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An effective method for enhancing oxygen evolution kinetics of $LaMO_3$ (M = Ni, Co, Mn) perovskite catalysts and its application to a rechargeable zinc–air battery



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ABSTRACT

Of the various non-precious catalysts that have been explored thus far, perovskite oxides have attracted much attention due to their intrinsic catalytic activity and structural flexibility. Here we report a new method for enhancing oxygen evolution reation (OER) activity of LaNiO₃ perovskite by a thin FeOOH coating. The resulting LaNiO₃@FeOOH demonstrates remarkably enhanced OER activity, much better than those of the pristine LaNiO₃ or the benchmark RuO₂. The excellent OER activity is attributed mainly to the optimized adsorption energy for oxygenated species and fast charge transfer kinetics. Similar enhancement effect of the FeOOH layer is also observed for other perovskite oxides, suggesting that the developed approach could be an effective strategy towards enhancing OER activity of many perovskite catalysts. Moreover, when the LaNiO₃@FeOOH is used as the OER catalyst in a rechargeable Zn–air battery, the overpotential of the cell is reduced while maintaining long cycling life, demonstrating the promising prospect for practical applications.

1. Introduction

Oxygen evolution reaction (OER) is a necessary step in many energy storage and conversion processes such as reversible fuel cells, electrolyzers, and rechargeable metal-air batteries [1–6]. Unfortunately, the rates of OER are relatively sluggish due to the complex multiple-electron transfer processes involved in the electrode reaction, leading to high anodic overpotential (η) and low energy efficiency [7–9]. While noble metal oxides (e.g., RuO₂ and IrO₂) demonstrate excellent OER activity, and have been widely deemed as the state-of-the-art electrocatalysts [10,11], the high cost and scarcity make them unsuitable for practical applications. Thus, exploration of low-cost, highly-efficient OER catalysts has attracted considerable attention. Among many materials that have been extensively investigated as alternative candidates to replace noble metal oxides [12–15], perovskite oxides have potential to be a promising family of cost-effective catalysts [16–18].

Perovskite oxides with a general formula of ABO₃ (where A is a rareearth or alkaline earth element and B is a transition metal) are of particular interests due to their high OER catalytic activity (mA cm_{oxide}^{-2}) in an alkaline electrolyte. Besides the aforementioned advantage of low cost and earth-abundance, perovskite oxides have flexible physical and chemical properties, strong tolerance to contaminants, and remarkable durability for many applications [19-22]. Unfortunately, the intrinsic electro-catalytic activity of the ABO3-type perovskite oxides is still inadequate in most cases. Accordingly, large overpotentials are needed to sustain a desired current density, due mainly to weak absorption energy of the oxygenated species (*O, *OH, *OOH) on active sites of perovskite surface [23]. In previous studies, different approaches have been explored to optimize the absorption energy. For example, proper cation substitution (A and/or B sites) resulted in elusive descriptor (e.g., eg filling factor) regulation and MO-H bond strength modification [24-26]. Another widely used approach is to create oxygen vacancies

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through annealing at high temperatures, which can be complicated and difficult to control under certain conditions [27–29]. To overcome these difficulties, direct growth of a thin layer of material with strong affinity for the oxygenated species may greatly boost the OER activity of perovskites. It is noted that FeOOH is seldom regarded as a highly-efficient catalyst due to poor electrical conductivity and inferior mass activity; however, it has strong adsorption energy for the oxygenated intermediates (*O, *OH, *OOH), implying that it could be used as a surface modifier for perovskite catalysts [30–32].

In this work, we report a new approach for enhancing the OER activity of LaNiO₃ perovskite catalyst by growth of a thin-film FeOOH on the perovskite surface. In LaNiO₃@FeOOH catalyst, coherent interfaces were observed under HRTEM, which favors the electron transfer as confirmed by the corresponding peaks shift in the core-level XPS spectra. Upon analysis, the relative weak absorption energy of the oxygenated species (*O, *OH, *OOH) on active sites of perovskite (vs. the relative strong nature of FeOOH) should be the main reason for the remarkably improved OER performance. Besides, the strong electron interaction evidenced by both XPS and electrochemical impedance spectroscopy also boost the catalytic kinetics. In order to demonstrate the approach (decorating thin FeOOH layers) is an effective strategy for boosting the oxygen evolution kinetics and suitable for other perovskite oxides as well, case study was also conducted for both LaCoO3 and LaMnO₃. After a suite of measurements, as expected, both engineered LaCoO₃ and LaMnO₃ exhibit enhanced OER activities, endorsing it to be an effective strategy for boosting the catalytic performance of LaMO₃ (M = Ni, Co, Mn) perovskites. Moreover, a home-made Zn-air battery with LaNiO₃@FeOOH catalyst as cathode and Pt/C as anode was also constructed and tested, exhibiting small overvoltage during charging/ discharging and decent cycling stability, confirming that the developed approach is suitable for practical application.

2. Experimental section

All chemical reagents were of analytical grade and directly used without further purification.

2.1. Preparation of LaNiO₃

LaNiO₃ was prepared with a modified sol-gel method similar to the reported literatures [19,33]. In a typical process, stoichiometric amount of 0.01 mol Ni(NO₃)₂.6H₂O and 0.01 mol La(NO₃)₃.6H₂O were firstly subject to 100 ml deionized (DI) water, and then 0.02 mol EDTA and 0.04 mol CA were added in sequence. The molar ratio of total metal ions (La³⁺ Ni²⁺)/EDTA/CA was 1:1:2, and the pH value of the solution was adjusted to be ~ 8 by adding some NH₄•OH. After carrying out the heat treatment at 100 °C in oil bath under stirring, a transparent blue gel was obtained, which was then subjected to further sintering at 250 °C for 5 h in air towards formation of a black solid precursor. Then, the solid precursor was re-calcined at 800 °C for another 5 h in air, after which the LaNiO₃ perovskite of LaCOO₃ and LaMnO₃ were also prepared using Co(NO₃)₂•6H₂O and (Mn(NO₃)₂•6H₂O as the raw chemical with quite similar approach, the detail of which will not give here.

2.2. Preparation of LaNiO₃@FeOOH

The as-prepared LaNiO₃ (0.5 mmol) was dispersed in DI water (50 mL) by sonication for 20 min, by which a homogenous suspension was formed. After adding 0.5 mmol FeSO₄•7H₂O and subsequent stirring for a while, the mixed suspension was heated to 80 °C and keep for 1 h. After that, the collected product was then washed with DI water and ethanol, respectively. Finally, the LaNiO₃@FeOOH sample (termed as LaNiO₃@FeOOH-1:1 as the same mole ratio of the two components) was dried in an oven at 80 °C overnight. In order to find the LaNiO₃@FeOOH sample that demonstrate the best catalytic behavior, LaNiO₃@

FeOOH samples with different mole ratio (LaNiO₃ vs. FeOOH = 3:1, 2:1, 1:2 and 1:3) were also prepared by changing the initial added iron-related precursors.

Moreover, the composites of $LaCoO_3@FeOOH-1:1$, $LaMnO_3@FeOOH-1:1$ were also fabricated and tested.

2.3. Material characterizations

The crystal nature of all samples were examined by Powder X-ray diffraction (XRD, Philips, X'pert Pro, Cu K α , $\lambda = 1.5406$ Å, 40 kV, 40 mA). The morphology of the samples was collected on a fieldemission scanning electron microscope (FESEM; JEOL JSM-7100 F), and transmission electron microscopy (TEM; Titan G2 60-300) with an accelerating voltage of 300 kV. The corresponding element mapping images were captured with image corrector. The chemical oxidation states were determined by X-ray photoelectron spectroscopy (XPS; Kratos AXIS Ultra DLD-600W) using Al Ka (1486.6 eV) X-ray source. The Fourier transform-infrared spectra (FT-IR) were recorded using an Equinox IFS55 spectrometer in the range of $400-4000 \text{ cm}^{-1}$. Raman spectra were tested on a Lab-RAM HR Evolution spectroscope with a laser excitation wavelength of 532 nm (HORIBA, France). The specific surface areas and the corresponding pore size distribution of the samples were measured on a Quadrasorb SI-MP system at 77 K. The oxygen evolution rate was determined using gas chromatography (GC-2014C, SHIMADZU).

2.4. Electrode preparation

For preparation of the catalyst ink, typically, 5.0 mg catalyst, 1 mg conductive acetylene black (AB), and 30 μ L Nafion solution (5.0 wt%) were dispersed in 1000 μ L mixed solution, composing of isopropyl alcohol and DI water (volume ratio of 1:1). In order to make the ink more homogeneously, ultrasonical treatment was carried out for ~40 min before using. 10 μ L in. was pipetted onto the glassy carbon (GC) electrode. The mass loading of the catalyst was calculated to be 0.306 mg_{total} cm⁻² (0.255 mg_{oxide} cm⁻²).

2.5. Electrochemical characterizations

The electrochemical measurements were performed in a threeelectrode cell with a CHI 760E electrochemical station. A Pt wire is chosen as the counter electrode, and a saturated Ag/AgCl works as the reference electrode, respectively, while a GC disk electrode (5 mm diameter, 0.196 cm⁻²) coated with catalysts connected to a rotatingdisk device serves as the working electrode. 1 M KOH aqueous solution was selected to work as the electrolyte. Before testing, the electrolytes were generally saturated with O₂, and the flow rate of oxygen was maintained during the whole test. The obtained potentials (vs. Ag/ AgCl) were calibrated to the reversible hydrogen electrode (RHE) according to the Nernst equation:

 $E_{RHE} = E_{Ag/AgCl} + 0.059pH + 0.197V$

Where $E_{Ag/AgCl}$ is the experimentally measured potential vs. Ag/AgCl reference electrode. All the potentials stated in this work were calibrated against RHE unless otherwise noted.

Cyclic voltammograms (CVs) were recorded in a range of 0.0 to 1.2 V with a scan rate of 50 mV s⁻¹; and RDE linear sweep voltammograms (LSVs) measurements were carried out from 0.2 to 1.0 V with a sweep rate of 10 mV s⁻¹ under disk rotation rate of 1600 rpm. The electrical double layer specific capacitor (C_{dl}) of catalysts were determined from CVs.

All the given potential values were iR-corrected ($E_{iR-corrected} = E$ -iR, where i is the current and R is the uncompensated ohmic electrolyte resistance). Prior to the electrochemical measurements, the catalysts were activated with CV scan at a scan rate of 50 mV s⁻¹ for ~20 cycles. Electrochemical impedance spectra (EIS) were recorded under an AC



Fig. 1. (a) Schematic illustration of the processing of LaNiO₃@FeOOH synthesis. (b) XRD patterns of LaNiO₃ and LaNiO₃@FeOOH-1:1. FESEM image of (c) LaNiO₃ and (d) LaNiO₃@FeOOH-1:1. (e, f) TEM images of LaNiO₃@FeOOH-1:1 with different magnification. (g) HRTEM image of LaNiO₃@FeOOH-1:1. (h) SAED pattern of the LaNiO₃@FeOOH-1:1. (i ~ n) HAADF-TEM image of LaNiO₃@FeOOH-1:1 and the corresponding elemental mapping images.

voltage of 5 mV with frequencies in range of 100 kHz to 0.1 Hz.

2.6. Zn-air battery assembly and measurements

A Zn-air battery was assembled from a Zn plate negative electrode, a

carbon paper positive electrode coated with catalysts (mass loading of 1 mg cm⁻²), and an electrolyte consisting of 0.2 M Zn(CH₃COO)₂ and 6 M KOH aqueous solution. The polarization curves were constructed from the LSV data collected at 5 mV s⁻¹ using a CHI 760E electrochemical workstation. The charge-discharge curves were acquired using



Fig. 2. (a) Raman spectra and (b) FT-IR spectra of LaNiO₃, FeOOH and LaNiO₃@FeOOH-1:1. (c) Nitrogen adsorption/desorption isotherm of LaNiO₃ and LaNiO₃@ FeOOH-1:1 (inset is the corresponding pore distribution). XPS spectra of (d) Fe 2P, (e) La 3d and Ni 2p, and (f) O 1s.

a Land CT2001A battery tester.

3. Results and discussion

3.1. Material characteristics and analyses

The preparation of the LaNiO₃@FeOOH composite is a two-step process, as schematically illustrated in Fig. 1a. First, LaNiO₃ was synthesized with a modified sol-gel method; second, a thin layer of amorphous FeOOH was grown on the LaNiO₃ surface by a chemical bath deposition method. The more specific experimental details can refer to the experimental section. Fig. 1b displays the powder XRD patterns of LaNiO3 and LaNiO3@FeOOH-1:1 samples. Nine pronounced peaks centered at 23.2°, 32.9°, 40.6°, 47.3°, 53.5°, 58.7°, 69.5°, 74.5° and 79.1° were observed, being well indexed to the planes of the orthorhombic phase LaNiO₃ structure (JCPDS card No. 88-0633; space group: Pnma). After growth of FeOOH on LaNiO₃ surface, no new peaks appeared compared with that of the parent LaNiO3 perovskite, indicating that either the as-prepared FeOOH is amorphous or the amount of the FeOOH is below the detection limit. Moreover, it was also noticed that when the amount of the encapsulated FeOOH increased, the peaks intensity of LaNiO₃ dwindled, which finally disappeared when thick layer of FeOOH was formed (e.g. $mole_{FeOOH}/mole_{LaNiO3} \ge 2$; see Fig. S1a). When encapsulating LaCoO3 and LaMnO3 with FeOOH layer, again, no iron oxyhydroxide signals were identified in both cases (Fig. S1b-c), again indicating the decorated FeOOH layers on these perovskites are also of amorphous nature or the amounts of the as-prepared FeOOH is below the detection limit. On the other hand, this observation implies that our approach for growth of FeOOH layer is also applicable to LaCoO₃ and LaMnO₃ perovskite materials. It is an effective strategy for enhancing oxygen evolution kinetics of $LaMO_3$ (M = Ni, Co, Mn) perovskite catalysts as well.

The morphology of the as-prepared samples was first captured by Field-emission scanning electron microscopy (FESEM). SEM image of the bare LaNiO₃ is depicted in Fig. 1c, disclosing that they are composed of interconnected nanoparticles with diameters of 200–400 nm in size. After growth of FeOOH layers, the smooth surface of the composite becomes very rough as shown in Fig. 1d. Energy dispersive X-ray spectroscopy (EDS) and element mapping analysis of LaNiO₃ and

LaNiO₃@FeOOH-1:1 were all implemented (Fig. S2), from which it confirms the successful growth of FeOOH as one more element (Fe) was identified compared with the pristine LaNiO3. To unveil the detail of the elaborated geometric structure, transmission electron microscope (TEM) images were also collected (see Fig. 1e). Particularly, a close-up of one nanoparticle at the edge the composites was captured (the dash red box region in Fig. 1e), in which it shows that a 5-10 nm thick FeOOH layers were uniformly and seamless bonded to the host LaNiO₃ nanoparticles, forming a core-shell structure (Fig. 1f). Furthermore, high-resolution TEM (HRTEM) characterization of the composites was also carried out at the edge of the specified core-shell structured nanoparticle (highlighted with the dashed red box in Fig. 1f), where the dspacing is measured to be 0.273 nm, indexing to the (110) plane of orthorhombic-phase LaNiO₃ perovskites. Interestingly, the amorphous FeOOH shell was also observed in the same TEM image (the yellow dash line separated part), and identified easily as no regular interplannar spacing can be found because of its amorphous nature. The sharp interface between LaNiO₃ and FeOOH again evidence the intact contact of the two catalysts towards forming the core-shell catalyst composites. In order to further investigate the crystalline structure of LaNiO₃ in the composites, the selected-area electron diffraction (SAED) pattern of LaNiO₃@FeOOH-1:1 was further collected (Fig. 1h). The explicit points impart the single crystalline nature of LaNiO₃, indexing to (110), (122), and (220) planes of orthorhombic crystal, being consistent with the XRD patterns that talked aforementioned. A high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was further carried out, in which it displays that La, Ni, O, and Fe are distributed uniformly over the whole surface of particle (Fig. 1i-n). Nonetheless, after scrutinizing carefully, it was noticed that the Fe and O mapping area is a little bit large than that of the counterpart La, Ni, validating the fact that the elements Fe and O are mainly distributed on the surface, consistent with the reality of our configured core-shell structured composite catalyst.

To further confirm the as-grown shell of the composites being FeOOH layer, Raman spectra and FT-IR spectroscopies were recorded. For comparison, the characterization of the bare $LaNiO_3$ and FeOOH were also carried out. As show in Fig. 2a, characteristic peaks at 258, 307, 394, 488, 538, 673 and 1307 cm⁻¹ were identified, corresponding to the dissymmetric stretching of metal and hydroxide group [34],



Fig. 3. (a) LSV curves of LaNiO₃, FeOOH, LaNiO₃@FeOOH-1:1 and RuO₂ in O₂ saturated 1 M KOH aqueous solution at 1600 rpm. (b) The corresponding comparison of overpotentials (η) required for a 10 mA cm⁻² current density. (c)The corresponding Tafel plots. (d) Differences in current density plotted against scan rate showing the extraction of the double-layer capacitances. (e) Chronopotentiometric measurements of LaNiO₃@FeOOH-1:1 at 10 mA cm⁻² (Inset is the LSV curves of LaNiO₃@FeOOH-1:1 after 10 h). (f) Nyquist plots of LaNiO₃, FeOOH and LaNiO₃@FeOOH-1:1. The insets of is the equivalent circuit diagram.

evidencing the successful formation of FeOOH layer. Different from the strong peaks observed in the pristine FeOOH sample, the intensity of all peaks in sample LaNiO₃@FeOOH-1:1 were decreased which could be due to the substrate effect as no stretching vibration mode was detected in LaNiO₃ perovskite. With increasing the counterpart amount of the host (LaNiO3 perovskite), the Raman intensity decreased according, for more of which it could refer to Fig. S3. Fig. 2b shows the FT-IR spectroscopy of the three designated samples. The bands at around 1135 and 1035 cm⁻¹ are associated to the Fe–OH bending vibrations and the Fe–O stretching vibration, respectively [35–37], again unambiguously confirming the as-grown material being FeOOH. The stronger and broader peak near $1135 \sim 1035$ cm⁻¹, appeared after growth of FeOOH layers on perovskite, could be attributed to the strong coupling effect between FeOOH and LaNiO₃ (LaCoO₃ or LaMnO₃) (Fig. S4a and b). Similar effect was also reported for graphene oxide (GO)-carbon nanotubes (CNTs)-a-FeOOH decorated composite aerogel (α-FeOOH@GCA); a similar peak near $1135 \sim 1035 \text{ cm}^{-1}$ was also observed in FT-IR spectrum [37]. Further, the same coupling effect was also observed for control samples of LaNiO3@FeOOH with different composition ratios (see Fig. S4c). On the other hand, FT-IR spectra also confirm the formation of FeOOH on perovskite surface.

Since the as-prepared composites is of nanoarchitecture, the specific surface areas of the catalyst were then accessed by N2 adsorption measurement. The Brunauer-Emmett-Teller (BET) surface area of LaNiO₃@FeOOH-1:1 composites is calculated to be ca. $3.6 \text{ m}^2 \text{g}^{-1}$ by determining from the typical type-III isotherm curves (Fig. 2c). Noteworthy, in case of no FeOOH layers were decorated on surface, the specific surface areas of LaNiO₃ was decreased to $3.1 \text{ m}^2 \text{ g}^{-1}$, being consistent with the SEM observation that the perovskite become rough after the growth of FeOOH layers on the surface. Meanwhile, the porous feature of the catalysts was also disclosed. In the inset of Fig. 2c, it presents that the pore sizes of LaNiO₃@FeOOH-1:1 composites is in range of 4 to 9 nm by using Barrett-Joyner-Halenda (BJH) method, while nearly no pore feature was identified in the bare LaNiO3 perovskite sample. The porous nature of the LaNiO₃@FeOOH enables larger contact area between electrolyte and LaNiO₃@FeOOH, increasing the reaction rate and boosting the electrocatalytic activity of LaNiO₃@FeOOH.

To study the chemical states and electron interactions between LaNiO₃ and FeOOH, X-ray photoelectron spectroscopy (XPS) spectra of the LaNiO₃, FeOOH and LaNiO₃@FeOOH-1:1 in Ni 2p, Fe 2p, and O 1s regions were collected. In the survey spectrum of LaNiO₃@FeOOH-1:1 (Fig. S5), La, Ni, Fe and O elements were well discerned. The core level spectrum of Fe 2p for LaNiO₃@FeOOH-1:1 is demonstrated in Fig. 2d, where two spin-orbit peaks at 725.2 and 711.1 eV are resolved, ascribing to Fe $2p_{1/2}$ and Fe $2p_{3/2},$ respectively. In more specific terms, the specific peaks at 710.8 eV is associated to $Fe^{2+} 2p_{3/2}$, and the peaks at 712.7 eV and 725.2 eV correspond to $Fe^{3+} 2p_{3/2}$ and $Fe^{3+} 2p_{1/2}$ [38,39]. Compared with those of the bare FeOOH, the Fe 2p peaks of LaNiO₃@FeOOH negatively shifts to $\approx 0.69 \text{ eV}$. The core-level spectra of La $3d_{3/2}$ and Ni $2p_{3/2}$ of LaNiO₃@FeOOH-1:1 are presented in Fig. 2e, of which $Ni^{3+} 2p_{3/2}$ (855.9 eV) and $Ni^{3+} 2p_{1/2}$ (872.6 eV) are deconvoluted with two satellite peaks located at 862.1 eV and 880.2 eV [40,41] and Ni $2p_{3/2}$ satellite overlaps with La $3d_{3/2}$ peak partially. Compared with that of the parent LaNiO₃, the peak of Ni 2p positively shifts to ≈ 0.27 eV. Considering the peak shift and charge density changes, it reasonably acknowledges that electrons transferred from LaNiO3 to FeOOH were occurred in the LaNiO3@FeOOH-1:1 [30,42,43], which may in turn influence the catalytic activity as well as the corresponding durability. Moreover, the core-level spectra of O 1s of LaNiO₃@FeOOH-1:1 was also recorded. As shown in Fig. 2f, the peak at 528.3 eV is ascribed to the lattice oxygen species (O²⁻), and another three peaks at 529.2 eV, 531.1 eV, and 532.2 eV should be corresponding to superoxidative oxygen species $(O_2^{2^-}/O_{-})$, surface adsorbed oxygen/hydroxyl groups (O₂/OH-), and surface adsorbed molecular water (H₂O) and/or carbonates (CO₃²⁻), respectively [19,44,45]. As can be observed, compared to the bare LaNiO₃, numerous oxygen/hydroxyl groups (O₂/OH-) were attached to LaNiO₃@FeOOH-1:1 (Table S1), which could effectively improve the hydrophility of the catalyst, and favor the adsorptions of H₂O and OH- groups on the catalysts surface, in turn boosting the OER kinetics.

3.2. Electrochemical activity of the catalysts

The evaluation of the electrocatalytic OER activity of the LaNiO₃@ FeOOH composite was carried out on rotating disk electrode (RDE) in a

typical three-electrode setup. Linear sweep voltammetry (LSV) polarization curves of LaNiO₃, FeOOH and LaNiO₃@FeOOH-1:1 were recorded at a scan rate of 5 mV s^{-1} in 1.0 m KOH aqueous electrolyte with a continuous rotating rate of 1600 rpm. For comparison, the benchmark RuO₂ was also test with equal mass loading. As expected, among all the catalysts, LaNiO3@FeOOH-1:1 enable the lowest overpotential (264 mV) to launch a current density of 10 mA cm⁻² (the critical value for the conversion of solar fuel [11]) (see Fig. 3a), which is much lower than those of LaNiO₃ (446 mV) and FeOOH (440 mV). Even compared with the benchmark RuO₂ catalyst that tested with the same mass loading under the same experimental condition, the superiority is still immensely obvious (264 vs. 358 mV) as plotted in Fig. 3b. To the best of our knowledge, the delivered OER activity should be the best one among ABO₃-type perovskite ever reported in literatures [16]. The overpotential for LaNiO₃@FeOOH-1:1 is smaller than those for most perovskite-based catalysts recently reported in the literature (Table S2). Besides, the LSV curves of LaNiO₃@FeOOH with different mole ratios (i.e. mol_{LaNiO3}:mol_{FeOOH}) were also collected toward finding the best advanced catalyst (Fig. S6). As can be observed, among all the samples, the catalyst with $mol_{LaNiO3}:mol_{FeOOH} = 1$ (designated as LaNiO₃@FeOOH 1:1), which is indeed the composite that talked in the main text, yields the lowest overpotential. Another thing that needs to point out is that, once LaNiO₃ is encapsulated with FeOOH layers, the catalytic OER activity will be effectively improved no matter how much it is, the evidence of which could be captured from the fact that LaNiO₃ and FeOOH show the most inferior catalytic activity among all the catalysts. Given the mechanical mixed catalyst (composing of LaNiO₃ and FeOOH with ratio of 1:1) possess the comparable overpotential to the pristine perovskite (Fig. S7), it can be unambiguously confirmed that the improved electrocatalytic activity should be due to the strong electron interaction between LaNiO3 and FeOOH, being consistent with XPS results. To ensure that the use of a Pt counter electrode has no unintended effect on the OER activity of the catalysts under study, we also performed control experiments by using Pt and graphite as the counter electrode, respectively. As expected, the performances of the cells with a Pt counter electrode were similar to those of the cells with a graphite counter electrode (see Fig. S8), consistent with what reported elsewhere [46] that Pt dissolution is negligible and will not affect the OER performance.

The Tafel slope of LaNiO₃@FeOOH-1:1 is calculated to be 66 mV dec^{-1} (Fig. 3c), which is much smaller than that of LaNiO₃ (98 mV dec^{-1}), FeOOH (97 mV dec^{-1}) as well as RuO₂ (88 mV dec^{-1}), further validating the fast kinetics toward OER. As we all know, Tafel slope is closely related to the rate determining steps (RDS) [47-50], which determines the catalytic kinetics. OH- electrosorption is the initial step of the OER process. Owing to the growth of FeOOH layers on the surface, the hydrophilic property could be effectively improved, which favors the OH- adsorption. After quickly building equilibrium of adsorbed OH- and its sequence intermediate species, the electron-transfer reaction is then dominated, being the RDS of the OER, yielding a low Tafel slope. Thus, it is understandable that OH- adsorption plays a decisive role for the advanced OER activity. In previous works, it has already been confirmed that FeOOH has a high adsorption energy of OH-[30], while Ni element involved catalysts possess a lower adsorption energy of OH- [51,52]. As such, aiming to improve OER activity of LaNiO₃ perovskite, combination of FeOOH and LaNiO₃, that is, optimization of the adsorption energy of OH- (the first step of OER reaction) could be an essential strategy. To deepen understand the intrinsic activity of the catalysts, the electrochemically active surface area (ECSA) were examined by measuring the electrochemical double-layer capacitance (C_{dl}), the scan of which is ranging from 0.68-0.78 V (Fig. S9). The calculated C_{dl} of LaNiO₃@FeOOH is 22.5 m F cm⁻², being almost 5.7 times higher than that of the parent ${\rm LaNiO_3}~(3.9\,{\rm m\,F~cm^{-2}})$ and 20.5 times higher than that of the FeOOH (1.1 m F cm⁻²) (Fig. 3d), implying that the LaNiO₃@FeOOH-1:1 possesses much more catalytic active sites than the counterpart single catalyst component. This observation is in

line with the BET results that talked aforementioned. Oxygen evolution rates was determined using gas chromatography (GC) (see Supporting information Fig. S10). The measured O_2 evolution rate of LaNiO₃@ FeOOH-1:1 is 2.573*10⁻⁸ mol/s, which is close to the theoretical value if the Faraday efficiency is assumed to be unity, indicating that the faradaic efficiency is very close to 100%.

Apart from the decent OER activity, another critical factor, the longterm durability, is evaluated using chronoamperometry measurements (j - t). The test was carried out at a current density of 10 mA cm⁻² in 1 M KOH. As shown in Fig. 3e, about 5.3% decrease in stability was seen after continuous testing for 10 h. Note that the zigzag-shape of the curve is due likely to the intense bubble generation and release during the cycling. Moreover, the robust stability feature against harsh water oxidation was also evident from the LSV measurement (inset in Fig. 3e), where about 17 mV activity loss was discerned after testing for 10 h. This observation is again consistent with the CV test, which yields only 14 mV potential increase after 1000 cycles (see Fig. S11). After these examinations, it is aware that the robust nature of the LaNiO₃@FeOOH-1:1 could be due possibly to the intact interface between the two catalysts. To gain further insight into the catalytic kinetics of water oxidation, electrochemical impedance spectroscopy (EIS) measurements were performed. Fig. 3f shows some typical impedance spectra (Nyquist plots) of cells with LaNiO₃, FeOOH, and LaNiO₃@FeOOH-1:1. The equivalent circuit is shown in the inset of Fig. 3f, consisting of an ohmic resistance (R_s), a charge transfer resistance (R_{ct}), and a constant phase element (CPE); among them, the charge-transfer resistance $(\mathrm{R}_{\mathrm{ct}})$ can be determined from the diameters of the semicircles in the high-frequency range [53,54]. Since R_{ct} of the cell with LaNiO₃@FeOOH-1:1 is much smaller than those of the cells with other two catalysts, the chargetransfer kinetics of the composite catalyst is much faster than that of the other two catalysts. More EIS measurements were also conducted for other LaNiO₃@FeOOH samples with different mole ratios. Consistent with the LSV test results (Fig. S6), Rct of the LaNiO₃@FeOOH-1:1 is the smallest one, while that of the LaNiO3@FeOOH-1:3 is the largest one (Fig. S12). To be more specific, the value of R_{ct} is in the order of LaNiO₃@FeOOH-1:1 < LaNiO₃@FeOOH-2:1 < LaNiO₃@FeOOH- $1:2 < LaNiO_3$ @FeOOH- $3:1 < LaNiO_3$ @FeOOH-1:3.

3.3. Applicability of the approach to other perovskite catalysts

Further, to determine whether the FeOOH boosting strategy is applicable to engineering other ABO3-perovskites, we decorated FeOOH layers on the surface of LaCoO3 and LaMnO3 under identical preparation condition. All the SEM, EDS mapping and XRD characterizations have been implemented and validated (See Figs. S1, S13 and S14). As expected, both LaCoO3@FeOOH-1:1 and LaMnO3@FeOOH-1:1 composites displayed significantly enhanced OER activity than the pristine perovskite without FeOOH coating (Fig. 4a, d). It can be easily seen that the overpotential for the engineered LaCoO₃ was decreased from 461 to 334 mV while the value for the engineered LaMnO3 was reduced from 630 to 470 mV, as shown in Fig. 4b, e. Similarly, the Tafel slope was decreased from 98 to 66 mV dec $^{-1}$ for LaCoO $_3$ and 128 to 83 mV dec $^{-1}$ for LaMnO₃ (Fig. 4c, f) confirming the dramatic enhancement of OER activity by the FeOOH decoration. Although enhancement in OER activity by a surface coating is observed for both cases, it was noted that the OER activity of the engineered LaMnO₃ (470 mV) is still inferior to that of the commercial RuO₂ (358 mV; tested at the identical condition), due most likely to its poor intrinsic electrocatalytic activity. However, it can be concluded that the synergistic coupling between the FeOOH layer and LaMO₃ (M = Ni, Co, Mn) perovskites is vital to boosting the electrocatalytic activity.

3.4. Application to Zn-air batteries

To demonstrate the practical application of the as-prepared LaNiO₃@FeOOH-1:1 in rechargeable Zn-air batteries, a home-made Zn-



Fig. 4. (a) LSV curves of LaCoO₃, FeOOH, LaCoO₃@FeOOH-1:1 and RuO₂ in O₂ saturated 1 M KOH aqueous solution at 1600 rpm. (b) The corresponding comparison of overpotentials (η) required for launching a current density of 10 mA cm⁻². (c) The corresponding Tafel plots for LaCoO₃, FeOOH, LaCoO₃@FeOOH-1:1 and RuO₂ in O₂ saturated 1 M KOH aqueous solution at 1600 rpm. (e) The corresponding comparison of overpotentials (η) required for 10 mA cm⁻². (f) The corresponding Tafel plots for LaMnO₃@FeOOH-1:1 and RuO₂ in O₂ saturated 1 M KOH aqueous solution at 1600 rpm. (e) The corresponding comparison of overpotentials (η) required for 10 mA cm⁻². (f) The corresponding Tafel plots for LaMnO₃@FeOOH-1:1 and RuO₂.



Fig. 5. (a) Schematic illustration of electrochemical processes in Zn-air battery. (b) Photograph of the Zn-air battery with an open circuit voltage of 1.434 V with LaNiO₃@FeOOH-1:1 as the air-cathode. (c) Charge and discharge polarization curves for Zn-air batteries at different current densities. (d) and (e) Discharge and charge voltage profiles of Zn-air batteries with LaNiO₃@FeOOH-1:1 and RuO₂ catalysts as the air-cathode at a current density of 5 mA cm⁻² and a cutoff time of 10 min per cycle (5 min discharge and 5 min charge per cycle).

air battery prototype was built. The schematic model of the designed rechargeable Zn-air battery is shown in Fig. 5a, in which Zn plate serves as the anode (or negative electrode), the tested catalyst that supported on gas diffused carbon paper works as the cathode (or the positive electrode), and the mixed 0.2 M Zn(CH₃COO)₂ and 6 M KOH solution was chosen as the electrolyte. The open-circuit voltage of the Zn-air battery with the LaNiO₃@FeOOH-1:1 catalyst as the cathode was measured to be \sim 1.434 V (Fig. 5b), which is higher than similar cells with other perovskite catalysts' [55–57]. Fig. 5c exhibits the charging/ discharging polarization curves of the Zn-air cell with LaNiO₃@FeOOH-1:1 or commercial RuO₂ as the OER catalyst and Pt/C as the ORR catalyst of the positive electrode. As can be seen, the discharge voltage gap of the Zn-air battery with LaNiO₃@FeOOH is very close to that of the Zn-air battery with RuO₂, suggesting that the OER activities of the two catalysts are comparable. When cycled at a current density of 5 mA cm⁻², the Zn-air cell with LaNiO₃@FeOOH-1:1 displayed an initial charge potential of 1.94 V and discharge potential of 1.21 V, yielding high round-trip voltage efficiency of 62.4% (Fig. 5d). The excellent cycling stability of the LaNiO₃@FeOOH-1:1 catalyst is evident from the stable charge/discharge profile over time. After 90 cycles, only a small lost was observed, an increase of ~0.09 V in overpotential, corresponding to a loss of 3.7% round-trip efficiency. In contrast, the Zn-air cell with RuO_2 displayed an increase of ~0.13 V in overpotential, corresponding to a loss of 5.8% round-trip efficiency. The enhanced performances of the cell with LaNiO₃@FeOOH-1:1 once again demonstrate the effect of FeOOH towards boosting the catalytic activity of perovskite.

4. Conclusion

In summary, we have developed an effective strategy for fabrication of a FeOOH layer on LaNiO₃ in order to enhance the electrocatalytic performance. The remarkable OER activity of the LaNiO₃@FeOOH catalyst is attributed to its favorable absorption energy of the oxygenated species, exposure of more active sites, and acceleration of charge transfer kinetics, as confirmed by HRTEM, XPS, and impedance analyses. In particular, the approach is also applicable to the enhancement of OER activities of other perovskite oxides (e.g., LaCoO₃ and LaMnO₃). Additionally, a Zn-air battery was assembled using LaNiO₃@FeOOH perovskite as the air-cathode and Pt/C as the air-anode, demonstrating promising performance and remarkable cycle life. Thus, this simple approach is very effective for boosting OER activity of perovskite or other non-precious metal-based catalysts for metal-air batteries and reversible fuel cells.

Declaration of Competing Interest

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcatb.2019.118291.

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