

HIGH THROUGHPUT STUDIES OF HYDROGEN EVOLUTION ELECTROCATALYST FOR WATER ELECTROLYSIS

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Abstract

This thesis presents a study of hydrogen evolution electrocatalyst for alkaline water electrolysis. Hydrogen production through the electrolysis of water requires the development of new electrocatalysts in order to reduce the hydrogen evolution over-potential of the cathode in order to make water electrolysis more competitive and efficient. An alternative approach in the optimisation of water splitting electrocatalyst may be the modification of the metal electrocatalytic behaviour by supporting nano-particles on oxide support. Development of the electrocatalyst material for hydrogen evolution reaction in alkaline electrolyte may obtain more stable hydrogen evolution reaction.

Pt on TiO₂ electrocatalyst has been synthesized by applying high throughput Physical Vapor Deposition (HT PVD) method. Electrochemistry measurements of Pt on TiO₂ have been used to study the characteristic and stability of the electrocatalyst for hydrogen evolution reaction in alkaline electrolyte for water electrolysis. XRD confirmed that the phase of TiO₂ were amorphous and anatase after annealing for 6 hours at the temperature of 450°C. The thicknesses of TiO₂ both for amorphous and anatase were 200 nm.

Similar electrocatalytic behavior are presented both for Pt on amorphous TiO₂ and Pt on anatase TiO₂ from electrochemistry measurements using cyclic voltammetry and potential step on the 10 x 10 E-chem arrays in alkaline electrolyte (0.5 M NaOH). Higher currents are seen in the larger particle size of platinum in TiO₂ both for amorphous and anatase phase. The hydrogen evolution reaction starts at the potential below -0.8 V vs RHE. The potential for hydrogen evolution reaction is shifted to the low potential. Larger particle size of platinum shows lower potential of hydrogen evolution reaction.

Pt on TiO₂ tends to be a stable electrocatalyst for hydrogen evolution reaction in alkaline water electrolysis. It is because hydrogen evolution reaction occurs at low potential. Anatase phase of TiO₂ is more stable than amorphous TiO₂, hence, Pt on anatase TiO₂ could be better than Pt on amorphous TiO₂ for hydrogen evolution reaction in alkaline water electrolysis.

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1. Introduction

The development of electrochemical technology, e.g. fuel cells, brings contribution to a cleaner, more efficient, and more stable energy production and energy storage. This therefore can create the possibility of a cleaner environment. Chemical reactions in fuel cells involve hydrogen and oxygen from the air to produce electricity, heat, and water. Fuel cells are pollutant free because the only emission is water. Of particular interest are polymer electrolyte membrane fuel cells (PEMFCs) that promise to be the most appropriate technology for transport applications. However, PEMFCs need more development to overcome the problems related with the supply and the storage of hydrogen. Hydrogen can be obtained from water electrolysis which is a renewable source. Alkaline water electrolysis offers simplicity and easy method for hydrogen production.

Hydrogen production through the electrolysis of water requires the development of new electrocatalysts in order to reduce the hydrogen evolution over-potential of the cathode in order to make water electrolysis more competitive and efficient. Water electrolysis which is renewable hydrogen production method is commonly used to produce hydrogen for fuel cells. Direct current on water electrolysis dissociates hydrogen and oxygen from water molecules (Macsic *et al.*, 2011 and Kaninski *et al.*, 2011). Water electrolysis is suitable for the application of hydrogen fuel production and the most environmentally

friendly because water is a renewable resource (Ni *et al.*, 2007, Park *et al.*, 2006, Lee *et al.*, 2004, Galinska *et al.*, 2005, Kruger, 2000), and of course, water can be recycled.

Water electrolysis requires new electrocatalyst development for the hydrogen evolution reaction (HER) to reduce the hydrogen evolution overpotential of the cathode in the process. This will make water electrolysis more economically, competitive and efficient (Yazici, 1999 and Nikolic *et al.*, 2010). An alternative approach in the optimisation of water splitting electrocatalyst may be the modification of the metal electrocatalytic behaviour by supporting nano-particles on oxide support. Development of the electrocatalyst material for hydrogen evolution reaction in alkaline electrolyte may obtain more stable hydrogen evolution reaction.

The study of the HER may be used as the development of modern concepts of electrochemistry and it is important for electrochemical technology. Hydrogen evolution applied to this research is the cathode reaction in water electrolysis. The kinetic behavior of HER plays important role for the electrolysis efficiency, hence the performance of cathode must be considered in the research and development in this area. Combinatorial high throughput method in this research was developed to achieve higher efficiency in the research and development of catalyst synthesis.

Pt supported on the mesoporous TiO_2 is a good catalyst for the photocatalytic reaction of HER (Bamwenda *et al.*, 1997). Pt/ TiO_2 surface area influence the HER activities in alkaline electrolyte, higher surface area gives better HER activities. Pt supported on mesoporous anatase TiO_2 exhibits higher HER activity than Pt supported on bulk TiO_2 (Noel and Vasu, 1990).

HT method for this experiment was developed by Guerin and Hayden (2006) by fabricating arrays with a gradation of catalyst particle sizes in a physical vapor deposition (PVD) system while the selection of the support material occurs. Research and development in the area of high-throughput screening methodologies and combinatorial electrochemistry has been developed by many researchers and the approach can be used to identify the catalytic activity of different materials (Al-Odail *et al.*, 2010, Guerin *et al.*, 2006, Guerin and Hayden, 2006, Reddington *et al.*, 1998, Guerin *et al.*, 2004, Guerin *et al.*, 2006).

2. Research Methodology

Platinum on TiO_2 electrocatalysts were successfully synthesised by applying high throughput physical vapour deposition method. Samples were prepared by a HT-PVD (High Throughput Physical Vapor Deposition) system which allows simultaneous deposition of elements on the substrate. The substrates were silicon substrate arrays for calibration, surface and bulk characterization and microfabricated (10 x 10) electrode (electrochemical, E-chem) arrays for electrochemical screening. Titania layers were deposited at room temperature, $T = 298 \text{ K}$, on the silicon substrate using Ti (99.995%, Alfa Aesar metals) from e-gun 1 and oxygen directed to the substrate. During the process, the oxygen condition was maintained at plasma source power 300 W, oxygen plasma flow rate at 300, and oxygen pressure of $9.7 \pm 0.2 \times 10^{-6}$ torr. The chamber pressure was controlled at 3.6×10^{-6} torr. AFM measurement confirmed that the thickness of TiO_2 was 200 nm at the deposition rate 4 \AA/s for 75 minutes deposition time. Platinum was deposited on uniform titania layer at room temperature, $T = 298 \text{ K}$ and the chamber pressure was maintained at 3.6×10^{-6} torr. The deposition rate was 0.15 \AA/s at deposition times of 5 minutes.

Electrochemical measurements were carried out in 0.5 M sodium hydroxide electrolyte (NaOH) prepared using ultra-pure water (ELGA Ultrapure, $18.2 \text{ M}\Omega \text{ cm}$) and solid NaOH (GFS Chemicals, double distilled). The gases used in the experiments were Ar (BOC, 99.999%) and H_2 (BOC, 99.999%). Electrochemical measurements on the 10 x 10 electrode (E-chem) array as the working electrode were conducted using three electrode cell system, a Pt wire as counter electrode and a saturated calomel reference electrode (SCE, Cole Parmer, $+0.268 \text{ V vs SHE}$). Potentials reported here are given against the standard hydrogen electrode (SHE). Electrolyte was purged with Ar gas for 20 minutes before starting cyclic voltammetry in order to remove oxygen and dissolved gasses from the solution.

Standard conditions for recording cyclic voltammograms were to use a sweep rate of 50 mV s^{-1} and potential limits as follows: Amorphous phase: upper limit =

0.5 V , lower limit = -1.1 V , and an initial potential = -0.8 V ; Anatase phase: upper limit = 0.5 V , lower limit = -1.1 V , and an initial potential = -0.8 V . Hydrogen evolution experiments were carried out as the potential was stepped at 90s intervals from -0.8 V to -1.1 V . The data were obtained from the PC which directly installed to the measured electrochemical cell. It allowed to control and monitor the current, CV, and potential step at each electrode.

Data interpretations are done by correlating the thickness of platinum with the voltages, currents, and charges to take conclusion related with the behaviour and stability of the electrocatalyst for water electrolysis. We can conclude the stability of the electrocatalyst by analyzing the kinetic behaviour which can be seen on the relation between voltages and currents and the relation between charges and surfaces of the electrocatalyst.

3. Results And Discussion

The phase of TiO_2 were amorphous (figure 1) and anatase (figure 2), confirmed by XRD.

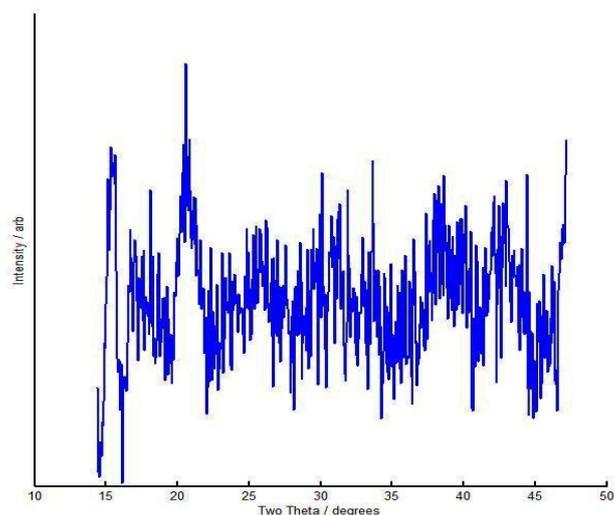


Figure 1. X-Ray Diffractogram of amorphous TiO_2

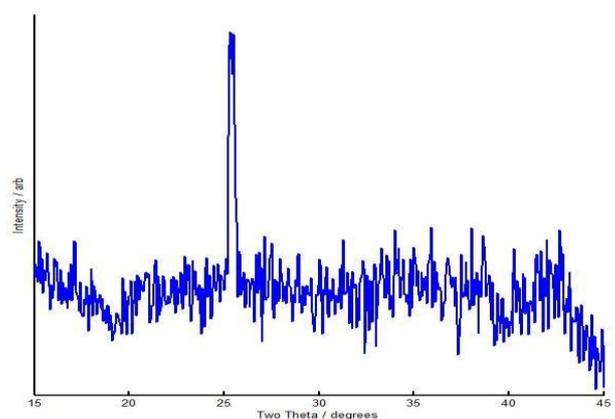


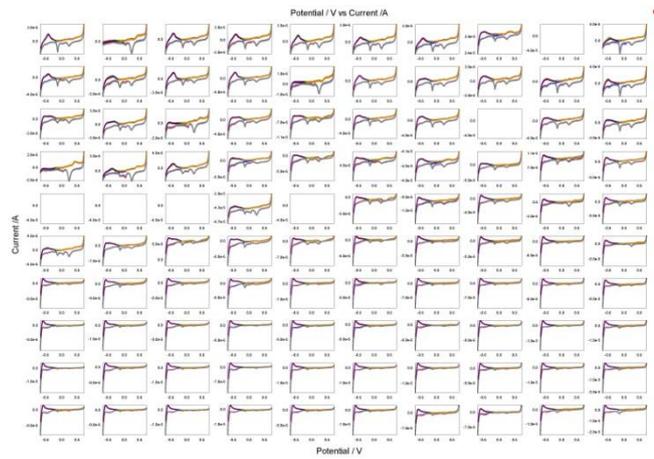
Figure 2. X-Ray Diffractogram of anatase TiO_2

Pt on amorphous and anatase TiO_2

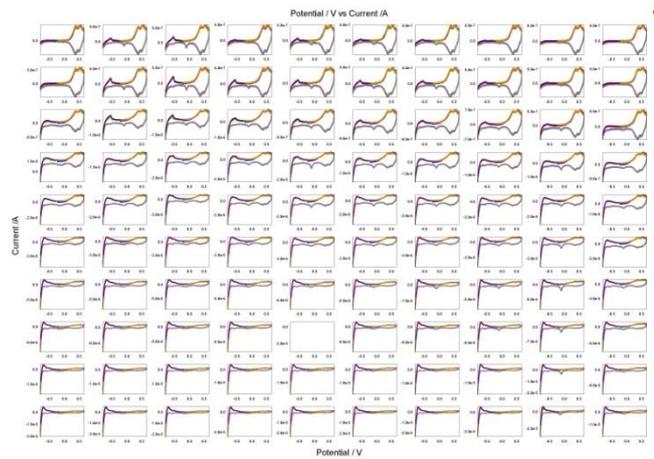
Cyclic voltammograms and potential step of 10 x 10 E-chem array of Pt on TiO_2 were carried out in argon purged

0.5 M NaOH at 25°C for both amorphous and anatase phase of TiO₂. The scan rate was 50 mV s⁻¹, the upper limit (anode limit) was 0.4 V vs SHE, the lower limit (cathode limit) was -1.1 V vs SHE, the initial potential was -0.5 V vs SHE, and the final potential was -0.5 V vs SHE. The potential was stepped at interval 90s at -0.8 V – -1.1 V vs SHE. Compared to Pt on anatase TiO₂, due to unstable amorphous phase of TiO₂, Pt on amorphous TiO₂ electrode results many bad electrodes which do not work well in the cyclic voltammetry and potential step measurements (figure 3).

The characteristics of cyclic voltammograms for Pt on amorphous TiO₂ and Pt on anatase TiO₂ are similar (figure 4). Hydrogen adsorption occurs in the negative scan between -0.45 V and -0.65 V vs SHE. Hydrogen desorption region is indicated in the negative scan of potential between -0.65 V and -0.80 V vs SHE. Kinetic performance as indicated from the current responses, higher current is seen in the hydrogen desorption process.

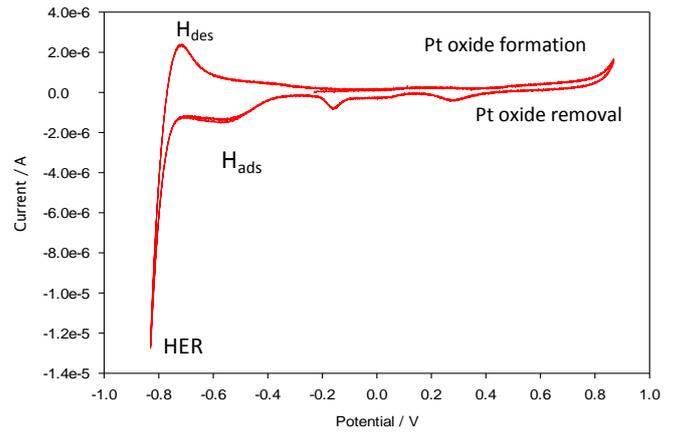


a. Pt on amorphous TiO₂

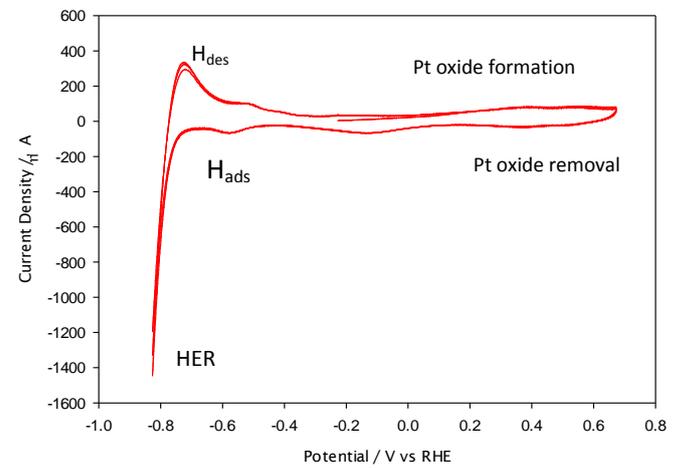


b. Pt on anatase TiO₂

Figure 3. Cyclic Voltammograms for 10 x 10 E-chem array of Pt on amorphous TiO₂ (a) and anatase TiO₂ (b) and in Ar purged 0.5 M NaOH at 25°C; increasing Pt thickness from top to bottom



a. Pt on amorphous TiO₂



b. Pt on anatase TiO₂

Figure 4. Cyclic Voltammograms of 10 x 10 E-chem array of Pt on amorphous (a) and anatase (b) TiO₂ in Ar purged 0.5 M NaOH at 25°C for electrode 1

Different particle size of platinum gives different response in cyclic voltammograms. The current increases as the particle size of platinum increases. The larger Pt particles have the higher currents. For Pt on anatase TiO₂, both large and small particle size of platinum, higher currents are seen in the hydrogen desorption formation region at the larger thickness of platinum. These trends are also applied for larger particle size of Pt on amorphous TiO₂. For small particle size of platinum, there are different trends of voltammograms for Pt on amorphous TiO₂, compared to Pt on anatase TiO₂ which have broader peak in the region of platinum oxide formation and removal than in hydrogen adsorption and desorption region. Higher currents are seen in the platinum oxide formation region. Smaller particle size of platinum has higher kinetic performance for the platinum oxide process.

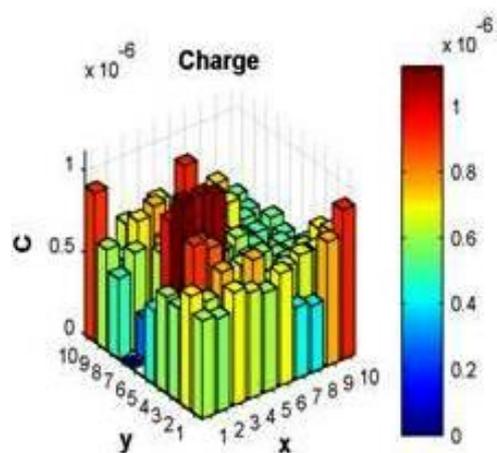
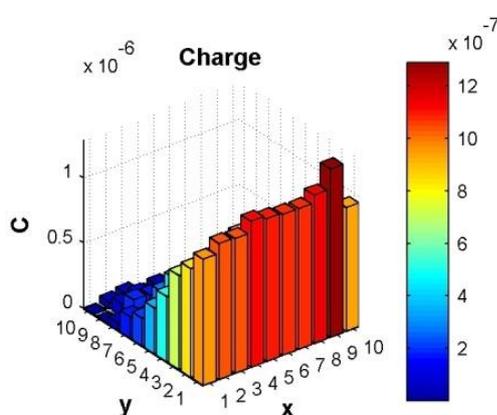
a. Pt on amorphous TiO₂b. Pt on anatase TiO₂

Figure 5. The distribution of charge of the 10 x 10 E-chem arrays of Pt on (a) amorphous TiO₂ and on (b) anatase TiO₂

The charge area of hydrogen desorption is larger than the hydrogen adsorption region. It is noted both for Pt on amorphous TiO₂ and anatase TiO₂. The peak area indicates charge of larger particle size of platinum is larger than of smaller particle size of platinum for Pt on amorphous TiO₂ and anatase TiO₂ respectively. It is differ for small particle size Pt on anatase TiO₂ which the charges are larger in the region of platinum oxide formation. These results show the evidence that the thickness of platinum gives influences on the electrocatalyst activity.

The distribution of charge on Pt deposited on amorphous TiO₂ (figure 5a) shows that the increasing platinum thickness increases the charge trends, so it increases the surface area of platinum. However, the charges are unstable due to unstable amorphous phase of titania. The distribution of charge on Pt deposited onto anatase TiO₂ (figure 5b) shows that the increasing platinum thickness increases the trend of charge, so it increases the surface area of platinum.

HER of Pt on TiO₂

a. Pt on amorphous TiO₂b. Pt on anatase TiO₂

Figure 6. Potential step of the 10 x 10 E-chem array of Pt on amorphous TiO₂ (a) and Pt on anatase TiO₂ (b); increasing Pt thickness from top to bottom

Platinum was deposited onto the amorphous and anatase TiO₂ on the 10 x 10 arrays of electrode with the thickness of TiO₂ is 200 nm both for amorphous and anatase phase, measured by AFM. The potential was stepped from -0.8 – -1.1 V vs SHE, each for 90 s to study the HER of Pt on amorphous and anatase titania. Potential steps of electrodes show the current response for the 10 x 10 array in the interval time of 90s (figure 6).

When the potential is stepped negative, -0.8 V vs SHE and further to -1.1 V vs SHE, the strong current occurs and it indicates the onset of hydrogen evolution reaction. The hydrogen evolution reaction begins approximately in potential below -0.8 V vs SHE (figure 4).

Electrodes show different characteristic of potential step for different particle size of platinum on amorphous TiO₂. As potential was stepped, larger particle size of platinum results lower current response. Larger particle size of platinum on amorphous TiO₂ results lower current responses for hydrogen evolution reaction. However, the current responses for different size of Pt on anatase TiO₂ are similar, the current responses for hydrogen evolution reaction are similar.

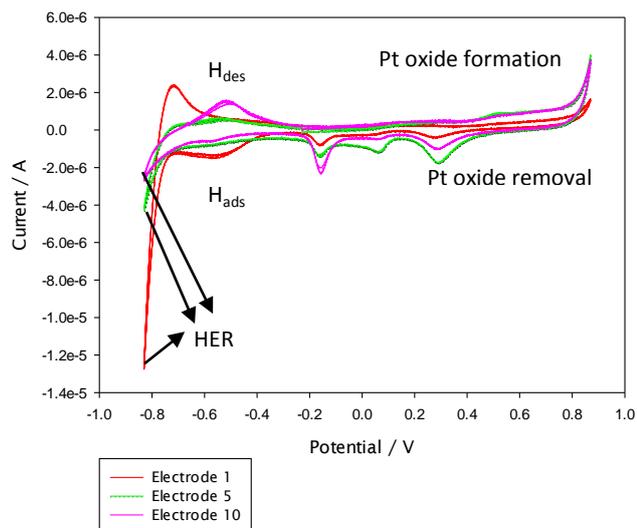
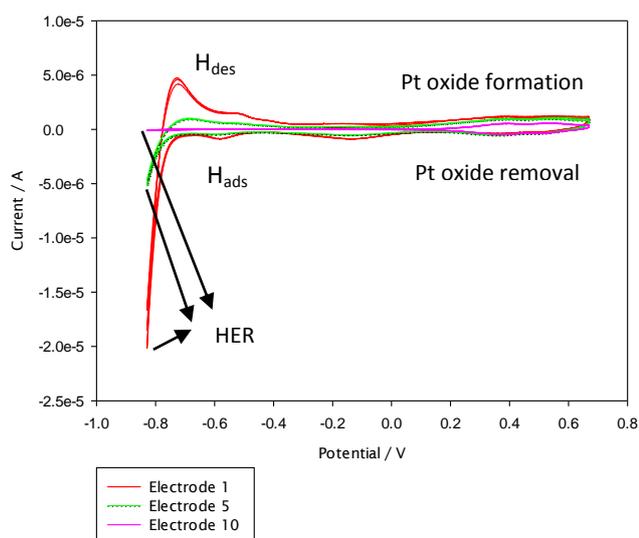
a. Pt on amorphous TiO₂b. Pt on anatase TiO₂

Figure 7. Cyclic Voltammograms of 10 x 10 E-chem array of Pt on amorphous TiO₂ in Ar purged 0.5 M NaOH at 25°C for electrode 1, 5, and 10: a. Pt on amorphous TiO₂; b. Pt on anatase TiO₂

As we can see in figure 7 for both Pt on amorphous and anatase TiO₂, the potential for HER is shifted to lower potential as the particle size of Pt increase. The larger Pt particles have lower potential for HER. Larger particles size of Pt on TiO₂ is more stable for HER on low potential for both amorphous and anatase phase of TiO₂. Based on the references (Noel and Vasu, 1990 and Cao *et al.*, 2011), Pt on TiO₂ surface area influence the HER behaviour in alkaline electrolyte, higher surface area gives better HER activities. Nanocrystallite TiO₂ increases the current density

to increase water electrolysis rate by providing a large specific surface area and suitable size.

Development of Pt on amorphous and anatase TiO₂ for the HER in alkaline water electrolysis can reduce the hydrogen evolution overpotential of the cathode in the process. Yazici (1999) and Nikolic *et al.* (2010) showed that reducing the hydrogen evolution overpotential of the cathode makes water electrolysis more economically, competitive and efficient.

4. Conclusions

After all the research activities undertaken in this thesis it can be drawn a conclusion as follows:

Pt on TiO₂ electrocatalyst tends to be a stable electrocatalyst for hydrogen evolution reaction in alkaline water electrolysis. However, the anatase phase is more stable than amorphous phase, hence, Pt on anatase TiO₂ is a better electrocatalyst than Pt on amorphous TiO₂ for hydrogen evolution reaction in alkaline water electrolysis.

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