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Abstract: We introduce a fast and non-destructive method for Pt catalyst loading mass determination in catalyst sheet of proton exchange membrane fuel cell using a benchtop EDXRF analyzer. We made a calibration curve by analyzing in-house samples with different Pt loading masses and determined catalyst loading mass of a sample using the curve. Our result showed that the curve had a good linearity ($R^2 > 0.999$) and that the calculated result was consistent with the labeled value of the sample with good repeatability.

Keywords: Proton exchange membrane fuel cell (PEMFC), Catalyst loading mass, EDXRF

Introduction

A catalyst is one of the significant components in a proton exchange membrane fuel cell (PEMFC). The catalyst plays a role to boost the reaction in catalyst layers shown below in Figure 1. Platinum (Pt) is one of the most popular catalyst materials used in both anode and cathode catalyst layer of PEMFC.^[1] However, Pt is expensive and a main contributor to PEMFC manufacturing cost. Therefore, it is important for manufacturers to optimize the catalyst loading mass (mg/cm^2) in a catalyst layer.

ICP-OES is one of the elemental analysis methods to determine catalyst content used in PEMFC^[2]. However, it is a destructive approach, and it needs time-consuming sample pretreatment to make a sample into a liquid state with a strong acid digestion.

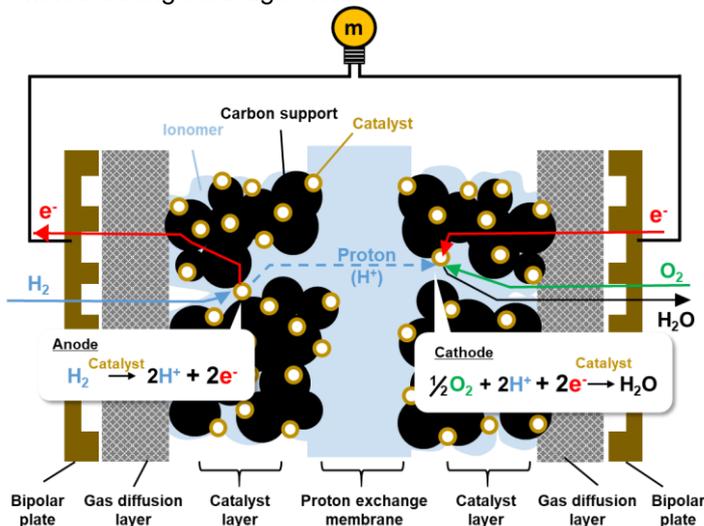


Figure 1. Schematic diagram of the chemical reactions in PEMFC.

In this application note, we introduce a fast and non-destructive approach using the HORIBA MESA-50 EDXRF analyzer to determine Pt catalyst loading mass.

MESA-50 X-ray fluorescence analyzer

The MESA-50 (Figure 2a) is a benchtop energy-dispersive X-ray fluorescence analyzer. The schematic diagram of the instrument is represented in Figure 2b. It irradiates primary X-rays from the bottom and detects fluorescent X-rays from a sample on the diagonal position. Various peaks in a XRF spectrum correspond to the spectroscopic emission of the elements in a sample, and the intensity is correlated to the elemental composition in the volume of the interaction of the incident beam. For this reason, the intensity of an element peak in the XRF spectrum can be a function of loading mass of the element in a sample.

(a)



(b)

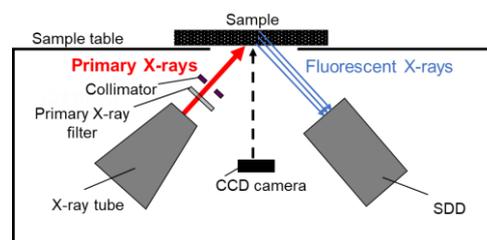


Figure 2. (a) Appearance and (b) schematic diagram of MESA-50.

1. Calibration curve creation and linearity check

The first step consists of calibration curve creation and the linearity check. In this application note, we prepared five in-house catalyst sheet samples with known loading mass of Pt. We made a slurry by mixing carbon supported Pt, ionomer, and solvent (NPA and water). We coated the slurry on a film by spray coating. The five known samples as shown in Table 1 and made a calibration curve of Pt loading mass. We decided our Pt loading mass range according to the possible range used in commercial PEMFC.^[3]

We mounted each sample onto the measurement position of the MESA-50 chamber (Figure 3), and we carried out spectrum analysis at the center of the sheet using a 7 mm collimator (maximum spot size of the instrument) to get a representative result of the sample, and a primary X-ray filter to reduce the background around the peak of Pt L lines. The other parameters were set as shown in Table 2.

Figure 4 shows a layered spectrum of the five samples' results, and we could see a trend that 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-L α counts, and it showed a good regression coefficient by using a linear model (Figure 4b). This is a good indication that EDXRF is a suitable method for this kind of application.

Table 1. The sample information for calibration curve [mg/cm²]

	a	b	c	d	e
Pt loading mass [mg/cm ²]	0 (blank)	0.052	0.21	0.31	0.39

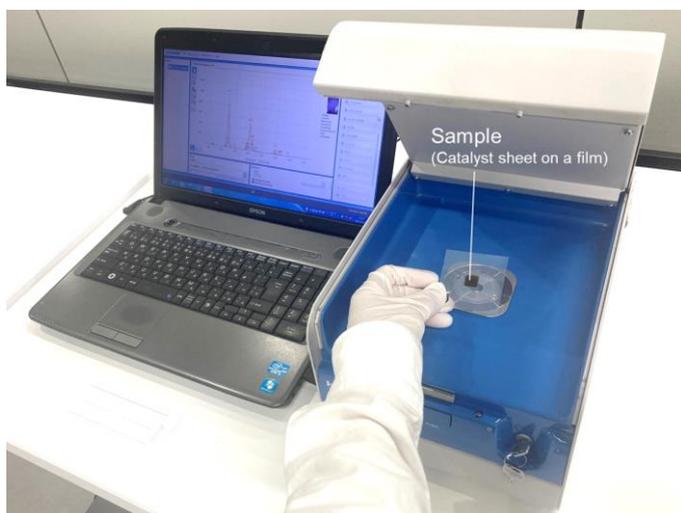


Figure 3. Sample setting inside the MESA-50 chamber.

Table 2. Measurement condition used in this application note.

	Condition
Spot size	7 mm
Voltage	50 kV
Current	200 μ A
Measurement time	60 s
Processing time	Process 4
Filter	Mid

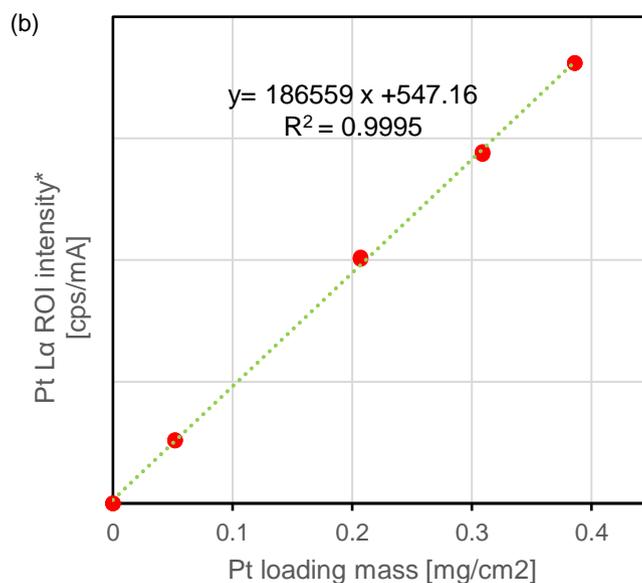
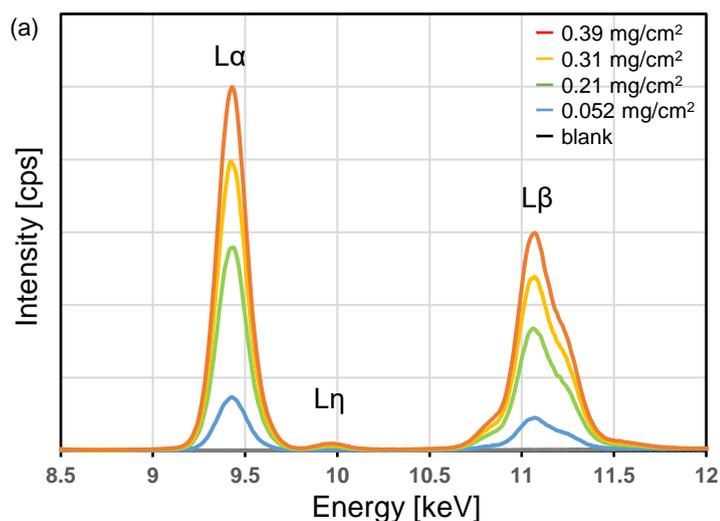


Figure 4. (a) Layered XRF spectrum of the five known samples (b) Calibration curve plots: Pt loading mass [mg/cm²] vs Pt-L α ROI [cps/mA] (after background subtract and peak separation).

2. Loading mass determination and accuracy check

In the second step, we prepared another in-house catalyst sheet sample whose Pt loading mass was known to be 0.10 mg/cm². We used it as an unknown sample to evaluate our determination accuracy.

The measurement condition was set to be the same condition shown in Table 2. We carried out spectrum analysis 3 times ($n=3$) at the same position of the sample. Table 3 shows the calculated Pt loading mass using the calibration curve. The calculated result showed 0.11 mg/cm², on the average. The value was consistent with the labeled value of the sample with a good repeatability.

Table 3: Pt loading mass determination using the calibration curve made in the first section.

	Pt loading mass [mg/cm ²]
1	0.11
2	0.11
3	0.11
Average	0.11
Expected value	0.10

Conclusion

We analyzed multiple catalyst sheet samples with different Pt loading masses using a HORIBA MESA-50 EDXRF analyzer. We were success in seeing the clear peaks of Pt even on a sample with 0.052 mg/cm² of Pt loading mass, and we could also see a consistent trend of Pt peak intensities with their Pt loading mass. The calibration curve showed a good linearity ($R^2 > 0.999$), and our calculated result was consistent with the provide value and with good repeatability. Thus, we could show that EDXRF analysis based on calibration curve method provides a fast and non-destructive determination of catalyst loading mass for PEMFC application.

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References

- [1] Kaewsai and Hunsom (2018) Comparative study of the ORR activity and stability of Pt and PtM (M=Ni, Co, Cr, Pd) supported on polyaniline/carbon nanotube in a PEM fuel cell. *Nanomaterials*, 8(5), p.299-319.
- [2] Chou et al (2014) Effects of reduction temperature and pH value of polyol process on reduced graphene oxide supported Pt electrocatalysts for oxygen reduction reaction. *Energy*, 70(1), pp.231-238.
- [3] Sánchez-Ramos et al. (2022) Modeling the effect of low Pt loading cathode catalyst layer in polymer electrolyte fuel cells. Part II: Parametric analysis. *J. Electrochem. Soc.*, 169 (7), 074503.