Electrochemical degradation of perfluorooctanoic acid (PFOA) by Yb-doped Ti/SnO\textsubscript{2}-Sb/PbO\textsubscript{2} anodes and determination of the optimal conditions.

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ABSTRACT

Model aqueous solutions of perfluorooctanoic acid (PFOA, 100 mg/L) were electro-oxidized in a homemade container. The electrocatalytic behavior and anodic performance of Ti/SnO\textsubscript{2}-Sb/Yb-PbO\textsubscript{2}, Ti/SnO\textsubscript{2}-Sb-PbO\textsubscript{2} and Ti/SnO\textsubscript{2}-Sb-Yb anodes in sodium electrolytes were compared. The SnO\textsubscript{2}-Sb/Yb-PbO\textsubscript{2} anode demonstrated better electrocatalytic performance compared with the SnO\textsubscript{2}-Sb-PbO\textsubscript{2} and SnO\textsubscript{2}-Sb-Yb electrodes in terms of both degradation and defluorination. Then a systematic experimental study was designed as follows to analyze the influencing factors: initial concentration of PFOA (10mg/L to 200 mg/L), current density (1 mA/cm\textsuperscript{2} to 40 mA/cm\textsuperscript{2}), initial pH value (3 to 11) and electrode distance (5 mm to 20 mm). After a 150 min electrolysis, the optimum reaction conditions were obtained and the degradation and defluorination ratios reached 95.11±3.9% and 75.7±2.8%,
respectively. Under the optimum conditions, the degradation of PFOA followed pseudo-first-order kinetics (0.0193 min\(^{-1}\)) and the degradation half-life was 35.9 min. The produced \(\text{F}^-\) was measured using a fluoride ion selective electrode, whereas the intermediate PFCAs with short-chain lengths were measured using HPLC-MS. A detailed degradation pathway was proposed in this study by analyzing the intermediates and the recovery of fluoride.

**Keywords:** Electro-chemical degradation; Ytterbium-doped; Perfluorooctanoic acid (PFOA); Optimal conditions; Mechanisms
1. Introduction

Perfluorooctanoic acid compounds are considered important surfactants and emulsifiers because of their hydrophobic and oleophobic characteristics. Since the 1960s, the electrochemical fluorination method has been applied to the production of perfluorinated compounds, perfluorooctanoic acid, and many other kinds of perfluorinated carboxylic acids (PFCAs) and salts that contain sulfonyl perfluorinated organic compounds. Over the recent decades a large number of these products have been developed for both industrial and domestic uses [1,2]. The extensive use of these products and the strong bond energy of the C-F bond (116 kcal/mol) [3] have driven the accumulation of these compounds in various environmental niches worldwide [4-6]. In fact, these compounds have also been observed in many animal [7] and human tissues [8, 9] because of the amplification of the food chain. Some reports suggested that this class of compounds are toxic to experimental animals and humans [10, 11]. Therefore, in the fourth session of the Stockholm Conference in 2009, perfluorinated compounds including perfluorooctane sulfonic acid, perfluorooctane sulfonate and perfluorooctanesulfonyl fluoride were included in the new list of persistent organic pollutants thereby establishing the harmfulness of such substances.

Several methods for degrading perfluorinated acids under specific situations have been investigated. Among these methods, sonochemical degradation [12] and thermolysis [13] can achieve high decomposition ratios for PFOA, but these techniques require strict reaction conditions and high energy consumption. Although
the persulfate radical ($\text{S}_2\text{O}_8^{2-}$) oxidation [14] and $\text{H}_3\text{PW}_{12}\text{O}_{40}$ [15] methods can degrade PFOA under mild reaction conditions, the defluorination process is slow and inefficient. Membrane separation [16, 17], adsorption [18, 19] and ion exchange [20, 21] have also been investigated, but these merely transfer the contaminants to a second phase. The effect of disposal of the generated waste disposal on the environment and the consumption of resources must also be managed.

Unlike the above methods, electrochemical oxidation can overcome the limited oxidizing abilities of conventional advanced oxidation processes because of its many advantages, such as high oxidation efficiency, fast reaction rate, easy operation, amenable to automation, and environmental compatibility. Previous studies have demonstrated the effectiveness of boron-doped diamond, $\text{SnO}_2$ and $\text{PbO}_2$ in the degradation and mineralization of perfluorocarboxylic and perfluorosulfonic acids in a model solution [22]. Some reports have also reported the strong ability of the lead dioxide electrode in producing hydroxyl radical [23-25]. Other researchers have incorporated materials, such as $\text{Nb}^{5+}$[27], $\text{Bi}^{4+}$[28], $\text{Ce}^{4+}$[29], $\text{Mn}^{4+}$[30], and carbon aerogel [31] into the $\text{PbO}_2$ coating to enhance its catalytic activity for wastewater treatment [32].

In the previous report [32, 33], cerium was doped in the preparation of electrodes for degrading PFOA. Ytterbium and cesium, which both belong to Lanthanide, share the similar chemical properties. The configuration of Ytterbium is $[\text{Xe}]4f^{14}6s^2$, which is the most stable element among the rare earth (RE) element because of the saturation state. At the same time, the resistivity of Ytterbium is 28 $\mu\Omega$ / cm, which is the
smallest among the rare earth. The structural superiority above makes Yb$^{3+}$ being studied extensively for many applications, such as the preparation of lithium ion batteries [34]. The photoluminescence properties of Yb-doped Si oxide [35] have been investigated, but the performance of Yb-doped electrode in degrading PFOA by electrochemical method has been rarely examined.

In this study, we attempt to decompose PFOA using a novel Yb(III)-doped PbO$_2$ anode that is selected from three types of anodes (e.g., Ti/SnO$_2$:Sb/Yb-PbO$_2$, Ti/SnO$_2$:Sb-PbO$_2$ and Ti/SnO$_2$:Sb-Yb) and propose a decomposition pathway. We prepared and doped the electrode, investigated the effects of different factors on the electrochemical decomposition and defluorination of PFOA and studied the decomposition kinetics and defluorination pathways of PFOA by measuring the degradation rate and identifying the intermediate products. The Yb-doped anode can be an effective technology for dealing with PFOA pollution in the future.
2. Material and methods

2.1. Chemical reagents and Instruments.

SnCl$_4$·5H$_2$O (99%, Hushi, Shanghai), SbCl$_3$ (98%, Kemiou, Tianjin), HCl (36%, Tieta, Shandong), Pb(NO$_3$)$_2$ (99%, Damao, Tianjin), iso-propanol (99.7%, Fuyu, Tianjin), HNO$_3$ (68%, Kangde, Laiyang), NaF (99%, Damao, Tianjin), Yb(NO$_3$)$_3$·6H$_2$O (99%, Bailingwei, Beijing), Oxalic acid (99%, Xilong, Guangdong), NaOH (96%, Yongda), Na$_2$SO$_4$ (99%, Tianda, Tianjin) and Ti sheet (99%, Taiye, Baoji) were used to prepare the electrodes and for the electrolysis procedures. Perfluorooctanoic acid (PFOA, 95%) was purchased from Wongjiang (China). Perfluoropropropionic acid (PFPrA, 97%) was supplied by Aladdin (China). Perfluoroheptanoic acid (PFHpA, 98%), perfluorohexanoic acid (PFHxA, 98%), perfluoropentanoic acid (PFPeA, 97%), perfluorobutanoic acid (PFBA, 98%) and trifluoroacetic acid (TFA, 99%) were obtained from Bailingwei (China). Na$_3$C$_6$H$_5$O$_7$·2H$_2$O (98%, Beichen, Tianjin) and NaNO$_3$ (98%, Aibi, Shanghai) were used when measuring the concentration of fluorine ion. The instruments involved during the experiment as follows: ultrasonic instrument (KQ-250B, Kunshanyiqi), drying cabinet (101A-2, Shuangwuqin), muffle furnace (XS1-25-1200, Zhongda), pH meter (PXS-215, Lieci), magnetic stirrer (79-1, Guohua), DC power supply (DYY-6B, Liuyi). All chemicals were used without further purification and deionized water was used in all of the experiments.
2.2. Electrode fabrication.

The titanium (Ti) sheet was cut to a rectangular shape (50 mm × 20 mm, with a thickness of 0.4 mm). After polishing with two grades of sandpaper (280-grid and 600-grid), the sheets were placed in the ultrasonic instrument for 10 min to remove the particles on its surface. The sheet was then soaked in a NaOH solution (5%, m/m) at 95°C for 1 h to remove grease. The Ti sheet was washed with distilled water and etched in boiling oxalic acid solution (10%, m/m) for about 2 h until gray pits were observed on its surface. The middle layers of the Ti/SnO$_2$:Sb/Yb:PbO$_2$ and Ti/SnO$_2$:Sb:PbO$_2$ anodes are the same, while that of the Ti/SnO$_2$:Sb:Yb anode is different. The coating solution was prepared as follows using the sol-gel technique: SnCl$_4$·5H$_2$O and SbCl$_3$ were dissolved in 50 ml iso-propanol at a Sn:Sb atomic ratio of 95:5. Next, 15 mL of concentrated HCl solution was added, and the resulting solution was diluted to 100 mL using iso-propanol. This solution was marked as solution A. For the Ti/SnO$_2$:Sb-Yb anode, we added trace ytterbium nitrate to the iso-propanol solution (which contained dissolved Sn and Sb) at a Sn: Sb: Yb atomic ratio of 95:5:0.5. This solution was marked as solution B and was used to make the Ti/SnO$_2$:Sb-Yb electrode only. We prepared three identical Ti sheets, of which two (marked as sheets 1 and 2, respectively) were dipped in solution A, while the other sheet (sheet 3) was dipped in solution B for 5 min. The sheets were then dried at 130°C for 10 min, and the organics were thermally decomposed at 490°C for 5 min. This dipping-annealing cycle was repeated 12 times. In the final stage, the coating was annealed for 1 h at 490°C. Sheet 3 was the Ti/SnO$_2$:Sb-Yb electrode.
Electro-deposition was employed for the preparation of Ti/SnO$_2$-Sb/Yb-PbO$_2$ and Ti/SnO$_2$-Sb-PbO$_2$. Sheet 1 was placed into an acidic (pH 1, adjusted with HNO$_3$) electro-deposition solution, which contained 200 g/L Pb(NO$_3$)$_2$, 2 g/L NaF, and 2.36 g/L Yb(NO$_3$)$_3$·6H$_2$O at a constant anode current density of 20 mA/cm$^2$ for 90 min under room temperature (25°C). The anode was used as the Ti/SnO$_2$-Sb/Yb-PbO$_2$ electrode. Sheet 2 was treated similarly as sheet 1 except without the addition of Yb(NO$_3$)$_3$. The preparation of Ti/SnO$_2$-Sb-PbO$_2$ was thus completed.

### 2.3. Electrochemical Experiments

The 200 mL electrochemical reaction container was made of organic glass (Polymethyl Methacrylate). During the experiments, 200 ml PFOA (100 mg/L) was electrolyzed using 0.1 M Na$_2$SO$_4$ as a supporting electrolyte. The prepared Ti/SnO$_2$-Sb/Yb-PbO$_2$, Ti/SnO$_2$-Sb-PbO$_2$ and Ti/SnO$_2$-Sb-Yb electrodes were used as the anodes, and a same size Ti sheet was used as the cathode. The effective electrolytic area was 10 cm$^2$, and the stirring rate was 500 r/min. The distance between the two electrodes and the electrolysis current density can be changed. The reaction solution was sampled for analysis every 15 min or 30 min during the experiments. All experiments were performed triplicate and performed at room temperature.

### 2.4. Instrumental Analysis

The PFCAs concentration were measured by using a high-performance liquid chromatography-mass spectrometry (HPLC-MS, Dionex U3000, USA), which was
equipped with a Thermo C18 column (100 mm × 2.1 mm, 3 µm). A mixture of
methanol (80%, volume percent) and distilled water (20%, containing 0.1%
methanoic acid) was used as the mobile phase. The sample injection volume was 10
µL at a flow rate of 0.2 mL min⁻¹. Room temperature was regarded as the column
temperature (25°C). Electrospray negative ionization mass spectrometry (Thermo
LCQ Fleet, USA) was used to identify the intermediate products of PFOA. The
capillary temperature was 320°C. The full scan range of the mass spectra ranged from
100 m/z to 600 m/z. The gas flow rates of sheath, aux, and sweep were 30, 10 and 0
units, respectively, and the spray voltage was -4 kV. Given that the sodium sulfate
electrolyte could harm the mass spectrometer, solid-phase extraction was performed
to remove the salt from all samples before measurement. The analyte-specific mass
spectra and standard curves of the PFCAs are shown in Figure S1 and S2(a to g) in the
supporting information section.

The concentration of F⁻ was measured using a fluoride ion selective electrode. Given
that the acidity of the electrolyzed solution (pH < 4) affects the determination of
fluoride ion concentration, the total ion strength adjustment buffer (TISAB) should be
added to the test solution. TISAB was prepared as follows: 58.8 g sodium citrate and
85 g sodium nitrate were dissolved in a beaker, then the pH was adjusted between 5
and 6 with HCl, and the solution was diluted to 1000 mL using distilled water. The
concentration of fluoride (C_F⁻) and the defluorination ratio (R) were calculated as
follows:

\[ E = E_0 - \frac{2.303RT}{F} \cdot \log C_{F^-} \]  

(1)
\[ R = \frac{C_{F^-}}{C_0 \times 15} \times 100\% \]  

where \( E_0 \) (mV) represents the steady electromotive force, \( E \) (mV) is the determined electromotive force, \( C_{F^-} \) is the concentration of fluoride ion (mg/L), and \( C_0 \) is the initial concentration of PFOA in mg/L. The stoichiometric factor of 15 indicates to the number of fluorine atoms in a PFOA molecule. Under the condition that the total ion strength in the solution is constant and sufficient, the electromotive force \( (E) \) has a linear relationship with \( \lg C_{F^-} \), and \( -\frac{2.303RT}{F} \) represents the slope of this line. The concentration of \( F^- \) can be obtained from the standard curve of \( F^- \) (Fig. S3).

\[ ACE = \frac{(COD_0 - COD_t)FV}{8lt} \times 100\% \]  
The average current efficiency (ACE) is calculated by the formula as above. Where \( COD_0 \) and \( COD_t \) are the chemical oxygen demands (mg/L) at the initial and the final moments, respectively. The difference between \( COD_0 \) and \( COD_t \) is COD removed. \( F \) is the Faraday constant (96487C/mol), \( V \) is the volume of electrolyte (L), 8 is the equivalent mass of oxygen (g/mol), \( I \) is the current (A), and \( t \) means the electrolysis time (s).
3. Results

3.1. Selection of the anode material.

As shown in Fig. 1, under the standard reaction conditions, the degradation ratios of PFOA were 95.11±3.9%, 83.94±1.6, and 80.14±3.8% for the Ti/SnO$_2$:Sb/Yb:PbO$_2$, Ti/SnO$_2$:Sb:PbO$_2$ and Ti/SnO$_2$:Sb-Yb anodes, respectively. Kinetic behavior was observed and modeled as a probable pseudo-first-order reaction. The electrochemical degradation rate constants ($k$, $k = \ln \frac{C_0}{C}$) of the three anodes were 0.0193, 0.012 and 0.011 min$^{-1}$, respectively, and their defluorination ratios of PFOA were 76.7±2.8%, 61.4±1.1% and 52.8±2.8%, respectively, as shown in Fig. 1. According to the rate constants, the degradation had the optimal reaction conditions. A 200 mL PFOA solution was used in the electrochemical experiments to examine the effects of current density (1 mA/cm$^2$ to 40 mA/cm$^2$), initial concentration (10 mg/L to 200 mg/L), electrode distance (5 mm to 20 mm), and initial pH (3 to 7).

3.2. Initial PFOA concentration

The effects of PFOA concentration are described in this section. Table 1 shows four samples with initial PFOA concentrations of 10, 50, 100 and 200 mg/L. The concentrations of PFOA for the three anodes were reduced by 90.90±0.1%, 93.75±0.7%, 95.11±3.9% and 83.86±2.8%, respectively (Fig. 2(a)), indicating the excellent performance of the Ti/SnO$_2$:Sb/Yb-PbO$_2$ electrode in degrading PFOA for low-concentration solutions (<100 mg/L).
Fig. 2(b), shows that with an increasing initial concentration of PFOA, the pseudo-first-order kinetic constant \((k)\) is reduced at first, eventually increases; correspondingly, the electrochemical reaction rates increased and then decreased. This phenomenon might be explained as follows. When the concentration of initial PFOA is low (<100 mg/L), the PFOA around the anode is degraded but cannot be replenished quickly. Given the turbulence in the electrolytic cell, the PFOA located far from the anode is degraded slowly, thereby affecting the degradation rate of PFOA. In contrast, higher concentrations of shorter-chain intermediates were produced under high concentrations of PFOA. The reaction of the intermediates would consume \(\text{HO}^\cdot\) and gather on the surface of the electrode to transfer electrons, which would restrain the degradation reaction of PFOA.

3.3. Effect of current density

By influencing the electron transfer capability and the hydroxyl radical production in electrolytic systems, the current density affects the degradation and defluorination rates of PFOA [30]. Fig. 3(a) shows the different current densities (1, 5, 10, 20, 30, and 40 mA/cm\(^2\)) used to investigate the degradation of 100 mg/L PFOA. The degradation rate is very low at a low current (1 mA/cm\(^2\)), where less than 60% of the PFOA can be degraded after 150 minutes of electrolysis. Compared with this result, the degradation rate gradually increased with the increasing of applied current density. When the current density increased from 20 mA/cm\(^2\) to 40 mA/cm\(^2\), the rate of degradation remained above 95% and the \(k\) value increased greatly as well, to 0.0193
As we can see from Fig. 3 (b), when the X coordinate is 20 mA/cm², the Yb-doped electrode has the highest average current efficiency (ACE). The degradation of COD is low (<250 mg/L) under a low current intensity (1, 5, 10 mA/cm²). However, in spite of the high removal, a low ACE was obtained as well when the current intensity is higher than 20 mA/cm² because of the high power consumption. This experiment also proved that the 20 mA/cm² is the best degradation current density in this electro-chemical system. This finding may be attributed to two reasons. First, the mass transfer rate of PFOA molecules toward the anode is limited and the degradation is inadequate. Second, the oxidation reaction at the anode is gradually enhanced by the increasing applied current density. As a result, the current oversupply leads to a lower average current efficiency (ACE) [36, 37].

3.4. Effect of initial pH value

The electrochemical degradation of PFOA was evaluated for five integral initial pH values ranging from 3 to 11. Fig. 4 shows the degradation rates and the fitted pseudo-zero-order kinetic curves after 150 minutes at different initial pH values. When the pH value was 5, the best degradation rate of 95.11±3.9% was achieved, which was 1.1 times higher than that in pH 3 and pH 7, 1.2 times higher than that in pH 9, and 1.5 times higher than that in pH 11. The PFOA solutions with a lower initial pH value had a higher oxidation rate than those with a higher initial pH value, thus indicating that the oxidation process was more favorable in acidic solutions. This conclusion also mentioned in previous literatures [38, 39]. However, low pH value will increase the concentration of H⁺ and hamper the positive direction to produce
Therefore, the trend in Fig. 4 was present. Thus, pH 5 was the most beneficial pH value for the degradation of PFOA.

3.5. Effect of gap distance between two plates

At the same current density, the effect of different electrode gap distances on degradation of PFOA is equivalent to that of electrode voltage. The degradation ratios of PFOA were 95.11±3.9%, 89.05±1.1%, 85.23±1.4%, and 67.92±3.8% for the plate distances of 5, 10, 15, and 20 mm, respectively (Fig. 5). As shown in Table 1, the highest k value (0.0193 min⁻¹) was obtained at 5 mm, the k values of 0.0151 and 0.0122 min⁻¹ were obtained at 10 and 15 mm, respectively; and the lowest k value (0.0193 min⁻¹) was obtained at 20 mm. The t₁/₂ value ranged between 35.9 min and 87.7 min. These data indicate that within a certain distance, a shorter electrode space will lead to a higher degradation efficiency. However, the voltages between two electrodes were 2.4, 2.9, 3.2 and 3.8 V for the distances of 5, 10, 15, and 20 mm, respectively. The longer electrode distance, the more electrolysis time was required due to the longer diffusion distance. Unlike degradation, the defluorination of PFOA required higher potential to activate electron transfer. Energy-band theory argues that the electron transfer reaction can be activated [33] when the energy level of an unoccupied electron given by the anode is lower than that of the highest occupied molecular orbital of PFOA.

3.6. The production of intermediates.

To investigate the production of intermediates during the electrochemical process,
HPLC-MS was used to measure the concentration of PFCAs (C₂ to C₇). As shown in Fig. 6(a), six different shorter-chain perfluoroalkyl groups (e.g., TFA, PFPA, PFBA, PFPeA, PFHxA, and PFHpA) were identified and quantified by using the mass spectra, which were produced during PFOA degradation as the intermediates. Fig. 6(a) also shows the formation of intermediates over the electrolysis time. As we can see from the diagram, during 150 min of degradation, the concentrations of PFHpA (C₇) and PFPeA (C₆) reached their maximum values at 30 min and 60 min, respectively, which decreased afterward. The concentrations of PFPeA (C₅) and PFBA (C₄) increased slightly since the beginning of electrochemical reaction but began to decrease after reaching their peaks at 90 and 120 min, respectively. The concentrations of PFPA (C₃) and TFA (C₂) slowly increased throughout the electrolysis time. The observed degradation process is similar to that seen by other researchers [30, 40]. In summary, the appearance of the maximum concentrations of the intermediates follows the order of the number of carbon atoms and PFCAs, with longer carbon chains showing higher concentrations. These phenomena indicate that the intermediates with longer chains are formed at the beginning of electrochemical reaction and are further decomposed into shorter chain intermediates as the reaction continues [33]. The incomplete degradation also indicates that some PFOA degradation products have not been fully decomposed.

\[ \eta = \sum_{i=0}^{5} (3 + 2i) \times C_{C_{F_{3}(C_{F_{2}})_{i}}} \text{COO}^- \] (4)

The mass balance of fluorine after 150 min electrolysis was investigated to analyze the electro-chemical degradation pathway of PFOA. Using Eq.(3), the mass balance
values of fluorine (i.e., \( F_\text{in intermediate PFCAs, undegraded} + F_\text{in PFOA, undegraded} + F_\text{in solution} \))/
\( F_\text{in PFOA initial} \), \( F_\text{in intermediate PFCA, undegraded} \) were calculated to be 95.8%, 95.8%, 96.8%, 95.3%, 93.6%, and 89.0% at different times, as shown in Fig 6(b). The recovery rates of fluoride were less than 100% (i.e., \( F_\text{unknown} \)), indicating that other intermediate products were quantified or detected in the solution. For example, volatile 1-C fluorocarbons may accumulate along with an increasing of electrolysis time [41]. However, the high recovery rates of fluoride allow us to describe the main reaction mechanism of the PFOA degradation in an aqueous solution.

3.7. Degradation pathway of PFOA.

Based on the results presented above and in the previous literature, a possible pathway by electrochemical oxidation could be expressed as follows: PFOA was ionized when dissolved in the solution (Eq. (5)) [42, 43]. Using the electrochemical device, PFOA underwent direct electron transfer from the carboxyl group on the anode to form perfluorooctanoic acid carboxyl radical (\( \text{C}_{15}\text{F}_{15}\text{COO}^- \)) (Eq. (6)). This radical was then decarboxylated to form the perfluoroheptyl radical (\( \text{C}_{15}\text{F}_{15}^- \)), where the method of bond cleavage was similar to the Kolbe decarboxylation mechanism in Eq. (7) [44-46].

\[
\begin{align*}
\text{C}_{15}\text{F}_{15}\text{COOH} + \text{H}_2\text{O} & \rightarrow \text{C}_{15}\text{F}_{15}\text{COO}^- + \text{H}_3\text{O}^+ \quad (5) \\
\text{C}_{15}\text{F}_{15}\text{COO}^- & \rightarrow \text{C}_{15}\text{F}_{15}\text{COO}^- + e \quad (6) \\
\text{C}_{15}\text{F}_{15}\text{COO}^- & \rightarrow \text{C}_{15}\text{F}_{15}^- + \text{CO}_2 \quad (7)
\end{align*}
\]

After the degradation process, \( \text{C}_{15}\text{F}_{15}^- \) followed two pathways. As shown in Eq. (8), the perfluoroheptyl radical was oxidized by radical species to form \( \text{C}_{15}\text{F}_{15}\text{OH} \) [47, 48],
which could be largely produced by the typical active electrode [23]. Given that
C$_7$F$_{15}$OH was a terminally unstable alcohol [49], this radical underwent
intramolecular rearrangement to form C$_6$F$_{13}$COF and eliminate HF (Eq. (9)) [15, 50].
The C$_6$F$_{13}$OF was then hydrolyzed to form shorter-chain PFCAs by removing of CF$_2$
units [15] and releasing fluoride ions into the aqueous solution (Eq. (10)).

\[
\begin{align*}
C_7F_{15}^- + HO^- &\rightarrow C_7F_{15}OH \quad (8) \\
C_7F_{15}OH &\rightarrow C_6F_{13}COF + H^+ + F^- \quad (9) \\
C_6F_{13}COF + H_2O &\rightarrow C_6F_{15}COO^- + 2H^+ + F^- \quad (10)
\end{align*}
\]

In the previous literature, another reaction pathway was proposed after the Kolbe
decarboxylation. In Eq. (11), the C$_7$F$_{15}^-$ reacted with the oxygen produced via water
electrolysis [46]. The existence of this pathway was proven by using oxygen isotope
tracers [40]. The produced C$_7$F$_{15}$COO$^-$ was then combined with another
perfluorinated carboxylic acid radical (RFCOO$^-$) to form C$_7$F$_{15}$CO$^-$ and RFCO$^-$ (Eq.
(12)) [29]. According to Eq. (13), the C$_7$F$_{15}$CO$^-$ was decomposed to produce
C$_7$F$_{13}^-$ and COF$_2$ [46]. The obtained carbonyl fluoride was hydrolyzed to produce
carbon dioxide and HF (Eq.14). In the degradation process, some volatile fluorinated
organic contaminants, such as CHF$_3$, CF$_4$ and C$_2$F$_6$, may be produced during the
electrolysis of the PFCs [13, 51].

\[
\begin{align*}
C_7F_{15}^- + O_2 &\rightarrow C_7F_{15}COO^- \quad (11) \\
C_7F_{15}COO^- + RFCOO^- &\rightarrow C_7F_{15}CO^- + RFCO^- + O_2 \quad (12) \\
C_7F_{15}CO^- &\rightarrow C_7F_{13}^- + COF_2 \quad (13) \\
COF_2^+ + H_2O &\rightarrow CO_2 + 2HF \quad (14)
\end{align*}
\]
In the two pathways above (Eq. (5-10), and Eq. (5-7, 11-14) ), PFOA was degraded to shorter-chain PFCAs by repeating the CF₂ unzipping processes in a step-wise manner as time progressed, and PFOA was then entirely mineralized to CO₂ and F⁻.
4. Conclusion

Typical anodes, such as Ti/SnO$_2$-Sb-PbO$_2$ and Ti/SnO$_2$-Sb-Yb, can be used in the electrochemical degradation of PFOA, whereas the addition of the rare earth ytterbium (Ti/SnO$_2$-Sb/Yb-PbO$_2$ anode) can increase the decomposition of PFOA from 83.94±1.6 and 80.14±3.8% to 95.11±3.9%. The reaction follows the pseudo-first-order kinetics, and the $k$ values of PFOA follow the order of Ti/SnO$_2$-Sb/Yb-PbO$_2$ ($0.0193$ min$^{-1}$) $>$ Ti/SnO$_2$-Sb-PbO$_2$ ($0.012$ min$^{-1}$) $>$ Ti/SnO$_2$-Sb-Yb ($0.011$ min$^{-1}$). The degradation of PFOA showed a positive correlation with the increase of current density (1 mA/cm$^2$ to 40 mA/cm$^2$), reduction of initial concentration (10 mg/L to 200 mg/L) and shorter electrode distance (5 mm to 20 mm). The degradation rate reached to the peak at pH 5, which was higher than the other tested pH values (3 to 11). The intermediate products of PFCAs ($C_2$ to $C_7$) and fluoride ion were detected, and a possible pathway for the PFOA electrochemical degradation was proposed by analyzing the intermediate products. Compared with other metal-doped electrodes that have been recently used (between 2011 to 2015) in the decomposition of PFOA, the linear fit of the kinetic plot was $k = 0.0193$ min$^{-1}$, which was higher than that of the Mn-doped electrode ($0.004$ min$^{-1}$) [30], but lower than that of the Ce-doped ($0.037$ min$^{-1}$) electrode [29]. In addition, the degradation of the Yb-doped electrode was 95.1%, which was higher than the reduction of Bi-doped electrode (93.3%) [28]. These results indicate that electro-chemical oxidation with Yb-doped electrode is an efficient method for decomposing PFOA.
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Fig. 1 Electrochemical degradation and defluorination ratio of PFOA at the reaction conditions including applied current density (20 mA/cm$^2$), initial concentration (100 mg/L), electrode distance (5 mm), initial pH (5) and with a 0.1 M sodium sulfate supporting electrolyte solution during 150 min, T=25 °C.
Fig. 2 (a) Effect of the initial PFOA concentration and (b) fitted pseudo-first-order kinetic curve. (Initial pH 5, plate distance 5 mm, current density 3.0 mA/cm², applied voltage 9.0 V, and electrolysis time 0-150 min.
density 20 mA/cm$^2$, 0.1 M Na$_2$SO$_4$, T=25 °C)

Fig. 3(a) PFOA concentration as a function of electrolysis time at current density 1, 5, 10, 20, 30, 40 mA/cm$^2$. Initial pH 5, plate distance 5 mm, 0.1 M Na$_2$SO$_4$,  

Fig. 3(b) COD removal as a function of current density
T=25°C. (b) COD removed and average current efficiency (ACE) as a function of current density.

Fig. 4 Effect of initial pH value. Initial concentration 100mg/L, current density 20 mA/cm², plate distance 5 mm, 0.1 M Na₂SO₄, T=25°C.
Fig. 5 PFOA concentration change as a function of electrolysis time at gap distance of 5, 10, 15, 20 mm. Initial pH 5, current density 20 mA/cm², initial PFOA concentration 100 mg/L, 0.1 M Na₂SO₄, T=25 °C.
Fig. 6 (a) Concentration of intermediates (C₂-C₇) formed during electrochemical decomposition of PFOA and (b) fluorine element mass balance with the progress of reaction. The operation conditions are given in the caption of Fig. 1.
Table 1 The efficiency and kinetics for PFOA degradation by Ti/SnO$_2$-Sb/Yb-PbO$_2$ electrode. (electrolysis time: 150 min)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>$\eta^a$</th>
<th>$k^b$</th>
<th>$t_{1/2}^c$</th>
<th>$R^2^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Current density (mA/cm$^2$)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>58.50±3.1%</td>
<td>0.0061</td>
<td>113.63</td>
<td>0.991</td>
</tr>
<tr>
<td>5</td>
<td>78.10±2.7%</td>
<td>0.0094</td>
<td>113.63</td>
<td>0.984</td>
</tr>
<tr>
<td>10</td>
<td>86.33±3.6%</td>
<td>0.0135</td>
<td>51.34</td>
<td>0.995</td>
</tr>
<tr>
<td>20</td>
<td>95.11±3.9%</td>
<td>0.0193</td>
<td>35.91</td>
<td>0.995</td>
</tr>
<tr>
<td>30</td>
<td>96.68±2.1%</td>
<td>0.0234</td>
<td>29.62</td>
<td>0.997</td>
</tr>
<tr>
<td>40</td>
<td>99.30±0.2%</td>
<td>0.0306</td>
<td>22.65</td>
<td>0.987</td>
</tr>
<tr>
<td><strong>Initial PFOA concentration (mg/L)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>98.10±0.1%</td>
<td>0.0272</td>
<td>25.48</td>
<td>0.994</td>
</tr>
<tr>
<td>50</td>
<td>97.19±0.7%</td>
<td>0.0230</td>
<td>30.14</td>
<td>0.996</td>
</tr>
<tr>
<td>100</td>
<td>95.11±3.9%</td>
<td>0.0193</td>
<td>35.91</td>
<td>0.995</td>
</tr>
<tr>
<td>200</td>
<td>83.86±2.8%</td>
<td>0.0127</td>
<td>54.58</td>
<td>0.991</td>
</tr>
<tr>
<td><strong>Initial pH value</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>87.65±1.4%</td>
<td>0.0139</td>
<td>49.87</td>
<td>0.994</td>
</tr>
<tr>
<td>5</td>
<td>95.11±3.9%</td>
<td>0.0193</td>
<td>35.91</td>
<td>0.995</td>
</tr>
<tr>
<td>7</td>
<td>87.13±0.9%</td>
<td>0.0130</td>
<td>53.32</td>
<td>0.990</td>
</tr>
<tr>
<td>9</td>
<td>78.34±1.4%</td>
<td>0.0103</td>
<td>67.30</td>
<td>0.994</td>
</tr>
<tr>
<td>11</td>
<td>62.71±2.2%</td>
<td>0.0067</td>
<td>103.45</td>
<td>0.988</td>
</tr>
<tr>
<td><strong>Gap distance (mm)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>95.11±3.9%</td>
<td>0.0193</td>
<td>35.91</td>
<td>0.995</td>
</tr>
<tr>
<td>10</td>
<td>89.05±1.1%</td>
<td>0.0151</td>
<td>45.90</td>
<td>0.998</td>
</tr>
<tr>
<td>15</td>
<td>85.23±1.4%</td>
<td>0.0122</td>
<td>56.82</td>
<td>0.986</td>
</tr>
<tr>
<td>20</td>
<td>67.92±3.8%</td>
<td>0.0079</td>
<td>87.74</td>
<td>0.985</td>
</tr>
</tbody>
</table>

Other operating conditions are the same as Fig. 3-6.

a Degradation ratio of PFOA. (%)

b Pseudo-first-order rate constant of electrochemical degradation. (min$^{-1}$)

c The time of half-left. (min)

d Goodness of fit.