A study on Electrosynthesis of 2,5-dichlorophenol Using Titanium Anode Coated with Metallic Oxide

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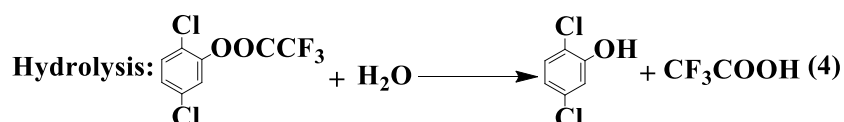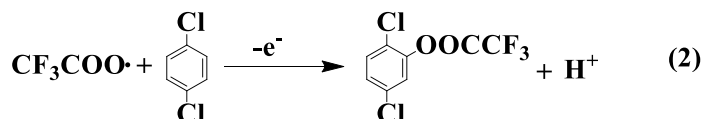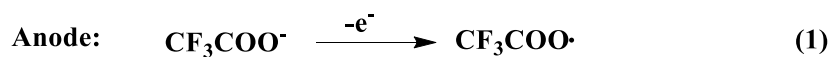
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A conventional thermal decomposition method was used to prepare Sn-Ir electrodes modified with Sb-, Co-, and Ce-based oxides, which were applied to synthesize 2,5-dichlorophenol by the electro-oxidation of 1,4-dichlorobenzene. The morphology of the electrodes was investigated by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) tests were employed to analyse the electrolysis experiment and electrocatalytic activity of the electrodes. The results showed that Sn-Ir electrodes doped with designated amounts of Sb, Co or Ce could compact the coating, and improve the stability of the electrode. Typically, Sn-Ir doped with 1% Ce had a good response in the LSV measurement, which yielded a 2,5-dichlorophenol concentration of 45% with a selectivity of 85%. The conversion rate of 1,4-dichlorobenzene was 53%, which indicated that the Sn-Ir-Ce electrode had a better catalytic activity.

1. INTRODUCTION

It is known that 2,5-Dichlorophenol is a key intermediate used for dicamba [1]. This intermediate is usually synthesized by conventional chemical methods [2-4], as shown in Scheme 1. It is well known that the conventional chemical method has many problems such as harsh reaction conditions, scarce raw materials, and various side reactions. In contrast, the electrochemical strategy [5] is highly controllable with fewer by-products [6-8]. Fujimoto *et al.* reported that phenol was synthesized from benzene by anodic oxidation [5]. A similar reaction was proposed in previous work

[9]. The electrolyte contains trifluoroacetic acid and triethylamine. CF_3COO^- was oxidized to $CF_3COO\cdot$ at the anode, and the radical combined with 1,4-dichlorobenzene to form the intermediate of 2,5-dichlorophenol. Then, 2,5-dichlorophenol was generated by hydrolysis [Reactions (1)-(4)]. Although the formation of 2,5-dichlorophenol was believed to occur directly in the water phase for $OH\cdot$ to be generated easily, O_2 could be formed as well, and O_2 could react with 2,5-dichlorophenol. Therefore, the reaction was complex in the water phase.

Anode: $\quad CF_3COO^- \xrightarrow{-e^-} CF_3COO\cdot \qquad (1)$

$CF_3COO\cdot + $ [2,5-dichlorobenzene] $\xrightarrow{-e^-}$ [2,5-dichlorophenyl trifluoroacetate] $+ H^+ \qquad (2)$

Cathode: $\quad 2H^+ \xrightarrow{+2e^-} H_2 \qquad (3)$

Hydrolysis: [2,5-dichlorophenyl trifluoroacetate] $OOCCF_3 + H_2O \longrightarrow$ [2,5-dichlorophenol] $OH + CF_3COOH \qquad (4)$

Typically, conditions such as the anode materials, current density, electrolysis time and type of electrolyte could influence the yield of 2,5-dichlorophenol in the electrolysis experiments. It is known that electrodes with high electrocatalytic activity can enhance the yield. A platinum electrode is usually used in electrolysis for its stability and higher catalytic activity; however, platinum electrodes are expensive, and they are not feasible for large-scale industrial applications. Furthermore, the electrochemical catalytic activity of the platinum electrode still needs to improve to meet the needs of practical applications. Actually, a new type of anode, which is a Ti-based dimension stable anode (DSA), has attracted a great deal of attention in recent decades, and it is widely applied in the chlor-alkali industry, electrosynthesis, oxygen evolution reaction, and sewage disposal because of its advantages of superior performance and facile fabrication [10-14]. Ti is chosen as the substrate for its availability and corrosion resistance compared with Zr, Nb, Hf, and Ta [15]. It is known that the electrochemical performance of DSAs can be improved by altering the composition and morphology of the coating [16]. SnO_2 and IrO_2 are usually selected as the metallic oxide coating for their good performance in electrocatalysis [17-21]. To get a better electrode in terms of service and electrochemical performance, other metallic oxides are doped in the electrode because the physical structure of the electrode is changed, and the metallic oxides dopants can increase the adhesion between the coating and the substrate [22-25].

In a previous study, a $Ti/SbSnO_x/IrSnO_x$ electrode was prepared by a conventional thermal decomposition method. The accelerated life of the electrode is 115h in 1 mol L^{-1} H_2SO_4 at a current density of 5 $A\cdot cm^{-2}$. The electrocatalytic performance of the electrode is higher than that of a Pt electrode, commercial oxygen evolution electrode, and chlorine evolution electrode [9]. However, the stability and electrocatalytic activity of the electrode still needs improvement. In this work, a Ti/Sn-Ir-Ce electrode with a long service life and high electrocatalytic activity was obtained after comparing the performance of electrodes via electrochemical measurements and electrolysis experiments.
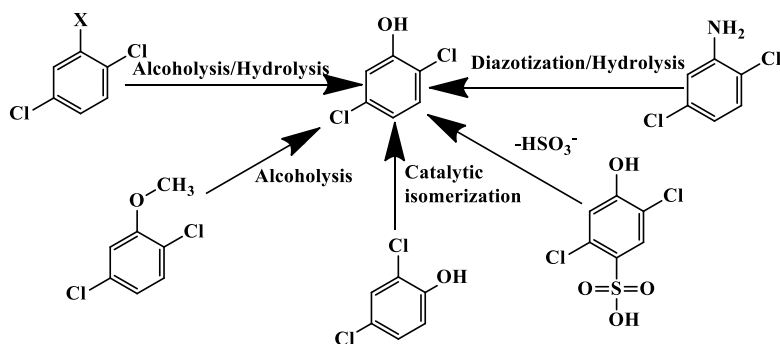
Scheme 1. Chemical methods for the synthesis of 2,5-dichlorophenol

2. EXPERIMENTAL

2.1 Preparation of electrodes

Titanium mesh (5 cm × 5 cm) was pretreated by thermal oxidation (500 °C) to degrease the sample. Next, it was sand blasted to obtain a rough surface. Then, to remove the oxides and strengthen the adhesion between the coatings and the substrate, it was etched in 30 wt % sulfuric acid heated to 80 °C for 30 min, and the Ti substrate was subsequently washed with deionized water. Different mole ratios of $SnCl_4 \cdot 5H_2O$ (99%, Aladdin Co., Ltd., Shanghai, China), $HIrClO_4$ (Ir wt %=35%, Aladdin Co., Ltd., Shanghai, China), $CoCl_2 \cdot 6H_2O$ (99%, Aladdin Co., Ltd., Shanghai, China), $SbCl_3$ (99%, Aladdin Co., Ltd., Shanghai, China) and $CeCl_3 \cdot 7H_2O$ (99%, Aladdin Co., Ltd., Shanghai, China) (Table 1) were added to n-butyl alcohol as a brush solution. The brush solution was dipped on the Ti substrate, dried at 120 °C for 10 min and heated up at 500 °C in air atmosphere for 10 min. The electrodes were cooled naturally to avoid cracking on the electrodes surface. The above process was repeated 12 times, and the final time it was heated at 500 °C for 1 h. Total metal mass of the coating was 20 g·m^{-2}.

Table 1. The various compositions of prepared electrodes

| Entry	Sn	Ir	Co	Sb	Ce
E1	95	5			
E2	90	10			
E3	85	15			
E4	80	20			
E5	78	20	2		
E6	76	20	4		
E7	74	20	6		
E8	75.2	20		4.8	
E9	75	20			0.5
E10	70	20			1
E11	65	20			1.5
E12	60	20			2

2.2 Accelerated life test of electrodes

Accelerated electrolysis life test was carried out to compare the adhesion of metallic oxides with Ti substrates in a solution containing 1 mol L^{-1} H_2SO_4 at a current density of 10 $A \cdot cm^{-2}$. The Ti electrode was used as the counter electrode, and the thermostat water bath was used to keep the temperature at 40 °C. When the voltage increased 5 V, the electrode was considered invalid [26]. The purpose of the accelerated life test of the electrodes was to select the electrodes that had a longer service life for the anode in the electrolysis experiments.

2.3 Electrochemical characterization

The electrochemical behaviour of 1,4-dichlorobenzene oxidation was investigated by using a CHI660B electrochemical workstation (Shanghai Chenhua Instruments Co., Ltd., China). The electrochemical cell was assembled with a conventional three-electrode system with a Pt plate working electrode, a saturated calomel reference electrode (SCE), and a graphite plate counter electrode. The working and counting electrodes were chosen because the Pt plate has the characteristics of an active anode as well and the graphite shows superior conductivity, making them suitable for this purpose. The electrolyte was a mixed solution of trifluoroacetic acid and triethylamine (mol ratio was 2:1) containing 0.1 $mol \cdot L^{-1}$ 1,4-dichlorobenzene.

2.4 Synthesis of 2,5-dichlorophenol
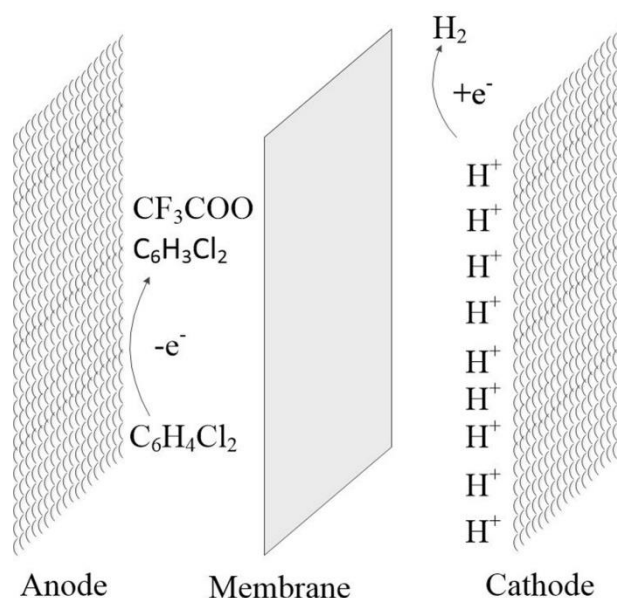
Scheme 2. The electrolysis device

2,5-Dichlorophenol was synthesized by the electro-oxidation of 1,4-dichlorobenzene. The electrode (2 cm × 2 cm) had been selected (in 2.3) as the anode, and the Ti electrode was used as the

cathode (2 cm × 2 cm). A polypropylene diaphragm was used to divide the chambers. The current density was 7.5 mA·cm^{-2}. The electrolyte was a mixed solution of trifluoroacetic acid and triethylamine (mol ratio was 2:1), which were added with 1,4-dichlorobenzene (0.1 mol·L^{-1}) in the anode chamber (50 ml), and cathode chamber contained 50 ml of a mixed solution of trifluoroacetic acid and triethylamine (mol ratio was 2:1). The electrolysis was conducted in the plate and frame electrolytic cell showed in Scheme 2, and the electrolysis time was calculated by the faradaic efficiencies, which were determined to be 100% by equation (5). With electrolysis time, the by-product could be formed by CF$_3$COO· and the intermediate of 2,5-dichlorophenol.

$$\eta = \frac{ZnF}{It} = 100\% \quad (5)$$

2.5 Analysis method

The electrolyte was hydrolysed to form 2,5-dichlorophenol after electrolysis and extracted by methylbenzene. Because the boiling points of methylbenzene, 1,4-dichlorobenzene, and 2,5-dichlorophenol are 110.6 °C, 173.4 °C, and 210 °C, respectively, the extract was analysed by gas chromatography (HP6890N, Agilent Technologies Co., Ltd.). The temperature programming was set from 50 °C to 230 °C at a speed of 20 °C per minute. The standard curve of the peak area and concentration of 1,4-dichlorobenzene and 2,5-dichlorophenol were drawn to precisely calculate the concentration of 1,4-dichlorobenzene and 2,5-dichlorophenol. In addition, the conversion rate, selectivity and yield could be calculated by the following equations:

$$\alpha_{conversion} = \left(1 - \frac{C_{paracide}}{0.01}\right) \times 100\% \quad (6)$$

$$\omega_{yield} = \left(\frac{C_{2,5-dichlorophenol}}{0.01}\right) \times 100\% \quad (7)$$

$$Y_{selectivity} = \frac{\alpha_{conversion}}{\omega_{yield}} \times 100\% \quad (8)$$

2.6 Physical characterization

A Hitachi S-4800 SEM was utilized to observe the surface microtopography of the electrodes. XRD analysis (D/MAX-2500, Rigaku, Japan) was used to measure the microstructure of the electrodes using a diffractometer with Cu K-Alpha radiation (λ=1.54425 nm) working at 40 KV/40 mA. The diffraction patterns were collected in the range of 2θ=10-80° at a rate of 10° per minute.

3. RESULTS AND DISCUSSION

3.1 Accelerated life test

Figure 1 shows the accelerated life of the different electrodes, and Figure 1 (a) shows the influence of the variated content of Sn and Ir on the accelerated life. The order of the accelerated life is E4＞E3＞E2＞E1. The results indicate that when the content of Ir increases or the content of Sn

decreases, the accelerated life was obviously increased. Ir is a metal that was previously taken into consideration, and the amounts of Sn and Ir were determined as 80% Sn and 20% Ir (mol ratio). E5, E6 and E7 were prepared by using E4 doped with different amounts of Co, as is shown in Figure 1 (b). Here, E5 had a longer accelerated life. As the content of Co increases, the accelerated life decreases. Figure 1 (c) reflects that E4 doped with Sb at a ratio of Sn: Sb=94:6 (mol ratio) [27] could improve the accelerated life of the electrode. E9, E10, E11 and E12 were prepared by E4 doped with different amounts of Ce, as is shown in Figure 5 (d), and E10 had a longer accelerated life. Ce is a rare earth metal that can improve the performance of the electrode when doped with an appropriate amount [28]. An electrode surface with fewer cracks could protect the Ti substrate and slow corrosion. Xu *et al.* [29] reported that the accelerated life of an IrO_2-Ta_2O_5-coated titanium electrode could last 800 h at 2 $A \cdot cm^{-2}$ in 1 mol L^{-1} H_2SO_4 at room temperature. According to the equation, $\tau_2 = \tau_1 \left(\frac{i_1}{i_2}\right)^2$ **(9)**, (i_2 and i_1 are the actual current density and the accelerated current density, respectively; τ_2 and τ_1 are the actual service life and accelerated life, respectively), the accelerated life of E4, E5, E8 and E10 are longer than the life of the IrO_2-Ta_2O_5 electrode (70% content of Ir).
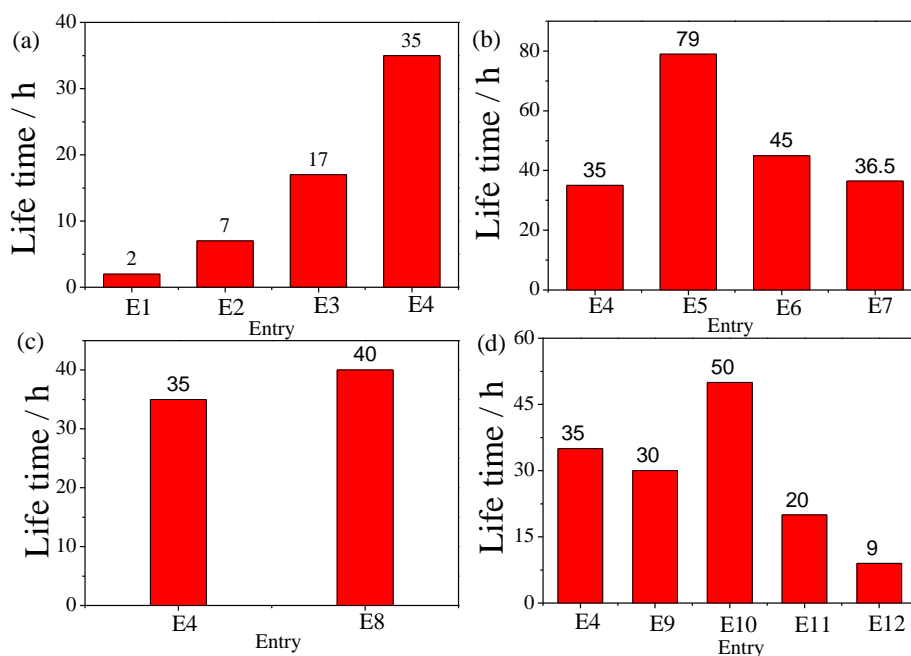

Figure 1. The accelerated life of different electrodes in 1 mol L^{-1} H_2SO_4 at a current density of 10 $A \cdot cm^{-2}$.

3.2 Cyclic voltammetry

Figure 2 (1) shows the potential corresponding to the peak at 1.2 V *vs* SCE for different scan rates. The peak reflects the reaction (1), and $CF_3COO\cdot$ was formed which can combine with 1,4-dichlorobenzene. With a higher scan rate, the peak current increases. Additionally, with an increase of the scan rate, the peak potential increased gradually in the positive direction, which indicates the reaction was irreversible. Figure 2 (2) shows the plotted results according to Figure 2 (1). As seen from

Figure 2 (2), the relationship between the peak current (I_p) and the scan rates is linear, indicating that the electrode reaction was a surface controlled process and that the electrolytic reaction could be influenced by the electrode [30]. It was necessary to seek out an electrode with a high electrocatalytic activity.
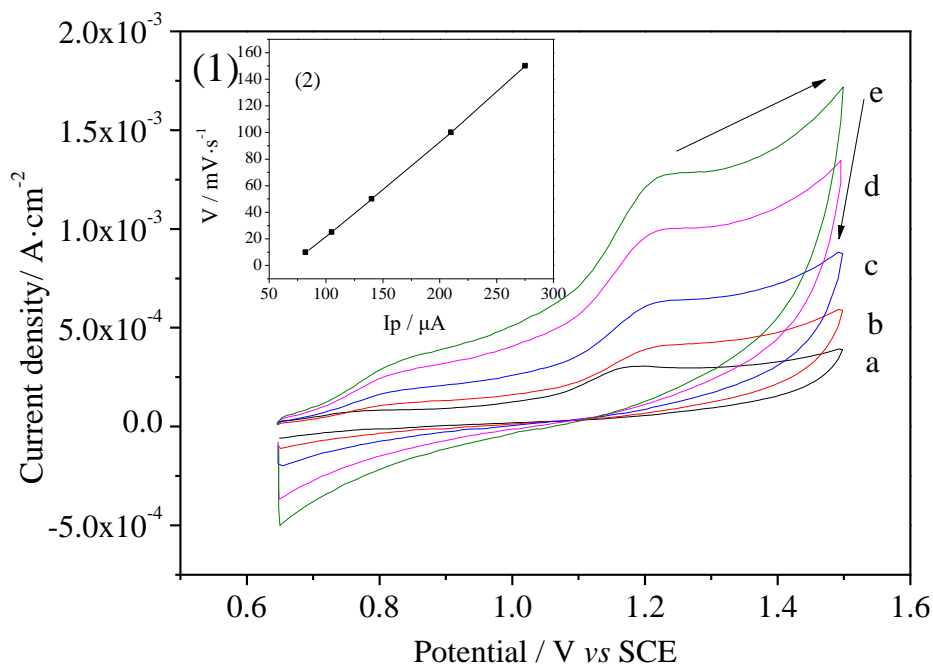

Figure 2. (1) Cyclic voltammograms of 0.1 mol·L^{-1} 1,4-dichlorobenzene at a Pt electrode at the different scan rates of (a) 10 mV/s, (b) 25 mV/s, (c) 50 mV/s, (d) 100 mV/s, and (e) 150 mV/s. (2) Linear relationship obtained between the peak current and the increase of the square root of scan rates.

3.3 Electrolysis experiments

Gas chromatography was used to examine the product and calculate the yield. As is shown in Figure 3 (a), the retention times of 6.62, 8.06, and 9.37 correspond to 1,4-dichlorobenzene, 2,5-dichlorophenol, and a by-product (deep oxidation), respectively. In theory, 2,5-dichlorophenol was the only product of the electro-oxidation of 1,4-dichlorobenzene. However, during deep oxidation, it was difficult to prevent the formation of 2,5-dichlorophenol. Figure 3 (b) shows the standard curves, in which $y = 31440x - 60.4$ (1,4-dichlorobenzene), $y = 27982.8x - 59.9$ (2,5-dichlorophenol), such that x is the concentration (mol·L^{-1}), and y is the peak area.

Table 2 presents the results of electrolysis by using different electrodes as the anode. The order of the yield was E10＞E4＞E5＞E8，the order of the conversion was E4＞E10＞E5＞E8, and the order of the selectivity was E8＞E10＞E4＞E5. The yields of E4 and E10 were obviously higher than those of E5 and E8. Of the high-yield electrodes, E10 had the highest electrocatalytic activity, longest life time and best selectivity for the electro-oxidation of 1,4-dichlorobenzene. Compared with the conventional chemical methods of preparing 2,5-dichlorophenol and other electrolysis reactions, the products of this reaction were not complex, and the selectivity was high [31].
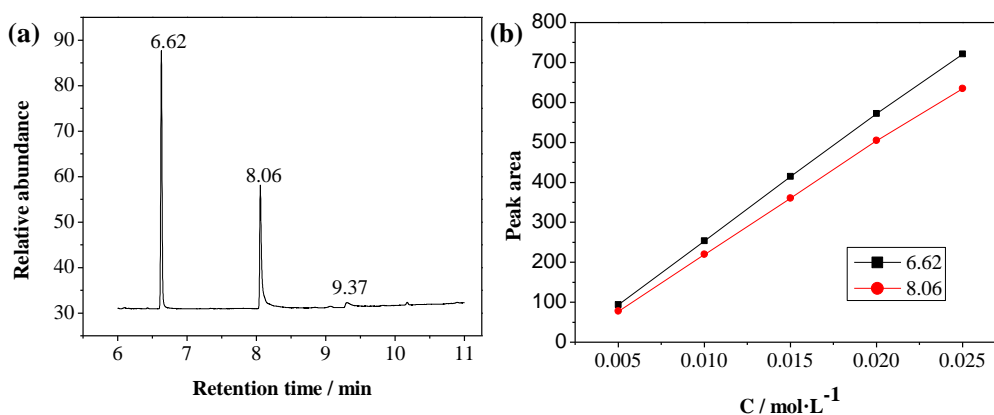
Figure 3. (a) Metrological chromatograph of the products, the retention times of 6.62, 8.06, and 9.37 correspond to 1,4-dichlorobenzene, 2,5-dichlorophenol, and a by-product, respectively. (b) Standard curve of the peak area corresponding to the concentration of products. 6.62 is 1,4-dichlorobenzene, 8.06 is 2,5-dichlorophenol.

Table 2. The results of gas chromatography after calculations

Entry	1,4-Dichlorobenzene (peak area)	2,5-Dichlorophenol (peak area)	Yield	Conversion	Selectivity
E4	84	60	43%	54%	79%
E5	106	42	36%	47%	77%
E8	143	28	31%	35%	89%
E10	89	65	45%	53%	85%

3.4 Surface analysis

Figure 4 shows the surface morphologies of different electrodes prepared by conventional thermal decomposition. The results show that the surfaces of all the electrodes exhibit pores and unavoidable cracks from the mechanical tension and cooling shrinkage after sintering resulting from the difference in the thermal expansivity of the Ti substrate and the metallic oxide coatings [32]. E4 shows more pores, cracks and particles, which led to a relatively unstable coating. E5, E8 and E10 showed fewer cracks and holes. E5, E8 and E10 were doped with a suitable amount of metal from E4, which is the reason that the surface structure of the electrode can be improved when doped with a proper amount of metal [33]. As is shown in Figure 5, all the diffraction patterns display a series of diffraction peaks (35.3°, 38.4°, 40.4°, 53.2°, 63.2°, 70.8°, 73.9°) representing the Ti substrate and a few diffraction peaks of SnO_2 (26.6°, 38.1°, 54.9°) and IrO_2 (28.1°, 34.7°). This may be a result of the thin coating thickness, and it may also have been that the diffraction peaks of the other metallic oxides were covered. The diffraction patterns indicate that the electrode consisted of oxides of Sn and Ir. The diffraction peaks of TiO_2 were not shown in the figure indicated that the Ti substrate was covered by other metallic oxides, and the Ti was not oxidized during the preparation process [23].
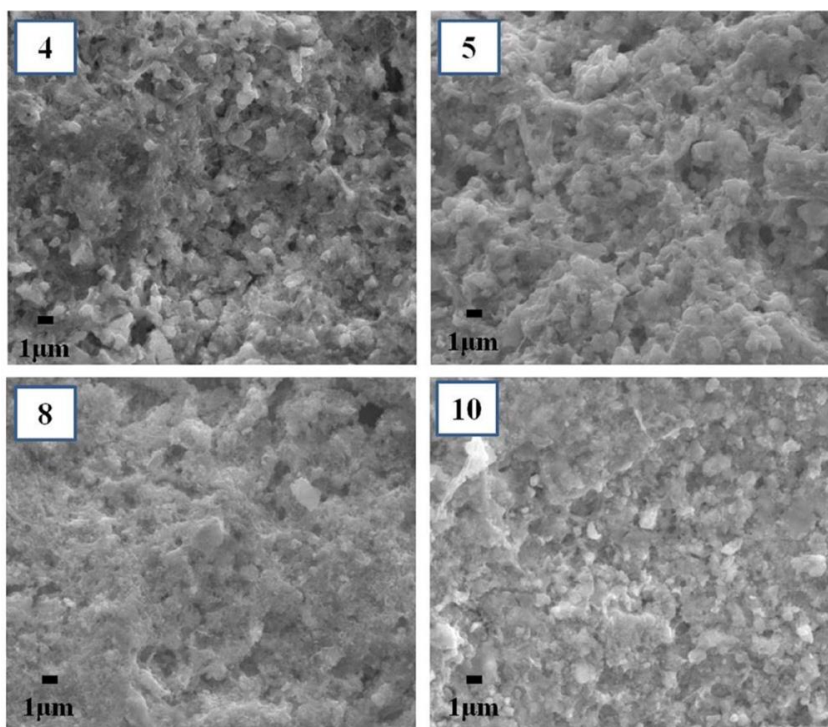
Figure 4. SEM images showing the surface morphologies of E4, E5, E8 and E10.
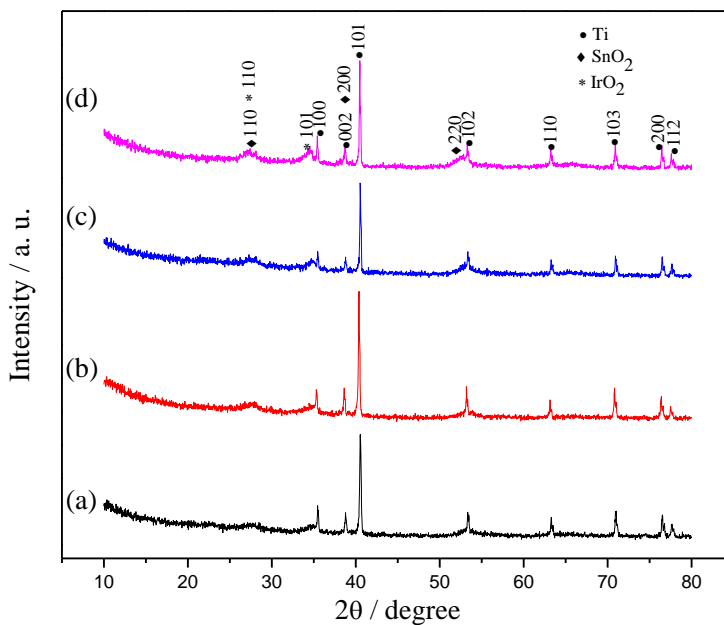

Figure 5. XRD patterns of electrodes (a) E4, (b)E5, (c) E8, and (d) E10.

3.5 Liner sweep voltammetry

LSV was used to study the electrocatalytic activity of the electrodes [34]. As shown in Figure 6, the response current of all the electrodes was lower in the blank solution than in the solution containing 1,4-dichlorobenzene, and the response potential was approximately 1.2 V *vs* SCE. This is

attributed to the participation of 1,4-dichlorobenzene in the reaction. The net current of the E4 and E10 samples was notably larger than that of E5 and E8, which reflects that E4 and E10 have a better catalytic activity for the electro-oxidation of 1,4-dichlorobenzene. The surface structure should also be considered for this result. The SEM images of E4 and E10 show many thin particles that enhance the real area of the electrode and improve its the electrocatalytic activity. Based on the results of the cyclic voltammetry, E4 and E10 are more suited for use as anodes in the electrolysis experiments. These results are consistent with the electrolysis experiments.
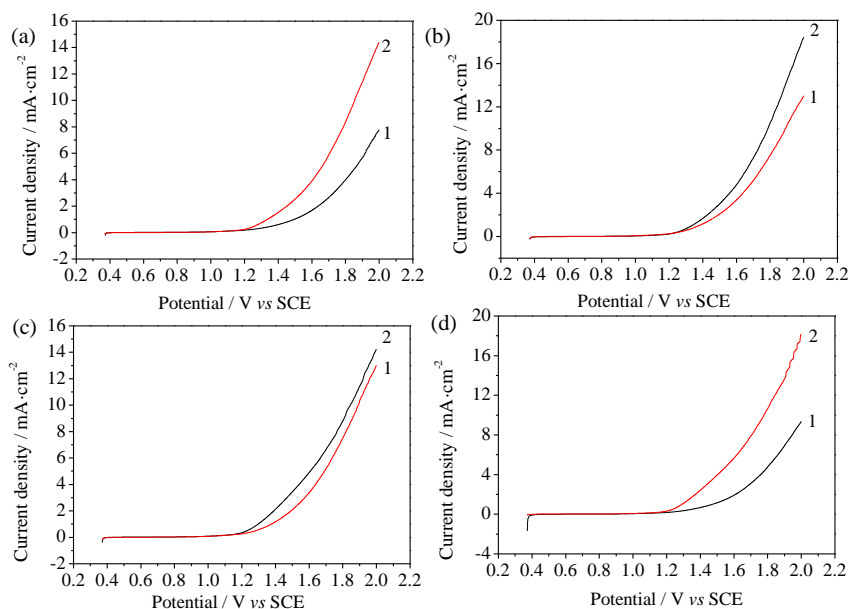

Figure 6. LSV of different electrodes (a) E4, (b) E5, (c) E8, (d) E10 in the blank solution (1) and in the sample solution (2).

4. CONCLUSIONS

In summary, we prepared Sn-Ir electrodes modified with Sb-, Co-, and Ce-based oxides, which were used to synthesize 2,5-dichlorophenol by the electro-oxidation of 1,4-dichlorobenzene. It was found that the type and proportion of the electrode materials influence the morphology, life time, and catalytic activity of the electrodes. Typically, Sn-Ir electrodes doped with an appropriate amount of Sb, Co, and Ce could improve the life time of electrodes. When the ratio of Sn:Ir:Ce is 79:20:1, the accelerated life of the electrode is 50 h in 1 mol L^{-1} H_2SO_4 at a current density of 10 A cm^{-2}. In addition, the catalytic activity of the electrode is high, and the yield of the 2,5-dichlorophenol can reach 45%. The selectivity reaches 85% and the conversion rate of 1,4-dichlorobenzene is 53%, indicating that Sn-Ir-Ce electrode is promising for the electrosynthesis of 2,5-dichlorophenol via the electro-oxidation of 1,4-dichlorobenzene.

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