Electrochemical Calorimetry of D_2O Electrolysis Using a Palladium Cathode in a Closed Cell System

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ABSTRACT

Electrolysis of D_2O containing LiOD using palladium cathode was studied with a closed type calorimeter. The electric power input was kept constant, and all D_2 and O_2 generated and liberated to a gas phase were recombined on a catalyst, palladium black supported on a platinum wire. When the electric power of 0.2 W was employed, excess heat generation (2.4%) was observed once out of 5 experiments. No significant generation of excess heat was observed for LiOH/H_2O electrolysis. In the case where the electric power of 0.3 W was employed, excess heat was observed (2.7%) for more than one month in the presence of 200 ppm aluminum. Depositon of aluminum onto the palladium surface was examined by means of in situ electrochemical quartz crystal microbalance.

1. Introduction

Since the observation of excess heat generation in D_2O electrolysis using a palladium cathode was reported (Fleischmann *et al.*, 1989), we have been addressed ourselves to the evaluation of excess heat. In the recent paper, we reported on the observation of excess heat generation in an open system (Oyama *et al.*, 1990). In the open system, however, the evaluation procedure for excess heat is complicated because several parameters must be considered and thus the evaluated value may contain some error (Balej and Divisek, 1989, Divisek *et al.*, 1990, Lewis and Skold, 1990 and Wilson *et al.*, 1992). That is, heat generation through the recombination of D_2 and O_2, the heat uptake through vaporization of D_2O, heat loss by radiation or conduction, and so forth must be taken into account. Thus we constructed a closed system in which D_2 (or H_2) and O_2 generated are recombined on a catalyst so that the errors contained in the open system are much smaller and excess heat can be evaluated more precisely in the present system.

2. Experimental

Electrolysis of D_2O containing LiOD (0.1 M) or H_2O containing LiOH (0.1 M)was performed with a two-electrode system in a twin cell (Figure 1). A palladium

rod (2.0 mm in diameter and 5.0 mm in length) of >99.9% purity (Tanaka Kikinzoku, Japan) and a platinum gauze were used as the cathode and anode, respectively. The product of the electrolytic current and the voltage was kept constant (0.200 or 0.300 W) by a computer (PC9801, NEC, Japan). The other twin cell as a reference was filled with a solution of the same amount and the same composition as was the electrolytic cell. Those twin cells were closed and set in a calorimeter (model MM 5111, Tokyo Riko, Japan) which is kept at 8.0°C. Difference in generated heat between the twin cells was measured and transferred to the computer every 10 seconds together with other parameters, applied voltage and current, for subsequent data processing and analysis. All D_2 (or H_2) and O_2 generated and liberated to a gas phase were recombined on a catalyst, palladium black supported on a platinum wire.

3. Results and Discussion

Calorimetry of LiOD/D₂O Electrolysis. In the case where electric power was kept at 0.200 W, excess heat generation was observed once out of 5 experiments. Figure 1 shows the time-course of the ratio of excess heat (W_{ex}) to input power (W_{in}). Continuous generation of excess heat was observed since the 12th day after beginning of D_2O electrolysis. The total energy produced for 27 days was 11.2 kJ, that means 2.4% of the power input. Excess heat per unit volume was 0.31 W cm^{-3}. Thus obtained excess heat was statistically examined and the value was certified to be larger than the error. Generation of ca. 4 ppm ^4He was observed by means of gas chromatography, though reproducibility and experimental error has not been examined. This value roughly agrees with that expected for the fusion of two D_2 molecules (Miles *et al.*, 1991). Then, another experiment was made with this palladium cathode and a newly prepared LiOD/D₂O solution, and slight excess heat (0.4% of the power input) was observed. On the other hand, no significant generation of excess heat has been observed for H_2O electrolysis.

Next the electric power was kept at 0.300 W to improve the reproducibility of excess heat generation. Further, aluminum (200 ppm) was added to the LiOD/D₂O solution. Aluminum is speculated to exist in the solution as AlO_2^-. In this case, continuous generation of excess heat was observed from the beginning of the electrolysis for more than one month. Figure 2A shows the time-course of the W_{ex}/W_{in} ratio. The total energy produced for 32 days was 22.7 kJ, which corresponds to 2.7% of the power input. Excess heat per unit volume was 0.52 W cm^{-3}. Addition of 50 ppm aluminum to a LiOD/D₂O solution resulted in observation of no significant excess heat generation (Figure 2B). Thus, it was found that aluminum content of the LiOD/D₂O solution might affect reproducibility of the excess heat generation.
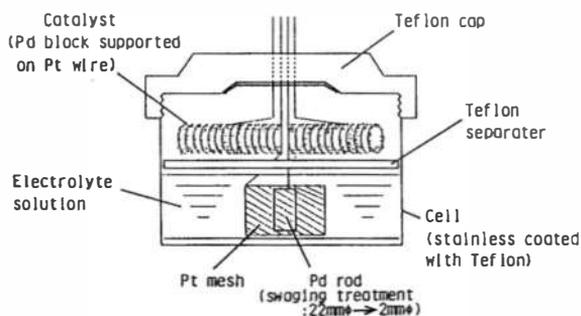

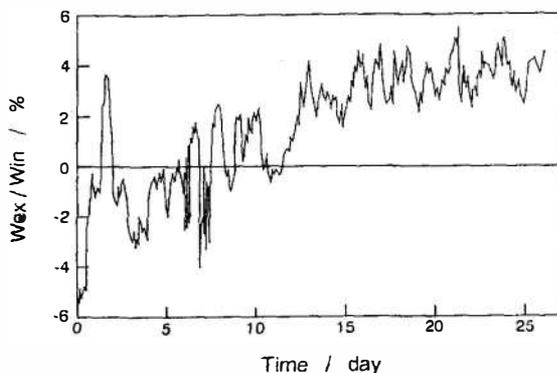Fig. 1. Schematic depiction of the closed electrolytic cell.

Fig. 2. Energy balance for the electrolysis of D_2O containing 0.1 M LiOD at a palladium cathode at 8.0°C. Input power = 0.20 W.
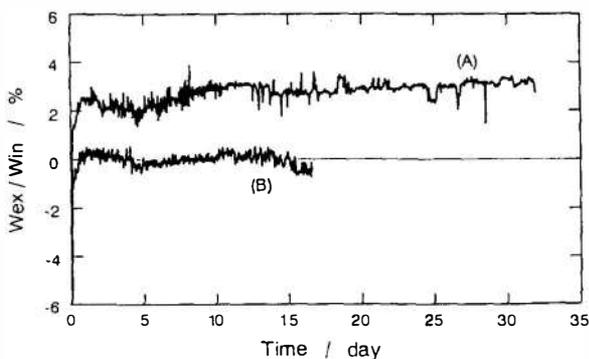

Fig. 3. Energy balance for the electrolysis of D_2O containing 0.1 M LiOD and 200 (A) or 50 (B) ppm aluminum at a palladium cathode at 8.0°C. Input power = 0.30 W.
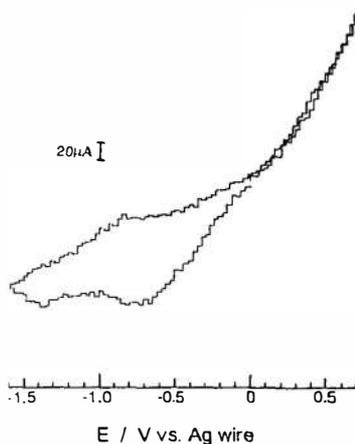

Fig. 4. Typical cyclic voltammogram obtained at palladium electrode in propylene carbonate containing 0.1 M tetrabutylammonium chloride as supporting electrolyte and 10 mM $AlCl_3$. Electrode area = 0.5 cm^2, scan rate = 20 mV s^{-1}.

Electrochemistry of Lithium and Aluminium on the Palladium Electrode. In the studies on calorimetry of $LiOD/D_2O$ or $LiOH/H_2O$ electrolysis, it is important to elucidate electrochemical behavior of lithium. In view of this, we have studied underpotential deposition of lithium by means of electrochemical quartz crystal microbalance (EQCM) (Oyama *et al.*, 1992). Lithium was found to be deposited at negative potential of -700 mV vs. Ag in propylene carbonate. In the present study, as mentioned above, aluminum may also play important role for the excess heat generation. Thus, EQCM technique was employed to study electrochemical behavior of aluminum. Palladium-coated quartz crystal oscillators and propylene carbonate containing 0.1 M tetrabutylammonium chloride as supporting electrolyte and 10 mM $AlCl_3$ were used here. The propylene carbonate solution is presumed to contain about 0.1% (vol) water. Resulted cyclic voltammogram was shown in Figure 4. Cathodic current was observed at a potential region more negative than 0 V vs. Ag and the current showed two peaks at about -0.8 V and -1.4 V. Anodic current increase was observed from 0 V. When the potential was swept between 0 V and -1.6 V, peak height of the cathodic peaks was decreased gradually. Resonant frequency of the quartz crystal was decreased with potential scanning; this indicates that mass of the electrode increased. Next the potential step measurements were performed. When the potential was stepped from 0 V to -1.6 V, mass increase was observed together with a cathodic current. Following step from -1.6 V to 0 V resulted in no significant change in mass, and further step from 0 V to 0.7 V caused mass decrease down to the initial value together with an anodic current. Thus, the cathodic and anodic currents were attributed to the electroreductive deposition and electrooxidative dissolution of aluminum, respectively. Similar behavior might be observed in an $LiOD/D_2O$ solution, though it will be examined elsewhere.

4. References

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