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## Introduction

Lattice oxygen of PbO<sub>2</sub> induces crystal facet dependent electrochemical ozone production<sup>†</sup>

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The on-site production of ozone *via* electrochemical water electrolysis has attracted increasing interest because of its security and efficiency. However, the underlying mechanism of the facet effect and the influence of lattice oxygen on  $\beta$ -PbO<sub>2</sub> for electrochemical ozone production (EOP) remain unclear. Here,  $\beta$ -PbO<sub>2</sub>-120 nanorods ( $\beta$ -PbO<sub>2</sub>-120 NRs) were prepared to investigate the mechanism of the facet effect and the influence of lattice oxygen during the EOP process. The  $\beta$ -PbO<sub>2</sub>-120 NRs assembled as an anode in a membrane electrode assembly show a remarkable EOP performance. Measurements using *in situ* <sup>18</sup>O isotope-labeling differential electrochemical mass spectrometry confirm that all three oxygen atoms in the ozone originate from the lattice oxygen of  $\beta$ -PbO<sub>2</sub>. Theoretical calculations verify that the EOP reaction pathway on  $\beta$ -PbO<sub>2</sub> follows the lattice oxygen mechanism (LOM), and surface lattice oxygen migration and coupling to  $O_2/O_3$  are favorable on the (101) and (110) surfaces of  $\beta$ -PbO<sub>2</sub>. Different reaction mechanisms are proposed on the two surfaces, and (101) exhibits higher reactivity for  $O_2$  and the formation of  $O_3$ . This valuable insight into the facet effect and LOM of metal oxide-based electrocatalysts can be extended to other applications.

The relationship between the structure and the reactivity of catalysts has attracted considerable attention in recent decades.<sup>1-3</sup> The structures of the crystallographic surface of catalysts are determined by their exposed surfaces, which could also introduce steps, kinks, or dangling bonds to promote effectively the reactivity of these substances.<sup>4,5</sup> In recent years, the facet and size-dependent effects of nanoparticles have also been well investigated in electrocatalytic reactions.<sup>6,7</sup> However, in these studies, the facet effect of nanocatalysts is generally suggested by providing different adsorption sites for reaction intermediates,<sup>8-10</sup> and investigations on the facet effect originating from the surface are insufficient. For instance, the electrocatalytic oxygen evolution reaction (OER) is mostly adopted to occur via four-step proton-couple-electron-transfer (PCET),<sup>11,12</sup> which was also termed the "adsorbate evolution mechanism" (AEM). Rajan and co-workers used the AEM to systematically investigate the reaction intermediates (O\*, OH\*, OOH<sup>\*</sup>, H(OH)O<sup>\*</sup>, H<sub>2</sub>O<sup>\*</sup>, and O<sup>\*</sup><sub>2</sub>) adsorbed on the different active sites from the  $\beta$ -NiOOH (0001) and (10<sup>†</sup>0) facets.<sup>13</sup> The thermodynamic overpotentials were calculated to evaluate the OER reactivity. The intrinsic reason for the promotion of the electrocatalytic performance by the facet effect, which is dependent on the AEM, is the provision of effective adsorption sites for the reaction intermediates. Volcano plots were mapped out to correlate the overpotentials and the adsorption energies of  $\Delta G_{\rm O}^{*} - \Delta G_{\rm OH}^{*}$ .<sup>14,15</sup> The results show that a moderate energy difference is required to reach the minimum overpotentials.

Another type of mechanism known as the lattice oxygen mechanism (LOM) has been proposed,16-18 in which the surface lattice oxygen is the active species and participates in the formation of O2 in the OER. In the first step of the LOM proposed by Mefford and co-workers,19 the adsorbate OO\* is generated by a surface lattice oxygen atom and OH\* from water. With the LOM, the various crystallographic facets are likely to exhibit different reactivities toward the migration of lattice oxygen and formation of surface vacancies.<sup>20</sup> The surface lattice oxygen atoms were only partially involved within the entire reaction network of oxygen evolution through the LOM.<sup>21-23</sup> Electrochemical ozone production (EOP), which involves three oxygen atoms and a six-electron reaction process, is the competing reaction of the OER during water electrolysis. β-Lead dioxide  $(\beta$ -PbO<sub>2</sub>) with high oxygen overvoltage has been demonstrated as a good anode material for a feasible EOP process. However, the mechanism of the EOP pathway is still controversial. Previous studies have suggested that the production of  $O_3$  is mediated by the adsorption of  $O_2^*$ , which further bonds with an adsorbed O\* to generate O3.24

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#### Paper

Nevertheless, the specific role of the crystal facets and lattice oxygen of  $\beta$ -PbO<sub>2</sub> during the EOP process is still poorly understood. Therefore, the rational design and preparation of  $\beta$ -PbO<sub>2</sub> with a regular structure and high EOP efficiency and the comprehensive disclosure of the specific role of the crystal facet effect and lattice oxygen during the EOP process are worth exploring.

In this work, novel  $\beta$ -PbO<sub>2</sub> nanorods (NRs) (named  $\beta$ -PbO<sub>2</sub>-120 NRs) with a high (101) facet were prepared by using a surfactant-free hydrothermal route and presented as effective electrocatalysts for EOP. Experimental and theoretical approaches were applied to study the mechanism of the formation of O<sub>3</sub> with the participation of lattice oxygen. The specific role of the facet effect and lattice oxygen of  $\beta$ -PbO<sub>2</sub>-120 NRs during the EOP reaction was clarified *via in situ* <sup>18</sup>O isotopelabeling differential electrochemical mass spectrometry (DEMS) experiments and density functional theory (DFT) calculation. A possible reaction network was then proposed with all oxygen atoms in O<sub>3</sub> originating from the surface lattice oxygen of  $\beta$ -PbO<sub>2</sub>.

## Materials and methods

#### Materials

NaOH (97%), Pb(CH<sub>3</sub>COO)<sub>2</sub>·3H<sub>2</sub>O (99.5%), and NaClO (AR, 5%) were purchased from Aladdin Industrial Inc. Commercial  $\beta$ -PbO<sub>2</sub> ( $\geq$ 97%) was purchased from Merck. Nafion (5%) was purchased from Johnson Matthey. H<sub>2</sub><sup>18</sup>O was purchased from Heowns. The commercial Pt/C catalyst (20% Pt) was purchased from Shanghai Hesen Electric Co., Ltd. All chemicals were used as received without any further purification. Deionized water (18 M $\Omega$ ) from a Barnstead E-pure system was used in all experiments.

# Synthesis of the $\beta\mbox{-PbO}_2\mbox{-}120$ NR and the $\beta\mbox{-PbO}_2\mbox{-}150$ NR catalysts

In a typical synthesis, 6.0 g of Pb(CH<sub>3</sub>COO)<sub>2</sub> (18.5 mmol) was added to 12 mL of deionized water with ultrasonic treatment for 5 min. The mixture was stirred for 30 min. Afterward, 0.3 g of NaOH (7.5 mmol) was added into the solution under stirring, forming a homogeneous transparent solution. Then, 48 mL of NaClO solution (5% available chlorine, 30 mmol) were added into the above solution. After strongly stirred for 10 min, the mixture was transferred into a 100 mL Teflon-lined autoclave. The autoclave was sealed and maintained at 120 °C for 6 h. After the reaction was completed, the autoclave was cooled down naturally to room temperature. Black-brown products (β-PbO<sub>2</sub>-120 NRs) were collected. The product was washed several times with deionized water and ethanol and then dried at 60 °C for 24 h in a vacuum. The  $\beta$ -PbO<sub>2</sub>-150 NRs were synthesized by the same method except for changing the hydrothermal temperature to 150 °C.

#### Characterization

The morphology of the catalysts was determined by SEM by using a Hitachi FE-SEM S-4700 operated at 15.0 kV and TEM by using

a Tecnai G2F30S-Twin microscope equipped with a field emission gun operated at 300 kV. The HAADF-STEM, EDX, and EDS mapping images were obtained by using an FEI Titan Themis 60-300 "cubed" microscope fitted with a series of aberration-correction factors for the imaging lens and the probe forming lens. Powder XRD was conducted by employing an X-ray diffractometer with graphite monochromatized Cu K $\alpha$  irradiation ( $\lambda = 1.54$  Å) at 40 mA and 40 kV. Based on the XRD results, the corresponding cell parameters of the catalysts were calculated by using Jade software. XPS was performed using a Kratos AXIS Ultra DLD instrument with 300 W Al K $\alpha$  radiation, and the C 1s peak was located at 284.5 eV as the internal standard.

#### **Electrode preparation**

A carbon fiber (CF) cut into 2 cm  $\times$  2 cm was ultrasonicated successively in HNO<sub>3</sub> (40 wt%), acetone, ethanol, and deionized water for 30 min. Then, the CF was dried at 60 °C in a vacuum for 24 h. The catalyst (8 mg) was dispersed by ultrasonication in 900 µL of ethanol and 100 µL of Nafion solution. The catalyst was slowly added dropwise onto the 2 cm  $\times$  2 cm carbon cloth (2 mg cm<sup>-2</sup>) and then dried under infrared light.

#### Electrochemical ozone production measurements

The electrochemical ozone generation of the catalysts was performed by using an electrochemical workstation (CHI 760E) with a typical three-electrode cell. The CF with catalysts was employed as the working electrode, a platinum plate was employed as the counter electrode, and an Ag/AgCl (3 M KCl) electrode was employed as the reference electrode. The polarization curve results were measured in the range of 0-3.5 V vs. Ag/AgCl (5 mV  $s^{-1}$ ). The electrochemically active surface area (ECSA) was evaluated in terms of double-layer capacitance  $(C_{dl})$ . Cyclic voltammetry (CV) was performed in the 0-0.2 V range vs. Ag/AgCl at different scan rates (20, 40, 60, 80, 100 and 120 mV  $s^{-1}$ ). Electrochemical impedance spectroscopy (EIS) was performed at 2.0 V vs. Ag/AgCl from 100 000 to 1 Hz with an amplitude of 5 mV. All measurements were performed in a saturated K<sub>2</sub>SO<sub>4</sub> solution at room temperature. The potentials were referenced to the reversible hydrogen electrode (RHE) by using the Nernst equation as follows:

$$E_{\rm RHE} = E_{\rm Ag/AgCl} + 0.059 \times \rm pH + 0.197$$

#### Determination of the concentration of the gaseous ozone

Experiments on the EOP were carried out in a membrane electrode assembly (MEA) electrolyzer with  $\beta$ -PbO<sub>2</sub> and Pt/C coated on a Nafion membrane as the electrodes, and deionized water as the electrolyte. The ozone gaseous products were determined by using an Ozone Analyzer (UVIZ-1200). The Faraday efficiency (FE) (%) of the evolution of the gaseous ozone was calculated as follows:

$$FE(\%) = \frac{5 \times F \times Q}{3 \times M_{O_3} \times I} \times 100$$

where  $M_{O_3}$  is the molecular weight of  $O_3$  (48), *I* is the current (A), *F* is Faraday constant (9.6485 × 10<sup>4</sup> C mol<sup>-1</sup>), and *Q* is the O<sub>3</sub> production rate (kg h<sup>-1</sup>).<sup>25</sup>

#### In situ differential electrochemical mass spectroscopy

The DEMS data were collected on a QAS 100 from Linglu Instruments (Shanghai) Co. Ltd. to perform an in situ analysis of gas. The gaseous products were analyzed with a commercial quadrupole mass spectrometer (Pfeiffer Prisma) in the main chamber. The electrolytic chamber and main chamber were separated by a porous PTFE membrane. Instead of deionized water, H<sub>2</sub><sup>18</sup>O was applied to dissolve K<sub>2</sub>SO<sub>4</sub>, and the solution was employed as the electrolyte for the electrolysis at a constant voltage (1.5 mL). The working electrode was prepared by depositing the electrocatalyst ink on gold foil with a loading of around 0.6 mg cm<sup>-2</sup>. The saturated Ag/AgCl electrode as the reference electrode and the Pt wire as the counter electrode were positioned near the liquid surface, while the working electrode was positioned at the bottom of the electrolyte such that the gaseous products could be directly introduced into the main chamber. Experiments for the electrolysis at a constant voltage were performed using a CHI 600 station. The O2 species were determined by monitoring the values of m/z signals of 32, 34, and 36, while the  $O_3$  species were determined by monitoring the values of *m*/*z* signals of 48, 50, 52, and 54.

#### **Calculation section**

Periodic DFT calculations were performed using the Vienna ab initio Simulation Program (VASP) package.26,27 The projectoraugmented wave (PAW) method<sup>28,29</sup> was applied at a planewave cutoff of 400 eV to decouple the core from the valence electrons. The Perdew-Burke-Ernzerhof exchange-correlation function<sup>30</sup> was used in the calculations. The electronic configurations were 2s<sup>2</sup> 2p<sup>4</sup> for O and 5d<sup>10</sup> 6s<sup>2</sup> 6p<sup>2</sup> for Pb. A Gaussian smearing method with a width of 0.05 eV was applied throughout the calculations. Spin polarization was also considered in all calculations. The electronic energy of the supercell was converged to  $10^{-6}$  eV, with the force on each relaxed atom converged to 0.02 eV Å<sup>-1</sup> in the ionic relaxation calculations. Transition states were optimized with the climbing image nudged elastic band (CI-NEB) approach and the dimer method.<sup>31,32</sup> The vibrational frequencies of the transition states were calculated, and only one imaginary frequency was predicted, confirming the structures as right transition states.

A symmetric and stoichiometric slab model of PbO<sub>2</sub> (101) and PbO<sub>2</sub> (110) was constructed from the optimized bulk  $\beta$ -PbO<sub>2</sub> structure. For the PbO<sub>2</sub> (101) surface, a p-(2 × 2) supercell with a lattice constant of 12.25 Å × 10.11 Å was constructed. For the PbO<sub>2</sub> (110) surface, a p-(3 × 2) supercell with a lattice constant of 10.30 Å × 14.17 Å was constructed. The bottom half layers were kept constant in the calculations for the PbO<sub>2</sub> (101) and (110) surfaces. A vacuum layer of 15 Å was added in the *z* direction, and a Monkhorst–Pack *k*-point mesh of (2 × 2 × 1) was applied for both surfaces.

The Gibbs free energy for each species was calculated as follows:

$$G = E_{\text{elec}} + E_{\text{ZPE}} - T \times S$$

where  $E_{elec}$  is the electronic energy at 0 K from the DFT calculation and  $E_{ZPE}$  is the zero-point energy term. For the gaseous species, including O<sub>2</sub> and O<sub>3</sub>, the entropic term was obtained from the NIST-JANAF thermochemical tables.<sup>33</sup> For the surface-adsorbed species, all 3 N degrees of freedom of the adsorbates were treated as harmonic vibrations, and the entropy was calculated as the sum of the contributions from these vibrational motions.

#### Results and discussion

#### Structural and morphological characterization of the samples

 $\beta$ -PbO<sub>2</sub>-120 NRs were prepared through a non-surfactant assisted hydrothermal reaction. Fig. 1a presents the scanning electron microscopy (SEM) image of the  $\beta$ -PbO<sub>2</sub>-120 NRs. The asprepared catalyst features a typical NR-shaped structure 100 nm in length and 20 nm in diameter, which is confirmed by the transmission electron microscopy (TEM) images (Fig. 1b and S1<sup> $\dagger$ </sup>). For comparison, the SEM images of the  $\beta$ -PbO<sub>2</sub>-150 NRs and commercial β-PbO<sub>2</sub> (β-PbO<sub>2</sub>-CM) are also shown in Fig. S2 and S3,<sup>†</sup> respectively. β-PbO<sub>2</sub>-150 NRs feature a NRshaped structure over 150 nm in length and 50 nm in diameter, and  $\beta$ -PbO<sub>2</sub>-CM presents block structures with an irregular size of  $\sim 1$  to 5 µm, while the  $\beta$ -PbO<sub>2</sub>-120 NRs are markedly smaller and more uniform. These differences in the morphology would lead to an immense influence on the adsorption of key O intermediates. In addition, the energydispersive X-ray (EDX) elemental mapping analysis (Fig. 1c) exhibits that the Pb and O elements are evenly distributed on the NRs. To further understand the  $\beta$ -PbO<sub>2</sub>-120 NRs, colored images from atomic-scale scanning transmission electron microscopy (STEM) (Fig. 1d) verify the ordered surface along with very high crystallinity. The appearance of continuous lattice fringes oriented in the same direction across the β-PbO<sub>2</sub>-120 NRs indicates their quasi-single-crystalline nature. This



**Fig. 1** (a) SEM image, (b) TEM image, (c) EDX elemental map, and (d) colourized atomic-scale STEM image of the  $\beta$ -PbO<sub>2</sub>-120 NRs with the fast Fourier transform (FFT) pattern of the lattice image. (e, h) Partially enlarged image of (d). (f) Schematic illustration of the (110) facet. (g) Intensity profiles of (110) facets in (e). (i) Schematic illustration of the (101) facet. (j) Intensity profiles of (101) facets in (h).

#### Paper

structure is beneficial for the in-plane electron transport during the EOP process. In addition, the crystal structure is further confirmed by the fast Fourier transform (FFT) patterns of the lattice image (Fig. 1d, inset) along the (110) and (101) axes. Moreover, the major interplanar spacings measured in the magnified atomic-scale STEM images and intensity profiles (Fig. 1g and j) from Fig. 1e and h are 0.346 nm and 0.286 nm, respectively, which well match the corresponding (110) and (101) lattice fringes of  $\beta$ -PbO<sub>2</sub>. Furthermore, the symmetric and stoichiometric PbO<sub>2</sub> (110) and (101) surfaces were used as the model of the  $\beta$ -PbO<sub>2</sub>-120 NRs due to their high concentrations (Fig. 1f and i). DFT calculations show that the lattice distances between two repeating units are 0.368 nm and 0.282 nm for the (110) and the (101) surface, respectively. These values are also consistent with that obtained from colourized atomic-scale STEM. Overall, these results confirm the successful synthesis of highly crystalline ordered  $\beta$ -PbO<sub>2</sub> NRs with thermodynamically stable crystal facets.

To further investigate the states of composition, a series of Xray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurements were carried out. The XRD patterns of the  $\beta$ -PbO<sub>2</sub>-120 NRs,  $\beta$ -PbO<sub>2</sub>-150 NRs and  $\beta$ -PbO<sub>2</sub>-CM are displayed in Fig. 2a. Three evident strong peaks can be observed at 25.4°, 32°, and 49°, which belong to the (110), (101), and (211) facets of  $\beta$ -PbO<sub>2</sub> (PDF#41-1492),<sup>34,35</sup> respectively, consistent with the STEM results. The  $\beta$ -PbO<sub>2</sub>-120 NRs and the  $\beta$ -PbO<sub>2</sub>-150 NRs reveal the most intense peak corresponding to the (101) facets, which is considerably higher than that of the  $\beta$ -PbO<sub>2</sub>-150 NRs and  $\beta$ -PbO<sub>2</sub>-CM. Such a phenomenon is due to the regular NR morphology of the  $\beta$ -PbO<sub>2</sub>-120 NRs. The X-ray photoelectron survey spectra (Fig. 2b) illustrate that the  $\beta$ -PbO<sub>2</sub>-120 NRs contain only Pb and O elements,<sup>36,37</sup> and this result corresponds



Fig. 2 (a) XRD patterns and (b) full survey X-ray photoelectron spectra of the  $\beta$ -PbO<sub>2</sub>-120 NRs,  $\beta$ -PbO<sub>2</sub>-150 NRs and  $\beta$ -PbO<sub>2</sub>-CM. High-resolution X-ray photoelectron spectra of (c) Pb 4f and (d) O 1s of the  $\beta$ -PbO<sub>2</sub>-120 NRs,  $\beta$ -PbO<sub>2</sub>-150 NRs and  $\beta$ -PbO<sub>2</sub>-CM.

to those from EDX. The normalized high-resolution Pb 4f and O 1s spectra are displayed in Fig. 2c and d. The typical XPS peaks of Pb 4f (Fig. 2c) at 142.4 eV and 137.5 eV in the  $\beta$ -PbO<sub>2</sub>-120 NRs,  $\beta$ -PbO<sub>2</sub>-150 NRs and  $\beta$ -PbO<sub>2</sub>-CM are assigned to Pb<sup>4+</sup>, while the peaks at 141.6 eV and 136.8 eV correspond to Pb<sup>0</sup>.<sup>38,39</sup> The ratio of Pb<sup>4+</sup>/Pb<sup>0</sup> in the  $\beta$ -PbO<sub>2</sub>-120 NRs and the  $\beta$ -PbO<sub>2</sub>-150 NRs are larger than that in  $\beta$ -PbO<sub>2</sub>-CM (Table S1†), indicating a higher degree of crystallinity in the surface of the  $\beta$ -PbO<sub>2</sub>-120 NRs and the  $\beta$ -PbO<sub>2</sub>-150 NRs. Meanwhile, the O 1s peak (Fig. 2d) can be fitted with two peaks at 528.8 eV and 530.3 eV, which are associated with the Pb–O and surface O–H groups, respectively.<sup>40</sup> The higher content of surface O–H groups comes from the hydrothermal reaction.<sup>41,42</sup>

#### **Electrocatalytic performance**

The electrocatalytic activity of the  $\beta$ -PbO<sub>2</sub>-120 NRs,  $\beta$ -PbO<sub>2</sub>-150 NRs and  $\beta$ -PbO<sub>2</sub>-CM toward EOP was investigated by employing a typical three-electrode configuration in saturated K<sub>2</sub>SO<sub>4</sub> solution (pH = 7.0) at room temperature. Fig. 3a reveals the steady-state polarization curves of the  $\beta$ -PbO<sub>2</sub>-120 NRs,  $\beta$ -PbO<sub>2</sub>-150 NRs and  $\beta$ -PbO<sub>2</sub>-CM. The  $\beta$ -PbO<sub>2</sub>-120 NRs exhibit a potential of 2.63 V *vs.* RHE at a current density of 10 mA cm<sup>-2</sup>, which is higher than that of  $\beta$ -PbO<sub>2</sub>-150 NRs (2.60 V *vs.* RHE) and  $\beta$ -PbO<sub>2</sub>-CM (2.55 V *vs.* RHE). The higher overpotential indicates that O<sub>3</sub> is more conducive to generate on the  $\beta$ -PbO<sub>2</sub>-120 NRs, demonstrating the importance of the facet effect and nanostructure engineering in enhancing the EOP activity. In addition, the Tafel plots of these catalysts were investigated to determine their EOP kinetics. Fig. 3b displays the Tafel slopes of



Fig. 3 (a) Steady-state polarization curves, (b) Tafel plots, and (c) charging current density at 0.71 V vs. RHE as a function of various scan rates for the  $\beta$ -PbO<sub>2</sub>-120 NRs,  $\beta$ -PbO<sub>2</sub>-150 NRs and  $\beta$ -PbO<sub>2</sub>-CM. (d) Schematic of the membrane electrode assembly (MEA) electrolyzer. (e) Ozone output, (f) power consumption per unit of ozone, and (g) Faraday efficiency for the MEA electrolyzer with the anode of the  $\beta$ -PbO<sub>2</sub>-120 NRs,  $\beta$ -PbO<sub>2</sub>-150 NRs and  $\beta$ -PbO<sub>2</sub>-CM at a constant current density of 0.25–1.0 A cm<sup>-2</sup>. (h) Ozone output and Faraday efficiency for the MEA electrolyzer with the anode of the  $\beta$ -PbO<sub>2</sub>-120 NRs for 50 h at a constant current of 0.5 A cm<sup>-2</sup> with the photograph of the MEA electrolyzer.

the  $\beta$ -PbO<sub>2</sub>-120 NRs,  $\beta$ -PbO<sub>2</sub>-150 NRs and  $\beta$ -PbO<sub>2</sub>-CM, and two apparent linear segments can be observed. The larger value of the Tafel slope of the  $\beta$ -PbO<sub>2</sub>-120 NRs indicates more efficient EOP electrocatalytic kinetics.43 Moreover, the electrochemically active surface area (ECSA) was obtained by determining the double-layer capacitance  $(C_{dl})$  via cyclic voltammetry (CV) measurements at different scan rates (Fig. S4-S6<sup>†</sup>). As extracted in Fig. 3c, the  $C_{\rm dl}$  value of the  $\beta$ -PbO<sub>2</sub>-120 NRs is 40.76 mF cm<sup>-2</sup>, which is almost two times higher than that of the  $\beta$ -PbO<sub>2</sub>-150 NRs (21.22 mF cm<sup>-2</sup>) and  $\beta$ -PbO<sub>2</sub>-CM (22.70 mF cm<sup>-2</sup>).  $C_{dl}$  was also used to calculate the value of the normalized exchange current density  $(J_{0, normalized})$  to estimate the relative electrochemically active surface area, and the results are listed in Table S2.<sup>†44</sup> The  $J_{0, \text{ normalized}}$  of the  $\beta$ -PbO<sub>2</sub>-120 NRs is slightly smaller than that of the β-PbO<sub>2</sub>-150 NRs and β-PbO<sub>2</sub>-CM, which indicates that the high performance of EOP can be attributed to the different ratios of crystal facets. Hence, the ratio of (101) and (110) facets plays a crucial role in ozone production. These findings suggest that the facet effect significantly influences the local environment, greatly improving the intrinsic EOP activity. This phenomenon also shows that the  $\beta$ -PbO<sub>2</sub>-120 NRs are efficient electrocatalysts toward EOP in media with neutral pH.

A membrane electrode assembly (MEA) electrolyzer was built to explore the feasibility of the electrocatalyst for high current densities required in industrial potential applications. The schematic of the MEA is shown in Fig. 3d. The core of this system was a catalyst-coated membrane, which employed the β-PbO<sub>2</sub>-120 NRs, β-PbO<sub>2</sub>-150 NRs or β-PbO<sub>2</sub>-CM and 20% commercial Pt/C coated on a Nafion 117 membrane as the anode and cathode, respectively. Ultrapure water was employed as the electrolyte. The catalysts were uniformly coated on both sides of the membrane by using a benchtop ultrasonic spray coating system. The EOP performance was evaluated in a constant current density range of 0.25-1.0 A cm<sup>-2</sup> and within the voltage range of 3-6 V. The gaseous ozone output (Q) of the constant-current electrolysis under different current densities is shown in Fig. 3e. The gaseous ozone output produced by the  $\beta$ -PbO<sub>2</sub>-120 NRs and the  $\beta$ -PbO<sub>2</sub>-150 NRs is markedly higher than that of  $\beta$ -PbO<sub>2</sub>-CM, and the yield can reach 442.1 mg h<sup>-1</sup> and 403.1 mg  $h^{-1}$  at a current density of 1.0 A cm<sup>-2</sup>, respectively, while the yield of  $\beta$ -PbO<sub>2</sub>-CM is only 288.0 mg h<sup>-1</sup>. These results show the excellent EOP performance of the  $\beta$ -PbO<sub>2</sub>-120 NRs and the  $\beta$ -PbO<sub>2</sub>-150 NRs. The power consumption (PC) per unit of ozone by the  $\beta$ -PbO<sub>2</sub>-120 NRs is also considerably lower than that by  $\beta$ -PbO<sub>2</sub>-CM (Fig. 3f). The PC of the ozone for the  $\beta$ -PbO<sub>2</sub> NR-based electrolyzer is 115.6 W h  $g^{-1}$  O<sub>3</sub> at a current density of 0.5 A cm<sup>-2</sup>, which is markedly lower than that of the  $\beta$ -PbO<sub>2</sub>-150 NR-based (131.4 W h g<sup>-1</sup> O<sub>3</sub>) and the  $\beta$ -PbO<sub>2</sub>-CM-based (146.0 W h g<sup>-1</sup> O<sub>3</sub>) electrolyzer. This result implies that the  $\beta$ -PbO<sub>2</sub>-120 NRs as an anode can significantly reduce the energy consumption to facilitate ozone production. As the current density increases, the PC decreases at first and then stabilizes. Additionally, the slight fluctuation in the PC indicates that the EOP electrolyzer has a limitation because of heat dissipation. A high temperature will lead to the decomposition of O<sub>3</sub>. Moreover, the heat loss also affected the Faraday efficiency (FE), as shown in Fig. 3g. The FE of the  $\beta$ -PbO<sub>2</sub> NR-based electrolyzer

reaches a maximum of 14.9% at a current density of 0.5 A cm<sup>-2</sup>, which is superior to that of the  $\beta$ -PbO<sub>2</sub>-150 NRs (11.8%) and  $\beta$ -PbO<sub>2</sub>-CM (8.4%). Nevertheless, as the current density increases, the FE does not increase because of the thermal loss. This result is consistent with the foregoing heat inference. According to the evaluation of the EOP activity of the MEA electrolyzer, the  $\beta$ -PbO<sub>2</sub>-120 NRs have the highest gaseous ozone output and lowest power consumption, and the  $\beta$ -PbO<sub>2</sub>-150 NRs also exhibit better EOP performance compared with  $\beta$ -PbO<sub>2</sub>-CM. This finding further demonstrates that the crystal facet ratio of  $\beta$ -PbO<sub>2</sub> has a significant impact on the EOP performance.

To further evaluate the stability of the  $\beta$ -PbO<sub>2</sub>-120 NRs, electrolysis was also continuously performed using the electrolyzer (Fig. 3h, inset) for 50 h at a constant current of 0.5 A  $cm^{-2}$ . The ozone output and FE are shown in Fig. 3h. The ozone output first increases rapidly and exceeds 210 mg  $h^{-1}$  after 2 h of electrolysis, exhibits negligible degradation, and holds an FE of over 14% even after 48 h. The excellent durability of the  $\beta$ -PbO<sub>2</sub>-120 NRs is also confirmed by the TEM and XRD data after the stability measurements. Impressively, no obvious breakdown in the NR structure is observed (Fig. S7†), which clearly confirms the maintenance of the original framework of the β-PbO<sub>2</sub>-120 NRs. The XRD pattern also shows that the peak ratio of the (101) and (110) facets after the reaction is similar to those of the pristine  $\beta$ -PbO<sub>2</sub>-120 NRs (Fig. S8<sup>†</sup>). These results further verify that the NR structure and the composition of the  $\beta$ -PbO<sub>2</sub>-120 NRs are unchanged after the long-term durability test. The robust stability under industrial current density highlights prospects for the use of the β-PbO2-120 NRs as ideal electrocatalysts for the large-scale implementation of an EOP electrolyzer.

#### In situ DEMS measurements

To gain more insight into the mechanism of the generation of  $O_3$  on the  $\beta$ -PbO<sub>2</sub>-120 NRs, *in situ* <sup>18</sup>O isotope-labeling DEMS measurements were designed and carried out.45-47 The experiments were conducted with the  $\beta$ -PbO<sub>2</sub>-120 NR (<sup>16</sup>O) catalyst deposited on gold disk electrodes scanned in a saturated K<sub>2</sub>SO<sub>4</sub> solution of H<sub>2</sub><sup>18</sup>O. Controlled potential electrolysis was performed at 3.0 V vs. Ag/AgCl (Fig. S9<sup>†</sup>). Unexpectedly, the intensity of the O<sub>3</sub> (<sup>16</sup>O<sup>16</sup>O<sup>16</sup>O) signal with a mass-to-charge ratio of 48 is the strongest, which is over 100 times higher than those of the other O<sub>3</sub> signals. This result shows that the three lattice oxygen atoms couple with each other and generate the <sup>48</sup>O<sub>3</sub> product. The weak m/z signals at 50, 52, and 54 indicate that the EOP proceeds via the LOM pathway. Meanwhile, different O2 signals are also shown in Fig. 4b, and three isotopologues  ${}^{32}O_2$ , <sup>34</sup>O<sub>2</sub>, and <sup>36</sup>O<sub>2</sub> are detected. Interestingly, the intensity of the  ${}^{36}O_2$  ( ${}^{18}O^{18}O$ ) signal is the strongest, and the intensity of  ${}^{34}O_2$ (<sup>16</sup>O<sup>18</sup>O) and <sup>32</sup>O<sub>2</sub> (<sup>16</sup>O<sup>16</sup>O) signals demonstrates that lattice oxygen participates in the production of O2. These results indicate that the OER proceeds via the AEM and LOM pathways, and the AEM pathway plays a dominant role in the OER process,45,48 which is remarkably different from the EOP process. The DEMS results provide evidence for the participation of the lattice oxygen of  $\beta$ -PbO<sub>2</sub> during the EOP process.



**Fig. 4** Differential electrochemical mass spectrometry measurements of (a) <sup>16</sup>O<sup>16</sup>O<sup>16</sup>O (*m*/*z* = 48), <sup>18</sup>O<sup>18</sup>O<sup>16</sup>O (*m*/*z* = 52), and <sup>18</sup>O<sup>18</sup>O<sup>18</sup>O (*m*/*z* = 54) signals and (b) <sup>16</sup>O<sup>16</sup>O (*m*/*z* = 32), <sup>18</sup>O<sup>16</sup>O (*m*/*z* = 34), and <sup>18</sup>O<sup>18</sup>O (*m*/*z* = 36) from the reaction products for the β-PbO<sub>2</sub>-120 NRs (<sup>16</sup>O) in a H<sub>2</sub><sup>18</sup>O aqueous electrolyte. Free energy diagrams (298 K) of lattice oxygen migration and coupling to O<sub>2</sub>/O<sub>3</sub> over the (c) (101) and (d) (110) surfaces of β-PbO<sub>2</sub> are calculated by using density functional theory. Proposed reaction network for the electrocatalytic O<sub>2</sub>/O<sub>3</sub> production originating from the lattice oxygen on the (e) (101) and (f) (110) surfaces of β-PbO<sub>2</sub>.

#### Theoretical calculation

To further elucidate the intrinsic mechanism for the enhancement of EOP activity, DFT calculations were also applied to investigate the LOM in the EOP reaction over the  $\beta$ -PbO<sub>2</sub>-120 NR catalyst. Gibbs free energy diagrams at a reaction temperature of 298 K were predicted to elucidate the catalytic mechanism of the diffusion of lattice oxygen and formation of O<sub>2</sub>/O<sub>3</sub>. The possible reaction pathway on the  $PbO_2$  (101) surface was first investigated. As shown in Fig. 4c and S10,† the formation of the O<sub>2</sub><sup>\*</sup> adsorbate involves the diffusion of the exposed O<sub>latt</sub> atom and the direct coupling with the neighboring Olatt site. A moderate apparent energy barrier of 0.74 eV is predicted for the direct coupling process, and this step is also considered as the rate-determining step due to its highest apparent energy barrier. The corresponding Gibbs reaction energies and energy barriers for each elementary step are shown in Table S3.<sup>†</sup> The subsequent diffusion and desorption of the O<sub>2</sub><sup>\*</sup> species are also calculated to be very thermodynamically favorable with the reaction energy determined to be -0.43 eV and -0.40 eV, respectively. Thus, the overall Gibbs reaction energy of the coupling of surface lattice oxygen to form the gaseous  $O_2$  is calculated to be highly exothermic by -2.03 eV. Alternatively,

the  $O_2^*$  fragment can also migrate and interact with the neighboring  $O_{latt}$  to yield the  $O_3^*$  intermediate, with the free energy barrier and reaction energy calculated to be only 0.41 eV and -0.05 eV, respectively. In the  $O_3^*$  intermediate, the  $O_2$  fragment is first weakly bonded to the lattice oxygen atom, with the  $O_2$ -O\* distance found to be 1.56 Å. After the couple of  $O_2$  and an additional O to form  $O_3^*$  intermediate, the  $O_3^*$  intermediate rotated with two oxygen atoms bonding with one Pt atom, the energy barrier for this rotation process was calculated to be 0.08 eV. The gaseous ozone is then generated with the desorption of  $O_3^*$ , producing three oxygen vacancies, and the reaction energy is found to be slightly endothermic by 0.30 eV.

For the  $PbO_2$  (110) surface, calculations show that the LOM reaction follows the "oxygen hopping" mechanism instead of the direct coupling mechanism. As shown in Fig. 1d and S11,† the corresponding Olatt atom will continuously migrate to the bridge site between two Pb atoms and the top site of the neighboring Pb atom, with the reaction energy calculated to be endothermic by 0.73 eV and 0.42 eV, respectively, for the two diffusion steps. The free energy barrier of the O<sub>latt</sub> atom coupling with the neighboring lattice oxygen to yield the  $O_2^*$ intermediate is only 0.11 eV. Thus, the transference of the first Olatt atom is most likely to limit the reaction due to its high endothermicity, which results in a significant apparent energy barrier of 1.25 eV. Upon the formation of the surface  $O_2^*$  species, its direct desorption is also very likely to occur to form the gaseous  $O_2$  molecule, with a reaction energy of -1.08 eV. The reaction pathway of  $O_2^*$  further coupling with an additional  $O_{latt}$ to form ozone was also investigated, and the reaction energy and free energy barrier for this step are determined to be 0.19 eV and 0.92 eV, respectively. The  $O_3^*$  fragment further desorbs from the surface to form the gaseous ozone with a desorption energy of 1.15 eV. After the desorption of  $O_3$ , we consider that the catalyst could be regenerated via H2O adsorption and dissociation, and the oxygen vacancy sites were fulfilled during this process. The free energy diagram of H2O adsorption and dissociation on the (110) and the (101) surface with one oxygen vacancy is shown in Fig. S12.<sup>†</sup> For the PbO<sub>2</sub> (110) surface, the Gibbs reaction energy for H2O adsorption and dissociation was calculated to be -0.10 eV and -0.76 eV, respectively. And the oxygen vacancy site was fulfilled by the OH\* fragment, and O-Pb bond lengths were calculated to be 2.28 Å and 2.31 Å. For the PbO<sub>2</sub> (101) surface, the Gibbs reaction energy for H<sub>2</sub>O adsorption and dissociation was calculated to be -0.15 eV and -0.67 eV, respectively. The O-Pb bond lengths were calculated to be 2.24 Å and 2.41 Å. The above results suggested that for both the (110) surface and the (101) surface, the catalyst could be regenerated via H<sub>2</sub>O dissociation and fulfilling the oxygen vacancy, which also explains the stability of the  $\beta$ -PbO<sub>2</sub>-120 NRs.

Thus, the results show that for the PbO<sub>2</sub> (101) and the PbO<sub>2</sub> (110) surfaces, the first-step lattice oxygen migration and coupling to the  $O_2^*$  adsorbate is the rate-determining step for the surface lattice oxygen evolution to  $O_2/O_3$ . Different reaction mechanisms for the formation of  $O_2^*$  are observed on the above surfaces, in which the reaction occurs by direct coupling between neighboring surface oxygens on the (101) surface. By contrast, for the (110) surface, the reaction occurs indirectly, in

which the relevant lattice oxygen atom first migrates to the top site of the Pb site nearby and then couples with another surface  $O_{latt}$  to yield  $O_2^*$ . A possible reaction network originating from the surface lattice oxygen is proposed via the previously mentioned reaction mechanism (Fig. 4e and f). For the (101) and (110) surfaces, the reaction path for the formation of  $O_2$  is thermodynamically more favorable than that for the formation of  $O_3$ . This phenomenon explains the necessity of a higher overvoltage to obtain O<sub>3</sub>. By comparing the two Gibbs potential energy of the (101) and (110) surfaces, the potential energy of the (101) surface was much lower than that on the (110) surface, indicating a more favourable reaction pathway. In addition, the effective energy barrier for the (101) surface was calculated to be 0.74 eV, whereas for the (110) surface, the effective energy barrier was calculated to be 1.25 eV, which was mediated by two Olatt migrating steps. Thus, we were able to conclude that the (101) surface was more reactive than the (110) surface for O<sub>latt</sub> migration and O<sub>3</sub> formation.

## Conclusions

In summary,  $\beta$ -PbO<sub>2</sub>-120 NRs with a high ratio of (101) facets were synthesized by a hydrothermal method for EOP. A  $\beta$ -PbO<sub>2</sub>-120 NRassembled MEA electrolyzer exhibits remarkable EOP performance. The results from in situ <sup>18</sup>O DEMS measurements show that the OER and EOP on the β-PbO2-120 NRs follow different reaction processes, and the ozone products mainly originate from the three lattice oxygen atoms of the  $\beta$ -PbO<sub>2</sub>-120 NRs. Theoretical investigations reveal the possibility of the formation of O2/O3 from the surface lattice oxygen on the (101) and (110) facets of  $\beta$ -PbO<sub>2</sub>. Different reaction mechanisms are proposed for the evolution of the surface oxygen on the two surfaces, in which the reaction follows direct and indirect routes for O<sup>\*</sup><sub>latt</sub> coupling to O<sup>\*</sup><sub>2</sub> on (101) and (110) facets, respectively. The results provide new insights for the studies of the facet effect originating from the surface lattice oxygen. New ideas are also provided for designing EOP electrocatalysts with higher efficiency.

## Author contributions

W. B. Jiang and J. Liu synthesized the samples and performed the characterization. S. B. Wang contributed to theoretical calculations. H. Y. Zheng and Y. Gu synthesized the  $\beta$ -PbO<sub>2</sub>-150 NRs. W. W. Li assisted in theoretical calculations. H. J. Shi and S. Q. Li contributed to the discussion of the results. X. Zhong and J. G. Wang designed the research, and wrote the paper. All the authors commented on and revised the manuscript.

## Conflicts of interest

The authors declare no competing financial interests.

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## Notes and references

- 1 D. Lei, K. Yu, M.-R. Li, Y. Wang, Q. Wang, T. Liu, P. Liu, L.-L. Lou, G. Wang and S. Liu, *ACS Catal.*, 2016, 7, 421–432.
- 2 X. Wang, J. Wang, Z. Cui, S. Wang and M. Cao, *RSC Adv.*, 2014, 4, 34387–34394.
- 3 X. Zhou, Z. Wang, X. Xia, G. Shao, K. Homewood and Y. Gao, *ACS Appl. Mater. Interfaces*, 2018, **10**, 28199–28209.
- 4 D. Cai, T. Yang, B. Liu, D. Wang, Y. Liu, L. Wang, Q. Li and T. Wang, *J. Mater. Chem. A*, 2014, **2**, 13990–13995.
- 5 U. Diebold, Surf. Sci. Rep., 2003, 48, 53-229.
- 6 A. X. Yin, X. Q. Min, Y. W. Zhang and C. H. Yan, *J. Am. Chem. Soc.*, 2011, **133**, 3816–3819.
- 7 T.-T. Zhao, H. Wang, X. Han, K. Jiang, H. Lin, Z. Xie and W.-B. Cai, *J. Mater. Chem. A*, 2016, 4, 15845–15850.
- 8 D. Gao, H. Zhou, J. Wang, S. Miao, F. Yang, G. Wang, J. Wang and X. Bao, *J. Am. Chem. Soc.*, 2015, **137**, 4288–4291.
- 9 Q. Zhang, Y. Cao, Y. Yan, B. Yuan, H. Zheng, Y. Gu, X. Zhong and J. Wang, *J. Mater. Chem. A*, 2020, **8**, 2336–2342.
- 10 B. Yuan, Z. Yao, C. Qiu, H. Zheng, Y. Yan, Q. Zhang, X. Sun, Y. Gu, X. Zhong and J. Wang, *J. Energy Chem.*, 2020, **51**, 312– 322.
- 11 J. Rossmeisl, A. Logadottir and J. K. Nørskov, *Chem. Phys.*, 2005, **319**, 178-184.
- 12 Á. Valdés, Z. W. Qu, G. J. Kroes, J. Rossmeisl and J. K. Nørskov, J. Phys. Chem. C, 2008, 112, 9872–9879.
- 13 A. Govind Rajan, J. M. P. Martirez and E. A. Carter, *J. Am. Chem. Soc.*, 2020, **142**, 3600–3612.
- 14 I. C. Man, H. Y. Su, F. Calle-Vallejo, H. A. Hansen, J. I. Martínez, N. G. Inoglu, J. Kitchin, T. F. Jaramillo, J. K. Nørskov and J. Rossmeisl, *ChemCatChem*, 2011, 3, 1159–1165.
- 15 G. Murdachaew and K. Laasonen, J. Phys. Chem. C, 2018, 122, 25882–25892.
- 16 A. Grimaud, W. T. Hong, Y. Shao-Horn and J. M. Tarascon, *Nat. Mater.*, 2016, **15**, 121–126.
- 17 T. Liu, Z. Feng, Q. Li, J. Yang, C. Li and M. Dupuis, *Chem. Mater.*, 2018, **30**, 7714–7726.
- 18 D. N. Mueller, M. L. Machala, H. Bluhm and W. C. Chueh, *Nat. Commun.*, 2015, 6, 6097.
- 19 J. T. Mefford, X. Rong, A. M. Abakumov, W. G. Hardin, S. Dai, A. M. Kolpak, K. P. Johnston and K. J. Stevenson, *Nat. Commun.*, 2016, 7, 11053.
- 20 X. Rong, J. Parolin and A. M. Kolpak, ACS Catal., 2016, 6, 1153–1158.
- 21 D. A. Kuznetsov, M. A. Naeem, P. V. Kumar, P. M. Abdala, A. Fedorov and C. R. Muller, *J. Am. Chem. Soc.*, 2020, **142**, 7883–7888.
- 22 D. Liu, H. Ai, J. Li, M. Fang, M. Chen, D. Liu, X. Du, P. Zhou, F. Li, K. H. Lo, Y. Tang, S. Chen, L. Wang, G. Xing and H. Pan, *Adv. Energy Mater.*, 2020, **10**, 2002464.

- 23 A. Zagalskaya and V. Alexandrov, *ACS Catal.*, 2020, **10**, 3650–3657.
- 24 G. Gibson, A. Morgan, P. Hu and W.-F. Lin, *Chem. Phys. Lett.*, 2016, **654**, 46–51.
- 25 F. Okada and K. Nay, Electrolysis, *Electrolysis for Ozone Water Production*, ed. J. Kleperis, IntechOpen Limited, London, 2012, p. 245. DOI: 10.5772/51945.
- 26 G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, 6, 15–50.
- 27 G. Kresse and J. Furthmüller, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, **54**, 11169–11186.
- 28 G. Kresse and D. Joubert, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **59**, 1758–1775.
- 29 P. E. Blöchl, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **50**, 17953–17979.
- 30 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, 77, 3865–3868.
- 31 K. Mathew, R. Sundararaman, K. Letchworth-Weaver, T. A. Arias and R. G. Hennig, J. Chem. Phys., 2014, 140, 084106.
- 32 S. Smidstrup, A. Pedersen, K. Stokbro and H. Jonsson, J. Chem. Phys., 2014, **140**, 214106.
- 33 *NITS-JANAF Thermochemical Tables*, https://webbook.nist.gov/chemistry/, DOI: 10.18434/T4D303.
- 34 G. Xi, Y. Peng, L. Xu, M. Zhang, W. Yu and Y. Qian, *Inorg. Chem. Commun.*, 2004, 7, 607–610.
- 35 Y. Yan, Y. Gao, H. Zheng, B. Yuan, Q. Zhang, Y. Gu,
  G. Zhuang, Z. Wei, Z. Yao, X. Zhong, X. Li and J. Wang, *Appl. Catal.*, B, 2020, 266, 118632.

- 36 C. H. Lee and M. W. Kanan, ACS Catal., 2015, 5, 465-469.
- 37 Y. Hu, J. Yang, J. Hu, J. Wang, S. Liang, H. Hou, X. Wu, B. Liu, W. Yu, X. He and R. V. Kumar, *Adv. Funct. Mater.*, 2018, 28, 1705294.
- 38 W.-H. Yang, Q.-H. Zhang, H.-H. Wang, Z.-Y. Zhou and S.-G. Sun, New J. Chem., 2017, 41, 12123–12130.
- 39 J. Morales, G. Petkova, M. Cruz and A. Caballero, *J. Power Sources*, 2006, **158**, 831–836.
- 40 X. Duan, W. Wang, Q. Wang, X. Sui, N. Li and L. Chang, *Chemosphere*, 2020, **260**, 127587.
- 41 Z. Liu, D. D. Sun, P. Guo and J. O. Leckie, *Chem.-Eur. J.*, 2007, 13, 1851–1855.
- 42 S. Han, Q. Ye, S. Cheng, T. Kang and H. Dai, *Catal. Sci. Technol.*, 2017, 7, 703–717.
- 43 C. Zhang, Y. Xu, P. Lu, X. Zhang, F. Xu and J. Shi, *J. Am. Chem. Soc.*, 2017, **139**, 16620–16629.
- 44 Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, T. Regier and H. Dai, *Nat. Mater.*, 2011, **10**, 780–786.
- 45 L. Zhang, L. Wang, Y. Wen, F. Ni, B. Zhang and H. Peng, *Adv. Mater.*, 2020, **32**, e2002297.
- 46 D. Yao, C. Tang, L. Li, B. Xia, A. Vasileff, H. Jin, Y. Zhang and S. Z. Qiao, *Adv. Energy Mater.*, 2020, **10**, 2001289.
- 47 A. M. Ullman, C. N. Brodsky, N. Li, S. L. Zheng and D. G. Nocera, J. Am. Chem. Soc., 2016, 138, 4229–4236.
- 48 Y. Pan, X. Xu, Y. Zhong, L. Ge, Y. Chen, J. M. Veder, D. Guan, R. O'Hayre, M. Li, G. Wang, H. Wang, W. Zhou and Z. Shao, *Nat. Commun.*, 2020, **11**, 2002.