NOVEL CLASS OF CATALYSTS BASED ON PLATINUM AND ORGANIC COMPLEX FOR METHANOL OXIDATION IN DIRECT METHANOL FUEL CELLS

T. Okada, Y. Suzuki, T. Toda, T. Hirose*

National Institute of Advanced Industrial Science and Technology, Higashi 1-1, Tsukuba, Ibaraki 305-8565, Japan.

* Department of Applied Chemistry, Faculty of Engineering, Saitama University, 255 Shimo-Ohkubo, Urawa, Saitama 338-8570, Japan.

INTRODUCTION

Methanol oxidation reaction (MOR) is of recent technological interest, because of its application in direct methanol fuel cells (DMFCs). Since the reaction is strongly hindered by CO adsorption, the electrode catalyst free from CO poisoning is desired in order to realize high conversion efficiency in DMFC.

Several kinds of MOR electro-catalysts have been proposed including platinum based ally catalysts,[1] platinum finely dispersed with oxide-like TiO_2, MoO_2, WO_3, etc.[2] The best catalyst so far known is Pt-Ru, the function of Ru being the sites of CO elimination by oxidation.[3] However, high cost and poor natural abundance of Ru is a drawback of this catalyst for practical uses.

In this study, a new class of catalysts is proposed using organic metal complexes, because these have potentiality to generate a new function by proper molecular designing.

MATERIALS AND METHODS

The aqueous mixture of 8-hydroxyquinoline, o-phenylenediamine and sodium disulfate was refluxed for a week at 110 ℃. Recrystalization from methanol gave amber colored cubic. Equi-molar amount of cobalt acetate tetrahydrate was added at room temperature in ethanol under nitrogen atmosphere and the resulting solution was concentrated and refrigerated to get Co(mqph) in claret or reddish purple powder.

Mixed catalysts of platinum tetraammine chloride $Pt(NH_3)_4Cl_2 \cdot xH_2O$ and cobalt complex Co(mqph) were prepared in various mixing ratios. Mixed catalysts and graphite powder (1-2 μm, Aldrich) in 1:4 ratio were nixed in ethanol in a mortar, dried at 80 ℃ and then heat-treated in Ar atmosphere at 600 ℃ for 2 h in a furnace. The catalyst powder thus obtained was transferred with 5% Nafion solution (Aldrich) to the disk electrode made of basal plane of high density pyrolytic graphite (BHPG). The amount of the catalyst was 1.8×10^{-4} g cm^{-2}, for the apparent electrode area.

Cyclic and linear sweep voltammetry (CV and LSV) were measured for the disk electrode in 1 mol dm^{-3} CH_3OH + 0.05 mold dm^{-3} H_2SO_4 at 25 ℃. Potential was scanned at a scan rate of 0.1 V s^{-1} and 0.001 V s^{-1}, in a range -0.2 to 1.0 V vs. SCE (+0.316 V in RHE scale).

RESULTS AND DISCUSSION

Figure 1 shows the polarization curves of MOR for mixed catalysts of platinum and Co(mqph)/C of various mixing ratios. Results for 10 wt% Pt-Ru/C and 10 wt% Pt/C as similar catalyst loading are also superposed. Neither Pt/C nor Co(mqph)/C show catalytic ability towards MOR, but the mixture of them at 40-60 % mixing ratio revealed extraordinarily high MOR current density. Using $Co(NH_3)_6Cl_3$ in place of Co(mqph) as precursor material failed to get MOR activity (Fig. 2), showing that the initial structure of the complex affects the catalytic function after the heat treatment.

XRD and XPS analyses of mixed catalysts showed no evidence of alloying Co with Pt. Small extent of demetallation of Co complex was observed, but still N ligand coordinated to Co was apparent above 400 ℃.

All these results indicate strong potentiality of the combination of platinum (or other) and organic complex mixed catalysts as replacements of Pt-Ru electro-catalysts for MOR in DMFC or as CO tolerant H_2 oxidation catalysts in polymer electrolyte fuel cells.

REFERENCES

1. M. M. Janssen, J. Moolhuysen, *Electrochim. Acta*, **21**, 861; 869 (1976).

2. P. K. Shen and A. C. C. Tseung, *J. Electrochem. Soc.*, **141**, 3082 (1994).

3. M. Watanabe, S. Motoo, *J. Electroanal. Chem.*, **60**, 267 (1975); **69**, 429 (1976).

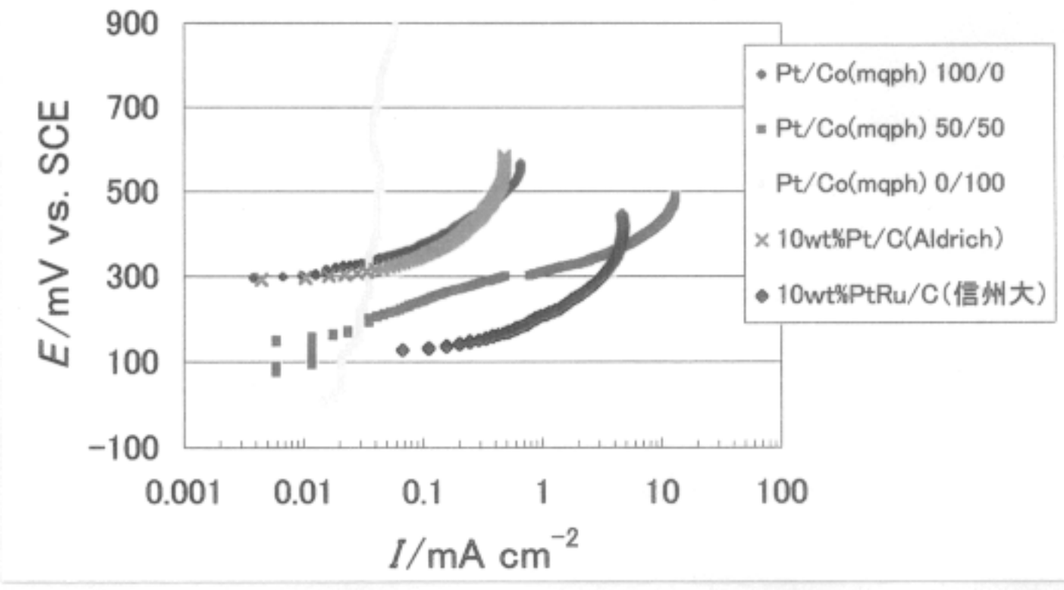

Fig. 1 Polarization curves of MOR on mixed catalysts Pt+Co(mqph)/C in 1M CH_3OH + 0.05 M H_2SO_4.

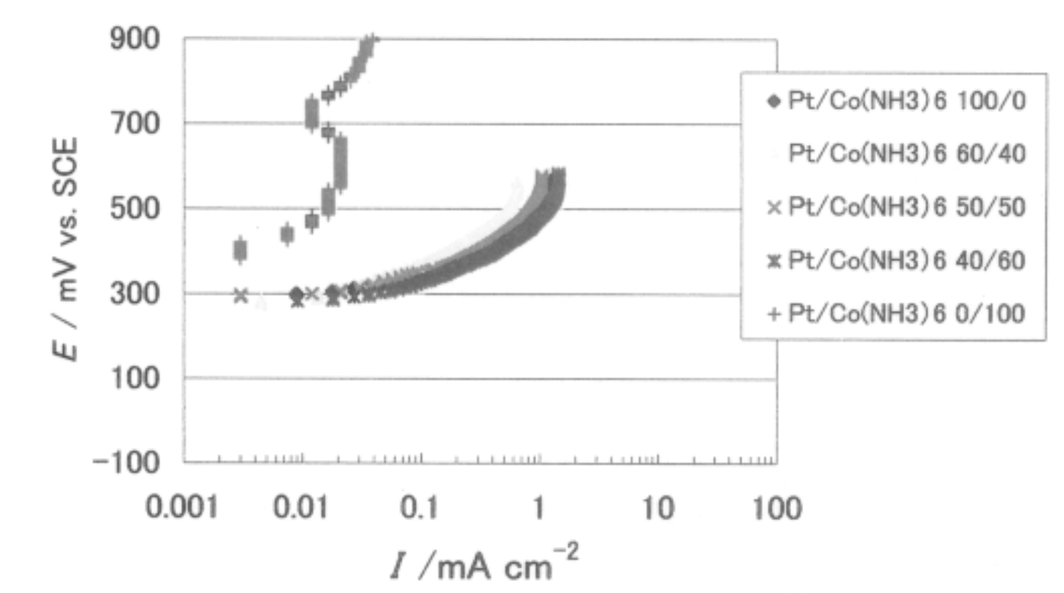

Fig. 2 Polarization curves of MOR on mixed catalysts Pt+$Co(NH_3)_6$/C in 1 M CH_3OH + 0.05 M H_2SO_4.