Vietnam Journal of Catalysis and Adsorption
Vietnam Catalyst and Adsorption Magazine

Fabrication of platinum coating on titanium transport layer for Proton exchange membrane water electrolyzer (PEMWE)

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ARTICLE INFO

ABSTRACT

Proton exchange membrane water electrolysis (PEMWE) combined with renewable energy sources such as wind, solar, geothermal provides a sustainable solution for green hydrogen production. In structure of a PEMWE, the porous transport layers (PTL) is a key component of a PEMWE. In order to meet the primary requirement of a PEM water electrolyzer, PTL should be corrosion-stable, have good electrical conductivity, and be mechanically stable for operation at differential pressures. Material porous titanium is the most typically used to construct PTL of PEMWE. However, titanium is also oxidized under the harsh conditions of PEMWE. Forming a passive layer of titanium oxide on the surface of titanium greatly reduces the conductivity of titanium. To limit these disadvantages, in this study, a thin layer of platinum was deposited onto the porous transport layers using DC plating technique. The conditions of DC plating were investigated, experimented and evaluated, from which the current density of 3 mA/cm^2 for the platinum coating has the best electrical conductivity and corrosion resistance, which contributes to reducing the precious metal content in PEMWE.

Introduction

Hydrogen is one of the most potential energy carriers because it has a high specific energy and environmentally friendly. However, hydrogen is mainly produced from fossil fuels, so when mined and used, it increases pollution levels and greenhouse gas emissions [1, 2]. Currently, the world is undergoing a rapid transition towards the use of sustainable energy conversion devices such as water electrolyzers for energy-to-gas conversion applications [3, 4]. In the near future, these electrochemical systems will be deployed worldwide, especially in areas with abundant renewable energy sources [5].

Water electrolysis is the process of using electricity to split water into hydrogen and oxygen, which can produce sustainable green hydrogen when combined with renewable energy sources such as wind and solar energy [6, 7]. Compared to traditional alkaline electrolysis, proton exchange membrane water electrolysis (PEMWE) offers advantages including high hydrogen purity, fast speed, flexibility, and a more compact design [8]. PEM water electrolyzer is mainly composed of: a catalyst-coated proton exchange membrane sandwiched between two porous transport layers (PTL) and two bipolar plates (aka flow separator plates). The anode foam transport layer is the main component of the PEM water electrolyzer which has the

function of transporting water to the anode electrode, conducting electrons and removing the oxygen generated on the anode electrode surface. In order to achieving the main requirement of PEMWE water electrolyzer, PTL must have corrosion resistance, has good electrical conductivity and mechanical strength when operating at high differential pressures [9]. Titanium-based materials with high corrosion resistance are most commonly used to fabricate PTL on the anode side due to their excellent chemical stability, good electrical conductivity, and high corrosion resistance. To apply as PTL for PEMWE, titanium material is fabricated as porous. In recent years, several teams have studied the effects of parameters such as thickness, particle size, pore diameter, or porosity of titanium-based PTLs. Grigoriev and colleagues optimized the microstructure of sintered titanium powder (porous titanium). They showed that the optimal spherical particle size of PTL titanium powder was 50÷75 μm and the optimal pore size was 12÷13 μm [10]. Normally, the anode and cathode of a PEMWE cell operate at 1.8 to 2 V(RHE) and -0.2V(RHE) respectively at current density of 1÷2 A/cm^2, and the pH value in the cell can reach 2 to 4. In such a potential and pH environment, the porous titanium PTL plate will be passivated, leading to severe degradation of the PEM aqueous electrolysis cell [11, 12]. According to the literature, the thickness of the naturally formed passive titanium layer can range from 3÷7 nm under the conditions of the electrolytic environment of PEMWE [13]. The entire surface of the titanium PTL in the PEMWE cell is covered with a layer of passive oxide (TiOx). This passive layer is very stable and durable, drastically reducing the conductivity of PTL. Therefore, PTL surface treatment such as coating with a protective layer is essential to prevent titanium components from passivation. The current common remedy is to transform the surface by different methods such as spraying, coating and plating precious metal coatings on the surface of PTL.

Rakousky, et al in their study concluded that PEMWE cells with uncoated titanium PTL at the anode had an attenuation rate of 194 μv/h at a constant current density of 2 A/cm^2 in a 1000-hour long-term test, they attributed 78% of the attenuation to an increase in ohmic resistance. The reason is that the PTL on the titanium-based anode side is passivated. However, by using the Pt coating on the PTL anode, the degradation rate drops to only 12 μv/h [14]. Gago and colleagues agglomerated Ti and then coated the Ti-Pt alloy (8 wt% Pt/Ti) on the stainless steel bipolar plate by physical vapor deposition (PVD) sputtering magnetron for the

PEM aqueous electrolysis cell, the results showed that the conductivity and corrosion resistance of the surface in contact with the coating increased. The average degradation rate is 26.5 μV/h with 200 hours durability of [15]. Another similar study of showed that PEMWE cells with a Pt coating on PTL anode were stable at a current density of 2 A/cm^2.

In this study, we used the plating method, which is a fairly simple and effective technique to create a platinum coating on the surface of the porous titanium that protects the titanium from corrosion and the formation of oxide layers, which is both highly conductive and durable and good adhesion to the porous titanium substrate. The plating conditions have been studied, tested and evaluated, thereby providing the optimal parameters for the plating process to be prepared at the platinum coating on a porous titanium substrate applied as a PTL diffuser for PEM water electrolyzers.

Experimental

Preparation platinum plating solution:

Dissolve $H_2PtCl_6.xH_2O$ in 100 ml of distilled water; dissolve 45 g of $(NH_4)_2HPO_4$ in 200 ml of distilled water; dissolve 240 g of $Na_2HPO_4.12H_2O$ in 600 ml of distilled water. Pour $(NH4)_2HPO_4$ solution into H_2PtCl_6 solution, precipitate $(NH_4)_2PtCl_6$ and platino hydrochloric acid. Pour the Na_2HPO_4 solution into this precipitate, boil the mixture until the ammonia smell is lost and the solution is light lemon yellow. Add distilled water to the 1-liter mark, adjust pH = 7 with 25% NH_4OH solution.

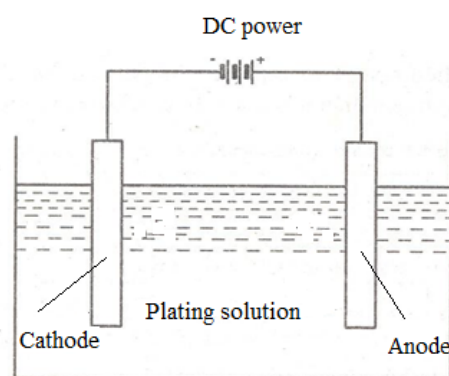### *Platinum plating process on porous titanium substrate:*

Figure 1: Electroplating diagram

Platinum plating process on a porous titanium substrate: the substrate material is Fuelcellstore's porous titanium sheet with a thickness of 1.5 mm; an average hole size of 100÷120 μm is cut into small samples of 50×10 mm. These samples are processed according to the following

steps: first, the samples are ground with sandpaper with a fineness of 100-300-600, respectively. Then degreasing in a solution containing 30 g/L NaOH; 50 g/L Na₃PO₄; 30 g/L Na₂CO₃; 5 g/L Na₂SiO₃ at 60°C for 30 minutes. The next step is chemical eatching to remove the titanium oxide layer from the surface raft: the titanium sample is eatched in a 20% HCL solution at 100°C for 5 minutes. Finally the sample is plated in the plating bath with the composition and conditions in table 1. The sample after plating is rinsed under cold water, rinsed with distilled water and then dried in a drying oven at 100°C for 30 minutes.

Table 1: Platinum plating bath components and conditions

Components and conditions	Parameter	Unit
Chemical:		
H₂PtCl₆.xH₂O	5	g/L
(NH₄)₂HPO₄	45	g/L
Na₂HPO₄ .12H₂O	240	g/L
Current Strength	1; 2; 3; 4; 5	mA/cm²
Plating time/sample	60	minute
Stirring speed	200	rpm
Plating tank temperature	65-70	°C
DC Power Supply (Uni-T-China)		
Current	10	A
Voltage	32	V
Cathode electrode	Titanium sample	
Anode electrode	MMO Electrode	

Methods for evaluating the properties of Pt/Ti plating.

Scanning electron microscopy method (SEM, HITACHI S-4800, 20 kV) to study the morphological and structural changes of the plating layer when changing the plating parameters.

The X-ray spectroscopy method (EDS, Hitachi S-4800, 20 kV potential) is used to analyze the elements and their components present in the plating layer.

Methods of anodic polarization, tafel measurement, and impedance spectra are used to evaluate the electrochemical properties of platinum plating on a titanium substrate in a 0.5 M H₂SO₄ solution. Electrochemical measurements are performed in a

three-electrode system with the opposite electrode being the platinum electrode and the comparison electrode being the Ag/AgCl electrode at room temperature with the electrochemical device used is Autolab–Nova 1.10. CV curves are scanned in the range of 0.2÷1.4 /AgCl with a potential scan rate of 50 mV/s. Anode polarization measurements are measured within 0÷1.3/AgCl around a stable potential at a potential sweep rate of 1 mV/s. Tafel measurements are measured within −0.25÷0.25 $V_{Ag/AgCl}$ around a corrosive potential at a potential sweep rate of 1 mV/s. Impedance spectra measurements are scanned from a frequency of 0.01÷1000 Hz to calculate transfer resistance R_{ct} of the coating. The conductivity and corrosion resistance of the platinum plating will be evaluated through the following parameters: total charge, I_C corrosion current density, E_C corrosion potential, R_{ct} charge transfer resistance calculated through electrochemical measurement curves.

Results and discussion

Figure 2 shows an image of a porous titanium substrate and porous titanium samples after plating platinum at different current densities. The surface of the samples shows a color change in the direction of getting darker as the current density increases. This change is due to the deposition of platinum on the titanium surface as the current density increases.
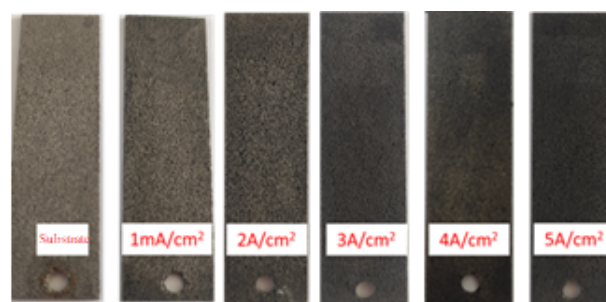

Figure 2: Photograph of Pt/Ti plating with different current densities

Figure 3a shows the surface morphology of the porous titanium and platinum plating received from different current densities. With the porous titanium subtrace surface, it can be seen that the rough surface has many pores of different sizes. When the platinum layer is plated onto the porous substrate surface, the porous surface structure has a clear change. At a current density of 1 mA/cm², spherical platinum particles begin to adhere to the sites around the pores. As the current density gradually increases, the platinum particles begin to go deep into the pores. When the current density of

3 mA/cm^2 is reached, it appears that the platinum particles have packed up on the titanium surface and the pores of the titanium substrate.
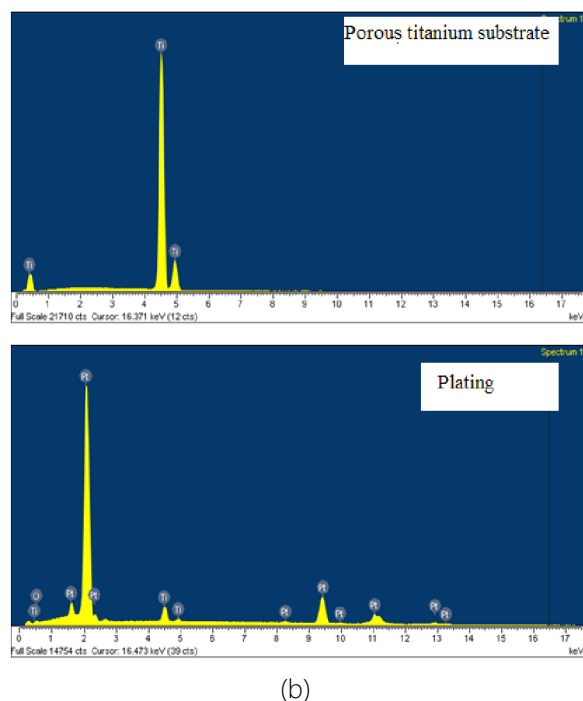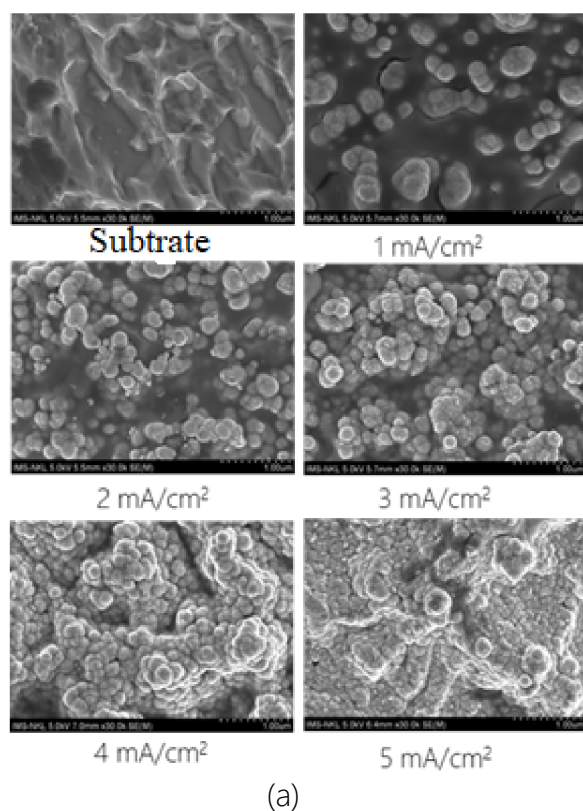

(a)

(b)

Figure 3: (a) SEM image with 30,000 times magnification of Pt/Ti plating layers with different current densities; (b) EDS spectrum of porous titanium substrate and of Pt/Ti plating

As the current density continues to increase, the platinum particles continue to cling, accumulating, and filling the porous conduction. Relatively uniform platinum plating particles range in size from 100÷300 nm and tend to be small conductors when the current density increases. Initially, it can be judged that the plating and plating tank are suitable for creating platinum plating on a titanium substrate. The appropriate current density is from 3÷4 mA/cm^2 because the plating layer at this current density is moderately thick, the platinum particles cover the pores evenly and the surface around the pores.

In order to accurately determine the formation of platinum on a porous titanium substrate after plating, EDS measurements were conducted on the sample before and after plating. Figure 3b shows that, when unplated, only titanium is represented on the EDS spectrum, when plating is formed, on the EDS spectrum, the platinum element signal has completely replaced titanium.

Figure 4a is the CV curves of the plating samples at different current densities, the total charge is calculated from the CV curves and listed in table 2.
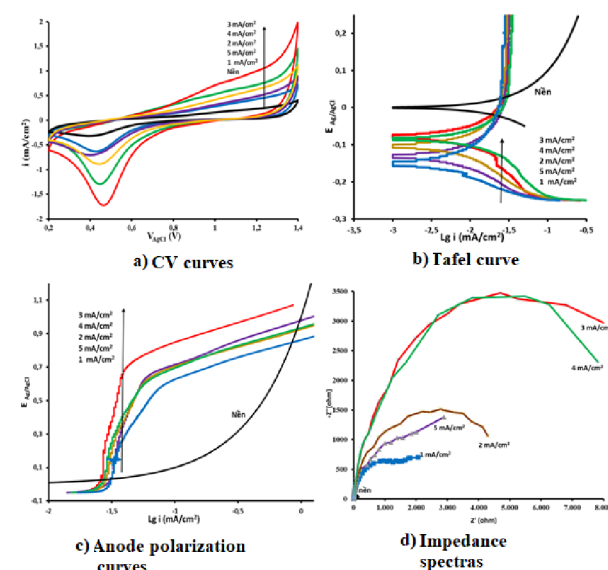

Figure 4: Electrochemical measurement results of Pt/Ti plating at different current densities measured in 0.5 M H$_2$SO$_4$ solution

The total charge value reflects the conductivity of the sample, the greater the total charge, the better the conductivity. In general, CV curves have a similar shape. The CV curve of the porous titanium substrate has the smallest area because there is always a layer of non-conductive titanium oxide on the titanium surface,

making the conductivity of the porous titanium substrate the smallest. The total charge of the plating layer gradually increases with the current density, but to the current density of 4÷5 mA/cm^2 the total charge of the plating layer gradually decreases, this may be due to the change in the structure of the plating layer, the plating particles at this current density have gradually filled the pores, causing the surface active area to decrease, leading to the conductivity of the layer plating decrease (shown on SEM). At a current density of 3 mA/cm^2, the Pt/Ti plating gives the best conductivity.

The results of tafel measurement and anode polarization curve measurement of plating samples in 0.5M H$_2$SO$_4$ solution are shown in figures 4b and 4c. The corrosion potential and corrosion current parameters calculated from these two curves are listed in Table 2. The corrosion potential datas shows that when the potential polarization is in the range of –0.25÷0.25 V$_{AgCl}$, the porous titanium substrate has the best strength (the most positive corrosion potential) due to the existence of a stable titanium oxide layer on the porous titanium surface. However, when polarizing towards the anode (Figure 4c), this titanium oxide layer being dissolved, so the porous titanium substrate has the least strength (the largest corrosion potential). As for platinum plating samples, the results are stable, the strength is the same as the conductivity measurement results, the plating samples when polarized at high voltages have a wide passivity range (from 0 ÷ 0.7 V *vs*. Ag/AgCl), and the corrosion resistance is much better than that of porous titanium substrates. Pt/Ti plating sample at a current density of 3 mA/cm^2 provide the best durability and high polarization potentials in acidic environments.

Figure 4d shows the impedance spectras of Pt/Ti plating samples at different current densities. The impedance spectra of a porous titanium substrate has a very small circular arc corresponding to the smallest value of charge transfer resistance. The impedance spectras of Pt/Ti plating samples exhibits a passive layer covering the sample surface and has a much greater resistance than porous titanium substrates. This demonstrates the very fast passive film formation of the platinum plating due to the very small plating particles adhering to the surface. The charge transfer impedance values characterize the higher corrosion resistance of the platinum plating compared to the porous titanium substrate and are consistent with the results obtained from the measurement of the anode polarity in a 0.5 M H$_2$SO$_4$ solution.

Table 2: Electrochemical parameters of Pt/Ti plating

Current density mA/cm^2	Total charge (C/cm^2/mg)	E$_{corr}$ /AgCl	i$_{corr}$ mA/cm^2	IDR Ω.cm^2
Background	0,006	-0.022	34.45	1385
1	0.010	-0.154	2.01	3699
2	0.015	-0.103	1.75	5581
3	0.025	-0.076	1.16	12250
4	0.019	-0.083	1.23	9356
5	0.012	-0.132	1.93	4579

Thus, the platinum plating on the porous titanium substrate has significantly improved the electrical conductivity and corrosion resistance of the porous titanium substrate, helping the titanium surface not to be oxidized into a passive layer that does not conduct electricity on the surface. Electrochemical measurements to evaluate the properties of the platinum plating are carried out in an acidic environment and high potential polarity, which is a simulation of the working environment in a proton exchange membrane water electrolyzer. From the data obtained, it can be seen that the current density of 3 mA/cm^2 for platinum plating is not too thick but has the best electrical conductivity and corrosion resistance, which contributes to the reduction of precious metal content in PEMWE in order to promote the commercialization of PEMWE.

Conclusion

The platinum coating on the foam titanium substrate has been successfully fabricated using the plating method. The platinum plating consists of particles of 100÷300 nm in size, which relatively evenly cover the entire surface of the porous titanium. The current density greatly affects the structure, conductivity and corrosion resistance of the plating layer. Coatings formed at current densities of 1 ÷5 mA/cm^2 all have electrical conductivity and corrosion resistance and potential polarization in acidic environments. The plating mode at a current density of 3 mA/cm^2 with a plating time of 60 minutes has the best electrical conductivity and corrosion resistance, making it suitable for the fabrication of coatings on porous titanium substrates for use as diffusion plates in proton exchange membrane electrolyzers.

Acknowledgments

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