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Multimaterial 3D-printed water electrolyzer with earth-abundant electrodeposited catalysts

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ABSTRACT Additive manufacturing (AM) is reaching a stage of development that enables high throughput fabrication of end products/devices. An important contribution to the advancement of this technology is given by the possibility to combine different materials into a single printing process or integrate diverse technologies for the fabrication of different components. Here we show how a prototype water electrolyzer can be fabricated using two different AM technologies, named selective laser melting (SLM) and fused deposition modeling (FDM) to produce the metallic components (electrodes) and the liquid/gas handling components (cells) of the electrolyzer, respectively. Both components are produced following a precise design which enables their perfect integration and assembly. The electrodes are produced in stainless steel which can be directly used for both the cathodic hydrogen evolution reaction (HER) and the anodic oxygen evolution reaction (OER). However we

propose to introduce a simple and rapid electrochemical surface modification of the steel electrodes with more efficient earth-abundant catalysts in order to enhance the overall water splitting performance. For the HER we deposited a thin film of Ni-MoS₂ composite while a NiFe double hydroxide film is deposited on the anode. Scanning electron microscopy (SEM) combined with energy dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy are employed to characterize the electrode surface before and after the electrodeposition with the catalysts. Electrochemical testing is then used to optimize the composition of the catalysts by verifying the catalytic performance of the electrodes. As proof-of-concept, a electrochemical testing is performed with the 3D printed and assembled device.

KEYWORDS: 3D-printing, electrochemistry, water splitting, hydrogen evolution reaction, oxygen evolution reaction

The well-known intermittent nature of renewable energy sources demands a concomitant development of ways to store the produced energy.^{1,2} Beside the electrical energy storage devices such as batteries and capacitors, another convenient way to store electricity is to convert it into molecular hydrogen by the electricity-driven splitting of water into H₂ and O₂.³ Hydrogen is a chemical fuel that can be stored, transported where needed, used as clean combustion fuel or, if necessary, recombined with oxygen in fuel cells to efficiently regenerate electricity with no CO₂ emission. However the water splitting route is still economically limited by the high energy costs required due to the sluggish kinetics of the process, which, particularly for the anodic production of oxygen, demands the application of large overpotentials. Catalysts based on noble metals such as Pt for the cathodic hydrogen evolution reaction (HER) and Ir or Ru for the oxygen evolution reaction (OER) have been used to decrease the energy barrier and improve the efficiency of the overall process, but due

to their scarcity they are expensive and therefore not suitable for sustainable large scale production.⁴ Several noble metal-free catalysts have been proposed as less costly alternative which are generally based on transition metals. Phosphides,⁵ carbides⁶ and chalcogenides⁷ have demonstrated particularly good performance with regard to the HER, while oxides of Ni, Fe, Co and Mn showed excellent catalytic activity towards the OER.^{8,9} Due to their large availability, earth-abundant electrocatalysts will be therefore essential for future developments of water splitting technologies.

For a large-scale production of H₂ and O₂, in addition to find novel active materials that can improve the efficiency of the process, it is also equally important to develop innovative fabrication methodologies that enable easy and cost-effective production of the active electrodes as well as the water/gas handling electrolyzer components. Additive manufacturing (AM, also known as 3D-printing) is lately attracting a gigantic interest from a variety of industries and research institutions since it enables rapid prototyping as well as the fabrication of components and devices with unprecedented design freedom.¹⁰ Several different materials can today be processed into functional components by AM ranging from polymeric materials, metals, to ceramic materials.¹¹⁻¹³ Combination of different materials into a single printing process (multi-material printing) represents the ultimate goal since it would allow the fabrication of functional devices from scratch without the need of assembly.¹⁴⁻¹⁷ Alternatively, combination and integration of different AM technologies driven by a common structural design, could facilitate the fabrication of functional devices at lower costs with respect to traditional methods.

In view of this, we propose to show here how the potential combination of two different AM technologies, selective laser melting (SLM) for metal printing and fused deposition modeling (FDM) for plastic material printing, can be adopted to produce the functional metal electrodes and the polymeric gas/liquid handling components, respectively, of a water electrolyzer. The

metal electrodes are primarily fabricated in stainless steel which represents itself a viable and known electrode material for water splitting.¹⁸ However, we propose a rapid and easy electrodeposition method to modify the stainless steel electrode surface with highly active earth-abundant electrocatalysts for improved HER and OER. Precisely, we deposited a layer of MoS₂-Ni composite onto the electrode surface to be used as cathodic H₂ generation catalyst, while a layer of Ni/Fe double hydroxide deposited onto the 3D-printed steel electrode operates as the oxygen evolution electrocatalyst. The electrodes as-printed and after the electrochemical modification have been carefully characterized by scanning electron microscopy (SEM), energy-dispersive X-ray analysis (EDX) and X-ray photoelectron spectroscopy (XPS), before testing their electrocatalytic properties in alkaline solution. A tentative water electrolyzer design is finally proposed, fabricated and assembled as proof-of-concept prototype.

RESULTS AND DISCUSSIONS

The main components of a water electrolyzer are represented by the metallic electrodes, the liquid/gas handling cells and the ion exchange membrane which separates the cathodic and anodic compartments with their respective gaseous products (H₂ and O₂) while ensuring ionic migration. For demonstration purposes of this prototype we replace the ion exchange membrane with a polymeric solid barrier carrying two small holes to ensure ionic movements between the compartments. As summarized in Figure 1 the fabrication of the electrolyzer follows three phases: 1) Firstly the metallic electrodes and the cell components (including the separating barrier) are designed using CAD software. The dimensions and geometrical features of all components are established in order to enable a perfect fit and integration once assembled. 2) Next, each component is fabricated by the corresponding AM machine, precisely a SLM printer is used to fabricate stainless steel electrodes and a FDM printer is

employed to fabricate the cell components using polylactic acid (PLA) thermoplastic material. Stainless steel electrodes possess intrinsic catalytic properties towards HER and OER but the efficiency is generally poor. We propose to use a simple electrochemical deposition method to modify the electrode surface by introducing a thin film of earth-abundant catalysts in order to significantly enhance the overall process. More details on this modification step will be given in the next section. 3) Once the fabrication of the electrodes and components is completed, they are assembled into a complete prototype device ready for testing.

Figure 1. Schematic of the fabrication process: 1) Design of the electrodes and the electrolyzer components are created using CAD software; 2) A metal 3D printer fabricates the electrode (steel) by selective laser melting technology (SLM) while a fused deposition modeling (FDM) printer fabricates the components (thermoplastic) according to the design. Electrochemical surface modification of the electrode is then performed to tune its catalytic properties; 3) Components and modified electrodes are assembled into a complete prototype water electrolyzer ready for testing.

Particularly important for the current project is the electrode surface modification. As shown in our previous works, different electrodeposition procedures can be adopted for the surface modification of conductive electrodes.^{16, 19-21} Here we opted to employ a common procedure for both the cathodic and anodic electrode consisting in a time-controlled potentiostatic method. Precisely, a fixed potential of -1 V (vs Ag/AgCl) is applied to the electrode in the presence of ionic species of the catalyst dissolved in solution. During the process the ionic species deposit on the electrode as solid films of varying thickness depending on the process duration. Amorphous MoS₂ films can be deposited onto conductive electrodes employing both potentiostatic electrochemical methods and cyclic voltammetry starting from thiomolybdate ionic precursors dissolved in solution.^{22, 23} These amorphous MoS₂ films are highly active towards HER in acidic solutions but have lower performance in alkaline conditions. Combination with transition metals (M) such as Co, Fe and Ni and the formation of M-MoS₂ composites demonstrated enhancing effects,²⁴ particularly with Ni in alkaline solutions.²⁵ For this project we propose to modify the cathode with a Ni-MoS₂ film, employing a simple co-electrodeposition procedure in the presence of Ni and thiomolybdate ionic precursors in the plating solution at potentiostatic conditions. Optimal deposition conditions have been preliminarily investigated using glassy carbon (GC) electrode as

conductive substrate. GC substrate is ideally suited for testing catalytic properties of materials since it presents extremely low catalytic performances. Different deposition times and molar ratios have been tested using LSV in a three-electrode setup and measuring the HER performance (Figure S1 of Supporting Information). Figure 2A summarizes the polarization curves obtained depositing onto the GC electrode, a Ni-only, a MoS₂-only and a Ni-MoS₂ composite film with the best performances. It is evident the synergistic effect obtained when mixing Mo ionic precursors and Ni ions in the plating bath at a ratio of 3:1 which resulted the optimal for the best performing HER catalyst composites in alkaline conditions. As it can be seen in Figure 2A, the Ni-MoS₂ composite showed a significant catalytic enhancement decreasing the overpotential of about 140 mV compared to the MoS₂ film requiring a potential of about -0.23 V to reach the current of -20 mA/cm².

Other ratios and deposition times were tested and summarized in Figure S1 of Supporting Information. Electrodeposition of Ni results generally in an improvement of the catalytic process compared to GC although still inferior to the performance offered by a MoS₂ film (Figure S1A and S1B). The introduction of Ni ions during the deposition of MoS₂ for a co-deposition process produced composites with better performances at MoS₂: Ni molar ratio of 3:1 (Figure S1C).

For the OER we chose to deposit a NiFe doublehydroxide composite film following a modified procedure optimized in another work.²⁶ Figure 2B summarizes the polarization curves obtained using the individual catalysts and the combined co-deposited film. Again a synergistic effect was observable with the NiFe film obtained by the codeposition of Ni and Fe at equal molar ratio. This film produced the best performance requiring overpotential of about 300 mV to reach 20 mA/cm² current density. Different deposition times and experimental conditions were tested as summarized in Figure S2 of Supporting Information.

Figure 2. A) Polarization curves for hydrogen evolution reaction in 1 M KOH solution using bare glassy carbon electrode (GC) and GC modified by electrodeposition with Ni (blue), MoS₂ (orange) and the co-deposited Ni-MoS₂ composite film (ratio MoS₂: Ni of 3:1, red). Polarization curve obtained using Pt disk electrode (Pt) is also presented for comparison. B) Polarization curves for oxygen evolution reaction in 1M KOH solution using bare GC electrode and GC modified by electrodeposition with Ni (blue), Fe (green) and the co-deposited film NiFe composite (ratio 1:1, red). Scan rate for both measurements is 5 mV/s.

We then moved to the preparation of the electrodes to be used for the electrolyzer. 3D-printed stainless steel electrodes have been tested for HER and OER in alkaline solution before and after electrochemical surface modification. Figure 3 summarizes polarization curves and the corresponding Tafel plots. Clearly bare steel electrodes already possess intrinsic catalytic properties towards both HER and OER as evidenced by the polarization curves. At 10 mA/cm² current density overpotential required using steel electrode is about 0.45 V. HER catalysis is improved by modifying the electrode surface with a Ni film or a MoS₂ film requiring overpotential of 0.4 V and 0.35 V, respectively at 10 mA/cm² current. However, as demonstrated previously using GC electrode, the best performance is obtained when a Ni-MoS₂ composite is deposited using the optimized conditions. Ni-MoS₂ film decreased the overpotential of about 150 mV compared to bare steel electrode requiring a potential of -0.3 V to reach 10 mA/cm² current density. Tafel plot corresponding to the polarization curves for HER confirmed the Ni-MoS₂ film as the most efficient catalyst producing a Tafel slope of 106 mV/dec (Figure 3B). Being made of Fe and Ni, steel shows also solid catalytic properties for the OER. Interestingly, the modification of the electrode surface by depositing a Fe film seems not generating any significant performance improvement despite a reduced onset potential. A larger Tafel slope of 65 mV/dec for Fe modified steel electrode versus 42 mV/dec for the bare steel clearly indicates a slower and less efficient process generating lower currents at higher potentials. Improvements could be measured by modifying the surface with a Ni film which decreased the overpotential of about 80 mV compared to the bare steel electrode. It could be clearly noticed the presence of an oxidation signal starting at about 1.4 V which is due to the oxidation of Ni(OH)₂ to NiOOH and which precedes OER. Once again, as evidenced when using the GC electrode, the best performance was obtained by co-deposition of Ni and Fe precursors at equal ratio which generated a NiFe doublehydroxide film. An overpotential of 300 mV can generate oxygen with a current

density of 20 mA/cm² (Figure 3C). An oxidative wave at the region 1.45-1.5 V could be noticed prior the OER and which is due to the oxidation of Ni(OH)₂ to NiOOH. Such signal practically overlaps with the OER and therefore hindering a clear evaluation of the Tafel slope. We provide two values for the Tafel slope: one at the onset (37 mV/dec) and another after the Ni(OH)₂ oxidation signal (76 mV/dec) (Figure 3D) but we believe they should not be used for performance comparison. Figure S2 of Supporting Information shows polarization curves obtained with different electrodeposited films using various deposition conditions. NiFe double-hydroxide film prepared from a plating solution with equal molar ratio of Fe and Ni precursors is clearly confirmed as the most performing for OER.

Figure 3. A) Polarization curves for hydrogen evolution reaction in 1 M KOH solution using bare 3D-printed steel electrode before (black) and after modification by electrodeposition with Ni (blue), MoS₂ (orange) and the co-deposited Ni-MoS₂ composite film (ratio MoS₂: Ni of 3:1, red). B) Corresponding Tafel plots for HER. C) Polarization curves for oxygen evolution reaction in 1M KOH solution using bare 3D-printed steel electrode before (black) and after modification by electrodeposition with Ni (blue), Fe (green) and the co-deposited film NiFe composite (ratio 1:1, red). Scan rate for both measurements is 5 mV/s. D) Corresponding Tafel plots for OER.

SEM and EDX were used to confirm the film deposition onto the 3D-printed steel electrodes. Figure 4 shows images at different magnifications of the electrode surface before (Figure 4A) and after modification with NiFe double-hydroxide film (Figure 4B) or Ni-MoS₂ film (Figure 4C). It can be clearly seen that a film of sub-micrometer thickness is deposited onto the stainless steel surface in both cases.

Figure 4. SEM images of as-printed stainless steel electrode before A) and after the deposition with NiFe double-hydroxide film B) and Ni-MoS₂ film C). Scale bars from left to right correspond to 1mm, 10 μ m and 1 μ m, respectively.

EDX element analysis provides the elemental composition of the electrode surface as shown in Figure 5. It can be seen for the steel electrode that O, Ni and Fe are the main elements while C and Si should be attributed to contamination impurities. Fe and Ni represent the main components of steel and are therefore expected while the oxygen is due to the presence of oxides of these elements. After the deposition of NiFe film it is evident the increase of the oxygen signal due to the formation of the hydroxide film of Ni and Fe which are also confirmed. The spectrum for the electrode modified with Ni-MoS₂ film shows the presence of the Mo+S signal while the O, Ni and Fe signals appear diminished due to the masking effect of the MoS₂ film covering most of the surface. Corresponding EDX element mapping for all electrodes is available in Figure S3 of Supporting information. It can be clearly seen how all the elements are homogeneously distributed on the entire surface. In addition, it is visible the strong presence of Ni, Fe and O for the NiFe modified electrode and the strong presence of Mo and S (with diminished Ni, Fe and O) for the MoS₂ modified electrode.

Figure 5. EDX spectra of A) As-printed steel electrode; B) NiFe modified steel electrode and C) Ni-doped MoS₂ modified steel electrode.

XPS was employed to further confirm elemental composition of the electrode surface after the electrodeposition. Figure S4A of Supporting Information shows the wide spectra for the electrodes modified with NiFe and Ni-MoS₂ films in comparison with electrodes modified by the individual materials. Both Ni and Fe are detected for the Steel-NiFe electrode and both Ni and Mo are detected for the Steel-Ni-MoS₂ electrode. High resolution XPS spectra are

recorded for Ni 2p, Fe 2p and Mo 3d signals to evaluate the oxidation state (Figure S4B-H). From the high resolution spectra it appears clear that Fe and Ni are present as oxide/hydroxide state given the signal of Fe 2p_{3/2} and Ni 2p_{3/2} at binding energy of 710 eV and 855 eV, respectively, which corresponds to Fe oxides and Ni oxides (Figure S4B-D). Also the Mo 3d_{5/2} signal appears at 232 eV which suggests the presence of Mo oxides together with Mo sulfides (Figure S4H).

A prototype water electrolyzer was finally assembled combining the metal electrodes and the plastic components fabricated through 3D-printing. Figure 6A show a detailed design of each component while pictures of the printed components can be seen in Figure 6B-D before and after assembly. A full electrolysis polarization curve was recorded for the assembled device after introducing 1 M KOH solution and connecting the electrodes to a bipotentiostat in a two-electrode setup (Figure 6E). We measured the overall water splitting using the bare 3D-printed steel electrodes and the electrodes after modification with the NiFe and Ni-MoS₂ catalysts. As it can be seen in Figure 6E a significant enhancement could be obtained with the electrodeposited catalytic films with over 250 mV decrease for the overall potential difference. Using the modified electrodes a current of 10 mA/cm² could be obtained at an overall potential difference of about 1.72 V.

Figure 6. A) Schematic of the electrolyzer components with a top and side-view. B) Picture of the printed components. C) Picture of the assembled electrolyzer. D) Picture of the assembled electrolyzer with liquid tubing and electrical connectors. Scale bare corresponds to 2 cm. E) LSV curve of the electrolyzer recorded after filling with KOH 1 M and using the bare printed steel electrodes (black) and the steel electrodes modified with NiFe and Ni-MoS₂ catalysts (red).

CONCLUSIONS

Different AM technologies have been applied here to fabricate different components of a water electrolyzer. 3D-printing with different materials enabled the preparation of the metallic electrodes by SLM and the liquid/gas cell plastic components by FDM. Both were designed to allow their perfect integration and assembly into a complete device. In order to enhance the catalytic properties of the electrodes, a simple electrodeposition method has been applied to modify the electrode surface with the deposition of a NiFe double-hydroxide film onto the anode electrode and a Ni-MoS₂ composite film onto the cathode. A synergistic effect

resulted evident when combining Ni and Fe into a composite for the anode and when combining Ni and MoS₂ for the cathode. The presence of the earth-abundant electrocatalysts produced a significant enhancement for the overall process with a decrease in overpotential of more than 250 mV compared to the unmodified 3D printed steel electrodes, measured with the assembled device.

EXPERIMENTAL SECTION

Materials. Potassium chloride, nickel nitrate, iron nitrate, ammonium tetrathiomolybdate and potassium hydroxide were purchased from Sigma–Aldrich, Singapore.

Apparatus. Metal 3D-printing was performed with a Mlab cusing machine (ConceptLaser, Germany). Fused deposition modelling printing was performed using a FlashForge Dreamer (FlashForge, China). Voltammetric experiments were performed using a three-electrode configuration. A platinum foil served as an auxiliary electrode, while an Ag/AgCl served as a reference electrode. All electrochemical tests were performed on a PGSTAT101 electrochemical analyzer (Methrom Autolab B. V., The Netherlands) controlled by NOVA software Version 1.8 (Methrom Autolab B. V.). XPS was performed with a Phoibos 100 spectrometer and a monochromatic Mg X-ray radiation source (SPECS, Germany). Both survey and high-resolution spectra are calibrated against the C 1s signal at 284.5 eV. Scanning Electron Microscopy (SEM) images and EDX mapping/element analysis were obtained by using JEOL 7600F SEM (JEOL, Japan) operating at 5 kV.

Procedures

3D-printing of stainless steel electrodes. Electrode design was firstly drawn using sketch-up 3D modelling open-source software. Slicing and g-code file was obtained with Simplify3D

software. Metal 3D printing was carried out with an Mlab cusing machine printer (Concept Laser GmbH, Germany) which uses a selective laser melting (SLM) technique. A focused, high-energy laser beam fuses and link metallic particles deposited on a printing stage in a layer by layer fashion according to the established design. Stainless steel particles (CL 20ES, Concept Laser, GmbH) were employed to produce stainless steel electrodes.

3D-printing of plastic electrolyzer cell components. Plastic cell components were firstly designed using the sketch-up 3D modeling open-source software. Slicing and g-code file was obtained with Simplify3D software. FDM printing was done with a commercially available 3D printer FlashForge model Dreamer using polylactic acid (PLA) thermoplastic filament.

Deposition of NiFe film on GC electrode or stainless steel 3D-printed electrodes. NiFe plating solution consisted of 3 mM $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 3 mM $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Molar ratio 1:1 was previously optimized elsewhere showing the best OER performance.²⁶ A potentiostatic electrodeposition was carried out by applying a fixed potential of -1 V (vs Ag/AgCl) at RT. Preliminary optimization study was performed using a glassy carbon (GC) working electrode. The GC electrode surface was renewed before modification by polishing with 0.05 μm alumina particle slurry on a polishing pad followed by thorough washing with ultrapure water. Different deposition intervals were tested between 10-30 min. Stainless steel 3D-printed electrode was used as-printed with no prior treatment procedure. A Pt foil and a Ag/AgCl were used as auxiliary and reference electrode, respectively. After the deposition the electrode was carefully washed with ultrapure water and let drying at room temperature.

Deposition of Ni-doped MoS_2 film on GC or stainless steel 3D-printed electrodes.

Preliminary optimization study was carried out using GC as the working electrode, a commercial Pt disk as auxiliary electrode and a Ag/AgCl as reference electrode in a glass voltammetric cell. The GC electrode surface was preliminarily renewed by polishing with

0.05 μm alumina particle slurry on a polishing pad followed by thorough washing with ultrapure water. Electrodeposition solution consisted of 3mM $(\text{NH}_4)_2\text{MoS}_4$ and 1 mM $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in the presence of 0.1 M KCl electrolyte. Molar ratio between Mo and Ni was optimized during the preliminary study. Deposition was obtained by applying a fixed reducing potential of -1 V (vs Ag/AgCl) for interval time between 10 - 30 min. After deposition the electrode was gently rinsed with ultrapure water and left to dry at room temperature before electrochemical measurements.

Electrochemical measurements. Both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) were tested in a three-electrode setup using Ag/AgCl and Pt foil as reference and auxiliary electrode, respectively and using linear sweep voltammetry (LSV) at 5 mV/s scan rate in 1 M KOH solution. Water splitting tests were carried out in a two-electrode setup using LSV at 5 mV/s scan rate in 1 M KOH solution with the stainless steel electrodes as printed and after modification as cathode and anode.

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Notes

The authors declare no competing financial interest.

ASSOCIATED CONTENT

Supporting Information. Additional polarization curves for HER and OER; EDX and XPS data. Supporting Information is available from the Wiley Online Library or from the author.

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The combination of 3D-Printing with electrochemical deposition of earth-abundant catalysts is used to fabricate functional bespoke water electrolyzer as sustainable energy-related device.