

Excess Heat Produced during Electrolysis of H₂O on Ni, Au, Ag and Sn Electrodes in Alkaline Media

T.OHMORI and M.ENYO

Catalysis Research Center, Hokkaido University

Sapporo, 060, Japan

ABSTRACT

Excess heat evolution was measured on Ni, Au, Ag and Sn 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 Sn in K₂SO₄.

Introduction

Mills and Kneizys reported a production of 130 mW excess heat in Ni/K₂CO₃-H₂O system [1]. Later, Bush reported 310 - 580 mW in the same system and claimed the detection of Ca of the amount that may correspond to the amount of excess energy [2]. The present study is aimed at the reproduction of their results on Ni, and further to investigate similar possibilities on several other metal electrodes. The reasoning of this extension is that the underpotential deposition (upd) of alkali metals is known to occur under high cathodic polarization [3].

Experimental

The electrolytic cell used was a 300 ml Pyrex glass vessel with a 5 cm thick silicon rubber stopper equipped with the test electrode, counter and reference electrodes, a thermocouple, inlet and outlet glass tubes for H₂ gas and a heater. The cell was placed in an air

thermostat maintained at $25 \pm 1^\circ\text{C}$. The test electrodes used were plates of various metals (Ni, Au, Ag, Sn, etc). Surface of these electrodes was abraded with emery papers and then rinsed with ethyl alcohol and Milli-Q water in a ultrasonic bath. The counter electrode was a platinum net. The reference electrode was of a rhodium wire. The heater used for the cell constant measurement is a nichrome wire (1.6Ω) covered with a teflon tube (2 mm diam.).

The cell constant was measured by applying a current to the heater using 100 ml 0.5 M K_2CO_3 solution under stirring with a flow of H_2 gas (several ml per min.). The electrolyte solution was 100 ml of 0.5 M aqueous K_2CO_3 , Na_2CO_3 and Li_2SO_4 . The electrolysis was conducted galvanostatically usually for 20 hours by passing a constant current of 1.0 A and the variations of input potential and the temperature rise were monitored by a pen recorder.

Results and Discussion

Figure 1 shows typical variations of the solution temperature with polarization time obtained on a Ni electrode in K_2CO_3 and Na_2CO_3 solutions. The time variations of input potential are also shown in this figure. It can be seen from this figure that the increase in temperature in K_2CO_3 is $1 - 1.3^\circ\text{C}$ larger than in Na_2CO_3 in spite of the fact that the levels of input

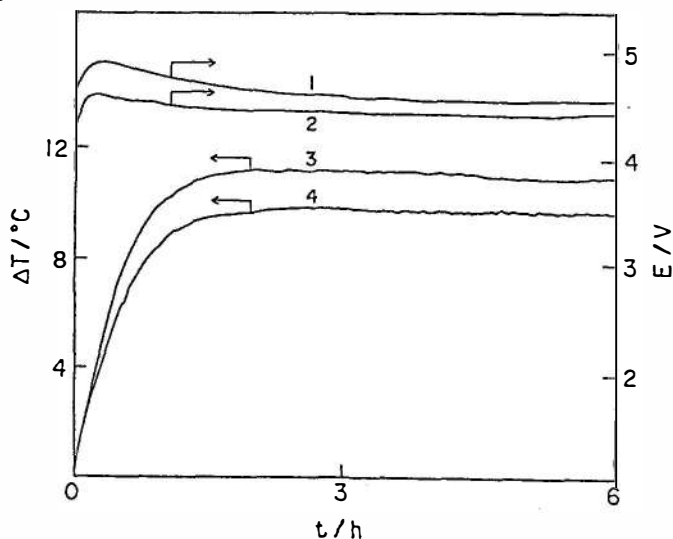


Fig.1 Variations of input potential and solution temperature with polarization time. (1),(4) in 0.5M Na_2CO_3 , (2),(3) in 0.5 M K_2CO_3 .

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 Ni/K₂CO₃ system.

The rate of excess heat evolution R_{ex} was 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 a steady-state is

$$R_{ex} = R_{rx} + R_L - R_{app} \quad (1)$$

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

$$R_L = \Delta T/k \quad (2)$$

from Eqns.(1) and (2) and using $R_{app} = EI$ where E is the total cell voltage, we have

$$R_{ex} = \Delta T/k - (E - 1.48)I \quad (3)$$

A preliminary heat measurement was first performed in the electrolysis on Au in 1M H₂SO₄ solution to check the precision of our method. Practically no excess heat was obtained in this system during 20 hours of observation. On the other hand, significant magnitudes of excess heat were observed on Ni, Au, Ag and Sn in K₂CO₃, Na₂CO₃, Na₂SO₄ and Li₂SO₄ solutions, except for Ni/Na₂CO₃, Ni/Na₂SO₄ and Ni/Li₂SO₄, as listed in Table 1 together with the data of cell potential and solution temperature shift. The excess heat evolution was almost steady, but a slight tendency to increase on prolonged time of polarization was noted. The largest excess heat evolution was observed on Sn electrode; the value reached after 65 hours of polarization was 907 mW, as compared with the input power of $(4.95 - 1.48) \times I = 3.47$ W. The magnitude of the excess heat evolution increases in the order Ag < Ni < Au < Sn. It was noteworthy that the excess heat was noticeable also in Na₂CO₃ and Li₂SO₄ for Au, Ag and Sn.

The total summed-up amount of the excess energy evolved during the electrolysis is too large to be regarded as the heat of any chemical reaction. For instance, the total excess heat evolved in the electrolysis on the Sn electrode for 65 hours of polarization was evaluated to be 176 kJ. Even if one supposes that all the amount of Sn (1 g) of the electrode was reacted

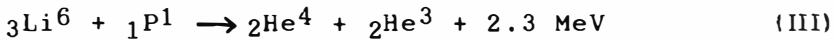
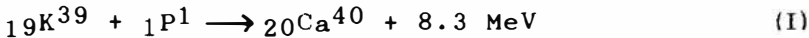
with certain species in the system (which is not the case), the heat produced would at most be 9.3 kJ (for $\text{Sn}(\text{OH})_4$) which is too small an amount to account for the excess heat observed.

Table 1 Rate of excess heat evolution on various metal electrodes

electrode	solution	E (V)	ΔT (°C)	R_{ex} (mW)
Ni	K_2CO_3	4.12	0.75	208
Ni	K_2CO_3	3.88	1.26	387
Ni	Na_2CO_3	3.94	0.02	6
Ni	Na_2SO_4	4.17	0.01	0
Ni	Li_2SO_4	4.50	0.01	0
Au	K_2CO_3	4.34	1.71	524
Au	Na_2CO_3	4.85	1.83	565
Au	Li_2SO_4	4.60	1.64	503
Ag	K_2CO_3	4.12	1.07	328
Ag	Li_2SO_4	5.10	0.31	95
Sn	K_2CO_3	5.04	2.31	708
Sn*	K_2CO_3	4.95	2.96	907
Sn-	Na_2CO_3	5.07	0.73	224

* electrolyzed for 65 hours.

The excess heat evolution observed in many systems other than $\text{Ni}/\text{Na}_2\text{CO}_3$, $\text{Ni}/\text{Na}_2\text{SO}_4$ and $\text{Ni}/\text{Li}_2\text{SO}_4$ may suggest the following nuclear reactions.



The excess heat evolution on Ni was observed only in K_2CO_3 . On Ag and Sn, it was larger in K_2CO_3 than in Na_2CO_3 or Li_2SO_4 solutions. On Au, no large difference was observed between these electrolytes. These results may suggest that all the reactions (I), (II) and (III) 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 upd species, etc.

1. Mills, R. L. and Kneizys, S. P., 1991, Fusion Technology, 20, 65.
2. Bush, R. T., 1992, Fusion Technology, 22, 301.
3. Ohmori, T. and Enyo, M., 1992, Electrochimica Acta, 37, 2021.