# **Supporting Information for**

# Highly conductive composite anode catalysts featuring fused Ir nano-network towards proton exchange membrane electrocatalysis

Lu Zhang,<sup>a</sup> Qiannan Wu,<sup>a,b</sup> Xiao Zhao,<sup>c</sup> Xiao Liang,<sup>a</sup> Xiaoxin Zou<sup>a</sup> and Hui Chen\*<sup>a</sup>

<sup>a</sup> State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012.

<sup>b</sup> Hefei conservation of momentum green energy Co., Ltd, Hefei, 231100, China.

<sup>c</sup> School of Materials Science and Engineering, Key Laboratory of Automobile Materials of MOE, State Key Laboratory of Automotive Simulation and Control, Electron Microscopy Center, Jilin University, Changchun 130012.

\*Corresponding Author: Hui Chen: chenhui@jlu.edu.cn

#### **1. Experimental Section**

## 1.1 Chemicals and reagents.

Titanium dioxide (TiO<sub>2</sub>), titanium dioxide, sodium chloride (NaCl) and potassium chloride (KCl) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Boron (B) and Dipotassium hexachloroiridate (K<sub>2</sub>IrCl<sub>6</sub>) were purchased from Shanghai Macklin Biochemical Co., Ltd. Hexachloroiridium Acid Hydrate (H<sub>2</sub>IrCl<sub>6</sub>·6H<sub>2</sub>O) was purchased from Hefei conservation of momentum green energy Co., Ltd. Sodium borohydride (NaBH<sub>4</sub>), absolute ethanol (C<sub>2</sub>H<sub>6</sub>O), isopropanol ((CH<sub>3</sub>)<sub>2</sub>CHOH) were purchased from Sinopharm Chemical Reagent Co., Ltd. Perchloric acid (HClO<sub>4</sub>, 70.0-72.0%), and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) were purchased from Tianjin Xinyuan Chemical Co., Ltd. Commercial Pt/C (40 wt<sub>Pt</sub>%) catalyst was purchased from Sigma-Aldrich. Highly purified water (>18 MΩ cm resistivity) was obtained from a PALL PURELAB Plus system.

## 1.2 Material Synthesis.

The synthetic method for titanium diboride can refer to previous work.<sup>1</sup>

The titanium diboride was synthetized by boron-thermal reduction in molten salts with equal molar ratio (KCl-NaCl). The titanium dioxide and boron were fully ground for about 15 min as well as the molten salt. The mixture was put in an  $Al_2O_3$  crucible and heated at 900 °C with a rate of 10 °C min<sup>-1</sup> for 1 h in a tubular furnace under Ar atmosphere. After cooling, the resulting product was washed with warm water and dried in an oven at 80 °C for 12 h to obtain TiB<sub>2</sub>.

To prepare Ir NN@TiO<sub>2</sub>, TiB<sub>2</sub> support (1.15 mmol) was firstly ultrasonically dispersed for 30 min in a solution with a 9:1 volume ratio of ethanol to deionized water, then H<sub>2</sub>IrCl<sub>6</sub>·6H<sub>2</sub>O (0.44 mmol) was added to the mixture. Once thoroughly stirred, the solution was transferred to a reaction kettle and then hydrothermal reaction at 180°C for 4 hours. After naturally cooling down, the resulting product was washed with water and the black catalyst powder was dried in an oven at 80 °C for 12 hours to yield Ir NN@TiO<sub>2</sub>.

The preparation of unsupported Ir NPs followed the same experimental procedure as that for Ir NN@TiO<sub>2</sub>, with the exception that TiB<sub>2</sub> support was not added.

To prepare of Ir NP@TiO<sub>2</sub>, TiO<sub>2</sub> support (0.75 mmol) and K<sub>2</sub>IrCl<sub>6</sub> (0.21 mmol) were firstly ultrasonically dispersed for 30 min in deionized water, then 10 ml of NaBH<sub>4</sub> solution (0.37 M) was added to the above mixture. The solution was subsequently heated in an oil bath at 180°C for 4 hours. After the reaction was complete, the resulting product was washed with water, and the black catalyst powder was dried in an oven at 80 °C for 12 h to obtain Ir NP@TiO<sub>2</sub>.

## **1.3 Material Characterizations.**

Powder X-ray diffraction (XRD) patterns were conducted by a Rigaku D/Max 2550 X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å). Scanning electron microscope (SEM) images of samples were captured with field emission scanning microscopy (FESEM, JEOL 7800F) at an accelerating voltage of 5 kV. Energy dispersive X-ray (EDX) analysis was obtained with an EDX system attached to JEOL JSM-7800F SEM. Transmission electron microscope (TEM) images were acquired using a Philips-FEI Tecnai G2S-Twin microscope equipped with a field emission gun operating at 200 kV. High-resolution TEM images were recorded on a JEM-2100F electron microscope (JEOL, Japan). The nitrogen adsorption and desorption investigation were tested on a Micromeritucs model. The Fourier transform infrared measurements were carried out on a Nicolet is50 FTIR spectrometer. Inductively coupled plasma atomic emission spectroscopy (ICP-OES) was carried out on a PerkinElmer Optima 3300DV ICP spectrometer. X-ray photoemission spectroscopy (XPS) measurements were test using a Thermo Fisher Scientific ESCALAB 250Xi with photoelectron spectroscopy system using a monochromatic Al Ka (1486.6 eV) The electrical conductivity was tested on four probe resistance tester (ST2722-SZ).

X-ray source. X-ray absorption fine structure (XAFS) spectra (Cu K-edge) were collected at the 4B9A beamline of the Beijing Synchrotron Radiation Facility (BSRF). The BSRF storage rings operated at 2.5 GeV with a stable current of 400 mA. Data collection was conducted in fluorescence mode using a Lytle detector with a Si (111) double-crystal monochromator, and all spectra were obtained under ambient conditions.

## **1.3 Electrochemical Measurements.**

The electrochemical properties of as-prepared catalysts were assessed using a threeelectrode setup with a CHI 660E workstation. The counter electrode and reference electrode were a Pt wire and a saturated calomel electrode (SCE), respectively. The working electrode consisted of either a glassy carbon electrode (GCE, 3 mm diameter), carbon paper, or a titanium plate coated with the catalyst (*e.g.*, Ir NN@TiO<sub>2</sub>). Before testing, the SCE reference electrode was calibrated to a zero net current potential of -0.247 V against a reversible hydrogen electrode (RHE). All electrochemical experiments were conducted in a 0.1 M HClO<sub>4</sub> electrolyte. Linear sweep voltammetry (LSV) was performed at a scan rate of 1 mV s<sup>-1</sup> with 85% *iR*-drop compensation. Chronopotentiometric measurements were taken without *iR*-drop compensation. The potential values were adjusted to the RHE using Equation (1):

$$E_{vs.RHE} = E_{vs.SCE} + 0.247 + 0.059 pH$$
(1)

where 0.247 (vs. SCE) is the zero net current potential.

The working electrode was prepared as follows: (i) 4 mg of catalyst was dispersed in a mixture of 200  $\mu$ L isopropyl alcohol and 200  $\mu$ L Nafion solution, followed by ultrasonic treatment for 30 minutes. (ii) 2.0  $\mu$ L of catalyst ink was carefully dropped onto the GCE surface. (iii) 1.0  $\mu$ L of Nafion solution was dropped onto the catalyst layer. (iv) The working electrode was air-dried. The catalyst loading on the electrode was 0.28 mg cm<sup>-2</sup>.

Chronopotentiometric curves were recorded using carbon paper as the working electrode  $(0.3 \times 0.3 \text{ cm})$  with a catalyst loading of 0.28 mg cm<sup>-2</sup>.

To detect the amount of iridium dissolved from catalysts during OER and collect catalysts post-test, 10 mg of catalyst was dispersed in a mixture of 100  $\mu$ L isopropyl alcohol and 100  $\mu$ L Nafion solution, followed by 60 minutes of ultrasonic treatment. The preparation of the working electrode was similar to the previously mentioned method, with the catalyst applied to the surface of a titanium plate (2 x 2 cm). Potentiostatic measurements were conducted at 1.53 V vs. RHE for 10 hours.

To calculate  $j_{geo}$ , the measured current was normalized by the geometric area of GCE (0.071 cm<sup>2</sup>) according to the Equation (2):

$$j_{geo} = \frac{\ddot{u} \times 1000}{S} \quad (\text{mA /cm}_{geo}^2) \tag{2}$$

where i (A) is the measured current (compensated by 85% *iR*-drop), and S is the geometric area of GCE (cm<sup>2</sup>).

To calculate  $j_{Ir}$ , the measured current was normalized by the loading mass of iridium on GCE according to the Equation (3):

$$j_{Ir} = \frac{i}{m \times Ir(wt_{.}\%)} (A/g_{Ir})$$
(3)

where i (A) is the measured current at 1.55 V vs. RHE, m (g) is the loading mass of catalysts on GCE, and Ir (wt.%) is the mass fraction of iridium in catalysts.

To calculate the Q, we conducted cyclic voltammetry (CV) measurement between 0.4 and 1.4 V vs. RHE at a scan rate of 50 mV/s.

To determine the amount of Ir leached during OER, chronoamperometry was performed at 1.53 V vs. RHE in 50 mL of 0.1 M HClO<sub>4</sub> electrolyte. At various time points during electrocatalysis, 1.0 mL of the electrolyte was sampled and diluted to 10 mL for ICP-OES analysis to measure the concentration of dissolved Ir. The total amount of leached Ir ( $n_{Ir}$ ) was then calculated.

To calculate the S-number of catalysts,<sup>2</sup> the procedure is similar to calculations of the amount of Ir leached during OER. The amount of produced oxygen  $\binom{n_{0_2}}{2}$  was determined based

on the total charge passed during electrocatalysis. The S-number was then calculated using  $n_{0_2}$  and  $n_{Ir}$  values within 10 hours according to Equation (4):

$$S-\text{number} = \frac{n_{O_2}}{n_{Ir}} \tag{4}$$

To calculate Faradaic efficiency, both the actual and theoretical amounts of  $O_2$  must be obtained. The actual amount of  $O_2$  produced at a current density of 20 mA/cm<sup>2</sup> was measured per 40 minutes using the drainage method. The theoretical amount of  $O_2$  was calculated based on Faraday's law, assuming that full current efficiency for  $O_2$  production. The Faradaic efficiency of the catalyst was then calculated as the ratio of the actual  $O_2$  produced to the theoretical value.

### **1.4 PEMWE Measurements**

The Nafion 115 membrane (N115, Dupont) was first successively treated with 3 wt%  $H_2O_2$ , 0.5 M  $H_2SO_4$  and deionized water for 1 hour at each step at an 80°C before fabricating catalyst-coated membrane (CCM). The treated N115 was then stored in deionized water for preservation. Our catalysts (*e.g.*, Ir NN@TiO<sub>2</sub>) were used as the anode, while commercial Pt/C (40%) served as the cathode. To prepare the catalyst ink, the catalyst was dispersed in a 1:1 (w/w) mixture of isopropyl alcohol and distilled water. Nafion was then added, with an ionomer mass fraction of 12 wt% for the anode or 35 wt% for the cathode. The suspension was ultrasonicated in an ice water bath for 1 hour to obtain the catalyst ink.

To fabricate the CCM, the prepared anode and cathode catalyst inks were sprayed onto both sides of the N115 membrane using an ultrasonic spraying device. The catalyst-coated N115 was hot-pressed at 130°C for 3 minutes under a pressure of 10 MPa to obtain the CCM. The load of cathode and anode were 0.44 mg<sub>pt</sub> cm<sup>-2</sup> and 0.30 mg<sub>lr</sub> cm<sup>-2</sup> respectively using ICP-OES. The CCM was then assembled in a single cell with an area of 5 cm<sup>2</sup>. A 0.19 mm thick pore titanium plate (with Pt coating) and 0.2 mm thick carbon paper were used as the gas transport layers for the anode and cathode, respectively. Before testing, the membrane electrode was conditioned in water at 80°C for at least 30 minutes. Subsequently, CCM underwent sequential testing for galvanostatic (at 0.1 A cm<sup>-2</sup> and 0.5 A cm<sup>-2</sup>) for 1 hour and then potentiostatic (at 1.70 V) for 2 hours at a flow rate of 60 mL min<sup>-1</sup>. Finally, polarization curves were recorded on a Gamry Instrument with a 30 A booster using a scan rate of 10 mV s<sup>-1</sup>.

The cell voltage ( $E_{cell}$ ) consists of the reversible cell potential ( $E_0$ ) and three primary overpotentials: kinetic overpotential ( $\eta_{Kinetic}$ ), ohmic overpotential ( $\eta_{Ohmic}$ ), and mass transport overpotential ( $\eta_{Transport}$ ). The value of  $\eta_{Ohmic}$  was determined from electrochemical impedance spectroscopy (EIS) results according to Equation (6):

$$H_{\rm Ohmic} = j \times HFR \,(\rm V) \tag{5}$$

where *j* is current density (A/cm<sup>2</sup>), *HFR* is the high frequency resistance ( $\Omega$  cm<sup>2</sup>).

To further analyze overpotential losses, the cell voltage ( $E_{cell}$ ) from the polarization curves was first corrected for ohmic resistance to obtain the ohmic-corrected voltage ( $E_{ohmic-corrected}$ ). Tafel slopes were then derived in the low current density region using these corrected curves. And extrapolated to the maximum current density to determine the kinetic overpotential ( $E_{kinetic}$ ). It was assumed that the hydrogen evolution reaction (HER) was non-polarizable, meaning the kinetic overpotential was dominated by the oxygen evolution reaction (OER), with a Tafel slope (b) of 2.303 × RT/4F, where R is the ideal gas constant, T is the temperature, and F is Faraday's constant. Finally, the kinetic overpotential ( $\eta_{Kinetic}$ ) was calculated using Equation (7).

$$H_{\text{Kinetic}} = \frac{b \times \log\left(\frac{j}{\dot{j}_0}\right)}{(V)}$$
(6)

where j and  $j_0$  are the applied current density and exchange current density, respectively.

The value of  $\eta_{\text{Transport}}$  was obtained by Equation (8):

$$H_{\text{Transport}} = E_{\text{ohmic-corrected}} - E_{\text{kinetic}} (V)$$
(7)



Figure S1. TEM images of Ir NN@TiO<sub>2</sub> with different Ir content of (a) 6%, (b) 20%, (c) 30%, and (d) 35%.



**Figure S2.** (a) Electrochemical polarization curves and (b) Ir mass activity of Ir NN@TiO<sub>2</sub> with different Ir content.

A series of Ir NN@TiO<sub>2</sub> samples with different iridium loading amounts (*i.e.*, 6, 20, 30 and 35 wt%) can be synthesized by varying the amount of the iridium precursor in the reaction system. At a low iridium loading of 6%, iridium is dispersed on TiO<sub>2</sub> support. When the Ir loading is more than 20%, iridium network begins to form on the surface of TiO<sub>2</sub> support. The sample with an iridium content of 30 wt% exhibits the highest iridium activity among the samples, and Ir NN@TiO<sub>2</sub> refers to this sample unless otherwise specified.



**Figure S3.** (a) XRD pattern and (b,c) TEM images of  $TiB_2$ . The standard XRD card of the Joint Committee on Powder Diffraction Standards (JCPDS) for  $TiB_2$  is shown in the Figure S3a, for comparison.



Figure

NP@TiO<sub>2</sub>.



Figure S5. Nitrogen adsorption-desorption isotherms of Ir NN@TiO<sub>2</sub>.





**Figure S7.** XRD pattern of Ir NN@TiO<sub>2</sub> and Ir NP@TiO<sub>2</sub>. The standard XRD card of the JCPDS for TiO<sub>2</sub> is shown in the Figure S7, for comparison.



Figure S8. High-resolution XPS spectra of (a) Ti 2p and (b) Ir 4f for Ir NN@TiO<sub>2</sub>.

The surface oxidation state of Ti for Ir NN@TiO<sub>2</sub> is 4+. In addition, the surface oxidation state of Ir for Ir NN@TiO<sub>2</sub> is the mix of 0 and 4+. The combination of the XPS data with the Ir L<sub>3</sub>-edge XANES result (**Figure 2b**) indicates that the formation of iridium oxide layer on the surface of metallic Ir NN.



**Figure S9.** CV curves measured in the non-Faradaic region at different scan rates for (a) Ir NN@TiO<sub>2</sub> and (b) Ir NPs. (c) Double-layer capacitance ( $C_{dl}$ ) deduced by the fitting slopes of current between anodic and cathodic sweeps versus different scan rates. (d) ECSAs and ECSA-normalized specific activities at 1.55 V<sub>RHE</sub>.



Figure S10. Fourier transform infrared spectroscopy of Ir NN@TiO<sub>2</sub> and Ir NPs.



**Figure S11.** Chronopotentiometric curve of Ir NN@TiO<sub>2</sub> with a current density of 10 mA cm<sup>2</sup>.



**Figure S12.** The amount of  $O_2$  theoretically calculated and experimentally measured during OER over Ir NN@TiO<sub>2</sub> catalyst versus time at a current density of 20 mA cm<sup>-2</sup>.



Figure S13. The SEM and TEM images of Ir NN@TiO<sub>2</sub> before(a-b) and after OER(c-d).



Figure S14. Fourier transform of EXAFS spectrum of Ir  $NN@TiO_2$  before and after OER electrocatalysis at 10 mA cm<sup>-2</sup> for 10 h.



**Figure S15.** XRD patterns of Ir NN@TiO<sub>2</sub> before and after OER electrocatalysis at 10 mA cm<sup>-2</sup> for 10 h. The weakened diffraction peaks of metallic Ir (at 38-45°) indicates an electrochemical oxidation from Ir to  $IrO_x$ .



Figure S16. Cross-section SEM image of CCM employing Ir  $NN@TiO_2$  in anodic catalyst layer and Pt/C in cathodic catalyst layer.

Because of much lower density of carbon support than  $TiO_2$  support, the Pt packing density (0.44 mg<sub>Pt</sub>/cm<sup>2</sup>) in Pt/C catalyst layer is lower than the Ir packing density (1.5 mg<sub>Ir</sub>/cm<sup>2</sup>) in Ir NN@TiO<sub>2</sub> catalyst layer. Additionally, the Pt loading at the cathode layer (0.44 mg<sub>pt</sub>/cm<sup>2</sup>) is larger than the Ir loading at the anode layer (0.30 mg<sub>Ir</sub>/cm<sup>2</sup>). The lower packing density and higher loading of Pt lead to higher catalyst layer thickness at cathode.



**Figure S17.** EIS curves of Ir NN@TiO<sub>2</sub>, Ir NP@TiO<sub>2</sub> and Ir NPs at large current densities of (a) 1A cm<sup>-2</sup> and (b) 2 A cm<sup>-2</sup>, respectively.



Figure S18. High frequency resistance (HFR) of Ir NN@TiO<sub>2</sub>, Ir NP@TiO<sub>2</sub> and Ir NPs.



Figure S19. The breakdowns of voltage losses for Ir NN@TiO<sub>2</sub>.



Figure S20. The breakdowns of voltage losses for (a) Ir NP@TiO<sub>2</sub>-based and (b) Ir NPs-based cells.

Sample	Shell	CN	R(Å)	$\sigma^2(\text{\AA}^2)$	$\Delta E_{\theta}(\mathrm{eV})$	R factor
Ir NN@TiO <sub>2</sub>	Ir-O Ir Ir	2.2	1.99	0.0053	10.3	0 0071
	Ir-O <sub>1</sub>	6.6	1.98	0.0040	10.5	0.0071
IrO <sub>2</sub>	Ir-Ir <sub>1</sub>	3.0	3.13	0.0022	10.7	0.0082
	lr-lr <sub>2</sub> Ir-O <sub>2</sub>	5.7 5.2	3.54 3.57	0.0012 0.0018		
Ir foil	Ir-Ir	12.0	2.71	0.0027	8.2	0.0044

Table S1. EXAFS Fitting Parameters at the Ir L<sub>3</sub>-edge for Ir NN@TiO<sub>2</sub> ,IrO<sub>2</sub>, and Ir foil.

Anode catalysts	Ir loading (mg/cm <sup>2</sup> )	Pt loading (mg/cm <sup>2</sup> )	Membrane	Current density at 1.9 V (A/cm <sup>2</sup> )	Reference
Ir NN@TiO <sub>2</sub>	0.30	0.44	N115	2.90	This work
<i>p</i> -L-IrO <sub>2</sub>	0.56	0.2	N115	2.70	3
Ir/Nb <sub>2</sub> O <sub>5-x</sub>	1.80	0.4	N115	3.20	4
IrO <sub>2</sub> @TaB <sub>2</sub>	0.15	0.27	N115	2.52	5
Ir/B <sub>4</sub> C	0.50	0.5	N115	2.60	6
IrO <sub>x</sub>	0.20	0.5	N115	2.51	7
Sr <sub>2</sub> CaIrO <sub>6</sub>	0.4	0.4	N212	2.45	8
Porous Ir <sub>0.7</sub> Ru <sub>0.3</sub> O <sub>2</sub>	1.5	0.5	N115	2.20	9
Ir/ATO	1.00	0.4	N212	1.92	10
Ir/WO <sub>x</sub>	0.14	0.4	N115	1.80	11
IrO <sub>2</sub> @TiN <sub>1+x</sub>	1.20	0.4	N117	1.95	12
Ta <sub>0.1</sub> Tm <sub>0.1</sub> Ir <sub>0.8</sub> O <sub>2</sub>	0.20	0.04	N117	1.75	13
IrO <sub>2</sub> /ATO	2.00	0.5	N115	1.70	14
IrO <sub>2</sub> /Ti <sub>1-x</sub> W <sub>x</sub> O <sub>2</sub>	2.14	0.5	N117	1.30	15
W <sub>0.7</sub> Ir <sub>0.3</sub> O <sub>y</sub>	0.4	0.2	N212	0.61	16

 Table S2. Performances of reported PEMWEs using advanced OER catalysts.

Anode catalysts	Membrane	Current density	Cell voltage	Lifetime	Referenc
	N115	1.0	(V)	<u>(h)</u>	e This was als
IF $NN(a) \Pi O_2$	INTT5	1.0	1.0/	1005	I his work
TiIrWO <sub>x</sub>	N117	1.0	1.77	120	17
Ir carbonyl formate	N115	1.0	1.69	100	18
IrO <sub>2</sub> @TaB <sub>2</sub>	N115	1.0	1.70	120	5
IrRuCoNiMo	N115	1.0	1.70	500	19
IrO <sub>x</sub> ·nH <sub>2</sub> O	N115	1.0	1.77	600	20
RuIrFeCoNiO <sub>2</sub>	N212	1.0	1.90	500	21
RuO <sub>2</sub> @IrO <sub>x</sub>	N117	1.0	1.72	300	22
Ir/TiO <sub>2</sub> -MoO <sub>x</sub>	N115	1.0	1.85	50	23

 Table S3. Lifetime of reported PEMWEs using advanced OER catalysts.

## Reference

- 1. F. Guo, Y. Wu, X. Ai, H. Chen, G.-D. Li, W. Chen and X. Zou, *Chem. Commun.*, 2019, **55**, 8627-8630.
- 2. S. Geiger, O. Kasian, M. Ledendecker, E. Pizzutilo, A. M. Mingers, W. T. Fu, O. Diaz-Morales, Z. Li, T. Oellers, L. Fruchter, A. Ludwig, K. J. J. Mayrhofer, M. T. M. Koper and S. Cherevko, *Nat. Catal.*, 2018, **1**, 508-515.
- 3. Z. Xie, X. Liang, Z. Kang, Y. Zou, X. Wang, A. Wu Yimin, G. King, Q. Liu, Y. Huang, X. Zhao, H. Chen and X. Zou, *CCS Chem.*, 2024, **0**, 1-13.
- Z. Shi, J. Li, J. Jiang, Y. Wang, X. Wang, Y. Li, L. Yang, Y. Chu, J. Bai, J. Yang, J. Ni, Y. Wang, L. Zhang, Z. Jiang, C. Liu, J. Ge and W. Xing, *Angew. Chem., Int. Ed.*, 2022, 61, e202212341.
- 5. Y. Wang, M. Zhang, Z. Kang, L. Shi, Y. Shen, B. Tian, Y. Zou, H. Chen and X. Zou, *Nat. Commun.*, 2023, 14, 5119.
- 6. J. Islam, S.-K. Kim, P. T. Thien, M.-J. Kim, H.-S. Cho, W.-C. Cho, C.-H. Kim, C. Lee and J. H. Lee, *J. Power Sources*, 2021, **512**, 230506.
- 7. F. Hegge, F. Lombeck, E. Cruz Ortiz, L. Bohn, M. von Holst, M. Kroschel, J. Hübner, M. Breitwieser, P. Strasser and S. Vierrath, *ACS Appl. Energy Mater.*, 2020, **3**, 8276-8284.
- M. Retuerto, L. Pascual, J. Torrero, M. A. Salam, Á. Tolosana-Moranchel, D. Gianolio, P. Ferrer, P. Kayser, V. Wilke, S. Stiber, V. Celorrio, M. Mokthar, D. G. Sanchez, A. S. Gago, K. A. Friedrich, M. A. Peña, J. A. Alonso and S. Rojas, *Nat. Commun.*, 2022, 13, 7935.
- 9. M. Faustini, M. Giraud, D. Jones, J. Rozière, M. Dupont, T. R. Porter, S. Nowak, M. Bahri, O. Ersen, C. Sanchez, C. Boissière, C. Tard and J. Peron, *Adv. Energy Mater.*, 2019, **9**, 1802136.
- 10. H.-S. Oh, H. N. Nong, T. Reier, M. Gliech and P. Strasser, *Chem. Sci.*, 2015, **6**, 3321-3328.
- 11. G. Jiang, H. Yu, Y. Li, D. Yao, J. Chi, S. Sun and Z. Shao, *ACS Appl. Mater. Interfaces*, 2021, **13**, 15073-15082.
- 12. S. Wang, H. Lv, S. Bi, T. Li, Y. Sun, W. Ji, C. Feng and C. Zhang, *Mater. Chem. Frontiers*, 2021, **5**, 8047-8055.
- S. Hao, H. Sheng, M. Liu, J. Huang, G. Zheng, F. Zhang, X. Liu, Z. Su, J. Hu, Y. Qian, L. Zhou, Y. He, B. Song, L. Lei, X. Zhang and S. Jin, *Nat. Nanotechnol.*, 2021, 16, 1371-1377.
- 14. V. K. Puthiyapura, M. Mamlouk, S. Pasupathi, B. G. Pollet and K. Scott, *J. Power Sources*, 2014, **269**, 451-460.
- 15. H. Lv, J. Zuo, W. Zhou, X. Shen, B. Li, D. Yang, Y. Liu, L. Jin and C. Zhang, *J. Electroanal. Chem.*, 2019, **833**, 471-479.
- 16. T. Yan, S. Chen, W. Sun, Y. Liu, L. Pan, C. Shi, X. Zhang, Z.-F. Huang and J.-J. Zou, ACS Appl. Mater. Interfaces, 2023, 15, 6912-6922.
- 17. Z. Guan, J. Li, S. Li, K. Wang, L. Lei, Y. Wang, L. Zhuang and Z. Xu, *Small Methods*, 2024, **8**, 2301419.
- 18. J. W. Guo, F. Mao, S. R. Fang, H. Y. Lin, H. Wang, W. J. Li, H. Y. Yuan, S. Yang, P. F. Liu and H. G. Yang, *J. Mater. Chem. A*, 2024, **12**, 27280-27285.
- 19. L. Yao, F. Zhang, S. Yang, H. Zhang, Y. Li, C. Yang, H. Yang and Q. Cheng, *Adv. Mater.*, 2024, **36**, 2314049.
- 20. J. Xu, H. Jin, T. Lu, J. Li, Y. Liu, K. Davey, Y. Zheng and S.-Z. Qiao, *Sci. Adv.*, 9, eadh1718.
- C. Hu, K. Yue, J. Han, X. Liu, L. Liu, Q. Liu, Q. Kong, C.-W. Pao, Z. Hu, K. Suenaga, D. Su, Q. Zhang, X. Wang, Y. Tan and X. Huang, *Sci. Adv.*, 9, eadf9144.
- 22. H. Lv, S. Wang, J. Li, C. Shao, W. Zhou, X. Shen, M. Xue and C. Zhang, Appl. Surface

*Sci.*, 2020, **514**, 145943.

23. E.-J. Kim, J. Shin, J. Bak, S. J. Lee, K. h. Kim, D. Song, J. Roh, Y. Lee, H. Kim, K.-S. Lee and E. Cho, *Appl. Catal. B.*, 2021, **280**, 119433.