

Ultra-low Pt loading electrocatalysts for H₂/CO and methanol oxidation

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Fuel cells have increasingly been expected to become one of major sources of clean energy. In spite of a large number of studies, however, enhancing activity of electrocatalysts and reducing the noble metal loading together with achieving the long term stability, still remain the requirements for the ongoing research in the fuel cell electrocatalysis.

We demonstrated a new approach in synthesizing fuel cell electrocatalysts based on placing atoms of a catalytically active metal on nanoparticles of suitable metal substrate, which facilitates its full utilization and an ultimate reduction of its loading[1]. This was obtained by electroless (spontaneous) deposition of Pt submonolayers in the form of two-dimensional (2D) islands on the surface of Ru nanoparticles. The basic idea of this approach is that all the Pt atoms at the surface of nanoparticles can be actively involved in reaction. The mass-specific activity for H₂ oxidation of the PtRu₂₀ was found to be 3-4 times higher than that of commercial PtRu alloy catalysts. Its CO tolerance appears considerably higher under the condition of the rotating disk experiments despite its three times smaller Pt loading[2]. Long-term tests of the PtRu₂₀ electrocatalyst under real operating conditions exhibited excellent stability. The tests were made using electrodes of 50 cm² with the catalyst of a Pt content of 18 μg/cm². No voltage losses were observed at a constant current of 0.4 A/cm² with H₂ or H₂ with 50 ppm of CO and 3% air after 870 h of testing.

In order to elucidate the origin of the observed CO tolerance, *in situ* XANES measurements were made to obtain the electronic properties of the PtRu₂₀ electrocatalyst. Fig. 1 shows the Pt L₃ (A) and L₂ (B) edge spectra of the electrocatalyst at 0.40V(RHE) in 1 M HClO₄, together with those of a Pt foil. The absorption peaks of the PtRu₂₀ at L₃ and L₂ are larger than those of the Pt foil. This indicates an increase in *d*-band vacancy caused by interaction between the Pt atoms and the Ru nanoparticle surface. As a consequence, CO adsorption on the Ru-supported Pt is weakened and the CO can react with RuOH species more facily to form CO₂. This is in agreement with the stripping voltammetry data. The observed CO tolerance of the PtRu₂₀ electrocatalyst appears to originate from the combined electronic effect and the bifunctional mechanism. The electronic effects are larger than previously assumed for PtRu alloys.

We also report a new approach to preparing electrocatalysts for methanol oxidation, *viz.*, a deposition of Pt on Ru nanoparticles by redox replacement of an underpotentially deposited (upd) Cu adlayer. Cu was underpotentially deposited on the Ru nanoparticles in a solution containing Cu²⁺ and the electrode surface was immersed into a solution containing Pt²⁺ to replace upd Cu by Pt. These operations were performed in a single cell with multi-compartments in an Ar atmosphere that prevents the oxidation of Cu adatoms in contact with oxygen. We deposited an amount of 6 nmol Pt on 15 nmol Ru nanoparticles by replacing a Cu monolayer

(Pt₆Ru₁₅). Cyclic voltammograms of the Pt₆Ru₁₅ electrocatalyst in 0.5 M CH₃OH/0.1 M H₂SO₄ show 2~3 times higher mass-specific activity for methanol oxidation compared with a commercial PtRu electrocatalyst.

Electrochemical properties of a Ru(10-10) surface were also examined. The CO displacement experiments demonstrated that the Ru(10-10) surface is associated with RuOH species at potentials between 0 and 0.3 V(RHE). The morphology of the Pt deposits obtained by replacement of a Cu monolayer was investigated by STM. The STM data showed a number of small Pt islands (*ca* 3 nm diameter) dispersed on the Ru surface, suggesting that for the Pt₆Ru₁₅ electrocatalyst 3D Pt clusters may be formed on the Ru nanoparticles, rather than flat 2D Pt clusters. Other details of these experiments and their implications will be discussed.

Acknowledgement

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References

- [1] S.R. Brankovic, J .X. Wang, R. R. Adžić, *Electrochem. Solid-State Lett.*, 4 (2001) A217.
- [2] K. Sasaki, Y. Mo, J.X. Wang, M. Balasubramanian, F. Uribe, J. McBreen, R.R. Adžić, *Electrochim. Acta*, 48 (2003) 3841.

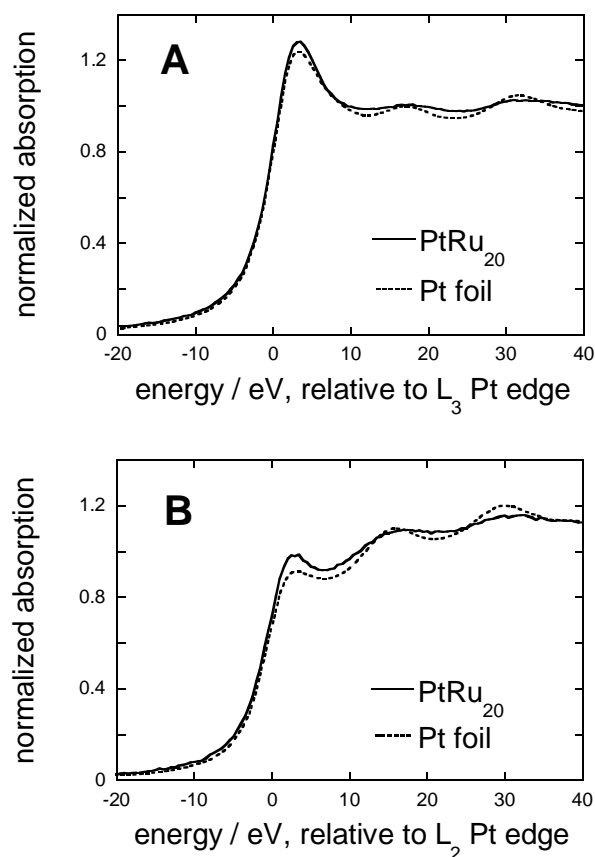


Fig. 1 *In situ* XANES at Pt L₃ (A) and L₂ (B) edges of the PtRu₂₀ electrocatalyst at 0.40V(RHE) in 1 M HClO₄ (solid lines), together with those of a Pt foil (dotted lines).