Catalysis



One-Step Fabrication of Ultralow Pt Loading High Efficiency Proton Exchange Membrane for Water Electrolysis by Conventional E-Beam Metal Deposition

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Proton exchange membrane water electrolysis (PEMWE) is known as an effective and environmental-friendly method for hydrogen production. However, the process is hindered by the necessity of large loading of high-priced noble metals in the conventional approaches. To resolve this problem, a highly efficient Nafion-based catalyst and proton exchange system are developed, which only need ultralow platinum loading by direct e-beam evaporation deposition. Scanning electron microscopy is performed before and after the deposition, which reveals a very smooth morphology. By assembling the PEMWE device with above-mentioned cathode and conventional iridium black anode, the current density reaches 500 mA cm⁻² with a platinum loading of only 0.00379 mg cm⁻² at 1.64 V under 80 °C. A mass activity of \approx 132 A mg⁻¹ is achieved, which is one order of magnitude higher than previously reported results. Moreover, powered by a commercial silicon solar cell, it realizes a solar-to-hydrogen conversion efficiency up to 8.26%. This work opens up an avenue of fabricating PEMWE with an ultralow catalyst loading, which may have enormous potential for future industrial scale applications.

1. Introduction

With the increasing energy demand globally, clean renewable energy sources, such as solar, wind, and biomasses, have attracted enormous research interests.^[1] However, due to the instability of producing cycles of aforementioned renewable energy, the challenges of energy utilization gradually shift from the generation to the storage.^[2] Hydrogen, as a zeroemission energy carrier has been considered as one of the best candidates for future energy storage.^[3] However, its production procedure has always been very energetically consuming and complicated. Moreover, when the procedure is powered

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by fossil fuel it even will inevitably create heavy pollution.^[4] To solve this problem, water electrolysis has become one of the most efficient and reliable approaches, which converts water into hydrogen directly without pollutions.^[4b,5] In general, two major low temperature water electrolysis processes have been developed: 1) alkaline water electrolysis and 2) proton exchange membrane water electrolysis (PEMWE).^[6] PEMWE is believed to have a faster response time and better dynamic behavior than alkaline water electrolysis as well as owns the higher energy density and water splitting efficiency.[3b,c,5a,7] Moreover, it also uses only pure water as reactant with the instant yielding and quick in situ separation of hydrogen (H₂) and oxygen (O_2) .^[3b,7c] Regarding the reliability and feasibility for solar panel integration, PEMWE is also highly superior to the alkaline water electrolysis.^[8] Since

the PEMWE process takes place in an acidic environment,^[6b,c,9] usually it needs plenty of noble metal catalysts against acidic corrosion (normally 0.5–1.0 mg cm⁻² in cathode for hydrogen evolution reaction (HER) and $1-3 \text{ mg cm}^{-2}$ in anode for oxygen evolution reaction (OER));^[10,11] this severely limits its large-scale industrial application.^[9b,11b,12] Currently, there are two hot spots in the research of HER catalysts. The first one is to search for nonprecious metal substitutions for the expensive noble metal catalysts.^[5d,e,13] The other one is to decrease the noble-metal catalysts loading.^[14] To lower the loading of noble metal catalysts usage, many deposition methods have been exploited including chemical-,^[15] electrochemical-reduction,^[7f,9b] atomic layer deposition (ALD),^[16] magnetron sputtering (MS),^[17] etc. Compared to wet chemistry methods, physical depositions are often superior in mass control precision, uniformity of catalyst sparsity, impurity concentration, and yielding rate.^[17c,18] For example, Grigoriev^[17c,18a] had deposited Pt and Pt-Pd nanoparticles by magnetron sputtering on various carbon carriers to lower noble metal usage. Similarly, Zhang^[17d] sputtered Pt on the liquid/gas diffusion layers achieving great catalyst mass activity. Besides, the deposited Pt on carbon nanotube and carbon paper by electron beam evaporation (e-beam evaporation) exhibits better Pt mass activity than commercial electrodes for fuel cells.^[18c,19,20]

Considering the advantages of e-beam evaporation, especially the highly precise deposition rate control (on the order of one angstrom per second), we have performed the e-beam



evaporations of extremely thin Pt films upon Nafion membranes, and achieved ultrahigh mass activity than conventional approaches. Furthermore, a photovoltaics–electrolysis (PV–E) system was constructed by a series of these fabricated PEMWE devices which was powered by a commercial silicon solar cell. This provides a novel method to prepare PEMWE devices with ultralow catalyst loading, which demonstrates a great potential contribution for solving the sustainable energy crisis.

2. Result and Discussion

Pt thin films with various thicknesses have been deposited on Nafion membranes by e-beam evaporation. The assembling processes of the membrane electrode assembly (MEA) and PEMWE device are shown in **Figure 1**a,b. In addition, the optical and scanning electron microscopy images of the Pt loaded on Nafion are shown in Figure 1c,d. In order to measure the thickness of deposited Pt on Nafion, Pt was deposited onto SiO₂ substrate parallel with the Pt deposition on Nafion simultaneously. Therefore, through measuring the height difference across the film boundaries using atomic force microscopy (AFM) the actual thickness of Pt on Nafion was determined, which is shown in Figure S1 (Supporting Information). The corresponding calculated Pt loading is shown in Table S1 (Supporting Information).

AFM has been employed to characterize the surface morphology of Nafion membrane before and after the Pt deposition

as shown in Figure 2a,b, the thickness being 6 nm. We can see that only a very slight increase of roughness was observed after the Pt deposition as indicated by the average root mean square (RMS) value increase from 2.33 nm (before) to 3.23 nm (after). This indicates the high uniformity and flatness Pt on the membrane.^[21] Figure 2c shows the XRD results of Nafion membrane with different Pt thickness samples. Almost identical XRD spectrum of Nafion membrane of without (black line) and with 6 nm Pt (red line) indicate that Pt amorphously loading on the Nafion surface.^[22,23] However, when the deposited Pt film is thicker than 30 nm, the spectrum (green line) clearly shows the Pt (111) and (200) characteristic peaks at 39.7° and 46.2°, respectively. This is a prominent feature of polycrystallization. In addition, EDS mapping is also performed on the 6 nm Pt film, verifying the evenly distribution of deposited Pt as shown in Figure 2d.

The linear sweep voltammetry (LSV) curves of PEMWEs assembled with e-beam evaporated Pt cathodes (with thicknesses ranging from 0 nm (Ir-Pt-0) to 8 nm (Ir-Pt-8)) as well as the commercial Pt/C cathodes were measured by an electrochemical workstation at room temperature, as shown in **Figure 3**. The current densities of the Ir-Pt-0, Ir-Pt-2, Ir-Pt-4, Ir-Pt-6, and Ir-Pt-8 are measured to be 2, 89, 167, 225, and 127 mA cm⁻² at 1.64 V bias voltage, respectively. This result indicates that Ir-Pt-6 possesses the best performance. As reported by Zhang,^[5a,7g] the PEMWE electrolysis performance is largely determined by the properties of tri-phase boundary of liquid gas diffusion layer, catalyst, and membrane. Thus, an



Figure 1. The schematic diagram of a) MEA (1, 5: Ti mesh, 2: carbon paper with Ti, 3: Nafion with deposited Pt, 4: carbon paper) and b) PEMWE device; c) optical photograph and d) SEM image of Pt on Nafion membrane.





Figure 2. a,b) AFM images of Nafion membrane without and with 6 nm thick Pt. c) XRD patterns of Nafion membrane with Pt (blank: pure Nafion, red: Nafion with 6 nm thick Pt, green: 30 nm thick Pt), d) EDS mapping of Pt element (green spot: Pt).

increasing performance from Ir-Pt-0 to Ir-Pt-6 was presumably a result of enhanced catalytically active surface area of the cathode while a decreasing performance from Ir-Pt-8 to Ir-Pt-8 oriented from the over blocking of membrane diffusion sites.^[21]

Next, electrochemical impedance spectroscopy (EIS) curves of the PEMWEs with different Pt loadings were obtained at 1.55 V, as shown in Figure 3b. The intersection point with *x*-axis in the high frequency represents the ohmic loss of the whole PEMWE device, including external circuit and electrodes contact resistances.^[24] No obvious ohmic loss was seen among difference samples. Commonly, two connected semicircles can be seen as shown by the Ir-Pt/C curve, the first semicircle toward the left direction of *x*-axis in the high frequency section represents the activation loss resulting from overcoming the electrode's activation barrier.^[21] The other semicircle toward the right direction of *x*-axis in low frequency



Figure 3. a) LSV curves and b) EIS curves of the MEA with different Pt thicknesses at room temperature.

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Figure 4. The a) LSV and b) EIS curves of Nafion with 6 nm thick Pt at different temperature.

section represents the mass transport loss.^[3c,7g,25] For all EIS curves, the first semicircle is very small compared to the second one for e-beam-deposited Pt cathodes which indicates a limited activation.^[7g,26] Besides, it can be seen the first semicircles of e-beam deposited Pt cathodes were always smaller than the commercial Pt/C cathode, indicating enhanced density of catalytic activations sites presumably resulting from the suppressed Pt nucleation. However, the second circles of the e-beam-deposited Pt cathodes were always larger than the commercial Pt/C cathode; this most likely results from the blocking of membrane pores which hinders the proton diffusion.^[21] By combining these effects, it can been see that the mass transport loss of Ir-Pt-6 sample is the lowest in all measured samples. This indicates that this is the right thickness of Pt as it balances the need of activation sites and avoids overblocking the diffusion channels of membrane. Moreover, the EIS curves of Ir-Pt-6 sample were tested at different cell voltages (Figure S2, Supporting Information). Mass transport loss is decreased with the increase of the applied voltage. With higher voltage, the second semicircle became more anomalous, most possibly attributed to the attachment of gas bubble on the surface.^[7c] These results have highlighted the crucial role of Pt thickness on affecting the activation and mass transport losses in the electrolysis process.

Notably, we also find that the operating temperature has a significant influence on the performance of MEAs and it

closely correlates to the reaction activation energy, membrane conductivity, and proton transport resistance.^[3c] As shown in **Figure 4**, as the temperature was increased from 20 to 80 °C, the current density of the MEA increased from 483 to 855 mA cm⁻² at the cell voltage of 1.75 V, and the slopes of the polarization curves also increased. We believe it attributes to the reduced catalytically activation barrier and increase proton transport rate.^[7d,11c] Figure 4b shows the change of the EIS curves at 1.55 V under different temperatures. There, the second arc represents the mass transport loss and it becomes much smaller at higher temperature, which indicates a faster proton transport.

Table 1 shows the detailed assembly and performance of the PEMWE devices in recently reported literatures.^[5a,9b,11c,17c,d,27,28] All current densities were measured under 1.64 ± 0.05 V bias. Also, the comparisons with this work of current density and mass activity (MA) (MA = $\frac{i_{1.64 \pm 0.05 \text{ V}}}{m}$, where *i* represents the current density and *m* represents Pt loading) have been shown in **Figure 5**.

In order to obtain the actual Pt loading of the Ir-Pt-6, inductively coupled plasma mass spectroscopy (ICP-MS) was performed. The measured Pt loading was 0.00379 mg cm⁻², as shown in Figure S4 (Supporting Information). The value is even lower than the value we calculated (0.01265 mg cm⁻²) based on the assumption that all evaporated Pt stick onto the

References	Cathode [mg cm ⁻²]	Membrane	Anode [mg cm ⁻²]	T [°C]	J at 1.64 \pm 0.05 V _{cell} [A cm ⁻²]
[5a]	Pt (0.033)	Nafion 115	IrRuOx (3)	80	0.651
[9b]	Pt300/CP (0.021)	Nafion 212	IrO ₂ /CP (0.1)	90	0.580
[11c]	Pd (0.7)	Nafion 115	RuO ₂ (1.2)	80	0.5
[17d]	Pt (0.086)	Nafion 115	IrRuOx (3)	80	0.642
[27]	Pt (0.051)	Nafion 212	IrO ₂ /CP (0.096)	90	0.374
[17c]	Pt-Pd/C (1)	Nafion 115	Ir black (1.3)	80	1
[28]	Pt (0.4)	Nafion 117	IrO ₂ (1.2)	80	1.5
This work	Pt 0.00379	Nafion 117	Ir black (2)	80	0.5

Table 1. Detailed operating conditions for every MEA in the literature.







Figure 5. a) Current densities measured at 1.64 \pm 0.05 V from this study and the literature, b) Pt mass activity from this study and the literature. [5a,9b,11c,17c,d,27,28]

membrane surface in a dense state. The thickness of ultrathin film coating layer on Nafion has rather large fluctuations which cause the rather large deviation between the calculated value and the measured values by using ICP-MS.

In Figure 5a, it clearly shows that the Ir-Pt-6 sample with almost negligible Pt amount (0.00379 mg cm⁻²) can obtain similar current density compared with these literatures and the best corresponding mass activities; the results are summarized in Figure 5b.^[5a,9b,11c,17c,d,27,28] The mass activities of Pt catalyst for HER are mostly in the range of 0.5–3 A mg⁻¹ at 1.64 \pm 0.05 V.^[9] In contrast, under the similar operating conditions, the mass activity of Ir-Pt-6 with Pt loading of 0.00379 mg cm⁻² reaches ≈132 A mg⁻¹; it is at least one order of magnitude higher than any of previously reported results. This PEMWE showing much superior mass activity proves that e-beam evaporation is a promising method of decreasing the noble metal loading for water electrolysis.

Finally, a commercial amorphous silicon solar cell was integrated with the PEMWE forming a device for hydrogen production.^[29] The *J*–*V* curve of the solar cell and the LSV curve of the device are shown in **Figure 6**a. The intersection point of *J*–*V* and linear sweep voltammetry curves denotes the operating point of integrated device,^[30] which is close to the maximum power point of the solar cell (7.22 mA cm⁻² at 1.31 V) with a solar-to-electric power conversion efficiency (PCE) of 9.46%. This intersection value with current density of 6.75 mA cm⁻² and voltage of 1.39 V gives the solar-to-hydrogen (STH) conversion efficiency around 8.26%.^[29,31,32] The current density–time curve is shown in Figure 6b, and the current density in an unbiased light-driven PEMWE is slightly lower than the operating current density because of the increase in resistance between the connecting wire and device.

3. Conclusion

A series of MEAs with different Pt loading, deposited by e-beam evaporation, were prepared for PEMWE devices. The one-step deposition fabricated low Pt loading Nafion membrane shows excellent mass activity. When Pt loading was as low as 0.00379 mg cm⁻², the MEA showed the unprecedented performance of mass activity, which is much better than any of those reported before. In addition, after integration with a commercial amorphous solar cell, the STH hits to 8.26%. It not only literally shows that this one-step e-beam evaporation is an applicable method in the preparation of cathode catalyst with ultrahigh mass activity but also sheds a bright light on finding of the completely environmental friendly approach for the hydrogen production. It carries an enormous potential for future industrial scale applications.



Figure 6. a) J-V curve of the solar cell under illumination, and the LSV curve of the PEMWE device. b) Current density-time curve of PEMWE device driven by solar cell without external bias with alternating 10 s light on-off cycles under AM 1.5 G, 100 mW cm⁻² illumination.



4. Experimental Section

Pretreatment of Nafion 117 membrane: All the chemicals were purchased without further purification before being used. Nafion 117 membranes (Hensen Corp., Shanghai, China) was pretreated by a three-step process as follows. First, the membranes were soaked into 5% H_2O_2 solution at 80 °C for 30 min. Then samples were rinsed by deionized water repeatedly to remove residual H_2O_2 . Second, these membranes were transferred into 0.5 M H_2SO_4 solution at 80 °C for 30 min, and rinsed by deionized water repeatedly after to remove the residual acid. Finally, these membranes were immersed in deionized water before the fabrication of membrane electrode assembly.

Pt Deposition by E-Beam Evaporation: An e-beam evaporator (DZS500, SKY Technology Development Co., Ltd., Shenyang, China) was used to deposit Pt. First, a Nafion membrane partially covered in SiO₂ substrate was mounted onto the e-beam evaporator stage and fixed by high-temperature vacuum tapes. The SiO₂ substrate lithography patterned, which was used to calibrate the thickness of Pt film for the subsequent calculation of Pt loading. The chamber was then pumped down around 6.6×10^{-5} Pa. Once it reached the vacuum setting, the electron gun started with the settled accelerating voltage of beam 6 kV, which gave Pt deposition rate of 0.1 Å s⁻¹. The deposition rate was monitored and controlled by a quartz crystal microbalance (QCM)-tuned PLD-controlling circuit. It guaranteed the deposition with constant set rate.

The Preparation of MEAs: The Nafion membrane, one side with Pt as cathode catalyst and the other side with iridium (Ir) black (Hensen Corp., Shanghai, China) as anode catalyst, was represented as "Ir-Pt-x" (x represents the thickness of Pt film). The control sample assembled with commercial Pt/C (20%, Aladdin, China) was indicated as "Ir-Pt/C." For all the experiments, the anode catalyst loading was about 2 mg cm⁻², and cathode catalyst loading was determined by the thickness of deposited Pt as shown in Table S1 (Supporting Information), which was calculated based on the film thicknesses and Pt density (ρ = 21.09 g cm⁻³).^[21] To prepare MEAs, the samples were sandwiched and compressed by two TGP-H-060 Toray carbon papers (TGP-H-060, Toray, Japan) using a power compressing machine (769YP-30T, Tianjin, China) under the pressure of 0.6 MPa with temperature of 120 °C for 2 min.

Characterization: The thickness of Pt on photolithography-patterned SiO₂ substrate was measured by atomic force microscope (AFM) (NX 10, Park, Korea), which was used to evaluate the thickness of the Pt on the Nafion membrane.^[21] The surface topographies of the membrane before and after the Pt deposition were also mapped with AFM. Scan electron microscope (SEM) (SU3500, Hitachi, Japan) and Energy Dispersive Spectrometer (EDS) (Model 550i, IXRF, America) were used to obtain the surface morphology and the spatial distribution of Pt. The θ -2 θ XRD spectra of Pt on membrane was recorded by a D/MAX-2500 system using Cu-K α radiation (λ = 0.154 nm) with a scan rate of 5° min⁻¹. The amount of Pt loading deposited on the Nafion 117 substrate was measured by inductively coupled plasma mass spectroscopy (ICP-MS; Agilent, 7900).

PEMWE Device Assembly: The carbon paper was used as gas diffusion layers of cathode. It was coated with 50 nm titanium (Ti) for lowering the contact resistance and protecting the anode from oxidization.^[17a] In addition, Ti mesh (100 mesh) was placed on the carbon paper as current collector. The schematic diagram of the MEA and PEMWE device are shown in Figure 1a,b, respectively.

Electrochemical Characterization: The catalytic activities of the prepared Pt catalysts deposited on the membrane by e-beam were measured in N₂-purged 1 \mbox{M} H₂SO₄ solutions through a conventional three-electrode system, which consists of Pt deposited on membrane as a working electrode, Pt wire as a counter electrode, and Ag/AgCl (3 \mbox{M} KCl) as a reference electrode. All applied potentials were converted to the reversible hydrogen electrode (RHE) scale. Cyclic voltammetry was measured to evaluate the electrochemical surface area (ECSA) at a scan rate of 0.1 V s⁻¹ at room temperature. The potential scan window was from -0.2 V to 1.2 V versus Ag/AgCl, as shown in Figure S3 (Supporting Information).

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The Performance of MEAs: The linear sweep voltammetry (LSV) curves were measured by measuring the current density when scanning the voltages from 1.2 to 2 V at interval rate of 0.02 V s⁻¹, by an electrochemical workstation (CHI 760E, CH Instruments Inc., Shanghai, China). Electrochemical impedance spectroscopy (EIS) were recorded at different voltages with frequencies range from 100 kHz to 0.1 Hz.^[7b] To measure the performance of commercial amorphous silicon solar cell, a Xenon lamp (CEL-HXF300, AuLight, China) with AM 1.5 G optical filter and optical power meter (NP2000, AuLight, China) was used to mimic the sun light (100 mW cm⁻²), and a CHI760E was used to obtain the current density–voltage (J–V) curve. Such a solar cell was then connected to the PEWME device as a power source.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

e-beam evaporation, proton exchange membrane water electrolysis, Pt mass activity, solar energy, ultralow loading

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