

Analysis of MEA (Membrane Electrode Assembly)

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User Benefits

- ◆ It is possible to analyze the performance deterioration behavior of fuel cells and other industrial products in which MEA (Membrane Electrode Assembly) is used.
- ◆ EPMA can also be utilized in research and development and quality improvement for cost reduction, long life, and enhanced stability of MEA.

Introduction

Electrochemical devices in which electrode catalyst layers are bonded on a solid polymer electrolyte membrane, which is a hydrogen ion conductor, are called membrane electrode assemblies (MEA), and are used in diverse applications including fuel cells, technologies for water electrolysis hydrogen production technologies, and dehumidifying cells.

The solid polymer electrolyte membrane consists mainly of tetrafluoroethylene (CF₂-CF₂) as the backbone chain and a side chain with a terminal sulfonic acid group (-SO₃H). Nafion™ is a representatively commercial product. The sulfonic acid group is hydrophilic and is filled with water molecules when humidified. When hydrogen ions are generated here, they bond with the water molecules, forming oxonium (hydronium) ions (H₃O⁺), and migrate by jumping successively by way of adjacent water molecules. The electrode catalyst layers on the two sides of the solid polymer electrolyte membrane are mainly made of Pt and have the function of activating the oxidation-reduction reaction.

In MEA, cost reduction, long life, and high stability have become important issues. For example, it is known that the chemical stability of the electrolyte membranes is reduced depending on temperature characteristics, and performance is deteriorated by agglomeration of the catalyst. An understanding of the layer structure, the distribution of each element, and the deterioration behavior of the MEA is required in order to suppress these problems.

This article introduces an example of an analysis by a comparative evaluation of a new MEA before use and a product with deteriorated performance using a Shimadzu EPMA-8050G EPMA™ electron probe microanalyzer.

Surface Analysis of MEA

Fig. 1 shows a structural diagram of the MEA which was the target of this analysis. The surface of the anodic side is covered with an electrode catalyst layer and is coated with a mixture of a Pt catalyst and an ionomer (solid polymer electrolyte membrane). The solid polymer electrolyte membrane is positioned under this coating, and a lattice-shaped (+) electrode grid is embedded in the membrane.

Fig. 2 shows the results of a mapping analysis of the surface of the anodic side of this MEA. The left side shows the results for a new product, and the right shows a product with deteriorated performance. A relative comparison of intensity values is possible by measuring the new product and deteriorated product under the same conditions. Looking at the distribution of Pt, in the deteriorated product, the intensity has decreased, while the intensity of S, which is an ionomer component (sulfonic acid), has increased. Because C and O display particularly high intensities in the electrode grid part, and conversely, the intensity of F has decreased in this grid part, the elevated levels of C and O are thought to show the effects of adhering contamination and surface oxidation.

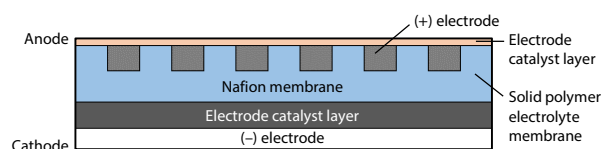


Fig. 1 Structural Diagram of MEA

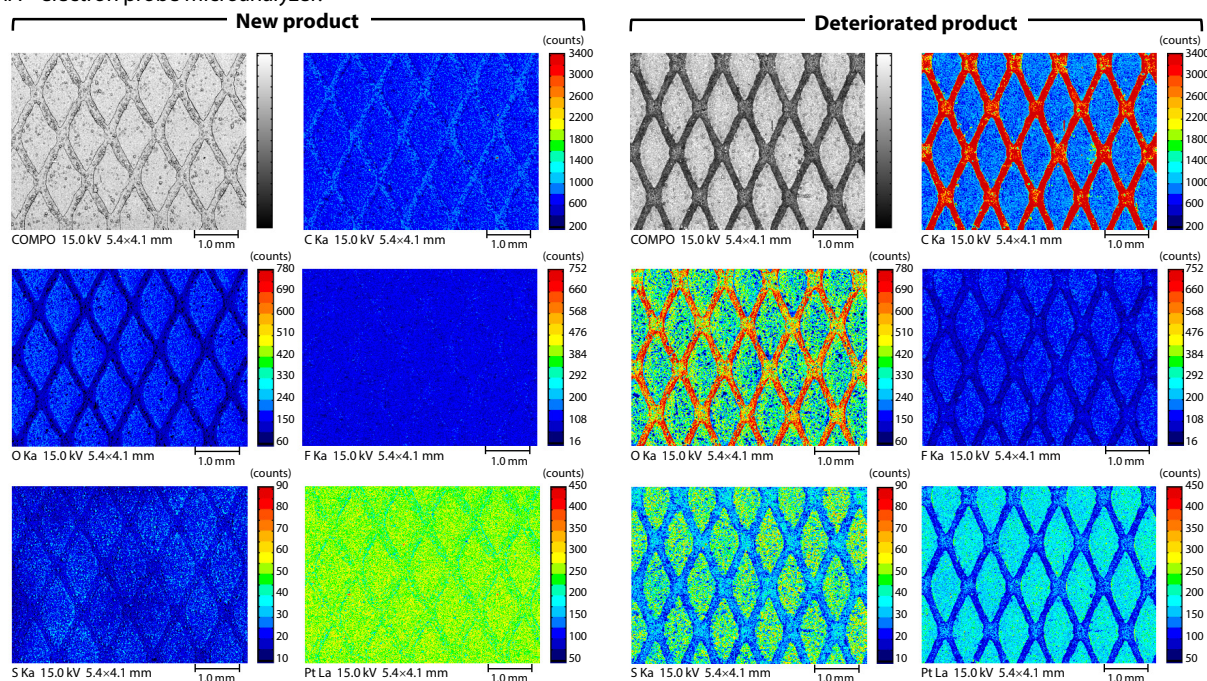


Fig. 2 Mapping Analysis of MEA Surface (Left: New, Right: Deteriorated)

■ Cross-Sectional Analysis of MEA (Wide Region)

In order to identify the cause of the changes observed in the surface analysis, cross-sectional samples of the new product and deteriorated product were prepared by embedding in resin and observed (Fig. 3). Here, a mapping analysis of a $500 \times 140 \mu\text{m}$ region was conducted (Fig. 4).

First, comparing the backscattered electron compositional images (COMPO), the thickness of the electrode catalyst layer on the solid polymer electrolyte membrane on the anodic side is comparatively uniform in the new product, but in the deteriorated product, this layer displays many parts with irregular thicknesses, and the surface undulations tend to be large.

Comparing S, in the deteriorated product, the intensity of S in the solid polymer electrolyte membrane is generally low, while conversely, the intensity of S tends to be high in the electrode catalyst layer, suggesting that S has migrated from the solid polymer electrolyte membrane to the electrode catalyst layer. When Pt is compared, in the deteriorated product, a tendency to concentrate from the electrode catalyst layer toward the interior of the solid polymer electrolyte membrane can be observed along the periphery of the (+) electrode, which consists mainly of Ti. Focusing on the interior of the electrode catalyst layer, the distribution of Pt is dispersed comparatively finely in the new product, whereas the Pt in the deteriorated product tends to have a biased distribution. Based on these results, it can be inferred that a phenomenon of diffusion and agglomeration of the Pt has occurred.

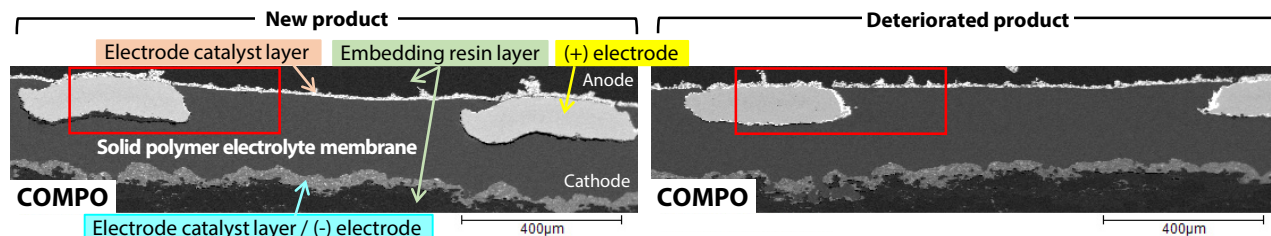


Fig. 3 Compositional Image of MEA Cross Section (Left: New, Right: Deteriorated)

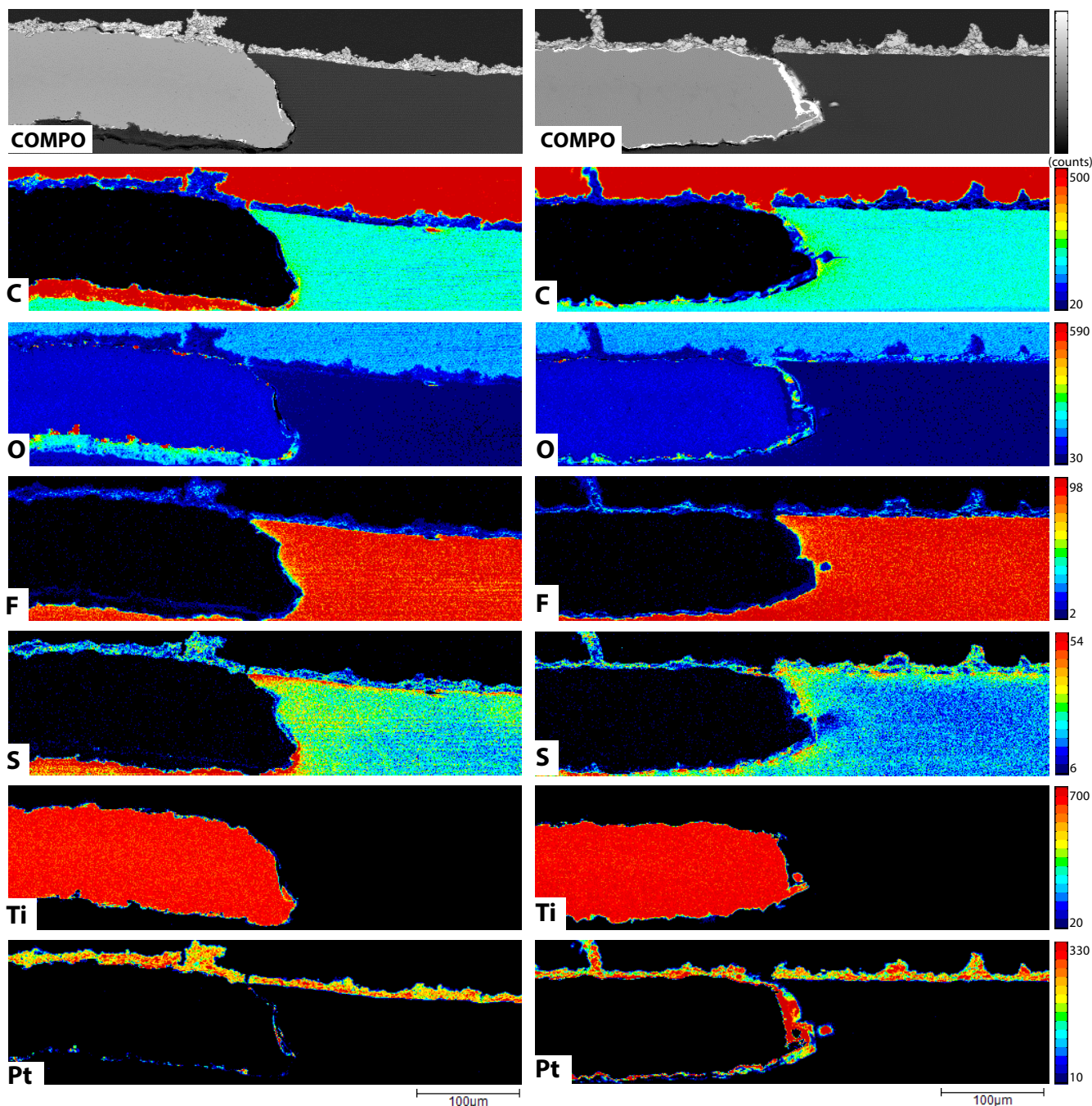


Fig. 4 Mapping Analysis of MEA Cross Section (Wide Area) (Left: New, Right: Deteriorated)

■ Cross-Sectional Analysis of MEA (Electrode Catalyst Layer)

Next, Fig. 5 shows the results of a mapping analysis of a $150 \times 45 \mu\text{m}$ region, focusing on the electrode catalyst layer of the MEA.

Looking first at the distributions of O and Pt in the electrode catalyst layer, the distribution of O is negligible in the new product, but in addition to the distribution of Pt, the intensity of O has also increased in the deteriorated product. Here, it is considered possible that oxidation has proceeded in the process of agglomeration accompanying dissolution and coarsening of Pt.

Next, focusing on the distribution of S in the electrode catalyst layer, since the intensity of S shows an overall increase in the deteriorated product in comparison with the new product, it is thought that S has diffused from the solid polymer electrolyte membrane toward the surface side by way of the electrode catalyst layer. In the overlay of the distributions of S and Pt, comparing the deteriorated product with the new product, it can be understood that the red area of the deteriorated product, where the intensity of S is high and the intensity of Pt is low, has increased remarkably on the surface side of the electrode catalyst layer.

On the other hand, focusing on the distribution of F, which exists as an ionomer component not only in the solid polymer electrolyte membrane but also in the electrode catalyst layer, the distribution in the electrode catalyst layer of the new product is comparatively uniform, but tends to be segregated due to agglomeration of Pt in the deteriorated product. However, no large change in the intensity of F comparable to that of S was observed, indicating that changes in the distribution of F was limited to local segregation.

Based on these results, it is thought that the deterioration of the catalyst in the deteriorated product was caused by progressive coarsening of Pt by dissolution of fine Pt particles, followed by precipitation on larger particles, resulting in a decrease in the surface area of the Pt particles. Moreover, it is also considered possible that the terminal sulfonic acid groups ($-\text{SO}_3\text{H}$) of the solid polymer electrolyte membrane compound separated, and S infiltrated into the electrode catalyst layer, migrated to the surface as a result of agglomeration of the Pt particles, and then desorbed to the outside.

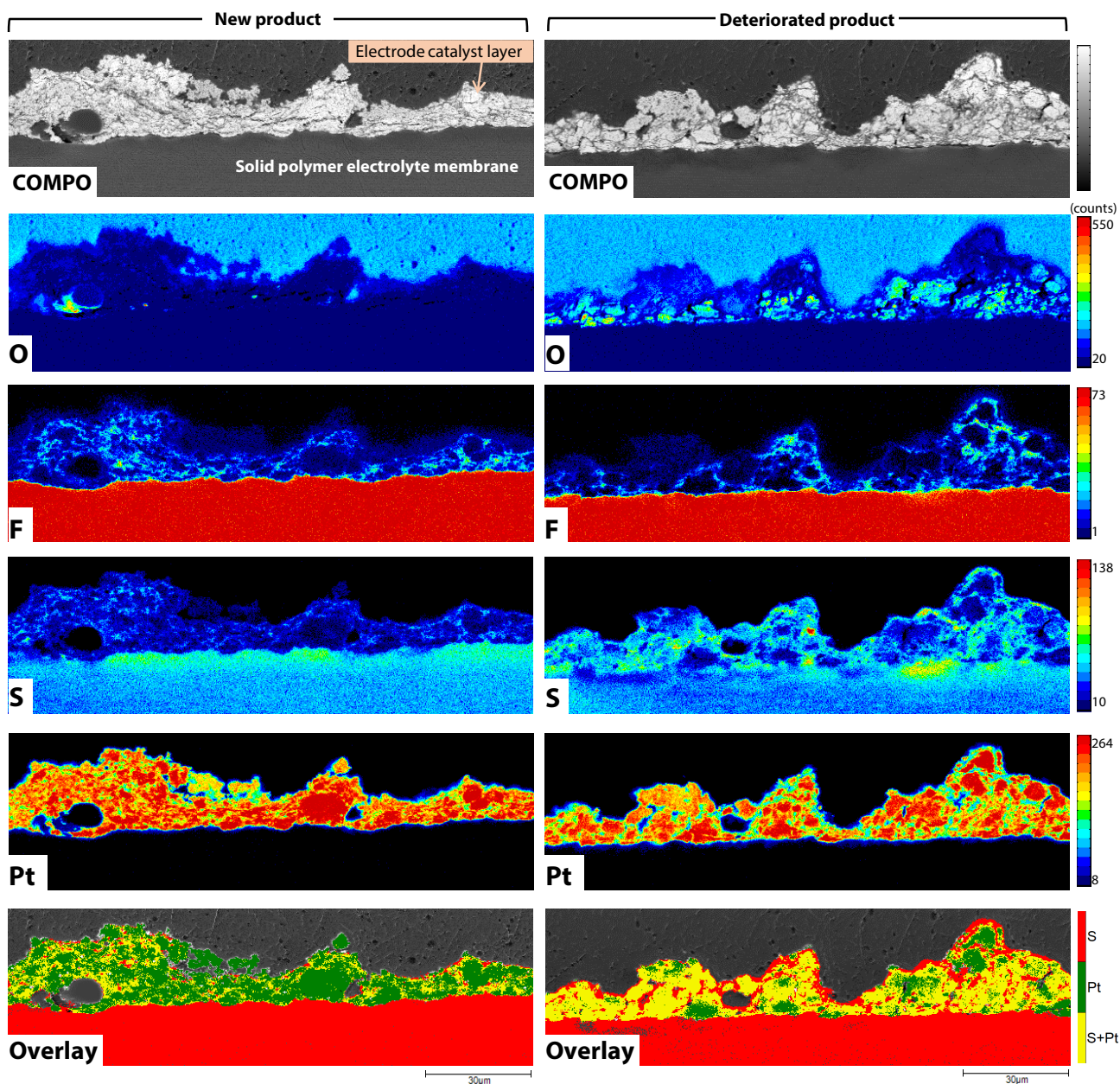


Fig. 5 Mapping Analysis of MEA Cross Section (Electrode Catalyst Layer) (Left: New, Right: Deteriorated)

■ Cross-Sectional Analysis of MEA (Partial Enlargement of Electrode Catalyst Layer)

Fig.6 shows the results of a mapping analysis of a further enlarged part of the electrode catalyst layer in Fig.5. The accelerating voltage was 10 kV, and the measured region was $24 \times 18 \mu\text{m}$.

As could be seen in Fig.5, the distribution of O shows a high intensity at parts where Pt has agglomerated in the deteriorated product, and conversely, F has segregated in voids at parts where Pt has agglomerated. The intensity of S shows an overall increase in the deteriorated product, and in particular, a tendency of S to segregate toward the surface side can be seen. The distribution of Pt also displays segregation in the deteriorated product, suggesting progressive agglomeration of Pt accompanying a process of dissolution and coarsening. In the overlay of the distributions of S and Pt in the new product, the S- and Pt-rich areas (red and green areas, respectively) are dispersed relatively uniformly, but in contrast, these areas are segregated in the deteriorated product, and in particular, S is clearly concentrated at the surface side.

■ Conclusion

The elemental distributions at the surface and in the cross section of a new MEA and a deteriorated MEA were compared by an EPMA mapping analysis. At the anodic surface, the deteriorated product displayed a higher intensity of S, while the intensity of Pt tended to be low. Cross-sectional samples were prepared and compared in order to identify the cause of these differences, revealing that Pt had diffused from the electrode catalyst layer along the periphery of the (+) electrode and concentrated in the interior in the deteriorated product. When the cross section of the electrode catalyst layer was enlarged further, it was found that oxidation and agglomeration of Pt by dissolution and coarsening had proceeded, and S had migrated and concentrated at the surface as a result of separation of terminal sulfonic acid groups ($-\text{SO}_3\text{H}$) of the solid polymer electrolyte membrane compound.

As demonstrated here, mapping analysis utilizing a high sensitivity and high resolution EPMA makes it possible to analyze and evaluate deterioration of performance in MEA by grasping the composition and intensity distribution changes of the individual layers of the MEA, and thus is a powerful tool for research and development and quality improvement of MEA.

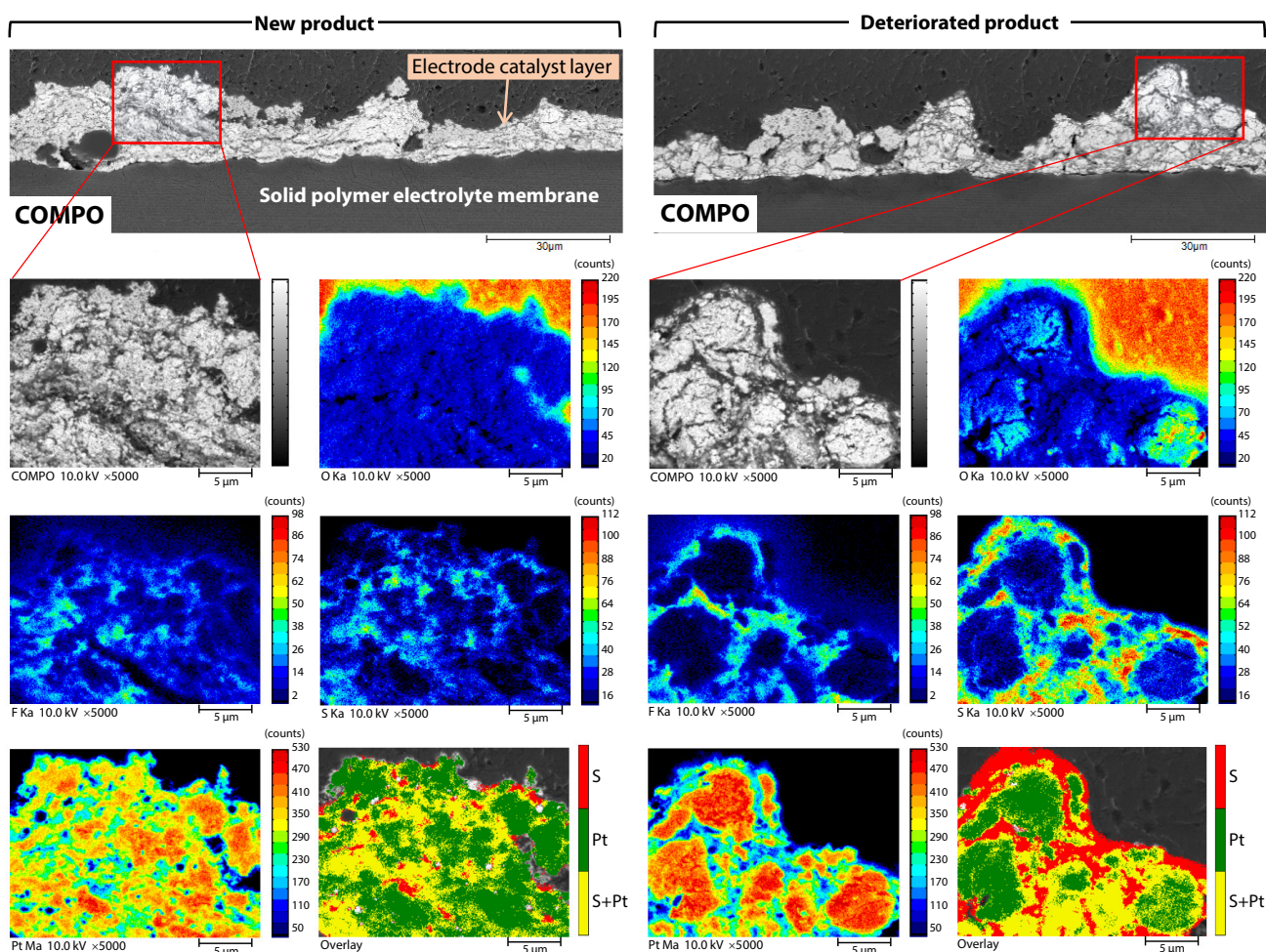


Fig. 6 Results of Mapping Analysis of MEA Cross Section (Partial Enlargement of Fig. 5) (Left: New, Right: Deteriorated)

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