RSC Advances



View Article Online

View Journal | View Issue

PAPER



Cite this: RSC Adv., 2015, 5, 8778

The electrocatalytic activity of $IrO_2-Ta_2O_5$ anode materials and electrolyzed oxidizing water preparation and sterilization effect⁺

Zhandong Ren,* Shanshan Quan, Jie Gao, Wenyang Li, Yuchan Zhu,* Ye Liu, Bo Chai and Yourong Wang

 $Ti/IrO_2 - Ta_2O_5$ anode electrocatalysts with different contents and preparation temperatures were prepared by thermal decomposition in this work. The crystallite characterization and morphology were examined via XRD and SEM. The electrochemical properties were examined via cyclic voltammetry (CV) in $0.5 \text{ M H}_2\text{SO}_4$ and linear sweep voltammetry (LSV) in saturated sodium chloride. Through the study of different series of Ti/ $IrO_2-Ta_2O_5$ anodes, we find that the preparation conditions have a great impact on the electrode catalytic activity. Experimental results indicate that the electrochemically active surface area is determined by the content and morphology of the anode coating. When the IrO₂ content and the preparation temperature are 70% and 500 °C, the surface of the electrode is aggregated with segregated crystallite flower-like particles, which brings about the best electrode catalytic activity. The current density in the chlorine evolution reaction of $IrO_2-Ta_2O_5$ (70% and 500 °C) is 0.4 A cm⁻² in saturated sodium chloride. The properties and sterilization effect of EO water are closely related to the electrode catalytic activity. The higher the current density is in chlorine evolution, the higher the available chlorine and HClO content. When the IrO₂ content is 70% and the preparation temperature is 500 °C, the maximum values of the killing logarithm value and killing rate are 3.01-3.05 and 99.9023-99.9109%, respectively. In addition, when the Ti substrate undergoes 40 minutes of activation treatment, the Ti/IrO2-Ta2O5 anodes have the highest stability.

Received 16th November 2014 Accepted 18th December 2014

DOI: 10.1039/c4ra14671a

www.rsc.org/advances

1. Introduction

Diseases caused by food are widespread throughout the world. Food-borne diseases are the most prominent health problems in the world and are directly related to people's lives, safety and health. Therefore, new food sterilization technology which has wide adaptability, high efficiency, broad spectrum, safety and no residues is very important for the food industry. Electrolyzed oxidizing water (EO water), with low pH (2.2-2.7), high oxidation-reduction potential (ORP, >1100 mV), and an available chlorine content of 30 to 80 mg L⁻¹, has high bactericidal activity and wide adaptability against many food-borne pathogens.1 EO water has been designated as a food fungicide in Japan² and has high sterilization ability for agricultural products, including lettuce³ (Escherichia coli); carrot⁴ (aerobic bacteria, molds, yeasts); fish⁵ (Listeria monocytogenes, Morganella morganii); shrimp⁶ (Vibrio parahaemolyticus); pork⁷⁻⁹ (Escherichia coli, Listeria monocytogenes); egg¹⁰ (Salmonella enteritidis);

apple¹¹ (Escherichia coli, Listeria innocua, Salmonella choleraesuis); peanut¹² (aflatoxin B1); and cabbage² (Escherichia coli). In addition, several studies have shown that EO water can be effective in killing fungi (Candida spp.; Aspergillus spp.), blood viruses (Hepatitis B virus; hepatitis C virus; human immunodeficiency virus) and toxins (Staphylococcal enterotoxin-A; Aspergillus parasiticus aflatoxin).¹ Regarding the sterilization mechanism of EO water, there are two main theories: one is physical (high ORP and low pH),¹³⁻¹⁹ and the other is chemical (available chlorine concentration and active oxygen).²⁰⁻²⁵ Nevertheless, there is no definite conclusion about the disinfection targets of EO water for lack of authentic evidence at the molecular biological level.

EO water is generated by electrolysis of a dilute salt (NaCl) solution in an electrolysis chamber where anode and cathode electrodes are separated by a membrane. In 2005, Hsu first explored the influence of velocity, salinity and temperature on the preparation of EO water.^{26,27} However, little information concerning preparation of the electrode materials has been investigated until now.²⁸ For example, commercial electrode materials were still dominated by platinum for a long time because of its electrolysis stability. However, the performance in chlorine evolution of platinum is very poor compared with that of ruthenium (see Table S1[†] and ref. 29). Ruthenium has good activity not only for chlorine evolution in saturated sodium

School of Chemical and Environmental Engineering, Wuhan Polytechnic University, Wuhan, 430023, China. E-mail: renzhandong@163.com; zhuyuchan@163.com; Tel: +86 27 83943956

[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ra14671a

Paper

chloride solution used in the chlor-alkali industry,29-35 but also for oxygen evolution in sulfuric acid or sodium sulfate solution.³⁶⁻⁴¹ It should be noted that the chloride concentration (0.05 wt%) in EO water preparation is much lower than that in the chlor-alkali industry. Thus, a large quantity of oxygen would be produced by an evolution reaction in the electrolysis process of EO water preparation, which may result in low current efficiency. This would destroy the low-oxygen solid solution structure of the oxide electrode surface, resulting in a reduction in electrolysis efficiency and lifetime of the electrode.42-46 Iridium has a stable structure in acid medium and can effectively catalyze the oxygen evolution reaction.^{33,34,46-52} Although there are a few literature references about the chlorine evolution reaction of IrO₂ electrodes,^{47,53,54} the activity of the chlorine evolution reaction on iridium is also poor in contrast to ruthenium (see Table S1[†]). So the activity of the chlorine evolution reaction on iridium should be further enhanced and this is very important for EO water preparation. It would enhance the activity in the chlorine evolution reaction of the electrode through alloying with other metals.28

In this work, $IrO_2-Ta_2O_5$ electrocatalysts with different contents and preparation temperatures were prepared by thermal decomposition. XRD, SEM and XRF characterizations were employed to study the performance of the $IrO_2-Ta_2O_5$. The relationship between the physicochemical properties of the $IrO_2-Ta_2O_5$ electrode and its electrochemical behavior was established through cyclic voltammograms (CV) and the chlorine evolution reaction (CER). Furthermore, the values of pH, ORP, ACC and the sterilization effect of EO water using a series of $IrO_2-Ta_2O_5$ electrodes (different compositions and preparation temperatures) as anode materials has been systematically discussed in this article. In addition, the stabilities of $IrO_2-Ta_2O_5$ electrodes with different activation treatment times of the Ti substrate were also investigated for their further industrial application.

2. Materials and methods

2.1 Electrode preparation

A titanium plate of grade TA1 (1 cm \times 1 cm) was utilized as the electrode substrate, which was sandblasted, degreased in acetone and then in boiling 10% oxalic acid at 96 °C for 2 h to produce a gray surface with uniform roughness. The preparation of the titanium-based IrO2-Ta2O5-coated anode by the conventional method of thermal decomposition is described elsewhere in detail.33,47,55-57 The precursors H2IrCl6 and TaCl5 were dissolved in 1:1 volume ratio isopropanol and ethanol mixed solutions, in which the total metal concentration was kept at around 0.2 mol L^{-1} . When the mole ratios of H_2 IrCl₆ and $TaCl_5$ were 1:18, 4:12, 6:8, 7:6 and 9:2, titanium-based IrO₂-Ta₂O₅-coated anodes with nominal contents of 10%, 40%, 60%, 70% and 90% IrO_2 would be obtained. The precursors were applied with a brush to the pretreated titanium substrate, which was dried at 100 °C for 10 min in an oven, and then sintered in a furnace at 500 °C for 10 min. The above steps were repeated 10 times, with a total oxides loading of about 1.5

mg cm⁻², after which the samples were heated at the same annealing temperature for 1 h.

2.2 Material characterization

X-ray diffraction (XRD) was used to analyze the structure of the electrode coating. The inspection was carried out at room temperature on a D/Max-IIIA diffractometer (Rigaku, Japan), using Cu K_{α} radiation operating at 40 kV and 30 mA. The surface morphology of the oxide electrode was characterized by scanning electron microscopy (SEM: S-3000N, Hitachi Co., Japan). The analysis of the composition of the electrode was carried out by X-ray fluorescence (XRF: EDX-720, Shimadzu, Japan).

2.3 Electrochemical measurements

All the electrochemical measurements were carried out in a typical three-electrode electrochemical glass cell. A platinum plate was used as the counter electrode, and KCl saturated calomel electrode (SCE) as the reference. Cyclic voltammetry (CV) measurements were performed in 0.5 mol L⁻¹ H₂SO₄ solution at 25 °C with a CHI760D potentiostat. Linear sweep voltammetry measurements were performed in saturated NaCl solution. Accelerated electrolysis life tests were carried out under conditions of 0.5 mol L⁻¹ H₂SO₄ solution, 2 A cm⁻² anodic current density, Ti plate as counter electrode and temperature 40 °C. For electrochemical tests, the surface of the specimen was covered with epoxy resin except for the working area (1 cm²) on one side.

2.4 Preparation and analysis of EO water

The generation of EO water involved electrolysis of NaCl in a three-compartment cell containing inert positively charged and negatively charged electrodes separated by an anion membrane and a cation membrane as shown in Fig. 1. The anode was $IrO_2-Ta_2O_5$ and the cathode was titanium plate. A salt solution (0.5 wt% NaCl) was pumped into the EO water generator. The current densities were 40 mA cm⁻² and 160 mA cm⁻² and the electrode distance was 2 cm. Two types of water possessing different characteristics were generated: electrolyzed oxidizing water (pH < 2.6, ORP > 1100 mV) containing dilute hypochlorous acid (HOCl) was produced from the anode side with approximately 20–200 mg L⁻¹ free chlorine, and electrolyzed reduced water (pH > 11, ORP < -795 mV) containing dilute NaOH was produced by the cathode.

The values of pH and ORP were analyzed by a pH meter (3-Star, Thermo Orion). The concentration of total active chlorine dissolved in the solution was determined using the TMB (3,3',5,5'-tetramethylbenzidine) colorimetric method. In this method, TMB was oxidized to form a yellow product and its concentration was analyzed immediately using a spectrophotometer (UV-2102PC, UNICO, US) at 450 nm. The content of HClO was measured directly by a spectrophotometer at 233 nm, where the absorption coefficient ε was 100.⁵⁸ These were measured three times and the average values were obtained.



Fig. 1 Schematic representation of the electrolyzed oxidizing water preparation, detection and sterilization.

2.5 Bactericidal effect of EO water

Bacillus subtilis var. *niger* (ATCC 9372) (purchased from China General Microbiological Culture Collection Center) was employed as an indicator bacterium in all disinfection experiments. The initial population of *B. subtilis* for each disinfection experiment was approximately 7.53 log CFU mL⁻¹. During the experiments, 1.0 mL bacteria suspension was mixed with 9.0 mL EO water in a sterile tube and was immediately quenched with excess $Na_2S_2O_3$ (10 mmol L⁻¹) to eliminate residual disinfectants in the sample solution after 30 min.

The survival of *B. subtilis* was determined by the colony counting method using a tryptic soy agar (TSA) plate with serial dilutions in Butterfield's phosphate buffer (pH 7.2–7.4). To prepare the counting plate, 1 mL of each appropriate dilution of *B. subtilis* culture was mixed carefully with 15 mL TSA at 45–47 °C and then transferred into a Petri dish at ambient temperature for solidification. After complete solidification, an overlay adding 5 mL to 10 mL VRBL was poured onto the surface of the inoculated medium. The plates were incubated at 35 °C for 48 h and the colonies formed on the plates were counted. Significant differences between treatments were established at a significance level of p = 0.05.

3. Results and discussion

3.1 Composition analysis of IrO₂-Ta₂O₅

The actual compositions of the oxide electrodes with different proportions and preparation temperatures were examined by XRF and the results are listed in Table S2.† The majority of electrode actual compositions are consistent with the nominal compositions, such as 60% (450 °C), 70% (450 °C, 500 °C, 550 °C, 650 °C) and 90% (450 °C). However, for the 10% sample, there is a large deviation between the actual composition and the nominal composition. A possible reason is that when the

content of $TaCl_5$ is too high, hydrolysis of $TaCl_5$ will easily occur due to its unstable nature and reduce the content of $TaCl_5$ in a solid solution.

3.2 Effect of IrO₂ content on surface morphology

Since the kinetics of the chlorine evolution reaction is very fast, the main active site is the outer surface. In order to improve the catalytic activity of a chlorine electrocatalyst it is necessary to specifically increase the outer surface area. So the surface morphology plays an important role in the chlorine gas-evolving catalysis reaction. As can be seen from Fig. 2, dried-mud cracks appear in all the samples as a result of the sintering process, which is quite typical for oxide electrodes. The reasons are the quick volatilization of organic solvents and the stress caused by different coefficients of thermal expansion between the substrate and the coatings. But the surface morphologies are different with varying IrO2 content in the coating. It can be seen that there are islands separated by wide and deep cracks and a few crystallite particles in Ti/IrO2-Ta2O5 anodes with 10% IrO2 in Fig. 2a. In Fig. 2b, it is found that the cracks become fewer and narrower in comparison with the sample in Fig. 2a, while there are some large IrO2 crystallite particles with average sizes about 20-30 nm. As for Ti/IrO2-Ta2O5 anodes with 60% and 70% IrO₂ (Fig. 2c and d), the surfaces of the anodes are covered by more and more fine crystal particles in flower-like agglomerates which tend to connect to form networks without cracks. In addition, the film thickness is about 150 µm from a crosssection SEM of a 70% IrO₂ anode in Fig. 2f and the oxide crystals are lined up tightly. However, it was found that the crystallite particles disappeared and dried-mud cracks appeared again in Ti/IrO₂-Ta₂O₅ anodes with 90% IrO₂ in Fig. 2e, which indicates that IrO₂ crystallite agglomerates emerged when the content of IrO2 was too high. So the existence of proper quantities of Ta₂O₅ modification in the coating results in a typical



Fig. 2 SEM images for Ti/ IrO_2 -Ta₂O₅ anodes with (a) 10% IrO_2 , (b) 40% IrO_2 , (c) 60% IrO_2 , (d) 70% IrO_2 , (e) 90% IrO_2 , (f) a cross-section of 70% IrO_2 .

morphology of the oxide solid solution, which features driedmud cracks, networks and fine crystal particles.

This deduction has been confirmed by XRD curves as shown in Fig. 3. The resulting peak positions and intensities were compared with the JCPDS reference files for IrO₂ (no. 15-870), Ta₂O₅ (no. 25-0922) and Ti (no. 44-1294). There is no evident diffraction peak of Ta₂O₅ in any XRD curve except 10% IrO_2 , which indicates that crystallization of Ta_2O_5 is restrained by the existence of IrO₂. The obvious diffraction peaks of β -Ta₂O₅ (22.8°, 28.7°, 36.8°) only appear in the 10% IrO₂ coating, although their intensities are not very strong. IrO2 rutile began to appear in 40% IrO2 films and the peaks of β -Ta₂O₅ had disappeared. As the IrO₂ content reaches 60%, the crystallite phase in the mixture exists entirely as a rutile phase with 110 (27.9°) and 101 (34.6°) crystals. This result indicates that crystallization of Ta_2O_5 is affected by the IrO₂ component. The intensity of the diffraction peaks of IrO₂ appears to increase at high IrO2 concentrations (60%, 70% and 90%), which means that aggregation of IrO₂ crystallites occurs with increasing content of IrO2 in the coating. In addition, diffraction peaks corresponding to the Ti support are also observed but no TiO₂ is detected. Ti peaks may arise from the penetration of X-rays reaching the substrate in some thin areas and/or diffusion into the coating from the substrate during the thermal preparation.33 SEM observation, together with XRD results, indicates that the composition plays a vital role in determining the surface morphology and structure.



Fig. 3 X-ray diffraction curves for Ti/IrO₂-Ta₂O₅ anodes with (a) 10% IrO₂, (b) 40% IrO₂, (c) 60% IrO₂, (d) 70% IrO₂, (e) 90% IrO₂.

3.3 Effect of IrO₂ content on electrocatalytic activity

Cyclic voltammograms of Ti/IrO₂–Ta₂O₅ anodes with different contents of IrO₂ recorded at a potential scan rate of 20 mV s⁻¹ in 0.5 mol L⁻¹ H₂SO₄ solution are shown in Fig. 4. The anodes with different IrO₂ contents exhibit voltammograms typical of oxide electrodes with pseudocapacitive behavior, while the electrochemical response is typical of a capacitor, exhibiting accurately rectangular mirror images and rapid reversals of the direction of the response current. The process of charge and discharge of IrO₂ is as follows: IrO_a(OH)_b \leftrightarrow IrO_(a+ δ)(OH)_(b- δ) + δ H⁺ + δ e⁻. When the potential was higher than 0.2 V, the process of OH adsorption and further oxidation with oxygen species began. In the cyclic voltammetric curves, the peak at 0.69 V (*vs.* SCE)



Fig. 4 Cyclic voltammograms of Ti/IrO₂-Ta₂O₅ anodes with different contents of IrO₂ in 0.5 mol L^{-1} H₂SO₄ solution at a sweeping rate of 20 mV s⁻¹.

corresponds to the conversion of Ir(III)/Ir(IV) and the conversion of Ir(IV)/Ir(V) or Ir(IV)/Ir(VI) is 1.0 V (vs. SCE).^{30,47,57,59} Regarding the Ir(III)/Ir(IV) transformation, a = 1, b = 1, $\delta = 1$; for the Ir(IV)/Ir(V) transformation, a = 1, b = 2, $\delta = 1$; for the Ir(IV)/Ir(VI) transformation, a = 1, b = 2, $\delta = 2$. The pair of peaks at 0.69 V (vs. SCE) shows good reversibility, which is deduced from the symmetrical shape of the peaks. This indicates that the surface electrochemistry of the electrode is governed by the active component IrO₂.

As shown in Fig. 4, it is quite obvious that the voltammetric current of the Ti/IrO₂-Ta₂O₅ anode with 70 mol% IrO₂ content is greater than that of the other anodes. The voltammetric charge capacity (q^*) obtained by integration of the cyclic voltammograms indicates the amount of protons exchanged with the solution. Therefore, the value of q^* is expected to be proportional to the electrochemically active surface area and is thought to be able to represent the number of electrochemically active sites on the surface.^{30,47,57} Fig. S1[†] gives the value of q^* at different contents of IrO2. The electrochemically active surface area increases gradually as the content of IrO₂ increases in the beginning. When the content of IrO₂ reaches 70%, the sample has the highest electrochemically active surface area because of its special morphology, then the electrochemically active surface area of the 90% IrO2 electrode decreases evidently because of the aggregation of IrO2 crystal particles. So the addition of Ta₂O₅ can improve the dispersion of iridium oxide grains and change the electrode morphology, and therefore increase the electrochemically active surface area. From the above discussion, it is evident that the electrochemically active surface area is determined not only by the content of the active component, but also by the structure and morphology of the anode coating.

In consideration of the fact that the electrolytic production of chlorine and hypochlorous acid from chloride could be used for food disinfection, the electrocatalytic activity was investigated by studying the model chlorine evolution reaction (CER). Linear sweep voltammetry curves of Ti/IrO₂–Ta₂O₅ anodes with different contents of IrO₂ are shown in Fig. 5. The results show that, accounting for the intrinsic catalytic activity and morphology,^{41,44,51,60,61} significant differences in current density still remain at a constant electrode overpotential. In agreement with the electrochemically active surface area, the current in the CER reaches a maximum at an IrO₂ content of 70%. This result confirms that the electrochemically active surface area plays an important role in determining the chlorine evolution.

Furthermore, the mechanism of the CER was studied *via* a Tafel plot. In Fig. 6, the Tafel curve shows a deviation from linearity at high overpotentials, requiring correction for ohmic drop in order to permit an appropriate interpretation. A single linear segment is obtained showing the kinetics of the CER is independent of potential. The Tafel slope is 46.8 mV dec⁻¹ for the 70% IrO₂ electrode, indicating that desorption is the rate-determining step of the reaction (Volmer–Heyrovsky).^{34,47} The reaction process is divided into two steps; the second step is the reaction rate-controlling step (S represents the active site).

$$S + Cl^{-} \xleftarrow[k_{-1}]{k_{-1}} S - Cl' + e$$
 (1)

$$\mathbf{S} - \mathbf{Cl}^{-} + \mathbf{Cl}^{-} \xrightarrow{k_{2}} \mathbf{S} + \mathbf{Cl}_{2} + \mathbf{e}$$
 (2)

3.4 Effect of IrO₂ content on EO water preparation

The properties of EO water prepared by Ti/IrO₂–Ta₂O₅ anodes with different contents of IrO₂ are shown in Table 1. The available chlorine content (ACC) and the content of HClO are very important characteristics in EO water preparation.^{47,62} From Table 1, it is clear that EO water has a maximum value of ACC at an IrO₂ content of 70%, which confirms again that the Ti/IrO₂–Ta₂O₅ anode with 70% IrO₂ has the best electrocatalytic activity for chlorine evolution. It can also be seen from Table 1 that the higher the chlorine content is, the better the sterilization effect of EO water is. When the IrO₂ content is 70%, the maximum values of the killing logarithm value and killing rate are 3.05 and 99.9109%, respectively. So this is the most suitable IrO₂ content for the preparation of EO water. Among different forms of chlorine, hypochlorous acid is the main active substance in sterilization; its sterilization efficiency is 80 times



Fig. 5 Linear sweep voltammetry curves of Ti/IrO₂-Ta₂O₅ anodes with different contents of IrO₂ in saturated sodium chloride solution at a sweeping rate of 20 mV s⁻¹.



Fig. 6 Tafel plot curve of Ti/IrO₂-Ta₂O₅ with 70% IrO₂ and preparation temperature 500 $^\circ$ C.

Content/mol%	Physicochemical property			Sterilization effect	
	рН	ORP/mV	$ m ACC/mg \ L^{-1}$	Killing logarithm value ^{a} /log CFU mL ^{-1}	Killing rate ^{<i>a</i>} /%
10	2.24	1146	31.64	2.30	99.4988
40	2.24	1149	69.83	2.76	99.8682
60	2.24	1152	85.66	2.92	99.8798
70	2.20	1150	90.17	3.05	99.9109
90	2.17	1150	83.56	2.90	99.8741

Table 1 Sterilization effect and EO water physicochemical properties depending on the IrO₂ content of Ti/IrO₂-Ta₂O₅ anodes

that of sodium hypochlorite.⁶² From Fig. 7, the HClO content is low for 10% IrO₂, so the killing logarithm value and killing rate are also lower than for the others. For 60%, 70% and 90% IrO₂, the contents of HClO are similar, so the sterilization effects are also similar. However, we can see that the HClO content is the highest for 70% IrO₂, so this has the best bactericidal activity.

3.5 Effect of preparation temperature on the surface morphology and electrocatalytic activity

Fig. 8 and 9 show SEM images and X-ray diffraction curves of Ti/ IrO2-Ta2O5 anodes with 70% IrO2 prepared at different temperatures. From Fig. 8 and 9, it was observed that the morphology and surface composition of the electrodes are different when prepared at different temperatures. The obvious differences indicate that the temperature has a significant effect on the surface microstructure and the elemental distribution. At a sintering temperature of 450 °C, there is no obvious peak of the oxide component (IrO_2) in Fig. 9. The amorphous phases of IrO₂ were formed due to incomplete firing of the gel coating. When the sintering temperature was increased to 500 °C, the amount of IrO2 agglomerated particles increased quickly (Fig. 8). As can be seen from the XRD patterns, the diffraction peak of IrO₂ is extremely broad and unsymmetrical, which suggests unsatisfactory crystallinity of IrO₂. When the sintering temperature rose to 550 $^\circ$ C and 650 $^\circ$ C, the amount of IrO₂



Fig. 7 Absorbance of HClO from Ti/IrO $_2$ -Ta $_2O_5$ anodes with different contents of IrO $_2$ at 233 nm.



Fig. 8 SEM images for Ti/IrO₂-Ta₂O₅ anodes with 70% IrO₂ prepared at different temperatures: (a) 450 °C, (b) 500 °C, (c) 550 °C, (d) 650 °C.

agglomerated particles decreased quickly and cracks began to increase and deepen, which greatly reduced the active area.

Cyclic voltammograms of Ti/IrO₂-Ta₂O₅ anodes prepared at different temperatures tested in 0.5 mol L^{-1} H₂SO₄ solution at a sweeping rate of 20 mV s^{-1} are shown in Fig. 10. It can be seen that the sample prepared at 500 °C has the highest electrochemically active surface area in Fig. S2.† Then the electrochemically active surface area decreases evidently with the increase in sintering temperature. The reduction in the active area should be attributed to the high temperature, which leads to grain growth and aggregation. Secondly, Ta enrichment occurs easily at high temperatures, reducing the distribution of the IrO2 active component. This phenomenon can lead to a decrease in the number of active surface sites. In addition, the Ti substrate tends to be oxidized at temperatures higher than 500 °C, leading to a decrease in electrode conductivity and a decline in apparent electrode activity. This result proves again that the electrochemically active surface area is determined by the structure and morphology of the anode coating.

Linear sweep voltammetry curves of Ti/IrO₂–Ta₂O₅ anodes prepared at different temperatures tested in saturated sodium chloride solution at a sweeping rate of 20 mV s⁻¹ are shown in Fig. 11. It can be seen that the current during chlorine evolution also reaches a maximum for anodes prepared at 500 °C. This is in line with the above study as shown in Fig. 4 and 5.



Fig. 9 X-ray diffraction curves for Ti/IrO₂-Ta₂O₅ anodes with 70% IrO₂ prepared at different temperatures: (a) 450 °C, (b) 500 °C, (c) 550 °C, (d) 650 °C.



Fig. 10 Cyclic voltammograms of Ti/IrO₂-Ta₂O₅ anodes with 70% IrO₂ prepared at different temperatures tested in 0.5 mol L^{-1} H₂SO₄ solution at a sweeping rate of 20 mV s⁻¹.

3.6 Effect of preparation temperature on EO water preparation

The properties of electrolyzed oxidizing water prepared by Ti/ IrO₂-Ta₂O₅ anodes at different preparation temperatures are shown in Table 2. It can be seen that EO water has maximum values of ACC and HClO content when prepared at 500 °C, which also proves again that Ti/IrO₂-Ta₂O₅ anodes prepared at 500 °C have the best electrocatalytic activity for chlorine evolution. It can also be seen from Table 2 that when the preparation temperature is 500 °C, the maximum values of the killing logarithm value and killing rate are 3.01 and 99.9023%, respectively. Therefore, when the anode



Fig. 11 Linear sweep voltammetry curves of Ti/lrO₂-Ta₂O₅ anodes prepared at different temperatures tested in saturated sodium chloride solution at a sweeping rate of 20 mV s⁻¹.

preparation temperature is 500 °C, this is most suitable for EO water preparation. In Fig. 12, the hypochlorous acid content first increased and then decreased with the increase in preparation temperature. We can see that the HClO content is the highest at 500 °C, which makes it have the best bactericidal activity.

3.7 The accelerated lifetime of Ti/IrO₂-Ta₂O₅ anodes

An accelerated lifetime test (ALT) of Ti/IrO₂-Ta₂O₅ anodes with different activation times under constant current electrolysis in $0.5 \text{ mol } L^{-1} H_2 SO_4$ solution at current density 2 A cm⁻² is shown in Fig. 13, showing the change of cell voltage with electrolysis time per unit loading during the ALT. The whole period can be divided into three stages: activation, stable and deactivation periods. In the beginning, the potential stays at the activation stage, when the electrolyte does not penetrate into the inner surface. After a certain time, it tends to stabilize; this period occupies the main portion of the whole electrolysis time. The potential starts to increase abruptly at the end and within a short time (less than 15 h) the anode is deactivated. As can be seen from Fig. 13, the IrO₂-Ta₂O₅-coated Ti substrate without activating treatment has the shortest accelerated life (35 h). The stability of a Ti/IrO₂-Ta₂O₅ anode can be improved significantly when the Ti substrate undergoes activating treatment. Therefore activating treatment for the Ti substrate is an effective method to improve the stability of Ti/IrO2-Ta2O5 anodes. On the other hand, the Ti/IrO2-Ta2O5 anodes differ greatly in terms of anode stability with different activation times. When the activation time increases from 0 min to 40 min, the anode stability also increases significantly. However, when the activation time reaches 60 min, the anode stability decreases. The change in ALT may be attributed to the different structure of the Ti substrate. So the surface morphologies of Ti substrates with different activation times were studied by SEM images as shown in Fig. S3.[†] Fig. S3(a)[†] shows that the Ti substrate has a smooth surface. When activating treatment is used, the surface morphologies become increasingly rough. With the increase in the activation time of the Ti substrate, the corrosion pits formed

Temperature/°C	Physicochemical property			Sterilization effect	
	pН	ORP/mV	$ACC/mg \ L^{-1}$	Killing logarithm value ^{a} /log CFU mL ^{-1}	Killing rate ^a /%
450	2.24	1146	83.51	2.71	99.8050
500	2.29	1150	90.17	3.01	99.9023
550	2.30	1141	83.96	2.90	99.8741
650	2.27	1146	66.22	2.88	99.8682

Table 2 Sterilization effect and EO water physicochemical properties depending on the preparation temperature of Ti/IrO2-Ta2O5 anodes

^{*a*} Positive control group (*Bacillus subtilis* var. *niger*): 7.53 log CFU mL⁻¹, killing time: 30 min.



Fig. 12 Absorbance of HClO from $Ti/IrO_2-Ta_2O_5$ anodes with different preparation temperatures at 233 nm.



Fig. 13 Accelerated lifetime test of Ti/lrO₂-Ta₂O₅ anodes with different activation times under constant current electrolysis in 0.5 mol L^{-1} H₂SO₄ solution at 2 A cm⁻².

on the surface of the Ti substrate become deeper. However, if the activation time is too long, it would cause excessive corrosion of the substrate surface. Gas can easily enter electrochemically active sites within the oxide coating, so that it will fall off and electrochemical dissolution will occur, resulting in consumption of electrochemically active sites, and so the accelerated life will be reduced.

4. Conclusions

Through the study of different series of Ti/IrO₂-Ta₂O₅ anodes, it can be seen that the preparation conditions have a large impact on the electrode catalytic activity. The influences of IrO2 content, preparation temperature and activation time on the electrode catalytic activity for Ti/IrO2-Ta2O5 anodes were investigated by SEM, XRD, CV, LSV and accelerated lifetime test. The experimental results indicate that the electrochemically active surface area is determined by the structure and morphology of the anode coating. IrO2 aggregated as segregated crystallite particles at a content of 70% prepared at 500 °C produces the best electrode catalytic activity. The properties and sterilization effect of EO water are closely related to the electrode catalytic activity. When the IrO2 content is 70% and the preparation temperature is 500 °C, the maximum values of the killing logarithm value and killing rate are 3.01-3.05 and 99.9023-99.9109%, respectively. In addition, when the Ti substrate undergoes 40 minutes of activation treatment, the Ti/ IrO₂-Ta₂O₅ anodes have the best stability.

Acknowledgements

The authors would like to acknowledge financial support from The National Natural Science Foundation of China (31101370) and The Natural Science Foundation of Hubei Province (2012FFB04803).

References

- 1 R. M. S. Thorn, S. W. H. Lee, G. M. Robinson, J. Greenman and D. M. Reynolds, *Eur. J. Clin. Microbiol. Infect. Dis.*, 2012, **31**, 641–653.
- 2 H. C. Zhang, Y. C. Zhu, Z. D. Ren, D. Pan, Y. Liu, Y. R. Wang and B. Cai, *Trans. Chin. Soc. Agric. Eng.*, 2013, **29**, 277–283.
- 3 L. A. Keskinen, A. Burke and B. A. Annous, *Int. J. Food Microbiol.*, 2009, **132**, 134–140.
- 4 S. Koide, D. Shitanda, M. Note and W. Cao, *Food Control*, 2011, 22, 452–456.
- 5 S. McCarthy and W. Burkhardt III, *Food Control*, 2012, 24, 214–219.
- 6 J. Xie, X. H. Sun, Y. J. Pan and Y. Zhao, *Food Control*, 2012, 23, 320–324.

Published on 18 December 2014. Downloaded by San Diego State University on 28/01/2015 11:19:33.

- 7 S. M. E. Rahman, J. Wang and D.-H. Oh, *Food Control*, 2013, **30**, 176–183.
- 8 Z. D. Ren, Y. C. Zhu, Y. Liu, Z. Y. Zhang and Q. Zhang, *Trans. Chin. Soc. Agric. Mach.*, 2009, **12**, 139–143.
- 9 Y. Liu, Z. D. Ren, Z. K. Liu and X. W. Zhang, *Food Science*, 2009, **14**, 119–122.
- 10 W. Cao, Z. W. Zhu, Z. X. Shi, C. Y. Wang and B. M. Li, *Int. J. Food Microbiol.*, 2009, **130**, 88–93.
- 11 A. Graca, M. Abadias, M. Salazar and C. Nunes, *Postharvest Biol. Technol.*, 2011, **61**, 172–177.
- 12 K. Xiong, H. J. Liu and L. T. Li, *J. Agric. Food Chem.*, 2012, **60**, 9770–9778.
- 13 C. Kim, Y. C. Hung and R. E. Brachett, *J. Food Prot.*, 2000, **63**, 19–24.
- 14 L. B. Liao, W. M. Chen and X. M. Xiao, *J. Food Eng.*, 2007, **78**, 1326–1332.
- 15 S. Koseki and K. Itoh, J. Food Prot., 2001, 64, 1935-1942.
- 16 Z. D. Ren, Y. C. Zhu, Y. Liu, X. R. Zhou and Z. Y. Zhang, *Chin. J. Prev. Med*, 2008, 8, 578–581.
- 17 Z. D. Ren, Y. C. Zhu, Y. Liu, X. R. Zhou and Z. Y. Zhang, *Chin. J. Hosp. Pharm.*, 2009, **17**, 1448–1450.
- 18 Z. D. Ren, Y. C. Zhu, Y. Liu and Z. Y. Zhang, J. Chem. Ind. Eng., 2009, 10, 2583–2589.
- 19 J. X. Hao, S. Qiu, H. Y. Li, T. P. Chen, H. J. Liu and L. T. Li, *Int. J. Food Microbiol.*, 2012, **155**, 99–104.
- 20 H. Kiura, K. Sano, S. Morimatsu, T. Nakano, C. Morita, M. Yamaguchi, T. Maeda and Y. Katsuoka, *J. Microbiol. Methods*, 2002, **49**, 285–293.
- 21 Y. R. Huang, Y. C. Hung, S. Y. Hsu, Y. W. Huang and D. F. Hwang, *Food Control*, 2008, **19**, 329–345.
- 22 J. Jeong, J. Y. Kim and J. Yoon, *Environ. Sci. Technol.*, 2006, 40, 6117–6122.
- 23 J. X. Hao, S. Qiu, H. Y. Li, T. P. Chen, H. J. Liu and L. T. Li, *Int. J. Food Microbiol.*, 2012, **155**, 99–104.
- 24 S. D. Stan, J. S. Woods and M. A. Daeschel, J. Agric. Food Chem., 2005, 53, 4901–4905.
- 25 T. Mokudai, K. Nakamura, T. Kanno and Y. Niwano, *PLoS One*, 2012, **9**, e46392.
- 26 S. Y. Hsu, J. Food Eng., 2003, 60, 469-473.
- 27 S. Y. Hsu, J. Food Eng., 2005, 66, 171-173.
- 28 X. P. Zeng, M. Zhang, X. D. Wang, X. Y. Chen, X. Z. Su and W. W. Tang, J. Electroanal. Chem., 2012, 677–680, 133–138.
- 29 S. Neodoa, D. Rosestolato, S. Ferro and A. D. Battisti, *Electrochim. Acta*, 2012, **80**, 282–291.
- 30 L. K. Xu, Y. L. Xin and J. T. Wang, *Electrochim. Acta*, 2009, **54**, 1820–1825.
- 31 K. S. Exner, J. Anton, T. Jacob and H. Over, *Angew. Chem., Int. Ed.*, 2014, **53**, 1–5.
- 32 N. Menzel, E. Ortel, K. Mette, R. Kraehnert and P. Strasser, *ACS Catal.*, 2013, **3**, 1324–1333.
- 33 Y. Zeng, K. N. Chen, W. Wu, J. R. Wang and S. Lee, *Ceram. Int.*, 2007, 33, 1087–1091.
- 34 M. H. P. Santana and L. A. D. Faria, *Electrochim. Acta*, 2006, 51, 3578–3585.
- 35 A. R. Zeradjanin, N. Menzel, W. Schuhmann and P. Strasser, *Phys. Chem. Chem. Phys.*, 2014, **16**, 13741–13747.

- 36 I. Katsounaros, S. Cherevko, A. R. Zeradjanin and K. J. J. Mayrhofer, *Angew. Chem., Int. Ed.*, 2014, 53, 102–121.
- 37 A. R. Zeradjanin, A. A. Topalova, Q. V. Overmeereb, S. Cherevkoa, X. X. Chen, E. Ventosac, W. Schuhmannc and K. J. J. Mayrhofer, *RSC Adv.*, 2014, 4, 9579.
- 38 V. Petrykin, K. Macounova, O. A. Shlyakhtin and P. Krtil, Angew. Chem., 2010, 122, 4923–4925.
- 39 V. Petrykin, K. Macounova, J. Franc, O. Shlyakhtin, M. Klementova, S. Mukerjee and P. Krti, *Chem. Mater.*, 2011, 23, 200–207.
- 40 T. Reier, M. Oezaslan and P. Strasser, ACS Catal., 2012, 2, 1765–1772.
- 41 R. Y. Chen, V. Trieu, A. R. Zeradjanin, H. Natter, D. Teschner, J. Kintrup, A. Bulan, W. Schuhmann and R. Hempelmann, *Phys. Chem. Chem. Phys.*, 2012, 14, 7392–7399.
- 42 S. Y. Chen, Y. H. Zheng, S. W. Wang and X. M. Chen, *Chem. Eng. J.*, 2011, **172**, 47–51.
- 43 V. Petrykin, K. Macounová, M. Okube, S. Mukerjee and P. Krtil, *Catal. Today*, 2013, **22**, 63–69.
- 44 V. Trieu, B. Schley, H. Natter, J. Kintrup, A. Bulan and R. Hempelmann, *Electrochim. Acta*, 2012, **78**, 188–194.
- 45 J. Jirkovský, H. Hoffmannová, M. Klementová and P. Krtil, *J. Electrochem. Soc.*, 2006, **153**, E111–E118.
- 46 N. W. Fan, Z. K. Li, L. Zhao, N. M. Wu and T. Zhou, *Chem. Eng. J.*, 2013, **214**, 83–90.
- 47 X. L. Zhou, Z. G. Ye, X. Z. Hua, A. H. Zou and Y. H. Dong, *J. Solid State Electrochem.*, 2010, **14**, 1213–1219.
- 48 L. Vazquez-Gomez, S. Ferro and A. De Battisti, *Appl. Catal., B*, 2006, **67**, 34–40.
- 49 P. Lakshmipathiraj, G. B. Raju, Y. Sakai, Y. Takuma,
 A. Yamasaki, S. Kato and T. Kojima, *Chem. Eng. J.*, 2012,
 198–199, 211–218.
- 50 B. Johnson, F. Girgsdies, G. Weinberg, D. Rosenthal, A. Knop-Gericke and R. Schlögl, J. Phys. Chem. C, 2013, 117, 25443–25450.
- 51 E. Ortel, T. Reier, P. Strasser and R. Kraehnert, *Chem. Mater.*, 2011, 23, 3201–3209.
- 52 R. Tolba, M. Tian, J. L. Wen, Z. H. Jiang and A. C. Chen, *J. Electroanal. Chem.*, 2010, **649**, 9–15.
- 53 K. C. Pillai, T. O. Kwon, B. B. Park and I. S. Moon, J. Hazard. Mater., 2009, 164, 812–819.
- 54 T. L. Luu, J. Y. Kim and J. Y. Yoon, *J. Ind. Eng. Chem.*, 2015, **21**, 400–404.
- 55 L. K. Xu and J. D. Scantlebury, Corros. Sci., 2003, 45, 2729–2740.
- 56 J. M. Hu, H. M. Meng, J. Q. Zhang and C. N. Cao, *Corros. Sci.*, 2002, 44, 1655–1668.
- 57 Z. W. Yan and H. M. Meng, Rare Met., 2011, 30(5), 439-446.
- 58 J. Carrell Morris, J. Phys. Chem., 1966, 70(12), 3798-3805.
- 59 S. Ardizzone, C. L. Bianchi, G. Cappelletti, M. Ionita, A. Minguzzi, S. Rondinini and A. Vertova, *J. Electroanal. Chem.*, 2006, 589, 160–166.
- 60 A. R. Zeradjanin, F. L. Mantiab, J. Masaa and W. Schuhmann, *Electrochim. Acta*, 2012, 82, 408–414.
- 61 H. Z. Cao, D. H. Lu, J. P. Lin, Q. Ye, J. J. Wu and G. Q. Zheng, *Electrochim. Acta*, 2013, **91**, 234–239.
- 62 C. Kim, Y. C. Hung and R. E. Brackett, *Int. J. Food Microbiol.*, 2000, **61**, 199–207.