

EXCESS HEAT EVOLUTION DURING ELECTROLYSIS OF H₂O WITH NICKEL, GOLD, SILVER, AND TIN CATHODES

COLD FUSION

TECHNICAL NOTE

KEYWORDS: excess heat, electrolysis, alkali-metal carbonate-light water system

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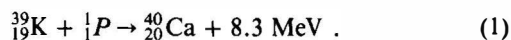
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Excess heat evolution was measured on nickel, gold, silver, and tin in aqueous K₂CO₃, Na₂CO₃, Na₂SO₄, and Li₂SO₄ solutions under galvanostatic electrolysis conditions. Steady evolution of excess heat in various electrode-electrolyte systems, but not in Ni/Na₂CO₃, Ni/Na₂SO₄, and Ni/Li₂SO₄, was observed for at least several days of observation. The largest excess heat observed was 907 mW on tin in K₂SO₄.

INTRODUCTION

Mills and Kneizys¹ recently reported production of 130 mW of excess heat in a Ni/K₂CO₃ system. Later, in the same electrode-electrolyte system, Noninski,² Bush,³ and Srinivasan et al.⁴ observed several hundred milliwatts of excess heat. The excess heat found by Noninski and Srinivasan et al. correspond to 23 to 160% of input energy. Bush claimed the detection of calcium in an amount that may correspond to the amount of excess energy. He suggested that this heat may originate from the following nuclear reaction:



To our surprise, Srinivasan et al. claimed the detection of tritium even in several Li₂CO₃ and K₂CO₃-H₂O solutions.

This study aims to reproduce these results on nickel and further to investigate similar possibilities on other metals, such as gold, silver, and tin. The reasoning behind this extension is that the underpotential deposition of alkali metals on, or their inclusion in, these metals is known to take place under high cathodic polarization.⁵⁻⁹

EXPERIMENTAL

The electrolytic cell was a 300-ml flat-bottomed Pyrex glass vessel with a 5-cm-thick silicon rubber stopper equipped with a test electrode, counterelectrode, and reference electrode; a thermocouple; glass inlet and outlet tubes for hydrogen gas; and a heater. The cell was placed in an air thermostat whose temperature was regulated at 25 ± 1°C with a period-

ical variation of ~10 cycle/h. This technique enabled solution temperature measurement with a precision of ±0.03°C. The test electrodes used were 3-cm × 20-cm × 0.15-mm nickel (99.997%) plates, 2-cm × 10-cm × 0.2-mm gold (99.95%) and tin (99.9%) plates, and 2-cm × 10-cm × 0.3-mm silver (99.98%) plates. The surfaces of these electrodes were abraded with emery paper and then rinsed with ethyl alcohol and Milli-Q water in an ultrasonic bath. A nickel electrode annealed at 600°C in helium and a gold electrode prepared by electrodeposition on a gold plate were also tested. The counterelectrode was a 1- × 7-cm, 80-mesh platinum net placed at the bottom of the cell. The distance between the test electrode and the counterelectrode was 1 to 2 cm. The reference electrode was a 0.2-mm-diam × 1-cm-long rhodium wire placed close to the test electrode.

The heater used for the cell constant measurement was a 0.3-mm-diam × 1.6-Ω Nichrome wire covered by a 2-mm-diam Teflon tube. The Nichrome wire was connected to copper wires at both ends by welding, and it was placed within the electrolytic solution. The cell constant was measured by applying a current to the heater using 100 ml of 0.5 M K₂CO₃ solution while stirring with a weak flow of purified hydrogen gas (several millilitres per minute).

The electrolytic solution was 100 ml of 0.5 M aqueous K₂CO₃, Na₂CO₃, Na₂SO₄, or Li₂SO₄, prepared with Milli-Q water. The electrolysis was conducted galvanostatically, usually for 20 h, by a constant 1.0-A current, and the variations of input potential and temperature were monitored by means of a pen recorder. During the electrolysis, the solution was stirred by hydrogen gas with the same flow rate as that used during the cell constant measurement.

RESULTS AND DISCUSSION

Figure 1 shows a typical calibration curve for solution temperature and input power. A very reproducible linear relationship was obtained if the hydrogen gas flow rate was in the range of 5 to 20 ml/min. The cell constant *k* calculated from the gradient was 3.26 ± 0.04°C/W.

Figure 2 shows typical variations of the solution temperature with polarization time obtained on a nickel electrode in K₂CO₃ and Na₂CO₃ solutions. The time variations of input potential are also shown. It can be seen that the increase in temperature in K₂CO₃ is 1 to 1.3°C larger than in Na₂CO₃

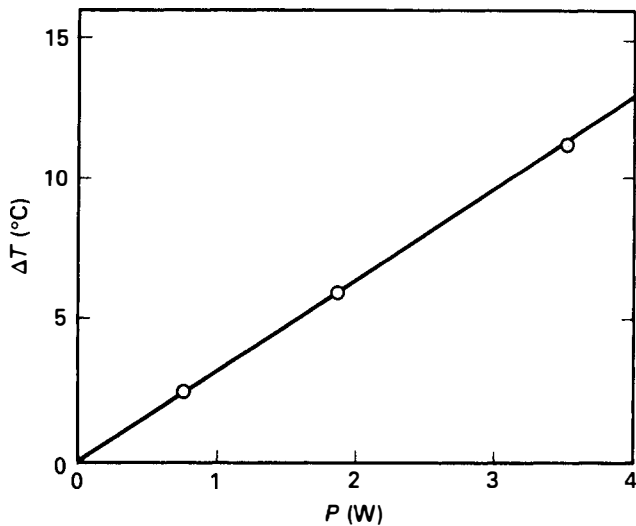


Fig. 1. Calibration curve between solution temperature and input power.

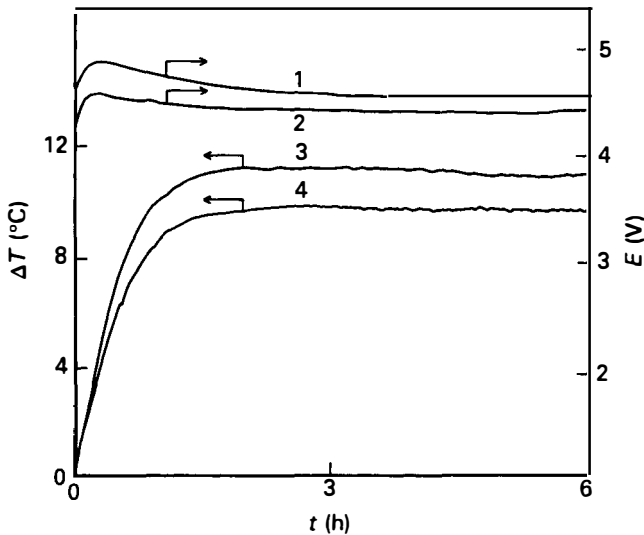


Fig. 2. Variations of input potential and solution temperature with polarization time: (1) and (4) in 0.5 M Na₂CO₃; (2) and (3) in 0.5 M K₂CO₃.

even though the levels of input power are in the opposite order. The difference was essentially unchanged during the polarization over several days. This result indicates that a noticeable amount of excess heat is produced in the Ni/K₂CO₃ system, in support of the reports by Mills and Kneizys,¹ Noninski,² Bush,³ and Srinivasan et al.⁴ On the other hand, no excess heat evolution was noted in the Ni/Na₂CO₃, Ni/Na₂SO₄, and Ni/Li₂SO₄ systems.

The rate of excess heat evolution R_{ex} can be determined quantitatively from the shift of solution temperature ΔT and the applied electrolysis power R_{app} in the following way. The energy balance equation for the cell in steady state is

$$R_{ex} = R_{rx} + R_L - R_{app} \quad (2)$$

where R_{rx} is the rate of heat removed by the endothermic reaction $H_2O \rightarrow H_2 + \frac{1}{2}O_2$, which is equal to the product of the thermoneutral potential E_{th} (1.48 V for H₂O) and the polarization current I , and R_L is the thermal loss rate. When a steady state is reached, the latter is given by

$$R_L = \Delta T/k \quad (3)$$

From Eqs. (2) and (3) and using $R_{app} = EI$, where E is the total cell voltage, we have

$$R_{ex} = \Delta T/k - (E - 1.48)I \quad (4)$$

A preliminary heat measurement was first performed in the electrolysis on gold in 1 M H₂SO₄ solution to check the precision of our method. Practically no excess heat (−0.9 mW on average) was obtained in this system during 20 h of observation.

On the other hand, significant amounts of excess heat were observed in every electrode-electrolyte solution system of nickel, gold, silver, and tin in K₂CO₃, Na₂CO₃, Na₂SO₄, and Li₂SO₄ solutions, except for Ni/Na₂CO₃, Ni/Na₂SO₄, and Ni/Li₂SO₄, as listed in Tables I through IV (for nickel, gold, silver, and tin, respectively) together with the data of input power ($R_{app} - IE_{th}$) and the increase in solution temperature. The evolution of excess heat was almost steady, but a slight tendency to increase with prolonged time of polarization was noted. On nickel, the excess heat seems to be

TABLE I
Results on Nickel Electrodes

Electrode	Solution	$R_{app} - IE_{th}$ (W)	ΔT (°C)	R_{ex} (mW)	$\frac{R_{ex}}{R_{app} - IE_{th}}$ (%)
Nickel	K ₂ CO ₃	2.86	1.71	524	18
Nickel	K ₂ CO ₃	2.40	1.26	387	16
Nickel	K ₂ CO ₃	2.81	1.23	377	13
Nickel ^a	K ₂ CO ₃	2.44	0.38	105	4
Nickel	Na ₂ CO ₃	2.46	0.02	6	0.2
Nickel	Na ₂ CO ₃	2.82	0.10	31	1
Nickel ^a	Na ₂ CO ₃	2.46	0.05	15	0.5
Nickel ^a	Na ₂ SO ₄	2.69	0.01	0	0
Nickel ^a	Li ₂ SO ₄	3.02	0.01	0	0

^aAnnealed at 600°C in helium atmosphere. In this case, an electrolytic cell with a cell constant of 3.60 was used.

TABLE II
Results on Gold Electrodes

Electrode	Solution	$R_{app} - IE_{th}$ (W)	ΔT (°C)	R_{ex} (mW)	$\frac{R_{ex}}{R_{app} - IE_{th}}$ (%)
Gold	K ₂ CO ₃	2.86	1.71	524	18
Gold	Na ₂ CO ₃	3.37	1.83	561	17
Gold	Li ₂ SO ₄	3.12	1.64	503	16
Gold ^a	K ₂ CO ₃	3.00	2.02	620	21

^aElectrodeposited.

TABLE III
Results on Silver Electrodes

Electrode	Solution	$R_{app} - IE_{th}$ (W)	ΔT (°C)	R_{ex} (mW)	$\frac{R_{ex}}{R_{app} - IE_{th}}$ (%)
Silver	K ₂ CO ₃	2.64	1.07	328	12
Silver	Li ₂ CO ₄	3.62	0.31	95	3

TABLE IV
Results on Tin Electrodes

Electrode	Solution	$R_{app} - IE_{th}$ (W)	ΔT (°C)	R_{ex} (mW)	$\frac{R_{ex}}{R_{app} - IE_{th}}$ (%)
Tin	K ₂ CO ₃	3.56	2.31	708	20
Tin ^a	K ₂ CO ₃	3.47	2.96	907	26
Tin	Na ₂ CO ₃	3.59	0.73	224	6

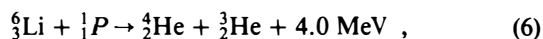
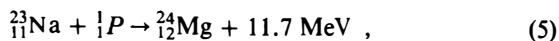
^aElectrolyzed for 65 h.

smaller for the annealed electrode (Table I). The largest amount of excess heat was observed on the tin electrode whose surface was mechanically abraded (Table IV); the value reached after 65 h of polarization was 907 mW, i.e., 26%, as compared with the input power of $(4.95 - 1.48) \times 1 = 3.47$ W.

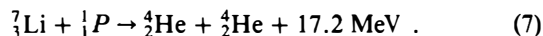
The magnitude of the excess heat increased in the order silver < nickel < gold < tin. It was noteworthy that excess heat was also noticeable in Na₂CO₃ and Li₂SO₄ for gold, silver, and tin.

The total amount of excess energy evolved during the electrolysis is too large to be regarded as the heat of any chemical reaction between the electrode material and some species present in the solution. For instance, the total excess heat evolved in the electrolysis on the tin electrode during 65 h of polarization was evaluated to be 176 kJ. Even if one supposes that all of the 1 g of tin in the electrode reacted with certain species in the system (which was not the case), the heat produced would be at most 9.3 kJ [for Sn(OH)₄], which is too small an amount to account for the excess heat observed. Furthermore, no reaction may be conceivable in the case of gold.

The excess heat evolution observed in many systems other than Ni/Na₂CO₃, Ni/Na₂SO₄, and Ni/Li₂SO₄ may suggest, in addition to the proposed nuclear reaction, Eq. (1), the following nuclear reactions:



or



Excess heat evolution on nickel was observed only in K₂CO₃. On silver and tin, it was greater in K₂CO₃ than in Na₂CO₃ or Li₂SO₄. On gold, no large difference was observed among these electrolytes. These results may suggest that reactions (1), (5), and (6) all occur in general, but the degree of the progress of each reaction depends on the nature of the electrode material, surface and bulk conditions of the electrode, adsorbed or underpotential deposited species, etc.

REFERENCES

1. R. L. MILLS and S. P. KNEIZYS, "Excess Heat Production by the Electrolysis of an Aqueous Potassium Carbonate Electrolyte and the Implications for Cold Fusion," *Fusion Technol.*, **20**, 65 (1991).
2. V. C. NONINSKI, "Excess Heat During the Electrolysis of a Light Water Solution of K₂CO₃ with a Nickel Cathode," *Fusion Technol.*, **21**, 163 (1992).
3. R. T. BUSH, "A Light Water Excess Heat Reaction Suggests that 'Cold Fusion' May Be 'Alkali-Hydrogen' Fusion," *Fusion Technol.*, **22**, 301 (1992).
4. M. SRINIVASAN, A. SHYAM, T. K. SANKARANARAYANAN, M. B. BAJPAI, H. RAMAMURTHY, U. K. MUKHERJEE, M. S. KRISHNAN, M. G. NAYAR, and Y. P. NAIK, "Tritium and Excess Heat Generation During Electrolysis of Aqueous Solutions of Alkali Salts with Nickel Cathode," presented at 3rd Annual Conf. Cold Fusion, Nagoya, Japan, October 21-25, 1992.
5. T. OHMORI and A. MATSUDA, "Intermediates of Hydrogen Evolution Reaction on Nickel in Aqueous Sodium Hydroxide," *J. Res. Inst. Catalysis, Hokkaido Univ.*, **26**, 53 (1978).
6. T. OHMORI and M. ENYO, "Hydrogen Evolution Reaction on Gold Electrode in Alkaline Solutions," *Electrochim. Acta*, **37**, 2021 (1992).
7. I. G. KISELEVA, N. N. TOMASHOVA, and B. N. KABANOV, "Investigation of the Inclusion of Alkali Metals in Electrodes by the Potential-Time Curve Method," *Zh. Fiz. Khim.*, **38**, 1188 (1964).
8. B. N. KABANOV, I. G. KISELEVA, I. I. ASTAKHOVA, and N. N. TOMASHOVA, "Overvoltage and the Mechanism of Cathodic Incorporation of Alkaline Metals into Solid Electrodes," *Elektrokhimiya*, **1**, 1023 (1965).
9. B. N. KABANOV, I. I. ASTAKHOVA, and I. G. KISELEVA, "Electrochemical Incorporation of Alkali Metals," *Usp. Khim.*, **34**, 1813 (1965).