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Platinum electroless deposition on Nafion membrane for PEM fuel cells

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Abstract−The aim of this research was to study the deposition of platinum on Nafion117 membrane by using an electroless technique. The investigated parameters were electroless time (30 to 90 min) and Pt : N_2H_4 ratio (from 1 : 1 to 1 : 3.85). The results indicated that the platinum deposition on the 1*st* side of membrane was lower than that on the 2*nd* side because of the effect of N_2H_4 on the property of membrane. Platinum deposition increased when the Pt : N_2H_4 ratio decreased. The optimum condition was found at electroless time of 60 min and Pt : N_2H_4 ratio of 1 : 1.95. At this condition, more than 89% of platinum was deposited on both surfaces. The coated membrane was used to make a membrane electrode assembly (MEA) of a proton exchange membrane fuel cell (PEMFC) which was tested at 60 °C in a saturated H_2/O_2 system. The maximum current density was 80 mA/cm^2 at 0.3 V.

Key words: Electroless Deposition, PEMFC, Platinum, Reducing Agent

INTRODUCTION

Due to the energy crisis in this century, the planet needs a new energy source for the future. With its excellent capacity to convert hydrogen, the energy carrier of the future, the fuel cell is on the road to fame and fortune. In addition, for reasons mainly relating to reliability and mass production requirements, the proton exchange membrane fuel cell (PEMFC) is more attractive. It is one of the most promising candidates as a clean power source for electric vehicles in automotive transport, because of (i) its high energy conversion efficiency, (ii) the possibility of using regenerative fuels, (iii) low or zero noxious emission of environmental pollutant, (iv) low operating temperature, and (v) relatively quick start-up [Shinichi et al., 1997; Bron et al., 2001]. Its performance is strongly dependent on not only operating conditions such as temperature and pressure but also cathode and anode electrocatalyst layer and water management in the cell [Park et al., 2005]. The best electrocatalyst for both the anode and the cathode is platinum [Larminie and Dicks, 2003]. A novel deposition method of Pt catalysts onto Nafion membranes impregnated with polypyrrole (PPy) to produce Pt/PPy/Nafion composite has been proposed for PEMFC by Park et al. [2004]. From the result of single cell tests, the current density of 888 mA/cm^2 at 0.3 V has been observed for MEA contained with this composite material. Yang et al. [2002] have improved the electrode performance for polymer electrolyte membrane fuel cell by direct coating of catalyst on membrane. It was shown that the solvent of 3-methyl butanol for catalyst slurry coated directly on membrane gave the highest performance at 1.2 A/cm^2. Kim et al. [2004] demonstrated that the preparation of Pt/C for PEMFC by alcohol-reduction method using polyvinylpyrrolidone as a stabilizer provided the high dispersion and uniformity of nanoparticles. The impregnation-reduction method was carried out to prepare the Pt/C catalyst by Tian et al. [2004]. They reported that heat treatment under suitable conditions for carbon black played an important role in the improvement of the electrocatalytic activity of Pt/C. The obtained catalyst exhibited the narrow size distribution and [111] orientation of Pt particle. Chang et al. [2000] used Pt/Vulcan XC to prepare the MEA by painting method on electrode (catalyst electrode) and spray-coating method on membrane (catalyst membrane). They reviewed that the MEA prepared from the catalyst membrane at 0.2 mg Pt/cm^2 provided higher current density than that from catalyst electrode with 0.4 mg Pt/cm^2 at the same potential; namely, it provided approximately 2,200 mA/cm^2. Besides previous techniques, the electroless deposition technique is currently used to prepare the catalyst for the reaction in PEMFC. The main advantage of this technique is that coating may be deposited on electrically nonconductive materials with more uniform thickness. In addition, the deposition is simple and possible to obtain the coatings having unique mechanical, magnetic and chemical properties [McDermott, 1972]. Bessarabov et al. [2001] investigated the effect of the membrane modification by using cetyltrimethylammonium bromide surfactant ($CH_3(CH_2)_{15}N(CH_3)_3Br$) on the morphology of deposition of a Pt catalyst. They demonstrated that the Pt particles were small in size and pyramidally textured. Furthermore, sodiumtetrahydroborate was also used as a reducing agent for preparing the Pt catalyst by electroless deposition. The results indicated that the morphology and composition of the platinum deposition were related to their preparation conditions in terms of platinum salt concentration, electrolyte flow and surface roughness of membrane. At best, Pt surface areas of 30-50 m^2/g Pt were achieved at platinum penetration depth of 5-30 μm into the membrane surface [Sheppard et al., 1998].

The problems of catalyst layer preparation for PEM fuel cell are poor contact between catalyst layer and electrolyte membrane and low quantity of platinum utilization. These problems can be attributed to the acquired preparation technique, such as screen printing or spray methods. In this work, the authors attempted to coat the platinum catalyst on membrane by using the electroless deposition technique in order to avoid such problems. The investigated parameters were electroless time, ratio of Pt and reducing agent on the

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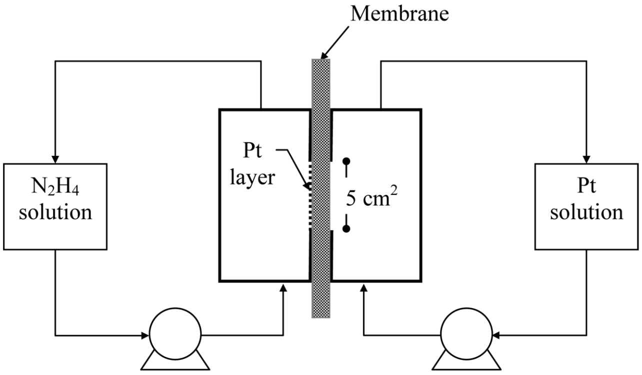


Fig. 1. Scheme of electroless deposition experiment.

catalyst morphology and its performance.

EXPERIMENTAL

The commercial membrane (Nafion117, Electrochem, Inc.) was first treated to improve the properties of the membrane in the boiled solution of 3 wt% H_2O_2, 0.5 M H_2SO_4, and distillated water at 80 °C for 1 hr. The treated membrane was then sensitized and activated by dipping in 0.05 M $SnCl_2$ for 10 min and consequently in 0.01 M $PdCl_2$ for 10 min [Sheppard et al., 1998; Mutreja, 1979; Takenaka et al., 1982]. After these steps, the black and thin film of palladium was thoroughly observed on the membrane. Membrane was cleaned with distilled water before depositing platinum. To deposit platinum on the membrane by electroless deposition, the treated membrane was placed in the middle position of the apparatus shown in Fig. 1.

The platinum solution prepared from $H_2(PtCl_6)\cdot 6H_2O$ (40%, Fluka) was pumped from the reservoir to the first side of membrane. Simultaneously, N_2H_4 (98% Merck) as a reducing agent was fed to the other side. The flow rate of both platinum and N_2H_4 solutions was equally fixed at 80 ml/min. The concentration of N_2H_4 and the reactive area of membrane were fixed at 5×10^{-4} M and 5 cm^2, respectively. Electroless time and ratio of Pt to N_2H_4 were varied to determine the optimum condition. After platinum deposition on both sides of membrane was completed, the prepared membrane was dried to eliminate moisture at 60 °C for 30 min and kept in a desiccator. The amount of platinum deposition was calculated from the difference between Pt content in the solution before and after the process by using Inductive Coupled Plasma or ICP (Perkin Elmer Optima 3000). The prepared membrane was cleaned with distilled water before being assembled with 5 cm^2 carbon paper at pressure of 50 kg/cm^2, 130 °C for 1.5 min to construct the MEA and continuously extended to construct the single fuel cell. The performance of the prepared fuel cell was tested in the H_2/O_2 system by using the flow rates of hydrogen and oxygen of 10 sccm and 80 sccm, respectively [Sanguanrak, 2001]. The humidification of both streams was set to 100% relative humidity and the temperature of fuel cell was fixed at 60 °C.

RESULTS AND DISCUSSION

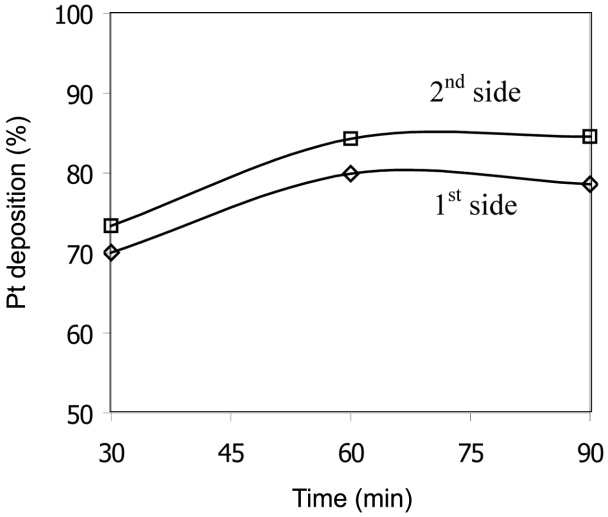


Fig. 2. Percentage of platinum loading as a function time at Pt : N_2H_4=1 : 1.

Effect of electroless time ranging from 30-90 min on platinum deposition by using N_2H_4 as a reducing agent was first carried out at a Pt : N_2H_4 ratio of 1 : 1 in laboratory scale at ambient temperature. For both sides of the membrane, the percentage of platinum deposition increased sharply from 70-73% at 30 min to approximately 79-84% at 60 min (Fig. 2) and after that the platinum deposition was constant at around 78-85%. The reaction of electroless deposition can be simply written as Eq. (1) and Eq. (2).

$$\text{Reduction reaction: } PtCl_6^{2-}+4e^-\rightarrow Pt+6Cl^- \quad (1)$$

$$\text{Oxidation reaction: } N_2H_4\rightarrow N_2+4H^++4e^- \quad (2)$$

Consider the percentage of platinum deposition on both sides, a slight difference between them was observed in that the platinum deposition on the 2nd surface was higher than that on the 1st surface for all electroless times. The percentages were around 78% and 84% on the 1st and the 2nd side, respectively. Fig. 3 reviews the effect of

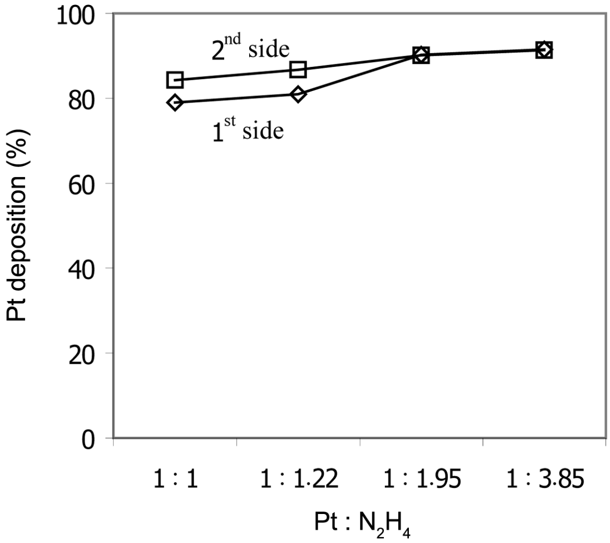


Fig. 3. Effect of platinum-N_2H_4 ratio on platinum deposition at 60 min reaction time.

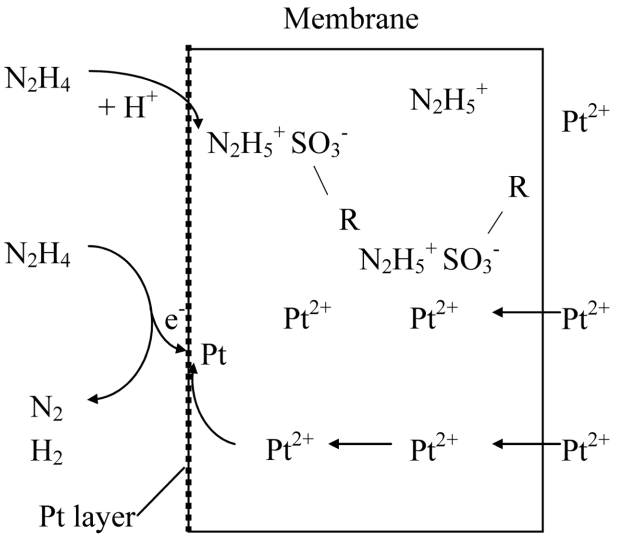


Fig. 4. Proposed mechanism of electroless deposition of platinum on membrane by using N_2H_4 as a reducing agent.

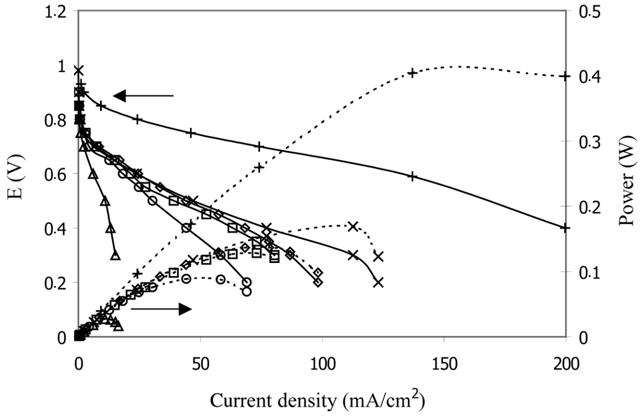


Fig. 6. Performance curve of the prepared single cell in H_2/O_2 system. Voltage (—); power (·····): Pt 1 mg/cm², EC (+); Pt 0.79 mg/cm², anode (×); Pt 0.79 mg/cm², both sides (◇); Pt 0.65 mg/cm², both sides (□); Pt 0.45 mg/cm², both sides (○); Pt 0.23 mg/cm², both sides (△).

Pt : N_2H_4 ratio on platinum deposition at 60 min electroless time. The results indicate that the percentage of platinum deposition increased slightly when the Pt : N_2H_4 ratio increased. At low Pt : N_2H_4 ratio (<1 : 1.95), it can be seen that the platinum deposition on the 2nd side was higher than that on the 1st side. At high Pt : N_2H_4 ratio (≥1 : 1.95); however, the percentage of platinum deposition on both sides was similar.

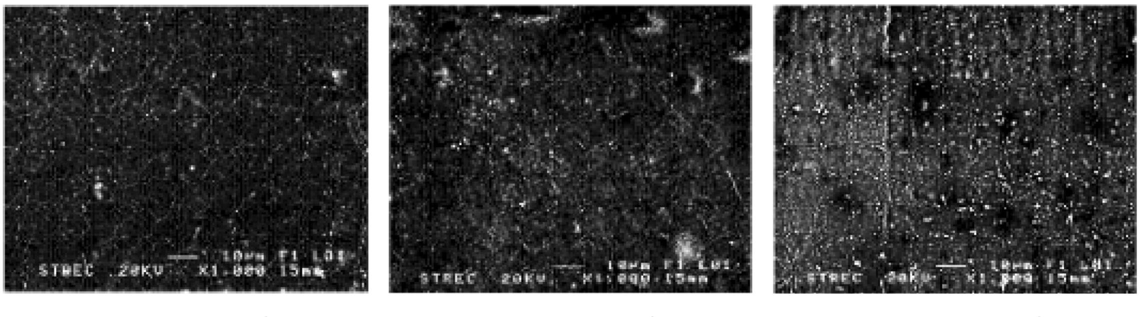
This behavior can be partly described as that the oxidation of N_2H_4 (Eq. (2)) in the acidic condition could produce the side species such as hydrazinium ion ($N_2H_5^+$) as expressed by Eq. (3) which led to a significant decrease in N_2H_4 in the solution [Ananiev, 2003]. For this reason, the amount of N_2H_4 is probably not enough to reduce Pt^{2+} to metallic platinum, resulting in small amount of platinum deposition on the 1st side of membrane.

$$N_2H_4 + H^+ \leftrightarrow N_2H_5^+ \tag{3}$$

Simultaneously, the $N_2H_5^+$ moved through the membrane and reacted with SO_3^- group in the membrane as shown in Fig. 4. After all SO_3^- groups were occupied by $N_2H_5^+$, the remaining N_2H_4 and $N_2H_5^+$ could be oxidized and reversed, respectively, as Eqs. (2) and (3) leading to high platinum deposition on the 2nd side. However, if excess N_2H_4 was used (Pt : N_2H_4 ratio >1 : 1.95), the quantity of N_2H_4 was adequate to reduce Pt^{2+} to metallic platinum. Consequently, the difference in percentage of platinum deposition on both surfaces was not observed in the latter case.

The platinum distribution on the prepared MEA was then analyzed by using scanning electron microscopy (SEM) as shown in Fig. 5. The result showed that the distribution of platinum particle had small uniformity because of the thickness of the deposited layer. More platinum particles could be observed with more platinum loading. The particle size of platinum was nearly constant at around 2-3 μm.

Fig. 6 demonstrates the plot of voltage and power as a function of current density of the MEA prepared by different electrodes (1 mg Pt/cm² of Electrochem, Inc.; 0.79 mg Pt/cm², anode and 1 mg Pt/cm² of Electrochem. Co., Ltd at cathode and MEA of 0.79, 0.65, 0.45 and 0.23 mg Pt/cm² for both sides). The curve shows that high platinum loading provided high current density. The maximum current density was obtained at 80 mA/cm² at the potential of 0.3 V with the platinum density of 0.79 mg/cm². Comparing the results of the MEA from this work and those from the commercial MEA, the results indicated that the performance of MEA from this work was lower especially during the activation region (0.7-0.9 V). It implies that the prepared catalyst has a low potential to promote the oxidation-reduction reaction. It is probably due to the crystal struc-



Pt 0.5 mg/cm² Pt 1.0 mg/cm² Pt 1.5 mg/cm²

Fig. 5. Platinum distribution on Nafion membrane at 1,000 magnification.

Table 1. Power and cell voltage of the prepared MEA

Platinum loading (mg/cm^2)	Maximum power (W)	Cell voltage (V)	Current density (mA/cm^2)
0.23 (both sides)	0.027	0.5	10.9
0.45 (both sides)	0.088	0.4	44.3
0.65 (both sides)	0.13	0.4	73.2
0.79 (both sides)	0.14	0.4	78.2
0.79 (anode side)	0.17	0.3	112.7
1.0 (commercial)	0.41	0.6	137.0

ture of the Pt which is not present in the active form or [111] orientation [Lipkowski et al., 1998]. In addition, the particle size of platinum prepared in this work was still larger than that of commercial (approximately 2 nm). Furthermore, the slope during the ohmic resistance of the polarization curve of this work was higher than that from the commercial one. It implied that the former case had cell resistance higher than that of the latter case. The maximum power and current density of the prepared MEA as demonstrated in Table 1 were about 2.8 and 1.4 times lower than that of commercial, respectively. Increasing platinum loading, however, led to increasing both maximum cell voltage and current density.

Due to the complexity in the electrode behavior inside the fuel cell and the influence of several factors, electrochemical impedance spectroscopy (EIS) was carried out to investigate the performance of the prepared MEA at the frequency ranging from 10^{-1}-10^{7} Hz. The results, as shown in Fig. 7, demonstrate that the high frequency spectra did not alter with potential, whereas that at low frequency changed with the cell potential. At high voltage (0.9 V), the spectra did not produce the RC component associated with the cell reaction at low frequencies. Beyond 0.7 V to lower; however, the pseudo-RC circuit was observed especially at voltage lower than 0.5 V. This result implies that for the tested condition of this work, the high frequency region was not associated by either Faradaic process or mass transfer limitation. It may be contributed by structure feature of the prepared MEA. In addition, deviation of impedance spectra was observed at very low frequency. This may be the cause of the diffusion process of gaseous reactant. These results corresponded to the MEA prepared with 0.79 mg Pt/cm^2 for both sides and 1 mg Pt/cm^2 from Electrochem, Inc. for both sides.

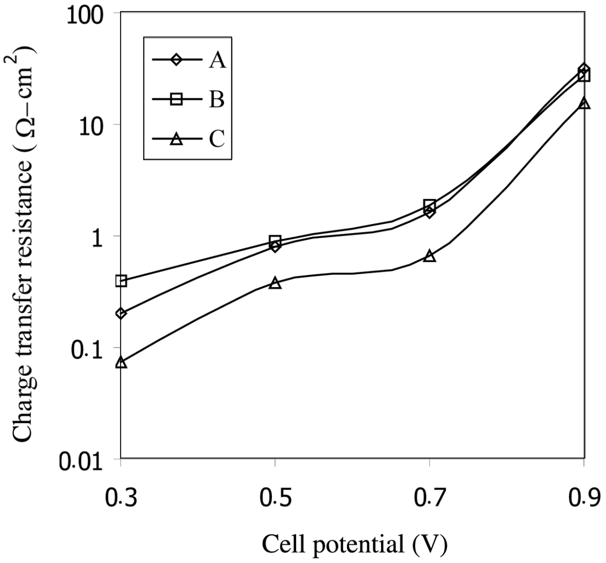
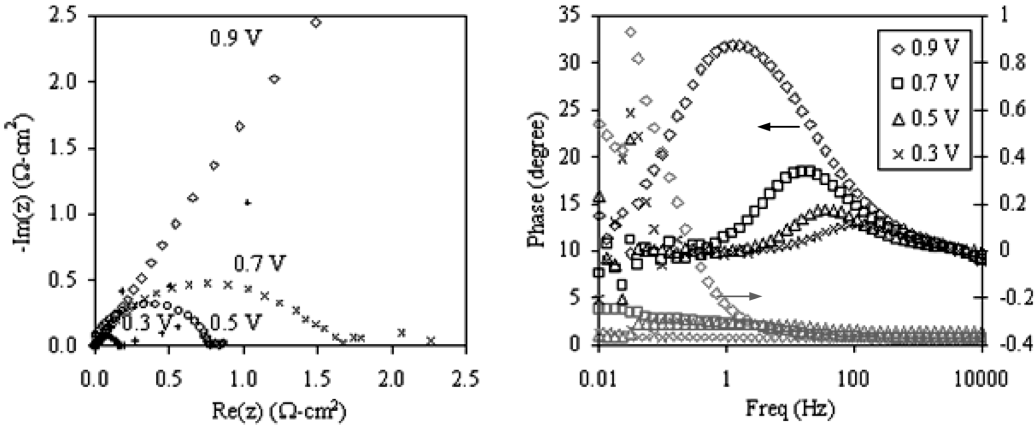


Fig. 8. Charge transfer resistance as a function of cell potential. 0.79 mg Pt/cm^2 for anode (A); 0.79 mg Pt/cm^2 for both sides (B); and 1 mg Pt/cm^2 (Electrochem Co. Ltd.) (C).

To further explore the performance of the prepared catalyst, the value of charge transfer resistance was calculated and plotted in Fig. 8. The charge transfer resistance seemed to decrease exponentially during the whole range of explored potential and the charge transfer resistance of the prepared catalyst was higher than that of the commercial one for all cell potentials. In addition, by using EIS, the ohmic resistance was found at 0.92, 0.95 and 0.73 Ω-cm^2 for platinum loading 0.79 mg/cm^2 (anode side), 0.79 mg/cm^2 (both sides) and 1 mg/cm^2, respectively. To improve the performance of prepared catalyst, the future work will study the improvement of platinum characteristics such as particle size, surface area, crystal structure, etc.



(a) (b)

Fig. 7. Nyquist (a) and Bode (b) plots of the prepared MEA 0.79 mg Pt/cm^2 for anode and 1 mg Pt/cm^2 (commercial) for cathode at several potentials for H_2/O_2 system.

CONCLUSIONS

The preparation of Pt electrocatalyst for PEMFC was carried out by using the electroless deposition technique. The results indicate that the electroless time and the Pt:N_2H_4 ratio have a significant effect on percentage of Pt deposition. The platinum deposition on the 1st side of membrane was lower than that on the 2nd side because of the effect of N_2H_4 on the property of membrane. Platinum deposition increased when the Pt : N_2H_4 ratio decreased. The optimum condition was found at 60 min electroless time and 1 : 1.95 Pt : N_2H_4 ratio. At this condition more than 89% of platinum was deposited on both surfaces. The distribution of the Pt particle was not uniform because of the membrane swelling. The maximum current density of the prepared MEA was 80 mA/cm^2 at 0.3 V in the testing condition of 60 °C in the saturated H_2/O_2 system. Furthermore, with EIS, the results demonstrated that the charge transfer resistance of the prepared catalyst was higher than that of the commercial one for all cell potentials. The ohmic resistance was found at 0.92, 0.95 and 0.73 Ω-cm^2 for platinum loading 0.79 mg/cm^2 (anode side), 0.79 mg/cm^2 (both sides) and 1 mg/cm^2, respectively.

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