Electrochemical Infrared Investigations of Ruthenium Stability between Platinum-Ruthenium Alloy Nanoparticles and Bulk Material

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Introduction

The CO oxidation on metallic catalyst systems is one of the important issues in direct methanol fuel cells (DMFCs) reaction. The platinum-ruthenium (PtRu) bimetallic catalyst has demonstrated a great performance for CO electro-oxidation [1]. But the full understanding of electrochemical and surface properties of PtRu nanoparticles (NPs) are still unclear.

Adsorbed CO exhibits a surface sensitive behavior of vibrational properties [2]. The electrochemical infrared absorption reflection spectroscopy (EC-IRAS) characterization technique could provide more details about the information of metal-CO bonding. The potential dependence of IR band wavenumber or so called "*Stark Tuning Rate*" (dv/dE; cm^{-1}/V) provides the degree of dπ-2π* back-donation of CO adsorbed on catalysts [3]. In the literature, the stark tuning rate of CO linearly (CO_L) adsorbed on Pt is around 25-30 (cm^{-1}/V) [4], which depends on it's particle size and interfacial conditions. However, the stark tuning rate of CO_L adsorbed on a bulk PtRu alloy material is higher than a Pt [4]. In this work, the behavior of stark tuning rate on PtRu alloying NPs was investigated by an EC-IRAS method.

Results and Discussions

Figure 1 (a) shows the potential dependence of C-O_L stretching wavenumber for the Pt NPs. The C-O_L stretching wavenumber increases with potential in the range of 0.05 and 0.45 V, indicating the degree of dπ-2π* back-donation of the CO adsorbed on Pt NPs decreases with increasing potential. A linear relation was observed in the range of 0.05 V and 0.30 V, the stark tuning rate (dv/dE) is 30.5 $cm^{-1}V^{-1}$.

Figure 1 (b) shows the potential dependence of C-O_L stretching wavenumber for the PtRu alloy NPs. The linear dependence in the range of 0.05~0.30 V was observed. The stark tuning rate of the PtRu alloy NPs is 28.3 $cm^{-1}V^{-1}$.

Table 1 shows the stark tuning rates for various catalysts. The lower stark tuning rate has been found in the PtRu alloy NPs than the Pt NPs. Meanwhile, the inverse trend of stark tuning rate is observed between bulk [4] and nanoparticle catalysts. It indicates the degree of dπ-2π* back-donation for the CO adsorbed on the PtRu alloy NPs is more difficult to be reduced than on a bulk material by the applied potential. As we known, the reduction potential of Ru is lower than Pt. The Ru would be oxidized more preferably than Pt in the PtRu alloy materials by the applied potential. The trend of stark tuning rates indicated that the electronic withdrawing effect caused by the applied potential in the Ru of the PtRu alloy NPs is more pronounced than in a bulk material.

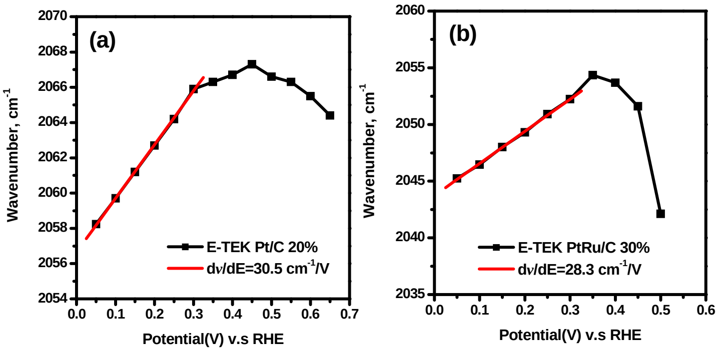

Figure 1. Potential dependence of linear C-O stretching wavenumber on (a) Pt NPs and (b) PtRu NPs

Table 1. The stark tuning rate (dv/dE) of various catalysts.

Catalyst	*dv/dE ($cm^{-1}V^{-1}$)*
Pt – bulk*	28
Pt – NPs	30.5
PtRu – bulk*	32
PtRu – NPs	28.3

* Reference 4

Reference

[1] C. Linda, F. K. Andreas, and S. Ulrich, Chemphyschem **1**, 162 (2000).
[2] S. Park, A. Wieckowski, and M. J. Weaver, J. Am. Chem. Soc. **125,** 2282 (2003).
[3] G. Blyholder, J. Phys. Chem., **68**, 2772 (1964).
[4] W. F. Lin, T. Iwasita, and W. Vielstich, J. Phys. Chem. B **103**, 3250 (1999).