On the Anomalous Gas Evolution in the Electrooxidation of Absolute Methanol

By Kazuo SASAKI, Chisato HAMAGUCHI and Shigeo NAGAURA

(Received April 9, 1964)

The mechanism of the electrooxidation of methanol has recently become the subject of great interest in connection with the present development of liquid fuel cells. Although this problem has thus been quite familiar to us, however, the mechanisms so far proposed can not be accepted with full agreement.

Here, we would like to report an interesting finding concerning the electrooxidation of a non-aqueous methanolic solution of inorganic salts. In this experiment, the methanol used had been dehydrated by single distillation in the presence of metallic magnesium. About 0.1 mol./l. each of sodium methylate, sodium hydroxide and sodium perchlorate were used as supporting electrolytes. The current densities were 2 to 5 mamp./cm^2 for the most part, but 10 to 20 mamp./cm^2 in some cases; these values of current density will be referred to as lower and higher current densities below. The solution was deaerated by nitrogen before the electrolysis.

The anodic product of the electrooxidation of absolute methanol is formaldehyde, in the case of an aqueous solution, on the other hand, methanol is oxidized to carbon dioxide via formic acid. Usually the gas evolution from the anode could hardly be observed except when a higher current density was applied; however, a minor amount of gas was found to be accumulated at the bottom of the sintered glass disk used to separate the cathode chamber and so prevent the mixing of the cathode gas. Through careful examination we have found an anomalous phenomenon, that is, the formation of the anode gas at the lower surface of the glass filter and not at the anode itself. This was quite reproducible.

We first suspected this to be a misconception caused by some errors. However, even when the anode was shielded from the cathode chamber by triplicated glass filters, the gas is still formed at the nearest glass filter surface. The shape of the electrolytic cell or the relative spacing of two electrodes and the separater in the electrolytic cell did not appreciably affect the anomaly. The effects of the kind of electrolyte, sodium methylate, sodium hydroxide and sodium perchlorate were also examined, but there was no appreciable effect.

Furthermore, the following facts were ascertained. When the abnormal gas formation once occurred, it continued during the electrolysis. The gas formation ceased upon the discontinuance of the current, but it resumed at the resumption of the current, provided that the time of the discontinuance of the current did not exceed two or three minutes. When the period of current discontinuance lasted more than five to ten minutes, the gas formation is not restored by the electrolysis. Thus, the gas formation disappeared when the electrodes had been kept in the solution for a prolonged time without passing a current through. However, even in such a case, we could see the anomaly when the anode was dried in air. This clearly indicates that the gas formation is a phenomenon induced by the anodic reaction and not by other reasons. Perhaps the existence of a catalytic amount of oxygen is required for this gas formation. The above experiments were made with platinized platinum anode. Although the anomaly was also found for the smooth platinum anode, it was occasional and the reproducibility was poor.

The relative composition of the gases evolved from the anode surface (at the higher current density) and of the separater was determined by a mass spectrometer; it is given in Table I.

TABLE I

	Methanol	Formaldehyde	CO
Gas evolved from the anode surface	0.84	0.06	0.19
Gas accumulated at the separater	0.79	0.21	0.00

Beside solvent methanol, formaldehyde was the only component of the gas, while carbon monoxide was the main component of the gas evolved from the anode surface.

At the end of the electrolysis for the gas collection, the concentration of formaldehyde could never exceed 10^{-3} in its mole ratio to methanol: this proportion could not cause such a high concentration of formaldehyde as was observed in the evolved gas.

On the basis of the facts described, we propose the following sequence of reactions:

At the anode

$$\mathrm{MeOH} \rightarrow \mathrm{MeO} + \mathrm{H}^+ + \mathrm{e} \tag{1}$$

Detachment and diffusion

$$\mathrm{MeO(ads)} \rightarrow \mathrm{MeO\ (bulk)} \tag{2}$$

Disproportionation

$$2\mathrm{MeO} \rightarrow \mathrm{MeOH} + \mathrm{HCHO} \tag{3}$$

We have some evidence that the radicals formed by electrooxidation are methoxyl (CH_3O) and not hydroxymethylene radicals (CH_2OH),[1] although it seems that the real process of methoxyl radical formation is not so simple as to be expressed by Eq. 1. The methoxyl radical is comparatively stable,[2] and the following decomposition is heavily endothermic ($q=-20$ to 35 kcal.[3]).

$$\mathrm{MeO} \rightarrow \mathrm{HCHO} + \mathrm{H}$$

Therefore, it is not surprising that an appreciable number of the radicals formed by Eq. 1 do not undergo further oxidation upon the electrode surface but detach from the electrode and diffuse into the bulk solution. If the association of two radicals occurs, large exothermic disproportionation ($q=+85$ kcal. for Eq. 3) would occur readily, presumably at the glass filter surface.

Faculty of Engineering
Osaka City University
Kita-ku, Osaka

---

[1] K. Sasaki, K. Uneyama, C. Hamaguchi and S. Nagaura, 17th Annual Meeting of the Chemical Society of Japan, Tokyo (1964).

[2] P. Gray and A. Williams, *Chem. Revs.*, 59, 239 (1959).

[3] N. Semenov, "Some Problems in the Chemical Kinetics and Reactivity" (Translated into Japanese), Iwanami, Tokyo (1963), p. 95.