PEM electrolyzer using Sb-SnO₂ anode for electrolyte free electrochemical oxidation

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Abstract. This study uses solvothermal method to fabricate PEM electrolyzer compatible Sb-SnO₂ anode catalyst with particle morphology, then load the catalyst with different arrangement of MEA, including CCG and CCM. Characterization of catalyst has been conducted using SEM, XRD and XPS. Performance of different MEA arrangement has been investigated through LSV, CV and EIS. Electrochemical oxidation of reactive blue 4 has been conducted on both arrangements. Moreover, MEA with tiny amount of Pt/C as cathodic catalyst or IrO₂ as anodic catalyst has been test to determine the bottleneck of electrolyzer. Results suggested promising EO performance can be achieved through electrolyte free electrochemical oxidation, further improvement should focus on anode catalyst.

1. Introduction
Waste water containing recalcitrant nonbiodegradable contaminants has becoming a worldwide water pollution source. For example, organic dyes from textile industry are difficult to decolorize through conventional treatment [1-4]. Discharge such nonbiodegradable contaminants to nature waters may cause detrimental environmental impact. Advanced Oxidation Processes (AOPs) are promising processes suitable for treatment of nonbiodegradable organic contaminants in water [5, 6]. AOPs use a variety of methods to produce hydroxyl radicals (·OH) in waste water to oxidize nonbiodegradable organic contaminants. Hydroxyl radicals are the second strongest oxidant known in nature environment, which has a standard redox potential of 2.8 V/SHE [1]. Moreover, hydroxyl radicals are non-stable in water, if didn’t react with contaminants, it will soon transform to O₂ and H₂O without further pollution [7, 8].

Electrochemical oxidation (EO) is one of AOPs that conduct without reagent addition, thus produce no secondary pollution and simplified treatment process. EO uses a water electrolyzer with special anode catalyst that has high oxygen evolution potential (OEP) to produce hydroxyl radicals through water electrolysis[9, 10]. Typical anode for EO including Sb-SnO₂ [11-24], PbO₂ [25, 26]and born-doped diamond (BDD) [27-30]. Among them, Sb-SnO₂ has lower cost than BDD, and presents lower toxicity than PbO₂, thus received increasingly consideration. However, relatively low electrochemical performance of Sb-SnO₂ anode hindered its widespread application. In order to increase electrochemical performance and stability of Sb-SnO₂ anode, many studies have been conducted through doping with third elements, like Eu, Gd [11, 12], Ru [13-15], Ce [11, 15], Pb [16], F [17] and so on.

Typical EO process uses conventional water electrolyzer, which demand electrolyte (salt, acid or alkaline solution) to support ion conducting. The electrolyte itself produces some kind of pollution to
environment, and increases cost. Thus, conducting EO process under electrolyte free polymer electrolyte membrane (PEM) electrolyzer presents distinctive advantage including no extra electrolyte, compact design and good scalability. Little research has carried on this area. Fernando M. Ribeiro [31] et al. and ER Faria [32] et al. reported using MOME-Ni(x)Co(1−x)Oy as anode onto a PEM electrolyzer for electrochemical degradation of diclofenac. Lindomar G. De Sousa [33] et al. use lead dioxide doped with Fe³⁺ as anode to composite a PEM electrolyzer for ozone generation. Study on PEM electrolyzer for EO with Sb-SnO₂ catalyst is rare to be seen.

This study used a solvothermal method to fabricate micro-particle Sb-SnO₂ catalyst, and loaded it onto a PEM electrolyzer. Both catalysts coated on membrane (CCM) and catalysts coated on gas diffusion layer (CCG) configuration have been tested through LSV, CV and EIS. EO performance have been investigated through EO of reactive blue 4. Moreover, extra test with tiny amount of Pt/C or IrO₂ as cathodic or anodic catalyst has been conducted to reveal the bottle neck of this electrolyte free EO process. Results suggested Sb-SnO₂ catalyst is applicable in PEM electrolyte free electrolyzer for EO process, but further study should be conducting to increase the electrochemical activity of Sb-SnO₂ on this kind of configuration.

2. Material and methods

2.1. Preparation and configuration of PEM electrolyzer for EO

2.1.1. Preparation of Sb-SnO₂ catalyst. All chemical materials employed are of analytical purity grade, used as received without any further purification. First, 0.9 g SnCl₂·2H₂O and proper dose of SbCl₃ were dissolved in 50 mL absolute ethanol with vigorous stirring to form a homogeneous solution, then 2.3 mL NaOH saturated ethanol solution was dipped into the above-mentioned solution with continuous stirring for 5 mins. Then the mixture was transferred into a Teflon-lined stainless-steel autoclave, and maintained at 180 ℃ for 12 h. The mole rate of SnCl₂·2H₂O/SbCl₃ is 40/1. After the solvothermal procedure, the autoclave cooled naturally at air to room temperature. The precipitates were collected by centrifugation, washed several times with distilled water and absolute ethanol, respectively, and dried at 80 ℃ for 12 h in air. The powder got from dry procedure was then milled in an agate mortar, and sealed to preserve.

2.1.2. Preparation of PEM electrolyzer. Most of electrolyzer components including fixture plate (Aluminum alloy), electrode plate (Pure copper), bipolar plate (Titanium) and sealing ring are commercial parts. The membrane electrode assembly (MEA) are fabricated using Nafion N115 (DuPont) PEM membrane. Sb-SnO₂ synthesized in this study are mixed with isopropanol, deionized water and

![Figure 1.](image-url)
Nafion solution (5wt%, DuPont) to form catalyst ink. On CCG MEA, catalyst ink is sprayed onto a 25 cm² square Ti felt (0.25 mm thick with 70% porosity), then the Ti felt will be hot-pressed onto Nafion N115 membrane with a 25 cm² square carbon paper (TGP-H-120, CeTech Co., Ltd.) as cathode. On CCM MEA, catalyst ink is sprayed directly onto Nafion N115 membrane with effective area of 25 cm² square. The same Ti felt and carbon paper without catalyst serve as anodic and cathodic diffusion layer, and been hot-pressed to assembled with catalyst loaded Nafion membrane to construct a CCM MEA. A schematic diagram of PEM electrolyzer for EO used in this study is presented in Fig. 1. (a).

2.2. Physicochemical characterization

The morphologies of anode powders, Ti felt and membrane were investigated by scanning electron microscope (SEM, JSM-7610F, JEOL). X-ray diffraction (XRD, Dmax-RB, Rigaku) was performed to obtain the crystalline patterns of powders. The chemical composition of powders was determined by X-ray photo-electron spectroscopy (XPS, PHI5000, ULVAC-PHI).

2.3. Electrochemical characterization

Electrochemical experiments were performed by an electrochemical workstation (interface 1000E, Gamry Instruments). Deionized water is used as electrolyte. The temperature of water is kept at 25 °C.

Linear sweep voltammetry (LSV) measurements were performed with a sweep speed of 10 mV s⁻¹. Cyclic voltammetry (CV) was performed with sweep rate at 50 mV s⁻¹ with the potential region of 0-2.5 V. Electrochemical impedance spectroscopy (EIS) was conducted in range of 10⁻⁴-10⁻¹ Hz at a potential of 1.9 V with an amplitude signal of 5 mV.

The EO experiments were performed using 100 ppm reactive blue 4 dissolved into deionized water as electrolyte with temperature of water is kept at 25 °C. The electrolysis was performed in the galvanostatic condition at 0.1, 0.2 and 0.3 A. The electrochemical decolorization process was monitored by a UV–vis spectrophotometer (Shimadzu UV Spectrophotometer UV1800), and the concentration of reactive blue 4 was measured by the absorbance intensity at the characteristic wavelength of 595 nm. The decolorization efficiency (η) was calculated according to Eq. (1), where $A_0$ and $A_t$ are the absorbance values at the initial time and $t$ (min), respectively.

$$\eta(\%) = \left( \frac{A_0 - A_t}{A_0} \right) \times 100$$

3. Results and discussion

3.1. Physicochemical characterization

Figure 2. (a) XRD pattern of as-prepared Sb-SnO₂ catalyst, (b) XPS survey spectra of as-prepared Sb-SnO₂ catalyst, inset presents Sb3d spectra.
Fig. 1. (b) presents the SEM morphology of as-prepared Sb doped SnO₂ catalyst. SnO₂ powders are composed of tiny crystal sheets. Typical size of SnO₂ tiny sheets is of 65 nm thick and 600 nm in diameter. Distribution in size is uniform.

Fig. 2. (a) presents the XRD pattern of as-prepared Sb-SnO₂ catalyst. Every diffraction peak coincides with cassiterite SnO₂ (PDF #71-0652). No extra peak presented on XRD pattern of Sb-SnO₂ catalyst, indicated that Sb atom has successfully been doped into SnO₂ crystal. Fig. 2. (b) shows XPS survey spectra of as-prepared Sb-SnO₂ catalyst, with inset presents Sb3d spectra. From XPS survey it can be observed that the powder contains C, O, Sn element. Tiny amount of C should be ascribed to impurity. Very weak Sb peak can be distinguished at around 441 eV binding energy. From inset of Fig. 2. (b), a clearly Sb3d₃/₂ can be found to confirm Sb doping. The molar ratio of Sb to Sn in as-prepared Sb-SnO₂ powder is 1:40, which cause the very weak peak of Sb in XPS spectrum.

Fig. 3. show the SEM morphologies and element mapping of catalysts sprayed membrane and Ti felt, respectively. It can be seen from morphological Fig. 3. (a) and Fig. 3. (d) that catalyst particles are uniformly distributed on surface of both configurations. Catalyst particle size are similar on both configurations. Whereas from Sb and Sn mapping images, firstly Sb distribution are absolutely identical with Sn distribution on both configurations, verified that Sb has been doped into SnO₂ crystals. Secondly, atoms distribution on Fig. 3. (b,c) of catalysts sprayed membrane are more uniform with less hollow void than Fig. 3. (e,f) of catalysts sprayed Ti felt, which shows advantage of CCM configuration.

3.2. Electrochemical performance and decolorization of RB4

Fig. 4. (a) presents LSV curves of two configurations of MEA. The oxygen evolution potential (OEP) of both configurations is at around 1.7 V. CCM configuration can provides greater current than CCG configuration at given potential, which could be ascribed to uneven surface of Ti felt observed in mapping results of Fig. 3. Uneven surface of Ti felt may case less electrochemical active area thus led to lower current.

Fig. 4. (b) presents EIS spectrum of two MEAs, with inset presents simulated circuit. The simulated circuit composed of One resistance (R1) and a circle contains a resistance (R2) and a constant phase element (CPE2). The simulated result of R1 represents solution and substrate resistance, the simulated
results of R2 and CPE2 stand for the electrochemical discharge process. The simulated results present in table 1. CPE2 and n of two configurations are similar due to same catalyst. R2 of CCM and CCG configuration is 0.11 and 0.29 Ω, respectively. R2 of CCM and CCG configuration is 75.5 and 102.8Ω, respectively. These results indicated better conductivity and electrochemical activity of CCM configuration.

![Image](image.png)

**Figure 4.** (a) LSV curves of MEAs, (b) EIS spectrum of MEAs, inset displays the simulated circuit model, (c) CV curves of MEAs with or without RB4, (d) RB4 decolorization efficiencies of MEAs, (e) LSV curves of MEAs with Pt/C or IrO2 catalysts, (f) CV curves of MEAs with Pt/C or IrO2 catalysts.

| Configuration | R1 (Ω) | R2 (Ω) | CPE2 (μF) | n  |
|---------------|--------|--------|-----------|----|
| CCG           | 0.29   | 102.8  | 452       | 0.846 |
| CCM           | 0.11   | 75.5   | 483       | 0.894 |

Table 1. EIS fitting results of MEAs.

Fig. 4. (c) shows the CV curves of two MEAs with or without RB4 at potential range from 0 V to 2.5 V. It can be observed that the CV curve are identical with or without RB4 on both configurations, which confirms the non-active property of both MEAs, which means RB4 will be decolorized by hydroxyl radicals produced from anode. Fig. 4. (d) shows the RB4 decolorization efficiencies of both configurations at different current. It can be observed from Fig. 4. (d) that, CCM configuration has slightly faster decolorization than CCG. This phenomenon may be ascribed to better current efficiency due to smoother catalyst distribution. In addition, at low current (0.1 A), decolorization is a lot slower than at higher current, which should be ascribed by lower electrolysis potential. At lower electrolysis potential OER rather than decolorization of RB4 tends to happen, which hinder the decolorization and decrease the current efficiency.

In order to determine the bottle neck of electrochemical performance of MEA used in this study, a set of extra experiments have been carried. A MEA with tiny amount of Pt/C (0.1 mg/cm^2 Pt loading) been sprayed on cathode and normal Sb-SnO2 sprayed on anode with CCM configuration has been
manufactured. Besides, a MEA with tiny amount of IrO₂ (0.1 mg/cm²) and normal amount of Sb-SnO₂ sprayed on anode and no cathodic catalyst with CCM configuration has been manufactured too. The electrochemical performance of three MEAs been compared in Fig. 4. (e,f). From LSV curves of Fig. 4. (e), it can be observed that with Pt/C added into cathode, no performance gaining has been achieved. Whereas, with IrO₂ added into anode, performance of LSV increased a lot. From CV curves of Fig. 4. (f), it can be observed that Pt/C cathode increased the cathodic area of CV curve and have no enhancement on anodic peak. Additional IrO₂ on anode increased anodic area, indicated larger electrochemical active charge for anodic reaction. These results indicated that in order to increase the electrochemical performance of this specific EO MEA, performance of anode catalyst should be improved, meanwhile cathode could continue to use simple non-active carbon paper.

4. Conclusion
This study synthesized particle shaped Sb doped SnO₂ catalysts with solvothermal method, and load the catalysts onto PEM membrane to form an electrolyte free MEA for electrochemical oxidation of organic wastewater. CCG and CCM configuration of MEA have been manufactured and tested. Results indicated that CCM configuration has an advantage on electrochemical performance and EO capability. Besides, MEA with tiny amount of Pt/C on cathode or tiny amount of IrO₂ on anode has been manufactured and compared to determine the bottle neck of this EO specific MEA. Results indicated that anode catalyst performance should be enhanced in the future, meanwhile non-active carbon paper cathode did not hinder the performance of this EO specific MEA.

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