



Effect of SnO₂ intermediate layer on performance of Ti/SnO₂/MnO₂ electrode during electrolytic-manganese process

Xin CHEN, Hua-jun GUO, Shu-liang LUO, Zhi-xing WANG, Xin-hai LI

School of Metallurgy and Environment, Central South University, Changsha 410083, China

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Abstract: SnO₂ intermediate layers were coated on the titanium (Ti) substrate by thermal decomposition. Scanning electron microscope (SEM) and X-ray diffraction (XRD) results show that uniform SnO₂ intermediate layers with rutile crystal structure were successfully achieved. According to the results of linear sweep voltammetry (LSV), oxygen evolution potential (OEP) of the Ti/SnO₂/MnO₂ electrodes decreases with increasing SnO₂ content, indicating that the electro-catalytic oxidation activity of the electrode increases. Accelerated service life tests results demonstrate that SnO₂ intermediate layer can improve the service life of the Ti/SnO₂/MnO₂ electrode. As the content of SnO₂ intermediate layer increases, the cell voltage and the energy consumption decrease apparently.

Key words: tin dioxide intermediate layer; oxygen evolution potential; accelerated service life; cell voltage, electrolytic-manganese

1 Introduction

Reducing energy consumption has been unremitting pursuit of electrolytic-manganese industry and many attempts have been carried out. Generally, reducing cell voltage and increasing current density are two effective ways to solve the problem. With increasing the current density, the current efficiency increases firstly and decreases thereafter [1]. The optimum current density is usually determined based on the deposit quality and electrodeposition time. Furthermore, the more important factor is that energy consumption closely relates to electrode materials, especially anode materials. Graphite, lead–silver alloy and titanium-coated electrode were generally used as anode materials in practical electrolytic-manganese process [2]. Graphite electrode, which shows low mechanical strength as well as short service life owing to severe oxidation, was used as anode at first. Moreover, iron mixed in graphite anode will be co-electrodeposited with manganese on cathode, decreasing the purity of manganese product and current efficiency. Lead–silver alloy electrode is a substitute for graphite electrode contributed to its stability. Unfortunately, high energy consumption is one of the

obvious shortcomings [3]. In addition, parts of lead would dissolve in the electrolyte solution, resulting in lead impurity in manganese product. Although titanium plate replaced lead–silver alloy electrode as anode due to its less energy consumption and corrosion resistance, the electrolytic manganese process cannot proceed regularly because of its serious passivation. The serious passivation leads to high cell voltage and limits its further application [4]. So, titanium substrate is usually covered by one or more metallic oxide layers, which is a pragmatic approach to prevent substrate from passivating [5–7]. SnO₂ is widely used as coating to modify titanium electrode [8,9] because of its high conductivity [10], strong combining ability, high electrocatalytic activity and oxygen evolution potential.

In this work, the main purpose is to study the effect of the SnO₂ intermediate layer on performance of Ti/SnO₂/MnO₂ electrode during the electrolytic manganese process. SnO₂ layer as an intermediate layer is mainly to improve the activity and service life of the electrode. Ti/SnO₂/MnO₂ electrodes with different contents of SnO₂ intermediate layer were prepared by thermal decomposition. The surface morphology, crystal structure and electrochemistry property were fully investigated. Meanwhile, the optimum content of SnO₂

intermediate layer was also determined.

2 Experimental

2.1 Electrode preparation

Ti substrate was firstly rubbed with fine sandpaper and degreased in 5% sodium hydroxide for 1 h, then etched in 10% oxalic acid for 1 h at 100 °C. Finally, it was rinsed with deionized water and finally dried at 60 °C.

The details of the electrodes preparation could be found in Ref. [11]. The precursor solution consisted of citric acid (CA) and ethylene glycol (EG) in molar ratio of 1:4.5, which reacted at 60 °C for 1 h. After that, $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ was added into precursor solution and kept at 90 °C for 1 h. Precursor solutions with five different molar ratios were prepared, where CA:EG: $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ was 0, 1:4.5:0.1, 1:4.5:0.21, 1:4.5:0.33, 1:4.5:0.45, respectively. Ti substrate was painted with precursor solution by brush, followed by drying at 130 °C for 10 min and heat-treating at 500 °C for 20 min. This process was repeated 10 times and the Ti/ SnO_2 electrodes were annealed at 500 °C for 1 h at the last time. After that, the Ti/ SnO_2 electrode was painted with 50% $\text{Mn}(\text{NO}_3)_2$ solution by brush and dried at 130 °C for 10 min followed by heat-treating at 500 °C for 20 min. This process was repeated 2 times and the Ti/ SnO_2 / MnO_2 electrodes were annealed at 500 °C for 1 h at the last time. Finally, Ti/ SnO_2 / MnO_2 electrodes were obtained.

2.2 Characterization and electrochemical measurements

The morphology of electrodes was observed by SEM (Sirion 200). The crystal structure of SnO_2 intermediate layer was determined by XRD (Cu K_α radiation, Rint-2000, Rigaku).

All electrochemical measurements were performed at 40 °C in a conventional three-electrode cell using an electrochemical workstation (CHI600A, Chenhua,

China). A large area 304 stainless steel plate was selected as the auxiliary electrode. The saturated calomel electrode (SCE) was used as the reference electrode. The interval distance between Ti/ SnO_2 / MnO_2 electrodes and auxiliary electrode always was 5 cm. The LSV curves were recorded from 0 to 2 V at a sweep rate of 2 mV/s.

2.3 Accelerated life test

Accelerated electrolysis was carried out with 1 mol/L H_2SO_4 solution as electrolyte, which was employed under galvanostatic electrolysis at a current density of 1 A/cm². The cell temperature was 40 °C. The 304 stainless steel plate was used as auxiliary electrode. The interval distance between Ti/ SnO_2 / MnO_2 electrode and auxiliary electrode was 1 cm. The cell voltage values were recorded in every 1 min. Electrode was defined as deactivated when the cell voltage was beyond 10 V.

2.4 Electrolysis

The electrolysis was conducted in a diaphragm cell with 300 mL electrolyte, which was placed in a thermostatic water bath to maintain the reaction temperature at 40 °C. The experimental facility for electrodeposition is presented in Fig. 1. Ti/ SnO_2 / MnO_2 electrode was employed as anode. A 304 stainless steel plate with the same dimension was used as cathode. Electrolyte solution consisted of 52.24 g/L $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, 110 g/L $(\text{NH}_4)_2\text{SO}_4$ and 0.04 g/L SeO_2 , and dissolved in deionized water. The pH value of the electrolyte solution was adjusted to 7.20 by adding dilute ammonium hydroxide. The current efficiency (η) was calculated based on the mass of manganese and manganese oxide on electrodes and the following equation:

$$\eta = \frac{m}{Iqt} \times 100\% \quad (1)$$

where m is the mass of deposits, q is electrochemical equivalent (g/(A·h)), I is the electrolysis current (A), t is the electrolysis time (h).

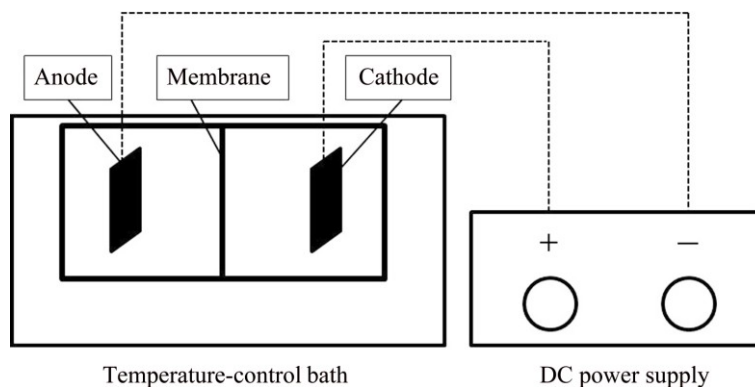


Fig. 1 Schematic diagram of experimental facility for electrodeposited manganese

3 Results and discussion

3.1 Morphology and structure of SnO₂ intermediate layers

Figure 2 shows the SEM images of the SnO₂ intermediate layers prepared from precursor solution at different mole ratios of CA:EG:SnCl₄·5H₂O. Uniform SnO₂ intermediate layers are observed on the surface of electrodes. When CA:EG:SnCl₄·5H₂O mole ratio is low, the surface of SnO₂ intermediate layer is smooth and no cracked mud is observed. However, the electrodes surface becomes more rough and a few of tiny holes appear as the CA:EG:SnCl₄·5H₂O mole ratio increases. Rough SnO₂ intermediate layers surface and tiny holes usually result in large specific surface, which could provide more active sites for electro-catalytic oxidation [12]. Furthermore, rough SnO₂ intermediate layer is in favor of combining with MnO₂ layer.

The mass of SnO₂ intermediate layers per unit area (ρ) is presented in Table 1. In addition, the MnO₂ layer is about 8 mg/mm². The mass of SnO₂ intermediate layers per unit area increases with increasing content of SnCl₄·5H₂O in the precursor solution. However, it is a little out of proportion with SnCl₄·5H₂O amount in the precursor solution due to part of SnO₂ peeling off electrode during preparation. In addition, the mass of MnO₂ layers is ten times that of SnO₂ intermediate layer on the electrode. The reason is that MnO₂ layer decomposed from manganese nitrite is loose and porous, which is in favor of adsorbing manganese nitrite.

Table 1 Mass of SnO₂ intermediate layer per unit area for electrode

x	$\rho/(\text{mg}\cdot\text{cm}^2)$
0	0
0.1	0.788
0.21	0.824
0.33	0.984
0.45	1.084

XRD patterns of the SnO₂ intermediate layers decomposed from precursor solution with different mole ratios of CA:EG:SnCl₄·5H₂O are shown in Fig. 3. The peaks at $2\theta=35.09^\circ$, 38.43° , 40.18° , 53.02° and 70.68° correspond to metallic titanium (JCPDS, No.65–3362). Clearly, several peaks at $2\theta=26.61^\circ$, 33.89° , 51.78° , 54.77° , 61.89° and 64.77° (JCPDS, No.72–1147) can be assigned well to the characteristic peaks of SnO₂ cassiterite with a rutile type structure, and these peaks become more intense with increasing the concentration of SnCl₄·5H₂O in the precursor solution. On the contrary, the characteristic peaks of metallic titanium become weaker. The results indicate that the SnO₂ intermediate layers become thicker and more compact so that they can prevent substrates from deactivating. No diffraction peak of TiO₂ was detected, so it effectively suggested that the titanium substrate was not oxidized in the process of preparation. According to the Scherrer equation, the crystalline size of SnO₂ intermediate layer with different mole ratios of CA:EG:SnCl₄·5H₂O were calculated based on the peak at $2\theta=27.44^\circ$ and their results are

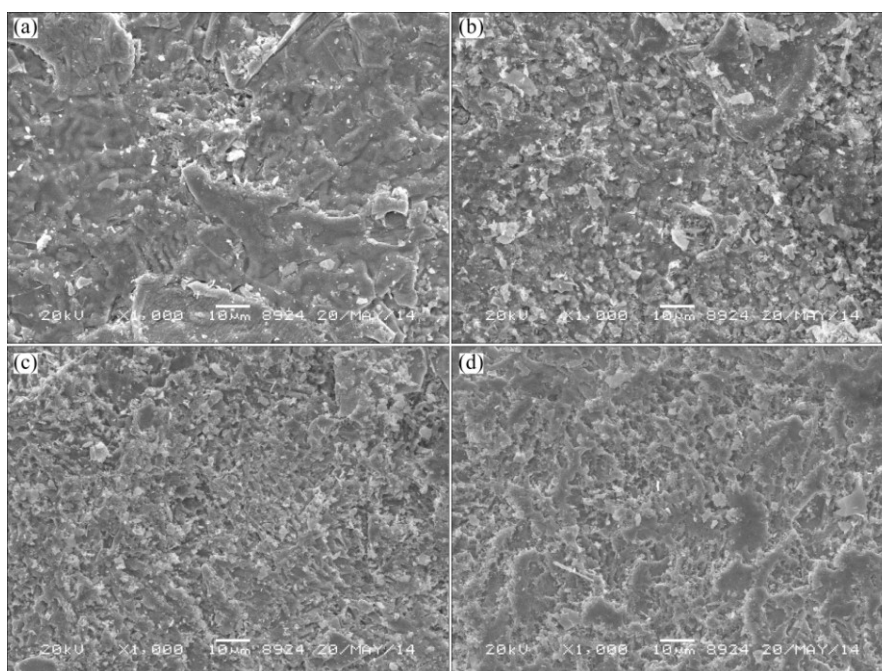


Fig. 2 SEM images of SnO₂ intermediate layer decomposed at different mole ratios of CA:EG:SnCl₄·5H₂O in precursor solution: (a) 1:4.5:0.1; (b) 1:4.5:0.21; (c) 1:4.5:0.33; (d) 1:4.5:0.45

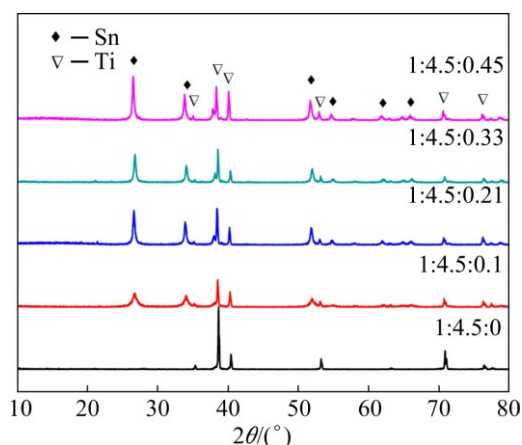


Fig. 3 XRD patterns of SnO₂ intermediate layer decomposed at different mole ratios of CA:EG:SnCl₄·5H₂O in precursor solution

shown in Table 2. When SnCl₄·5H₂O content is the lowest ($x=0.1$), the crystalline size of SnO₂ (11.4 nm) is much smaller than those of other samples. A high mole content of SnCl₄·5H₂O can facilitate the growth of grain.

Table 2 Crystalline size of SnO₂ layer

Mole ratio	Grain size/nm
1:4.5:0.10	11.4
1:4.5:0.21	32.7
1:4.5:0.33	32.1
1:4.5:0.45	34.4

3.2 Linear sweep voltammetry test

SnO₂ is an alternative electrode material for oxygen evolution [13]. For further exploring, the effects of SnO₂ content on the Ti/SnO₂/MnO₂ electrode, the linear sweep voltammetry was carried out to measure OEPs of the fresh Ti/SnO₂/MnO₂ electrodes [12]. The reaction current rises obviously on LSV curve when the potential increases above a certain value, which is marked as the oxygen evolution potential. The obviously increased reaction current corresponds to the oxygen evolution in solution. As shown in Fig. 4, the oxygen evolution current at high potential (for example, 1.75V) increases dramatically with increasing SnO₂ content in the Ti/SnO₂/MnO₂ electrode, and the OEPs for the Ti/SnO₂/MnO₂ electrode are 1.27, 1.32, 1.35, 1.39 and 1.44 V (vs SCE) respectively. Therefore, increasing the content of SnCl₄·5H₂O leads to an decrease of OEP for the electrode. This is caused by difference of the surface morphology as well as oxygen vacancies of SnO₂ crystal lattice [14,15]. Low OEP means that electrode owns good electron-catalytic oxidation performance and oxygen is easy to evolve. In other words, the higher the content of SnCl₄·5H₂O in precursor solution is, the better

the electro-catalytic oxidation performance of Ti/SnO₂/MnO₂ electrode has.

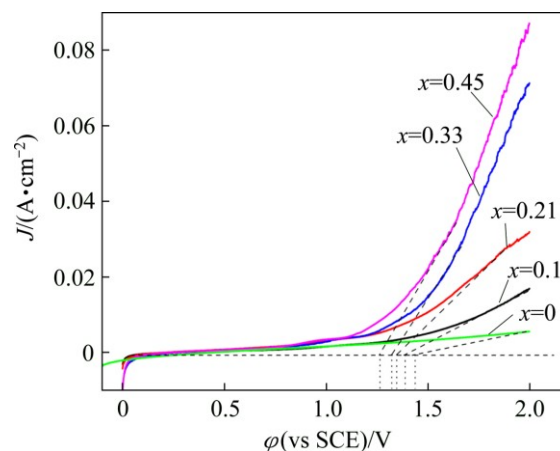


Fig. 4 Linear sweep voltammetry curves of Ti/SnO₂/MnO₂ electrodes

3.3 Accelerated life test

The electrode stability is another important parameter which determines whether the electrode could be applied in industrial scale finally [16]. A good electrode can often work effectively for a few years. The actual service life time is mainly influenced by the current density, temperature and pH of the electrolyte. Because a low current density is applied in practice, the actual service life time is usually long and difficult to evaluate. To reduce the test time, accelerated life test has been applied to evaluating electrode actual life. An empirical relationship between the accelerated service life (t_1) and the actual service life (t_2) was proposed, which could assess the actual service life of Ti/SnO₂/MnO₂ electrodes at different current densities [17].

$$t_2 = \left(\frac{J_2}{J_1} \right)^n t_1 \quad (2)$$

where n is a constant often equal to 2, J_1 is the actual current density and J_2 is the accelerated current density. The accelerated life test results and the cell voltage varied with time for Ti/SnO₂/MnO₂ electrodes are shown in Fig. 5. The accelerated service lives of Ti/SnO₂/MnO₂ electrodes are 0, 0, 3, 8 and 7 min, respectively. The accelerated service life increases obviously with increasing SnO₂ content. The cell voltage increases slowly when SnO₂ content is high. Specially, the cell voltages keep constant and the accelerated service life is the longest when the molar ratio of CA:EG:SnCl₄·5H₂O is 1:4.5:0.33. However, the cell voltage decreases when the molar ratio of CA:EG:SnCl₄·5H₂O increases to 1:4.5:0.45. It can be ascribed to the exfoliation of SnO₂ intermediate layer from the electrode during preparation. The reasons for the electrode deactivation are as follows. On one hand, the electrode surface is

corroded and washed by electrolyte solution coupled with gas bubbles. On the other hand, the more important reason is that electrolyte reacts with Ti substrate and forms a layer of passive film after permeating SnO_2 intermediate layer.

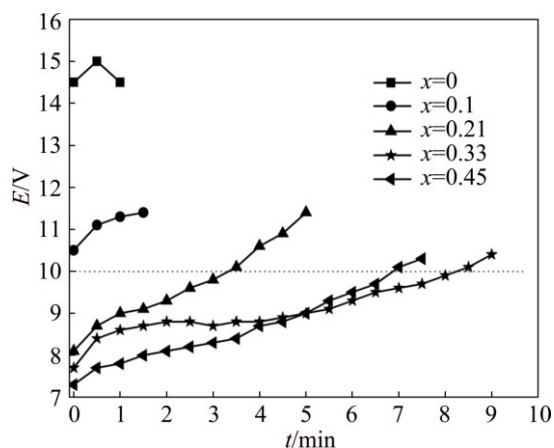


Fig. 5 Accelerated service life test on Ti/SnO₂/MnO₂ electrodes

3.4 Electrolysis

Figure 6 shows the cell voltage change of Ti/SnO₂/MnO₂ electrodes with different contents of SnO₂ intermediate layer in the process of electrolysis. Clearly, the cell voltage gradually decreases when the content of SnO₂ intermediate layers increases. The result is consistent with the trend of accelerated life test. Because the SnO₂ intermediate can effectively prevent the electrolyte solution from penetrating it. In addition, the cell voltages always go up at first and then remain constant. It could be attributed to that TiO₂ film formed on the Ti substrate [18]. As a consequence, the appropriate content of SnO₂ intermediate layer can protect the Ti substrate from passivation. Additionally, current efficiency on the anode and cathode was calculated and listed in Table 3. The results show that all the cathodic current efficiency is more than 80%, and the mass of MnO₂ on Ti/SnO₂/MnO₂ electrodes was almost

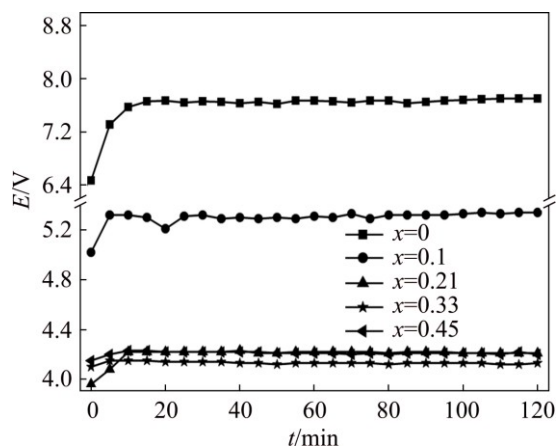


Fig. 6 Cell voltage of Ti/SnO₂/MnO₂ electrodes

similar. This suggests that the content of SnO₂ intermediate layer has little influence on anodic efficiency. After electrolysis, electrolyte solutions at anodic cell are colorless and no residue exists. MnO₂ can be regarded as raw material for lithium ion battery after further processing.

3.5 Energy consumption

The economic feasibility of Ti/SnO₂/MnO₂ electrodes as anode in electrolytic manganese industry was evaluated through the energy consumption. Energy consumption (W) can be calculated using the following equation:

$$W = \frac{1000V}{q\eta} \quad (3)$$

where V is the cell voltage (V). Energy consumption of Ti/SnO₂/MnO₂ electrodes is indicated in Fig. 7.

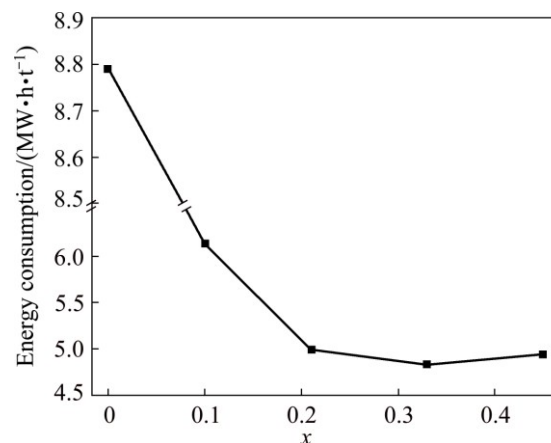


Fig. 7 Energy consumption of Ti/SnO₂/MnO₂ electrodes

It could be observed apparently that energy consumption is much higher than others if the content of $\text{SnCl}_4 \cdot \text{H}_2\text{O}$ in the precursor solution is low. Energy consumption is almost similar when the amount of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ changes from 0.21 to 0.45. Generally, energy consumption is about 6 MW·h/t in industry [19]. The results show that Ti/SnO₂/MnO₂ electrodes with appropriate content of SnO₂ intermediate layer can be used as anode in electrolytic manganese to save energy.

4 Conclusions

Ti/SnO₂/MnO₂ electrodes with different contents of SnO₂ were successfully synthesized by thermal decomposition. Oxygen evolution potentials (OEPs) of the Ti/SnO₂/MnO₂ electrodes decreases with increasing SnO₂ content. OEPs for Ti/SnO₂/MnO₂ electrodes made from different precursor solutions (CA:EG:SnCl₄·5H₂O=1:4.5:x, x=0, 0.10, 0.21, 0.33, 0.45) were 1.44, 1.39, 1.35, 1.32 and 1.27 V, respectively. SnO₂ intermediate

layer could prevent the electrode from forming the passive film, and then decreases energy consumption and extends the service life. Based on these experimental results, an optimum molar ratio of CA:EG:SnCl₄·5H₂O can be determined as 1:4.5:0.33.

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Ti/SnO₂/MnO₂ 电极的 SnO₂ 中间层对锰电解过程的影响

陈 鑫, 郭华军, 罗树亮, 王志兴, 李新海

中南大学 冶金与环境学院, 长沙 410083

摘 要: 通过热分解法在钛板表面沉积 SnO₂ 中间层。SEM 和 XRD 的结果显示得到了均匀的金红石型 SnO₂ 中间层。线性扫描结果表明, 随着 SnO₂ 中间层含量的增加, 氧气析出电势下降, 说明电极的电催化活性提高。强化寿命测试结果表明, SnO₂ 中间层可以提高电极的使用寿命。不同电极的槽电压随着 SnO₂ 含量的增加逐渐降低, 电解过程的能耗也随着 SnO₂ 含量的增加而减少。

关键词: SnO₂ 中间层; 锰电解; 析氧电位; 强化电解; 槽电压, 电解锰

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