The effect of Ce doped in Ti/SnO₂-Sb₂O₃/SnO₂-Sb₂O₃-CeO₂ electrode and its electro-catalytic performance in caprolactam wastewater

Qilin Zhang, Yaochi Liu, Dongming Zeng, Jingping Lin and Wei Liu

ABSTRACT

Ti/SnO₂-Sb₂O₃/SnO₂-Sb₂O₃-CeO₂ anodes were prepared by brush coating with high temperature oxidation. The anodes were characterized by X-ray diffractometer (XRD), scanning electron microscope and cyclic voltammetry. The surface of the electrode shows more compact and exist shallower mud cracks than the others by coating with 1% Ce to the surface of Ti/SnO₂-Sb₂O₃ electrode. The XRD patterns show that as-prepared electrodes are SnO₂ and TiO₂. The electrode with 1% Ce dopant shows the highest efficiency in the electrolysis of caprolactam wastewater. The oxygen evolution potential is about 1.75 V, the removal rate of chemical oxygen demand is 50%, and the biochemical oxygen demand is 353 mg/L for 5 h at a current of 0.12 A.

INTRODUCTION

Caprolactam wastewater is toxic, refractory, and difficult to be treated. Traditional wastewater technologies, such as incineration, biological and chemical methods have been proposed for caprolactam wastewater, but they are ineffective or high cost (Li et al. 2006).

Electrochemical (EC) processes are attractive for their high activity, low cost, ease of operation, high stability, wide range of treatment conditions and environmental friendliness for treatment of organic wastewater (Feng & Li 2003; Samet et al. 2006; Ali & Gupta 2007; Marco & Giacomo 2008; Cui et al. 2009; Gupta & Suhas 2009; Gupta et al. 2009). Organics can be oxidized to CO₂ and H₂O by OH radicals and chemisorbed active oxygen species produced during the EC reaction ( Parsa et al. 2009; Song et al. 2010).

In the EC processes, the effective and economical anodic oxidation of pollutants requires an appropriate choice of catalytic electrode materials. Ti/SnO₂ and Ti/PbO₂ electrodes exhibit higher oxygen evolution potentials compared with Ti/RuO₂, Ti/IrO₂ and other electrodes (Kelly & Sasha 2007; Li et al. 2009). Doping of rare earth into SnO₂ electrode changes the crystallinity of oxide films and enhanced the electrode capability on mineralization of phenolic compounds (Cui et al. 2009; Feng et al. 2010). The rare earth Ce has unique outer electronic structure. The electrons at the 4f orbital, which are not fully occupied, can occupy the 5d orbital and become valence electrons. It has been found when Ce is doped into metal oxide coatings, additional energy bands can be induced in the structure of coatings (Chen et al. 2009).

To the best of our knowledge, EC oxidation has not been explored for the degradation of caprolactam wastewater, especially the SnO₂ anode with Ce. In order to find an effective electrode to degrade caprolactam wastewater, in this paper, a systematic research was carried out to investigate the relationship of the structure and electro-catalytic activity with regards to the different amounts of Ce doped in Ti/SnO₂ anodes. The morphology and physical structures of the coating surface were examined by scanning electron microscope (SEM) and X-ray diffractometer (XRD). The electro-catalytic performance of the electrodes in caprolactam wastewater was evaluated by cyclic voltammetry measurements and bulk oxidation degradation.

EXPERIMENTS AND METHODS

Wastewater

The caprolactam wastewater from a chemical factory (Changsha, China) was adopted in this experiment. The
wastewater is difficult to treat due to its unstable and complicated characteristics. Its chemical oxygen demand (COD) is 3,000–6,000 mg/L, biochemical oxygen demand (BOD₅) is 10–50 mg/L, pH is 4–11 and the concentration of caprolactam is 100–500 mg/L.

Electrode preparation

Titanium net (2 × 3 cm) was used as the substrate for all oxide-coated electrodes. The substrates were polished using sand papers, degreased in 10 mol/L NaOH at 80°C for 2 h, and then etched in 6 mol/L oxalic acid at 90°C for 1 h followed by washing with distilled water, and dried. The electrode position of two layers was applied by thermal oxidation. The electrode includes the SnO₂–Sb₂O₃ inner layer and the SnO₂–Sb₂O₃–CeO₂ outer layer. For inner layer preparation, the solution was prepared by dissolving 2.5 g SnCl₄ · H₂O and 0.18 g SbCl₃ in 20 mL isopropanol with 1 mL 37% (by volume) concentrated HCl. The coating solution was painted onto the pretreated Ti substrate by a brush technique. The titanium net was dried in a drying oven at 80°C for 15 min and then placed into a preheated muffle furnace at 500°C for 10 min. This procedure was repeated for ten times. Finally, the titanium net was annealed at 500°C for 2 h in a muffle furnace (Feng et al. 2010; Tolba et al. 2010). For the outer layer preparation, the coating solution contained 2.5 g SnCl₄ · 5H₂O, 0.18 g SbCl₃, 1 mL 37% HCl and a variable amount of Ce(NO₃)₃ · 6H₂O (Ce/Sn mole ratios of 1.0, 2.0, 3.0, and 4.0%) in 20 mL isopropanol. The titanium nets were dried in an oven and then were heated in a muffle oven at 500°C for 10 min. After six times of above process, the titanium nets were individually heated in a muffle oven at 500°C for 2 h.

Structural characterization of the electrodes

Micrographs of the electrodes were obtained by SEM (Sirion200, Netherlands). The response information of phase identifications of the synthesized coatings were conducted by XRD (D/Max 2500 VB +, Japan).

Voltammetry measurements

Cyclic voltammograms were done at room temperature with a conventional three-electrode cell with a computer-controlled EC workstation (CH1660B, Shanghai Chenhua, China). A fabricated electrode (2 × 3 cm) was used as the working electrode; a graphite plate of the same size was employed as the counter electrode, and the reference electrode was a saturated calomel electrode (SCE) connected to the cell through a salt bridge (Yang et al. 2009). The working solution was 200 mL caprolactam wastewater contained 0.1 mol/L Na₂SO₄ at pH = 7. The blank solution was 100 mL distilled water contained 0.1 mol/L Na₂SO₄. The potential was scanned at a scan rate of 50 mV/s, and the scan range was from 0 to 2.5 V.

EC oxidation degradation

A fabricated electrode (2 × 3 cm) was used as the working electrode, whereas a graphite plate was employed as the counter electrode. The distance between anode and cathode was 7 cm. A DC potentiostat with a voltage range of 0–30 V was used as power supply for organic degradation studies. For each EC test run, 150 mL of caprolactam wastewater which contained 0.1 mol/L Na₂SO₄ was stirred by a magnetic stirrer. The bulk oxidation was performed at a current density of 20 mA/cm² for different electrolysis time (Kong et al. 2007).

The COD, BOD₅, and pH of the effluent were determined by using standard methods for the examination of water and wastewater (APHA 1995). UV (Cary 50 UV/vis Spectrophotometer, USA) absorbency over the range of 200–500 nm of the wastewater in the cell was analyzed. The total caprolactam concentration was measured by UV absorbance in a 3 cm quartz cell at 240 nm and pH 7. Linear results were obtained in the range of 100–200 mg/L with the regression equation \( A = 2.2702 \times C + 1.7735 \), \( R^2 = 0.9996 \) (Wei et al. 2003).

RESULTS AND DISCUSSION

XRD and SEM characterization of electrodes

SEM was used to characterize the morphology and surface structure of the five different electrodes. The SnO₂ coating without Ce doped (Figure 1(a)) is irregular and large mud-crack morphology. According to Figure 1(b), the surface coating of the 1% Ce doped Ti/SnO₂–Sb₂O₃ electrode is much more compact than other electrodes. The reduction of SnO₂ grain size with Ce addition suggest that improvement in catalytic ability is associated with a smaller grain size. The coating of the electrodes with 2% Ce (Figure 1(c)) is composed of heterogeneous and irregular cracks. The 3 and 4% Ce doping electrodes coatings have wide and deep cracks.

Figure 2 shows the phase behavior of the Ce inter layer of the modified Ti/SnO₂–Sb₂O₃ electrodes and the main
diffraction peaks are labeled. No diffraction peaks of Sb and Ce oxides are found from the XRD patterns due to low doping level or the incorporation of the doping ions into the SnO$_2$ unit cell (Cui et al. 2009). Compared with other electrodes, visible differences on the intensity of the SnO$_2$ and TiO$_2$ diffraction peaks are observed for 1% Ce doped Ti/SnO$_2$-Sb$_2$O$_3$ anode. The intensity of SnO$_2$ and TiO$_2$ peak in 1% Ce doped anode is lower than other Ce doped anodes.

**Voltammetry measurements**

According to the cyclic voltammogram, the oxygen evolution potential on the Ce doped electrodes is 1.75 V versus SCE. At this potential, the 0, 1, 2, 3 and 4% Ce anodic current are 15.74, 34.28, 30.47, 28.45 and 14.78 mA, respectively. It is clear that the 1% Ce dopant electrode own the best electro-catalytic capability. Along with the increase of Ce molar percent, the value of current...
peak decreases. The oxygen evolution potential of 1.75 V is higher than other electrodes (Ti/RuO₂), revealing that proper doping Ce could improve the current efficiency. Because oxygen evolution is a side-reaction and it reduces the overall current efficiency (Kong et al. 2007).

Figure 3(b) shows cyclic voltammetry (CV) of different materials in caprolactam wastewater. An oxidation current peak on the electrode appeared at 1.50 V, the anodic current of samples doping 0, 1, 2, 3 and 4% Ce, respectively, are 85.8, 117.3, 93.9, 98.7 and 37.9 mA. The peak current decreases gradually with increasing molar percent of Ce, it lies in the order: 1, 3, 2, 0 and 4%. This indicates that the Ce doped electrodes should have higher electro-catalytic activity in caprolactam solution.

**EC oxidation degradation**

EC oxidation degradation experiments were performed at pH 7 for 2 h with a current density of 20 mA/cm². The activity of five electrodes was evaluated based on their ability to oxidize organism. The UV/vis spectra of caprolactam wastewater were recorded over the range of 200–500 nm (Figure 4(a)).

The peak at about 240, 305 and 342 nm indicates the presence of the caprolactam, cyclohexanone-oxime, and nitrocyclohexane in caprolactam wastewater respectively (Wei et al. 2005; Zeng & Li 2005). In the 1 and 2% Ce electrodes, the peak at 305 and 342 nm decreases significantly after 2 h EC oxidation of caprolactam wastewater, indicating that the cyclohexanone-oxime and nitrocyclohexane are degraded rapidly. However, the decrease in 240 nm peak height shows a little loss of caprolactam. To investigate electrolysis of caprolactam, ln(C/C₀) versus time (Figure 4(b)) for the electrolysis in 200 mg/L caprolactam wastewater with a current density of 20 mA/cm² was tested (C is the concentration of the caprolactam after different electrolysis time in caprolactam wastewater; C₀ is the concentration of caprolactam wastewater not treated). The linear relationships suggest that the EC oxidation capability of caprolactam wastewater in these electrodes follows: 1, 2, 3, 0 and 4% Ce.

In order to further investigate the removal effect of wastewater and the influence of different Ce molar amounts on the electro-catalytic activity, degradation experiments were carried out on five electrodes. Figure 5 shows the variations of COD with different electrolysis time. After 5 h of electrolysis, the COD removal rates of samples doping 0, 1, 2, 3 and 4% Ce, respectively, are 36, 50, 41, 38 and 22%. In Figure 6, it shows the BOD₅ values of the five anodes. After 5 h of reaction, the BOD₅ for the anode with

---

**Figure 2** | XRD of Ti/SnO₂–Sb₂O₃–CeO₂ anodes prepared at different molar percent of Ce.

**Figure 3** | (a) Cyclic voltammograms of Ti/SnO₂–Sb₂O₃–CeO₂ anodes with different molar percent of Ce at the scan rate of 50 mv/s in 0.1 mol/L Na₂SO₄. (b) Cyclic voltammograms of Ti/SnO₂–Sb₂O₃–CeO₂ anodes with different molar percent of Ce at the scan rate of 50 mv/s in 0.1 mol/L Na₂SO₄ caprolactam solution.
0, 1, 2, 3 and 4% Ce increases from initial 32 to 266, 353, 301, 280 and 200 mg/L, respectively. From the dates of COD and BOD5, obviously, the 1% Ce doped electrodes is much more active than other electrodes. It concludes that 1% Ce dopant anode is more suitable for decomposition of caprolactam wastewater than other anodes.

CONCLUSIONS

The Ti/SnO2-Sb2O3 electrode coated with 1% Ce exists shallower mud cracks than other electrodes. Its oxygen evolution potential is about 1.75 V, the removal rate of COD is 50% and the BOD5 is 353 mg/L for 5 h at current density of 20 mA/cm2. The EC degradation capability of caprolactam wastewater lies in the order: 1, 2, 3, 0 and 4% Ce. It is suggested that proper and low doping Ce could improve the electro-catalytic capability. Higher Ce contents are not expected to show better performance.

ACKNOWLEDGEMENTS

We acknowledge the National Natural Science Foundation of China (No. 51074192) and the Planned Science and Technology Project of Hunan Province, China (2008FJ1009) for financial support of this research.

REFERENCES


Kelly, L. M. & Sasha, O. 2007 Sn0.86-Sb0.03-Mn0.10-Pt0.01-oxide/Ti anode for the electro-oxidation of aqueous organic wastes. Materials Chemistry and Physics 105, 143–147.


First received 5 January 2011; accepted in revised form 21 March 2011