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# Applications of micro-XRF for PEMFC catalyst research: Pt catalyst uniformity imaging and Pt loading mass determination

Application Note

Energy
XGT33

**Chiya Nishimura[1], Tsubasa Yamashita[1], Hitomi Nakano[2]**
[1]HORIBA, Ltd., Japan, [2]HORIBA Techno Service Co., Ltd., Japan.

**Abstract:** We introduce the “2-in-1” application of HORIBA micro-XRF for proton exchange membrane fuel cell (PEMFC) catalyst research: One is Pt catalyst uniformity imaging within a catalyst sheet thanks to the imaging capability. The other is Pt catalyst loading mass determination on average, which is a popular application of EDXRF. Through the experiments, we successfully visualized aggregates of Pt catalyst in our samples, and we also got a good linearity of calibration curve for Pt catalyst loading mass determination.

**Keywords:** Proton exchange membrane fuel cell, catalyst imaging, catalyst loading mass determination, micro-XRF

## Introduction

A catalyst layer is one of the most important components of proton exchange membrane fuel cell (PEMFC). The catalyst layer is made by catalyst slurry coated on a proton exchange membrane (Figure 1a) or sometimes on a gas diffusion layer. [1-3]

The catalyst slurry consists of the mixture of several ingredients, such as precious metal catalyst particles, carbon supports, an ionomer and solvents. Though there are various fabrication methods,[2, 4-9] it is challenging to achieve a uniform catalyst layer using this mixed slurry, and therefore, it is important for fuel cell researchers to check not only catalyst loading mass on average, but also the in-plane catalyst distribution in a catalyst layer.

We reported the application on a benchtop energy-dispersive X-ray fluorescence (EDXRF) analyzer for non-destructive determination of Pt catalyst loading mass on average.[10] However, the analyzer doesn’t have an imaging capability to see the distribution. On the other hand, a Transmission Electron Microscope (TEM) has an imaging capability with excellent spatial resolution in nano scale, and it is widely used to observe individual ingredient particles,[3,9] but it is difficult to get a representative distribution about an entire catalyst layer.

In this application note, we introduce a “2-in-1” application of a HORIBA micro-XRF called XGT-9000 X-ray analytical microscope for both in-plane Pt catalyst distribution imaging and Pt catalyst loading mass determination.

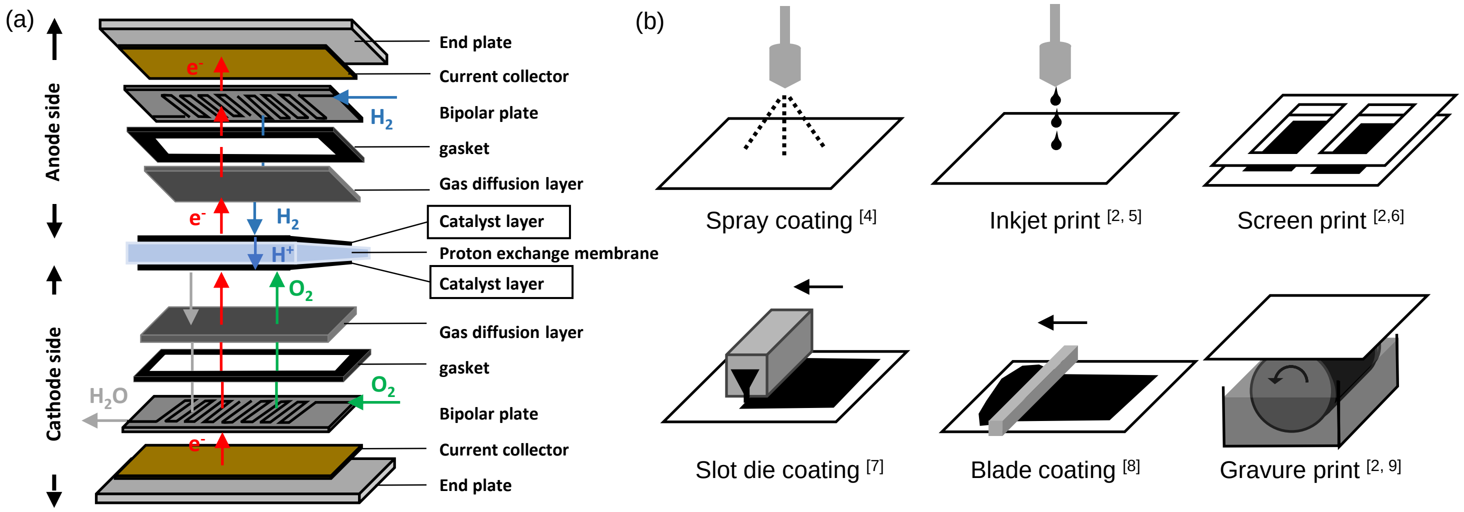


Figure 1. (a) Schematic diagram of PEMFC (b) Schematic diagrams of catalyst layer fabrication methods.

## HORIBA XGT-9000 X-ray Analytical Microscope

The XGT-9000 X-ray Analytical Microscope (Figure 2a) is micro-XRF, which is an elemental imaging analyzer based on energy-dispersive X-ray fluorescence. It is equipped with capillary optics to achieve micro-spot without sacrificing the intensity, a fluorescent X-ray detector, and a motorized XYZ stage. It allows elemental distribution imaging on a fuel cell test sheet.

## Sample information

In this application note, we prepared six in-house catalyst sheet samples with known loading mass of Pt (Table 1). We made a slurry by mixing carbon supported Pt, an ionomer, and solvent (NPA and water). We coated the catalyst slurry on a film by the spray coating method.

Table 1. Pt loading mass information of each sample [mg/cm$^2$]

| | A | B | C | D | E | F |
|---|---|---|---|---|---|---|
| Pt loading mass | 0 (blank) | 0.052 | 0.107 | 0.211 | 0.301 | 0.387 |

## Application -1: Pt catalyst uniformity imaging

We set all the sheet samples at once inside the sample chamber, as shown in Figure 2c. We used the partial vacuum condition, which keeps the optics part under vacuum and keeps the sample environment under air. We carried out elemental imaging on individual catalyst sheets with a 15 µm ultra-high intensity probe to see the micro distribution of Pt uniformity. The other measurement conditions were described in Figure 3.

Figure 3 shows the Pt distribution images of individual samples (darker color represents lower Pt intensity and brighter color represents higher Pt intensity). As shown in Figure 3, we could see the trend that the catalyst sheet sample with higher Pt loading mass showed a brighter color of the Pt image. We could also see micro aggregations especially in Sample E and Sample F.

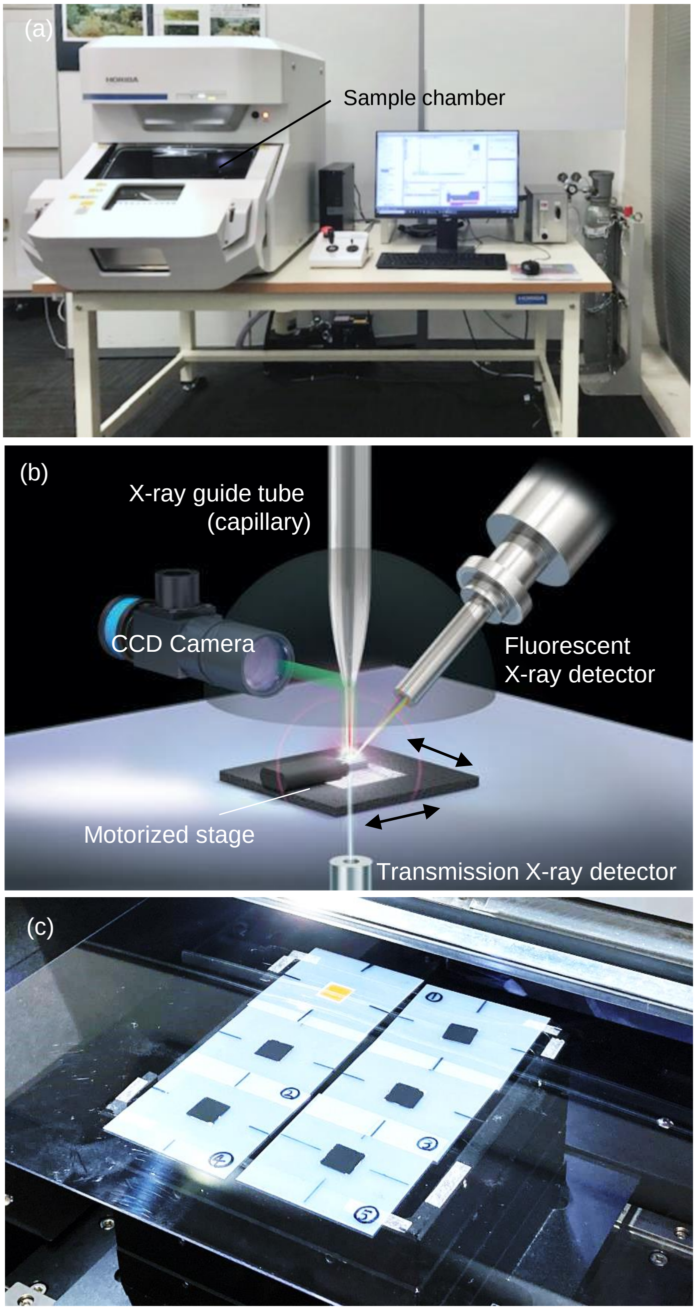


Figure 2. (a) Instrument set-up of the XGT-9000. (b) Schematic diagram of the optics inside the XGT-9000. (c) Sample setting in the sample chamber of the XGT-9000.

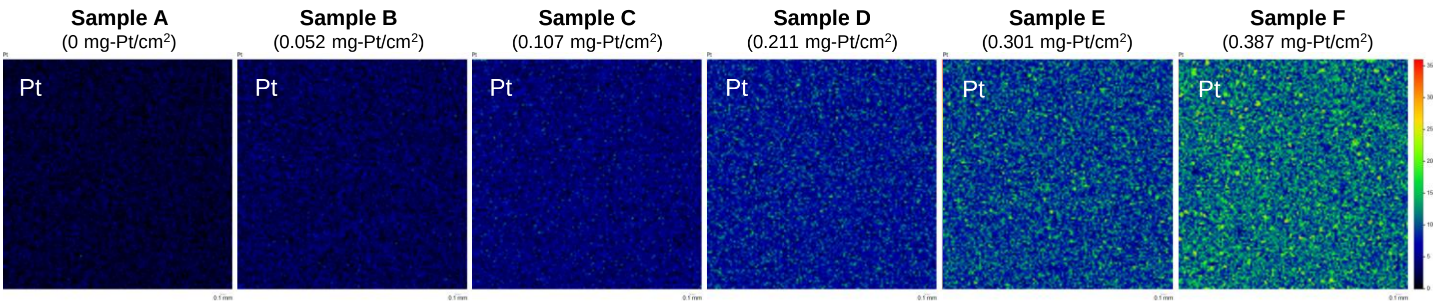


Figure 3. Pt distribution images obtained by the XGT-9000. [Condition] Voltage: 50 kV, Current:1000 µA, Capillary: 15 µm ultra-high intensity probe, Analysis environment: Partial vacuum, Mapping area: 3.84 mm x 3.84 mm, Mapping time: 6 min 33 sec per sample.

## Application-2. Pt loading mass determination

To show another capability of micro-XRF, in addition to the imaging capability, we created a calibration curve for Pt loading mass determination and checked the linearity of the curve. The HORIBA XGT-9000 software can obtain a map sum spectrum, which is an XRF spectrum consisting of the total X-ray counts obtained in the individual pixels. It is more suitable for representative discussions on a sample than an X-ray spectrum from a single micro-spot.

Figure 4a shows a layered spectrum of the six catalyst layers samples' results. We could see an expected trend that the higher loading mass sample had higher peak intensity of Pt. Using the result, we made a calibration curve of Pt loading mass value vs. Pt-Lα X-ray signal counts, and it showed a good regression coefficient by using a linear model (Figure 4b). This is a good indication that micro-XRF is also a suitable method for Pt loading mass determination in a PEMFC catalyst sheet.

## Conclusion

In this application note, we introduced two applications using a HORIBA micro-XRF on Pt catalyst sheet samples. We could visualize the Pt catalyst uniformity by imaging, and we could also get good linearity of the calibration curve for Pt loading mass determination. Thus, our results show the potentials of a micro-XRF as an analytical tool for catalyst fabrication optimization in PEMFC research.

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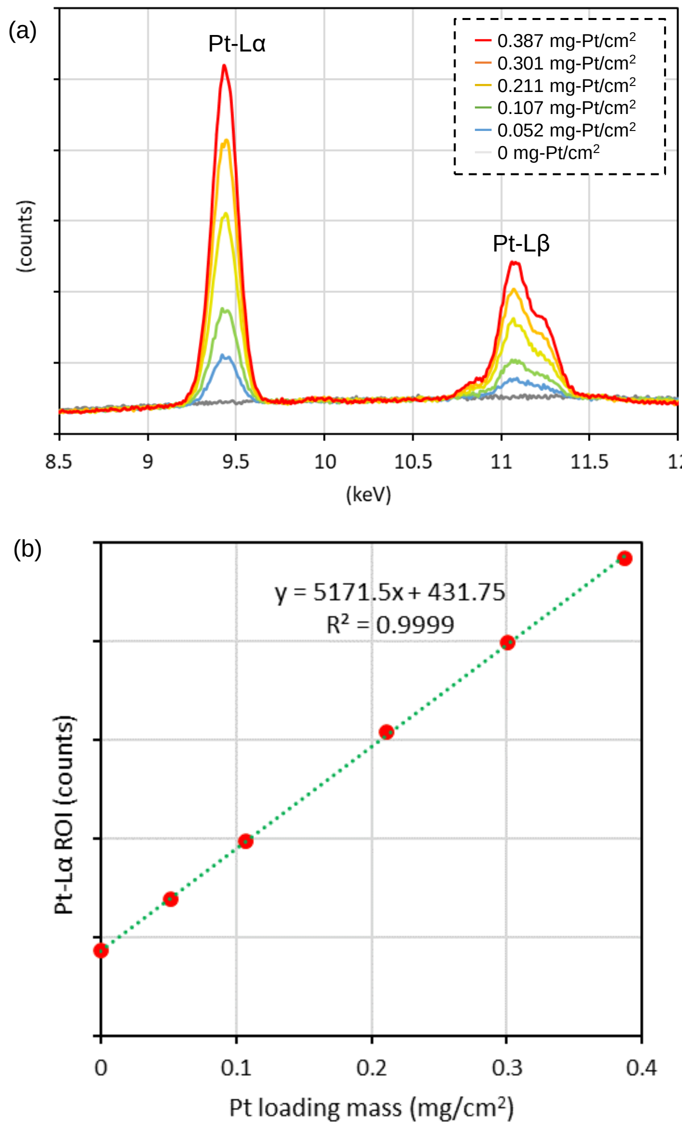


Figure 4. (a) Layered map sum spectrum of the six known samples (b) Calibration curve: Pt loading mass [mg/cm$^2$] vs Pt-Lα ROI [cps/mA]

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## Reference


[1] Grandi et al. (2023) Recent advancements in high performance polymer electrolyte fuel cell electrode fabrication – Novel materials and manufacturing processes. *J. Power Sources.* 562(1), 232734.

[2] Santangelo et al. (2019) Review of Catalyst-deposition Techniques for PEMFC Electrodes. *TECNICA ITALIANA-Italian Journal of Engineering Science*, 63(1), 65-72.

[3] Medina et al. (2023) Multi-technique characterization of spray coated and roll-to-roll coated gas diffusion fuel cell electrodes. *J. Power Sources.* 560(15), 232670.

[4] Sassin et al. (2017) Fabrication Method for Laboratory-Scale High-Performance Membrane Electrode Assemblies for Fuel Cells. *Anal. Chem.* 89(1), 511−518.

[5] Wang and Nagao (2014) Effects of Nafion impregnation using inkjet printing for membrane electrode assemblies in polymer electrolyte membrane fuel cells. *Electrochem. Acta.* 129 (20), 343-347.

[6] Ihm et al. (2004) High performance of electrode with low Pt loading prepared by simplified direct screen printing process in PEM fuel cells. *J. Mater. Sci.* 39, 4647–4649.

[7] Ding et al. (2016) A review of the operating limits in slot die coating processes. *AIChE J.* 62 (7), 2508-2524

[8] Yang et al. (2020) A Novel Approach to Fabricate Membrane Electrode Assembly by Directly Coating the Nafion Ionomer on Catalyst Layers for Proton-Exchange Membrane Fuel Cells. *ACS Sustainable Chem. Eng.* 8(26), 9803−9812

[9] Mauger et al. (2018) Gravure Coating for Roll-to-Roll Manufacturing of Proton-Exchange-Membrane Fuel Cell Catalyst Layers. *J. Electrochem. Soc.* 165 F1012.

[10] HORIBA Application note XRF 23: Pt Loading Mass Determination of PEMFC Catalyst Sheet Using a Benchtop EDXRF Analyzer. (https://www.horiba.com/int/scientific/applications/energy/pt-loading-mass-determination-of-pemfc-catalyst-sheet-using-a-benchtop-edxrf-analyzer/ Viewed on April 15th 2024)



HORIBA

info.sci@horiba.com

www.horiba.com/scientific

**USA:** +1 732 494 8660
**UK:** +44 (0)1604 542 500
**China:** +86 (0)21 6289 6060
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