}} = \frac{T_{\text{c}} - 3.65383}{0.22078 \, \text{W}}. \tag{2}$$

The calculation of the electrolysis power was made using the following formula, under the assumption that the factor of an output on a current is equal to unity

$$W_{\text{el}} = U_{\text{el}}(I_{\text{el}} - 0.0042) \, \text{W}, \tag{3}$$

where U_{el} is the electrolysis voltage (V), I_{el} the electrolysis current (A) and $0.0042 \, \text{A}$ is the amendment on a zero instrument reading. The excess of the measured power was calculated using the formula

$$\Delta W_1 = W_{\text{obt}} - W_{\text{heater}}^{\text{el}}, \tag{4}$$

where $W_{\text{heater}}^{\text{el}} = I_{\text{heater}}, U_{\text{heater}}$ is the heater power during electrolysis (W).
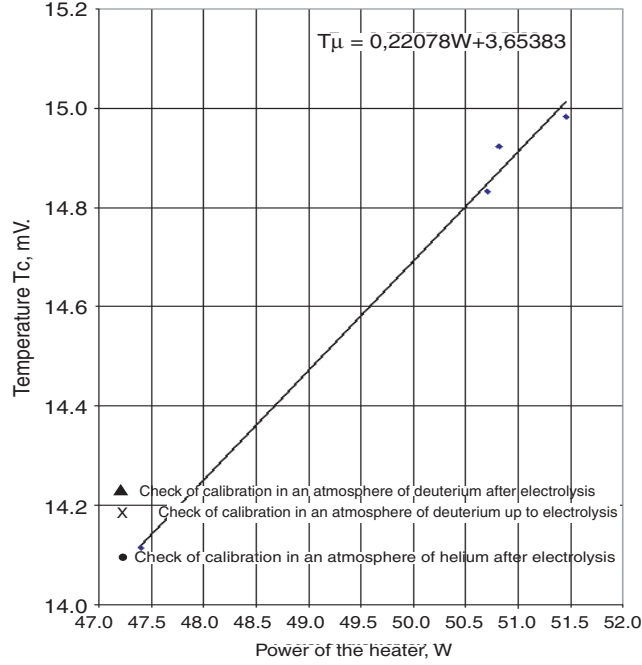
Figure 2. Temperature T_c calibration of the electrochemical as a function of heater power.

The excess power during electrolysis was calculated using the formula

$$\Delta W = \Delta W_1 - W_{el}. \tag{5}$$

The calculation of the allocated gas of deuterium D_2 for the electrolysis period (in moles) was made as in paper.[2] The charge for all experiment in an atmosphere of helium during electrolysis should be allocated

$$q_{He} = 0.10996\,A \times 7860\,s + 0.40987\,A \times 9600\,s = 4799.1\,C. \tag{6}$$

The quantity of the allocated deuterium on the anode is

$$m[D_2] = 4799.1/96520 \times 2.0016/1 = 0.09952\,[g/4\,g]\,mol$$
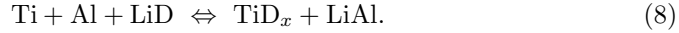
$$= 0.024880545\,mol\,D_2, \tag{7}$$

where $0.10996\,A$ is the average value of an electrolysis current for $7860\,s$ of electrolysis at constant external parameters for ten of the measured values that correspond to a current density of $80.15\,mA/cm^2$; and where $0.40987\,A$ is the average value of an electrolysis current for $9600\,s$ of electrolysis under different constant conditions

for 15 of the measured values—that corresponds to density of a current of 298.74 mA/cm^2.

The electrochemical cell reactions during electrolysis are:

$$LiD = Li^+ + D^-$$

$$Ti + xD^- = TiD_x + xe^- \quad \text{on the anode}$$

$$Al + Li^+ + e^- = LiAl \quad \text{on the cathode}$$
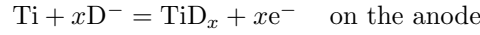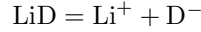
which gives the overall electrochemical cell reaction

$$Ti + Al + LiD \; \Leftrightarrow \; TiD_x + LiAl. \tag{8}$$

The associated enthalpies are $\Delta H_{670\,K} = -92.0\,\text{kJ/mol}$ for LiD; $\Delta H_{670\,K} = -132.9\,\text{kJ/mol}$ for TiD$_x$; and $\Delta H_{670\,K} = -53.72\,\text{kJ/mol}$ for LiAl. As a result of reaction (8), it should be allocated

$$-92.0 + 53.72 + 132.9 = 94.62\,\text{kJ/mol}.$$

If all allocated deuterium gas is absorbed by the titanium during electrolysis in a helium atmosphere, the following energy should be allocated

$$Q_\text{out} \; = \; 94.62 \times 0.024880545 \; = \; 2.3541971679\,\text{kJ}.$$

The change of excess power on the anode is shown in Fig. 3 during electrolysis in a helium atmosphere.

The integration of the excess power during electrolysis in a helium atmosphere gives a quantity of allocated excess heat on the anode which equals

$$Q_\text{exc} \; = \; -0.204\ \text{kJ}, \quad \text{for the entire experiment.}$$

The charge in experiment during electrolysis in a deuterium atmosphere was allocated

$$q_\text{D} = 0.067\,\text{A} \times 34800\,\text{s} + 0.21\,\text{A} \times 9900\,\text{s} + 0.16\,\text{A} \times 2100\,\text{s} + 0.34\,\text{A} \times 15900\,\text{s}$$

$$= \; 10152.6\,\text{C}.$$

The quantity of the allocated deuterium on the anode is

$$m[D_2] = 10152.6 \times 2.0016/96520/1 = 0.210541\,\text{g} = 0.052635\,\text{mol D}_2.$$

If we assume that all allocated gas was absorbed by the titanium, the energy should be allocated

$$Q \; = \; 94.62 \times 0.052635 \; = \; 4.9803237\,\text{kJ}.$$

The change of excess power on the anode is shown in Fig. 4 during electrolysis in a deuterium atmosphere.

The integration of the excess power during electrolysis in a helium atmosphere gives a quantity of allocated excess heat on the anode equal to
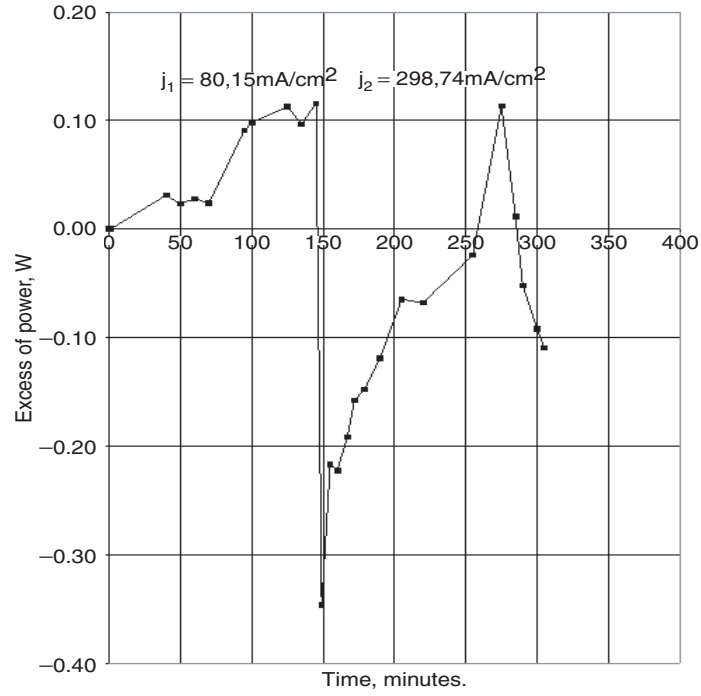
Figure 3. Excess power during electrolysis in a helium atmosphere on the anode as a function of time.

$$Q_{\text{exc}} = 18.163 \quad \text{kJ for all experiment.}$$

If the part of released heat occurs due to reaction of formation of deuteride titanium, the calculated quantity of heat at the anode under deuterium atmosphere has to equal

$$Q_{\text{exc}} = 18.163 - 4.9803237 = 13.18298732 \, \text{kJ.}$$

The total spent energy at experiment in a deuterium atmosphere:

$$Q_{\text{tot}} = 47.68581 \, \text{J/s} \times 62700 \, \text{s} + 0.108790 \, \text{J/s} \times 34800 \, \text{s} + 0.352549 \, \text{J/s} \times 9900 \, \text{s}$$

$$+0.228627 \, \text{J/s} \times 2100 \, \text{s} + 0.543644 \, \text{J/s} \times 15900 \, \text{s} = 3006.30018 \, \text{kJ.}$$

The fraction of excess heat is

$$Q_{\text{exc}}/Q_{\text{tot}} \times 100 \, \% = 100 \times 13.18298732/3006.30018 = 0.438 \pm 0.015\%.$$
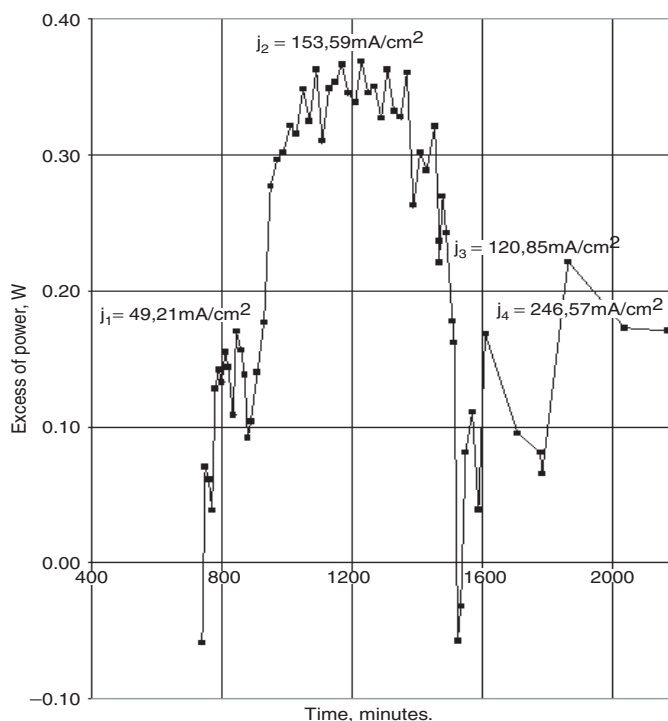
Figure 4. Excess power during electrolysis in a helium atmosphere on the anode as a function of time.

The relative error of measurement of excess heat is 3.5 %.

The Roentgen-phase analysis of a surface of a sample is shown on Fig. 5. Calculation of the contents of the deuteride titanium gives about 1–1.5 vol.% TiD_x in a sample. The optical analysis of a cut of a sample shows presence of the deuteride titanium at increase in 250 times under an electronic microscope (Fig. 6).

4. Discussion of Results

Steady thermal effects are observed during the experiments on a titanium electrode. The thermal effects may not be described by thermodynamics of electrochemical processes. Excess heat is measured at different current density. Heat absorption is observed at a sharp change of current density, and then excess heat is observed through 2 h all over again. This is shown in Fig. 3 during electrolysis in a deuterium atmosphere. For conservation of the released heat during long time it is necessary to define optimum density of a current for a concrete material which the electrode is made more carefully. In our case, the atmosphere from deuterium above electrolyte positively influences on process of excess heat at electrolysis. The process of development of heat at one density of a current has pulse character. All over again
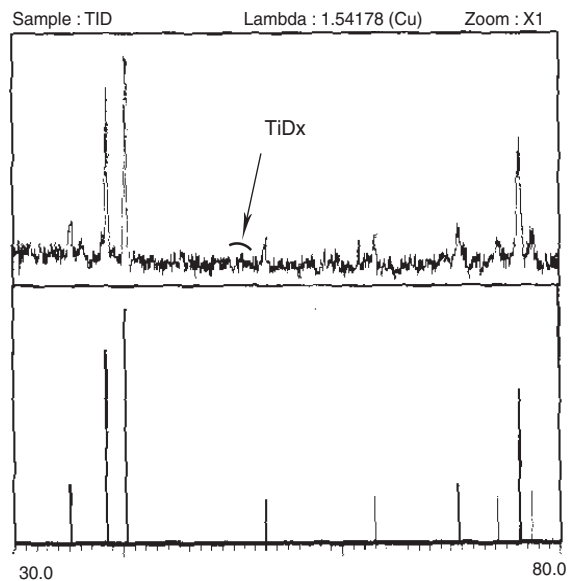
Figure 5.   The x-ray diffraction analysis of the surface of a sample after experiment.

development of heat is an increase and after achievement of the maximal value, there is a decrease of excess heat. The process of excess heat may be to support by gradual increase of density of an electrolysis current up to $150\,\text{mA/cm}^2$, the certain quantity of electrolyte and the certain weight of the titanium electrode.

In results of the x-ray diffraction analysis is possible to draw a conclusion. Not all of the weight of an electrode cooperated with molten salts in process of electrolysis.
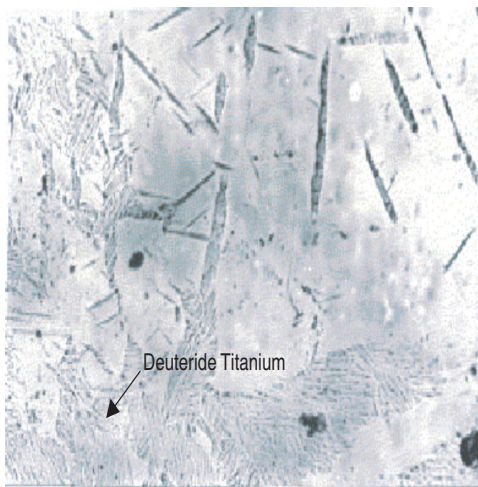

Figure 6.   Microstructure of the titanium (doubles and a thin plate of the titanium deuteride) after experiments (magnification of 250 times).

On the other hand, the calculated total of the deuterium, which reacted with the titanium is much more than the calculated quantity of deuterium in molten salts. Therefore, it is likely that the intensive process of deuterium saturation takes place at electrolysis in an atmosphere of deuterium not only from molten salts, but also from a gas phase.

Experiments on saturation of titanium electrodes are necessary to continue in molten salts in an atmosphere of deuterium for definition of the optimum parameters supporting of excess heat and to try thus to carry out the analysis of products of nuclear reactions, which are possible responsible for excess heat. The design of a device and an electrochemical cell is necessary to change for this purpose.

References

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2. B.Y. Liaw *et al.*, *J. Electroanal. Chem.* **319**, 161–175 (1991).