Detection of Methanol Cross-over Products in DMFCs by Infrared ATR Spectroscopy

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On the demand of high-energy sources, direct methanol fuel cell (DMFC) technology has emerged attractive particularly as a new portable power source. Much of development effort has been concentrated on identification of efficient electrocatalysts, new or modified membranes with reduced methanol crossover yet with high proton conductivity and fuel utilization. In this study, examination of the products from oxidation of methanol at the oxygen cathode under a condition similar to that of a DMFC was undertaken.

An infrared reflection-absorption spectroscopic technique based on an attenuated total reflection (ATR) mode using a FTIR spectrometer (Bio-Rad) was employed for probing the methanol oxidation products. A Pt catalyst supported on XC-72 as an ink form in a Nafion® solution was directly applied on to a commercial gas diffusion layer (ETEK) and then, the layer was placed onto a Si or Ge internal reflection crystal. A piece of graphite with a flow pattern was inserted for passing methanol vapor using oxygen as the carrier gas.

Figure 1 shows *in situ* IR-ATR spectra collected during passing methanol vapor and oxygen simultaneously through the flowfield. The spectrum collected for methanol carried by Ar shows the peaks of HO- stretching, CH_3- symmetric and asymmetric stretching, and CH_3- bending modes corresponding to liquid methanol. Additional peaks at 2035 and 1756 cm^{-1} were observed. These are associated with adsorbed CO and -CHO species (or -COOH), which are produced in the partial oxidation of methanol by oxygen initially present in the methanol reservoir. Upon purging oxygen, which has the same effect as setting the electrode potential at an operating oxygen cathode value in a DMFC, the methanol peaks decreased markedly. The twin peak centered at 2350 corresponding to the gas phase CO_2 was observed in addition to the large amount of liquid water (peaks at 3400 and 1640 cm^{-1}). The peak at 1756 cm^{-1} persisted whereas the CO peak disappeared completely as oxidized. Generation of formaldehyde from partial oxidation of methanol at Pt/Nafion® anodes under methanol-rich conditions have been reported earlier.[1, 2]

The experimental geometry and the methanol delivery condition mimic the situation of methanol crossover to the oxygen/air cathode in a DMFC using a proton exchange membrane under the open-circuit condition. More detailed data including the effects of operation temperature and oxygen to methanol mixing ratio will be discussed in the presentation.

Acknowledgment

This work was supported by the Gillette Company.

References

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2. R. F. Savinell, ARPA/URI Quarterly Report, Case Western Reserve University, 1994.

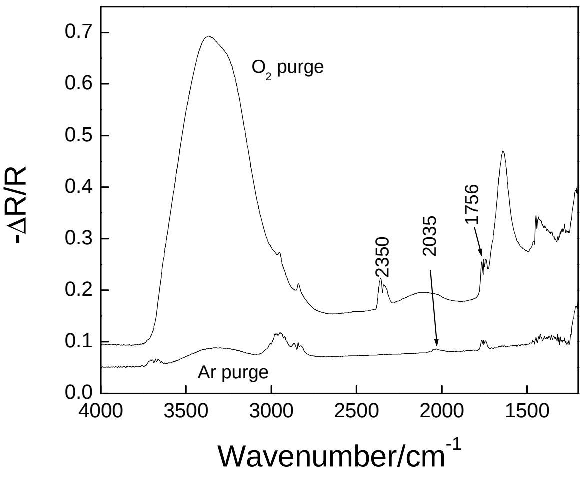

Fig. 1. IR-ATR spectra collected for the interface Pt-catalyzed GDL/Si exposed to methanol while purging Ar and O_2.