Large-Scale, Low-Cost, and High-Efficiency Water-Splitting System for Clean H$_2$ Generation

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Supporting Information

ABSTRACT: Scaling up electrochemical water splitting is nowadays in high demand for hydrogen economy implementation. Tremendous efforts over the past decade have been focused on exploring alternative catalytic materials, including a variety of earth-abundant transition-metal-based catalysts, to replace traditional noble metals such as Pt, Ir, or Ru. Nevertheless, few efforts have been carried out for (1) scalable catalyst synthesis on current collectors and (2) practical device design toward large-scale H$_2$ generation. Herein, we designed a modular alkaline water-splitting electrolyzer system with scaled-up metal foam electrodes covered by low-cost NiMo alloy and Ni$_3$Fe oxide for efficient hydrogen evolution and oxygen evolution, respectively. An electrolyte circulation system facilitates the mass transport and thus can further boost the H$_2$ generation particularly under large currents. As a result, the overall water-splitting performance of one-unit cell with a dimension of 10 × 10 cm$^2$ under room temperature presents an early onset voltage of 1.54 V and delivered practical currents of 20 and 55 A (9.1 and 25.0 L/h H$_2$ generation) under 2.2 and 2.9 V without $iR$ compensations, respectively. This demonstration could stimulate new focuses in water splitting toward more practical applications.

KEYWORDS: water splitting, hydrogen generation, large scale, mass transport, earth-abundant transition metal

INTRODUCTION

With more and more solar panels installed on family houses as well as the fast implementation of solar or wind farms all over the world, a powerful energy storage system is urgently needed to overcome the daily and seasonal mismatch between the generation and usage of clean electricity.¹ Hydrogen (H$_2$), which can be generated via electrocatalytic water splitting (2H$_2$O $\rightarrow$ 2H$_2$ + O$_2$; $E_0$ = 1.23 V) and converted back to electricity through fuel cell stacks, is becoming an increasingly attractive energy carrier for clean energy storage,²,³ with important advantages over battery systems particularly in grid-scale applications: (1) Although in battery systems the three-dimensional (3D) volume of electrode materials needs to be linearly scaled up to accommodate the increased energy capacities, the produced H$_2$ gas can be accumulated in high-pressure tanks without host materials, dramatically reducing the energy storage cost; (2) excess H$_2$ gas produced by solar panels during summer can be continuously accumulated and stored for use in winter, circumventing the self-discharging problems in batteries for long-term energy storage; (3) although stationary battery farms cannot be easily moved, clean H$_2$ produced from centralized solar or wind farms can be transported via pipelines or gas tanks to the end use in cities.

More importantly, the pipeline distribution to gas stations would further facilitate the popularization of H$_2$ fuel cell vehicles. Therefore, the development of a large-scale water-splitting system, which is made of earth-abundant catalysts and delivers high-energy-conversion efficiencies, holds the key to the deployment of H$_2$ economy in the future.⁴⁻⁷

Over the past decade, tremendous efforts in the research community have been focused on exploring alternative catalytic materials to replace traditional noble metal catalysts, such as Pt, Ir, and Ru, in both hydrogen evolution reaction (HER)⁸ and oxygen evolution reaction (OER).⁹,¹⁰ A variety of earth-abundant catalysts have been discovered to be promising candidates, including transition-metal (TM) chalcogenides,¹¹⁻¹³ metal phosphides,¹⁴⁻¹⁶ and TM alloys¹⁷⁻²⁰ for HER in acids or bases as well as perovskite oxides,¹¹,¹² TM oxides,²¹,²² and layer double hydroxides²³,²⁴ for alkaline OER. However, although many newly discovered catalysts have shown exciting performances, pairing different HER and OER catalysts in an integrated electrolyzer for practical H$_2$...
generation requires more strict criteria in the selection of candidates. For example, most OER catalysts made of earth-abundant materials are used in alkaline solutions and not stable in acids, which need to be paired with alkaline HER catalysts; second, although most of the performance tests in literature were based on small-scale electrodes (such as 1 cm² geometric area), the synthesis of catalytic materials should be easily and uniformly scaled up onto large-current collectors while maintaining the same catalytic activities. In addition to those challenges in catalytic materials, engineering issues related with large-scale currents under practical conditions, such as the mass transport as well as ohmic loss, need to be carefully addressed via the rational design of an efficient and scalable water-splitting system to deliver a practical performance for clean H₂ generation. The demonstration of a high-performance and large-scale electrolyzer system using low-cost catalysts for practical H₂ generation is therefore urgently needed for the next-stage development of water splitting. Here in this work, we designed a modular water-splitting electrolyzer system with scaled-up metal foam electrodes where low-cost NiMo alloy (HER) and Ni₃Fe oxide (OER) catalysts were uniformly synthesized without performance sacrifice. An alkaline electrolyte flow system was shown to substantially improve the water-splitting performance (∼44.7% improvement) by efficiently bringing out the H₂ and O₂ bubbles and thus refreshing the electrode surface. These positive electrodes, membranes, and negative electrodes can be alternatively stacked to deliver significant H₂ generation rates for practical applications. The overall water-splitting performance of one-unit cell under room temperature presents an early onset voltage of 1.54 V and can deliver a practical current of 55 A (per unit cell, ∼25 L/h H₂ generation rate) under 2.9 V without iR compensation. Over 10⁷ L of H₂ gas was accumulated during 1 day of continuous operation, without any performance degradation observed. This water-splitting system, including the low-cost catalytic materials, modular devices, and the electrolyte flow system, demonstrates a highly promising route toward the practical applications in energy storage as well as fuels/chemicals production.

RESULTS AND DISCUSSION
Electrocatalysts on current collectors/electrodes are usually prepared in two different ways. One approach is to synthesize catalytic materials separately and then apply them onto current collectors with polymer binders such as Nafton or poly(vinylidene fluoride) for strong adhesion. Although this method has been widely adopted on planar electrodes, it might be difficult to ensure a uniform coating of materials on porous electrodes such as metal foam for high surface areas. In addition, the adhesion between the catalysts and electrode via polymer binders could be weakened over a long-term operation. The other method, which is preferred for porous current collectors and long-term operation, is to synthesize catalytic materials directly onto the electrodes. This method involves hydrothermal deposition or electrochemical deposition in solutions where precursors can reach every corner of porous current collectors for a uniform coating. Compared to the polymer adhesion, the strong chemical bonds between the catalysts and current collector can prevent the materials from being peeled off under violent bubble evolutions and facilitate the electric conductivity.

NiMo alloy catalyst, which is made of low-cost metals and with excellent HER performance, becomes a promising candidate of H₂ electrode for our water-splitting electrolyzer. On the basis of the considerations mentioned above and previous components screening, we employed the electrodeposition method to reduce Ni and Mo ions into NiMo alloy on a current collector (Experimental Section). To make the two different metal ions to be co-deposited, low concentrations of metal ions and large overpotential were selected to overcome the differences in their electrochemical redox window. Cu foam with a relatively poor HER activity was used as the current collector to suppress extensive H₂ generation. A very uniform NiMo catalyst coating on the large-size (10 × 10 cm²) Cu foam was obtained as shown by the photograph in Figure 1A, suggesting the capability for large-scale production. X-ray diffraction (XRD) pattern in Figure S1 agrees well with Ni₃Mo phase, in which both Ni and Mo components show a partial oxidized chemical state (Figure S2). The scanning electron microscopy (SEM) image of NiMo shows nanometer-size grains nucleated together as large aggregations, maintaining a relatively high surface area (Figure S3 and Table S1). On the other side of the electrolyzer for water oxidation, the well-known NiFe oxide OER catalyst was selected due to its high OER performance and stability as well as the facile synthesis for scaled-up production. We employed a hydrothermal synthesis method to directly grow those amorphous NiFe oxide nanosheets onto Ni foam electrode (Experimental Section, Figure S1B). The SEM image in Figure 1B suggests a dense coating of nanosheets with ∼200 nm in width and only tens of nanometers in thickness. A uniform synthesis on current collector was obtained, as shown by the photograph with a size of 10 × 10 cm².

The HER and OER catalytic performances of as-synthesized NiMo and NiFe oxide were first evaluated in 30 wt % KOH alkaline electrolyte in a standard three-electrode cell by cutting the large electrode into small pieces (1 × 1 cm², Experimental Section). The potential has been scaled to a reversible hydrogen electrode (RHE) with iR compensation. The HER activity shows an early onset of less than 65 mV and rapidly ramp up to 170 mA/cm² at only −0.2 V. The corresponding
Tafel slope is 110.2 mV/dec (Figure S4), suggesting a facile bubble evolution even under significant current densities. The OER performance of NiFe oxide is also among the best compared to the existing literature, with an onset potential of only 1.46 V. The current density was quickly increased to 200 mA/cm² at only 1.5 V, with a Tafel slope of 58.3 mV/dec. By combining these two highly active catalysts, we can expect a 50 mA/cm² overall water-splitting current under a small cell voltage of 1.60 V, representing an energy-conversion efficiency of 77%.

The excellent water-splitting performance obtained in a standard three-electrode cell may not necessarily be translated into a two-electrode water-splitting device without proper engineering. A few important factors need to be taken into consideration for optimized performance. First of all, the anode and cathode should be separated by anion-exchange membrane (AEM), for separation of generated H₂ and O₂, in a compact way to minimize the gap and thus the ionic resistance between them. A small increase in the resistance could result in a large iR drop particularly under practical water-splitting currents. A compact and scalable cell was designed for this purpose as shown in Figure 2, where the current was collected by stainless-steel frames to ensure a uniform distribution of currents within the electrode and thus a minimized iR loss. A positive electrode, AEM, and a negative electrode can be alternatively stacked for scaled-up H₂ production. The photograph of a unit cell for our preliminary test is shown in Figure 2C, with two strong metal plate bases to clamp the stacks for good liquid and gas sealing.

The minimized gap between the electrode and AEM was balanced to allow both small ionic resistance as well as efficient electrolyte flow. Second, when the current density reaches a few hundreds of milliamps per centimeter square, the H₂ and O₂ bubble evolution become violent, which blocks the contact between the catalyst and electrolyte. This poor mass transport could dramatically limit the high catalytic performances of NiMo and NiFe oxide catalysts under high current densities. Therefore, we designed an electrolyte circulation system by a peristaltic pump to facilitate the bubble evolution and flush the surface of electrodes with fresh electrolyte without gases (Figure S5). The generated H₂ and O₂ were efficiently brought out into a gas−liquid separation tank, where H₂ was collected as the desired product and the electrolyte was circulated back into the cell (Movie S1).

Although we found out that the overall water-splitting performance under small current densities did not show much...
change with or without flowing the electrolyte, the flow rate does present a significant impact on the activity particularly in large-current regions. We therefore studied the electrolyte flow rate effects starting from 2 V of cell voltage with a current of ~10 A. All of the voltages presented were measured between the two electrodes without any iR compensations. First of all, without flowing the electrolyte in the unit cell, the water-splitting current showed a steady increase from 9 A at 2 V toward a 32 A at 2.6 V, followed by a flat plateau suggesting a mass-diffusion limited activity. With gradually increased electrolyte flow rate, the device performance under different cell voltages can be improved by varied degrees: the higher voltage and current the cell was operated, the more enhancement the flow of electrolyte can help to deliver. In
addition, as indicated in Figure 3, under the highest cell voltage of 2.9 V we applied, the water-splitting current can be dramatically increased from 38 to 49 A by starting the electrolyte circulation at a flow rate of 61 mL/min. By increasing the flow rate, the performance was further improved and also presented a plateau of 55 A with a flow rate of 253 mL/min or beyond. This suggests that with a fast-enough flow of electrolyte to facilitate the generated H2 and O2 bubbles, the water-splitting performance can be optimized to exclude the mass-diffusion limitation effect introduced by the violent gas evolution.

We maintained the highest electrolyte flow rate of 316 mL/min to examine the H2-generation performance of our device and catalysts without the limitations from mass transport. The I–V curve is plotted in Figure 4A, with the energy-conversion efficiencies from electricity to H2 marked in red; control experiment on measured H2 evolution rate versus constant current density is shown in Figure S6. The catalysts showed an excellent onset voltage of only 1.54 V with an overall current of 0.4 A, corresponding to a high efficiency of 80%. The current rapidly ramped up to a practical value of 20 A (200 mA/cm2) at only 2.2 V, representing a H2-generation rate of 9.1 L/h. The current can be further increased with higher cell voltages, with a maximum of 55 A under 2.9 V demonstrated in this current device. This current per unit cell represents a H2-generation rate of 25 L/h and is among the best performance demonstrated by earth-abundant catalysts in the literature to date (Table S2). A continuous operation under ~12 A has been performed (Figure 4B) to examine the overall stability including catalytic materials and device, in which ~107 L H2 was collected within 24 h, without any performance degradation observed.

### CONCLUSIONS

In summary, we present a low-cost and large-scale water-splitting system as a preliminary demonstration for practical applications in renewable energy storage and usage. The flow of electrolyte was shown to significantly boost the overall water-splitting performance due to the enhanced mass transport. The design of modular electrolyzer opens up opportunities in scalable capacity of H2 generation for potential deployment. This system-level study of overall water splitting for clean H2 generation reveals challenges beyond catalytic materials design and could pave a promising way for clean hydrogen economy implementation.

### EXPERIMENTAL SECTION

#### HER Electrode Preparation.

Electrodeposition was performed in a 2 L beaker with electrodes connected to DSC power supply (Sorensen DC520-50E). A Cu Foam (JYS Tape) was cut into 11 × 11 cm² (0.5 cm edges were remained for electrical contact with stainless-steel frames) and connected to the cathode of the supply, whereas an osmium net was used as counter electrode and connected to the anode. Prior to electrodeposition, the working electrode was pretreated by electrochemical cathodic degassing in a solution containing 0.375 M NaOH, 0.236 M Na2CO3, and 0.066 M Na2SiO3 at a current density of 5 mA/cm² to remove oil. Then, Cu foam was sputtered in 0.5 M H2SO4 for 5 min to remove the oxide layer and further rinsed with distilled water. All of the agents were purchased from Sigma-Aldrich at ACS grade without further purification. The electrodeposition solution was prepared with 0.017 M nickel sulfate, 0.016 M sodium citrate, 3.6 × 10⁻⁴ M ammonium molybdate, and 0.285 M NaCl; the agents were added while stirring. The pH was maintained at around 8.5 with aqueous NH3·H2O. The electrodeposition process was conducted under a constant current of 22 A for 60 min with vigorous stirring. After electrodeposition, the electrode was rinsed with deionized water several times and dried at 25 °C in Ar flow.

#### OER Electrode Preparation.

The OER electrode was synthesized on Ni foam (JYS Tape) by a hydrothermal method. Nickel foam (11 × 11 cm²) was first cleaned with concentrated HCl solution (37 wt %) in an ultrasound bath for 5 min to remove the surface NiO layer and rinsed with deionized water and ethanol. Then, the Ni foam was folded and transferred to a 100 mL Teflon-lined stainless-steel autoclave containing a transparent solution of Ni(NO3)2·6H2O (0.02 M), Fe(NO3)3·9H2O (6.9 × 10⁻³ M), and CO(NH2)2 (0.14 M). The autoclave was sealed and kept at 120 °C for 12 h, followed by naturally cooling down.

#### Materials Characterizations.

All of the samples used for characterization were taken from the bulk electrode. The SEM characterization was performed on a Zeiss Supra55VP field emission scanning electron microscope with the in-lens detector. Powder X-ray diffraction data were collected using a Bruker D2 Phaser diffractometer in parallel beam geometry employing Cu Kα radiation and a one-dimensional LYNXEYE detector, at a scan speed of 0.02°/step and a holding time of 2 s/step. The nitrogen adsorption and desorption isotherms were measured on an Autosorb iQ Station 3 adsorption analyzer. Before the measurements, the samples were degassed at 200 °C under vacuum for 5 h. The corresponding surface areas were calculated according to the Brunauer–Emmett–Teller (BET) theory.

#### Electrochemical Measurements in Three-Electrode System.

All electrochemical measurements were run at 25 ± 1 °C. A BioLogic VMP3 workstation was employed to record the electrochemical response. In a typical three-electrode test system (Figure 1C), a graphite rod (Sigma-Aldrich) and a saturated calomel electrode (SCE, CH Instruments) were used as the counter and reference electrodes, respectively. All potentials measured against SCE were converted to the RHE scale in this work using $E_{\text{RHE}} = E_{\text{SCE}} + 0.244$ V + 0.0591 × pH. Solution resistance ($R_s$) was determined by potentiostatic electrochemical impedance spectroscopy at frequencies ranging from 0.1 Hz to 200 kHz and manually compensated as $E_{\text{IR-corrected vs RHE}} = E_{\text{vs RHE}} - R_s × I$ (amps of average current). The energy-conversion efficiency was calculated as $\eta = \frac{I_{\text{avg}} × E_{\text{RHE}}}{E_{\text{RHE}} − iR_s}$ × 100% in a three-electrode system or $\eta = \frac{I_{\text{avg}} × E_{\text{RHE}}}{E_{\text{RHE}} − iR_s}$ × 100% in a two-electrode device, where 1.23 V corresponds to the theoretical water-splitting voltage.

#### Device Construction.

The whole device model was designed by ourselves inspired by the solar cell stack, and it was fabricated by the machine and model shop at Rowland Institute at Harvard. The reaction tank was all made with poly(vinyl chloride), the metal plates were made of stainless steel, and the electrodes were made of brass. During the experiment, the electrocatalysts were placed into the groove of the electrode to make a highly close contact and aligned stack-by-stack separated by anion-exchange membranes (Figure 2B). A DSC power supply (Sorensen DC58-125E) was used to control the voltage and measure the current, and a multimeter was connected directly to the two electrodes to measure the exact potential between the two sides. Peristaltic pump (YZ15-1A, Huiyu Weiyue Fluid Equipment) was linked to the system to control the flowing rate; the flowing rate was calibrated by transporting water for a certain period of time and measuring the volume. Separated holes were applied to collect the two different gas products, which were connected to two Teflon tanks to recycle the alkaline. Deionized water (10 mL) was added to the system each hour to compensate the loss of water splitting in alkaline. The measurement method was basically as follows: using the method of collection of gases over water in a measuring cylinder, we can measure the time it needed each time for producing 300 mL of H2 and therefore calculate its generating rate. As we can directly read the current from the power supply, the relation between the theoretical yielding and the practical yielding can also be gained.

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