A Highly Stable Ti/TiHₓ/Sb–SnO₂ Anode: Preparation, Characterization and Application

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ABSTRACT: Low service life limits the industrial application of the titanium-based Sb–SnO₂ anode. To improve its stability, a titanium hydride interlayer is fabricated to construct a three-layer anode, Ti/TiHₓ/Sb–SnO₂. Titanium hydride was prepared by reducing precoated titanium oxide in aqueous solution via electrochemical process, and it acted as a binder between the Ti and Sb–SnO₂ phases. Cyclic voltammetry, electrochemical impedance spectroscopy, and the accelerated lifetime test were also conducted to elucidate the positive effect of the TiHₓ interlayer. Results show that Ti/TiHₓ/Sb–SnO₂ not only possesses better stability but has higher oxygen evolution potential and lower electron transfer resistance compared with Ti/Sb–SnO₂. Essential characterizations were conducted including scanning electron microscopy, energy disperse spectroscopy, and X-ray diffraction. The mechanism of lifetime enhancement is also proposed. The performances of the electrodes on degrading three different organics manifest that the degradation performance of the electrode strongly relies on the electrode stability.

1. INTRODUCTION

In the past two decades, more and more attention has been attracted on studying electrochemical oxidation treatment (EOT) of wastewater with high oxygen evolution potential (OEP), high stable and low cost anodes.1–10 Dimensional stable anodes (DSAs) are series of electrodes fabricated by coating transition metal oxides, such as RuO₂, IrO₂, TiO₂, SnO₂, PbO₂, MnO₂, and Ta₂O₅, onto a metal substrate (mainly titanium).5–9 RuO₂, IrO₂, SnO₂, and PbO₂ are the most commonly used four coating materials for DSAs, and their synthetical performances (catalytic activity, stability, and cost) are proved to be better than those of conventional anodes (metal, carbon, etc.) and newly developed anodes (boron-doped diamond, etc.).10–12 An antimony-doped SnO₂ (Ti–SnO₂) anode, which possesses high OEP (higher than RuO₂, IrO₂, and PbO₂), appropriate cost (lower than RuO₂ and IrO₂), and low secondary contamination (lower than PbO₂), is one of the most promising anodes for EOT of wastewater.12–15 However, the main drawback of the Ti/Sb–SnO₂ electrode is the short service life in anodic polarization conditions, which limits its further applications.6,17

The factors that affect the stability of the Ti/Sb–SnO₂ electrode are very complicated and have not been studied thoroughly. It is generally believed that the weak attachment between the Ti substrate and Sb–SnO₂, and the passivation of the Ti substrate are the main factors leading to its low stability.18–21

The most simple and effective method to enhance the stability of Ti/Sb–SnO₂ is introducing an interlayer.22 However, the OEP value of heterogeneous active interlayer (Pt, RuO₂, and IrO₂) is not as high as that of Sb–SnO₂, and the OEP of the electrode was lowered inevitably.17 Therefore, a novel and economical interlayer insertion technique is still desired.

In this paper, titanium hydride (TiHₓ) was introduced as an interlayer to enhance the stability of the Ti/Sb–SnO₂ electrode. It is worth noting that this idea was inspired by the previous work of Baronetto et al.,23 where it was demonstrated that the ohmic loss between the catalyst layer and the Ti substrate could be eliminated by creating a hydride layer on the titanium surface. We envisaged that such a TiHₓ layer would not lower the OEP of the Ti/Sb–SnO₂ due to the high OEP of TiO₂ transformed from TiHₓ calcination. But, the direct reduction of the Ti substrate that we have performed before could not improve the stability of the Ti/Sb–SnO₂ electrode effectively, which may be due to the poor protection of the Ti substrate (Figure S1 in the Supporting Information). Thus, it is decided to coat a TiO₂ layer on the surface of Ti to protect the Ti substrate first and then electrochemically reduce TiO₂ to TiHₓ prior to further Sb–SnO₂ coating.

The special contributions of this TiHₓ interlayer in terms of electrode electrochemical properties and stability were confirmed and analyzed through a series of material characterizations, electrochemical characterizations, and accelerated lifetime tests. Furthermore, a possible deactivation mechanism of Ti/TiHₓ/Sb–SnO₂ was also discussed to explore the reason for stability enhancement. In addition, three target pollutants model compounds, including acid red G (ARG), methylene blue (MB), and sodium lignosulphonate (lignin), which are typical contaminants in acid dye wastewater, basic dye wastewater, and papermaking wastewater, respectively, were used to confirm the significant impact of the electrode stability on the performance of the electrode in environmental wastewater treatment.

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2. EXPERIMENTAL SECTION

2.1. Electrode Preparation. Titanium plates (40 mm × 10 mm × 0.5 mm, BaoTi Ltd., China) were used as the substrate. The substrate pretreatment method is listed in the literature.24 The dried substrate was first dip coated using the solution comprising 80% tetrabutyl orthotitanate (TBOT), 20% alcohol, and 0.1 M HNO₃ and then dried in an oven at 373 K and heated at 773 K for 15 min to form a TiOₓ-loaded plate. The TiOₓ-loaded plate was reduced by an electrochemical cathodic reduction process (two-electrode system; graphite plate was used as the counter electrode) in a sodium sulfate aqueous solution (room temperature, cathodic current density 10 mA·cm⁻², reduction time 5 min), and its gray color turned black (Figure 1a represented this specific color change). Sb deposition was performed for 10 s in ethanediol solution containing 0.2 M SbCl₃, 0.1 M HNO₃, and 0.01 M sodium citrate at the cathodic current density of 15 mA·cm⁻². Following that, Sn deposition was performed in another ethanediol solution for 120 s containing 0.5 M SnCl₂, 0.1 M HNO₃, and 0.01 M sodium citrate at the cathodic current density of 4 mA·cm⁻². Then, the above electrodeposition procedure was repeated for several cycles. Coating loading amount could be regulated accurately by adjusting the number of electrodeposition cycles. After electrodeposition, the electrode was dried and then heated in oven at 773 K for 1 h for the transformation of the precursor tin and antimony into a Sb–SnO₂ oxide layer. In addition, electrodes without an interlayer (Ti/Sb–SnO₂) were prepared in the same way to compare the performance with Ti/TiHₓ/Sb–SnO₂ electrodes.

2.2. Characterizations. The morphology and element content of samples were examined by field-emission scanning electron microscopy (FE-SEM, JEOL, JSM-6700F) equipped with an energy-dispersive X-ray spectroscopy (EDS) detector. The crystal structure of prepared samples were identified by an X’pert PRO MRD diffractometer (XRD, PANalytical, Holland) using Cu K source (λ = 0.15416 nm), with a scanning angle (2θ) ranging from 10° to ~80°. Inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICPE-9000, Shimadzu, Japan) was used to determine the concentration of Sn and Sb element in the electrolyte versus time in the accelerated lifetime test. Aqueous samples were first filtered by a membrane (pore size of 0.45 μm) and then digested by microwave.

2.3. Electrochemistry Experiments. All electrochemistry experiments were performed in 0.5 M H₂SO₄ aqueous solution (0.5 L) at room temperature. Cyclic voltammetry (CV, scan rate: 0.05 V·s⁻¹) and electrochemical impedance spectroscopy (EIS) were performed on an electrochemical workstation (CHI 660D, Shanghai Chenhua, China) to analyze the electrochemical property of the electrodes. The fabricated electrode (double-faced, effective area 2 cm²) was used as the working electrode and two copper plates (3 cm × 3 cm) were used as the counter electrode. The equilibrium potential of the working electrode was set to 0 V (vs Ag/AgCl) in the EIS test. The frequency range was from 0.1 Hz to 10⁵ Hz. The amplitude of the potential was 5 mV. The accelerated lifetime test was carried out at high current density (200 mA·cm⁻²) using electrochemical workstation (LK3000A, Tianjin Lanlike, China). The electrode sample served as the working electrode (double-faced, effective electrode area 2 cm²) and two copper plates (3 cm × 3 cm) were employed as the counter electrodes. The sample was regarded as a deactivated electrode when the cell voltage of the test system reached to 10 V.

2.4. Environmental Pollutants Degradation. Chemical pure acid red G (ARG, C₁₈H₁₃N₃Na₂O₈S₂, CAS no. 3734-67-6), methylene blue (MB, C₁₆H₁₁ClN₃S, CAS no. 61-73-4), and sodium lignosulphonate (Lignin, C₃₀H₂₈Na₂O₁₀S₂, CAS no. 8061-51-6) were dissolved in pure water (18 MΩ·cm) as model...
wastewater samples. The pure water is fabricated in a water purification system (EPED-S2-D, EPED, China). The concentration of each solution was defined as 1000 mg·L⁻¹. The volume of each solution was 0.5 L. The adopted effective area of the anode (fabricated electrode) and cathode (graphite sheet) was 90 cm², respectively. The anodic current density was fixed to 20 mA·cm⁻².

The current efficiency of organics degradation on each electrode is used to assess the catalytic oxidizing ability of the electrode. According to Faraday’s law, the current efficiency is defined as the ratio of theoretical quantity of electric charge to actual passed quantity of electric charge. Theoretical quantity of electric charge is calculated by the measured COD removal of each target pollutant. The examination of the relationship between the electrode stability and its degradation performance was carried out at a fixed current density of 20 mA·cm⁻². The electrodes were tested continuously throughout 50 days. ARG, MB, and lignin solution were replaced twice a day. The current efficiency was measured every 10 days.

3. RESULTS AND DISCUSSION

3.1. Characterizations. 3.1.1. Morphology and Crystal Structure. Morphologies of the interlayer and the surface layer of the Ti/TiHₓ/Sb—SnO₂ are shown in Figure 1. The unreduced TiO₂ interlayer (Figure 1b) shows a microstructure with irregular column arrays (~5 μm height), like isolated islands. Figure 1c shows the microstructure of TiHₓ. The production of TiHₓ could be simply expressed by the following equation:

\[
\text{TiO}_2 + x\text{H}_2\text{O} + xe^- \rightarrow \text{TiH}_x + x\text{OH}^- \quad \text{(aqueous medium)}
\]

Interestingly, several bulges immersed between the islands, which may be the consequence of hydrogen incorporation. When the compact Sb—SnO₂ layer was loaded (Figure 1d), the interlayer was completely filled and covered. The crystal structures of the above layers could be revealed by Figure 2. The unreduced interlayer showed TiO₂ anatase structure (ICDD 01-083-2243, main diffraction peaks at 25.4°, 37.0°, 37.9°, 38.7°, and 48.2°) but with low diffraction peak intensity that means the crystallization was undeveloped; thus, the following hydrogen reduction may be realized easier on this undeveloped crystalline. After reduction, the anatase TiO₂ structure on the surface layer was replaced by the titanium hydride (ICDD 01-078-2216, diffraction peaks at 35.3°, 40.9°, 59.4°, 70.9°, and 74.6°). The external Sb—SnO₂ layer showed a unique SnO₂ cassiterite structure (ICDD 01-077-0447, three main diffraction peaks at 26.6°, 33.9°, and 51.8°) without Ti detection indicated the well coverage of the Ti substrate. Antimony was also undetected, which may due to its incorporation into the SnO₂ lattice.

3.1.2. Oxygen Evolution Potential. To ensure the electrode catalytic efficiency for electrooxidation, the OEP of the electrode should not be decreased by the interlayer. The CV curves of freshly prepared Ti/Sb—SnO₂ and Ti/TiHₓ/Sb—SnO₂ in 0.5 M H₂SO₄ solution are shown together in Figure 3a. It is found that the OEP of Ti/TiHₓ/Sb—SnO₂ (~2.15 V vs Ag/AgCl) is slightly higher than that of Ti/Sb—SnO₂ (~2.05 V vs Ag/AgCl). The transformation of the TiHₓ interlayer to TiO₂ (0 < x ≤ 2) during the heating process of electrode fabrication may be the dominant factor, since TiO₂ is inert for oxygen evolution and hence increased the OEP slightly.

3.1.3. Electron Transfer Resistance. The effect of the TiHₓ interlayer on the electrode impedance was analyzed by EIS. The Nyquist plots of freshly prepared Ti/Sb—SnO₂ and Ti/TiHₓ/Sb—SnO₂ are shown in Figure 3b. Qualitatively, the arc diameter for Ti/TiHₓ/Sb—SnO₂ is smaller than that for Ti/Sb—SnO₂, which indicates that the introduction of the TiHₓ interlayer lowers electrode impedance and favors electron transfer. The equivalent circuit that best fits the experimental EIS data is a \( R_s(R || Q) \) combination, as shown in Figure 3b. \( R_s \), \( R || Q \) and \( Q \) correspond to solution resistance, electrode film resistance, and the constant phase element (CPE), respectively. The calculated \( R_s \) value of Ti/TiHₓ/Sb—SnO₂ is 17.38 Ω·cm², which is less than that of Ti/Sb—SnO₂ (46.77 Ω·cm²). Since the same Sb—SnO₂ was coated on both electrodes, such a difference in electrode film resistance could be attributed to the improvement of the coating–substrate interface condition in Ti/TiHₓ/Sb—SnO₂. From the perspective of electron transfer, direct electron transfer from Sb—SnO₂ coating to Ti substrate will encounter an interface resistance. The introduction of a buffer layer may minimize this effect. This result is consistent with those reported by Baronetto et al.²³

3.2. Electrode Stability. 3.2.1. Loading Amount Effect. The loading amount of the coating strongly affected the electrode stability.²⁰ Zhao et al. reported that the loading amount of Sb—SnO₂ on a TiO₂ nanotube electrode (Ti/TiO₂—NTs) was 2.14 mg·cm⁻², two times larger than traditional Ti/Sb—SnO₂. The accelerated lifetime of Ti/TiO₂—NTs/Sb—SnO₂ was 45 h while that of traditional Ti/Sb—SnO₂ was only 22 h (0.1 M Na₂SO₄, 100 mA·cm⁻²).²⁷ Generally, the optimal loading amount for Ti/Sb—SnO₂ (without interlayer) existed as...
a peak value. In this study, it was similar for the Ti/Sb−SnO2 (Figure 4a, ∼3.1 mg·cm−2) electrode. The initial increase in service life with increase of oxide loading amount can also be explained by a mechanism in which the coating is detached layer by layer, which means that the thicker the coating the higher the service life; this is the case when the loading amount is below a critical value. The decrease of service life when the loading amount exceeds the critical value can be explained by the mechanical stress generated by the difference of thermal expansion between the coating and the Ti substrate. However, the Ti/TiHx/Sb−SnO2 electrodes show good performances with the loading amount of Sb−SnO2 between 2.5 and ∼5.1 mg·cm−2 (Figure 4b). It is worth noting that the longest accelerated lifetime for Ti/TiHx/Sb−SnO2 is 60−80 h and that for Ti/Sb−SnO2 is only 14−16 h (0.5 M H2SO4, anodic current density of 200 mA·cm−2, room temperature). It is clear that the TiHx interlayer improves the electrode service life and extends the optimum ranges of the Sb−SnO2 loading amount. Although an excessive loading amount is not necessary, the extended optimum ranges of the Sb−SnO2 loading amount may simplify the electrode preparation process and increase the qualification rate of the electrode once it is applied in industry.

3.2.2. Accelerated Lifetime Test. Figure 5a describes the recorded time profile of cell voltage during the accelerated electrolysis of the Ti/TiHx/Sb−SnO2 (0.5 M H2SO4, anodic current density of 200 mA·cm−2, room temperature). The electrode could be regarded as stable in the first 60 h for the slight variation of cell voltage. After 60 h, the cell voltage increased clearly. Interestingly, when the cell voltage reached to a relative high level around 7−8 V (broken circle in Figure 5a), it remained relative steady and lasted for about 3 h. When this transition period was completed, the cell voltage increased rapidly.

From Figure 5a, the electrode service process could be divided into two periods: a steady period and an unstable period. In the first period, the external Sb−SnO2 layer was dissolving or detaching. However, in the second period, the inner layer may play an important role on keeping for a relative high performance of this electrode, and SEM and XRD analysis could reveal this. When the cell voltage reached the specific platform (Figure 5b), the profile of the column arrays structure (islands) of the interlayer emerged again (dark area), and residual Sb−SnO2 component could also be found at that time (bright area). However, when the cell voltage increased to 10 V, the coating was hard to recognize except the cracked interlayer (Figure 5c). The XRD patterns corresponding to the above two SEM images also demonstrate such severe coating loss (Figure 5d). SnO2 was still the main component and at the beginning of the platform, and other multiple phases (TiO2, Ti, and Sb2Ox) just emerged. However, SnO2 is hard to identify on the deactivated electrode, and the anatase TiO2 phase is dominant.

From the above results, it could be found that the specific cell voltage platform may indicate the existence of an inner Ti−Sn−Sb ternary oxide solid solution layer, which struggled with the electrolyte penetration when the outer layer had already dissolved or detached. The element analysis (EDS results in Table 1) also provides a side proof. The atom ratios of Ti, Sn, and Sb on the freshly prepared Ti/TiHx/Sb−SnO2 surface are 6.34%, 24.46%, and 2.53%, respectively. However the atom ratios of Ti, Sn, and Sb on the freshly prepared Ti/TiHx/Sb−SnO2 surface are 20.03%, 8.80%, and 1.01% on the
presumed Ti−Sn−Sb ternary oxide solid solution layer. On the deactivated electrode, such ratios are 30.70%, 5.15%, and 2.88%, respectively. Relative content variation of these three elements reflects the loss of Sb−SnO₂ coating on the deactivated electrode surface. Especially, oxygen content of the deactivated electrode is only 61.27%, lower than 66.6%, which indicates the detection of Ti metal. The EDS result also proves that the Ti/TiHₓ/Sb−SnO₂ would not be deactivated until nearly all the Sb−SnO₂ was lost.

The typical accelerated lifetimes of Ti/Sb−SnO₂ and Ti/TiHₓ/Sb−SnO₂ are ∼14 h and ∼72 h, respectively. Table 2 has listed the results of accelerated lifetime tests of the Ti/Sb−SnO₂ electrodes in recent literatures. The Ti/TiHₓ/Sb−SnO₂ in this study shows good performance under the similar test condition, which indicates the importance of the TiHₓ interlayer.

3.3. Possible Mechanism of Stability Enhancement.
3.3.1. Formation of a Solid Solution Interlayer. According to above results, it could be concluded that the TiHₓ interlayer plays an important role in stability enhancement. Our hypothesis is that TiHₓ could be heated with electrodeposited Sn and Sb to form stable solid solution oxide structure. Theoretically, the formation of a metal oxides solid solution is highly dependent on the ionic radius among the metal elements. When the ratio of radii difference between two metal ions in oxides is less than 15%, the metal oxide mixture could be highly intermixed and exist in the form of solid solution. The ionic radii of Ti(IV), Sn(IV), Sb(V) are 68, 71, 62 pm, respectively. The different ratios of ionic radii among Ti(IV) and Sn(IV), Ti(IV) and Sb(V), and Sn(IV) and Sb(V) are 13%, 4%, and 9%, respectively, which indicates the possible formation of Ti−Sn−Sb ternary oxides solution.

Transformation of TiHₓ to a solid solution layer may actually consist of two stages (also illustrated in Figure 6). The first one is the TiHₓ decomposition:

\[
\text{TiH}_x \rightarrow \text{Ti} + \text{H}_2 \quad \text{(occurs beyond } \sim 673 \text{ K)}
\]
This new generated Ti may be amorphous and much active, and its structure may be much porous due to the H₂ release (foaming agent property). The melting Sn and Sb may also penetrate into the vacancies, which may increase the possibility of forming mixture of Ti, Sn, and Sb metals. The second stage is the combination of oxygen and metals, three reaction happen simultaneously and form a solid solution layer:

\[
\begin{align*}
\text{Ti} + \text{O}_2 &\rightarrow \text{TiO}_2 & (3) \\
\text{Sn} + \text{O}_2 &\rightarrow \text{SnO}_2 & (4) \\
\text{Sb} + \text{O}_2 &\rightarrow \text{Sb}_2\text{O}_3 & (5)
\end{align*}
\]

Simultaneous in situ reactions may also benefit the cocrystallization of TiO₂, SnO₂, and Sb₂O₃ and solid solution formation takes advantage of it.

However, pure Ti substrate lacks the advantage of the Ti–Sn–Sb mixture and does not have the same solid solution formation ability as TiHₓ.

3.3.2. Ti/Sb–SnO₂ Deactivation Mechanism. It is generally believed that the formation of an undoped TiO₂ layer between the substrate and the coating is the immediate cause of Ti/Sb–SnO₂ deactivation (which is as mentioned in the abstract). The remote cause depends on the properties of the Sb–SnO₂ coating. However, besides severe dissolution in strong acid media, Sb–SnO₂ coating has other inherent defects, which could not be completely overcomed. For instance, traditional Ti/Sb–SnO₂ (via dip or brush coating-pyrolysis) electrodes possess typical “crack-mud” structure due to the inner mechanical stress of the coating. Such a loosened coating layer would be penetrated by electrolyte during electrolysis.

Another defect of Sb–SnO₂ may be the easy detaching (layer by layer), which can be explained on the mechanism for oxygen gas evolution in which a certain degree of nonstoichiometry (SnO₂₋ₓ) is present in the Sb–SnO₂ coating as discussed elsewhere. Initial defect involves many active sites, where the reaction

\[
\text{SnO}_2₋ₓ + \text{H}_2\text{O} \rightarrow \text{SnO}_2₋ₓ(\cdot \text{OH}) + \text{H}^+ + \varepsilon^- 
\]

happens with generation of adsorbed hydroxyl radicals ·OH. A further reaction may take place with an increase in oxygen stoichiometry, which is still below 2 at this stage:

\[
\text{SnO}_2₋ₓ(\cdot \text{OH}) \rightarrow \text{SnO}_2₋ₓ₋₁ + y\text{H}^+ + ye^- 
\]

This modification of the electrode surface increases the surface coating inner stress resulting in coating detachment. Underlying coating layers then undergo series of detaching cycles. Even when the coating is compact (fabricated through the electrodeposition-thermal oxidation method), such an effect is still unignorable.

No matter electrolyte penetration or coating detachment, when the electrolytes reach to the interface between the substrate and the coating, Ti substrate corrosion begins, and the
amount of Sn and Sb lost from the Ti−Sn−Sb ternary oxide inner layer was evaluated by ICP-AES when the cell voltage reached the platform nearby in the accelerated electrolysis (0.5 M H₂SO₄ anodic current density of 200 mA cm⁻², effect electrode area of 2 cm²).

Figure 8. Dissolved Sn and Sb element weight of Ti/TiHₓ/Sb−SnO₂ electrode (Sn−SnO₂ loading 2.5 mg) when the cell voltage reached the platform nearby in the accelerated electrolysis (0.5 M H₂SO₄ anodic current density of 200 mA cm⁻², effect electrode area of 2 cm²).
electrode means the effective use of precious electrode material because the electrode would not need to be recreated and replaced.

A highly stable electrode also saves electric energy as the total energy consumption is proportional to the total cell voltage that is dependent on the electrode conductivity. Table 3 listed the variations of electric energy consumption (kWh·gCOD⁻¹) of the Ti/Sb–SnO₂ electrode and the novel Ti/TiHₓ/Sb–SnO₂ electrode in ARG, MB, and lignin treatment. The data of the novel Ti/TiHₓ/Sb–SnO₂ electrode changed slightly during 50 days, while the data of the less stable Ti/Sb–SnO₂ electrode increased obviously (its energy consumption values were nearly doubled when 50 days passed).

The above results demonstrate that the pollutants degradation performance of the electrode relies on the electrode stability strongly. The previous effort on the electrode stability enhancement is meaningful. Environmental cost-effective strategy is working on the novel Ti/TiHₓ/Sb–SnO₂ electrode. The novel electrode is proved to be better than the Ti/Sb–SnO₂ electrode in many ways for organic wastewater treatment.

### 4. CONCLUSIONS

A specific titanium hydride interlayer (electrochemically reduced from titanium oxide in aqueous medium) has been used for the service lifetime improvement of the titanium-based antimony-doped tin dioxide anode. The typical accelerated lifetimes of Ti/Sb–SnO₂ and Ti/TiHₓ/Sb–SnO₂ are ~14 and ~72 h, respectively (in 0.5 M H₂SO₄, anodic current density: 200 mA·cm⁻², Sb–SnO₂ loading: 2.5 mg·cm⁻²). It must be noted that the oxygen evolution inhibition property of Ti/Sb–SnO₂ is also maintained. The film resistance is also slightly decreased, which is consistent with the previous report.²³ The mechanism of stability improvement could be ascribed to the well protection of the substrate by a firm Ti–Sn–Sb oxide solid solution interlayer. The solid solution layer changes the electrode deactivation mechanism, and the electrode would not be deactivated until nearly all the Sb–SnO₂ coating is lost. Coating consumption rate determined the lifetime of the novel electrode.

### Table 3. Electric Energy Consumption of ARG, MB, and Lignin Degradation by the Ti/Sb–SnO₂ Electrode and the Ti/TiHₓ/Sb–SnO₂ Electrode during 50 Service Days

<table>
<thead>
<tr>
<th>Service Day</th>
<th>Ti/Sb–SnO₂</th>
<th>Ti/TiHₓ/Sb–SnO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ARG</td>
<td>MB</td>
</tr>
<tr>
<td>1</td>
<td>0.048</td>
<td>0.068</td>
</tr>
<tr>
<td>10</td>
<td>0.056</td>
<td>0.072</td>
</tr>
<tr>
<td>20</td>
<td>0.064</td>
<td>0.079</td>
</tr>
<tr>
<td>30</td>
<td>0.073</td>
<td>0.091</td>
</tr>
<tr>
<td>40</td>
<td>0.084</td>
<td>0.097</td>
</tr>
<tr>
<td>50</td>
<td>0.109</td>
<td>0.106</td>
</tr>
</tbody>
</table>

Figure 9. Performance of the electrodes of ARG, MB, and lignin degradation. (a) UV–vis spectra variation of ARG after 1 h treatment (1, Ti/Sb–SnO₂; 2, Ti/TiHₓ/Sb–SnO₂) and COD removal efficiency (triangle, Ti/Sb–SnO₂; dot, Ti/TiHₓ/Sb–SnO₂); (b) UV–vis spectra variation of MB after 1 h treatment (1, Ti/Sb–SnO₂; 2, Ti/TiHₓ/Sb–SnO₂) and COD removal efficiency (triangle, Ti/Sb–SnO₂; dot, Ti/TiHₓ/Sb–SnO₂); (c) UV–vis spectra variation of lignin after 1 h treatment (1, Ti/Sb–SnO₂; 2, Ti/TiHₓ/Sb–SnO₂) and COD removal efficiency (triangle, Ti/Sb–SnO₂; dot, Ti/TiHₓ/Sb–SnO₂); (d) COD removal current efficiency variations during the 50 service days of the electrodes.
electrode. In addition, the pollutants degradation performance of the electrode relies on the electrode stability strongly, and the highly stable Ti/TiH2/Sb–SnO2 electrode exhibits better degradation efficiency and consistency than the Ti/Sb–SnO2 electrode.

**ASSOCIATED CONTENT**

Supporting Information

SEM image of Ti substrate after direct electrochemical reduction. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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