Combined ATR-SEIRAS and IRAS Study of Dissociation and Oxidation of Alcohols at Palladium Electrode in Alkaline Media

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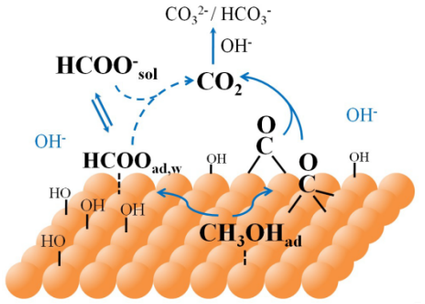
Nowadays, Pd-based catalysts are brought to use in the anode of direct alkaline alcohol fuel cells (DAAFCs), in consideration of their higher electrocatalysis towards alcohol oxidations in basic media than in acidic media [1]. In this regard, the fundamental study of alcohol dissociation and oxidation at Pd electrode in alkaline media is of great importance for designing new efficient and economic catalysts for next-generation DAAFCs [1-2]. Here, we initially combined attenuated total-reflection surface-enhanced infrared spectroscopy (ATR-SEIRAS) and infrared reflection adsorption spectroscopy (IRAS) to investigate the dissociation and electro-oxidation of alcohols at Pd electrode in NaOH solution [3].

Spectral results have shown that methanol can dissociate to form CO_{ad} at Pd electrode at open circuit potential as well as at potentials lower than ca. -0.10 V (vs. Ag/AgCl), involving the initial dissociation of O-H bond followed by the stepwise cleavage of C-H bonds. Meanwhile, A dual-pathway mechanism for a complete methanol oxidation to CO_2 (or (bi)carbonate) at Pd electrode have been put forward, involving CO_{ad} and interfacial formate as the intermediates. The formate is also a by-product due to an incomplete methanol oxidation. The proposed reaction pathway at Pd electrode is to some extent similar to that at Pt electrode in alkaline media. Nevertheless, a higher potential is required to oxidize the two intermediates, and the conversion rate from formate to CO_2 (or (bi)carbonate) at Pd electrode is less than that at Pt electrode, leaving more formate in the solution as the by-product.

In addition, the dissociation and electro-oxidation of ethanol at Pd electrode in 0.1 M NaOH ethanol is also preliminarily measured by combined ATR-SEIRAS and IRAS methods.

Furthermore, this work demonstrated that the combination of ATR-SEIRAS and IRAS measurements is more reliable for elucidating electro-catalytic reaction mechanism, thus may be regarded as a new development of electrochemical surface infrared spectroscopy.



Scheme 1. Schematic diagram for methanol dissociation and electro-oxidation at Pd electrode in alkaline media [3].

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References:

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