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A Novel Impregnation-Reduction Method Combined with Galvanic Replacement for Fabricating Low Cost MEA with High Performance for PEM Fuel Cells

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The fuel cells have outstanding advantages in the new energy application, but the membrane electrode assembly (MEA) of fuel cells is difficult to produce at low-cost and large-scale, which restricts their applications. To simplify the preparation of MEA, for the first time, we successfully develop a novel impregnation-reduction method combined with galvanic replacement to grow Ag/Pt bimetallic nanocatalyst onto a Nafion membrane (Nafion-Ag/Pt membrane), and the deposited Ag/Pt catalyst is very stable, which can be directly used as a novel ultra-thin catalyst layer in MEA. This novel method possesses mild conditions, simple procedure, good repeatability and practicability in a large-scale production. Moreover, a very low Pt loading amount of Nafion-Ag/Pt membrane can be achieved by regulating experimental conditions, which brings excellent Pt utilization. Therefore, the MEA made from Nafion-Ag/Pt membrane exhibits a Pt mass specific power (1.519 W mgPt⁻¹) that is 12.3 times higher than that of a conventional MEA. These results demonstrate that this novel impregnation-reduction method can reduce the cost of fuel cells by reducing the difficulty of MEA preparation and the Pt loading amount of MEA and simultaneously enhancing its performance, which shows great potential in fuel cell application.

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with galvanic replacement to grow Ag/Pt bimetallic nanoparticles (NPs) onto Nafton membrane as a simplified catalyst layer.

The combination of impregnation-reduction method and galvanic replacement to fabricate simple Ag/Pt catalyst layer shows great potential in fabricating MEA with high performance. Firstly, the uniform growth of nano-size Ag NPs onto Nafton membrane can be achieved by applying surfactant and controlling pH of the reaction solution. It is of great importance to limit the size of grown Ag NPs to 15 nm or smaller, or the subsequent galvanic replacement between Ag NPs and Pt ion would not happen under mild condition. Secondly, the loading amount of Pt can be controlled by regulating the experimental parameters and a low Pt loading amount of MEA (0.069 mg cm$^{-2}$) can be realized, which can dramatically reduce the cost of MEA. Finally, it provides a very simple and efficacious fabrication process of MEA by directly hot-pressing the Nafton-Ag/ Pt membrane with carbon papers, which reveals excellent performance in PEMFC.

Therefore, the MEA made from Nafton-Ag/Pt membrane with Pt loading amount of 0.110 mg cm$^{-2}$ exhibits a peak mass specific power (1.519 W mgPt$^{-1}$) that is 12.3 times higher than that of a conventional MEA (GDL MEA) at a lower Pt loading amount, which is only 9.8% of the usage of conventional MEA, which shows an efficient Pt utilization. In conclusion, the MEA made from Ag/Pt catalyst modified Nafton membrane (Nafton-Ag/Pt membrane) combines the advantages of advanced low-cost bimetallic catalyst, simplified catalyst layer structure and simple preparation method, which has the excellent performance and could be serviceable in reducing the cost of PEMFC and promoting its commercial application.

**Experimental section**

**Materials.—** Silver nitrate (AgNO$_3$, 99.8%) and sodium borohydride (NaBH$_4$, 98%) were purchased from Aladdin Industrial Co. Ltd (Shanghai, China). And the potassium tetrachloroplatinate (K$_2$PtCl$_4$, 99.95%) was bought from J&K Scientific Ltd (Beijing, China). Citric acid (analytical grade), sodium citrate (analytical grade), aqueous ammonia (25%), hydrogen peroxide (30 wt% H$_2$O$_2$), perchloric acid (HClO$_4$, analytical grade) and polyvinylpyrrolidone (PVP, K-30) were obtained from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Nafion 117 membrane, Nafion solution (5 wt%), carbon paper (the gas diffusion layer (GDL) with microporous layer (MPL)) (Model HCP120) and commercial Pt/C (Johnson Matthey, 60 wt% Pt, HiSPEC™ L100) were bought from Shanghai Hesen Electrical Ltd (Shanghai, China). The materials were used without any further purification, and the purity quotient of other reagents was analytical grade.

**Synthesis and preparation.—** Pretreatment of Nafton membrane.—Nafton 117 membrane was cut into 3 cm × 3 cm pieces for the experiment. The Nafton membrane pieces were boiled in H$_2$O$_2$ solution (5 wt%) under 60 °C for 6 h to remove the impurities on the surface, and fully active the Nafion membrane pieces. Then, the Nafion membrane pieces were immersed in the NaCl solution of 0.0010 M or a specific concentration of 0.0020 M, 0.0030 M, 0.0500 M, 0.1000 M, 0.2000 M, 0.3000 M for 24 h to transform the H$^+$ (Nafion-H$^+$ membrane) on the surface of Nafion membrane into Na$^+$ (Nafion-Na$^+$ membrane), which could accelerate the combination of Ag ions and the Nafton surface.

Deposition of Ag NPs onto Nafton membrane.—The Nafton-Na$^+$ membrane was immersed in the AgNO$_3$ solution of 0.0200 M or specific concentration of 0.0050 M, 0.0100 M, 0.0500 M, 0.1000 M, 0.2000 M for 12 h or a certain time of 3 h, 6 h, 9 h, 18 h, 24 h, 36 h, 48 h. The Na ions on the Nafton membrane surface would be replaced by Ag ions, which produced the Nafton-Ag$^+$ membrane.

After that, 0.1000 g polyvinylpyrrolidone, 0.0118 g AgNO$_3$, 0.0420 g sodium citrate, 0.0420 g citric acid, and 50 ml deionized water were mixed in a beaker and sonicated into a transparent solution. The Nafion-Ag$^+$ membrane was immersed in the above solution for 10 min. Then, 1 ml deionized water with 0.0100 g NaBH$_4$ was added very slowly. The color of the solution became brownish black immediately, indicating the Ag ions on the surface of the Nafion membrane were reduced to Ag NPs, which turned the Nafion membrane into a yellow membrane. After 24 h, the Ag deposited Nafion membrane (Nafion-Ag membrane) was taken out and washed with deionized water.

The roles of the above reagents are stated as follows. PVP is a surfactant, which limits the growth and aggregation of Ag nanoparticles. Sodium citrate and citric acid are similar, which possess the role of chelating agent to stabilize Ag nanoparticles and are also used as weak reducing agents to reduce Ag$^+$ ions to Ag nanoparticles. In addition, citric acid can adjust the pH of the reaction solution into acidic. Sodium borohydride (NaBH$_4$) shows strong reducibility and is the main reducing agent to reduce Ag$^+$ ions to Ag nanoparticles.

Deposition of Pt metal onto Nafion-Ag membrane.—The galvanic replacement between the K$_2$PtCl$_4$ and the Ag NPs on Nafion membrane was applied to deposit Pt onto Nafion membrane, which would form hollow Ag-Pt alloyed bimetallic structure as previously reported. During the reaction, PtCl$_4^{2−}$ would be reduced to Pt atoms through the galvanic replacement reaction involving Ag nanoparticles. The oxidized Ag atoms dissolved into solution and appeared a small hole on the Ag nanoparticles, which was the beginning of continuous dissolution of Ag nanoparticles. During this process, Ag nanoparticles acted as sacrificial template for the hollow cavity of the product. Finally, the internal Ag nanoparticles were removed by the galvanic replacement and resulted in the formation of a hollow Ag/Pt alloy shell. Alloying the Pt with Ag metal can enhance the catalytic activity of Pt because the introduction of Ag atoms can change the electronic structure of Pt. What’s more, the hollow structure of Ag/Pt alloys increases the utilization of Pt atoms. So, Ag/Pt nanoparticle reported in this work shows better performance as catalyst.

The Nafion-Ag membrane was immersed in K$_2$PtCl$_4$ solution of 0.0241 M with 20 ml, then the galvanic replacement reaction was taken place immediately without heating, which had be indicated by the formation of white AgCl precipitation. After 24 h, the Ag/Pt bimetallic NPs deposited Nafion membrane (Nafion-Ag/Pt membrane) was washed with ammonia solution and deionized water to remove the AgCl precipitation. Then, the Nafion-Ag/Pt membrane was immersed in 0.1000 M HClO$_4$ for subsequent characterization. The preparation route is shown in Fig. 1, and the images taken during the experiment which record the color change of Nafion membrane are shown in Fig. S1 (available online at stacks.iop.org/JES/168/034522/mmedia).

**Characterization of the materials.—** The crystal structure of the metal NPs loaded on the Nafion membrane was investigated by the X-ray diffraction (XRD), which was carried out on Mini Flex 600 X-ray diffractometer (Rigaku) adopting Cu K$\alpha$ radiation with a scan rate of 2.0° min$^{-1}$. The samples were stuck on a slide plate for measurement.

The scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS) (Model Hitachi S-4800) was conducted to characterize the surface morphology and the element distribution of the samples. To obtain the morphology and element distribution of the cross-sectional images of MEAs by SEM (Model ZEISS GeminiSEM 500), MEAs were sectioned with a scalpel. To obtain the morphology and element distribution of cross-sectional images of the Nafion-Ag/Pt membrane with Pt loading amount of 0.110 mg cm$^{-2}$ by the backscatter mode of the SEM (Model ZEISS GeminiSEM 500) with an accelerating voltage of 2 kV and an emission current of 0.2 nA, the Nafion-Ag/Pt membrane was cryo-fractured in liquid nitrogen. The samples were loaded into the microscope without platinum or gold spraying.
The distribution of Ag/Pt nanoparticles throughout the Naﬁon-Ag/Pt membrane (Pt loading amount: 0.110 mg cm\(^{-2}\)) was captured by FEI Tecnai G2 F30. To prepare thin ﬁlms (∼100 nm) for TEM imaging, the small pieces of Naﬁon-Ag/Pt membrane was encased with epoxy and sectioned with ultramicrotomy (Leica UC-7 RT ultramicrotome with a diamond knife to cut the samples).

The inductively coupled plasma-atomic emission spectrometry (ICP-AES) method was used to identify the metal loading amount of the samples, using NSC Plasma 1000. The Naﬁon-Ag/Pt samples were immersed in the aqua regia, which would completely dissolve the metal NPs on the membrane (As shown in Fig. S2).

To measure the water uptake rate, the samples were soaked in the deionized water at 25 °C. After 12 h, the samples were weighed after removing the surplus water from the surface. Then the samples were weighed again after drying at 60 °C under vacuum for 24 h. The water uptake is obtained by the equation below.

\[
W(\%) = \frac{(M_w - M_d)}{M_w} \times 100
\]

where the W is the water uptake, the \(M_w\) and \(M_d\) stand for the weight of wet and dried samples, respectively.

The attenuated total reﬂection Fourier transform infrared spectroscopy (ATR-FTIR) method was applied to obtain the infrared spectra of the fully dehydrated samples on a Nicolet IS5 infrared spectroscopy.

The in-plane sheet resistivity of the Naﬁon membrane and the Naﬁon-Ag/Pt membrane with different Pt loading amount was obtained using a four-point probe resistance measurement connected to a semiconductor resistivity of the powder tester (Model ST2558BF02 and ST2722-SZ, respectively, Suzhou Jingge Electronic Co., LTD). The in-plane electronic conductivity \(\sigma\) of the Naﬁon membrane and the Naﬁon-Ag/Pt membrane with different Pt loading amount is obtained by the following equation:

\[
\sigma (S \text{ cm}^{-1}) = \frac{1}{\rho},
\]

where \(\rho\) is the in-plane sheet resistivity (Ω ⋅ cm) of the Naﬁon membrane and the Naﬁon-Ag/Pt membrane with different Pt loading amount obtained from the four-point probe resistance measurement at 20 °C. The samples were dried in a vacuum oven at 80 °C for 12 h before testing.

The through-plane proton conductivity of the Naﬁon membrane and the Naﬁon-Ag/Pt membrane with different Pt loading amount was tested by the two-electrode AC impedance method on Princeton Parstat 263 electrochemical station with AC frequency from 0.1 Hz to 100 kHz. The method was described in previous works.\(^{32}\) The through-plane proton conductivity \(\sigma\) is obtained by the following equation:

\[
\sigma (S \text{ cm}^{-1}) = \frac{1}{(R \times A)},
\]

where the \(l\) (cm) stands for the distance between the electrodes, the \(R\) (Ω) is the measured resistance of the samples, the \(A\) is the contact area of the membrane and the electrodes. The samples were soaked in the deionized water at 25 °C for 12 h before testing.

The through-plane electronic conductivity of the Naﬁon membrane and the Naﬁon-Ag/Pt membrane with different Pt loading amount was determined by assembled 2032 type coin cells with the sample (Ø = 18.5 mm) sandwiched between two stainless-steel sheets (Ø = 16 mm) and one stainless-steel shrapnel (Ø = 16 mm), and using a multimeter (Model DE78A+, DELIXI\(^{\text{TM}}\)). The through-plane electronic conductivity \(\sigma\) of the Naﬁon membrane and the Naﬁon-Ag/Pt membrane with different Pt loading amount is obtained by the following equation:
where $l$ (cm) stands for the distance between the electrodes, $A$ is the contact area of the membrane and the electrodes, $R$ ($\Omega$) is the bulk resistance of the samples, which was obtained by using a multimeter at 20 °C. The samples were dried in a vacuum oven at 80 °C for 12 h before testing.

**Fuel cell performance test.**—The size of all MEAs in this work was 2 cm $\times$ 2 cm. The conventional MEA (GDL MEA) was prepared by the conventional GDL method. The conventional anode and conventional cathode were prepared through painting catalyst inks onto carbon papers. Catalyst ink was prepared by dispersing an appropriate amount of commercial Pt/C catalyst (Johnson Matthey, 60 wt% Pt) and 5 wt% Nafion solution into an isopropanol and sonicating and magnetic stirring overnight to yield a slurry containing 5 wt% of commercial Pt/C catalyst. For the GDL MEA, the Nafion 117 membrane was sandwiched between the conventional cathode electrode and conventional anode electrode, followed by hot-pressing at 80 °C under 5 MPa for 5 min. Since the Pt loading amount of conventional cathode and conventional anode was 0.780 mg cm$^{-2}$ and 0.340 mg cm$^{-2}$, respectively, the total Pt loading amount of the GDL MEA was 1.120 mg cm$^{-2}$.

For the sake of preparing MEA with lower Pt loading amount using CCM method, an ultrasonic spraying instrument (Model EXACTACOAT OP3, Sono-Tek Co.) was used and the catalyst ink for spray with the mass concentration of 1 mgPt ml$^{-1}$ was prepared by dispersing an appropriate amount of commercial Pt/C catalyst (Johnson Matthey, 60 wt% Pt) and 5 wt% Nafion solution into an isopropanol and sonication for 3 h. Then, a Nafion 117 membrane was sprayed with catalyst ink on two sides with a Pt loading amount of 0.2 mg cm$^{-2}$ and 0.4 mg cm$^{-2}$, respectively, and the spraying area was 2 cm $\times$ 2 cm, the total Pt loading amount of the Nafion membrane was 0.600 mg cm$^{-2}$. For a MEA made by CCM (CCM MEA), the Nafion membrane sprayed with catalyst ink was sandwiched between two carbon papers (2 cm $\times$ 2 cm), followed by hot-pressing at 80 °C under 5 MPa for 5 min.

For the New MEA, the different Pt loading amount of Nafion-Ag/Pt membranes were hot pressed directly with the carbon papers, followed by hot-pressing at 80 °C under 5 MPa for 5 min. The total Pt loading amount of Nafion-Ag/Pt membrane was 0.069 mg cm$^{-2}$, 0.090 mg cm$^{-2}$, 0.101 mg cm$^{-2}$, and 0.110 mg cm$^{-2}$, respectively. The images, cross-section SEM images and element mapping results of the GDL MEA with the Pt loading amount of 1.120 mg cm$^{-2}$ and the New MEA with Pt loading amount of 0.110 mg cm$^{-2}$ are shown in Fig. S3 to illustrate the structural differences between these two MEAs.

Polarization curves of the PEMFC were obtained on an fuel cell test system (Arbin FCTS, Arbin Instrument Inc. USA) at the working temperature of 70 °C. The anode and the cathode was fed with hydrogen and oxygen, respectively. The gas velocity of hydrogen and oxygen gas was 0.15 slpm (standard liter per minute). The gas relative humidity (RH) of hydrogen and oxygen gas was 60% RH. The fuel cells were worked at a constant current density of 0.050 A cm$^{-2}$ for 24 h to completely activate the MEA. In order to test the stability of MEAs, the GDL MEA with Pt loading amount of 1.120 mg cm$^{-2}$ and the New MEA with Pt loading amount of 0.110 mg cm$^{-2}$ was worked at a constant current density of 0.300 A cm$^{-2}$ for 24 h, respectively, and then measured their polarization curves again, followed by the same test conditions. Because the current density of 0.300 A cm$^{-2}$ corresponded roughly to a maximum power density for both GDL MEA and New MEA, these tests that operated MEAs at a maximum power density could demonstrate the stability of overall PEMFC performance under demanding life-test conditions as Gottesfeld et al. reported.33 For the sake of testing the anti-flooding performance of the New MEA, the New MEA with Pt loading amount of 0.110 mg cm$^{-2}$ was tested at a constant current density of 0.25 A cm$^{-2}$ for 2000 s, at a 100% RH.

**Results and Discussion**

**Control of Metal loading amount on the Nafion-Metal membrane.**—During the developing of the preparation method, we find that the concentration of the NaCl solution in the process of the pretreatment of Nafion membrane or the AgNO$_3$ solution in the process of the deposition of Ag NPs onto Nafion membrane has a great effect on the metal loading amount of Naion-Ag membrane or Nafion-Ag/Pt membrane.34 Hence, we could regulate the metal loading amount by simply controlling these two conditions.

Figure 2a shows the relationship between the concentration of AgNO$_3$ solution in the process of the deposition of Ag NPs onto Nafion membrane and the Ag loading amount of intermediate product Nafion-Ag membrane and the Pt loading amount of final product Nafion-Ag/Pt membrane, respectively. The trend of Ag loading amount is consistent with the final Pt loading amount, which proves that the amount of Pt loading is determined by the amount of Ag loading. The tendency of the metal loading indicates that the rise of the AgNO$_3$ concentration will raise the metal loading at low concentration range, but as further increasing the AgNO$_3$ concentration, the metal loading will reach an upper limit. The reason for this phenomenon is that the Ag loading amount is determined by the number of Ag$^+$ on the surface of Nafion membrane, which may be increased by exchanging Na$^+$ with the Ag$^+$ in AgNO$_3$ solution of higher concentration, but there is an equilibrium of the ion exchange, which limits the number of Ag$^+$ that Nafion membrane gets and, hence, the melting loading amount on Nafion membrane.

Figure 2b displays the relationship between the Pt loading amount of Nafion-Ag/Pt membrane and the soaking time in the AgNO$_3$ solution of 0.0200 M in the process of the deposition of Ag

![Figure 2](https://example.com/figure2.png)
A high concentration of NaCl will bring a maximum Ag loading amount of 0.203 mg cm$^{-2}$ and the Pt loading amount of 0.110 mg cm$^{-2}$. The XRD patterns of the Na$_2$Ag sample and Na$_2$Ag/Pt sample are shown in Figure 3. The XRD patterns of the Na$_2$Ag sample with Ag loading amount of 0.203 mg cm$^{-2}$ and the Na$_2$Ag/Pt sample with Pt loading amount of 0.110 mg cm$^{-2}$.

The morphology of the Na$_2$Ag/Pt bimetallic NPs is shown in Figure 4. The SEM images and the mapping results of the Na$_2$Ag/Pt bimetallic NPs are also compared with the Na$_2$Ag sample. The SEM images show that the Ag particle size of the Na$_2$Ag/Pt bimetallic NPs is smaller than that of the Na$_2$Ag sample. The Ag/Pt bimetallic NPs on the Na$_2$Ag membrane are also revealed due to the disappearance of large Ag particles. The Ag mapping result indicates that the Pt loading amount of Na$_2$Ag/Pt membrane is almost uniform and the Ag coverage can still be observed in the Ag mapping result. The SEM images and the mapping results of Na$_2$Ag/Pt membrane with Pt loading amount of 0.110 mg cm$^{-2}$ (prepared from Na$_2$Ag/Pt membrane with Ag loading amount of 0.421 mg cm$^{-2}$) is so compact that it looks like a mirror made from silver. The SEM images show that the Ag particles growing on the mirror like Nafion-Ag membrane have an average particle size of about 100 nm, and agglomerated together to fully cover the surface of Nafion membrane, which would block the mass transfer between the Nafion membrane and the carbon paper.

Our previous work demonstrated that the galvanic replacement reaction could only take place between the Pt salt and the Ag NPs at room temperature when the size of Ag is very small (under 15 nm) due to the high surface energy of small NPs. So it is impossible to load Pt onto the Nafion as the Ag loading is over about 0.300 mg cm$^{-2}$, and it should be avoided to deposit too much Ag on the Nafion membrane while preparing the Nafion-Ag membrane. The above results indicate that the Pt loading amount can be controlled by the concentration of NaCl solution, and their relationship is linear like positive correlation, which can be used to easily regulate the Pt loading amount of Na$_2$Ag/Pt membrane by simply controlling the NaCl concentration in the process of the pretreatment of Nafion membrane in a certain range. And owing to the impact of the particle size of the deposited Ag on the feasibility of the galvanic replacement, the maximum Pt loading amount of the Na$_2$Ag/Pt membrane may be limited to 0.110 mg cm$^{-2}$ (the total Pt loading amount of both sides on Nafion membrane).

Figure 3. The XRD patterns of the Nafion-Ag sample with Ag loading amount of 0.203 mg cm$^{-2}$ and the Nafion-Ag/Pt sample with Pt loading amount of 0.110 mg cm$^{-2}$.
0.203 mg cm$^{-2}$) are shown in Figs. 4e–4i. As shown in the SEM images, the Nafion-Ag/Pt membrane still looks like a flat film with scattered particles, but we can find the differences from the Ag and Pt element mapping results. In Fig. 4g, the distribution of Pt element is dense and uniform, demonstrating the existence of Pt element. In Fig. 4h, there exists aggregation of signals in the distribution of Ag element, which can correspond to the irregular small particles distributed on the surface of the Nafion-Ag/Pt membrane in Fig. 4f, but there is no obvious agglomeration of signals in the same place in Fig. 4g. Therefore, it is proved that the irregular small particles are Ag particles, which doesn’t react with Pt ions because of their big size.

Figures 5a–5b are the cross-section backscatter SEM images of the Nafion-Ag/Pt membrane with Pt loading amount of 0.110 mg cm$^{-2}$. It shows that the Ag/Pt NPs deposition zone has a depth about 4 μm in the cross section of the Nafion-Ag/Pt membrane, and there is an obvious interface between Nafion membrane with and without Ag/Pt NPs. Considering the thickness of Nafion-117 is 175 μm, the Ag/Pt alloy layer with the thickness of 4 μm on each side of the Nafion membrane will not critically affect the application of it. And as shown in the cross-section EDX results of the the Nafion-Ag/Pt membrane in Fig. S7, the existence of C and F is indicative of Nafion membrane, and it is clear that Ag and Pt are detected, which is the evidence of the existence of Ag/Pt alloy NPs in cross section. As shown in Figs. 5c–5d, the element mapping results of Ag and Pt indicate that the distribution of these two elements is mainly concentrated near the surface of the Nafion membrane, which is consistent with the results of the backscatter SEM images.

Figures 6a–6e shows the TEM images and elemental line scan result of an ultramicrotomed sample of the Nafion-Ag/Pt membrane with Pt loading amount of 0.110 mg cm$^{-2}$ to examine the
morphology and composition of Ag/Pt NPs on Nafton-Ag/Pt membrane. As shown in Figs. 6a–6d, the average particle size of nanoparticles is about 15 nm with a hollow structure, as expected, which proves the success of the novel impregnation-reduction process.
method combined with galvanic replacement. As shown in Fig. 6d, the crystal lattice fringes of the nanoparticles on the Naﬁon-Ag/Pt membrane is about 0.2300 nm, which is between the space of pure Pt (111) (0.2265 nm) and pure Ag (111) (0.2359 nm), making clearly that these nanoparticles should be Ag/Pt alloy NPs, and it is clearly that the Ag/Pt alloy nanoparticle shows a hollow structure with a shell of ~4 nm. The elemental distribution of the Ag/Pt alloy NPs on the Naﬁon-Ag/Pt membrane was investigated by line scan EDX. The results are shown in Fig. 6e. For Ag/Pt nanoparticle, both Ag and Pt reveals a trapezoidal curve, and the upper side of the curve is concave, which proves that preparing Ag/Pt alloy NPs successfully with a hollow structure.

Figure 7 shows the ATR-FTIR spectra of the fully dehydrated Naﬁon membrane, Naﬁon-Ag membrane (Ag loading: 0.203 mg cm$^{-2}$) and Naﬁon-Ag/Pt membrane (Pt loading: 0.069 mg cm$^{-2}$ and 0.110 mg cm$^{-2}$) samples. All the samples display two strong peaks at 1204 cm$^{-1}$ and 1140 cm$^{-1}$ due to the stretching vibration of C-F, which is characteristic for the Teflon framework of Naﬁon membrane. The peak at 974 cm$^{-1}$ is ascribed to the stretching vibration of C-O-C. The peak at 1055 cm$^{-1}$ and the shoulder peak at 1310 cm$^{-1}$ belong to the symmetric stretching vibration and antisymmetric stretching vibration of −SO$_3^-$, respectively. The comparison among the curves indicates the growth of Ag or Ag/Pt on the Naﬁon membrane does not affect the nanostructure of Naﬁon membrane, demonstrating that the Naﬁon membrane is stable under the deposition process, which is the foundation of the availability of the MEA made from Naﬁon-Ag/Pt membrane.

The stability of the binding of the Naﬁon membrane with the deposited Ag/Pt NPs is tested by sonicating the Naﬁon-Ag/Pt sample, as shown in the video named “Stability Test.mp4” in the supporting files. The Naﬁon-Ag/Pt sample remains unchanged after being sonicated for 1 min. This result states clearly that the Naﬁon-Ag/Pt membrane made in this paper is more stable than the Pt NPs on the Naﬁon membrane sub-surface does not affect the growth of Pt loading amount, which makes clear that the growth of Ag/Pt NPs on the Naﬁon membrane is more stable than the Pt NPs on the Naﬁon-Ag/Pt membrane.

As shown in Fig. S9a, the Naﬁon membrane without Ag/Pt NPs has no electronic conductivity in plane. And with the increase of Pt loading amount, the increase of the Ag/Pt alloy layer density and thickness leads to an increased in-plane electronic conductivity of the Naﬁon-Ag/Pt membrane as more Ag/Pt nanoparticles are connected together to promote the transmission of electrons. As shown in Fig. S11, the ohmic resistance and the corresponding through-plane electronic conductivity of the Naﬁon membrane and the Naﬁon-Ag/Pt membrane with different Pt loading amount is in the order of 10$^7$ Ω and 10$^{10}$ cm$^{-1}$, respectively. This result indicates that the cross-section of the Naﬁon membrane is non-electronically conductive regardless of the growth of Ag/Pt nanoparticles, which can avoid internal short circuit during running MEA fabricated by Naﬁon-Ag/Pt membrane.

As shown in Fig. S9b, compared with the Naﬁon membrane without Ag/Pt NPs, the through-plane proton conductivity of the Naﬁon-Ag/Pt membrane basically remains constant with the increase of Pt loading amount, which makes clear that the growth of Ag/Pt NPs on the Naﬁon membrane sub-surface does not affect the transmission of proton in cross section. What’s more, as shown in Fig. S10, when compared with the Naﬁon membrane, the Naﬁon-Ag/Pt membrane with the Pt loading amount of 0.110 mg cm$^{-2}$ possesses slightly higher through-plane proton conductivity at high temperature as the improvement of water uptake makes difference at high temperature.

The MEA made from Naﬁon-Ag/Pt membrane with different Pt loading amount is abbreviated as New MEA, the MEA prepared by the CCM method with Pt loading amount of 0.600 mg cm$^{-2}$ is abbreviated as CCM MEA, and the MEA prepared by the conventional GDL method with Pt loading amount of 1.120 mg cm$^{-2}$ is abbreviated as GDL MEA for comparison. The all MEAs are tested in the same H$_2$-O$_2$ fuel cell test system.

Figure 8a shows the polarization curves of different MEAs. The maximum power density of the New MEA increases as the Pt loading amount increases, and, unexpectedly, the peak power density of the New MEA with Pt loading amount over 0.100 mg cm$^{-2}$ is higher than that of GDL MEA. The potential drops of the New MEA in the region of activation polarization (0.000 ~ 0.025 A cm$^{-2}$) should be larger than that of the GDL MEA as a result of the much lower Pt loading amount of New MEA. But in contrast, the potential drop of New MEA with Pt loading amount of 0.110 mg cm$^{-2}$ (181.5 mV) is slightly smaller than that of the GDL MEA (187.6 mV), which could be contributed to the excellent catalytic activity of Ag/Pt bimetallic catalyst. In the ohmic polarization area (0.025 ~ 0.363 A cm$^{-2}$) of the polarization curves, the potential drops of the New MEA are also less than that of the GDL MEA, indicating that the internal resistance of the New MEA is lower than that of the GDL MEA. The lower internal resistance of the New MEA may be caused by the direct growth of Ag/Pt on Naﬁon, which binds the metal NPs with the membrane tightly, and thus reduces their contact resistance. And the higher ionic conductivity of Naﬁon-Ag/Pt may also decrease the resistance of the MEA made from Naﬁon-Ag/Pt membrane.

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As shown in Fig. 8b, benefiting from the higher electrocatalytic activity of hollow Ag/Pt bimetallic NPs and the better oxygen diffusion and lower internal resistance of the simplified catalyst layer structure, the New MEAs show a higher Pt utilization. The New MEA with Pt loading amount of 0.110 mg cm$^{-2}$ exhibits the highest value of 167.1 mW cm$^{-2}$, which is 1.2 times higher than that of the GDL MEA, and it is worth mentioning that its Pt mass speciﬁc power (1519.1 mW mgPt$^{-1}$) is 12.3 times to that of the GDL MEA (124.0 mW mgPt$^{-1}$), which is outstanding.

To test the stability of the samples, we run the fuel cells with the GDL MEA with Pt loading amount of 1.120 mg cm$^{-2}$ and the New MEA with Pt loading amount of 0.110 mg cm$^{-2}$ at a constant current.
density of 0.300 A cm\(^{-2}\) for 24 h, and then measure their polarization curves again, the results are displayed in Figs. 8c−8d. After the stability test, the peak power density of the GDL MEA reduces to 117.7 mW cm\(^{-2}\), which is 85% of the original value, but the New MEA with Pt loading amount of 0.110 mg cm\(^{-2}\) only loses 9% of its maximum power density, which is still about 1.1 times higher than that of the fresh GDL MEA. The comparison result demonstrates that the New MEA possesses better performance stability during the long-term operation in fuel cells when compared with the conventional GDL MEA.

To make the performance comparison more convincing, we compare the polarization curves and corresponding powers of the more advanced CCM MEA and the New MEA, the results are shown in Fig. S12. As shown in Figs. S12a−S12b, due to the uniform distribution of catalysts on the Na\(_{\text{fif}}\)on membrane and relatively higher Pt loading amount, the CCM MEA possesses higher peak power density than the New MEA. However, as shown in Figs. S12c−S12d, because the New MEA possesses a higher Pt utilization, the peak mass specific power of the New MEA is still about 2.5 times higher than that of the CCM MEA.

Water flooding is a common problem in the working process of MEA. To test the anti-flooding performance of New MEA in this work, the New MEA with Pt loading amount of 0.110 mg cm\(^{-2}\) is run at constant current density of 0.25 A cm\(^{-2}\) at 100% RH for 2000 s. As shown in Fig. S13, the voltage of New MEA shows a small fluctuation as the interface of the carbon paper and the Na\(_{\text{fif}}\)on-Ag/Pt membrane in MEA exists a dynamic process of exhausting water. And no obvious reducing in the power output is observed during the test, which indicates no flooding in the New MEA during working at 100% RH.

### Conclusions

This work is a successful attempt to grow hollow Ag/Pt bimetallic nanocatalyst onto Na\(_{\text{fif}}\)on membrane, for the first time, through a novel impregnation-reduction method combined with the galvanic replacement reaction between Ag and Pt ions. This method possesses mild condition and simple operation, which is highly reproducible and potential for large scale production. The successful deposition of hollow Ag/Pt NPs onto the Na\(_{\text{fif}}\)on membrane is proved by the XRD, SEM, TEM. The Pt loading amount can be regulated and the binding of Pt with the Na\(_{\text{fif}}\)on membrane is very stable. By hot-pressing it with bare carbon paper, the Na\(_{\text{fif}}\)on-Ag/Pt membrane can be manufactured into a MEA easily, which greatly reduces the difficulty of preparing a MEA. The prepared MEA exhibits a power density that is 1.2 times higher than that of the GDL MEA, meanwhile its loading amount of Pt is only 10% of that of the GDL MEA. In addition, the performance stability in fuel cells of the prepared MEA is also better than that of the GDL MEA. The prepared MEA has a certain anti-flooding capability. These experimental results demonstrate that although this novel impregnation method is nascent, but it has showed the potential to reduce the cost of fuel cells in the ways of simplifying the MEA preparation process and lowering the Pt loading amount on the MEA, which could be useful in the applications of fuel cells after being continually improved.
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