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Dedicated to Prof. Menachem Steinberg on the occasion of his 65th birthday

CALORIMETRIC STUDIES ON THE ELECTROREFINING PROCESS OF COPPER

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Abstract

Calorimetric measurements were carried out on the electrorefining of copper using different current densities with a Calvet type microcalorimeter at room temperature. The ratio (R) of the measured heat (Q_m or W_m) to the input electric energy (Q_{in} or W_{in}) and the excess heat (Q_{ex} or W_{ex}), i.e. the difference between Q_m (or W_m) and Q_{in} (or W_{in}) during the electrorefining process were discussed in terms of general thermodynamics. It was found that R and Q_{ex} were related to the current density employed in the experiment and varied as a logarithmic function. The results obtained here 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

There may exist no process taking place anywhere in the universe without heat generation. It must be admitted that an electrochemical process should be accompanied by heat generation as well. Therein, the energy consumption (or work dissipation), which is mostly dissipated in heat generation, is one of the important problems in electrochemical engineering which attracts the attention of electrochemists. Many articles have been published about the heat generated during the electrolysis process of heavy water (even light water!) since the article entitled 'Electrochemically induced nuclear fusion of deuterium' reported by Fleischmann and Pons [1] appeared. This calorimetric study not only attracted scientists to explore that a nuclear process may be induced by such a

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change in chemical conditions but also urged more and more electrochemical engineers to investigate it with great interest.

It was found that the work consumption as heat in the electrolysis of water, during which the gases (H_2 and O_2) must be produced, absolutely depends on the current density, (the cell voltage-essentially overvoltage) and the current efficiency [2–3]. In the electrolysis of water it is a typical irreversible process because gases are produced. It is necessary to investigate how the heat will be generated during the electrochemical process without gases being produced, such as the electrorefining of a metal.

The purpose of this work is to carry out calorimetric measurements during the process of electrorefining copper and to find a correlation between the results of these measurements and the electrochemical conditions of the experiment.

Experimental

Electrochemical cell

The cell for electrorefining copper consists of a copper rod as axis, with coils made of copper which wound around the rod, placed in a glass test tube filled with copper sulphate solution, as shown in Fig. 1. The concentration of the solution is about 5%.

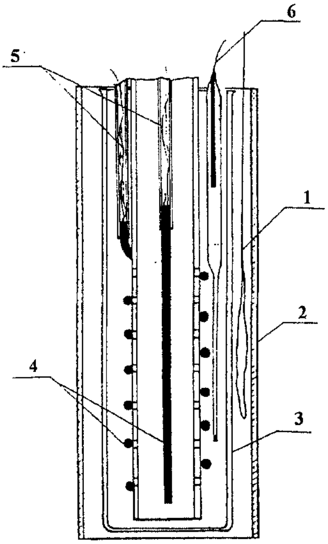

Fig. 1 Cross sectional view of the calorimetric chamber being placed in the electrorefining cell and a calibration heater, 1 – calibration heater, 2 – calorimetric vessel, 3 – glass cell, 4 – Cu rod and coils, 5 – electrode connections, 6 – reference electrode

Calorimetric system

Around the cell was wound an isolated resistance wire as a heater for calibration of the calorimetric system and the whole cell set was placed in a gilded copper vessel as a calorimetric chamber employed in this work.

A Calvet type microcalorimeter was used in this work as described before [3].

An electronic-constant current source or a dry cell was employed as a power supply in different processes.

Procedure

The calorimeter was calibrated in situ with electric current before and after the electrorefining process. The calorimetric constant was determined from the average of the calibration data.

The heats generated by the electrorefining of copper were measured in the current density range from 0.379 to 1.759 mA cm^{-2}. During the process, the energy consumptions were determined with the central rod-axis electrode used either as the anode, or as the cathode. For examining the effect of the current source on the calorimetric measurements, we used a dry cell instead of an electronic-constant current power supply.

Results and discussion

The results of calibration of this calorimeter are summarized in Table 1. The mean error of the determination on the calorimeter is better than ±4%. Therefore, the results obtained in this work should be reliable.

Table 1 Results of calibration of the calorimeter used in this work

No.	P1	I_e/mA	V_e/V	T_e/S	Q_{ei}/J	A/μV S	E/J (μV S)$^{-1}$
5120930	100	0.401	0.365	600	0.0876	0.6728	$1.30_2 \cdot 10^{-3}$
5121555	100	0.400	0.366	600	0.0878	0.6934	$1.26_7 \cdot 10^{-3}$
5130920	150	0.603	0.549	600	0.1986	0.9906	$1.33_7 \cdot 10^{-3}$
5141014	100	0.504	0.449	600	0.1358	1.0852	$1.25_1 \cdot 10^{-3}$
5141348	100	0.504	0.450	600	0.1361	1.0123	$1.34_4 \cdot 10^{-3}$

$E_{mean}=(1.30_0 \pm 0.04_1) \cdot 10^{-3}$ J/(μV S)±3.2%

The calorimetric measurements during the electrorefining of copper under different electrochemical conditions are shown in Tables 2–6. From these and

Table 2 Results of calorimetric measurements on the electrorefining process of copper in aqueous solution of $CuSO_4$ at room temeperature

No.	Cd/mA cm^{-2}	V_e/V	T_e/S	Q_{ei}/J	Q_m/J	R	Q_{ex}/J
4221615$^{\#}$	0.379	0.162	600	0.0379	0.0673	1.78	0.0294
4151015	0.972	0.293	600	0.1758	0.2103	1.20	0.0345
4151110	1.351	0.398	600	0.3321	0.3771	1.14	0.0450
4151425	1.759	0.525	600	0.5695	0.6234	1.09	0.0539

A copper rod (ø 0.12×2.7 cm) was used as the anode in this work.
A copper wire (ø 0.002 cm) coiled on a polyethylene tube (ø 0.5 cm) was used as the cathode.
$^{\#}$ the mass of the cathode determined before and after refining process.
An electronic-constant current supply was used during these runs.
Cd is the current density. V_e is the cell voltage. T_e is the duration of runs.
Q_{ei} is the electric energy input. Q_m is the heat measured. Q_{ex} is the excess heat.

Figs 2–10, we can conclude the heat generated during the refining of copper changes significantly with the current density employed. It is apparent that the heat generated during these processes changes nearly as a logarithmic function of the current density employed.

The ratio of the measured heat to the electric input energy (Q_m/Q_{in}) increases with the current density as a logarithmic function when the central electrode is used as the anode, but decreases when the central electrode is the cathode, with the same surface areas of the electrode, except one which has a larger surface area as shown in Fig. 1.

The excess heat (Q_{ex}) is defined as the difference between Q_{in} and Q_m calculated from the results of calorimetric measurements. The results shown in Figs 6–10 indicate that the excess heat also depends on the current density employed. Furthermore, the excess heat (Q_{ex}) increases with the current density according to a logarithmic function while the central electrode is employed as the anode but decreases while it is employed as the cathode.

The results for W_m/W_{in} and W_{ex} from our earlier work [3] shown in Figs 11–12 indicate a similar dependence on the current density.

Assuming that the excess heat might be generated by an unknown voltage caused by the electronic-constant current supply, we used a dry cell instead of it. From the results obtained during the electrorefining of copper, which are shown in Tables 2–4 and 5–6, do not suggest any significant effect of the power supply employed, whether it is an electronic-constant current supply or a dry cell.

For testing the reliability of the calorimetric measurements in this work, two calibrations were done before and after the determinations of heats generated during the electrorefining of copper. The results shown in Table 7, agree well with other data obtained.

Table 3 Calorimetric measurements on the electrorefining process of copper in aqueous solution of $CuSO_4$ at room temperature

No.	Cd/mA cm^{-2}	V_e/V	T_e/S	Q_{ei}/J	Q_m/J	R	Q_{ex}/J
5121050	0.391	0.122	600	0.0294	0.0319	1.09	0.0025
5131100	0.875	0.155	600	0.0837	0.1076	1.28	0.0239
5181800	0.777	0.146	600	0.0701	0.0996	1.42	0.0295
5161410	0.810	0.190	600	0.0950	0.1159	1.22	0.0209
	0.793	0.168	600	0.0826	0.1078	1.32	0.0252
5171300	0.963	0.229	600	0.1362	0.1992	1.46	0.0630
5181715	0.987	0.176	600	0.1073	0.1717	1.60	0.0644
	0.975	0.203	600	0.1218	0.1855	1.53	0.0637
5181515	1.156	0.209	600	0.1492	0.1637	1.10	0.0145
5171420	1.272	0.240	600	0.1885	0.2893	1.53	0.1008
	1.214	0.225	600	0.1689	0.2265	1.34	0.0577
5171525	1.412	0.260	600	0.2266	0.3346	1.48	0.1080
5181415	1.380	0.246	600	0.2096	0.2865	1.38	0.0769
	1.396	0.253	600	0.2181	0.3106	1.42	0.0925
5171645	1.530	0.300	600	0.2833	0.3926	1.39	0.1093
5181115	1.565	0.275	600	0.2656	0.3477	1.31	0.0821
	1.547	0.288	600	0.2745	0.3702	1.35	0.0957
5180915	1.632	0.320	600	0.3224	0.4672	1.45	0.1448
5181020	1.759	0.320	600	0.3475	0.4003	1.15	0.0528
	1.695	0.320	600	0.3350	0.4338	1.29	0.0988

A copper rod (ø 0.12×2.7 cm) was used as the anode in this work.
A copper wire (ø 0.12×7.5 cm) coil (ø1.0 cm) was used as the cathode.
An electronic-constant current power supply was used during these runs.
Cd, V_e, T_e, Q_{ei}, Q_m and Q_{ex} are as explained in Table 2.

Table 4 Calorimetric measurements on the electrorefining process of copper in aqueous solution of $CuSO_4$ at room temperature

No.	Cd/mA cm^{-2}	V_e/V	T_e/S	Q_{ei}/J	Q_m/J	R	$Q_{ex.}$/J
5140854	0.613	0.122	600	0.0462	0.0607	1.45	0.0145
5141454	0.929	0.178	600	0.1021	0.1371	1.34	0.0350

A copper rod (ø 0.12×2.7 cm) was used as the anode in this work.
A copper wire (ø 0.12×7.5 cm) coil (ø 1.0 cm) was used as the cathode.
A dry cell was used as a source in this work.
Cd, V_e, T_e, Q_{ei}, Q_m and Q_{ex} are as explained in Table 2.

Table 5 Calorimetric measurements on the electrorefining process of copper in aqueous solution of $CuSO_4$ at room temperature

No.	Cd/mA cm^{-2}	V_e/V	T_e/S	Q_{ci}/J	Q_m/J	R	Q_{cx}/J
5121415	0.388	0.111	600	0.0266	0.0874	3.29	0.0608
5191545	0.659	0.153	600	0.0740	0.1536	2.08	0.0796
5161535	0.721	0.168	600	0.0810	0.1276	1.58	0.0466
	0.783	0.182	600	0.0880	0.1016	1.15	0.0136
5201250	0.991	0.181	600	0.1108	0.1767	1.59	0.0659
5200820	1.176	0.216	600	0.1568	0.2082	1.33	0.0514
5201030	1.370	0.243	600	0.2056	0.1912	0.93	–0.0144
5200930	1.565	0.277	600	0.2676	0.2662	0.99	–0.0014

A copper rod (ø 0.12x2.7 cm) was used as the cathode in this work.
A copper wire (ø 0.12x7.5 cm) coil (ø 1.0 cm) was used as the anode.
An electronic-constant current supply was used during these runs.
Cd, V_e, T_e, Q_{ei}, Q_m and $Q_{ex.}$ are as explained in Table 2

Table 6 Calorimetric measurements on the electrorefining process of copper in aqueous solution of $CuSO_4$ at room temperature

No.	Cd/mA cm^{-2}	V_e/V	T_e/S	Q_{ci}/J	Q_m/J	R	$Q_{cx.}$/J
5141604	0.914	0.163	600	0.0919	0.1175	1.28	0.0256
5150848	0.877	0.173	600	0.0936	0.1313	1.40	0.0377
	0.895	0.168	600	0.0928	0.1244	1.34	0.0316
5150955	1.312	0.237	600	0.1920	0.2197	1.14	0.0277
5160850	1.712	0.295	600	0.3118	0.3644	1.17	0.0298

A copper rod (ø 0.12x2.7 cm) was used as the cathode in this work.
A copper wire (ø 0.12x7.5 cm) coil (ø 1.0 cm) was used as the anode.
A dry cell was used as a source in this work.
Cd, V_e, T_e, Q_{ei}, Q_m and Q_{ex} are as explained in Table 2

For examining the current efficiency in the electrochemical process, the mass of the electrode before and after running an experiment was measured several times. The results are given in Table 8. The values calculated according to Faraday's law from the currents employed in the process are almost the same as the measured mass changes of the electrode.

It seems that the copper atom is dissolved from copper anode into the solution and the copper ion is deposited onto the surface of cathode, therefore, the whole

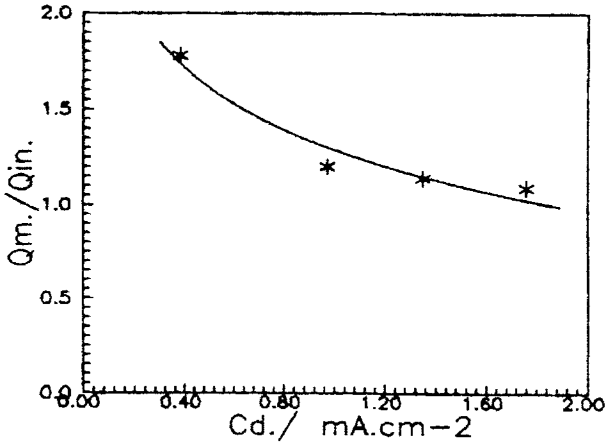

Fig. 2a Q_m/Q_{in} as a function of *Cd* during electrorefining of Cu. Power supply: an electronic-constant current supply, anode: copper rod (*D*=0.12 cm, *L*=2.7 cm), cathode: copper wire (*D*=0.02 cm, *L*>200 cm) coiled on a PE tube

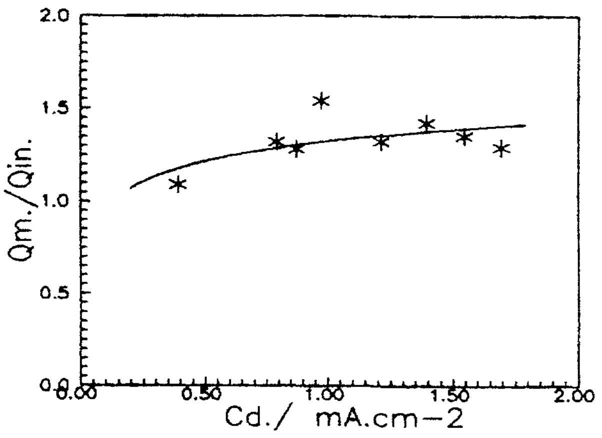

Fig. 2b Q_m/Q_{in} as a function of *Cd* during refining of Cu. Power supply: electronic-constant current supply, anode: copper rod (*D*=0.12 cm, *L*=2.7 cm), cathode: copper wire (*D*=0.12 cm, *L*=25.0 cm) coil (*D*=1.0 cm)

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 equal to one. However, it is greater than one in most cases. It appears that the heat observed in the experiment was 'more' than the input electric energy! The results obtained in this work compel us to accept a 'fallacy' in classical thermodynamics! In other words, the result seems to show that it does not abide by the first law of thermodynamics. In fact, that must be a 'false fallacy' in general thermodynamics. The problem is that we should understand correctly that the cell studied dur-

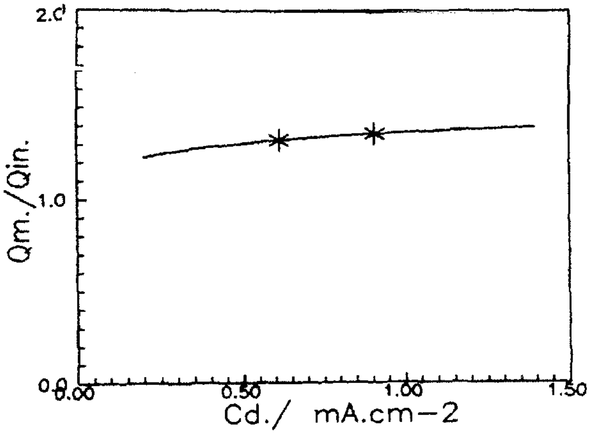

Fig. 3 Q_m/Q_{in} as a function of *Cd* during electrorefining of Cu. Power supply: dry cell, anode: copper rod (*D*=0.12 cm, *L*=2.7 cm), cathode: Cu wire (*D*=0.12 cm, *L*=25.0 cm) coil

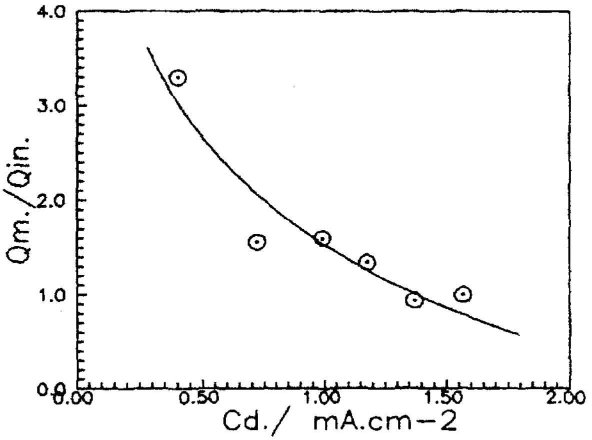

Fig. 4 Q_m/Q_{in} as a function of *Cd* during electrorefining of Cu. Power supply: electronic-constant current supply, anode: Cu wire (*D*=0.12 cm, *L*=25 cm) coil (*D*=1 cm), cathode: copper rod (*D*=0.12 cm, *L*=2.7 cm)

ing the electrorefining of copper is not a simple thermodynamic system. The process taking place in the cell may be irreversible and the final state may be a non-equilibrium state. All these results indicate that the mechanism of electrodeposition of a metal is very complex because it may occur in different stages and may change with the electrochemical conditions. The complexity of the electrodeposition system may be caused by these different conditions, and in particular, by the irreversibility of the process. Therefore, we have to investigate

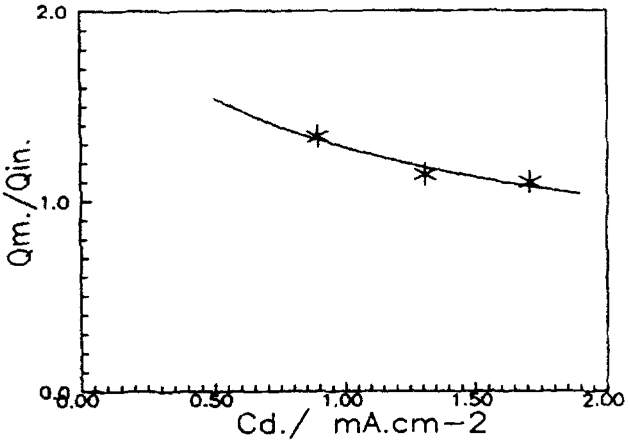

Fig. 5 Q_m/Q_{in} as a function of *Cd* during electrorefining of Cu. Power supply: dry cell, anode: Cu wire (*D*=0.12 cm, *L*=25 cm) coil (*D*=1.0 cm), cathode: copper rod (*D*=0.12 cm, *L*=2.7 cm)

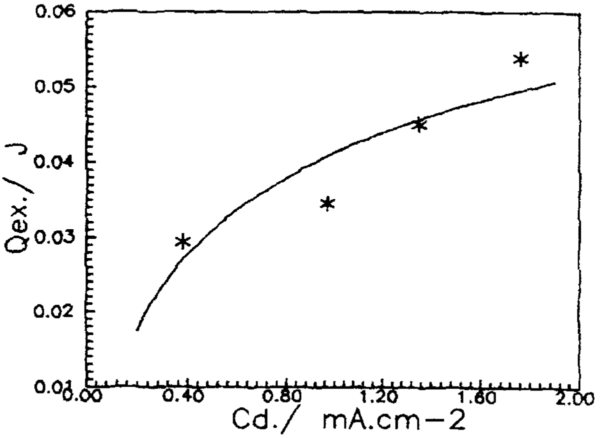

Fig. 6 Q_{ex} as a function of *Cd* during the electrorefining of Cu with the central rod as the anode and an electronic-constant current supply used

the character of an electrochemical cell and the behaviour of the electrochemical process. In particular, one has to understand how the heat generated during an electrochemical process can be affected by the irreversibility of the process and varied with the changes of the thermodynamic state. From our previous work [3], we know that the input power W_{in} in an electrochemical cell cannot be simply expressed in the common form

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

It should be a function of I, and should be described by the following equation

$$W_{in} = I[T\Delta S^{0}/nF - (RT/nF)\ln Q + (\eta_a + \eta_c + \eta_{mt} + IR_{ca})] \quad (2)$$

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, otherwide it must be irreversible. So the heat generated during an electrochemical process should depend on the cur-

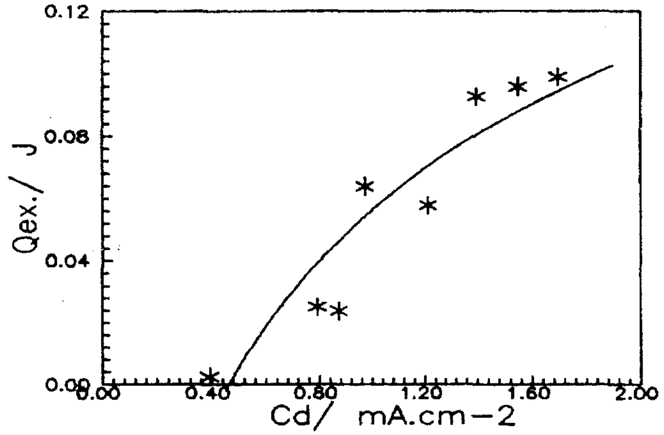

Fig. 7 Q_{ex} as a function of Cd during the electrorefining of Cu with the central rod as the anode and an electronic-constant current power supply

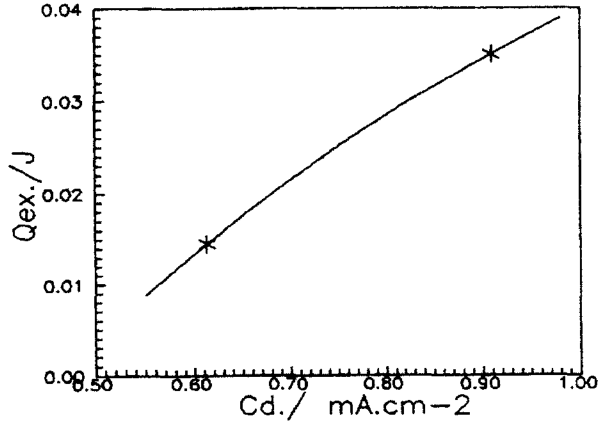

Fig. 8 Q_{ex} as a function of Cd during the electrorefining process of Cu with the central rod as the anode and a dry cell as a power supply

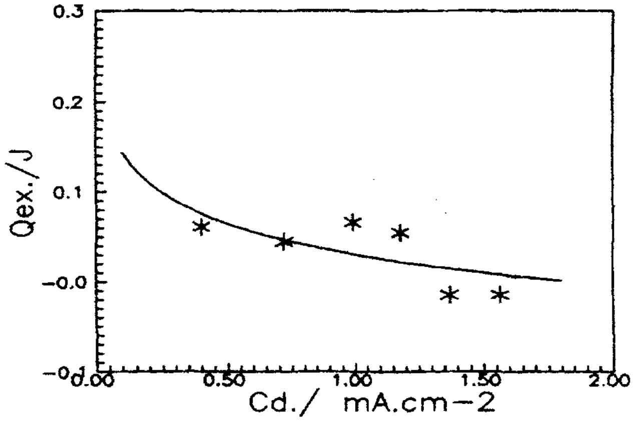

Fig. 9 Q_{ex} as a function of *Cd* during the electrorefining process of Cu with the central rod as the cathode and an electronic constant current supply

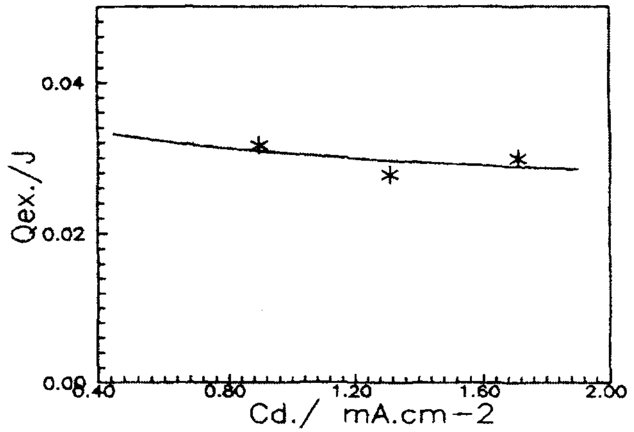

Fig. 10 Q_{ex} as a function of *Cd* during the electrorefining of Cu with the central rod as the cathode and a dry cell as a power supply

rent density (or cell voltage) employed in this practical process, i.e. the irreversible process.

Conclusions

From the results of calorimetric measurements made during the electrodeposition of copper, the following conclusions can be drawn:

1) The observed energy consumption as the heat measured during an electrochemical process (whether electrorefining of copper or electrolysis of water in an open system) always appear to be greater than the input electric energy.

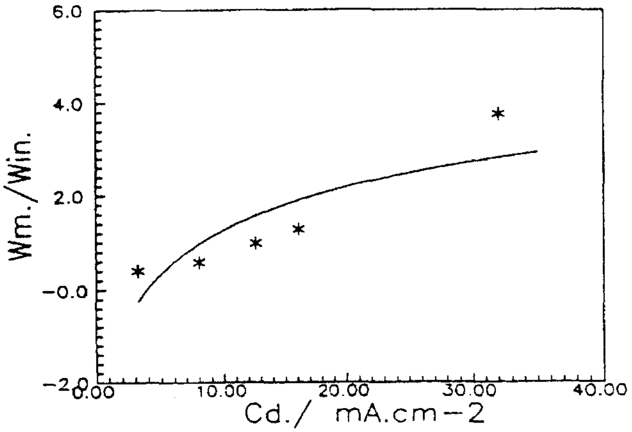

Fig. 11a W_m/W_{in} as a function of the current density (*Cd*) during the electrolysis of H_2O

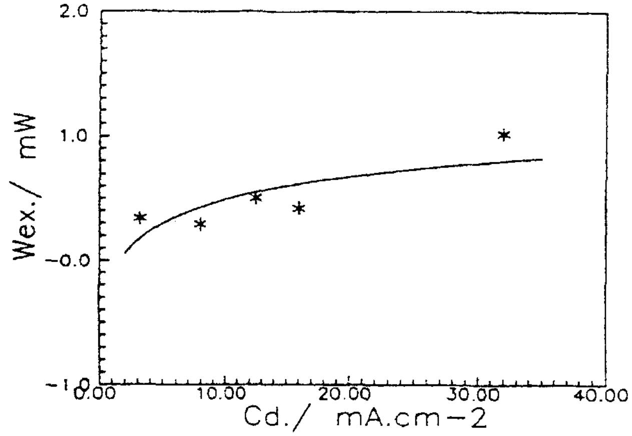

Fig. 11b W_{ex} as a function of *Cd* during the electrolysis of H_2O

2) The heat generated during an electrochemical process depends on the current density employed. The heat measured during the electrorefining of copper always increases with the current density in a cell with the central copper rod as the anode, but decreases with the current density in a cell with the central copper rod as the cathode.

3) The heat measured during the electrolysis of water in an open cell and the electrorefining of copper seems to change in a similar manner.

4) Both the generated heat and the excess heat determined during these processes are approximated as a logarithmic function of the current density employed.

Table 7 Calorimetric measurements on the electrorefining process of copper in aqueous solution of $CuSO_4$ at room temperature

No.	P1	I_e/mA	V_e/V	T_e/S	Q_{ei}/J	A/μV S	E/J (μV S)$^{-1}$
5120930	100	0.401	0.365	600	0.0876	0.6728	$1.30_2 \cdot 10^{-3}$
5121050 [α]	100	0.391	0.122	600	0.0294	0.3019	
5121415 [β]	100	0.388	0.111	600	0.0266	0.0874	
5121555	100	0.400	0.366	600	0.0878	0.6934	$1.26_7 \cdot 10^{-3}$

[α] A copper rod (ø 0.12×2.7 cm) was used as the anode in this work.
A copper wire (ø 0.12×7.5 cm) coil (ø 1.0 cm) was used as the cathode.
An electronic-constant current supply was used during these runs.
[β] A copper rod (ø 0.12×2.7 cm) was used as the cathode in this work.
A copper wire (ø 0.12×7.5 cm) coil (ø1.0 cm) was used as the anode.
An electronic-constant current supply was used during these runs.

Table 8 Change in mass of the cathode before and after the refining process

No.	I/mA	Cd/mA cm^{-2}	V_e/V	T_e/S	Mc/mg	Mm/mg	Rm
4251630#	0.397	0.331	0.195	900	0.118	0.105	0.89
4271000#	0.599	0.499	0.166	1020	0.202	0.191	0.95
4281050#	0.802	0.668	0.215	1260	0.332	0.304	0.91

Mc=63.55($I\Delta t$)/(2·96485)
Rm=Mm/Mc,
where Mm is the mass change of cathode determined from the masses before and after the run.

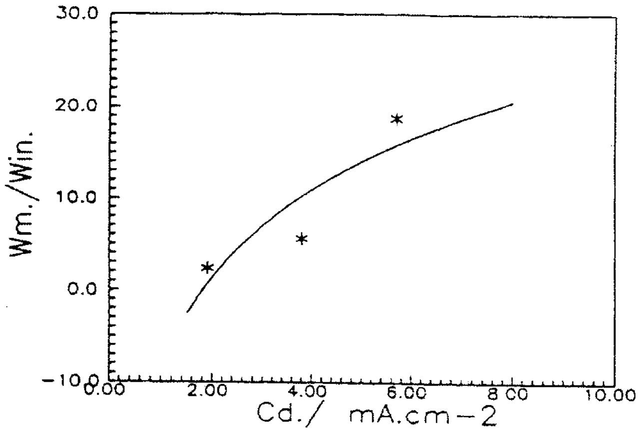

Fig 12a $W_{m.}/W_{in}$ as a function of the current density (Cd) during the electrolysis of D_2O

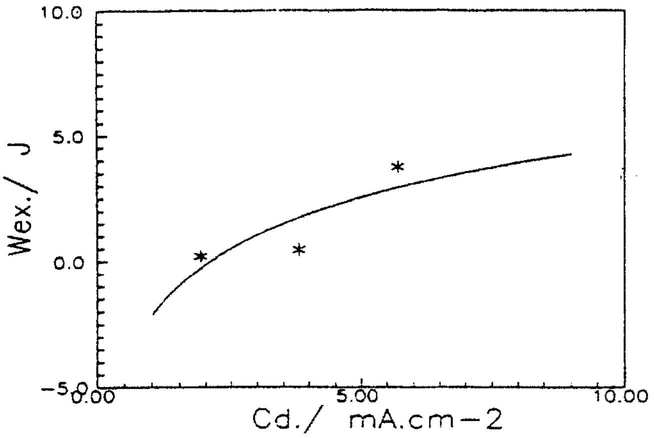

Fig. 12b W_{ex} as a function of Cd during the electrolysis of D_2O

5) From the generated heat being 'more' than the input electric energy, it appears that there may be a 'fallacy' in classical thermodynamics, but should be a 'false fallacy' in general thermodynamics.

6) If and only if i=0, the whole system of the electrochemical cell studied could 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 go through a reversible path, otherwise it must go through an irreversible path.

The above conclusions were drawn from the results of measurements first carried out by us. It is very clear that investigations in this area have to be continued to determine the processes taking place in systems involving the electrorefining of metals or to describe the final state attained after a refining process.

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