Synthesis and characterization of an IrO$_2$–Fe$_2$O$_3$ electrocatalyst for the hydrogen evolution reaction in acidic water electrolysis†

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Water electrolysis is one of the most promising processes for a hydrogen-based economy, so the development of highly active, durable, and inexpensive catalysts for the hydrogen evolution reaction (HER) is very important. IrO$_2$ is known to be one of the most active catalysts for the oxygen evolution reaction (OER) in a PEM electrolyzer, but the HER activity of IrO$_2$ is rarely studied because of its low cathodic current compared to platinum. Herein, an IrO$_2$–Fe$_2$O$_3$ composite oxide was prepared by a thermal decomposition method. The physical and electrochemical characterization of the material was achieved by scanning electron microscopy (SEM), X-ray fluorescence (XRF), X-ray diffraction (XRD), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Compared to that of IrO$_2$, the CV curves of the IrO$_2$–Fe$_2$O$_3$ electrode reveal that hydrogen is more easily adsorbed on the surface, which would lead to the H underpotential deposition (H–UPD) redox current increasing significantly. Therefore, the IrO$_2$–Fe$_2$O$_3$ electrode exhibits higher HER activity than that of the IrO$_2$ electrode in 0.5 M H$_2$SO$_4$ solution as shown by linear sweep voltammetry (LSV). It is attributed to the electronic structure modification of IrO$_2$ and synergetic effect between Ir and Fe in the IrO$_2$–Fe$_2$O$_3$ electrode. In addition, the Tafel slope of 36.2 mV dec$^{-1}$ suggests that the mechanism for the IrO$_2$–Fe$_2$O$_3$-catalyzed HER is Volmer–Heyrovsky.

Introduction

With increasing demands for clean and renewable energy and the development of a low carbon emission economy, hydrogen has attracted much attention as an ideal energy carrier.\textsuperscript{1–4} To date, extensive effort has been devoted to exploring advanced techniques for hydrogen production.\textsuperscript{5–8} Water electrolysis is the simplest electrochemical procedure for producing pure hydrogen and has been one of the most promising processes for a hydrogen-based economy. The development of highly active, durable, and inexpensive catalysts for the hydrogen evolution reaction (HER) is an attractive scientific and technological goal.\textsuperscript{11–17} A good catalyst for HER is required to be able to reduce the overpotential and consequently increase the reaction activity in terms of the exchange current density. To date, Pt and Pt-alloys have the highest activity for hydrogen evolution. But the high cost and rarity of Pt are big hurdles for practical application.\textsuperscript{18} Therefore, intensive effort has been applied to the investigation of non-platinum-metal alternatives such as Rh, Ru, Ir, Fe, Co or Ni as well as their alloys.\textsuperscript{19–39} Apart from pure metals or metal alloys, conductive metallic oxides, such as IrO$_2$, RuO$_2$, Co$_3$O$_4$ and NiO\textsuperscript{40–49} are also recognized to be good electrocatalysts for evolving hydrogen in acidic and alkaline solution without reducing to the metals.

It is generally known that IrO$_2$ is one of the most active catalysts for the oxygen evolution reaction (OER) in a PEM electrolyzer, exhibiting high electronic conductivity and stability in the electrochemical procedure. At the same time, IrO$_2$ is also highlighted as the most promising cathodic electrocatalyst because of its strong corrosion-resistance. The apparent current density of IrO$_2$ is in the order of 1.0 mA cm$^{-2}$ and the Tafel slope is 40–50 mV per decade at low current densities.\textsuperscript{48–49} The HER current density is about one order of magnitude lower than that of platinum and iridium\textsuperscript{48} and needs to be further improved. The volcano plot, which associates the intrinsic kinetic rate of HER with the chemisorption energy of hydrogen on metallic surfaces, has shown that an optimal hydrogen binding energy should be not too strong and not too weak to achieve high HER activity.\textsuperscript{50} For example, the strong chemical bond of Ir–H would hinder hydrogen desorption and decrease the reaction rate of HER. To further improve the HER activity of IrO$_2$, it is necessary to change its electronic structure to reduce the hydrogen binding energy, and thereby facilitate hydrogen desorption. Compared to iridium, iron exhibits a lower enthalpy of intermediate M–H adsorption for HER. Iron
composites have been widely applied in catalysis, especially in electrochemical water splitting. Iron has semi-empty d-orbitals, which would be available to facilitate H desorption in the electrochemical desorption step.²⁴ So, the addition of iron to IrO₂ may improve its hydrogen evolution activity. In addition, the well-known “spillover” effect in heterogeneous catalysis would exist in the synergism between iridium and iron.

In this paper, an IrO₂–Fe₂O₃ composite oxide was prepared by a thermal decomposition method. The structure of the IrO₂–Fe₂O₃ composite oxide was characterized by scanning electron microscopy (SEM), X-ray fluorescence (XRF), X-ray diffraction (XRD) and electrochemical methods. Then, the electrochemical catalytic activity and mechanism towards the HER of the IrO₂–Fe₂O₃ electrode was demonstrated in detail.

Results and discussion

The crystal structure of the IrO₂–Fe₂O₃ composite oxide was characterized by X-ray diffraction studies (Fig. 1a). The IrO₂–Fe₂O₃ composite oxide has a typical rutile phase crystal structure, in which the diffraction peaks at 28.1° and 34.9° correspond to the IrO₂(110) and IrO₂(101) crystal faces respectively, by comparison to the JCPDS 43-1019 standard card. The main peaks obtained at 40.1°, 54.0°, 69.4° and 73.2° belong to the rutile phase crystal structure of the (200), (211), (301) and (202) planes, respectively. As can be seen from Fig. 1a, the presence of an iron oxide crystalline phase was not observed in the whole range of 20–80° except in the diffraction peak of Fe₂O₃(113) located at 41.0°. This indicates that the Fe₂O₃ components have been fully incorporated into the IrO₂ lattice, forming a solid-solution composite oxide. In addition, compared to the IrO₂ standard card (the red line) in Fig. 1b, the diffraction peak position of the (101) crystal plane can be found to have a slight positive shift (0.24°), implying that the crystal lattice of IrO₂ has been contracted. The lattice parameter of IrO₂–Fe₂O₃ is found to be ~0.4486 nm, which is smaller than that of pure IrO₂ (0.4498 nm). The lattice shrinkage proves the formation of the IrO₂–Fe₂O₃ solid solution, in which iron atoms enter the rutile structure of IrO₂ or there is atomic substitution of some iridium atoms by smaller iron atoms. According to the Scherrer formula, the particle size of the IrO₂–Fe₂O₃ composite oxide was calculated to be 7.86 nm by fitting the (110) reflection.

Different degrees of agglomeration of the catalysts can been seen from the two SEM images in Fig. 2, which were caused by high temperature sintering during the process of preparation. In Fig. 2a, the IrO₂ particles are irregular in shape and uneven in size. In many places there are obvious agglomerated particles with an average size of about 1 μm. In the green regions of the image, some small crystalline grains with sizes of about 300–500 nm can also be seen at the same time. However, this phenomenon of agglomeration has been improved in the IrO₂–Fe₂O₃ composite oxide’s SEM image (Fig. 2b). The IrO₂–Fe₂O₃ composite oxide particles present rough morphology and the size of the tiny particles in the red regions is about 100 nm. The improvement in dispersion uniformity and decrease in particle size will greatly increase the specific surface area of the electrocatalyst. The BET specific surface area of the IrO₂–Fe₂O₃ composite oxide has reached 261.4 m² g⁻¹ (Fig. S1†), which is larger than that of IrO₂ (241.0 m² g⁻¹, see Fig. S1b†). This increase will be helpful to increase the probability of contact between the reactant and the catalyst.

X-ray fluorescence (XRF) was also carried out to confirm the Ir : Fe molar ratio in the IrO₂–Fe₂O₃ composite oxide, and the result turned out to be 88.39% : 11.61% (Fig. S2 and Table S1†). Specific surface area is a physical property of a catalyst itself. However, in electrochemical experiments, estimation of electrochemically active surface area (ESA) is critical in assessing intrinsic catalytic activity. A popular method for obtaining the ESA is based on the integration of the voltammetric charge (q*) associated with the surface electrochemistry between hydrogen and oxygen evolutions obtained by cyclic voltammetry. So, cyclic
volatammetry (CV) was used to characterize the ESA of the catalysts and is shown in Fig. 3. By integrating the CV curves, the q* of the IrO₂–Fe₂O₃ composite oxide is 26.65 mC cm⁻², which is 1.40 times that of pure IrO₂ oxide (19.00 mC cm⁻²). The increase in surface electrochemical active sites would be conducive to the improvement of electrocatalytic activity.

As shown in Fig. 3, the CV of the IrO₂ electrode accurately exhibits a rectangular mirror image and rapid reversals of the direction of the response current, which are typical electrochemical responses with pseudocapacitive behaviors. The voltammetric capacitance contains contributions from double layer capacitance and pseudo-capacitance, which depends on surface area. After Fe₂O₃ was doped with IrO₂, the electrochemical behavior changed obviously. The redox current, compared to that of IrO₂, increased significantly, especially in the region of hydrogen underpotential deposition (H-UPD, 0–0.3 V). The H-UPD reduction current of the IrO₂–Fe₂O₃ electrode is 4.06 mA cm⁻² @ 0 V, while the current of the IrO₂ electrode is only 1.12 mA cm⁻². The difference between the two catalysts is 3.56 times, which indicates that the IrO₂–Fe₂O₃ electrode would have good hydrogen evolution activity. In addition, the two quasi-reversible peaks seen in the CV can be attributed to changes in the Ir valence states (Ir(II)/Ir(III) at about 0.59 V vs. RHE and Ir(IV)/Ir(III) at about 1.0 V vs. RHE) taking place on the surface of iridium dioxide during potential scanning.

LSV measurements were performed from −0.2 to 0.2 V vs. RHE to investigate the activity of the hydrogen evolution reaction (HER) after the 150-segment CV measurements due to the hysteresis phenomenon of IrO₂. As displayed in Fig. S3, the IrO₂ electrode shows the most negative onset potential for an appreciable cathodic current density (η = 39 mV). The polarisation recorded for the IrO₂–Fe₂O₃ electrode revealed that the cathodic current rises rapidly beyond the zero overpotential. With an increase in polarization potential, the HER current is obviously enhanced and the i–V response of the IrO₂–Fe₂O₃ electrode exhibits higher catalytic activity than that of the IrO₂ electrode in Fig. 4. For instance, the overpotential at 10 mA cm⁻² (using the geometric surface area, GSA) is 155 mV for the IrO₂ electrode, while the overpotential for the IrO₂–Fe₂O₃ electrode is only 78 mV. For comparison, the same measurement was carried out for Pt disk and Pt/C (Fig. 4 and S4†). The electrochemical area of Pt/C is much larger than that of IrO₂–Fe₂O₃ (Fig. S5†) and has an excellent HER activity. But, comparison of IrO₂–Fe₂O₃ and Pt disk under the similar electrochemical area shows that the HER activities are close, which indicates that the IrO₂–Fe₂O₃ electrode is a good electrocatalytic material.

The superior HER activity of the IrO₂–Fe₂O₃ electrode could be attributed to two aspects including geometric and electronic effects. On the one hand, HER is essentially a surface reaction, so an increase in ESA would bring the enhancement in electrocatalytic activity. In addition, the high calcination temperature in the preparation of oxide electrodes has generated larger particle and agglomerate sizes, which intensify the bubble effect (hydrogen bubbles grow and stick on the surface) and result in higher overpotentials. Hence, the performance of electrodes has usually been improved by increasing the ratio between the real and geometric surface area of an electrode. On the other hand, it may be the change in the electronic structure of IrO₂. In the HER mechanism, the strength of the H₂O–M and M–H interactions appears to be very important. The H₂O–M interaction should be strong enough to favor the splitting of the water molecule, conversely, the M–H interaction should not be too strong so as to hinder hydrogen desorption. According to the volcano plot, the hydrogen binding energy of iridium is strong enough, while that of iron is weak. So, the addition of iron would decrease the binding energy and improve the activity of hydrogen evolution.

To understand which is the more important one of the two reasons mentioned above, it is necessary to exclude the effect of ESA on the HER activity. Therefore, the apparent activity of the IrO₂–Fe₂O₃ and IrO₂ electrodes should be normalized with respect to the unit of surface charge. As shown in the inset of Fig. 4, the IrO₂–Fe₂O₃ electrode also exhibited a high current density of 1.87 A cm⁻² at −0.2 V, which is 2.05 times higher than that for the IrO₂ electrode (0.91 A cm⁻²). Thus, we identified that the IrO₂–Fe₂O₃ electrode is truly more active than the IrO₂.
electrode and rationalized that the enhancement is principally
due to the boost in the intrinsic activity of IrO$_2$–Fe$_2$O$_3$. As the
IrO$_2$–Fe$_2$O$_3$ solid-solution formed, the shrinking crystal lattice (demonstrated by the XRD studies) may lower the hydrogen
binding energy to a relatively moderate binding strength, which
favors the desorption of H$_{ads}$ atoms on the surface. On the other
hand, the well-known “spillover” process would appear due to
the synergism between iridium and iron. In the cooperative
interaction, Ir sites facilitate electron transfer to the water
molecule and subsequent cleavage of the O–H bond, and
adjacent Fe sites facilitate the H desorption in the next step.

To study the kinetics of the HER process, the Tafel analysis
was carried out on the polarization curve of the IrO$_2$–Fe$_2$O$_3$
electrode (Fig. 5). The Tafel slope is calculated from the linear
portion of the plot in the low overpotential region. The Tafel
slope is an intensive quantity, and it does not depend on the
surface area of electrode. The Tafel slope of the IrO$_2$–Fe$_2$O$_3$
electrode is only 36.2 mV dec$^{-1}$, which is lower than that of the
IrO$_2$ electrode (42.9 mV dec$^{-1}$). In acidic solutions, the mecha-
nism of HER mainly involves three reactions. The common first
step is the Volmer reaction, where water dissociates and an
adsorbed hydrogen (H$_{ads}$) is formed, which is followed by either
the Tafel reaction (combination reaction) or the Heyrovsky
reaction (electrochemical desorption) to give H$_2$. Assuming
a small surface coverage of hydrogen, a fast discharge reaction
followed by a rate-determining combination reaction results in
a theoretical Tafel slope of 29 mV dec$^{-1}$ at 25 °C. If the elec-
trochemical desorption step is the rate-determining step, the
Tafel slope is 38 mV dec$^{-1}$ at 25 °C. If the Volmer step is rate
determining or the surface coverage is close to one, the Tafel
slope should be 116 mV dec$^{-1}$. Thus, the diagnostic criteria for
the HER on IrO$_2$–Fe$_2$O$_3$ clearly demonstrate a Volmer–Hey-
rovsky mechanism, i.e., the rate-controlling step is the electro-
chemical desorption of H$_{ads}$ and H$_2$O$^+$ to form H$_2$. So the
contraction of the crystal lattice of IrO$_2$–Fe$_2$O$_3$ has enhanced the
desorption of H$_{ads}$ atoms and accelerated the rate of the HER. In
addition, the exchange current density ($j_0$) is further calculated
by extrapolating the Tafel plot, which is the most inherent
measure of HER activity. As expected, the $j_0$ value (0.27 mA
cm$^{-2}$) for the IrO$_2$–Fe$_2$O$_3$ electrode is higher than that of the
IrO$_2$ electrode (0.05 mA cm$^{-2}$).

Electrochemical Impedance Spectroscopy (EIS) is a powerful,
nondestructive and informative technique used extensively to
study electrolyte–electrode interfacial properties. Fig. 6 shows
the Nyquist diagrams of the catalysts recorded at the over-
potential of 50 mV vs. RHE. The equivalent circuit corre-
spending to the EIS data of the IrO$_2$–Fe$_2$O$_3$ electrode was fitted
to a one time-constant model (the equivalent circuit $R_\text{ct}C_{dl}$
shown in Fig. 6f). The values of the electrolyte solution resis-
tance ($R_s$), the charge transfer resistance ($R_{ct}$) and constant
phase element ($C_{dl}$) are listed in Table S2.$^\dagger$ The low frequency
semicircle is ascribed to the charge transfer process, while the
high frequency semicircle could be associated to the mass
transfer processes of the adsorbed species at the cathode.
The charge transfer resistance ($R_{ct}$) data is obtained in the low
frequency zone, which is related to the electrocatalytic kinetics.
The $R_{ct}$ of IrO$_2$–Fe$_2$O$_3$ is 232.7 Ω, which is much lower than IrO$_2$
(693.2 Ω), suggesting a fast charge transport during the HER
process. The higher $C_{dl}$ values observed in the case of the IrO$_2$–
Fe$_2$O$_3$ electrode indicate that the active surface area has been
increased compared to the IrO$_2$ electrode.

In addition, accelerated CV tests were conducted to investi-
gate the stability of the catalysts in the potential range –0.2 to
0.2 V at a sweeping rate of 50 mV s$^{-1}$. As shown in Fig. 7, it is
obvious that the HER activities of the IrO$_2$–Fe$_2$O$_3$ and IrO$_2$
electrodes were both not significantly decreased after 600 cycles
of cyclic voltammetry measurements. The composition of the
IrO$_2$–Fe$_2$O$_3$ electrode did not significantly change, as the molar
ratio of Ir : Fe remained 89.62% : 10.38% (Table S1†). This
suggests that the IrO$_2$–Fe$_2$O$_3$ electrode is durable for hydrogen
evolution and the active sites were not destroyed for a long time
in electrocatalysis reactions.

As everyone knows, IrO$_3$ is one of the most active catalysts
for the oxygen evolution reaction (OER). As can be seen from
Fig. S7,$^\dagger$ the OER activity of IrO$_2$–Fe$_2$O$_3$ is slightly higher than
that of IrO$_2$. So, it can be used as a bifunctional catalyst for water
electrolysis.

![Fig. 5 Tafel plot curves of IrO$_2$–Fe$_2$O$_3$ (red line) and IrO$_2$ (black line) electrodes in 0.5 mol L$^{-1}$ H$_2$SO$_4$ solution.](image)

![Fig. 6 Complex plane plots of impedance of the IrO$_2$–Fe$_2$O$_3$ (red line) and IrO$_2$ (black line) electrodes in 0.5 mol L$^{-1}$ H$_2$SO$_4$ solutions at the overpotential of 50 mV vs. RHE.](image)
Conclusions

In the present work, an IrO$_2$–Fe$_2$O$_3$ composite oxide was prepared by a thermal decomposition method, and the electrochemical behavior and the catalytic activity of the IrO$_2$–Fe$_2$O$_3$ electrode towards HER were demonstrated in detail. When the IrO$_2$–Fe$_2$O$_3$ solid-solution formed, the shrinking crystal lattice modified the hydrogen binding energy to a relatively moderate binding strength, which favors the desorption of H$_{\text{ads}}$ atoms on the surface. On the other hand, the well-known “spillover” process would appear due to the synergism between iridium and iron. Ir sites facilitate electron transfer to water molecules and subsequent cleavage of O–H bonds, and adjacent Fe sites facilitate H desorption in the next step. In comparison to the Heyrovsky, where the electrochemical desorption of hydrogen is the rate-limiting step. In this work, an IrO$_2$–Fe$_2$O$_3$ electrode exhibits a higher catalytic activity towards HER, close to that of the Pt electrode. The Tafel slope suggests that the mechanism for the IrO$_2$–Fe$_2$O$_3$-catalyzed HER is Volmer–Heyrovsky, where the electrochemical desorption of hydrogen is the rate-limiting step. In addition, IrO$_2$–Fe$_2$O$_3$ also showed good activity for OER. Therefore, it can be used as a bifunctional catalyst for water electrolysis.

Material characterization

X-ray diffraction (XRD) was used to analyze the structure of the electrode materials. The inspection was carried out at room temperature on a XRD-7000 X-ray diffractometer (Shimadzu, Japan), using Cu Kz radiation ($\lambda = 0.15405 \text{ nm}$) operating at 40 kV and 30 mA. The analysis of the composition was carried out by X-ray fluorescence (XRF: EDX-7000, Shimadzu, Japan). The surface morphology was characterized by scanning electron microscopy (SEM: S-3000N, Hitachi Co., Japan).

Electrochemical measurements

The electrochemical experiments were carried out by a CHI 660 D electrochemical analyzer at 30 °C. All the electrochemical measurements were carried out in a typical three-electrode electrochemical glass cell. Carbon paper (TGP-H-090, Toray) was used as the counter electrode, the reversible hydrogen electrode (RHE) as the reference, and an IrO$_2$–Fe$_2$O$_3$ electrode (IrO$_2$ or Pt-disk) as the working electrode. Cyclic voltammetry (CV) measurements were performed from 0 to 1.4 V in 0.5 mol L$^{-1}$ H$_2$SO$_4$ solutions at a scan rate of 100 mV s$^{-1}$. Linear sweep voltammetry (LSV) was used as a systematic and effective method to investigate the electrochemical activity of the electrocatalysts. After obtaining a stable cycle between 0 and 1.4 V with 150 segments, the HER polarization curves were obtained by sweeping the potential from $-0.2$ to 0.2 V (vs. RHE) at a scan rate of 5 mV s$^{-1}$ in Ar-saturated 0.5 mol L$^{-1}$ H$_2$SO$_4$. The durability tests were carried out by repeating the potential scan from $-0.2$ to 0.2 V (vs. RHE) with 600 cycles in Ar-saturated 0.5 mol L$^{-1}$ H$_2$SO$_4$ solution. Electrochemical impedance spectroscopy was performed with the working electrode biased at a constant of $-0.05$ V vs. RHE with the frequency ranging from 100 kHz to 0.1 Hz with an amplitude of 10 mV.

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Figure 7: Long-term HER stability tests for IrO$_2$–Fe$_2$O$_3$ (red line) and IrO$_2$ (black line) electrodes in 0.5 mol L$^{-1}$ H$_2$SO$_4$.
44 T. Bhowmik, M. K. Kundu and S. Barman, ACS Appl. Mater. Interfaces, 2016, 8, 28678–28688.
45 U. Ć. Lačnjevac, V. V. Radmilović, V. R. Radmilović and N. V. Krstajić, Electrochim. Acta, 2015, 168, 178–190.
46 X. D. Yan, L. H. Tian, M. He and X. B. Chen, Nano Lett., 2015, 15, 6015–6021.
47 M. K. Bates, Q. Y. Jia, N. Ramaswamy, R. J. Allen and S. Mukerje, J. Phys. Chem. C, 2015, 119, 5467–5477.
48 X. D. Yan, L. H. Tian and X. B. Chen, J. Power Sources, 2015, 300, 336–343.
49 J. B. Cheng, H. M. Zhang, H. P. Ma, H. X. Zhong and Y. Zou, Electrochim. Acta, 2010, 55, 1855–1861.
50 W. C. Sheng, M. Myint, J. G. Chen and Y. S. Yan, Energy Environ. Sci., 2013, 6, 1509–1512.
51 F. Rosalbino, G. Scavino and M. A. Grande, J. Electroanal. Chem., 2013, 694, 114–121.