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Oxygen evolution catalyst on antimony doped tin oxide nanowire structured support for proton exchange membrane liquid water electrolysis

Gaoyang Liu, Junyuan Xu, Yituo Wang and Xindong Wang

Developing catalysts with high electrocatalytic activity has recently attracted much attention due to the slow reaction kinetics for oxygen evolution reaction (OER) and poor durability under harsh operating environments. Aiming at enhancement of oxygen electrode kinetics and durability, a facile and scalable electrospinning method is employed to fabricate antimony doped tin oxide nanowire (Sb-SnO$_2$ NW) as support materials for iridium oxide. Both the scanning electron microscope (SEM) and transmission electron microscope (TEM) results show that the as prepared Sb-SnO$_2$ NW is stacked from primary Sb-SnO$_2$ nanoparticles (Sb-SnO$_2$ NP) with diameters of 15-25 nm and exhibits uniform porous nanowire structure with diameter in the range of 200-300 nm. The synthesized Sb-SnO$_2$ NW has a BET surface area of 60 m$^2$ g$^{-1}$ and an electronic conductivity of 0.83 S cm$^{-1}$. Benefiting from porous nanowire structure and high electronic conductivity of the Sb-SnO$_2$ NW support, the supported IrO$_2$ catalyst exhibits significant enhancement of mass activity toward OER in acidic electrolytes comparing with Sb-SnO$_2$ NP supported IrO$_2$ catalyst and pure IrO$_2$. The improved catalytic performance for OER is further confirmed by proton exchange membrane (PEM) electrolyzer tests at 80 °C. A test of such an electrolyzer cell at 450 mA cm$^{-2}$ shows good durability within a period of up to 646 h.

Introduction

Renewable sources have been utilized via various methods for power generation, but not all the electricity is fed into the grid. Storage of the excess energy in the form of hydrogen is essential for the realization of large scale deployment of renewable sources. The method to generate hydrogen is the key in hydrogen energy development. So far, water electrolysis is one of the most practical ways to produce pure hydrogen from renewable energy sources. Compared with the traditional alkaline electrolysis, proton exchange membrane (PEM) water electrolysis has been considered as the most promising system in the future due to its higher current densities, energy efficiency and purity of the hydrogen product. Especially for the PEM water electrolyser based on Nafion* membranes operated below 80 °C or room temperature, it has advantages for practicability, and little demanding for thermal management and the subsequent gas product compression operations.

The high positive anode potential and the oxygen evolution in acid environment represent a very severe test for electrocatalysts. Only precious metal oxides are relatively stable. Typically, the currently used oxygen evolution reaction (OER) catalysts are based on IrO$_2$ and/or RuO$_2$. The major challenge of OER catalysts research is to reduce (noble metal) investment cost, while offer fast kinetics and is stable in a harsh oxidising environment of low pH values and high electrode potentials. One method to achieve this is to prepare composite oxide catalysts, i.e. iridium oxides doped with oxides of Sn, Ti, Si, Mn, Co, Ce+Nd, Ta and Mo metals. General speaking, these doping metal oxides could increase the active surface area by the mechanisms of the grain refinement, pore morphology, porosity and surface enrichment of the active phase. However, these doping metal oxides showed little beneficial effects other than serving as diluent matrices. Besides, these doping metal oxides are electrochemically inert and poor electronic conductivity. Excessive addition of the doping metal oxides in the composited oxide catalysts will dilute the IrO$_2$ and/or RuO$_2$ oxide content and lead to a decrease of the active area. As a result, the normalized catalytic activity of the composite oxide catalysts is low compared with that of catalysts made of pure IrO$_2$ and/or RuO$_2$, especially when the content of IrO$_2$ and/or RuO$_2$ is much lower than 60-80%.

To optimize the utilization of IrO$_2$ and/or RuO$_2$ and at the same time to improve the catalyst activity towards the OER, another effective approach is to disperse the noble metal...
active phase on high surface area non-noble supports. In essence, both of the doping metal oxides and the supports are used to increase the active surface area and then improve the apparent reaction rate. While, an obvious advantage of using a support comparing with the doping metal oxides is that the morphology of the support can be tailored to achieve higher degree of dispersion of the IrO₂ and/or RuO₂ nanoparticles and therefore maximized surface area of the active phase. However, from a materials science point of view, the chemical and electrochemical stability of the OER catalyst supports are the primary challenge due to the high positive anode potential and the oxygen evolution environment. High specific surface area carbon and their nanostructured analogues e.g. carbon nanotubes are no longer applicable as the OER catalyst supports. The investigated materials are a few of oxides and ceramics e.g. SiC-SiN₁⁰, TiO₂, and SnO₂, Ti₃O₇, TiC, TaC, TiC₀.²⁰ and antimony doped tin oxide, Ta₂O₅, and antimony doped tin oxide. Among these, antimony doped tin oxide has a wide range of applications such as water electrolysis¹², fuel cells,²² lithium-ion batteries, solar cells¹⁰¹, and gas sensors.²⁵ Antimony doped tin oxide could be a good alternative for OER catalyst supports, since it exhibits relatively high electronic conductivity and stability. Even though in an acidic medium and on long term polarisation at high anodic potentials, antimony doped tin oxide has much higher corrosion resistance and could hardly be oxidized electrochemically.²⁷ Except for the limitation of the support materials, sufficient charge transport, high specific surface area and preferable pore-size distribution²⁸ is also required to favor the availability of active phase.

At present, IrO₂ and/or RuO₂ supported on nanoparticle structured materials have been widely researched. Nanostructured supported catalysts could be easily synthesized through simple sol-gel method³⁰ or chemical co-precipitation method³¹, etc. The greatest advantages of nanoparticle structured supports are that high specific surface area could be obtained by optimization of the preparation method to refine the particle size. However, on the one hand, the tiny nanoparticles supported catalysts tend to aggregate in the preparation of the anode electrode or degrade the maintenance of their catalytic activity over the long term use under highly oxidizing conditions. On the other hand, the nanoparticle supported catalysts could be wrapped by the added ionomers. Since the ionomers are electron resistant, the charge transfer rate may be decreased due to the hinder of ionomers, which resulting in decreasing of the electronic conductivity of the catalyst layers and leading to high ohmic overpotential.

Fortunately, there are quite a few successful examples and theoretic predictions in other research filed that we can borrow to address the above issues. Very recently, one-dimensional (1-D) nanostructure materials such as nanowires and nanotubes have been considered as the most promising architectures to enhance the electrocatalytic activity. Typically, the nanowire structured materials consisting of conductive oxide nanoparticles represent the advantages of the good charge transport properties, high surface areas and preferable pore-size distribution. The replacement of nanowire structure materials by new conducting 1-D nanostructure materials are of great interest as catalyst support materials.

In the present work, we explored the use of nanowire structured conductive oxide to support the active phase IrO₂. To the best of our knowledge, there were very few reports on the application of nanowire structured oxide supported catalysts in water electrolysis. We successfully introduced a new supported catalyst for OER by combining iridium oxide and antimony doped tin oxide nanowire. The antimony doped tin oxide nanowire was firstly synthesized via an electrosprinning method, which was a facile and versatile process for producing webs of long and continuous metal oxide nanowires. Finally, the supported IrO₂ catalysts were prepared and characterized with respect to the OER activity by electrochemical evaluation and tested in a PEM water electrolyzer. To elucidate the superior catalytic activity of the antimony doped tin oxide nanowire supported catalyst, antimony doped tin oxide nanoparticle had also been prepared by chemical co-precipitation method for comparison.

**Experimental**

**Materials and methods**

**Chemicals**

All the chemicals used in the present work were used as received without further purification. Nafion® solution (5 wt%) and Nafion® 212 were supplied by Dupont. H₂IrCl₆·H₂O, PTFE emulsion (6 wt%) and 40 wt% Pt/C were received from Beijing Nonferrous Metal Research Institute, Shanghai Organic Fluorine Material Research Institute and Johnson Matthey, respectively. All other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd.

**Synthesis of catalyst supports**

The antimony doped tin oxide nanowires were prepared using the electrosprinning method. Firstly, 3 g of Polyvinylpyrrolidone (PVP, Mw≈1300,000) was dissolved in 40 mL methanol under stirring. For antimony doped tin oxide precursor solution, 0.1 g of SnCl₂·2H₂O with 0.018 g of SbCl₃·2H₂O were dissolved in 40 mL methanol under stirring. The PVP and antimony doped tin oxide precursor solution were then mixed together. After the solution was loaded into a syringe that was part of the electrosprinning setup, the solution was ejected into the multi-nozzle with a throughput of 1.2 ml h⁻¹ for single-nozzle electrosprinning systems. The metallic nozzles were connected to a high-voltage power supply (15 kV), and a rotating cage collector was placed 12 cm away from the tip of the multi-syringe needle. Referring to the TG-DSC curves (Fig S1), the as-spun antimony doped tin oxide nanowires precursor was firstly heated to 290 °C and kept at that temperature for 1 h to volatilize the moisture residual solvent in the precursors. The temperature was subsequently slowly increased to 450 °C and kept for 1h. This step allowed completely decompose the PVP to obtain the nanowire structure of antimony doped tin oxide. Finally, the
The crystalline structures of the prepared Sb-SnO$_2$ NW were characterized by X-ray diffraction (XRD) using a Marcogroup diffractometer (MXP21 VAHF) with a Cu-Kα radiation source ($\lambda=1.54056$ Å) to identify the crystal structure. The micromorphology of the prepared Sb-SnO$_2$ NW, Sb-SnO$_2$ NP was studied using scanning electron microscopy (SEM) (ZEISS and LEO-1530 FESEM).

The physical surface area was determined by N$_2$ adsorption-desorption measurements (Micromeritics ASAP 2020, Micromeritics). Brunauer-Emmett-Teller (BET) formulations were used to calculate the surface area. Pore size distributions were estimated by applying the Barrett-Joyner-Halenda (BJH) method to the desorption branch of the isotherms.

Transmission electron microscopy (TEM) analysis was carried out with a Tecnai G2 F20 microscope operating at an accelerating voltage of 300 kV. The samples were first ultrasonically dispersed in ethanol for 10 minutes, and then a drop of the dispersion was deposited on a holey C/Cu TEM grid.

The conductivity measurement of the supports was operated according to a previously reported procedure. The samples were placed in a homemade stainless steel chamber with a PTFE inner sleeve (the conductivity cell) and pressed by two stainless steel pressure levers with a diameter of 10 mm. The pressure was firstly increased to $3 \times 10^8$ Pa for 60 s and then to $3 \times 10^9$ Pa. Measurements were performed at 25 °C in dry ambient atmosphere and the thickness of the pellet in the chamber was measured before and after the measurement by calipers. Electrochemical impedance spectroscopy was used for the conductivity measurement with frequency in a range of 1-10$^6$ Hz and ac amplitude of 10 mV.

For electrochemical evaluations, the catalyst powders were dispersed in isopropyl alcohol, into which Nafion® solution (5 wt%) and PTFE emulsion (6 wt%) was added. The mixtures were then homogenized for 1 h in an ice ultrasonic bath to form an ink. A 50 µL of the ink was pipetted on the surface of a glassy carbon working electrode with 7 mm diameter, followed by drying under a nitrogen atmosphere. For all the catalyst inks, the mass ratio of IrO$_2$ to Nafion® and PTFE was 14:2:1 and the loading of IrO$_2$ in the working electrode was 0.125 mg cm$^{-2}$. The electrochemical properties of the catalysts were characterized with a VMP2 electrochemical workstation by CV, EIS, and chronopotentiometry in a 0.5 mol L$^{-1}$ H$_2$SO$_4$ solution at 25 °C. A Pt coil and a saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. The potential window of CV was from 0 to 1 V vs. SCE using a scan rate from 2 to 300 mV s$^{-1}$. The EIS measurement was conducted at 1.25 V vs. SCE for the frequency between 5 mHz to 99 kHz with a sinus amplitude of 10 mV. The impedance data were modeled with ZSimpWin software. The polarization curves were acquired between 1.2 to 1.8 V vs. SCE with a scan rate of 1 mV s$^{-1}$.

**Electrolyser cell test**

An ink composed of the prepared catalysts, Nafion® solution, PTFE emulsion and isopropyl alcohol was sprayed on a PTFE sheet to form anode catalyst layer. After being dipped in the sodium chloride solution for 2 h and annealed at 340 °C for 30 min, the anode catalyst layer was dipped in 0.5 mol L$^{-1}$ H$_2$SO$_4$ solution for 2 h and then in water for 2 h successively. An ink composed of 40 wt% Pt/C as cathode catalyst, Nafion® solution and isopropyl alcohol was sprayed on a PTFE sheet to form cathode catalyst layer. The loading of IrO$_2$ was 0.75 mg cm$^{-2}$ (determined gravimetrically within ±0.01 mg cm$^{-2}$) for the anode side and 0.2 mg cm$^{-2}$ Pt for the cathode side.

Pretreatment of Nafion® 212 was accomplished by being successively treated in 5 wt% H$_2$O$_2$ solution, distilled water, 0.5 mol L$^{-1}$ H$_2$SO$_4$ solution and distilled water at 80 °C and 60 min for each step. The catalyst coated membrane (CCM) was obtained by transferring the catalyst film from the PTFE film to the pretreated Nafion® 212 by the decal method under the conditions of 135 °C, 75 kg cm$^{-2}$ for 3 min. The performance test was performed in a PEM electrolyser under ambient pressure at 80 °C. Membrane electrode assembly (MEA) (with a 1 cm$^2$ active area) was fabricated by placing the CCM between two carbon cloths. Distilled water was fed to the anode and cathode at a flow rate of 3 mL min$^{-1}$. The cathode of the cell was used as both the counter and reference electrode. Polarization curves were measured in constant current mode.
by increasing the current density from 0 to 2 A cm\(^{-2}\). As for the stability test under ambient pressure at 35 °C, the gas diffusion layers in the anode side were replaced for tantalum coated stainless steel felts.

**Results and discussion**

The schematic illustration of the synthetic route for the IrO\(_2\)/Sb-SnO\(_2\) NW and IrO\(_2\)/Sb-SnO\(_2\) NP is shown in Fig 1. Two different structured antimony doped tin oxides were selected for preparation of supported iridium oxide catalysts. The pore volume, surface area and electronic conductivity of the synthesized supports in the present work are summarized in Table 1.

For the as prepared Sb-SnO\(_2\) NP, the electronic conductivity was 0.76 S cm\(^{-1}\) at 25 °C in ambient atmosphere. A slightly increase of the electronic conductivity for the as prepared Sb-SnO\(_2\) NW was observed when the nanoparticles were assembled into nanowire structure, and the electronic conductivity of 0.83 S cm\(^{-1}\) was obtained at 25 °C in ambient atmosphere. It was a little higher than the values reported in the literatures, which were found to be of up to 10\(^{-1}\) S cm\(^{-1}\) level.

Structural characterization

Fig 2 shows the microstructure of Sb-SnO\(_2\) NW and Sb-SnO\(_2\) NP. The as prepared Sb-SnO\(_2\) NW (Fig 2a) exhibited continuous lengths of up to a few micrometers and uniform 1-D nanostructures (diameter: in the range of 200–300 nm). A magnified image (Fig 2b) revealed that the surface of thus prepared Sb-SnO\(_2\) NW was rough at the nano-scale. Each nanowire had protrusions which consist primarily of fine Sb-SnO\(_2\) nanoparticles. As shown in the elemental mapping from the EDX mapping image (inset in Fig 2b), both tin and antimony were observed in the same sample area. Antimony doping could give rise to enhance electrical conductivity of Sb-SnO\(_2\) oxides. The morphology and phase structure of the Sb-SnO\(_2\) NW was further examined using transmission electron microscopy (TEM) of an individual Sb-SnO\(_2\) NW. The nanowire structured Sb-SnO\(_2\) was clearly demonstrated in Fig 2c, indicating that the Sb-SnO\(_2\) NW was stacked from primary Sb-SnO\(_2\) nanoparticles with diameters of 15-25 nm. As could be observed, the pore structure was formed and mainly caused by the gases produced from the decomposition of the organic material in the precursor. During the calcination process in air, the organic material was oxidized to gas. The produced gases diffused rapidly at the high temperature, which prevented the agglomeration of the Sb-SnO\(_2\) particles. The pore structure of Sb-SnO\(_2\) NW was of importance for allowing easy access of the active surface sites to the electrolyte. Fig 2d shows the high resolution transmission electron microscopy (HRTEM) image of Sb-SnO\(_2\) NW.
the synthesized Sb-SnO$_2$ NW, it revealed that the Sb-SnO$_2$ NW was crystalline rutile structures and showed the lattice fringes with the d spacing of 0.333 nm corresponding to the (110) lattice plane of tetragonal rutile SnO$_2$. Meanwhile, the selected area electron diffraction (inset in Fig 2d) showed that the electron diffraction pattern of the Sb-SnO$_2$ NW was composed of a series of concentric rings corresponding to the (110), (101) and (211) lattice planes, revealing the polycrystalline character of the Sb-SnO$_2$ NW. The morphologies and particle sizes of Sb-SnO$_2$ NP were investigated by SEM and TEM (Fig 2e and Fig 2f). As can be seen, the Sb-SnO$_2$ NP was in form of spheres within a diameter range of 40-50 nm, this was further confirmed by the TEM imaging. Moreover, the HRTEM image (inset in Fig 2f) of the Sb-SnO$_2$ NP demonstrated a fringe spacing of 0.333 nm, and this value agrees well with the spacing of the (110) lattice plane of tetragonal rutile SnO$_2$. On account of primary fine nanoparticles and thus fabricated pore structure of Sb-SnO$_2$ NW, the specific surface area and electrical conductivity slightly increased compared with Sb-SnO$_2$ NP.

X-ray diffraction patterns of the Sb-SnO$_2$ NW, Sb-SnO$_2$ NP were shown in Fig 3. The analysis of the diffraction data revealed that both of Sb-SnO$_2$ NW and Sb-SnO$_2$ NP possessed poly-crystalline structures and the patterns were matched well with the tetragonal rutile SnO$_2$ structure as indexed with the JCPDS 21-1250 file. This observation is corresponded well with the lattice fringes in the HRTEM micrograph (Fig 2d) and the SEAD pattern (inset in Fig 2d) above. Furthermore, no visible diffraction peaks of antimony oxide were observed for the samples, indicating that the antimony oxide entered the tin oxide lattice without formation of a second distinct phase. However, one should take into account that the concentration of antimony oxide is less than 5% in the oxide phase. On the other hand, Wang et al. have reported no structural changes in the SnO$_2$ lattice when up to 15 mol% antimony was accommodated.

Fig 4 shows the N$_2$ adsorption/desorption isotherms of the Sb-SnO$_2$ NW and Sb-SnO$_2$ NP. As shown in Fig 4, the corresponding BJH pore size distribution analysis based on the desorption branch (inset in Fig 4) showed that the Sb-SnO$_2$ NW exhibited relatively uniform mesopores centred at around 75 nm, while the Sb-SnO$_2$ NP contained less uniform mesopores with diameters spanning a range from 30 nm to 250 nm. The calculated pore volumes and surface areas are summarized in Table 1. The pore volume and BET surface area of Sb-SnO$_2$ NW was 0.191 cm$^3$ g$^{-1}$ and 60 m$^2$ g$^{-1}$, respectively. While, the pore volume and BET surface area of Sb-SnO$_2$ NP was 0.178 cm$^3$ g$^{-1}$ and 54 m$^2$ g$^{-1}$, respectively, which were slightly lower than those of Sb-SnO$_2$ NW.

As seen from above, the Sb-SnO$_2$ NW could be viewed as assembling Sb-SnO$_2$ nanoparticles together randomly into nanowire structure via a simple and effective electrospinning method. The structural improvement of Sb-SnO$_2$ NW contributed to tiny beneficial effects on the specific surface area and the electronic conductivity except for more uniform pore size distribution compared with Sb-SnO$_2$ NP. However, the Sb-SnO$_2$ NW was designed to support active phase IrO$_2$ for OER catalyst. The characteristic nanowire structure and the fabricated pore structure of the support were expected to promote the charge transport in the catalyst layer, as to be discussed below.
Fig 5 shows the TEM and HRTEM images of the synthesized IrO$_2$ catalysts using Sb-SnO$_2$ NW and Sb-SnO$_2$ NP as supports. Both the TEM image (Fig 5a and Fig 5c) and the SEM image (Fig 5a and Fig 5b) of the as-prepared catalysts showed that, after the IrO$_2$ nanoparticles were loaded on the different supports, the corresponding catalysts maintained the original structure of the supports, respectively. As shown in Fig 5b, it appeared that the small and uniformly distributed IrO$_2$ nanoparticles (5-8 nm diameter) were well adhered to the Sb-SnO$_2$ NW support. The HRTEM images of IrO$_2$/Sb-SnO$_2$ NW (inset in Fig 5b) and IrO$_2$/Sb-SnO$_2$ NP (Fig 5d) showed the lattice fringes with distinct d spacing of IrO$_2$ (0.320 nm and 0.258 nm) and SnO$_2$ (0.333 nm) corresponding to those of the IrO$_2$ (110) plane, IrO$_2$ (101) plane and SnO$_2$ (110) plane, respectively. The elemental mapping (inset in Fig 5a) of the IrO$_2$ phase (Ir in red), the Sb-SnO$_2$ phase (Sn in pink) and the elemental composition of the supported catalysts (Fig 5c and Fig 5d) were also verified by using EDX analysis, and the results confirmed that the IrO$_2$ phases were present for both catalysts. We further examined the crystalline structures of the supported catalyst by means of a XRD analysis (Fig S3), which indicated that IrO$_2$/Sb-SnO$_2$ NW and IrO$_2$/Sb-SnO$_2$ NP samples were properly formed without any impurity phase.

**Electrochemical characterization**

To evaluate the catalytic activity of the prepared catalysts, the mass specific activity based on the IrO$_2$ loading of 0.125 mg cm$^{-2}$ was used in the following discussion. Cyclic voltammetry in double electrode layer region was used to characterize the electrochemical behavior of prepared catalysts. Fig 6a shows the representative cyclic voltammograms (CVs) of IrO$_2$/Sb-SnO$_2$ NW, IrO$_2$/Sb-SnO$_2$ NP, IrO$_2$ catalysts, Sb-SnO$_2$ NW and the bare glass carbon substrate at a scan rate of 10 mV s$^{-1}$ in N$_2$-saturated 0.5 mol L$^{-1}$ H$_2$SO$_4$ at 25 °C. As shown in Fig 6a, the capacitance of Sb-SnO$_2$ NW support and the bare glass carbon substrate is nearly negligible as compared with that of the prepared catalysts. The CVs of each catalyst exhibited the typical pseudo capacitive behavior with a broad redox peak which could be attributed to the reversible oxidation and reduction on the IrO$_2$ surface. From the CVs, an integration of the voltammogram between 0 and 1 V vs. SCE for the forward sweep was made to obtain the anode voltammetric charge, which previously was proposed to be related to the active surface areas of different catalysts.\cite{15,21}

Fig 6b showed the voltammetric charges for each catalyst obtained at different potential scan rate. It could be seen that the charges increased slightly with decreasing scanning rates especially at the lower scanning rates. According to Ardizzone\cite{40,42} and Trasatti\cite{43}, two kinds of information of the electrochemically active surface area of metal oxide electrodes, the “outer” voltammetric charge (Q$_o$) and the total voltammetric charge (Q$_t$), could be obtained as the scan rate approaches to the zero scan rate.\cite{189} At very high scanning rates, proton exchange took place only on more accessible “outer” active surface, but occurred on the total active surface (both the “outer” and less accessible “inner” surfaces) at very low potential scan rates. Correspondingly, the former (Q$_o$) related to the “outer” active surface was that directly exposed to the electrolyte, and the voltammetric charge (Q$_t$/Q$_o$) normally related to less accessible “inner” surfaces was that proton exchange took place relying on proton diffusion. The ratio of Q$_t$/Q$_o$ was therefore associated with the proton diffusion into subsurface regions through pores, cracks, etc., which depended on the porosity and particles wrapped by the proton conducting phase.

The obtained total charge, outer charge and charge ratio of all the prepared catalysts were investigated and are summarized in Table 2. Compared with IrO$_2$, an obvious increase of the total charge, or in other words, the number of the catalytically active sites was observed as well as an increase of Q$_t$/Q$_o$ ratio for IrO$_2$/Sb-SnO$_2$ NP. It could possibly be attributed to the better dispersion of the iridium oxide particles on Sb-SnO$_2$ NP. A more significant improvement in the catalytically active sites was achieved when IrO$_2$ was supported on Sb-SnO$_2$ NW. From the above BET surface area and conductivity test, the structural improvement of Sb-SnO$_2$ NW contributed to tiny beneficial effects on the specific surface area as well as the electronic conductivity. Thus, for the IrO$_2$/Sb-SnO$_2$ NW, the increase of the catalytically active sites might be attributed to the synergistic effect of the nanowire structure and preferable pore-size distribution of the support. This could be further confirmed by the evidence of enhanced Q$_t$/Q$_o$ ratio for IrO$_2$/Sb-SnO$_2$ NW compared with IrO$_2$/Sb-SnO$_2$ NP. It should be pointed that the limited Q$_t$/Q$_o$ ratio indicated that the charging process was limited by the slow proton diffusion. For IrO$_2$/Sb-SnO$_2$ NW, the nanowire structure of Sb-SnO$_2$ NW not only ensured that the active phase was well distributed, but also provided sufficient charge pathways required in the subsurface regions (as discussed in Fig 6c). Furthermore, the fabricated pore structure of the support could provide more accessible surface area for the electrolyte and accelerate the release of oxygen gas, which could facilitate the availability of active phase.

The charge transfer resistance is in fact of significance to OER activity of the supported catalysts. To shed light the charge transport properties afforded by support with different structures of the prepared catalysts, EIS characterization was carried out for the Sb-SnO$_2$ NW, Sb-SnO$_2$ NP supported IrO$_2$ catalysts, and pure IrO$_2$, respectively at 1.25 V vs. SCE, which corresponded to the oxygen evolution region. Fig 6c showed the EIS measurement in Nyquist plots and an appropriate equivalent electrical circle (ECC) shown in the inset of Fig 6c was selected to fit the impedance data. Among where R$_W$ was the ohmic resistance of working electrode and electrolyte between working electrode and reference electrode, R$_H$ was the charge transfer resistance of a faradic process occurring at the oxide/electrolyte interface, which was a measure of the polarization resistance or the catalytic activity of the electrode and was directly related to the OER kinetics.\cite{44} The impedance parameters for IrO$_2$/Sb-SnO$_2$ NW, IrO$_2$/Sb-SnO$_2$ NP and IrO$_2$ were described in Table 2. As seen from Table 2, the R$_H$ was decreased immensely from 3.415 ohm cm$^2$ for IrO$_2$ and 1.710 ohm cm$^2$ for IrO$_2$/Sb-SnO$_2$ NP to 0.812 ohm cm$^2$ for IrO$_2$/Sb-SnO$_2$ NW.
SnO$_2$ NW, and the IrO$_2$/Sb-SnO$_2$ NW exhibited significantly lower $R_{ohm}$ than that of pure IrO$_2$ and IrO$_2$/Sb-SnO$_2$ NP. It is speculated that the characteristic nanowire structure and the fabricated pore structure of the Sb-SnO$_2$ NW could enhance charge transport properties during the OER reactions. As for the $R_{ohm}$, it should be remarked that the loading of the catalyst on the glassy carbon electrode is relatively low. Better electron conductivity of the pure IrO$_2$ than that of Sb-SnO$_2$ resulted in lower ohmic resistance ($R_{ohm}$). While, slightly lower $R_{ohm}$ of IrO$_2$/Sb-SnO$_2$ NW was obtained than that of IrO$_2$/Sb-SnO$_2$ NP, which was consistent with the conductivity test of different supports.

The effect of catalyst supports with different structure on the catalytic activity of IrO$_2$ was further examined by steady state polarization curves of catalysts recorded in the potential region for the oxygen evolution reactions. For comparison, the polarization curves of Sb-SnO$_2$ NW and the bare glass carbon substrate were also recorded. The polarization curves of Sb-SnO$_2$ NW and the bare glass carbon substrate showed weak current densities within the test potential region (Fig 6d), and it could be concluded that the Sb-SnO$_2$ materials contributed negligible catalytic activity toward the OER. While the anodic current density of the prepared catalysts increased with the increase of the applied potential. As listed in Table 2, to reach a current density of 10 mA cm$^{-2}$, the overpotentials $\eta$ (against the thermodynamic equilibrium potential of OER, 1.23 V) of IrO$_2$/Sb-SnO$_2$ NW, IrO$_2$/Sb-SnO$_2$ NP and IrO$_2$ were measured to be 0.008 V vs. SCE, 0.030 V vs. SCE and 0.043 V vs. SCE, respectively. It should be pointed that the loading of IrO$_2$ in all test electrodes was 0.125 mg cm$^{-2}$, indicating that the IrO$_2$/Sb-SnO$_2$ NW showed the best electrocatalytic performance on mass activity, and it was further proved from the mass normalized polarization curves of the catalysts (Fig S4). It showed that Sb-SnO$_2$ NW support could help the dispersion of the active component and enhanced the catalyst efficiency. However, a problem in the enhancement of the mass activity of the IrO$_2$/Sb-SnO$_2$ NW was the separation of electronic effects (intrinsic activity) from geometric effects (related to catalytically active areas only). According to the previous literatures $^{45}$, normalizing the measured currents with the corresponding total charge could represent intrinsic activity of the corresponding materials. Thus obtained intrinsic activity of IrO$_2$/Sb-SnO$_2$ NW was almost identical with the pure IrO$_2$ (Fig 5S) at low current density. According to Rozain and Millet $^{46}$, at low current density, in the so-called activation governed potential region, the current-voltage relationship was controlled by the OER kinetics, and this potential region was used to evaluate the intrinsic activity of the catalyst. It could be concluded that the IrO$_2$/Sb-SnO$_2$ NW outperformed the IrO$_2$ in the mass activity may be mainly attributed to the improvement of catalytically active sites. Due to the negligible catalytic activity toward the OER of the Sb-SnO$_2$ materials, the higher mass activity of the IrO$_2$/Sb-SnO$_2$ NW than that of IrO$_2$ could be attributed to the better dispersion of the iridium oxide particles on the supports. Compared with the Sb-SnO$_2$ NP, although the physical surface area of the Sb-SnO$_2$ NW was not promoted substantially, higher mass activity might be contributed to the porous nanowire structure, which provide an open structure with appropriate pore-size distribution and enhanced charge transport properties. Fig S6 and Table 2 summarized the corresponding Tafel slopes of the catalysts for evaluating the catalytic kinetics of the catalysts towards the OER. At the applied overpotential ranges, the measured Tafel slopes of the catalysts were around 60 mV dec$^{-1}$, which were in agreement with literature data for pure IrO$_2$ and exhibited the similar reaction mechanism. $^{47}$ It should be noted that both the Tafel slopes of IrO$_2$/Sb-SnO$_2$ NW and IrO$_2$/Sb-SnO$_2$ NP were slightly lower than that of IrO$_2$, and better OER kinetics were probably related to a possible specific interaction between IrO$_2$ and Sb-SnO$_2$. As suggested in previous reports, $^{48}$ SnO$_2$ could facilitate the removal of adsorbed hydroxy species and increase the utilization ratio of the active phase.
Fig 6 (a) Representative CVs recorded with a scan rate of 10 mV s$^{-1}$, (b) Charge as functions of scan rate for IrO$_2$/Sb-SnO$_2$ NW, IrO$_2$/Sb-SnO$_2$ NP and IrO$_2$, (c) Nyquist diagram of three types of prepared catalysts measured at 1.25 V vs. SCE during oxygen evolution, the inset was equivalent circuit, (d) Steady-state polarization curves of the three types of prepared catalysts at scan rate of 1 mV s$^{-1}$. All the electrochemical characterization is tested in the 0.5 mol L$^{-1}$ H$_2$SO$_4$ at 25 °C.

Table 2 Summary of electrochemical characterization of prepared catalysts.

<table>
<thead>
<tr>
<th>J. Name</th>
<th>CV</th>
<th>EIS</th>
<th>Overpotentials</th>
<th>Tafel slopes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q_t^{(a)}$</td>
<td>$Q_{o}^{(a)}$</td>
<td>$Q_{t}/Q_{o}^{(a)}$</td>
<td>$R_{\text{ct}}^{(b)}$</td>
</tr>
<tr>
<td>IrO$_2$</td>
<td>105</td>
<td>71</td>
<td>0.676</td>
<td>0.216</td>
</tr>
<tr>
<td>IrO$_2$/Sb-SnO$_2$ NP</td>
<td>200</td>
<td>166</td>
<td>0.831</td>
<td>0.374</td>
</tr>
<tr>
<td>IrO$_2$/Sb-SnO$_2$ NW</td>
<td>286</td>
<td>246</td>
<td>0.860</td>
<td>0.277</td>
</tr>
</tbody>
</table>

(a) Total charge ($Q_t/C$ g-IrO$_2$)$^{-1}$, outer charge ($Q_{o}/C$ g-IrO$_2$)$^{-1}$ and charge ratio ($Q_{t}/Q_{o}$) of all prepared catalysts calculated from the cyclic voltammograms. (b) Ohmic resistance ($R_{\text{ohm}}$/ohm cm$^2$), charge-transfer resistance ($R_{\text{ct}}$/ohm cm$^2$). (c) Overpotentials ($\eta$/V vs. SCE). (d) Tafel slopes ($S$/mV dec$^{-1}$).

Single cell performance

By using a Nafion® 212 membrane as an electrolyte, MEAs based on IrO$_2$, IrO$_2$/Sb-SnO$_2$ NP, IrO$_2$/Sb-SnO$_2$ NW anodes and a cathode with 40% Pt/C as a catalyst were prepared and tested in a homemade electrolyser. In the present study, the cathode catalyst, loading and fabrication process remained unchanged in order to investigate the effect of anode catalysts with different supports. As seen from Fig 7a, the electrolysis cell performance operated at 80 °C under ambient pressure was steadily improved in the order: IrO$_2$ < IrO$_2$/Sb-SnO$_2$ NP < IrO$_2$/Sb-SnO$_2$ NW. No sign of transport hindrance was observed up to a current density of 2 A cm$^{-2}$. Therefore, the huge disparity in the performance was mainly because of ohmic resistance and the polarization resistance. Due to the better dispersion of iridium oxide on the Sb-SnO$_2$ nanowires, the performance of IrO$_2$/Sb-SnO$_2$ NP was improved compared with pure IrO$_2$ catalyst. For IrO$_2$/Sb-SnO$_2$ NW, a more significant improvement in the performance was achieved, which could be attributed to the improvement of the conductivity in the catalyst layers primarily due to the enhanced charge transport properties afforded by the Sb-doped SnO$_2$ nanowires support. The terminal voltage of electrolysis cell of MEA prepared with IrO$_2$/Sb-SnO$_2$ NW catalyst was 1.62 V at current density of 2 A cm$^{-2}$. It should be remarked that the electrodes were prepared by spraying the ultrasonic inks and then hot-pressed on the polymer membranes. During the procedure, the nanowire structure of the catalysts might be damaged to some extent. However, the performance was considerably improved, indicating the remaining effect of the nanowire structure of the support.

The durability of the electrolyser performance is one of the critical concerns for characterizations of materials and components. To evaluate the stability of the IrO$_2$/Sb-SnO$_2$ NW catalyst, an electrolysis cell was tested under a constant current density of 450 mA cm$^{-2}$ at 35 °C. As shown in Fig 7b, the cell presented reasonably good stability for 646 h and the degradation rate of cell voltage was about 0.76 mV h$^{-1}$. During the initial 90 hours, the voltage had a sharp increase from 1.73 to 2.09 V. It could be caused by the fact that the blocking of membrane exchanging sites by some metal cations and resulted in increasing the electrochemical overpotential. After stabilization period of the initial 90 h, the cell presented reasonably good stability for 556 h. In brief, the electrolyser
test confirmed high activity and stability for the supported catalysts. It should be noted that in terms of catalyst evaluation, comparison of the water electrolysis performance and stability with literature results is by no means straightforward, as membranes, electrode structures and cell assemblies are also playing a role. Moreover no systematic efforts were made to optimize the catalyst ink and hot-pressing procedure for the MEA fabrication, which could be expected to further improve both the cell performance and stability.

Conclusions

In summary, we rationally developed a novel catalyst support with functionalities of nanowire structure and pore structure via a simple and effective electrospinning method from antimony doped tin oxide. Compared with Sb-SnO$_2$ NP, the pore volume, BET surface area and electronic conductivity of Sb-SnO$_2$ NW were slightly increased. However, the structural improvement of Sb-SnO$_2$ NW contributed to more uniform pore size distribution and enhanced charge transport properties. The catalyst activity of Sb-SnO$_2$ NW supported iridium oxide catalyst toward the OER was investigated and showed about three times higher catalytic activity than that of the pure IrO$_2$ catalyst. The good catalytic activity was further confirmed by electrolysers operated at 80 °C, and the terminal voltage was 1.62 V at 2 A cm$^{-2}$ with an IrO$_2$ loading of 0.75 mg cm$^{-2}$, a Pt loading of 0.2 mg cm$^{-2}$. At 35 °C and 450 mA cm$^{-2}$ the cell showed good stability with a period of 846 hours.

Acknowledgements

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Notes and reference

Porous Sb-SnO$_2$ nanowires synthesized as support for IrO$_2$ by electrospinning method. Thus prepared catalyst exhibits enhanced mass activity toward OER.