



Effect of crystallographic structure of iridium based oxides on electrochemical degradation

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ARTICLE INFO

Article history:

Received 16 August 2017
Received in revised form
14 December 2017
Accepted 17 December 2017
Available online 18 December 2017

Keywords:

Electrochemical degradation
Tunnel structure
Iridium oxides
OER activity

ABSTRACT

Developing new anode materials is an effective strategy to overcome the growing challenges in electrochemical treatments. Material crystal structure is a critical factor in governing catalytic activity, but is often neglected in designing degradation electrodes. Here, we investigate the role of crystal structure using six different Ir-oxides with three different crystal structures in electrochemical degradation. Hollandite structure ($K_x\text{IrO}_2$ and $K_{1.6}(\text{Mn}_{0.78}\text{Ir}_{0.22})_8\text{O}_{16}$) with 2×2 tunnel size obtains higher removal performance than that of other structure oxides, such as packed pyrochlore ($\text{Pb}_2\text{Ir}_2\text{O}_{6.5}$ and $\text{Bi}_2\text{Ir}_2\text{O}_7$) and rutile (IrO_2 and $\text{Cu}_{0.3}\text{Ir}_{0.7}\text{O}_6$). Catalysts with same crystal structure show similar morphology features and have almost same degradation performance, although their electrochemical properties are quite different. The presence of tunnel structure in oxides may be responsible for excellent degradation performance of corresponding catalysts. Additionally, tunnel structure oxides with good oxygen evolution reaction (OER) activity can reduce the energy consumption due to low cell potential. Our findings bring an opportunity for developing new catalysts for electrochemical treatment technologies.

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1. Introduction

Electrochemical technologies have been paid more and more attention to degrade a wide range of organic and inorganic contaminants due to their flexible adaptability, zero-pollution or less pollution and easily combined with other advanced oxidation technologies [1]. The ability of electrochemical methods to destroy the organic structure, even to mineralization, stems from the strong oxidizing intermediates generated during electrochemical process [2,3], such as OH^\cdot , O_2 and Cl_2 et al. At present, there are three main types of electrode materials reported to have good removal efficiency: 1) BDD electrodes, 2) PbO_2 and its modified materials and 3) Sb-SnO_2 oxides and its modified materials. The degradation performance is strongly dependent on the nature of the electrode materials. Due their extremely high oxygen evolution potential (OEP), commonly higher than 1.7 V vs RHE, they have a “non-active” behavior for oxygen evolution reaction (OER) and favor complete oxidation of organics to CO_2 [4–6]. On the contrary, materials with good OER activity, such as IrO_2 and RuO_2 , often lack capability of removing contaminants.

Even though high OEP materials are capable of degrading organic contaminants efficiently, the high OEP gives rise to cell potential and reduces materials stability. These two factors are the main challenges for commercial application of electrochemical processes. Strategies for solving these problems are mainly concentrated on three aspects: 1) composition modifications (such as Gd [7] or Eu [8] doped Sb-SnO_2 , Y [9] doped $\text{SnO}_2\text{-Sb/PbO}_2$); 2) increasing activated area by using the porous tube [10] or nanotube [11]; 3) and multi coated architecture, such as $\text{SnO}_2\text{-Sb}_2\text{O}_3/\text{PbO}_2$ [12], $\beta\text{-PbO}_2/\alpha\text{-PbO}_2/\text{Sb-SnO}_2$ [13] et al. These methods, however, ignore the roles of crystal structure on degrading pollutants.

Actually, the crystal structure property plays a very important role in determining the catalytic activity of materials. Numerous oxides show that same chemical formula with different crystal structures will result in distinctly different catalytic activities. For example, outmost surface species distribution of spine structure oxides depends on its crystal structure, for normal spinel gives almost exclusively B site on surface while the inverse one shows half of A site and B site [14], even both of them have the same AB_2O_4 formula. Currently, layer double hydroxide (LDH) materials of NiOOH successes with good OER activity by transferring the crystal phase from $\gamma\text{-NiOOH}$ to $\beta\text{-NiOOH}$ [15]. The photocatalytic performances of three different crystal structure TiO_2 (rutile, anatase and

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brookite) are also inconsistent [16–18]. However, there is few reports studying the roles of materials crystal structure on electrochemical degradation processes.

Here, we compared the degradation performance of six different Ir-based oxides with three different crystal structures. Two are hollandite structure with special $[2 \times 2]$ tunnel size ($K_x\text{IrO}_2$, Ir doped cryptomelane-Cry-Ir), two belong to rutile structure (IrO_2 , Cu doped IrO_2) and the remaining two are Ir-pyrochlore structure ($\text{Pb}_2\text{Ir}_2\text{O}_6.5$ -Pb-Ir and $\text{Bi}_2\text{Ir}_2\text{O}_7$ -Bi-Ir). The results indicate that hollandite oxides have a better performance than two other crystal structure oxides. The sulphide (SP) is selected as target pollutant due to the fact that it is one kind of pharmaceuticals and personal care products (PPCPs), a class of products being paid closed attention by environmental researchers, and reported to be detected in water environment widely [19,20]. We also study the electrochemical properties of materials on removing SP, such as OEP, voltametrics charge and OER activity. Both of these two typical factors are unable to fully explain the performance tendency of different materials. However, the same crystal structure of catalysts exhibits similar removal even with varying compositions. Lastly, we find that catalyst with moderate OER activity will reduce the cell potential by dropping anodic over-potential, which will help decrease the total energy consumption.

2. Materials and methods

2.1. Preparation of materials and electrodes

All six catalysts are prepared using hydrothermal synthesis. More details are given in the **Supplementary Material**. The electrodes are prepared by depositing the catalyst ink (6–14 mg catalysts dispersed into 1.5 mL of 2:1 v/v isopropanol/water and then ultrasonicated for approximately 1 h to form a homogeneous ink) into three dimensional porous Ti foam several times. To precisely compare the removal using different catalysts, we also calculate the deposited Ir mass. All electrochemical measurements were conducted using a three-electrode cell. The working electrode was prepared by depositing catalyst ink into a $0.5 \text{ cm} \times 0.5 \text{ cm}$ (electrode area = 0.25 cm^2) Ti plate. A saturated calomel reference electrode (SCE) and a polished and cleaned Pt foil with a $1 \text{ cm} \times 1 \text{ cm}$ reaction area were used for the reference electrode and counter electrode, respectively. The SCE was calibrated respect to the RHE in the solution using a high purity hydrogen saturated electrolyte with a Pt foil as the working electrode.

2.2. Electrochemical analysis and SP degradation procedures

The electrochemical degradation experiments are carried out in a flow-press reactor at room temperature. A 4 cm^2 stainless steel sheet (200 mesh) is used for a counter electrode. The distance between anode and cathode is approximately 1.2 cm. SP concentration is set as 20 mg L^{-1} (considering its water solubility) in all experiments. The electrolyte is 100 mL with 0.1 M Na_2SO_4 . The electrolysis time is set at 4 h for all electrodes.

SP is determined quantitatively by high-performance liquid chromatography (LC-20AT, Shimadzu Inc., Japan) with a C-18 chromatographic column and detected at 254 nm using a UV-VIS detector. The mobile phase is a mixture of water and methanol 50/50 (vol %). The water phase also includes 2% formic acid and 2 mmol ammonium acetate to make the SP peak more symmetric. Mineralization efficiency of pollutant solution is estimated from the total organic carbon (TOC) removal (Vario TOC cube, Elementar Co., Germany).

The cell solution resistance is determined by EIS technique. The energy consumption is calculated as follows:

$$\begin{aligned} \text{Energy consumption} & \left(\text{kWh g}^{-1} \right) \\ & = \int_{t_0}^t I \times E(t) dt / [(TOC_{t_0} - TOC_t) \times V] \end{aligned} \quad (1)$$

Where $E(t)$ (V)-the cell potential change with time during constant current electrolysis. I -the electrolysis current (A). TOC_{t_0} -initial TOC concentration (mg L^{-1}). TOC_t -final TOC concentration (mg L^{-1}). V -the volume of solution (L).

3. Results and discussion

3.1. The performance of six different electrodes on removing SP

The crystal structures of six different Ir-based oxides are determined by X-ray diffraction (XRD) method (Fig. S1). The IrO_2 is a tetragonal rutile oxide with AO_2 formula. This crystallography shows a small $[1 \times 1]$ tunnel structure along the c axis. As our previous study [21] shows that although diffraction peaks of IrO_2 are shifted in 30% mole Cu doped IrO_2 , the rutile structure maintains as in Fig. S1b and without any observation of CuO_x peaks. The Fig. S1c shows that diffraction peaks of two Ir-pyrochlores (Pb-Ir and Bi-Ir) are very similar indicating same crystal structure. Currently, $K_x\text{IrO}_2$ is the only known 5d transition metal hollandite structure. Additionally, the diffraction peaks of Ir doped cryptomelane (define as Cry-Ir) are essentially in agreement with hollandite structure. Their detailed cell parameters calculated by refining their XRD patterns (Fig. S2) are listed in Table S2. We also performed X-ray photoelectrons spectra (XPS) to investigate the Ir valence states in six oxides (as shown in Fig. S3). From Fig. S4, we find that hollandite structure $K_x\text{IrO}_2$ and Cry-Ir have lower oxidation states than that of other oxides according to the binding energy of Ir-4f_{7/2}. The K^+ ions insertion in the crystal structure results in low oxidation states of Ir sites.

Fig. 1 shows the degradation performance of these six materials, which are conducted under same condition with four different applied currents at 30 mA, 50 mA, 80 mA and 100 mA, respectively. The IrO_2 and $\text{Cu}_{0.3}\text{IrO}_{0.7}\text{O}_8$ (Fig. 1a and b) under the 100 mA condition just have 15% and 25% SP removal, while under the lower currents, such as 30 mA or 50 mA, both of them only give degradation performance of less than 5%. Besides, two kinds of Ir-pyrochlore show some removal activity of 30% and 33% (for Pb-Ir and Bi-Ir, respectively) under 100 mA, still not satisfying. The similar performance indicates that the different A cations ($\text{A}_2\text{Ir}_2\text{O}_6$) in pyrochlore structure does not have any obvious effect on degrading SP. However, two kinds of hollandite structure Ir-oxides in Fig. 1g and h, $K_x\text{IrO}_2$ and Cry-Ir give an excellent degradation performance, obtaining 67% and 68% removal under 100 mA, respectively. Even at lower current conditions (50 mA case), the removal is also higher than four other electrodes under 100 mA. To precisely compare their specific degradation activity, we also take into consideration the Ir mass in each prepared electrode rather than the total coated mass. As shown in Table S2, it is clearly seen that Cry-Ir and $K_x\text{IrO}_2$ have the highest performance in all six materials, especially the relative performance of Cry-Ir is 6.6 times as much as IrO_2 , mainly due to its Ir mass is only 34% in catalyst. From their monetary activity ($\$/\text{mg}$) as shown in Fig. S5, we can find that both tunnel structure materials of $K_x\text{IrO}_2$ and Cry-Ir exhibits the best monetary activity, which is six times as much as that of IrO_2 . The comparisons indicate that both hollandite structure oxides have the intrinsic activity for degrading SP.

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