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In situ Analysis of Products in Electrocatalytic Reduction of CO_2 with Ni-cyclam by Differential Electrochemical Mass Spectroscopy during Cyclic Voltammetry on an Amalgamated-Gold Mesh Electrode

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The products of electrocatalytic reduction of CO_2 with Ni(II)-cyclam on Hg were analyzed *in situ* during cyclic voltammetry by Differential Electrochemical Mass Spectroscopy (DEMS) using an amalgamated gold mesh electrode in contact with a polytetrafluoroethylene (PTFE) inlet membrane.

An *in-situ* spectroscopic analysis of intermediates and products during electrochemical processes is one of the most interesting subjects in recent electrochemistry. Among versatile spectroelectrochemical methods,$^{1,2)}$ Electrochemical Mass Spectroscopy (EMS) developed by Bruckenstein and Gadde$^{3)}$ allows the most definite *in situ* analysis of the volatile intermediates and products. Their method uses a porous electrode, one side of which contacts the solution being electrolyzed, while the other side contacts the high-vacuum system of a mass spectrometer. The mass intensity detected after typical rise times of ca. 20 s was directly proportional to the amount of product. Heitbaum and his co-workers$^{4,5)}$ improved the method so that the time derivative of the amount of the species produced, i.e. its rate of formation, could be measured and they called the method Differential Electrochemical Mass Spectroscopy (DEMS). DEMS takes the advantage of a nonwetting porous electrode as the membrane inlet system, which is directly attached to the ionization chamber. Therefore, volatile products directly reach the ion source and they are ionized and detected shortly after their formation. At the same time, the chamber volume is continuously and effectively pumped thereby producing a mass signal which is proportional to the rate of the incoming flow of the product formed at the electrode.

In the present paper, we will describe application of DEMS to an *in situ* analysis of products of electrocatalytic reduction of CO_2 on Hg in an aqueous solution of Ni(II)-cyclam (nickel(II) complex of 1,4,8,11-tetraazacyclotetradecane) during cyclic voltammetry (CV). The exceptional efficiency and selectivity of the catalyst for the CO_2 reduction to CO were reported by Sauvage and his co-workers$^{6)}$ in a very narrow potential region. To analyze the products in the wide potential region during CV on Hg, the latest model of DEMS$^{5)}$ developed by Heitbaum and his co-workers was modified further, and in particular a new inlet system with an amalgamated gold (Hg-Au) mesh electrode was developed.

The experimental setup was composed of electrochemical apparatus, a membrane inlet system, and mass spectroscopic equipment as illustrated schematically in Fig. 1. The electrochemical apparatus together with the membrane inlet system is illustrated in more detail in Fig. 2. The working electrode was an Hg-Au mesh (made by amalgamating 100 mesh with Au wires of 0.07 mm in diameter) electrode placed on a PTFE film as the membrane inlet. The electrochemical control was made by a Nikko Keisoku potentiostat. All potentials given below were referred to SCE.

Since the solvent continuously evaporated into the mass spectrometer, a rather high back ground pressure of H_2O would be obtained at the ionizer if differential pumping was not used. Therefore, the mass spectrometer had two chambers connected with an orifice of 5 mm in diameter, i.e. a sample and

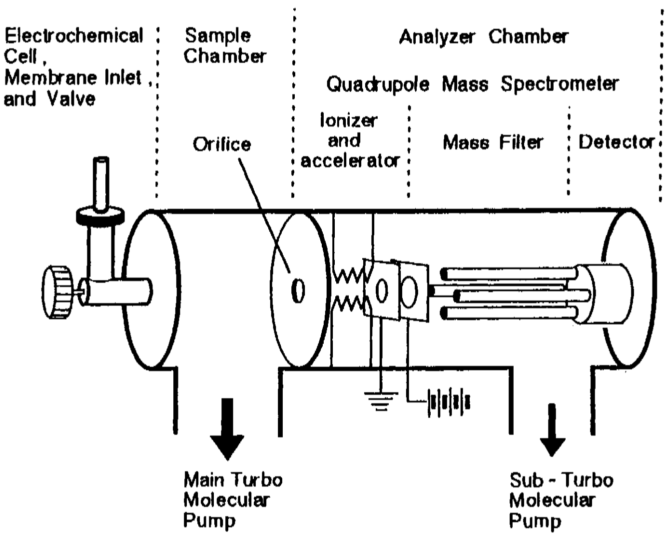

Fig. 1. Schematic diagram of DEMS apparatus.

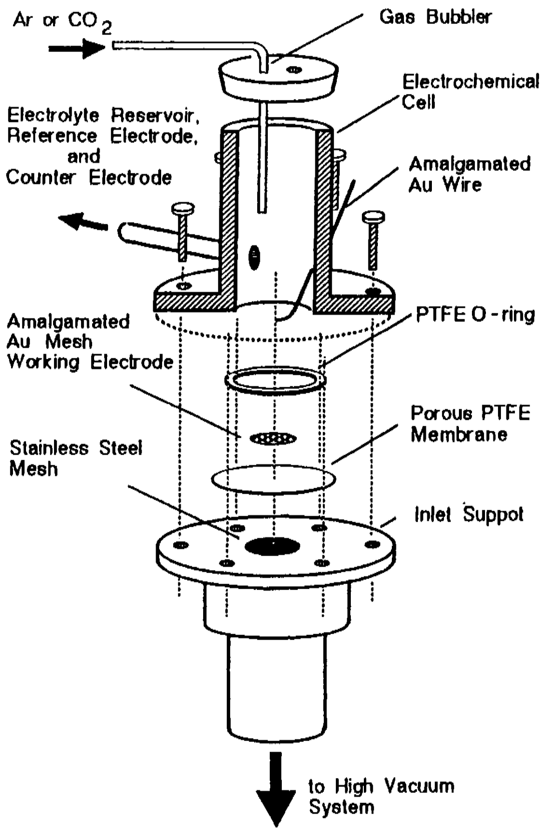

Fig. 2. Electrochemical cell and inlet system with an Hg-Au mesh.

an analyzer chamber pumped separately by an ULVAC UTM-300M main and an UTM-50 sub-turbo molecular pump, respectively, as shown in Fig. 1. The analyzer was an ULVAC MSQ-150A quadrupole mass spectrometer.

Figure 3 shows mass spectra for a background and a DEMS measurement. Respective spectra were recorded when a valve connecting the sample chamber and the membrane inlet system was closed and opened. A drastic increase in peak for H_2O by opening the valve clearly indicates the connection to the membrane which separated the aqueous electrolyte and the ultra-high vacuum.

In Fig. 4a is shown a cyclic voltammogram of 0.1 mM Ni(II)-cyclam under CO_2 in the electrochemical cell for DEMS. Fairly good similarity of the cyclic voltammogram to those recorded with an Hg-Au disk electrode in the same solution indicates that CV for DEMS was carried out properly.

Figures 4b - d show the mass intensity vs. electrode potential (MSCV) curves recorded simultaneously with CV with a potential sweep rate of 10 mV s^{-1} for CO at m/e = 28, CO_2 at m/e = 44, and H_2 at m/e = 2, respectively.

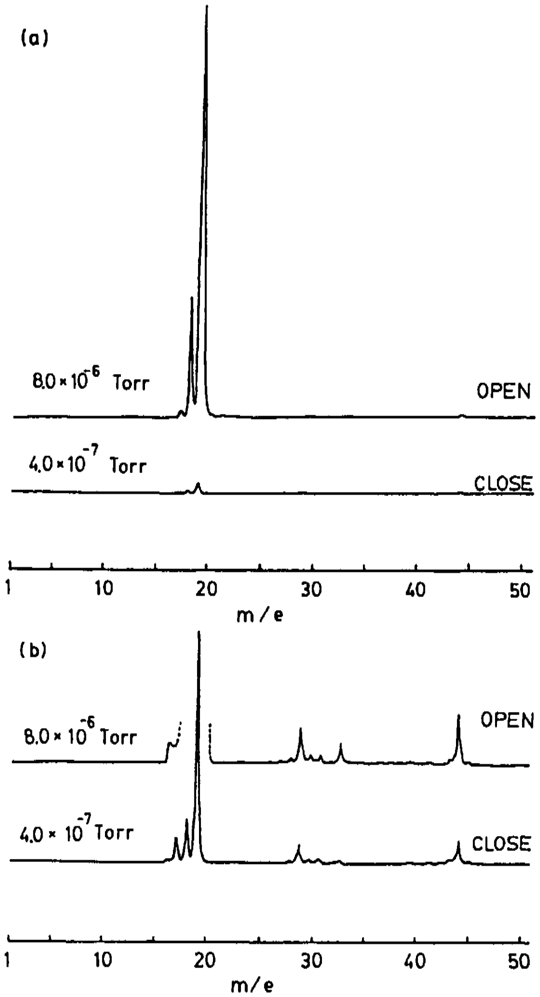

Fig. 3. Mass spectra for background (close) and DEMS (open). (a) low, (b) high sensitivity.

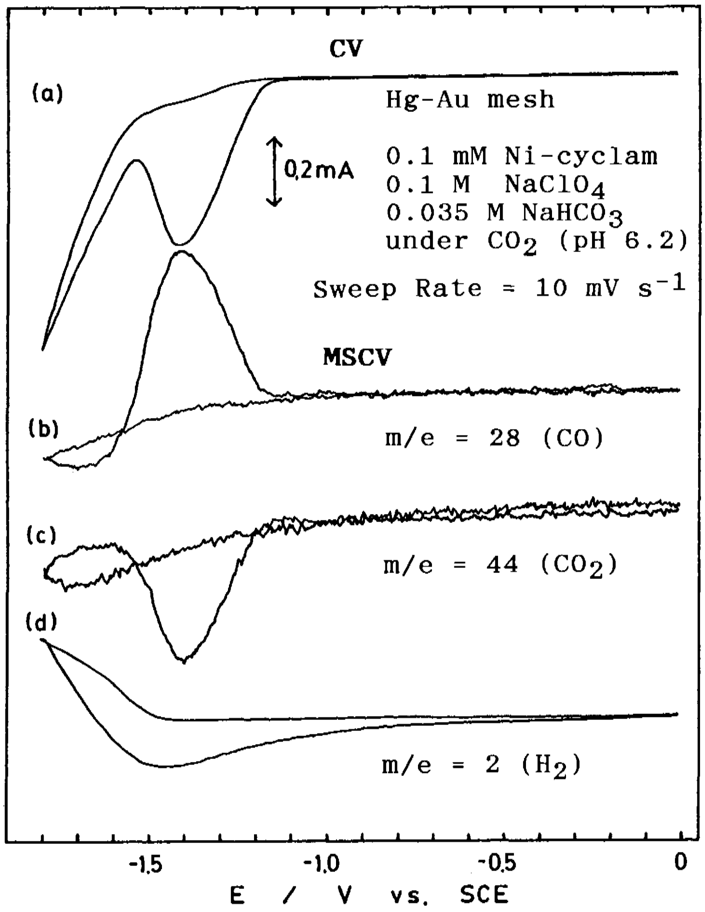

Fig. 4. (a) Cyclic voltammogram and MSCV's for (b) CO, (c) CO_2, and (d) H_2. Sweep rate: 10 mV s^{-1}.

On cathodic sweep of MSCV for CO, the mass intensity increased gradually from the onset potential of - 1.15 V, reached to a peak at ca. - 1.4 V, and then decreased up to a potential of ca. - 1.7 V. However, almost no change was observed except a small hysteresis at negative potentials during the anodic sweep. Similarity between the curves for CV and MSCV for CO during the cathodic sweep between - 1.15 and - 1.55 V clearly indicates that the cathodic wave with a peak potential of - 1.4 V is ascribed to the catalytic reduction of CO_2 to CO. By gas chromatography of gaseous products after a macroelectrolysis of CO_2 with Ni(II)-cyclam on Hg, CO was shown to be a main product (more than 98%) by the electrolyses at the narrow potential region from - 1.14 to - 1.29 V.⁶⁾ MSCV for CO_2 shown in Fig. 4c was almost an mirror image of MSCV for CO, indicating diminished concentrations of CO_2 in the vicinity of the electrode surface and thus the membrane surface during the formation of CO by the electrocatalytic reduction.

In Fig. 4d, we can clearly see the increase in the mass intensity for H_2 starting from the onset potential at ca. - 1.5 V for a steep rise of the cathodic current appearing after the electrocatalytic reduction of CO_2. The result for MSCV for H_2 confirms the conclusion from CV that the steep rise in the cathodic current was attributed to hydrogen evolution because the same steep rise was also observed in CV under N_2 in the same solution.

It is surprising that CO and H_2 evolution on the Hg-Au mesh electrode in contact with the PTFE membrane inlet was detected by the present DEMS without any appreciable delay, although the slow sweep rate at 10 mV s^{-1} was used. Of course, the delay in MSCV became apparent at 100 mV s^{-1}. This delay seems to be caused by longer mass transfer distance of gases evolved at the other side of the mesh electrode surface than that evolved at the surface near the PTFE membrane. The intrinsic response time of DEMS itself determined by the chamber volume and the pumping rate was calculated to be less than 10 ms according to the equation proposed by Heitbaum and his co-workers.⁴⁾

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References
1) R.J. Gale, "Spectroelectrochemistry," Plenum, New York (1988).
2) W.R. Heineman, F.M. Hawkridge, and H.N. Blount, "Electroanalytical Chemistry," ed by A.J. Bard, Marcel Dekker, New York (1984), Vol.13, p.1.
3) S. Bruckenstein and G.G. Godde, *J. Am. Chem. Soc.*, **93**, 793 (1971).
4) O. Wolter and J. Heitbaum, *Ber. Bunsenges. Phys. Chem.*, **88**, 2 (1984).
5) D. Tegtmeyer, A. Heindrichs, and J. Heitbaum, *Ber. Bunsenges. Phys. Chem.*, **93**, 201 (1989).
6) M. Beley, J.-P. Collin, R. Ruppert, and J.-P. Sauvage, *J. Am. Chem. Soc.*, **108**, 7461 (1986).

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