

Possible Scenario of Forming the Catalyst Layer for Proton Exchange Membrane Fuel Cells

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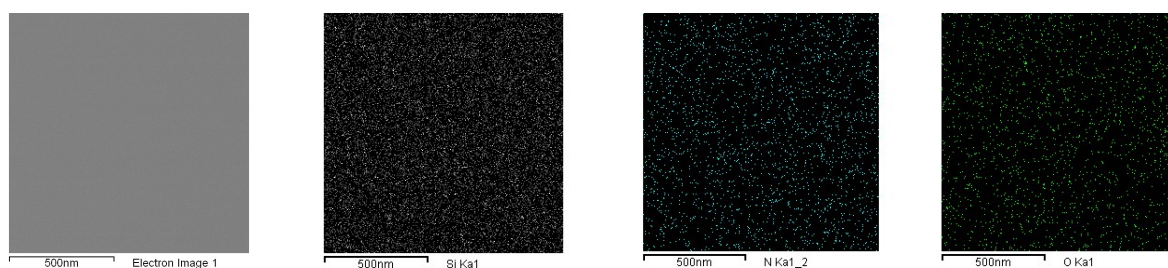


Fig S1. HAADF images and EDX maps with colored pixels

Si is grey; N is blue; O is green

The EDX mapping of the original SiN grid shows that Si, N and O were homogeneously distributed. Only Si, N, O and Cl are the detected. The SiN grid is free of the concerned C, F, S, Pt.

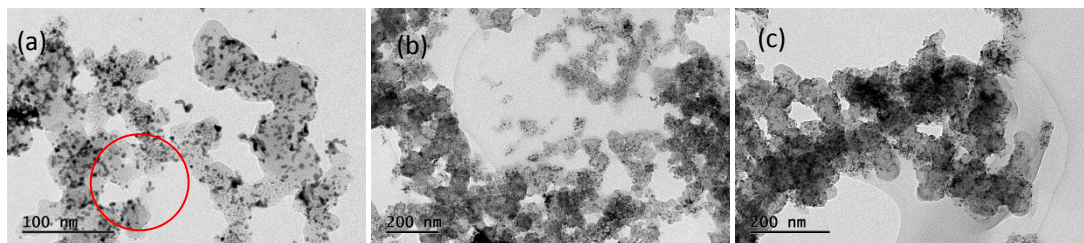


Fig. S2 TEM of catalyst with ionomer in (a) H⁺, (b) Al³⁺ and (c) Cu²⁺ form

It is hardly to discern the ionomer film in H⁺ from the SiN background as shown in Fig S2 (a). The possible ionomer film in H⁺ form was highlighted by the red circle. However, one can clearly discern the ionomer film in Al³⁺ and Cu²⁺ form from the SiN background. The AFM images of the catalyst layer show the ionomer thin film covered the aggregated Pt/C catalyst in different thickness.¹⁻⁸ The ionomer doesn't cover the catalyst in an aggregated state as expected but form thin film among the aggregated catalyst.

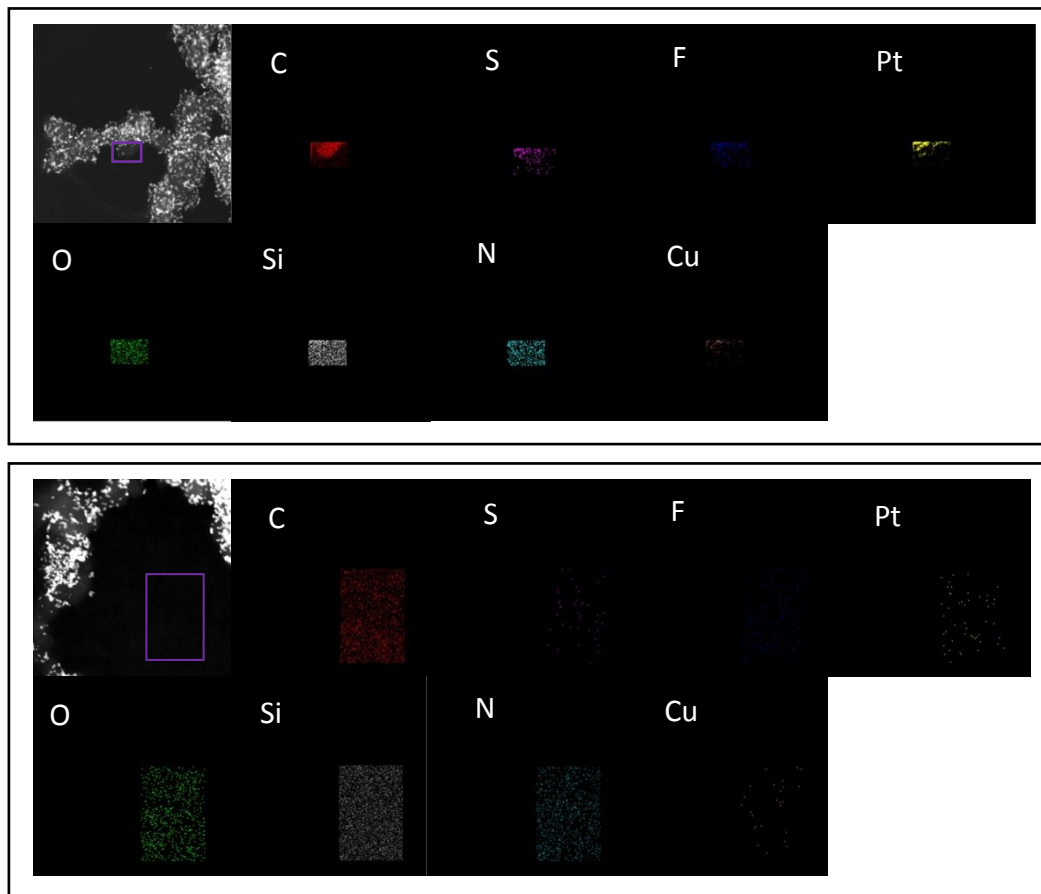


Fig. S3 HAADF images (where the purple rectangle show the mapping area) and EDX maps with colored pixels indicating where the element was detected above background in the area of the catalyst with ionomer in Cu^{2+} (the upper images) and away from the catalyst (the lower images). C is red; S is purple; F is blue; Pt is yellow; O is green; Si is grey; N is cyan. It clearly showed that S appeared at the position where Pt was.

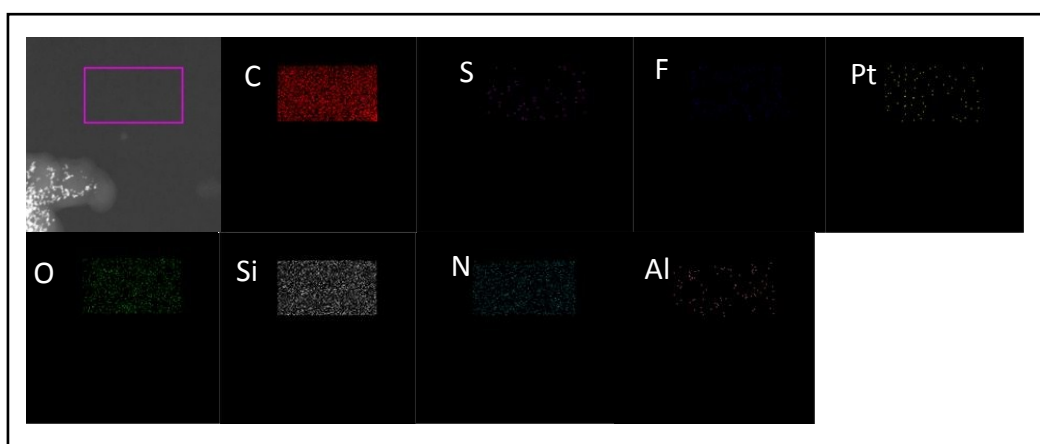
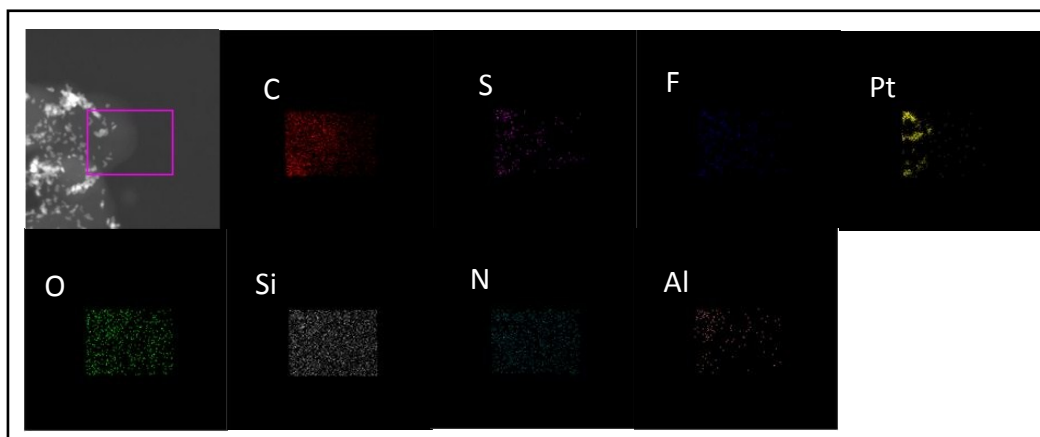


Fig. S4 HAADF images (where the purple rectangle show the mapping area) and EDX maps with colored pixels indicating where the element was detected above background in the area of the catalyst with ionomer in Al^{3+} (the upper images) and away from the catalyst (the lower images). C is red; S is purple; F is blue; Pt is yellow; O is green; Si is grey; N is cyan. It clearly showed that S appeared at the position where Pt was.

Table S1. Elemental content in the area of the catalyst and away from the catalyst using ionomer in Al³⁺, Cu²⁺

	Catalyst/in Al ³⁺	Away catalyst/in Al ³⁺	catalyst/in Cu ²⁺	Away catalyst/in Cu ²⁺
C(at%)	89.39	83.88	92.39	83.24
Pt(at%)	0.63	-	0.95	0.01
S(at%)	0.11	-	0.12	0.03
F(at%)	0.06	-	0.15	0.38
O(at%)	2.49	3.99	1.31	2.17
Si(at%)	7.27	12.04	4.93	14.15
N(at%)	-	-	-	-
Cl(at%)	-	-	-	-
Al(at%)	0.05	0.09	-	-
Cu(at%)			0.15	0.01

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