Int. J. Electrochem. Sci., 8 **(2013)** 11943 - 11950

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

TiO_2 Gel Thin Film Doped Ce and Sm Preparation and Cyclic Voltammetry Characteristics

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Received: 22 June 2013 / *Accepted:* 29 July 2013 / *Published:* 10 September 2013

TiO_2 gel films doped Ce and Sm were prepared by sol–gel methods on ITO conductive glass substrate surface with Butyltitanate($Ti(OC_4H_9)_4$),Cerium nitrate($Ce(NO_3)_3 \cdot 6H_2O$) and Samarium nitrate($Sm(NO_3)_3 \cdot 6H_2O$) as main raw materials. The Ce and Sm doping molar ratios are 0, 2%, 5% and 10% and the heat processing of film under different temperatures lasts 2 hours. Structural, thermogravimetric and electrochemical Properties were investigated by XRD, TG-DTA and Cyclic Voltammetry curves(CV).The result indicates that all prepared thin films have amorphous structure. When the doped amount of Ce and Sm is at 2%, the peak current of film reaches its maximum value with most powerful charge storage capability, injected charge density at 15.12 $mC \cdot cm^{-2}$, and cyclic reversibility K value at 0.7. When the heat processing temperature is at 250℃, the organic components in the thin film are almost completely decomposed and obtain the stable Ce and Sm doped TiO_2 gel film.

Keywords: rare earth doping, electrochromism, TiO_2 thin film, Cyclic Voltammetry

1. INTRODUCTION

TiO_2 thin film is a kind of very important functional material in electrochromic device[1], photochemical catalysis[2-3] and dye- sensitized solar battery[4-5]. The chemical doping of thin film especially the doping of rare earth element will effectively alternate the manufacturing technique and performance of thin film, which makes the study in this field become an important research direction[3,6-8].Rare earth element Ce doped TiO_2 thin film will make CeO_2 exist in the form of crystal in the thin film but most TiO_2 exists in non-crystal form[1,9]. When the Ce/Ti mole ratio is at 1:2, the optical modulation range of thin film is wide; when the Ce/Ti mole ratio is at 1:1, after lithium ion is injected, the thin film remains high transparency[3,9]. When TiO_2 thin film is doped with rare earth element Sm, it modifies the manufacturing technique of thin film but the optical modulation range of thin film is small in the process when the lithium ion is injected[10]. Currently, the study on the manufacturing of the TiO_2 thin film with joint doping of Ce and Sm in non-crystal-form and the influence on its cyclic voltammetry characteristics is less.

Taking $Ti(OC_4H_9)_4$），（$Ce(NO_3)_4 \cdot 6H_2O$）and（$Sm(NO_3)_3 \cdot 6H_2O$） as main components, it uses sol-gel method to prepare Ce and Sm Doped TiO_2 gel film on ITO conductive glass substrate surface and systematically studies the influence on TiO_2 film's cyclic voltammetry characteristics by Ce and Sm doping amount and heat processing temperature, which provides references for the study on its application in photic positive pole of solar battery, photocatalytic materials and electrochromism material.

2. EXPERIMENT

2.1 Sol Preparation

Vigorously stir certain amount of $Ti(OC_4H_9)_4$），（$Ce(NO_3)_4 \cdot 6H_2O$）and（$Sm(NO_3)_3 \cdot 6H_2O$） before drop them in ethanol solution to obtain uniform and transparent jasmine precursor solution A after 30-minute mixing. Vigorously stir the mixed solution composing of H_2O, glacial acetic acid and absolute ethyl alcohol, which goes through pH value adjustment by nitric acid, before drop it slowly at 3 drop/s into precursor solution A. Keep stirring it after mixing for 2 hours and place it aging for 10 hours to obtain jasmine TiO_2 precursory sol with different doping contents, in which the Ce and Sm doping molar ratios are 0,2%, 5% and 10%.

2.2 Thin Film Preparation

Prepare Ce and Sm doped TiO_2 gel film on ITO conductive glass substrate surface with sheet resistance at 40Ω in dip-coating method. Firstly, immerse conductive glass with acetone and ethanol, clean it with ultrasonic wave, dry it before slowing dip it in the aged sol for 15 minutes; dip the substrate at 100mm/min, place it in the oven at 80℃ for 30 minutes after 15-minute natural drying; finally, placed the filmed glass substrate in chamber electric furnace for heat processing at 150℃, 200℃, 250℃and 300 ℃for 2 hours. After the furnace cools down to room temperature, you will obtain the thin film with uniform and transparent surface and you can make it into 5mm*5mm working electrode.

2.3 Sample Characterization

Use X'Pert PRO X-ray diffractometer (Cu Kα radiographic source, voltage at 40KV, current at 40mA and wave length at 0.15405nm) manufactured by PANALYTICAL B.V. from Netherland to test the phase structure of sol powder; use DSC-7 thermal analysis instrument to test sol powder's TG-DTA curve; use CS300UA electrochemical workstation manufactured by Huazhong University of

Science and Technology to test the thin film's cyclic voltammetry curve; the test adopts the standard 3-electrode method: platinum black electrode is counter electrode, saturated calomel electrode is reference electrode and thin film sample is work electrode and the electrolyte is 1mol/L $LiClO_4$ +PC solution. In the test, the scan speed is at 50mv/s.

3. RESULT AND DISCUSSION

3.1 Structure and Thermogravimetric Analysis

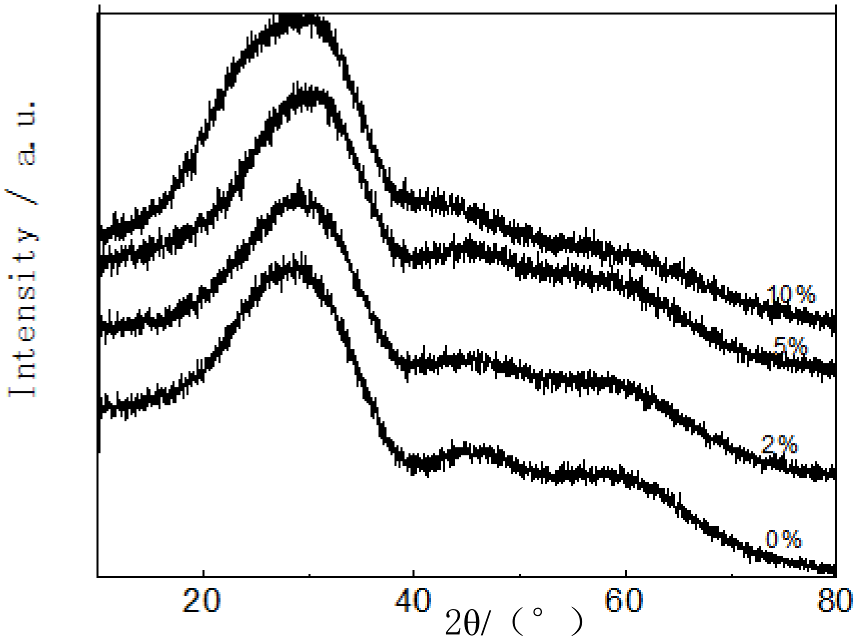

Figure 1. XRD spectra of TiO_2 powder doped Ce and Sm

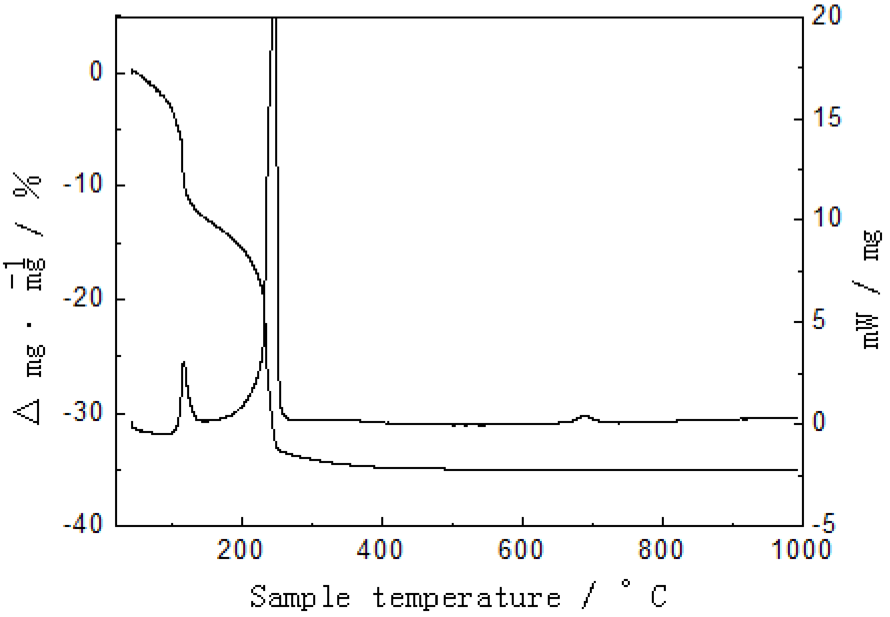

Figure 2. TG-DTA curves of TiO_2 powder doped Ce and Sm

Figure 1 is TiO_2 gel powder XRD graph with Ce and Sm doping at 0, 2%, 5% and 10% after heat processing at 300℃. We can see from Fig 1 that the prepared thin film has amorphous structure. With the increase of Ce and Sm doping content, the position of thin film's diffraction peak has slight offset with increased peak width and obviously enhanced diffraction peak intensity, which indicates that Ce and Sm doped film has higher amorphous degree in comparison with pure TiO_2 film. The research indicates that when the Ce/Ti mole ratio is at 1:1, after it goes through thermal processing at 300℃, it has obvious CeO_2 diffraction maximum (111), (200), (220) and (311)[3], which indicates that the crystallization status in the thin film is not only related to thermal processing temperature, but also related to the doping amount of CeO_2. Besides, the doping of Sm will also influence the CeO_2 crystallization performance. Nevertheless, the thermal processing temperature in this experiment is low with small doping of Ce and Sm, which makes the thin film remain in its non-crystal structure. But the non constancy of thin film is good for improving the ion storage capability[1]. Therefore, it contains the research value of preparing TiO_2 gel thin film with the doping of Ce and Sm.

Figure 2 is TiO_2 gel powder TG-DTA Curve when Ce and Sm doping at 2%. We can see form Fig 2 that the TG Curve of Ce and Sm doped TiO_2 powder can be divided into three stages: stage one from 20℃ to 116℃; in this stage, the weight loss rate is at around 11%, which mainly belongs to desorption release of the weakly absorbed water, alcohol and acetic acid in the gel; thermopositive peak at 116℃ indicates that the organic thermal decomposition has started; stage two from 116 ℃ to 246℃; in this stage, the weight loss rate is at around 33% and most of it is caused by the release of strongly absorbed water in gel network structure and the decomposition of most organics and the sharp thermopositive peak at 246℃ is mainly caused by organic thermal decomposition; stage three from 246℃ to 1000 ℃; in this stage, TG Curve is mild and almost unchanged with straight DTA Curve. Therefore, the joint doping of Ce and Sm in TiO_2 thin film will promote the decomposition of organic matter in the thin film and the function that played by Ce and Sm in it is similar with little difference[10].

3.2 Cyclic Voltammetry Characteristics Analysis

3.2.1 Influence of Ce and Sm doping content

Figure 3 is TiO_2 thin film's Cyclic Voltammetry Characteristics Curve with different Ce and Sm doping content after heat processing at 250 ℃. We can see from Fig 3 that both the positive extraction peak and negative injection peak of pure TiO_2 thin film are weak with small peak current. But the extraction peak and injection peak in Ce and Sm doped TiO_2 thin film are obviously enhanced. When the doping contents of Ce and Sm are different, the positions of positive extraction peak and negative injection peak, amount of peaks and peak current are also different.

When the Ce and Sm doping molar ratio is at 2%, the positive extraction peak is at -0.8V and negative injection peak is at -1.5V with basically same peak position in comparison with pure TiO_2 thin film without any doping. But when the Ce and Sm doping molar ratio is increased to 5% and 10%, the position of negative injection peak at -1.5V is unchanged but offset happens to positive extraction peak at -0.7V. At the same time, there is a minor negative injection peak at around -0.65V and the thin film starts expressing the characteristics of obvious double injection peaks at negative electrode.

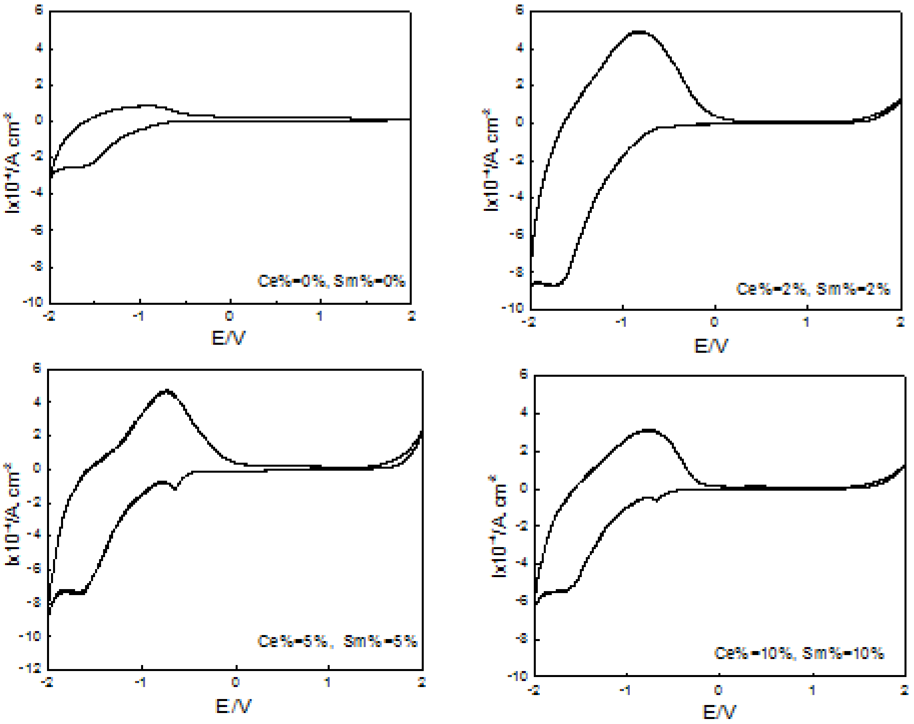

Figure 3. The CV curves of TiO_2 film doped Ce and Sm

We can also see from Fig 3 that Ce and Sm doping has obvious influence on peak current of positive extraction peak and negative injection peak of TiO_2 thin film and the peak current of TiO_2 thin film with Ce and Sm doping is as illustrated in Table 1. We can see from Table 1 that the peak current of positive extraction peak and negative injection peak of pure TiO_2 film is small, which is only at 0.08mA/cm^2 in extraction peak and is at 0.24 mA/cm^2 in injection peak; But the peak current of TiO_2 thin film with Ce and Sm doping is obviously enhanced. Besides, the influence on the peak current of TiO_2 thin film by Ce and Sm doping content expresses its rule, namely, with the increase of Ce and Sm doping content, the peak current of positive extraction peak and positive injection peak is gradually reduced. When the Ce and Sm doping molar ratio is at 2%, the peak currents reach their maximum value at 0.49mA/cm^2 and 0.91 mA/cm^2. Therefore, when the Ce and Sm doping molar ratio is at 2%, the TiO_2 film has best dynamic characteristics.

Table 1. Ce and Sm Doped TiO_2 Thin Film's Peak Current

Ce and Sm doping molar ratio/%	0	2	5	10
Peak current of positive extraction peak / (mA/cm^2)	0.08	0.49	0.46	0.31
Peak current of negative injection peak / (mA/cm^2)	0.24	0.91	0.73	0.52

Cyclic reversibility of electrochromic materials is often expressed by its K value for its quantitative description and its definition is as follows: $K=Q_{ex}/Q_{in}$， in which, Q_{ex} and Q_{in} respectively express the quantity of injected/extracted electric charges in corlering/bleaching process. When the K value approaches 1, it has better reversibility. Please refer to Table 2 for the calculating result of above-mentioned values.We can see from Table 2 that in comparison with pure TiO_2 film, in the Sm and Ce doped TiO_2 film, the Li^+ charge storage capacity is largely improved, which can reach 15.12mC/cm^2 at maximum and 10.3mC/cm^2 at minimum. Besides, the recylic reversibility of film is also obviously improved, which is increased from 0.46 to 0.7. At the same time, the principle of influence by Sm and Ce doping on TiO_2 thin film’s charge storage capacity is exactly same with above-mentioned principle of influence on peak current. Namely, the larger the Ce and Sm doping content is, the smaller the Li^+ charge storage capacity of TiO_2 film is. When the doping molar ratio is at 2%, TiO_2 film’s charge storage capacity reaches its maximum value with best recylic reversibility.

Table 2. Charge density inserted into or extracted from TiO_2 film doped Ce and Sm

Ce and Sm doping molar ratio/%	0%	2%	5%	10%
Q_{in} / (mC/cm^2)	4.95	15.12	14.34	10.3
Q_{ex} /(mC/cm^2)	2.27	10.55	9.29	7.14
K values	0.46	0.70	0.65	0.69

Above all, doping of Ce and Sm largely and obviously increases TiO_2 thin film’s peak current, charge storage capacity and recylic reversibility and it also largely improves the electrochromic performance because the doping of Ce and Sm makes the structure of regular octahedron become distorted and the thin film has higher amorphous degree, by which it provides more open spaces for the embedding of Li ions and make it easy for them to enter the crystal lattice. Nevertheless, the more the doping content is, the better the effect is, which is wrong because more and more Ce^{4+} and Sm^{3+} might be abundent in some place in the crystal lattice, which will devastate the crystal surface integrity of TiO_2 and reduce the amount of active TiO_2 phase points and reduce the Li ion injection volume. Therefore, in the process of preparing the TiO_2 film by doping Ce and Sm, it only needs small doping amount. When the doping molar ratio is at 2%, the thin film reaches its peak current with most powerful electric storage capacity and best recylic reversibility.

3.2.2 The influence by heat processing temperature

Figure 4 is the TiO_2 film’s Cyclic Voltammetry curve in different heat processing temperature when the Ce and Sm doping molar ratio is at 2%. We can see from Fig 3 that when the heat processing temperature rises, the TiO_2 thin film’s peak current gradually descends. When the heat processing temperature reaches 150℃, it has the largest current. When the heat processing temperatures reach 250℃ and 300℃, the thin film’s curves have similar appearance and similar peak current.

Table 3 is the Li^+ injection/extraction electric charge density value with calculation of K value. We can see from Table 3 that when the heat processing temperature rises, the injected and extracted electric charge's density gradually descends and the electric charge storage capability also drops with obvious increase of cyclic reversibility.

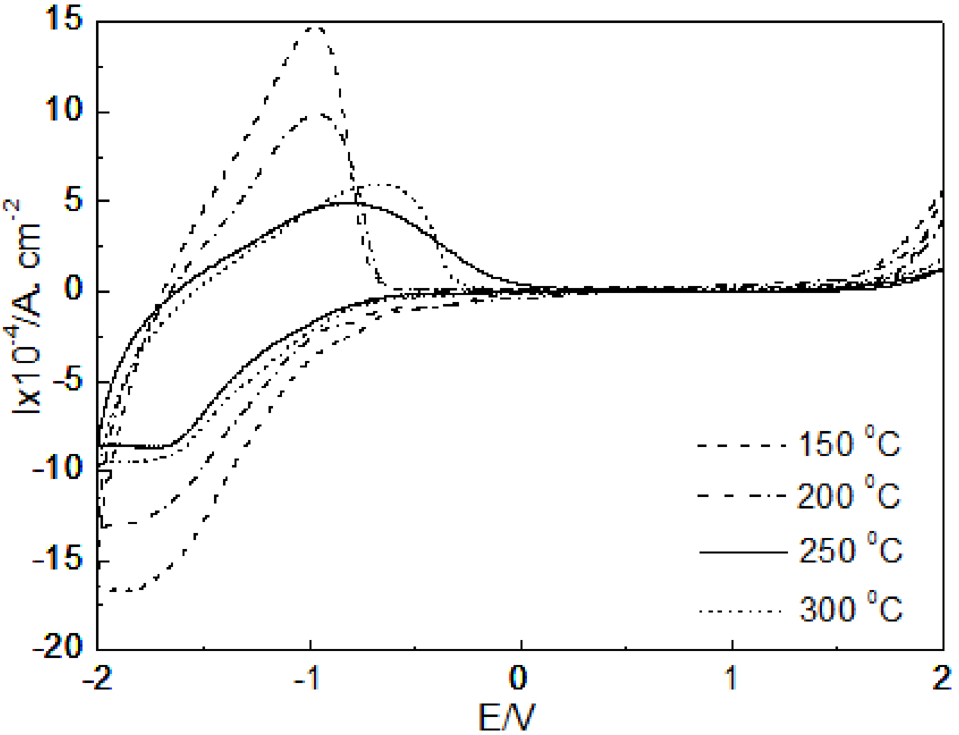

Figure 4. The CV curves of TiO_2 film doped Ce and Sm under different heat processing temperature

When the heat processing temperature reaches 150℃, the Li^+ storage capability reaches its maximum value at 26.94mC·cm^{-2} because when the heat processing temperature is at 150℃, a large amount of organic components in TiO_2 film are not decomposed and they form the frame in the thin film. Some injected Li^+ and electrons are stored in the film's organic frame in the form of Li^+ -e^- , which leads to the larger storage capacity for thin film's electric charges. But above-mentioned Li^+ have bad performance in injection/extraction cyclic reversibility with K value only at 0.52. Therefore, TiO_2 film is very unstable in this temperature. In the case that the heat processing temperature reaches 200℃, when the organic components are gradually decomposed in the film, the amount of Li^+ -e^- stored in the organic frame is reduced, which makes the electric charge storage capacity drop to 21.53 mC·cm^{-2} but with obvious increase of cyclic reversibility. In the case that the heat processing temperature reaches 250℃, electric charge storage capacity keeps dropping with K value increased to 0.7. In the case that the heat processing temperature reaches 300℃, when the organic components are almost completely decomposed in the thin film, there is no obvious change of the thin film's electric charge storage capability and cyclic reversibility, which is basically same with that in 250°C, and shares the same conclusion with the analysis of TG-DTA as mentioned above. Therefore we can draw a conclusion that the heat processing temperature for Ce and Sm doped TiO_2 thin gel film preparation should be at 250°C.

Table 3. Charge density inserted into or extracted from TiO_2 film doped Ce and Sm under different temperature

heat processing temperature /(℃)	150	200	250	300
Q_{in} /(mC/cm^2)	29.65	21.53	15.12	16.71
Q_{ex} /(mC/cm^2)	15.42	13.13	10.55	11.86
K values	0.52	0.61	0.70	0.71

4. CONCLUSION

By using sol-gel technique, it prepares Ce and Sm doped TiO_2 thin film with molar ratios at 2%, 5% and 10%, which goes through heat processing in accordance with 150℃×2h, 200℃×2h, 250℃×2h and 300℃×2h to form the amorphous TiO_2 thin film and the Cyclic Voltammetry curve test result indicates that :

(1) Ce and Sm doping increases the TiO_2 thin film's peak current, electric storage capability and cyclic reversibility: the electric storage capability is increased from 4.95mC·cm^{-2} to 10.3～15.12mC·cm^{-2} and the cyclic reversibility K value is increased from 0.46 to 0.7;

(2) The larger the Ce and Sm doping content is, the smaller the electric storage capability of TiO_2 thin film is; when the doping molar ratio is at 2%, the TiO_2 thin film has its largest electric charge storage volume with best cyclic reversibility.

(3) With the increase of heat processing temperature, the organic components in the film are gradually decomposed, the injected/extracted electric charge density gradually descends, and the cyclic reversibility is increased. When the heat processing temperature reaches 250℃, almost all organic components in the thin film are decomposed to obtain the Ce and Sm doped TiO_2 gel thin film with stable ingredients.

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