

ELECTRO-OXIDATION OF METHANOL ON PT-BASED CATALYSTS IN 7 M H₃PO₄

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The electro-oxidation of organic compounds, like methanol, is of interest in connection with the development of direct methanol fuel cells. Numerous investigations have been reported in the literature on this matter, however the presence of a parallel path in the reaction mechanism is still a matter of controversy. It is believed by many that a parallel path, where methanol is oxidised without the formation of CO as an intermediate, is a prerequisite for a successful development of low temperature direct methanol fuel cell. A deeper understanding of how one can facilitate the parallel reaction to occur is hence a key feature for catalysts development. In this paper the efficiency of electro-oxidation of methanol on various supported and unsupported Pt-based catalysts, prepared in-house, is reported.

Supported catalysts

Supported catalysts were prepared by impregnation of Vulcan XC-72. The effect of pre-treatment of the carbon support, as well as reducing agent, has been investigated by electrochemical measurements of the oxidation of methanol in 7 M H₃PO₄.

Thermal treatment of the carbon support at 500°C and 750°C in N₂ atmosphere showed that a certain improvement of the performance was observed for the support treated at the higher temperature. This observation could imply that organic impurities adsorbed on the surface, and which hence were inhibiting either the deposition of the noble metal or the methanol oxidation reaction, was removed by the thermal treatment [1]. Thermal treatment of the carbon support at 475°C with CO₂ atmosphere did not have a positive effect.

During the impregnation procedure, the noble metal precursor is partly reduced by carboxylic groups on the surface of the catalysts. A subsequent reduction procedure is required in order to reduce the catalyst to a metallic state. Four different reducing agents have been applied in this study: i) Formic acid, ii) Na-formiate, iii) Formaldehyde and iv) H₂. As can be observed from Fig. 1, the catalysts prepared by reduction with formic acid had the highest performance. Samples of the catalysts prepared by reduction with formic acid (i) and H₂ (iv) were studied with TEM, and clear differences in the particle distribution and size were observed. While the noble metal particles in case i) typically had a size of 5-10 nm, the particles on catalysts iv) had agglomerated to clusters of 50-100 nm. It is believed that the difference in the behaviour observed could be explained by the difference in size.

The effect of temperature was investigated by performing potential scans at 1 mV/s at four different temperatures (23°C, 50°C, 75°C and 98°C). The current density obtained at +900 mV vs RHE at the various temperatures was then plotted as a function of the inverse temperature, as shown in Fig. 2. The activation energy was then

calculated from the slope of the curve to be 30-35 kJ/mol for the prepared catalysts. This value is in the range earlier reported by Kauranen *et al* [1]

Unsupported catalysts

Unsupported catalysts were prepared by the method described by Adams and Schriener [3]. Two different catalysts were prepared, with the assumed composition of Pt_{0.5}Ru_{0.5}O₂. It was observed that a certain activation of the catalyst took place during a considerable amount of voltammetric sweeps. This is most likely due to a certain reduction of the oxide during the cathodic scan. A partly reduced surface might facilitate methanol adsorption and hence the methanol oxidation. Despite this activation, the performance of the unsupported catalysts, on weight basis, was considerably less than the supported catalysts. Attempts to develop unsupported catalysts with a porous structure, in order to increase the surface area, did apparently not improve the performance sufficiently.

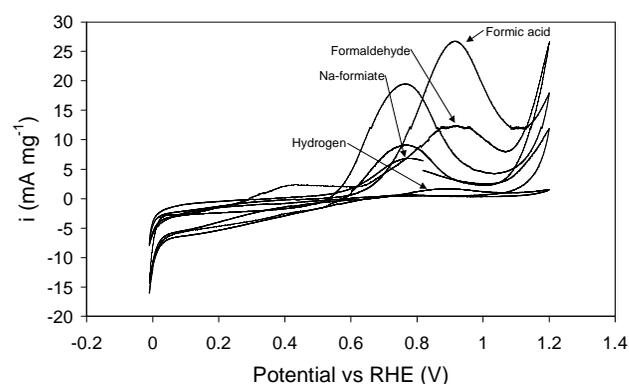


Fig. 1 Potential sweeps recorded at 1 mV s⁻¹ in 7 M H₃PO₄ + 2 M CH₃OH at 23±1 °C on catalysts reduced with formic acid, formaldehyde, Na-formiate and H₂.

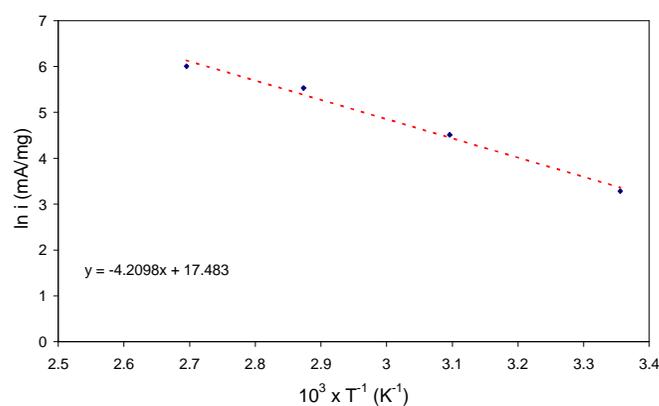


Fig. 2 Current density obtained at E=+900 mV vs T⁻¹ for the catalyst prepared by formic acid.

References

- 1) Carbon- Electrochemical and Physiochemical Properties, Kim Kinoshita, John Wiley & Sons, New York, 1988
- 2) P.S. Kauranen, E. Skou, J. Munk; J. Electroana. Chem., **404**, 1 (1996).
- 3) R. Adams and R.L. Shriener; J. Am. Chem. Soc., **45** (7), 2171 (1923).