



Short communication

Durability and characterization studies of polymer electrolyte membrane fuel cell's coated aluminum bipolar plates and membrane electrode assembly

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ABSTRACT

Coated aluminum bipolar plates demonstrate better mechanical strength, ease of manufacturability, and lower interfacial contact resistance (ICR) than graphite composite plates in polymer electrolyte membrane (PEM) fuel cell applications. In this study, coated aluminum and graphite composite bipolar plates were installed in separate single PEM fuel cells and tested under normal operating conditions and cyclic loading. After 1000 h of operation, samples of both the bipolar plates and the membrane electrode assembly (MEA) were collected from both the cathode and the anode sides of the cell and characterized to examine the stability and integrity of the plate coating and evaluate possible changes of the ionic conductivity of the membrane due any electrochemical reaction with the coating material. Scanning electron microscope (SEM) and energy dispersive X-ray (EDX) analysis were performed on the land and valley surfaces of the reactant flow fields at both the anode and the cathode sides of the bipolar plates. The measurements were superimposed on the reference to identify possible zones of anomalies for the purpose of conducting focused studies in these locations. The X-ray diffraction (XRD) analysis of samples scraped from the anode and cathode electrodes of the MEA showed the tendency for catalyst growth that could result in power degradation. Samples of the by-product water produced during the single fuel cell operation were also collected and tested for the existence of chromium, nickel, carbon, iron, sulfur and aluminum using mass spectroscopy techniques. The EDX measurements indicated the possibility of dissociation and dissolution of nickel chrome that was used as the binder for the carbide-based corrosion-resistant coating with the aluminum substrate.

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1. Introduction

The polymer electrolyte membrane (PEM) fuel cell is a promising power source to replace the internal combustion engine in transportation applications because of its fast start-up, relatively low operation temperature, high efficiency and high power density. The bipolar plate is one of the key components in the PEMFC system. It constitutes the backbone of the fuel cell power stack, collects electrons generated by electrochemical reaction in the membrane electrode assembly (MEA), and provides a uniform conduit for reactant gases passing through the cells. Currently, commercial bipolar plates are made of graphite composites, however their high cost

and poor durability have led researcher to look for an alternative bipolar plate material [1–5].

Metallic bipolar plates are being investigated by several researchers due to their durability and excellent potential for cost effective high volume manufacturing techniques such as stamping and die casting fabrication processes [4–7]. In addition, non-precious coatings for metals such as aluminum, stainless steel, titanium, etc. are effective for minimal permeability to gases combined with safer, more economical hydrogen consumption, and easier to manufacture by the stamping process than graphite, makes metal the recommended alternative bipolar plate material [4,8–10]. With these promising outcomes, stainless steel, aluminum, titanium and Ni–Cr-based alloy are suggested to be candidate material for bipolar plate component by many researchers [11–21].

Two different high corrosion-resistant metal coatings with high conductivity and graphite composite single cells were studied by Tawfik et al. [9,10]. Previous work from the same group showed

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that both metallic and graphite composite PEM cells exhibited a steady performance with negligible power degradation after 1000 h operation at 70 °C. Moreover, the average electric power output from the metallic cell exceeded considerably that from the graphite under the same engineering design and operating conditions. This is attributed to both the bulk and the interfacial contact resistance (ICR) values for the corrosion-resistant coatings on aluminum bipolar plates that are considerably lower than those for the graphite composites.

Generally, metallic bipolar plate fuel cells provided at least a 22% savings in hydrogen consumption in comparison to graphite cells [10]. This is attributed to lower bulk and surface contact resistances of the coated aluminum plates used in this study in relation to graphite composite. The results of the lifetime testing conducted at a temperature of 70 °C under cyclic loading condition ranging from 0 to 0.6 W showed no indication of power degradation due to metal corrosion for at least 1000 h of real time testing.

In this paper, the performance of aluminum bipolar plates fuel cells coated with carbide-based coating alloy was monitored for 1000 h at 70 °C. The characterizations of the coating and binder materials as well as MEA were conducted using scanning electron microscope (SEM), energy dispersive X-ray (EDX) and X-ray diffraction (XRD) techniques. The produced water from the reaction was also analyzed to detect any dissolved metals and these results are reported in this paper. Moreover, several groups have studied and provided evidence based on the SEM and TEM images showing coarsening of platinum (Pt) particles within the MEA and migration of Pt to the anode-membrane interface and into the membrane itself [20]. The coarsening of Pt particles occurred during the first 500 h of operation. The particles size changed from ~1–12 nm in the fresh anode layer to ~5–15 nm after 500 h that may result in power degradation due to loss of Pt surface area. Similar observations were indicated in this paper; however, power degradation was not detected in this work.

2. Experimental

Six single PEM fuel cells were identically designed, manufactured and operated under similar conditions as follows: cell temperature: 70 °C, relative humidity (RH): 95%, airflow rate: 470 standard cubic centimeter per minute (SCCM), back pressure: 0.052 MPa. The hydrogen pressure of 0.069 MPa was dead-ended at the exhaust manifold for all cells. Of the six fuel cells, four cells were fabricated of aluminum bipolar plates coated with high corrosion-resistant carbide-based alloy on both anode and cathode sides. The other two cells were fabricated of graphite composites that served as a benchmark for PEM fuel cell performance. Each single cell test fixture consisted of two bipolar plates that contained a serpentine flow field to allow the passage of hydrogen and air to the anode and cathode, respectively.

The electrode membrane assemblies (Series 14-W MEA) with carbon cloth, Nafion thickness <50 μm, <1.0 mg cm⁻² total platinum loading (anode and cathode) and 6.45 cm² active electrode areas were acquired from (E-TEK, DeNora.) and fitted in each cell with silicon gaskets and operated under identical conditions. To compensate for the thickness of the gasket, an extra carbon paper which acted as a gas diffusion layer (GDL) was added on each side of the electrodes. The data obtained from the two graphite composite cells and the coated aluminum cells were averaged and plotted on the same graph for comparison at various times of operation as shown in Fig. 1a and b.

After 1000 h of operation, the aluminum single cell coated with carbide-based coating was dismantled and the plates were cleaned with alcohol to remove excess carbon fibers in preparation for surface analysis.

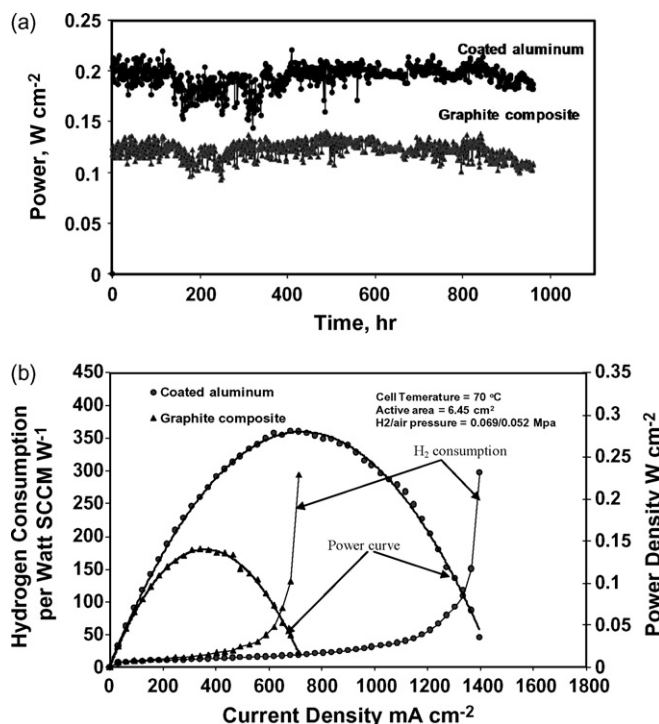


Fig. 1. (a) Lifetime test of coated aluminum and graphite composite bipolar plates operated under cyclic loading at 70 °C and (b) hydrogen consumption and power density.

For characterization studies, small portions of the surface from both the anode and the cathode sides of the MEA were scraped and ground into powder form. Three such samples were collected for XRD analysis and patterns that were obtained at beam line X7B of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory [6–8]. The beam line was equipped with MAR345 image plate detector and is capable of fast data collection. The wavelength of the beam was adjusted to 0.922 Å and is calibrated using LaB6. Each sample was filled inside a capillary and was rotated while the XRD patterns were taken to minimize the effect of preferred orientation.

The surface characterization of the bipolar plates was conducted by SEM (LEO 1550). The SEM was equipped with backscattered detector, secondary detector, in-lens detector and EDX detector. Fig. 2 shows the active areas of the cathode and anode fuel cell bipolar plates that were coated with carbide-based coating and examined with SEM and EDX analysis. The inactive areas of the bipolar plates and fresh (unused) MEA were used as a control for

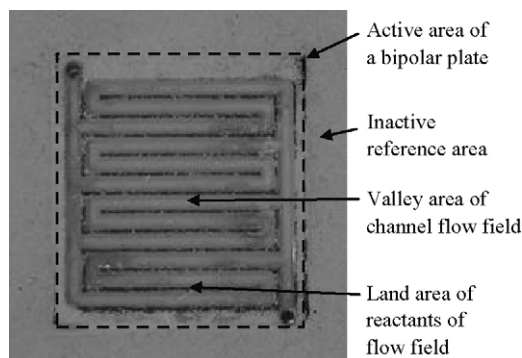


Fig. 2. Anode and cathode of aluminum coated bipolar plate.

comparison between before and after 1000 h of operation. Each of the X-ray spectrums was taken at 200 s real time and three X-ray spectrums were taken and then averaged in each area for consistent spectrums comparison.

3. Results and discussion

A comparison of time-resolved performance plots over 1000 h for coated aluminum and graphite composite bipolar plates operating under cyclic loading at 70°C are shown in Fig. 1a. Both plates show comparable and minimal degradation that continued after 1000 h. However, the metal plates sustain at least 50% higher power density throughout the operation compared to graphite composite. This is attributed to the higher aluminum coated bipolar plates electric conductivity compared to graphite composite and their improved corrosion resistance coating recently developed and patented at the Institute for Research and Technology Transfer (IRTT), State University of New York, College of Technology at Farmingdale. In addition, Fig. 1b exhibits the distribution of power density and hydrogen consumption per Watt versus current density for both coated metal and composite graphite bipolar plates. The results showed that the hydrogen consumption per Watt using coated aluminum is lower than graphite composite bipolar plate. For example, the hydrogen consumption per Watt at a current density of 200 mA cm⁻²; was 10.4 and 13.1 cm³ min⁻¹ W⁻¹ when coated metal and composite graphite were used as bipolar plates, respectively. This translates to approximately 26% savings in hydrogen consumption per Watt when coated aluminum plates were used in replacement of graphite composite that has higher electric resistance and heat losses. Preliminary experimental results measured showed at least 22% savings in hydrogen consumption. This is attributed to the higher output power of aluminum coated bipolar plates due to their lower bulk and contact resistances compared to graphite composite.

The image in Fig. 3 was taken at 6000× magnification on the inactive area of the bipolar plate in the cathode side of the single cell. A micro-scale crack in the surface layer of the coating was observed but it does not constitute a through crack that reaches the surface of the aluminum substrate. This is explained by the existence of approximately the same amounts of aluminum oxide in both metal and graphite fuel cells and attributed to the oxidation of the uncoated aluminum manifolds in the cell's end plates and was carried by the reactants to the active flow field.

Fig. 4 (cathode plate) and Fig. 5 (anode plate) show a comparison of the X-ray spectrum of the coatings on the land area, reference area and valley area for both the anode and the cathode bipolar plates that are described in Fig. 2 after 1000 h of operation. Chromium was the largest component of the coating therefore

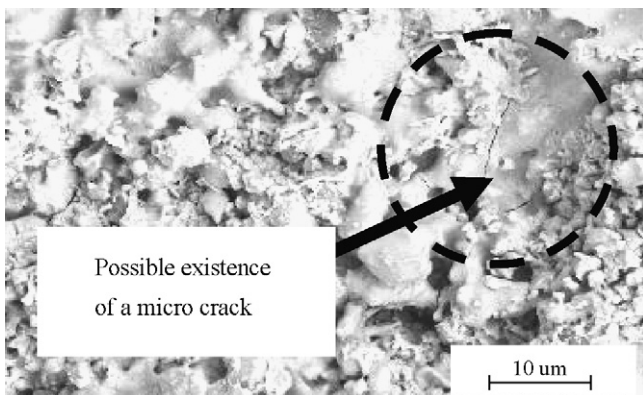


Fig. 3. SEM image of coating on aluminum bipolar plate after 1000 h of operation.

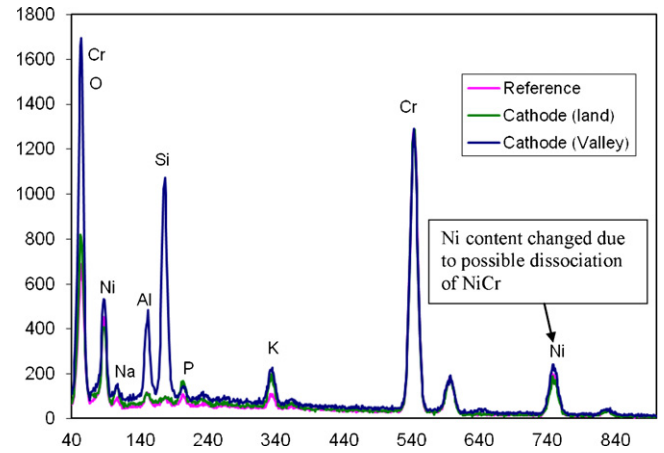


Fig. 4. Superimposed EDS analysis for the cathode plate samples (reference, valley and land).

its peaks, in each spectrum, were scaled to be the same and were superimposed for proper comparison. Carbon was found as part of the coating and the carbon fibers from the GDL were strongly stuck into the coating even after the coating was cleaned. Aluminum was also observed in the coating composition but was not necessarily brought to the corrosion resistance layer from the aluminum substrate by a possible through cracking in the coating layer (marked with a circle in Fig. 3). Instead, it was mainly attributed to the aluminum oxide carried by the reactant gases passing through the back plate and the gas inlets, because they were not covered by sealant or any other type of coating, and precipitated on the coating layer. Oxygen was also detected and was most likely linked to the same aluminum oxide developed from the oxidation of uncoated aluminum end plates and carried by reactant gases to the GDL and coated areas of the bipolar plate. In addition, small amount of silicon was detected and was assumed to originate from the silicon gaskets as shown in Fig. 4.

Fig. 4 also shows the possibility of partial dissociation of the NiCr alloy that is responsible for binding the coating layer material together and its adherence to the substrate. This was noted to take place in the cathodic side as was demonstrated by the change in Ni and shown in the EDX analysis. However, Fig. 5 shows that the change in Ni at the anodic side of the bipolar plate is less than the cathodic side and this is attributed to the lower humidity and anodic activity in relation to the cathode.

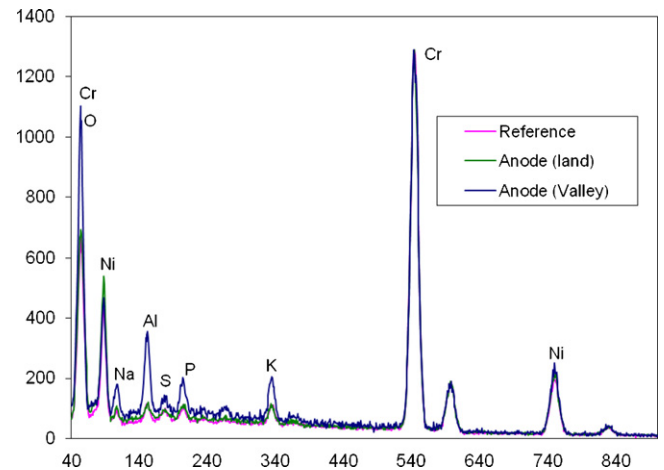


Fig. 5. Superimposed EDX analysis for the anode plate samples (reference, valley and land).

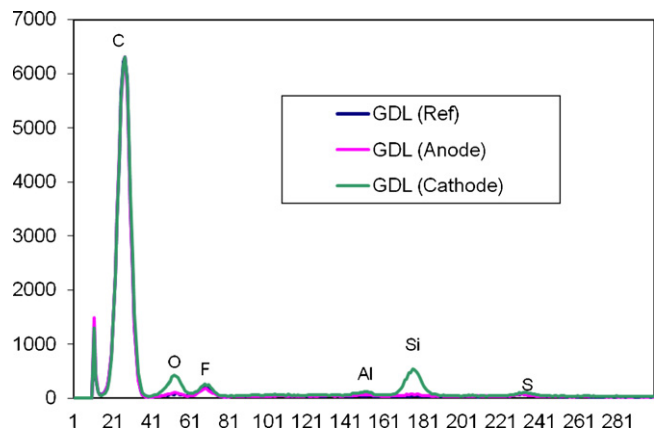


Fig. 6. Superimposed EDX analysis for the GDL (reference, land and valley) used in the metallic plate.

The EDX analysis showed that small amount of aluminum was detected in the GDL of the cathode for both coated aluminum and graphite composite cells as shown in Figs. 6 and 7, respectively. As indicated earlier, this small amount of aluminum could be introduced and carried to the GDL by the cathodic air flowing through the uncoated aluminum parts of the fuel cell in the back plates, fittings and manifolds.

Fig. 8 shows the EDX analysis of the MEA used in the coated aluminum bipolar plates fuel cell after 1000 h. Basic components such as Pt, F, and C as well as silicon were present in the MEA scraped sample from the cathodic side of the fuel cell. The Si was transported from the silicon gasket to the MEA due to steady flow of air and humidity. There were no other metals detected on both the MEA and GDL which agreed with the result obtained from the mass spectroscopy discussed later in this paper.

XRD analysis was performed on three samples that were scraped from each of the cathodic and anodic sides of the MEA after 1000 h of operation. Another three samples were also scraped from a fresh unused MEA and were considered as a control sample. The XRD analysis on the samples indicated catalyst clustering or coarsening on both anode and cathode side after the 1000 h of operation as demonstrated by the increase in the X-ray diffraction intensity as shown in Figs. 9 and 10. Similar observations were reported by other researchers [20,21]. This is explained by

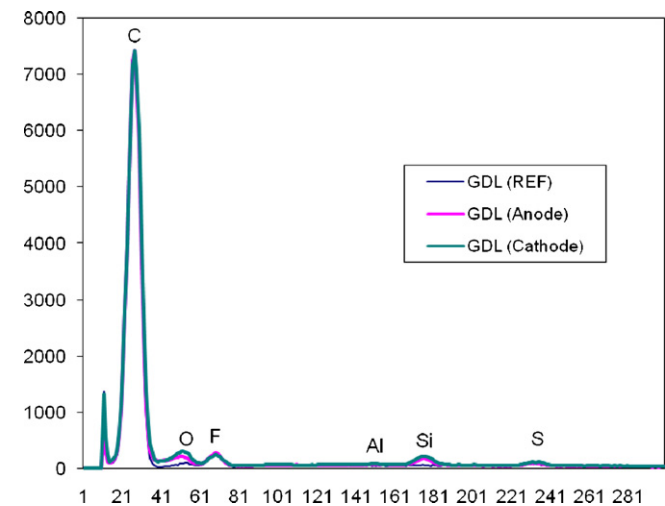


Fig. 7. Superimposed EDX analysis for the GDL (reference, land and valley) used in the graphite plate.

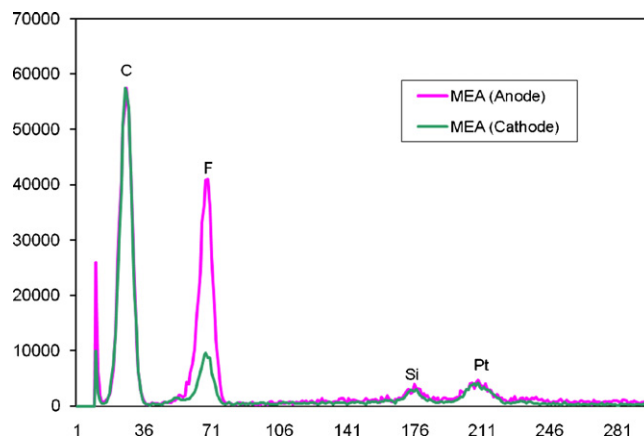


Fig. 8. Superimposed EDX analysis for the MEA (cathode and anode) used in the metal plate.

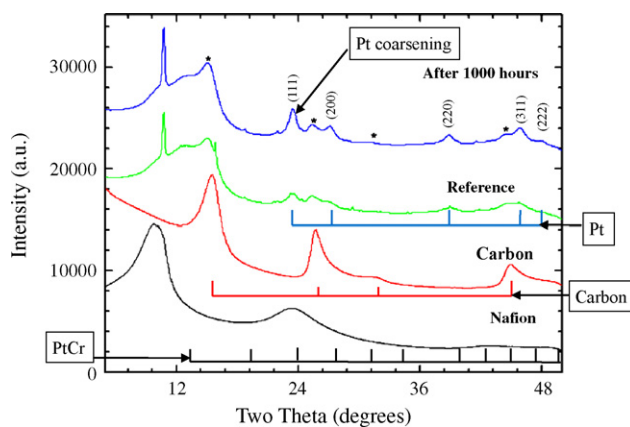


Fig. 9. XRD analysis for the MEA on the anode side.

the tendency of the catalyst to agglomerate to minimize its surface energy.

In addition, chromium was detected in one of the three cathode samples of the MEA as shown in Fig. 10. However, the free Pt catalyst did not react with the chromium to form PtCr alloy. Pure Pt normally has a fcc structure and PtCr alloy has a primitive cubic lattice (indexed by blue and black ticks, respectively) in diffraction patterns, these satellite peaks of the primitive PtCr alloy did not match with any XRD patterns as exhibited in both Figs. 9 and 10.

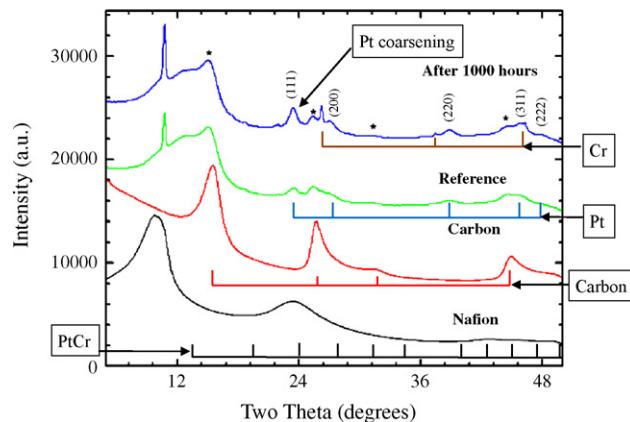


Fig. 10. XRD analysis for the MEA on the cathode side.

4. Mass spectroscopy

Samples of water as the by-product of the fuel cell electrochemical process were collected during the operation and analyzed by passing them into argon plasma at the commercial testing laboratory. The mass spectrometry emission intensity is measured for each element of interest and compared to the calibration curve to yield a concentration of each element in the sample solution. The results showed the presence of Al, Cr, Pt, Fe and Ni but at very low levels (<1 ppm each). Only carbon was found at ~0.12%. The carbon was likely extracted from the gas diffusion layer that was assembled and strongly adhered to the MEA. The lack of existence of Al in large quantities was noted as a significant evidence that the nano-cracks shown in Fig. 3 did not penetrate through the coating layer to the aluminum substrate.

5. Conclusions

Our data are consistent with the following conclusions:

1. The SEM/EDX analysis showed very small variation in the surface composition of the coated aluminum bipolar plate after 1000 h of operation.
2. The dissociation of the binding alloy (NiCr) was deduced from the SEM/EDX data analysis.
3. Chromium was observed in one of the three cathode simple of the MEA. However, it was confirmed that the released Cr did not react with Pt.
4. The micro-cracks that were observed in the corrosion resistance coating did not seem to completely penetrate through to the substrate layer.
5. Aluminum was detected in the GDLs that were used in both coated aluminum and graphite composite fuel cell. It is believed that aluminum was released mainly from aluminum oxide carried by the reactant gases from the uncoated back plate and gas manifolds.
6. The quantitative by-product water analysis was as follows: Pt, Al, Fe, Cr and Ni, all at <1 ppm. These data established the stability of the corrosion-resistant coating.
7. The catalyst (Pt) clustering effect was observed in the XRD data analysis for both the cathode and the anode sides.
8. Further studies are underway to establish reaction parameters such as corrosion resistance and contact resistance of the coating to enhance its lifetime.

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