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A Highly Sensitive Analysis of Electrochemical Reduction Products of CO_2 on Gold by New Differential Electrochemical Mass Spectroscopy (DEMS)

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The products of electrochemical reduction of CO_2 on gold were analyzed *in-situ* by new DEMS with a stationary gas-permeable gold electrode sputtered on a porous water-repellent membrane in a rotational flow produced by a rotating rod.

In modern electrochemistry, an in-situ spectroscopic analysis of intermediates and products in electrochemical reactions is necessary and provides us many valuable pieces of information. Among many spectroelectrochemical methods, the technique combining directly the mass spectroscopy and the electrochemical technique, i.e. Electrochemical Mass Spectroscopy (EMS), was developed initially by Bruckenstein and Gadde.1)

Heitbaum and his co-workers improved EMS so that the variation of the amount of the produced species with respect to time or to electrode potentials could be measured. They called the method Differential Electrochemical Mass Spectroscopy (DEMS).2) In addition to Heitbaum's group, Vielstich's3) and Enyo's group4) have studied various electrochemical processes with DEMS.

We have been studying the electrocatalytic reduction of CO_2 by using nickel complexes of cyclam5) and alkylated cyclams.6) In order to identify the products, we have developed a new type of DEMS with an amalgamated-gold mesh electrode.7) The conventional DEMS apparatuses including our previous one were equipped with electrochemical cells with stationary solution. When a volatile reactant such as CO_2 is dissolved in the electrolyte, however, the reactant in the vicinity of the electrode surface will be depleted by the mechanisms shown in Fig. 1, that is, i) the consumption of the volatile reactant by the electrochemical reaction, ii) the exhaust of the reactant by evacuation to a vacuum chamber for mass spectrometry, and iii) the degassing by concomitantly evolving gases such as H_2 and O_2 due to the electrolysis of water.

To cope with these problems due to the depletion of the gaseous reactants near the electrode surface, a hydrodynamic voltammetric method would be ideal as an electrochemical method for an improved DEMS apparatus. By promoting mass transfer of the gaseous reactants with the forced convection of the solution, the sensitivity of the quantitative analysis was expected to be improved drastically. Heitbaum and co-workers8) already reported DEMS with a rotating electrode inlet system, while Vielstich and co-workers9) positioned an inlet membrane window for mass spectrometry near a rotating cylinder electrode. In the former case, however, the inlet system became structurally complex, while in the latter case a collection efficiency was low and apparatus dependent and its careful calibration was required.

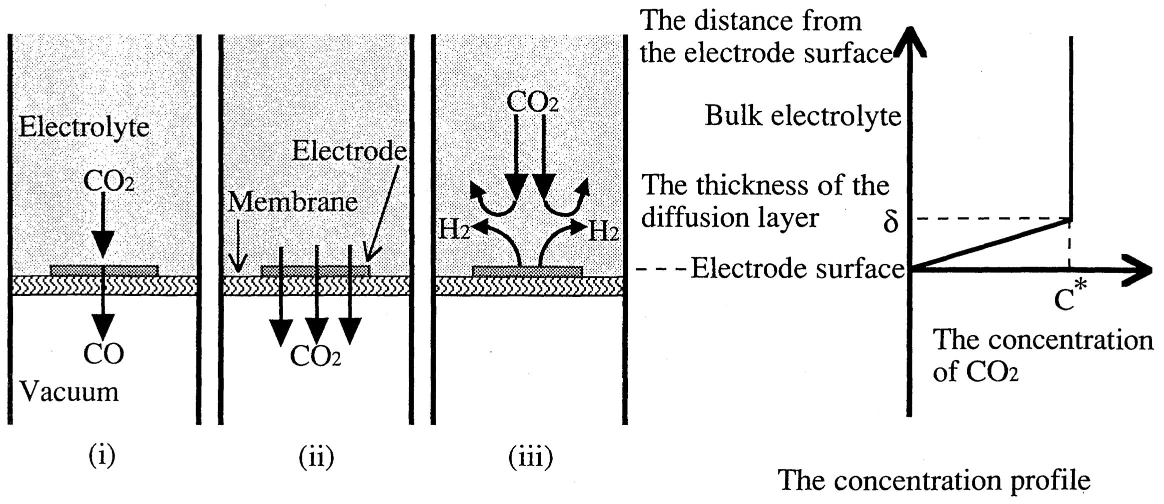

Fig. 1. The mechanisms by which the volatile reactant dissolved in the electrolyte is depleted.
(i) Consumption of the reactant by the electrochemical reaction, (ii) Exhaust of the reactant by evacuation to a vacuum chamber, (iii) Degassing of the reactant by concomitantly evolving gases due to the electrolysis of water.

Consequently, we examined another type of hydrodynamic electrochemical cell, that is, a stationary gas-permeable Au electrode sputtered on a water-repellent membrane in a rotational flow produced by a rotating rod. Such a stationary disk electrode placed in a rotational flow was already studied by Matsuda et al.10) and Bucur et al.11)

According to the investigation by Matsuda and co-workers,10) the same relation between the limiting diffusion current and the rotation speed as that for the conventional rotating disk electrode12) holds for the stationary electrode in the rotational flow except for the numerical coefficient as follows:

$$i_d = 0.422\, n\, F\, A\, c^*\, D^{2/3}\, \nu^{-1/6}\, \omega^{1/2} \qquad (1)$$

In our preliminary experiments, such Levich like electrochemical behavior was confirmed with our new electrochemical cell for DEMS shown in Fig. 2, but the numerical coefficient dependent on the cell geometry was determined experimentally to be 0.63 with 1 mM $K_3[Fe(CN)]_6$ aqueous solution containing 0.1 M Na_2SO_4. A porous gas-permeable and water-repellent membrane is made of polypropylene (DAICEL Chemical Industries,Ltd.). Working electrode was a gold porous thin film disk (8 mm in diameter) sputtered on the membrane. The inner diameter of the cell container was 25 mm and the diameter of the rotating rod was 20 mm. The counter and the reference electrode were a Pt wire and a saturated calomel electrode (SCE), respectively. Electrochemical control was done by a potentiostat (Nikko Keisoku,Ltd.). The rotation of the electrolyte was done by a rotating electrode system specially order-made (Nikko Keisoku,Ltd.).

With the above new DEMS apparatus, the electrochemical reduction of CO_2 on gold in 0.1 M Na_2SO_4 aqueous solution under CO_2 was studied as a function of the rotation speed. Hori et al. reported that the main product on gold was CO.[13)] Figure 3 shows current (i) - potential (E) and mass signal intensity (I_{MS}) - potential (E) curves at different rotation speeds. When the electrode potential was swept from - 0.5 to -3.5 V vs. SCE at 5 mV s^{-1}, the reductive current began to flow at ca. - 1.0 V vs. SCE and increased steadily with an increase in the negative potentials. The inherent Tafel like exponential increase in current was linearly increased by ohmic drop due to the high film electrode resistance and due to the solution resistance caused by the unfavorable location of the reference electrode which had to be chosen to avoid the disturbance of the rotational flow. The apparent applied electrode potentials more than - 3.0 V vs. SCE were due to the high ohmic drop. The I_{MS} - E curve for H_2 (m/z = 2) was similar to the i - E curve in shape, while the I_{MS} - E curve for CO (m/z = 28) became sigmoidal with an increase in the rotation speed. The latter change in shape indicates that the mass transfer of the gaseous reactant CO_2 was accelerated by the convection and thus the depletion of CO_2 due to the evacuation and the degassing with the evolving H_2 was almost overcome at 3600 rpm. The leveled off curve indicates that the reduction of CO_2 to CO was limited at very negative potentials by the convective mass transport.

This result indicates that the volatile products like CO could be detected in a high sensitivity in the presence of concomitantly evolving H_2 by promoting the mass transfer of the reactant CO_2 with the forced convection in the new DEMS. Further, it is also shown that the new DEMS has another advantage as follows. When the concomitant generation of gases of more than two kinds, like H_2 and CO in the present case, takes place at the same electrode potentials, it is difficult only from the i - E curve to know what kinds of gases evolve and what the composition of the evolved gases is. But, by the use of the present DEMS, the I_{MS} - E curves give us definite answers to these questions. The calibration methods are now under investigation to determine the mole fractions or the Faradaic efficiencies in a quantitative manner. .

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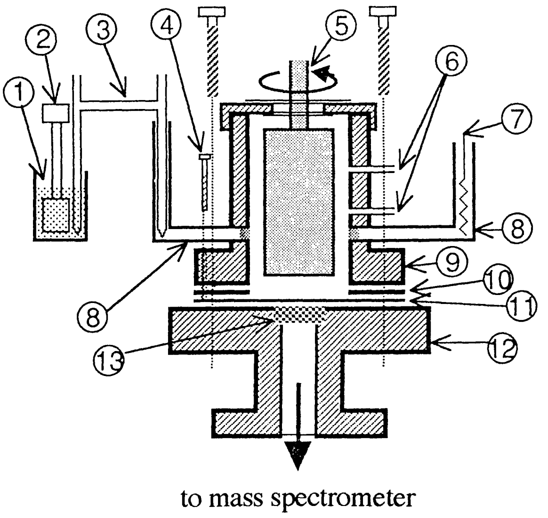

1. Saturated KCl solution, 2. SCE, 3. Liquid junction, 4. Current outlet from the working electrode, 5. Rotating rod, 6. Gas bubbler, 7. Counter electrode, 8.Glass pipe with a glass filter, 9.Cell container, 10. PTFE gasket, 11. Working electrode on the gas-permeable and water-repellent membrane, 12. Gas inlet, 13. Stainless steel mesh.

Fig. 2. Schematic diagram of the electrochemical cell and gas inlet system.

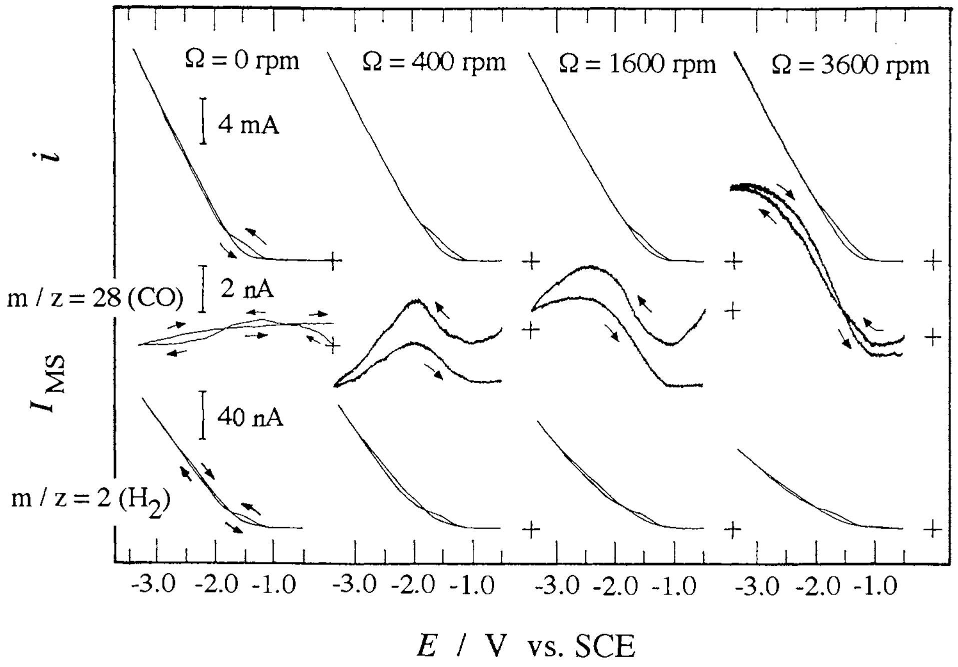

Fig. 3. Current (i) - potential (E) and mass signal intensity (I_{MS}) - potential (E) curves at different rotation speeds.
Electrolyte: 0.1 M Na_2SO_4 aqueous solution under CO_2 (pH 4.1, the temperature of the electrolyte: 26 ℃).
Working electrode: gold porous thin film disk (8 mm in diameter) sputtered on the membrane.
Sweep rate: 5 $mV \cdot s^{-1}$.

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