Electrocatalytic Activity of Ti/TiO$_2$ Electrodes in H$_2$SO$_4$ Solution

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Abstract: Ti/TiO$_2$ electrodes were prepared with the polymeric precursor method (PPM). The structure and morphology of Ti/TiO$_2$ electrodes were examined with XRD and ESEM. The voltammetric charge (q^*) of Ti/TiO$_2$ electrodes as cathode in 0.5 mol/L H$_2$SO$_4$ solution was investigated with cyclic voltammetry. It was found that the electrocatalytic activity of the Ti/TiO$_2$ electrodes was affected by the structure and morphology of the Ti/TiO$_2$ electrodes, in other words, was affected by the calcination conditions of preparing the electrodes. The value of q^*_{in} was considerably larger than that of q^*_{out}, which means that the 'inner' active surface area was much larger than the 'outer' active surface area, and 'inner' active surface played a main role in the electrocatalytic activity of the Ti/TiO$_2$ electrodes.
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1   INTRODUCTION

Since the important progress had been made in the research of photoelectric solar cell using Ti/TiO$_2$ electrodes in 1991[1], Ti/TiO$_2$ has been widely studied due to its superior photochemical, photoelectrochemical properties[2,3]. Recently, some experts have attached importance to the electrocatalytic properties of Ti/TiO$_2$ electrodes as cathode because it can behave as a stable redox electron carrier, and the electrodes have been used as electrocatalyst in the reduction of organic compounds, such as *o*-nitrophenol and *o*-aminophenol[4,5]. For electrocatalysts, improving surface availability is very important, while voltammetric charge (q^*) is one of the important parameters to evaluate the electrochemical active surface area of electrodes and has played an important role in the application of the electrodes.

As a rule, q^* varies with potential scan rate (v), which is attributed to difficulties for proton exchanging along pores, cracks and grain boundaries[6]. In fact, the total charge (q^*_{tot}), related to electrochemical active surface area which depends on the number of active sites of Ti/TiO$_2$ electrodes, can be separated into two parts: q^*_{out} and q^*_{in}. q^*_{out} correlates with 'outer' region of the electrodes which is directly exposed to the electrolyte. q^*_{in} correlates with 'inner' part of the electrodes which are hidden in loose grain boundaries, pores and cracks, and reflects the region of difficult accessibility for the proton-donating species assisting the surface redox-reaction. In order to obtain the relation between electrocatalytic properties of Ti/TiO$_2$ electrodes and calcination temperatures for preparing electrodes, it is necessary to study the voltammetric charge of a set of electrodes prepared at different temperatures[7,8].

Thus, Ti/TiO$_2$ electrodes were prepared by the thermal decomposition technology with the precursor method (PPM)[9−11] at several calcination temperatures. A systematical study on the

relation between active surface area of Ti/TiO$_2$ electrodes in H$_2$SO$_4$ solution and calcination temperatures was carried out in this work.

2 EXPERIMENTAL

2.1 Preparation of Ti/TiO$_2$ Film Electrode

The polymeric precursor solution of TiO$_2$ was prepared by dissolving critic acid (CA) and tetrabutyl titanate (TDT) in ethylene glycol (EG) at 60°C, keeping at n_{CA}:n_{TDT}:n_{EG}=1:0.33:4.5(mole ratio), then the solution was heated to the reflux temperature for certain time.

The polymeric precursor solution was dipped onto Ti substrate, which was then calcined at 250°C for 10 min to improve the adherence of the film. After that it was calcined in a muffle furnace for 10 min at different calcination temperatures. This step was repeated 5 times, at the last time, the calcination time of the sample was increased to 20 min.

2.2 Determination of Microstructure and Morphology of the TiO$_2$ Film

The microstructure and morphology of Ti/TiO$_2$ film electrodes layers were examined by a Type MO3XHF22 X-ray diffractometer (XRD) and a Type XL30 environment scanning electron microscope (ESEM) respectively.

2.3 Voltammetric Charge

The cyclic voltammetric curves were measured in 0.5 mol/L H$_2$SO$_4$ solution (25°C) with a three-electrode cell: working electrode (Ti/TiO$_2$), SSE (saturated K$_2$SO$_4$/Hg$_2$SO$_4$) as the reference electrode, and platinum electrode as the auxiliary electrode. The potential was between 0.0~-1.2 V at several scan rates. The voltammetric charge (q^*) was obtained by integrating the cyclic voltammetric curves of the fifth cycle. The relation of q^*_{tot} and its components are as follows[7]:

$$q^*_{tot}=q^*_{in}+q^*_{out}, \qquad (1) \qquad\qquad q^*=q^*_{out}+k_1 v^{-1/2}, \qquad (2) \qquad\qquad q^{*-1}=q^{*-1}_{tot}+k_2 v^{1/2}, \qquad (3)$$

where q^* is the voltammetric charge obtained by integration of the voltammetric curve at a given scan rate (v) and a certain calcination temperature for preparing Ti/TiO$_2$ electrodes. q^*_{out} and q^*_{tot} can be obtained by extrapolation from Eqs.(2) and (3), then q^*_{in} can be calculated from Eq.(1). k_1, k_2 are the constants.

3 RESULTS AND DISCUSSIONS

3.1 Voltammetric Charge q^* and Crystal Structure at Different Calcination Temperatures

The cyclic voltammetric curves of the Ti/TiO$_2$ electrodes which were prepared at the calcination temperatures of 400~650°C, were measured in 0.5 mol/L H$_2$SO$_4$ solution at 25°C. The cyclic voltammetric curve of electrodes prepared at the calcination temperature of 450°C is shown in Fig.1, and the voltammetric charge (q^*) for the temperature was obtained by integrating this cyclic voltammetric curves. A series of values of voltammetric charge (q^*) at different calcination temperatures were gained by integrating the corresponding cyclic voltammetric curves.

The relation between voltammetric charge and calcination temperatures is shown in Fig.2. It was found that q^* increased with the increase of temperatures when the temperature was below 475°C and it decreased when the temperature was above 475°C.
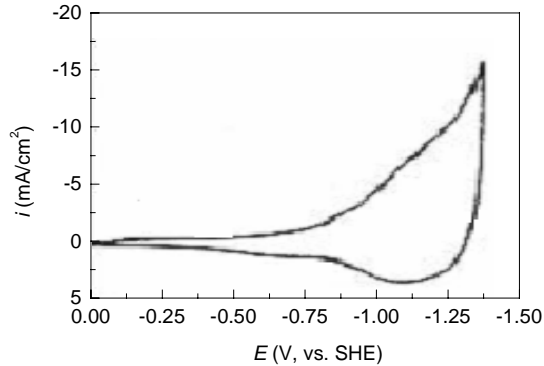
Fig.1 The cyclic voltammogram of electrode prepared
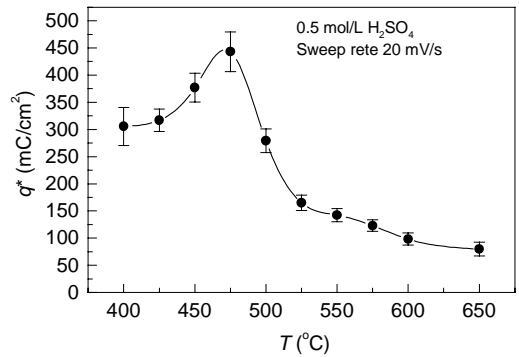at 20 mV/s and calcination temperature of 450°C

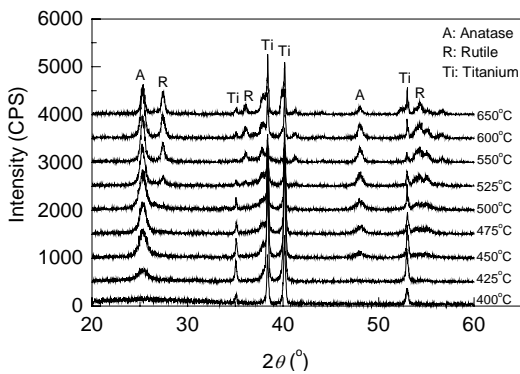Fig.2 Voltammetric charge vs. calcination
temperatures

Fig.3 XRD patterns of Ti/TiO$_2$ film at the different
calcination temperatures

Figure 3 showed the XRD patterns of TiO$_2$ film, from the analysis on the XRD patterns, it could be found that Ti standard peak could be found only at 400°C, and the standard peak of TiO$_2$ appeared at 425°C though TiO$_2$ crystal was not formed completely, indicating that 400°C was probably the lower limit of the useful temperature range for decomposition of tetrabutyl titanate. When the calcination temperature reached 475°C, the TiO$_2$ crystals were formed. Analysis of the XRD patterns showed that the TiO$_2$ crystals were of anatase below 475°C. The obvious changes could be observed from the pattern at 525°C, and a new peak appeared which represents rutile TiO$_2$. The quantity of rutile TiO$_2$ increased gradually while the quantity of anatase correspondingly decreased with increasing calcination temperatures.
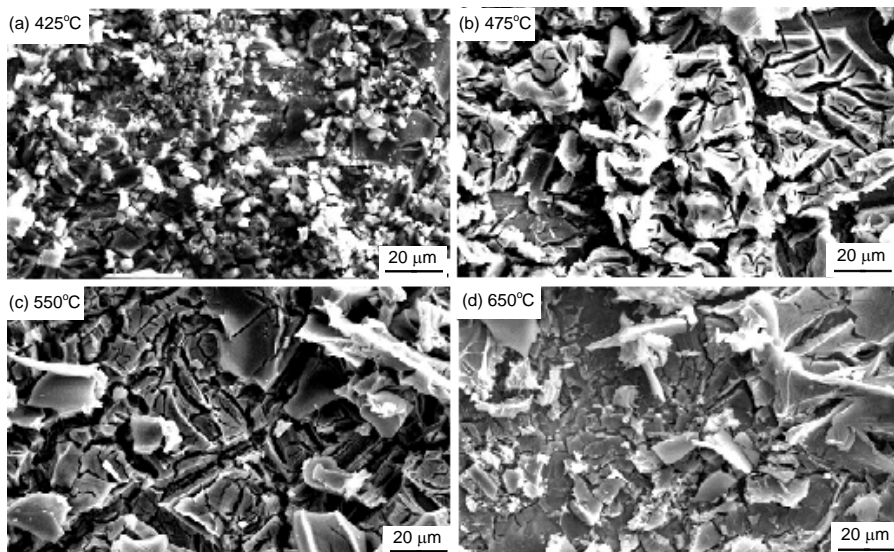

Fig.4 Surface morphology of Ti/TiO$_2$ electrode prepared at different calcination temperatures

　　The morphology of Ti/TiO$_2$ electrode, prepared at calcination temperatures of 425°C, 475°C, 550°C and 650°C, is shown in Fig.4(a)~(d). A little difference can be seen in the morphology of Ti/TiO$_2$ electrode made at several calcination temperatures.

　　From Figs.2~4, it could be found that the electrocatalytic activity of the electrodes was affected by the crystal structure and morphology of Ti/TiO$_2$ electrode. The activity of anatase TiO$_2$ was higher than that of rutile TiO$_2$, which was concordant with the literature[12,13].

3.2　Active Surface of Ti/TiO$_2$

　　A series of voltammetric charge (q^*) could be got from the cyclic voltammetric curves of Ti/TiO$_2$ electrodes at different scan rates and a certain calcination temperature. The plots of the curves of q^* vs. $v^{-1/2}$ and q^{*-1} vs. $v^{1/2}$ are respectively shown in Figs.5 and 6. According Eqs.(2), (3), the relation between q^* and v as well as q^{*-1} and $v^{1/2}$ is linear, and the result of linear regression for the data represented that the relation was indeed linear which as shown in Table 1. Extrapolating the straight line to $v^{-1/2}$=0 and to $v^{1/2}$=0 can gave q^*_{out} in Fig.5 and q_{in}^{*-1} in Fig.6.
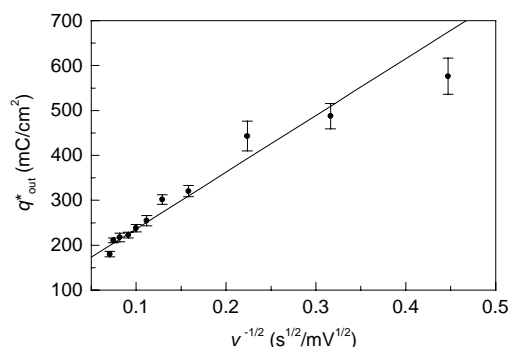

Fig.5 Typical plot of q^*_{out} at different sweep rates v for the Ti/TiO$_2$ electrode prepared at 475°C
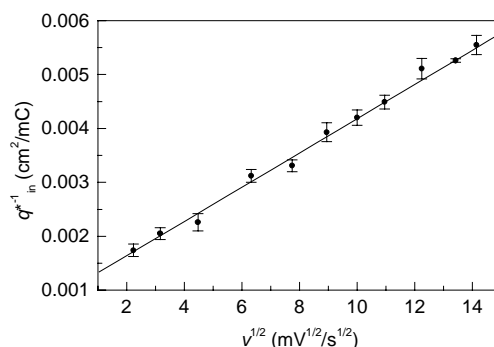

Fig.6 Typical plot q_{in}^{*-1} at different sweep rates v for the Ti/TiO$_2$ electrode prepared at 475

Table 1　Linear regression for the data of Fig.5 and Fig.6 ($Y = A + BX$)

Parameter	For the data of Fig.5		For the data of Fig.6	
	Value	Error	Value	Error
A	0.001	6.50294×10^{-5}	0.001	6.50294×10^{-5}
B	3.17528×10^{-4}	5.50163×10^{-6}	3.17528×10^{-4}	5.50163×10^{-6}
R	0.99865		0.99865	
SD	0.80093		0.80093	

　　The calcination temperatures affect the voltammetric charge, the relations between the calcination temperatures and q^*_{tot}, q^*_{in} as well as q^*_{out} in H$_2$SO$_4$ solution are shown in Fig.7. The experimental results showed that the change trends of q^*_{tot}, q^*_{in} and q^*_{out} with calcination temperatures were the same. The values of q^*_{in} were considerably larger than those of q^*_{out} at the same calcination temperatures, which means that the 'inner' active surface area was much larger than the 'outer' active surface area. In other words, the electrocatalytic activity of the electrodes was mainly affected by 'inner' active surface.

　　The relation between q^*_{in} and q^*_{out} at different calcination temperatures is shown in Fig.8. It can be seen that except for the point related to 400°C, the correlation was almost linear. The result showed that the 'inner' active surface area was in proportion to the 'outer' active surface area.
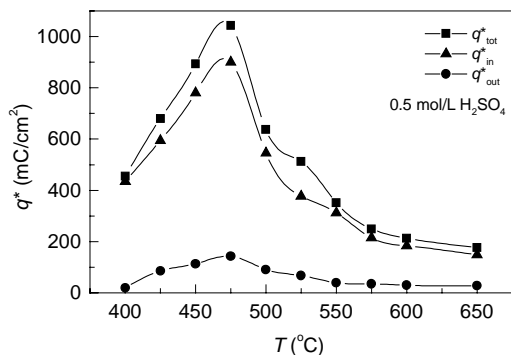
Fig.7 The charge densities related to 'total', 'inner' and 'outer' active surface of the Ti/TiO$_2$ electrode as function of calcination temperatures
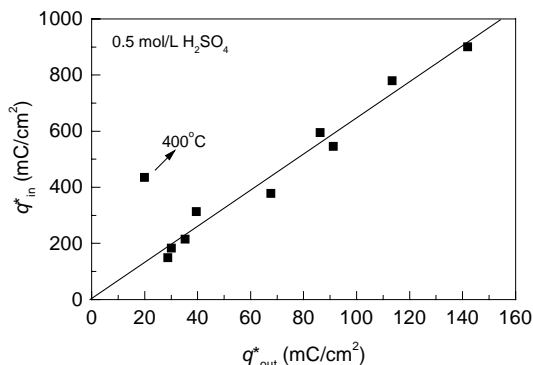
Fig.8 The relation of charge densities related to 'inner' and 'outer' active surface of the Ti/TiO$_2$ electrode

4   CONCLUTIONS

Voltammetric charge ($q*$) could characterize electrochemical active surface area of Ti/TiO$_2$ electrodes. For the electrode as cathode in H$_2$SO$_4$ solution, q^*_{in} values are considerably larger than those of q^*_{out}, which means that the 'inner' active surface area is much larger than the 'outer' active surface area, and is mainly responsible to the electrocatalytic behavior of the electrodes.

The structure of Ti/TiO$_2$ electrodes prepared below 475°C was mainly of anatase structure, and anatase TiO$_2$ changed gradually into rutile TiO$_2$ when the calcination temperature was up to 475°C, after which the active surface area began to decrease. The electrocatalytic activity of the electrodes was relevant to the structure of the crystal and morphology of the electrode surface. In other words, the electrocatalytic activity was affected by the calcination conditions of preparing the electrodes.

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