

## Pt skin layer thickness of Pt-Co cathode catalysts for PEFC

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### Introduction

The Polymer Electrolyte Fuel Cell (PEFC) system has been developed as an environmentally friendly power source for stationary, transportation and portable applications. Pt-Co alloy catalysts have been widely researched and developed to apply to PEFC cathode catalysts because of their high catalytic activity [1].

The surface of Pt-Co is reportedly covered with a platinum rich layer, named Pt skin layer [1, 2]. The Pt skin layer is formed by segregation during annealing or by acid leaching of cobalt from the surface [2]. Strasser *et al.* reported that the Pt skin layer of 0.6 nm is formed in Pt-Cu catalysts measured by high-resolution energy dispersive spectroscopy [3]. In this study, we have estimated the thickness of the Pt skin layer of the Pt-Co alloy catalyst.

### Experimental

Pt-Co nano-particles were loaded on the carbon support, which is carbon black.

The electronic states of cobalt in the Pt-Co alloy catalysts were measured using the soft X-ray photoemission spectroscopy (SXPES) in BL-7A of the Photon Factory. The measurement is conducted with various photon energies to change the escape depth of photo electron.

### Results and discussion

Figure 1 shows the SXPES spectra of the Pt-Co alloy catalyst. Photon energies are 850, 900 and 1000 eV. All measurement shows the peaks of cobalt in the catalyst. The peak positions of SXPES spectra measured with photon energy of 1000 eV are 778 and 793 eV, (solid lines in Fig. 1) indicating that the cobalt is in a metal phase [4]. On the other hand, the peak positions of spectra measured with 850 and 900 eV are 780 and 795 eV, respectively (dash lines in Fig. 1), which correspond to the positions of the CoO [4].

The metal phase cobalt may exist as the Pt-Co alloy in the core part of the catalysts. The CoO might exist on the surface to be oxidized.

The probing depth is estimated to be about three times of inelastic mean free path of the photoelectron from cobalt surrounded by platinum. The probing depth is 1.2

nm for 900 eV measurements and is 1.4 nm for 1000 eV. In our measurements, the spectrum of 1000 eV shows core Pt-Co alloy, while the spectrum of 900 eV shows surface cobalt oxide. Therefore the Pt skin layer thickness is evaluated to be from 1.2 to 1.4 nm, which is about two times thicker than that for the reported value [3]. This thicker Pt skin layer might improve the catalyst durability to prevent the cobalt dissolution from core part of the Pt-Co alloy catalysts.

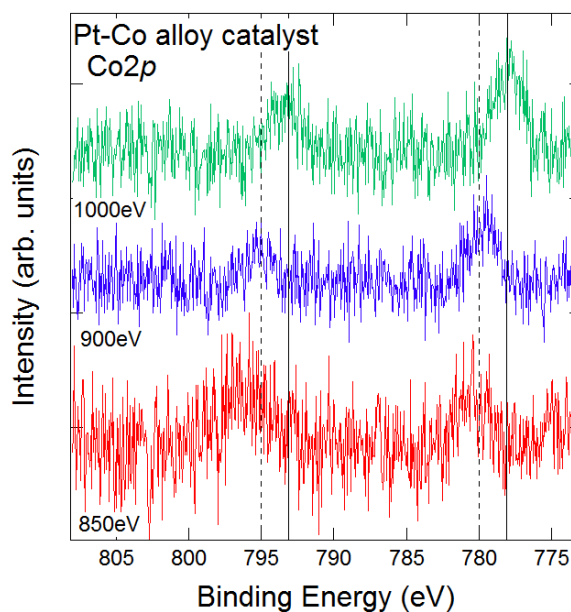


Fig. 1 Co 2p SXPES spectra measured with photon energies of 850, 900 and 1000 eV

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### References

- [1] T. Toda *et al.*, J. Electrochem. Soc. **146**, 3750 (1999).
- [2] V. R. Stamenkovic *et al.*, Nature Mater. **6**, 241 (2007).
- [3] P. Strasser *et al.*, Nature Chem., **2**, 454 (2010).
- [4] "Handbook of X-ray photoelectron spectroscopy" Parkin-Elmer corporation (1979).

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