



Thermolytic formation and microstructure of $\text{IrO}_2 + \text{Ta}_2\text{O}_5$ mixed oxide anodes from chloride precursors

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Abstract

The thermolytic formation of $\text{IrO}_2 + \text{Ta}_2\text{O}_5$ mixed oxides from chloride precursors is studied by thermogravimetry (TGA) and differential thermal analysis (DTA). The structure and morphologies of the corresponding oxide films coated on titanium bases are determined by X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM), respectively. The experimental results showed that, as a result of the interaction between Ir and Ta components, especially, the formation of solid solution phases during the thermolysis processes, the oxidative dissociation of the $\text{H}_2\text{IrCl}_6 + \text{TaCl}_5$ mixture is facilitated. The catalytic effect reached the maximum at a nominal IrO_2 content of 70 mol% in the expected product, i.e. $\text{IrO}_2 + \text{Ta}_2\text{O}_5$ mixed oxides, accompanied by the highest solid solubility between the two oxides and the finest rutile-structured crystalline grains in the oxides. For the mixed precursors with a low iridium content (e.g. 10 mol% nominal IrO_2 in $\text{IrO}_2 + \text{Ta}_2\text{O}_5$) or a low tantalum content (e.g. 80 mol% nominal IrO_2), however, the decomposition of the major component is inhibited by the minor one at high temperatures (610–800 °C). The results show that the solid solution at low Ir contents (<30 mol% IrO_2) is unstable since it decomposes at high temperatures (≥ 750 °C). Two or more IrO_2 based rutile-constructed solid solution phases are thermolytically formed from the mixed precursors with nominal IrO_2 contents ≥ 30 mol%. The rutile-structured phases stably exist only in the case of IrO_2 contents ≥ 60 mol%.

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1. Introduction

Conductive metallic IrO_2 is known to be one of the best electrocatalysis materials for the O_2 evolution reaction (OER) in acid solution [1,2]. In binary systems, the combination of $\text{IrO}_2 + \text{Ta}_2\text{O}_5$ has been verified to possess both the maximum activity and the highest stability for the OER [3–5]. Because of the convenience in preparation procedure and the high stability of the obtained oxides, the oxide electrodes are often prepared by thermolytic decomposition method from the

$\text{MCl}_3 \cdot n\text{H}_2\text{O}$ or $\text{H}_2\text{MCl}_6 \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Ru}, \text{Ir}, \text{Rh}, \text{etc.}$) precursors painted on valve metals (Ti, Zr and $\text{Ta}, \text{etc.}$) [6]. A lot of work has been done on the microstructure [7–9], oxygen evolution processes [10] and degradation mechanism [11,12] of IrO_2 based oxide catalysts. However, few works on fundamental research of thermolytic formation of these oxides by thermogravimetry (TGA) and differential thermal analysis (DTA) have been carried out. TGA and DTA of IrO_2 formation were investigated in the literatures [13–15], and those of Ta_2O_5 in the paper [14], respectively. Unfortunately, to our best knowledge, no work on the thermo-analysis on the formation of $\text{IrO}_2 + \text{Ta}_2\text{O}_5$ mixed systems has been reported previously.

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In the present paper, the thermolytic formation of $\text{IrO}_2 + \text{Ta}_2\text{O}_5$ from $\text{H}_2\text{IrCl}_6 + \text{TaCl}_5$ chloride precursors has been investigated by the combined use of TGA and DTA. These techniques are used in conjunction with X-ray diffraction (XRD) and scanning electron microscopy (SEM) observation on actually used titanium-supported oxide films prepared by thermo-decomposition in an attempt to gain an understanding of the microstructure of the obtained mixed oxides.

2. Experimental

2.1. TGA and DTA experiments

A certain amount of $x \text{H}_2\text{IrCl}_6 + (1 - x) \text{TaCl}_5$ precursors was mixed in alcohol solution (x is at mole fraction, H_2IrCl_6 was commercially available dissolved in concentrated HCl solution, and TaCl_5 dissolved in alcohol solution). The mixed solution was dried at 80°C for 10 h, and then the obtained product was mechanically powdered. The TGA and DTA measurements were carried out on a du pont Model 1090B system in air. The nominal heating rate was $10^\circ\text{C}/\text{min}$ for both the tests. The air flow rate was maintained at $\sim 75 \text{ ml}/\text{min}$. The weight of the tested sample was in the range 7–11.5 mg. Ignited alumina was used as reference in DTA. The TGA weight loss measurements had a nominal error of $\pm 0.5\%$, and nominal errors in the temperature measurement were $\pm 2^\circ\text{C}$.

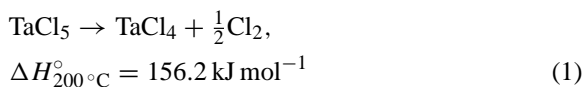
2.2. Characterization of Ti supported $\text{IrO}_2 + \text{Ta}_2\text{O}_5$ films

Ti supported oxide films were prepared by conventional thermo-decomposition [16]. The precursor solution thus obtained was painted over the Ti substrates, followed by drying at 80°C and then heated at a fixed temperature. The coating sample was subjected to an annealing treatment at the same temperature for 1 h after being painted for 10 layers. The XRD analysis was performed on D/MAX-R3 type diffractometer using $\text{Cu K}\alpha$ radiation and nickel filter. Surface morphologies and chemical composition were investigated with Cambridge S360 SEM, equipped with link X-ray energy dispersive (EDX) analyzer.

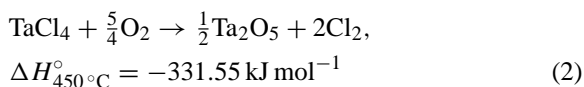
3. Results and discussion

3.1. $\text{TaCl}_5(n\text{H}_2\text{O})$ and $\text{H}_2\text{IrCl}_6(n\text{H}_2\text{O})$ thermolysis

Fig. 1a illustrates the thermal behavior of $\text{TaCl}_5(n\text{H}_2\text{O})$ as probed by TGA and DTA in air. Three stages of weight loss are shown in TGA curve. Stage A refers to the loss of free water molecules from the chloride matrix, with a wide endothermic DTA peak around 125°C . The TGA weight loss (12.5%) in stage B at $150\text{--}475^\circ\text{C}$, agrees well with the initial decomposition of TaCl_5 represented by reaction (1), with a weak endotherm at $\sim 235^\circ\text{C}$



In stage C ($>475^\circ\text{C}$) $\beta\text{-Ta}_2\text{O}_5$ is formed. This reaction can be written as follows:



The XRD analysis on the Ti supported tantalum oxide samples reveals that at low temperatures ($<450^\circ\text{C}$) many unidentifiable reflections are observed (uncompleted decomposition products), and only at the higher temperatures, the formation of $\beta\text{-Ta}_2\text{O}_5$ (PDF no. 21-1198) occurs (Fig. 2f shows the appearance of β phase at 450°C). The XRD results are found to be consistent with the work reported by Roginskaya et al. [7]. The TGA measurements carried out by Vercesi et al. [15] have shown that at temperatures higher than 580°C the precursor TaCl_5 could be completely decomposed to stable $\beta\text{-Ta}_2\text{O}_5$, a similar type of decomposition can be seen by a sharp exothermic DTA response at $\sim 575^\circ\text{C}$ in Fig. 1a. However, the total weight loss up to 800°C (26.4%) is far smaller than the totally theoretical loss of reaction (1) and (2). This indicates that although a plateau is shown in TGA curve after 700°C , the oxidative dissociation of TaCl_5 precursor is clearly not completed. A similar type of result can be seen for $\text{H}_2\text{IrCl}_6(n\text{H}_2\text{O})$ sample (see below). This phenomenon may be speculated that the surface of the initial reactant is protected (passivated) by the formation of upper oxidation products [13], which restricts the further thermolysis, however the

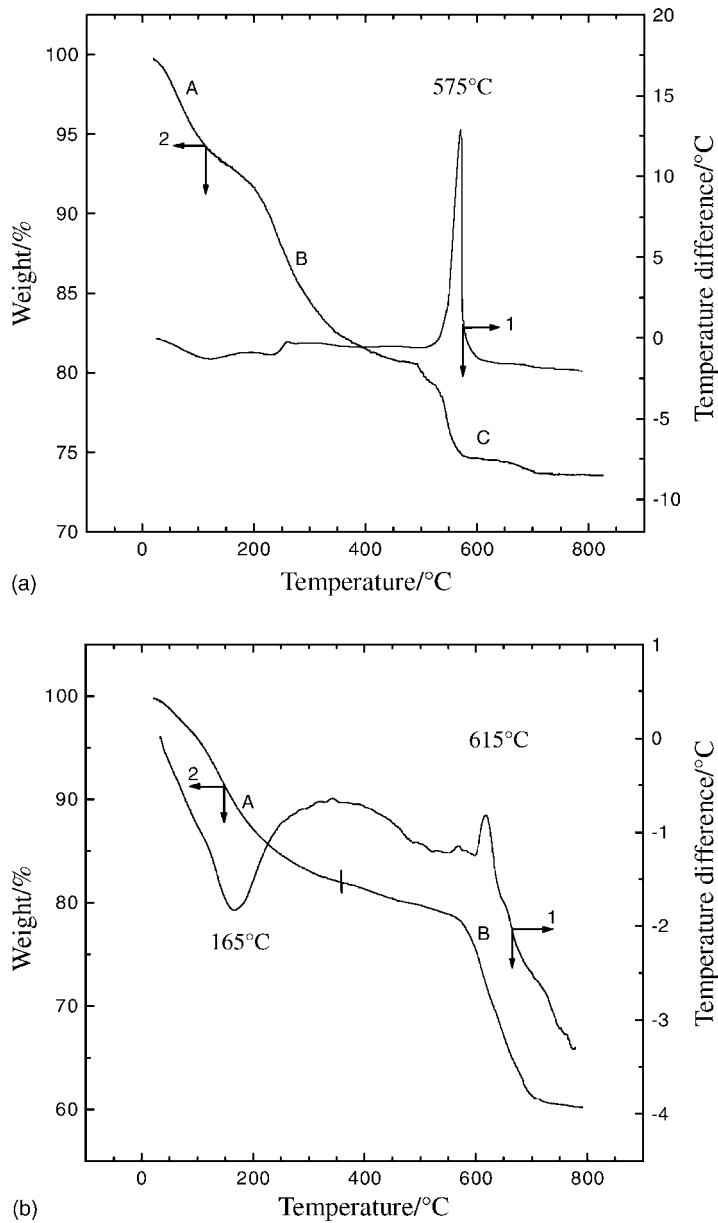
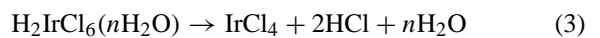


Fig. 1. DTA (1) and TGA (2) curves for TaCl₅ (a) and H₂IrCl₆ (b) obtained in air.

passivation effect is not seen in an inert atmosphere (such as in Ar).

The TGA curve for H₂IrCl₆(*n*H₂O) is much simpler (see Fig. 1b), containing two major weight loss stages (A and B). Stage A (≤360 °C) corresponds to the formation of IrCl₄ which is repre-

sented as



The *n* value calculated for this reaction from the TGA weight loss up to 300 °C is close to zero, implying the water molecules are already removed by the drying

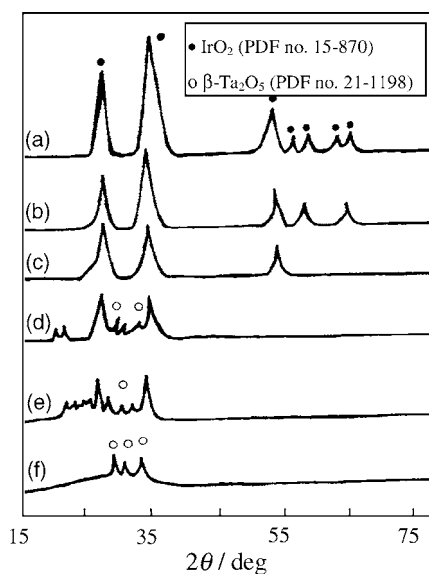
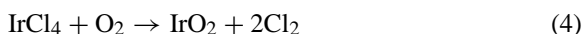


Fig. 2. Drafts of XRD patterns for Ti supported $\text{IrO}_2 + \text{Ta}_2\text{O}_5$ oxide coatings prepared at 450°C : (a) 100%, (b) 80%, (c) 70%, (d) 40%, (e) 10%, and (f) 0% IrO_2 content.

process at powder preparation stage (see Section 2). An endothermic response at 165°C is assigned to this reaction. Stage B ($>360^\circ\text{C}$) corresponds to the formation of IrO_2 , with an exotherm at 615°C . The reaction is represented by Eq. (4)



The crystalline reflections of IrO_2 (rutile-structured) (PDF no. 15–870) are also detected by XRD on Ti supported $\text{H}_2\text{IrCl}_6(n\text{H}_2\text{O})$ precursor heated at 350°C . Similarly, the total weight loss at 800°C (39.8%) is found to be still lower than that of the theoretical value of reactions (3) and (4) together (44.9%). The possible interpretation has been mentioned in the previous paragraph.

3.2. Thermolysis of $x\text{H}_2\text{IrCl}_6(n\text{H}_2\text{O}) + (1-x)\text{TaCl}_5(n\text{H}_2\text{O})$ mixed chloride precursors

Thermal behaviors of $\text{H}_2\text{IrCl}_6 + \text{TaCl}_5$ mixed chlorides with 5.3, 25.0, 42.9, 53.9 and 66.7% H_2IrCl_6 (at mole fraction) corresponding to 10, 40, 60, 70, and 80% nominal content of IrO_2 in $\text{IrO}_2 + \text{Ta}_2\text{O}_5$ mixed oxide products, respectively, are displayed in Fig. 3a–e. The calculated TGA curves are also shown

in these figures. The calculated curves are obtained by the combined use of TGA data for single H_2IrCl_6 and TaCl_5 (shown in Fig. 1a and b, respectively). The nominal residue weight percent of the mixed precursors, $(G_T\%)_x$, is calculated by the following equation:

$$(G_T\%)_x = \left(\frac{(G_T\%)_{x=100\%} x M_{\text{H}_2\text{IrCl}_6} + (G_T\%)_{x=0} (1-x) M_{\text{TaCl}_5}}{M_{\text{H}_2\text{IrCl}_6} x + (1-x) M_{\text{TaCl}_5}} \right) \times 100\% \quad (5)$$

where $(G_T\%)_{x=100\%}$ stands for the residue weight percent of the pure $\text{H}_2\text{IrCl}_6(n\text{H}_2\text{O})$ material at temperature T derived from Fig. 1b, $(G_T\%)_{x=0}$ the residue weight percent of the pure $\text{TaCl}_5(n\text{H}_2\text{O})$ material at temperature T derived from Fig. 1a, $M_{\text{H}_2\text{IrCl}_6}$ the molar weight of H_2IrCl_6 and M_{TaCl_5} the molar weight of TaCl_5 . The calculated TGA data result from merely mechanical mixing of these two chlorides. That is, the chemical interaction between the two individuals is ideally ignored.

Two classes of XRD patterns have been used to interpret the thermolytic behaviors of chlorides, with one emphasizing the influence of chloride composition (see Fig. 2), and the other on the effect of thermolytic temperature (shown in Fig. 4).

At $x = 5.3\%$, the TGA curve (Fig. 3a) is almost duplicate with that of pure $\text{TaCl}_5(n\text{H}_2\text{O})$ precursor (see Fig. 1a). Each characteristic stage mainly corresponds to different thermolysis reactions of Ta components. The DTA behavior, however, exhibits significant differences. The major exothermic peak characterizing the dramatic occurrence of $\beta\text{-Ta}_2\text{O}_5$ appears at 466°C , while at 575°C for $x = 0$. The declining of the $\beta\text{-Ta}_2\text{O}_5$ formation temperature is probably attributed to the solid solubilization of Ir component in $\beta\text{-Ta}_2\text{O}_5$ crystallite. According to the investigation of Roginskaya et al. [7], for the IrO_2 content of less than 30 mol% in $\text{IrO}_2 + \text{Ta}_2\text{O}_5$ mixed oxide films, β phase is a solid solution with Ir component penetration. Moreover, the XRD pattern (Fig. 2e) shows a highly better crystallinity for this composition than that of pure Ta component. Another exothermic peak at 751°C , accompanying by the absence of TGA weight loss is probably associated with the split of IrO_2 component from β solid solution, indicating a low stability of this solid solution phase at high temperatures.

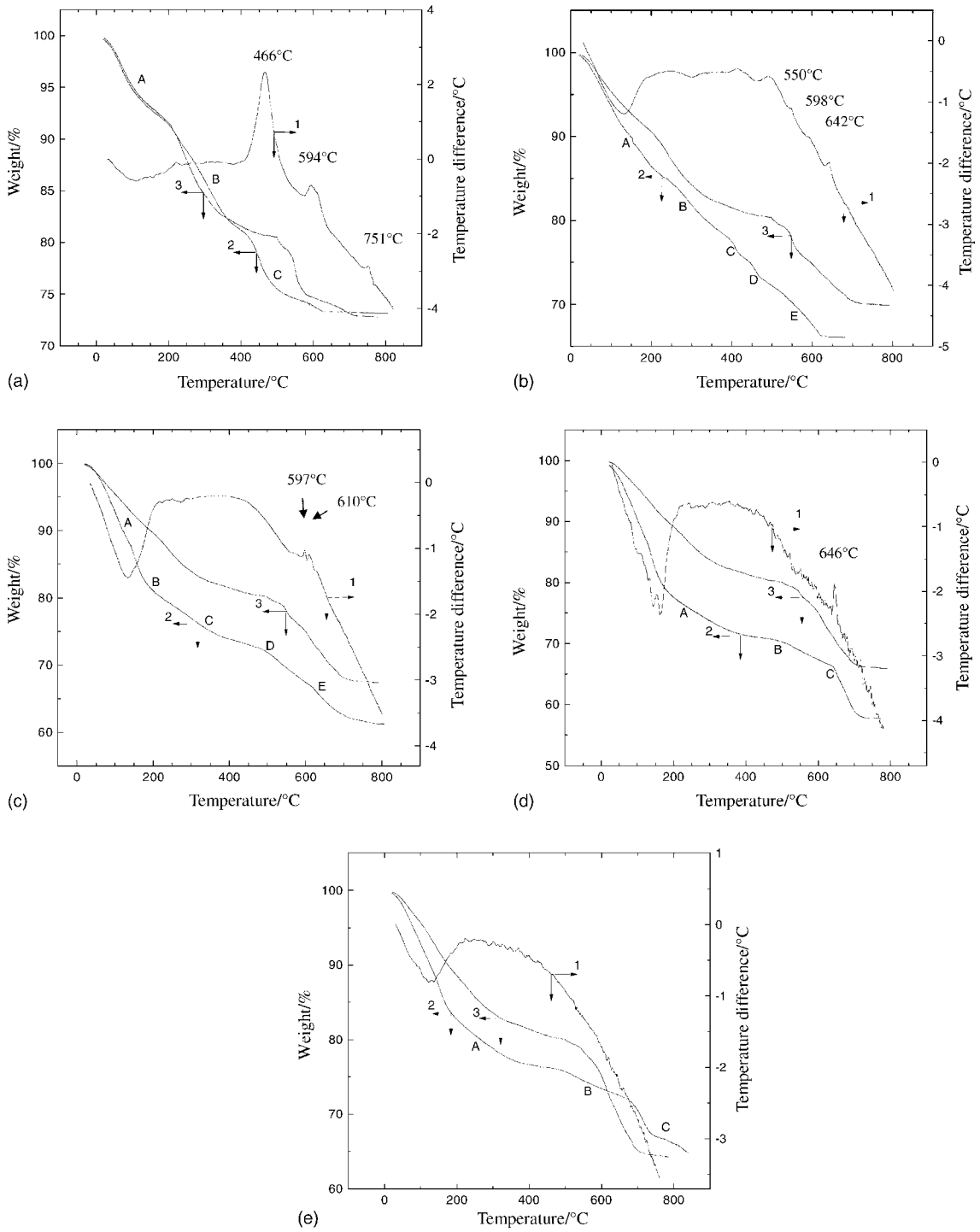


Fig. 3. DTA (1) and TGA (2: experimental and 3: calculated) curves for $x\text{H}_2\text{IrCl}_6 + (1-x)\text{TaCl}_5$ mixed chloride precursors obtained in air: (a) $x = 5.3\%$, (b) $x = 25.0\%$, (c) $x = 42.9\%$, (d) $x = 53.9\%$ and (e) $x = 66.7\%$.

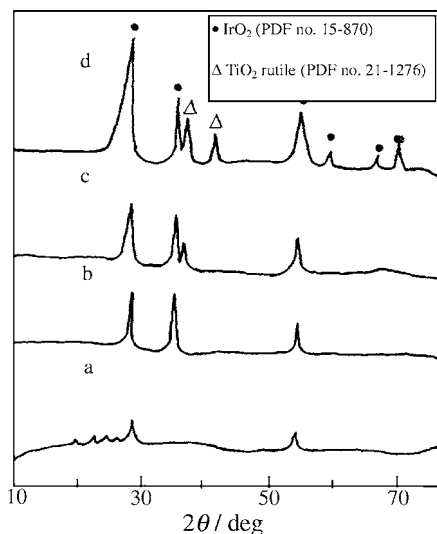


Fig. 4. Drafts of XRD patterns for Ti supported 70% IrO₂ + 30% Ta₂O₅ oxide coatings prepared at different temperatures: (a) 350 °C, (b) 450 °C, (c) 500 °C, and (d) 550 °C.

The TGA curve for the mixed chloride precursors with $x = 25\%$ is more complicated, containing five thermolysis stages as shown in Fig. 3b. Stages A and B correspond to the loss of water molecules and the elementary thermolysis of materials. The initial decomposition of H₂IrCl₆(n H₂O) (reaction (3)) occurs in the temperature range ≤ 368 °C, and the oxidative dissociation of TaCl₅ component (reactions (1) and (2)) takes place at the temperatures ≤ 438 °C. In stage C (368–438 °C) IrCl₄ starts to decompose and oxidize to form the first rutile-structured IrO₂, its occurrence temperature is approximately close to that of pure H₂IrCl₆(n H₂O) chloride (~ 360 °C as shown in Fig. 1b). The TaCl₄ begins to dissociate as represented by the reaction (2) in stage D (438–485 °C). The initial temperature of this reaction is slightly lower than that of pure TaCl₅ precursor (~ 475 °C) as shown in Fig. 1a, probably owing to the solid solubilization of Ta₂O₅ in rutile-structured IrO₂. The solubilization process can be supported by two minor exothermic peaks at 550 and 598 °C, respectively, corresponding to the formation of two solid solution compounds. The above assumption is consistent with the X-ray diffraction analysis on Ti supported IrO₂+Ta₂O₅ films [7], that is, at IrO₂ contents ≥ 30 mol% two or three rutile-structured phases exist with the first one com-

posed of pure IrO₂ crystal and the others the Ir/Ta oxide solid solutions. The XRD result for this composition at 450 °C (see Fig. 2d) indicates that, comparing to that of low Ir content mixture, the number of unidentifiable phases and the intensity of β phase decrease and the intensity of rutile-structured IrO₂ reflections increases. An exotherm at 642 °C, not accompanied by loss in TGA, is probably assigned to the phase transformation by which β -Ta₂O₅ phase is precipitated after split off from rutile-structured solid-solution. This result demonstrates that the rutile solid solution is unlikely very stable in IrO₂ + Ta₂O₅ mixture with low IrO₂ contents.

The TGA curve corresponding to $x = 42.9\%$ (Fig. 3c) is much similar to that for $x = 25\%$ (Fig. 3b). The reactions and productions in each thermolysis stage are comparable between the two compositions. However, the temperature regions for each stage are apparently changed. The start temperature of stage C (appearance of IrO₂ at ~ 261 °C) is clearly lower compared with that for $x = 25\%$ (~ 368 °C), and the temperature range of stage D is obviously broadened, and the two exothermic peaks for solid solution formation are both moved to higher temperatures (~ 597 and 610 °C, respectively). Interestingly, however, the phase transformation peaks in DTA curve before 800 °C are absent as shown in the DTA curve, indicating that the solid solution phases are stably presented in the IrO₂ + Ta₂O₅ mixed oxides with the IrO₂ content of 60 mol%.

Fig. 3d illustrates the thermolysis behavior of mixed chloride precursors with $x = 53.9\%$. Three thermolysis stages are also distinguished, i.e. the loss of water molecules, the primary thermolysis reactions of the mixed precursors and the IrO₂ formation take place in the stage A (≤ 435 °C), and the oxidative dissociation of Ta component in stage B (435–583 °C). The solubilization exotherm as indicated in Fig. 3b and c, however, is not observed in DTA curve for this composition. Fortunately, it has indicated that in IrO₂ + Ta₂O₅ films the highest solubility of Ta₂O₅ in IrO₂ rutile-structured phases is exhibited in the mixture corresponding to the composition (70 mol% IrO₂) (see below). The high thermo-stability of these rutile phases can also be indicated by the absence of phase transformation peaks around 800 °C. The exothermic peak at 646 °C is assigned to the complete oxidative decomposition of Ir components. The XRD measurements for

this composition are tested at different heat temperatures (shown in Fig. 4). When the heat temperature is higher than 450 °C, the mixed coatings show a good crystallinity (with a formation of IrO₂ rutile-structured phases). After 550 °C, TiO₂ rutile phase starts to form significantly in the interface between Ti substrate and oxide coatings. β-Ta₂O₅ phase can not be detected over the whole tested temperature range, indicating the solubilization of β phase into IrO₂ rutile(s).

The first two thermolytic stages of the material for $x = 66.7\%$ (stage A and B) are much similar to those of $x = 53.9\%$. When the temperature $\geq 620\text{ }^\circ\text{C}$, however, the TGA curve varies dramatically (see Fig. 3e). In this temperature range, the weight loss of samples is slowed down, indicating an uncompleted decomposition of the mixed precursors which results in further weight loss even after 800 °C (see stage C).

Table 1 provides a summary of the temperature range for different thermolysis stages in $x\text{ H}_2\text{IrCl}_6(n\text{H}_2\text{O}) + (1 - x)\text{ TaCl}_5(n\text{H}_2\text{O})$ precursors.

To directly understand the solubilization behaviors between Ir and Ta oxides, the lattice parameters of IrO₂ rutile in the films are calculated from the distance of different crystalline planes based on XRD results (Table 2). The systematic differences of the cell volume values with the change of composition at the same temperature indicate that this phase is a solid solution of Ta component in rutile-structured IrO₂. Since the ion radius of Ta^{IV}, Ta^V and Ir^{IV} are extremely close to each other (0.74, 0.72 and 0.71 Å, respectively [18]), Ir and Ta compounds are prone to form a solid solution during the thermolysis formation of the mixed oxides. The lattice of rutile-structured IrO₂ is deformed and the cell volume increases due to the access of a larger ion of Ta component. As shown in Table 2, at 450 °C the rutile-structured cell volume of the film

Table 2
Lattice parameters and cell volume of rutile IrO₂ in films $y\text{IrO}_2 + (100 - y)\text{Ta}_2\text{O}_5^a$

y (mol%)	T (°C)	a (nm)	c (nm)	V (nm ³)
10	450	0.4554	0.3165	0.0656
26	450	0.4571	0.3132	0.0654
40	450	0.4593	0.3111	0.0656
60	450	0.4560	0.3162	0.0657
70	450	0.4573	0.3185	0.0666
80	450	0.4554	0.3165	0.0656
100	450	0.4561	0.3174	0.0660
	^b	0.4498	0.3160	0.0638

^a The calculation of the lattice parameters was made using the (1 1 0) and (1 0 1) reflections.

^b Equilibrium lattice parameters of rutile IrO₂ [17].

with the content of 70% IrO₂ reaches the maximum value, indicating the maximum solubility of Ta with rutile-structured IrO₂ occurs.

Taking into consideration the complicated interaction between Ir and Ta chlorides in thermolysis process, it is very difficult to exactly determine the reaction products in each temperature regions. Nevertheless, it can be still possible to obtain some useful information on thermolysis kinetics of the mixed system by the combined analysis of the measured and calculated TGA curves as shown in Fig. 3. In a general trend, the value of weight loss in the former is larger than that in the latter over a wide temperature range. This means the oxidative decomposition of the individual chloride is catalyzed each other in the Ir/Ta mixture. As mentioned above, this catalysis effect is mainly attributed to the formation of solid solution between Ir and Ta oxides, with the β phase at nominal IrO₂ content <30 mol% and rutile-structured phases (Ta₂O₅ in rutile-structured IrO₂) at nominal IrO₂

Table 1
Temperature range (°C) of various thermolysis stages in TGA curves for $x\text{ H}_2\text{IrCl}_6 + (1 - x)\text{ TaCl}_5$ precursors

Thermolysis stages	x (mol%)						
	0	5.3	25.0	42.9	53.9	66.7	100
A	~150	~220	~215	~150	~435	~438	~360
B	150–475	220–440	215–368	150–261	435–583	438–650	360
C	475	440	368–438	261–477	583	650	583
D			438–485	477–610			
E			485	610			

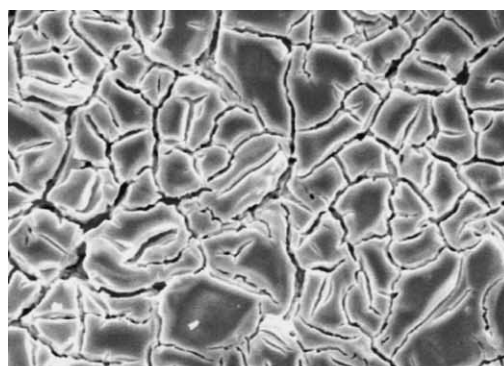
Table 3

Weight difference in TGA curves between calculated (W_3) and experimental (W_2) data at 450 °C

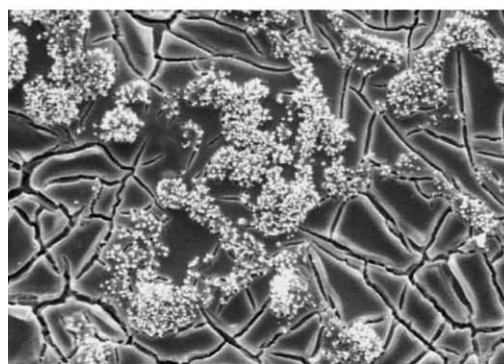
x (mol%)	$W_3 - W_2$ (%)
5.26	2.35
25.00	6.01
42.86	7.59
53.85	9.66
66.70	4.28

content ≥ 30 mol%. Accordingly, the thermolytic formation temperature of the major component in Ir/Ta mixed precursors decreases, then the total thermolysis process is facilitated. The differences of residue weight percent between the measured and calculated data obtained at 450 °C are listed in Table 3. As shown from the table, the order of thermolysis catalysis intensities of Ir and Ta components in the mixed chloride precursors is as follows: $x = 5.3\% < x = 25\% < x = 42.9\% < x = 53.9\% > x = 66.7\%$, with the maximum at $x = 53.9\%$ (i.e. 70 mol% nominal IrO_2 content in $\text{IrO}_2 + \text{Ta}_2\text{O}_5$ mixture). Relatively lower intensities are observed for the samples with a low Ir content ($x = 5.3\%$) and low Ta content ($x = 66.7\%$). Moreover, at high temperatures the decomposition process of the major component is inhibited by the minor one in the case of these two compositions. For instance, when $T > 700$ °C the measured weight loss of mixed precursors with $x = 5.3\%$ is surprisingly smaller than the calculated one (see Fig. 3a), indicating an inhibition of minor Ir component on the oxidative dissociation of major Ta chloride at a high temperature region. In the case of $x = 66.7\%$, the decomposition of Ir chloride is restricted by minor Ta component after 620 °C as shown in Fig. 3e.

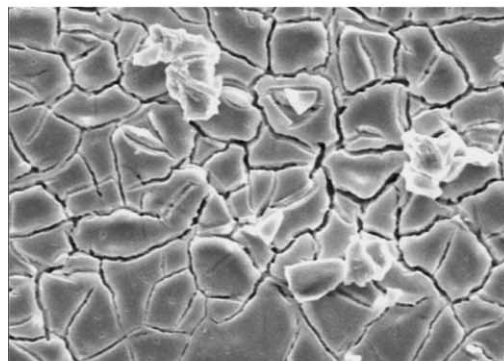
The maximum interaction force between the two components in 53.9% $\text{H}_2\text{IrCl}_6 + 46.1\%$ TaCl_5 mixture is in good agreement with the maximum solubility between Ir and Ta oxides measured on the $\text{IrO}_2 + \text{Ta}_2\text{O}_5$ mixed oxide films (with the nominal IrO_2 content of 70%) [9]. Fig. 5 displays typical micrographs of Ti supported $\text{IrO}_2 + \text{Ta}_2\text{O}_5$ prepared at 450 °C with different IrO_2 contents. Although, the previous work indicated the interaction between Ti substrate and IrO_2 oxides [19], according to our testing results TiO_2 rutile will only form in the Ti/oxide coatings interface at high temperatures (≥ 500 °C). From the XRD mea-



(a)



(b)



(c)

10 μm

Fig. 5. SEM surface images of Ti supported Ir/Ta oxide coatings with different IrO_2 contents prepared at 450 °C: (a) 10%, (b) 70%, and (c) 80% IrO_2 .

surements one cannot detect products regarding the Ti element participation at 450 °C. Moreover, according to the investigation of Krysa et al. [4] the surface morphology of oxide coatings is dependent to a great extent on the pretreatment of Ti substrate. In the present paper, the same pretreatment of Ti substrate for each experiment is employed, therefore the surface morphology of oxide coatings prepared at 450 °C (Fig. 5) is mainly determined by IrO₂ compositions in the mixed oxide coatings. The oxide surface exhibits a cracked-mud structure already observed by other authors on oxide layers by thermo-decomposition. Three typical surface features are observed: (i) islands separated by cracks, (ii) large amount of fine crystallites segregating on the surface of islands, and (iii) large size of crystallites segregating on the surface of islands. The segregation crystallites refer to IrO₂ based solid solution by the evidence of XRD analysis and of iridium enrichment in the region of the segregation by line scanning of X-ray energy dispersive analysis (EDX). It can be clearly shown that the finest grains exist on the surface of 70% IrO₂ containing oxide films. Both the maximum solubility and the finest segregation grains at a nominal IrO₂ content of 70% are attributed to the significant interaction between Ir and Ta chlorides during the thermolysis process. The above mentioned results are consistent with the viewpoint of Roginskaya and Morozova [8] who presented that the boundaries of IrO₂ crystallites are appreciably modified by Ta₂O₅ in mixed oxides, and the finer the crystallites the more the contribution of this mixed modified phase, and vice versa. The maximum activity and the highest stability of Ti/70 mol% IrO₂–30 mol% Ta₂O₅ electrodes for oxygen evolution reported by many workers [3,20–22] can be attributed to the characteristic thermolysis behaviors of the chloride precursors with the corresponding composition.

4. Conclusion

(1) As a result of the interaction between Ir and Ta components, especially, the formation of solid solution phases during the thermolysis process of mixed chloride precursors, the oxidative dissociation of H₂IrCl₆ + TaCl₅ mixture is facilitated. This promotion effect reaches the maximum at a nominal IrO₂ content of 70 mol% in the expected

product, IrO₂+Ta₂O₅ mixed oxides, accompanied by the maximum solubility between the two oxides and the finest crystal grains in oxides mixture. For the mixed precursors with a low Ir content (10 mol% nominal IrO₂ in IrO₂ + Ta₂O₅) or a low Ta content (80% nominal IrO₂ in IrO₂ + Ta₂O₅), however, the decomposition of the major component is inhibited by the minor one at high temperatures (610–800 °C).

(2) The β solid solution formed at low Ir contents (<30 mol% IrO₂) is unstable since it is subjected to decomposition at high temperatures (≥750 °C). Two or more IrO₂ rutile-structured solid solution phases can be thermolytically formed from the mixed precursors with nominal IrO₂ contents ≥30 mol%. The rutile-structured phases stably exist only in the case of IrO₂ contents ≥60 mol%, otherwise they are decomposed at higher temperatures.

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