Journal of Thermal Analysis and Calorimetry, Vol. 58 (1999) 421-433

THERMOKINETIC STUDIES OF THE PROCESS FOR ELECTROREFINING SILVER

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Abstract

In this work some calorimetric measurements were also carried out on the electrorefining silver by using different current densities with a Calvet type microcalorimeter at room temperature. The ratio (R) of the measured heat (Q_m) to the input electric energy (Q_{in}) and the excess heat (Q_{ex}), i.e., difference between Q_m and Q_{in} during the electrorefining process, were discussed in terms of general thermodynamics. It was found that the R and Q_{ex} for silver were related with the current density or cell voltage employed in the experiment. The results obtained here also indicate that the heat generation under different conditions, such as different currents or voltages may be caused partially by the irreversibility of the process or by some unknown processes.

Keywords: electrorefining, excess heat, general thermodynamics, irreversibility, microcalorimetry

Introduction

The work dissipation, as heat released, during the process electrorefining of metal is always generated. It is certainly very important for the investigation of thermodynamics.

The calorimetric study of electrorefining copper was reported in our previous work [1]. The heat generated during the process is always greater than the electric work input to it. That kind of heat may also be called excess heat as reported [2]. The process of electrorefining copper looks as if it was very simple, i.e. during the process a copper ion (Cu^{2+}) in electrolyte solution obtained electrons at cathode surface where it deposited as a copper atom (Cu), and at the same time a copper atom leaves its electrons at anode where a copper ion goes into solution, and thus the whole system of electrorefining copper apparently seems not to change. In that case, such excess heat may be caused by the fact that the copper ion in solution of the electrorefining system could not be completely reduced at cathode to be deposited Cu, or the copper atom at anode of the system could not be oxidized to be Cu^{2+}. In other words, the excess heat is generated during the electrorefining process because the copper presents its low oxidation state Cu^{+}.

The purpose of this work is to obtain the calorimetric measurements during the process of electrorefining silver and to investigate these measurements related with

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

electrochemical conditions in details. Silver was used for electrorefining because it does not present a low oxidation state.

Experimental

Electrochemical cell

The cell used here for electrorefining silver was almost the same as in previous work [1]. It was formed of a silver rod as axis, circulated around some metal wire coils, placed in a glass test tube filled with silver nitrate solution (0.1 M), as shown in Fig. 1.

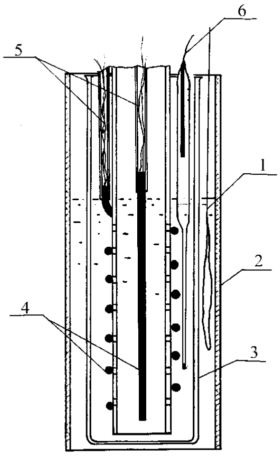

Fig. 1 Cross sectional view of the calorimetric chamber being placed in an electrorefining cell and a calibration heater; 1 – calibration heater; 2 – calorimetric vessel; 3 – glass cell; 4 – Ag rod and coils; 5 – electrode connections; 6 – reference electrode

Calorimetric system

The calorimeter and its system were the same as in our previous work [1].

In this study, an electronic-constant current source was also employed as a power supply in different processes.

Procedure

To test the reliability of our apparatus, the calorimetric system was calibrated again in situ with electric power in different ranges of energy. The results of the calibration are shown in Tables 1–3.

The results of heat generated by electrorefining silver were obtained in current density from 0.658 to 9.098 mA cm^{-2}. During the process, the energy consumption was determined with the centric rod – axis electrode used either as the anode, or as the cathode. These results are shown in Tables 4–7. We used an electronic-constant current power supply for the experiments.

Table 1 Calibration results of the calorimeter under S=3 and PP=40 condition

No.	$t_{heating}$/s	P_{in} / μW	E / μW nv^{-1} s^{-1}
4201305	300	82.0	92.8
4211040	300	45.1	125.0*
4211420	300	38.3	90.8

S=sensitivity; PP=decay parameter
E_{mean}=91.8±1.4 μW nv^{-1} s^{-1}
*There may be a random error, so that the E_{mean} was calculated without this result

Table 2 Calibration results of the calorimeter under S=10 and PP=30 condition

No.	$t_{heating}$/s	P_{in}/ μW	E / μW nv^{-1} s^{-1}
3061515	180	97.1	315.0
3061624	180	97.1	311.7
4171715	300	240.9	290.3

E_{mean}=305.7±13.4 μW nv^{-1} s^{-1}

Table 3 Calibration results of the calorimeter under S=30 and PP=40 condition

No.	$t_{heating}$/s	$P_{in.}$/ μW	E / μW nv^{-1} s^{-1}
4171435	300	884.0	876.8
4171555	300	738.9	882.1
4240817	180	70.1	890.7

E_{mean}=883.2±7.0 μW nv^{-1} s^{-1}

Results and discussion

From the results of calibration of the calorimeter summarized in Tables 1–3 it can be found out that the relative error of the power equivalent under low sensitivity conditions is better than ±4%. Therefore, the results obtained in this work should be reliable, even the relative error of power equivalent under high sensitivity is over ±4% as shown in Table 1.

The calorimetric measurements during electrorefining silver under different electrochemical conditions are shown in Tables 4–7. From these and Figs 2–13, we can find that the heat generated during refining silver is significantly changed, as in previous work [1], with current density, or cell voltage employed in this work.

The ratio of the measured heat to the electric input energy (Q_m/Q_{in}) decreases with current density whether in the centre electrode as a cathode, or as an anode.

The excess heat (Q_{ex}) is defined as before by a difference between Q_{in} and Q_m calculated with the results of calorimetric measurements. The results shown in Figs 6–9, indicate that the excess heat also depends on current density employed. In other words, the excess heat (Q_{ex}) decreases with current density whether in the center electrode as cathode, or as anode.

Table 4 Calorimetric measurements of the electrorefining process of silver in aqueous solution of $AgNO_3$ (0.1 M) at room temperature

No.	σ /mA cm^{-2}	V/V	t/s	Q_{in}/mJ	Q_m/mJ	R	Q_{ex}/mJ
3061554	0.913	0.048	210	7.62	6.96	0.91	–0.37
3061708	0.899	0.037	208	6.18	5.37	0.87	–0.81
3070824	0.656	0.033	302	5.88	9.73	1.65	3.85
3070946	0.658	0.033	310	5.92	10.52	1.78	4.60
3071107	0.658	0.035	303	6.27	14.65	2.35	8.38

*Silver rod (D=1.0 mm, L=26.0 mm) in the center axis as a cathode;
The anode formed a coil (D=10.0 mm) with silver wire (D=1.0 mm, L=97.0 mm)

Table 5 Calorimetric measurements of the electrorefining process of silver in aqueous solution of $AgNO_3$ (0.1 M) at room temperature

No.	σ /mA cm^{-2}	V/V	t/s	Q_{in}/mJ	Q_m/mJ	R	Q_{ex}/mJ
4201710	1.108	0.040	300	5.80	5.99	1.03	0.19
4131230	1.110	0.027	300	3.94	4.53	1.15	0.59
4131310	1.424	0.032	300	5.41	5.99	1.11	0.58
4131425	1.822	0.038	300	9.13	9.82	1.05	0.68
4141825	2.540	0.050	300	16.72	17.47	0.94	1.05
4171515	5.754	0.128	300	97.07	88.86	0.94	–8.22
4141410	6.027	0.148	300	117.26	109.67	0.93	–7.59
4141715	8.165	0.173	300	186.88	173.79	0.93	–13.09

*Silver rod (D=0.5 mm, L=31.0 mm) in the center axis as a cathode;
The anode formed a coil (D=10.0 mm) with silver wire (D=0.5 mm, L=150.0 mm)

Table 6 Calorimetric measurements of the electrorefining process of silver in aqueous solution of $AgNO_3$ (0.1 M) at room temperature

No.	σ/mA cm^{-2}	V/V	t/s	Q_{in}/mJ	Q_m/mJ	R	Q_{ex}/mJ
4171040	9.098	0.194	300	232.25	209.37	0.90	–22.88
4200915	5.709	0.129	300	96.88	91.65	0.95	–5.23
4200955	3.569	0.085	300	40.08	34.34	0.86	–5.74
4201030	1.551	0.044	300	9.08	9.16	1.01	0.08
4201405	1.176	0.037	300	5.78	6.67	1.16	0.90
4210830	1.110	0.038	300	6.03	7.03	1.17	1.00
4211340	0.755	0.030	300	2.98	5.82	1.95	2.84

*Silver rod (D=0.5 mm, L=31.0 mm) in the center axis as an anode;
The cathode formed a coil (D=10.0 mm) with silver wire (D=0.5 mm, L=150.0 mm)

Table 7 Calorimetric measurements of the electrorefining process of silver in aqueous solution of $AgNO_3$ (0.1 M) at room temperature

No.	σ /mA cm^{-2}	V/V	t/s	Q_{in}/mJ	Q_m/mJ	R
5271635	1.093	0.051	600	30.9	40.7	1.32
5230940	1.159	0.057	600	36.6	27.8	0.76
5301000	2.186	0.070	600	84.7	81.8	0.97
5301400	3.831	0.111	600	235.8	94.4	0.40
5301600	5.497	0.148	600	451.1	155.1	0.34

*Silver rod (D=1.0 mm, L=26.0 mm) in the center axis as a cathode;
The anode formed a coil (D=10.0 mm) with silver wire (D=1.0 mm, L=97.0 mm)

The process of electrorefining copper mentioned in the previous work [1] here seems that the silver atom is dissolved from silver anode into the solution and the silver ion is deposited onto the surface of cathode, therefore, the whole system never changes in the sense of thermodynamics. Thus the ratio of the measured heat (Q_m) to the input electric energy (Q_{in}) should be always less than one, or at most equal to one. However, it is also greater than one in most cases. It also appears that the heat observed in the experiment was more than the input electric energy! These kinds of results observed in this work compel us again to accept a 'fallacy' in classical thermodynamics! In other words, the result seems to show that it does not abide the first law of thermodynamics. As in previous work [1] it has to be pointed out that there

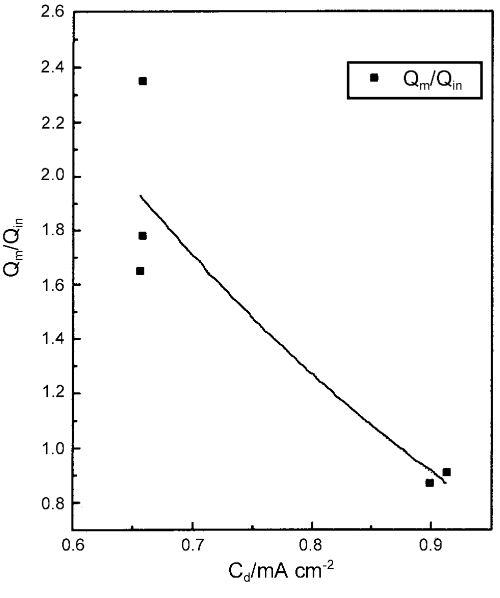

Fig. 2 Dependence of the ratio of work dissipation to the electric energy on the electric current density; silver rod (D=1.0 mm, L=26.0 mm) in the center axis as a cathode; the anode formed a coil (D=10.0 mm) with silver wire (D=1.0 mm, L=97.0 mm)

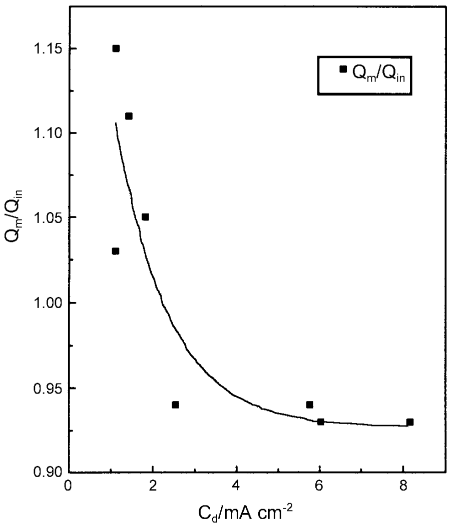

Fig. 3 Dependence of the ratio of work dissipation to the electric energy on the electric current density; silver rod (*D*=0.5 mm, *L*=31.0 mm) in the center axis as a cathode; the anode formed a coil (*D*=10.0 mm) with silver wire (*D*=0.5 mm, *L*=150.0 mm)

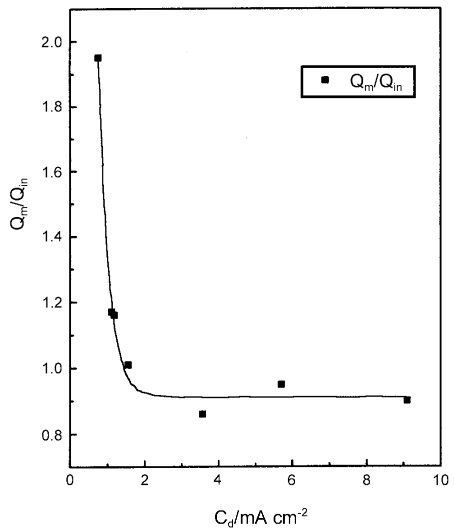

Fig. 4 Dependence of the ratio of work dissipation to the electric energy on the electric current density; silver rod (*D*=0.5 mm, *L*=31.0 mm) in the center axis as an anode; the cathode formed a coil (*D*=10.0 mm) with silver wire (*D*=0.5 mm, *L*=150.0 mm)

must be a ‘false fallacy’ in general thermodynamics. The problem here still is that the cell studied during electrorefining silver is not such a simple thermodynamic system. In previous work, such excess heat may be caused by the fact that the copper ion in solution of the electrorefining system could not be completely reduced at cathode to be deposited Cu, or the copper atom at anode of the system could not be oxidized to be Cu^{2+}, i.e. excess heat is generated during the electrorefining process because the copper presents its low oxidation state Cu^{+}. The calorimetric study of electrorefining silver in this work may be better because probably it avoids such a low

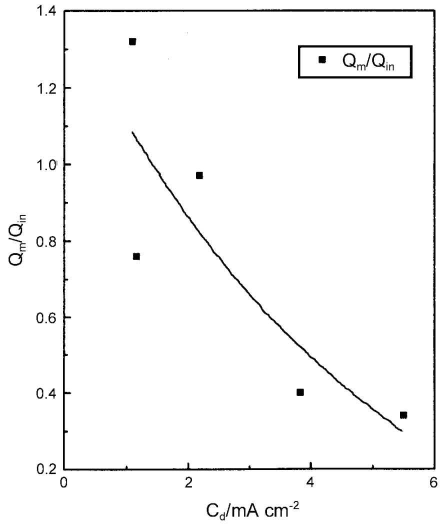

Fig. 5 Dependence of the ratio of work dissipation to the electric energy on the electric current density; silver rod (*D*=1.0 mm, *L*=26.0 mm) in the center axis as a cathode; the anode formed a coil (*D*=1.0 mm) with silver wire (*D*=1.0 mm, *L*=97.0 mm)

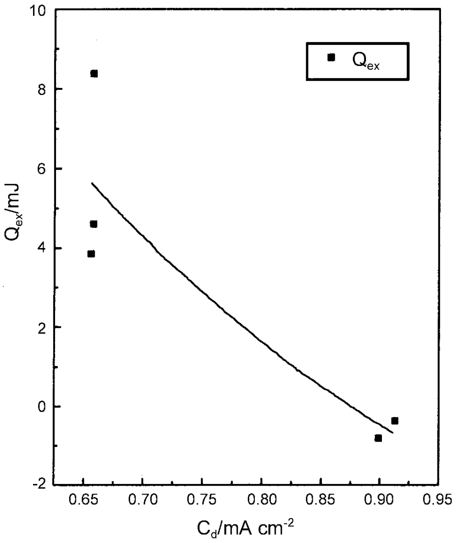

Fig. 6 Relation between the excess heat and the current density; silver rod (*D*=1.0 mm, *L*=26.0 mm) in the center axis as a cathode; the anode formed a coil (*D*=10.0 mm) with silver wire (*D*=1.0 mm, *L*=97.0 mm)

oxidation state Cu^+. The heat generated during the refining silver, however, is still changed, as in a previous work [1], with current density, or cell voltage employed. The ratio of Q_m/Q_{in} under different electrical conditions is still varied with current density whether in the centre electrode as a cathode, or as an anode. The excess heat (Q_{ex}) also depends on current density employed.

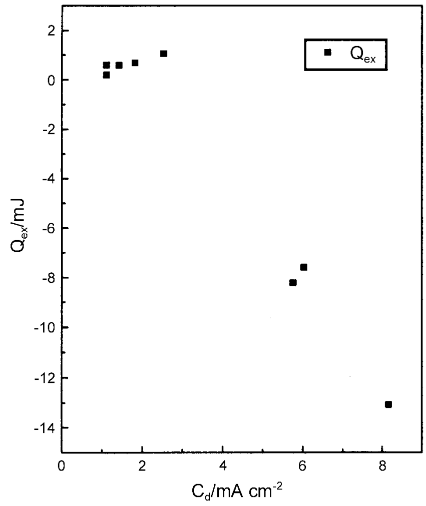

Fig. 7 Relation between excess heat and the current density; silver rod (D=0.5 mm, L=31.0 mm) in the center axis as a cathode; the anode formed a coil (D=10.0 mm) with silver wire (D=0.5 mm, L=150.0 mm)

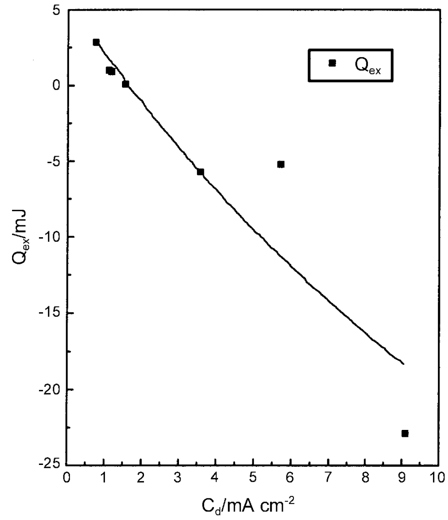

Fig. 8 Relation between excess heat and the current density; silver rod (D=0.5 mm, L=31.0 mm) in the center axis as an anode; the cathode formed a coil (D=10.0 mm) with silver wire (D=0.5 mm, L=150.0 mm)

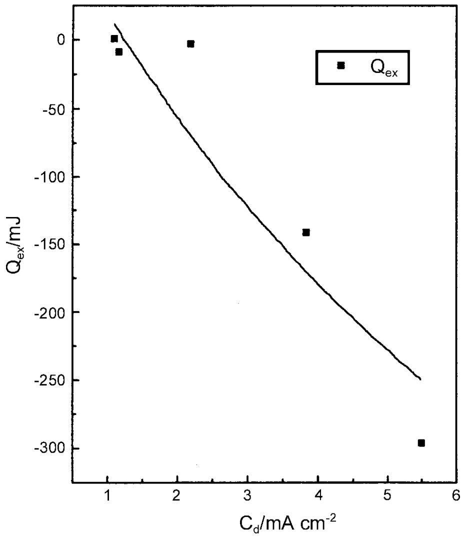

Fig. 9 Relation between excess heat and the current density; silver rod (*D*=1.0 mm, *L*=26.0 mm) in the center axis as a cathode; the anode formed a coil (*D*=10.0 mm) with silver wire (*D*=1.0 mm, *L*=97.0 mm)

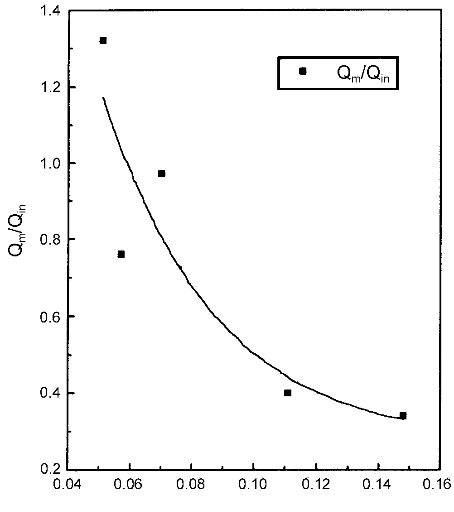

Fig. 10 Dependence of the ratio of work dissipation to the electric energy on the cell voltage; silver rod (*D*=1.0 mm, *L*=26.0 mm) in the center axis as a cathode; the anode formed a coil (*D*=10.0 mm) with silver wire (*D*=1.0 mm, *L*=97.0 mm)

As mentioned in a previous work [1], the process of electrorefining metal may be irreversible and the final state may be in non-equilibrium state. All of the calorimetric measurements of electrorefining silver, which is almost the same to copper, indicate that the mechanism of electrodeposition of a metal is very complex. The complexity of the electrodeposition system may be caused by these different conditions, in particular, by the irreversibility of the process in thermodynamics. These results

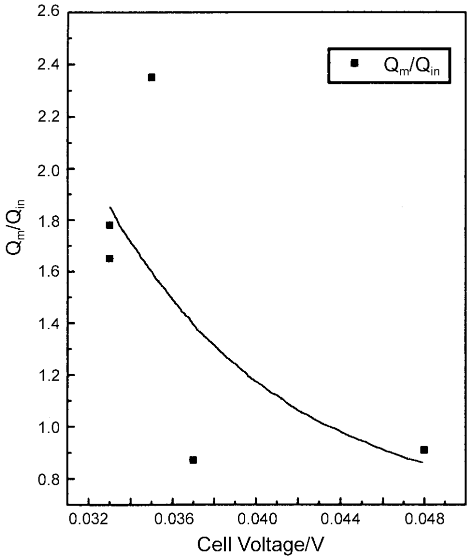

Fig. 11 Dependence of the ratio of work dissipation to the electric energy on the cell voltage; silver rod (*D*=0.5 mm, *L*=31.0 mm) in the center axis as a cathode; the anode formed a coil (*D*=10.0 mm) with silver wire (*D*=0.5 mm, *L*=150.0 mm)

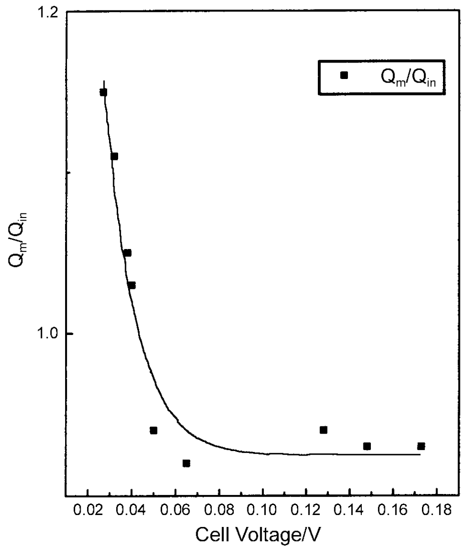

Fig. 12 Dependence of the ratio of work dissipation to the electric energy on the cell voltage; silver rod (*D*=0.5 mm, *L*=31.0 mm) in the center axis as a cathode; the anode formed a coil (*D*=10.0 mm) with silver wire (*D*=1.0 mm, *L*=150.0 mm)

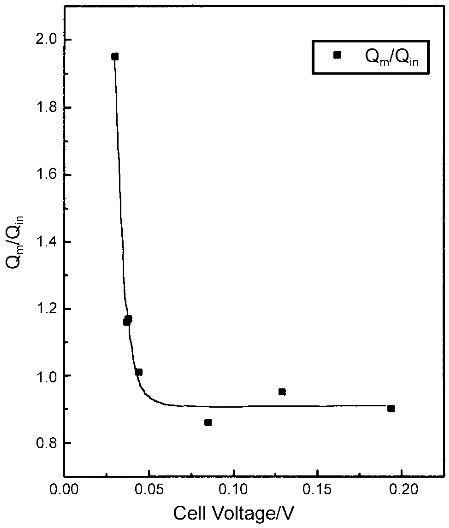

Fig. 13 Dependence of the ratio of work dissipation to the electric energy on the cell voltage; silver rod (D=1.0 mm, L=26.0 mm) in the center axis as a cathode; the anode formed a coil (D=10.0 mm) with silver wire (D=1.0 mm, L=97.0 mm)

are distinct in different stages of the process and be varied with electrochemical conditions such as current density or cell voltage. Therefore, we have to investigate the electrochemical character and behaviour of the process. In particular, one has to understand how the work dissipation as heat generated during an electrochemical process can be affected by the irreversibility of the process and varied with the changes of the thermodynamic state.

It is well-known, the input power W_{in} into an electrochemical cell is usually expressed as the common form [2]

$$W_{\mathrm{in}} = I(E_{\mathrm{ce}} - E_{\mathrm{th}}) \tag{1}$$

From our previous works [1, 3], however, one can know that the input power W_{in}, which may be totally output as heat to the surrounding of the calorimetric system during electrorefining silver in this work, should be a function of current I, and should be described by the following equation

$$W_{\mathrm{in}} = I\left(T\frac{\Delta S_{\mathrm{o}}}{nF} - \frac{RT}{nF}\ln Q + \eta_{\mathrm{a}} + \eta_{\mathrm{c}} + \eta_{\mathrm{mt}} + IR_{\mathrm{ce}}\right) \tag{2}$$

where T is the temperature of calorimetric system, R is the gas constant, ΔS_{o} is the entropy change of the whole cell reaction of electrorefining silver; n is the chemical valency of the ion concerned, which should be equal to one because of the silver ion in this work. F is the Faraday's constant. Q expresses, as in works [4–6], the activity quotient of product and reactant species raised to a power equal to each stoichiometric coefficient of the whole cell reaction. η_{a}, η_{c}, and η_{mt} express the activation overvoltages at the anode and cathode, and the polarization overvoltage due to mass transport of gaseous products away from the electrode surfaces, respectively. R_{ce} is the resistance of the electrorefining cell. The activation overvoltages at the anode and cathode can be given by the following equation as in work [7]

$$\eta_a = \frac{RT}{\alpha F}\ln\left(\frac{i_a}{i_{ao}}\right) \tag{3a}$$

and

$$\eta_a = \frac{RT}{\alpha F}\ln\left(\frac{i_c}{i_{co}}\right) \tag{3b}$$

where i is the current density, i_0 is the exchange current density, and α is the transfer coefficient.

The overvoltage arising from screening of part of the electrode surfaces from the electrolyte by gas films (gas bubble effect) is:

$$\eta_{mt} = \frac{lI}{A\,F(z_+\mu_+c_+ + z_-\mu_-c_-)} \tag{3c}$$

where l is the interelectrode spacing, A is the electrode area, z_+ and z_-, represent respectively the charge of the cation and anion in the electrolyte, μ_+ and μ_-, c_+ and c_-, represent such concerned mobility and concentration (mol l^{-1}), respectively. I is the cell current and F the Faraday constant.

From Eqs (2), (3a), (3b) and (3c), it is very clear that the work dissipation as heat generated, W_{in}, during the electrorefining process depends on the current density or cell voltage employed. The heat measured in the electrorefining silver always decreases with the current density or cell voltage in a cell with the center silver rod whether as the cathode or as the anode. It is in agreement with the experimental results, obtained in this work, shown in Tables 4–7 and Figs 2–13.

If and only if i=0, this equation expresses that the whole system of the electrochemical cell studied would be in an equilibrium state, otherwise it may be in a non-equilibrium state. If and only if i~0, the equation can also express that the electrochemical process may be reversible, otherwise it must be irreversible. So the W_{in} as heat totally generated, i.e. work dissipation, during an electrochemical process should depend on the current density (or cell voltage) employed in this practical process, i.e. the irreversible process.

Conclusions

From these results of calorimetric measurements of the electrochemistry obtained in this work, the following conclusions can be drawn:

1. The observed work dissipation i.e., energy consumption as the heat measured during the process of electrorefining silver also presents to be greater than the input electric energy.

2. The work dissipation during an electrochemical process depends on the current density or cell voltage employed. The heat measured in the electrorefining silver always decreases with the current density or cell voltage in a cell with the center silver rod whether as the cathode or as the anode.

3. The heat measured during the electrorefining silver and copper, and the electrolysis of water in an open cell seems to be varied with the same relation.

4. From the generated heat more than the input electric energy in electrochemical conditions, it appears there may be a 'fallacy' in classical thermodynamics, but should be a 'false fallacy' in general thermodynamics, as the result obtained from theoretical discussion above.

5. If and only if i=0, the state of the whole system of the electrochemical cell studied could just be in an equilibrium state, otherwise it should be in a non-equilibrium state. If and only if i~0, the equation form obtained by us can express that the electrochemical process could undergo through reversible path, otherwise it must undergo through an irreversible path.

The above conclusions were drawn according to such results of the theoretical discussion above and of the experimental measurements in this work. It is very clear that more experimental measurements in this area have to be continued to determine the processes taking place in the system of electrorefining metal or to describe the final state attained after a refining process.

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The authors would like to acknowledge the extreme encouragement and help of Professor Shuyi Liu (University of Science and Technology of China) and, Professors Fu Tan and Guoquan Liu (Institute of Chemistry, Academia Sinica).

This study was supported by the National Nature Science Foundation of China.

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