Self-Contained Polymer/Metal 3D Printed Electrochemical Platform for Tailored Water Splitting

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1. Introduction

Additive manufacturing is gaining enormous interest in recent years by a wide spectrum of entities ranging from industrial sector, research institutions, medical, engineering, art to also simple hobbyists.[1,2] Started as fabrication tool for rapid prototyping, 3D-printing has lately enormously progressed becoming an established manufacturing method complementing if not even replacing traditional molding procedures, hot embossing an established manufacturing method, or standard computer numerical control subtractive methods.[2,3] This growing interest in additive manufacturing is obviously accompanied by research and developments of a wider variety of materials to be 3D printed in order to be adopted in many different sectors.[4–6] In particular, efforts have lately been motivated by the idea of printing functional materials, which enable the fabrication of devices with specific operational abilities to perform certain tasks.[7–9] Materials with catalytic properties, to name one example, enable the fabrication of chemical reactors[10] combining in a single printing process structural material and functional catalytic materials. More and more often, however, efforts are focused on the development of printable materials with electric properties since these will enable the fabrication of a large variety of electronic devices (also defined as printed electronics) such as transistors,[11] sensors,[12–14] photovoltaics, and also energy storage devices such as batteries[15] and supercapacitors.[16,17] Conductive and/or functional inks have been developed recently to be employed in direct ink writing patterning technique. These include silver ink,[17] Li4Ti5O12, and LiFePO4 as anode and cathode of a microbattery assembly,[15] semiconductive quantum dots,[18] conductive polymer,[19] etc. While direct ink writing offers potentially the possibility to achieve multimaterial printing with diverse properties, it requires also a careful investigation on the ink formulation and its rheological properties including particle size, viscosity, hardening time, compatibility between solvents of different materials, etc. in order to be efficiently printed.[20]

Another approach that could be consider when fabricating devices based on conductive functional materials consists in the combination of an established 3D printing methodology to fabricate conductive parts with an electrochemical surface modification technique which can alter the surface composition by depositing a vast variety of materials and which would impart the desired functionality. The combination of the two technologies (3D printing and electrodeposition) can be easily performed enabling the creation of devices with a much wider range of functionalities.[21]

Water electrolysis represents a promising technology for the production of hydrogen given that renewable energy sources are being used. In particular, water electrolysis in alkaline media has demonstrated excellent performance compared to the operation in the acidic solution with also the advantage of simpler electrolyzer design and the use of more abundant transition metal based catalysts.[22]
Here we demonstrate that it is possible to build self-contained electrochemical system, consisting of electrodes and electrochemical cell via 3D metal and polymer printing. We show how electrodeposition procedures can be easily employed to confer and tune electrocatalytic properties of stainless steel metal 3D printed electrodes previously fabricated by the established selective laser melting (SLM) additive manufacturing method. Stainless steel electrodes have been first obtained with specific designs and different sizes by SLM process, then simple electrodeposition procedures have been applied to deposit thin layer of standard catalysts such as Ni, Pt, or iridium oxide (IrO₂) onto the electrode surface and then used for water splitting applications. The combination of 3D printing with electrodeposition provides extreme versatility allowing easy optimization not only of the electrode design and dimensions but also of the catalytic material to be used. The electrodes have been characterized by scanning electron microscopy (SEM) in combination with energy dispersive X-ray analysis prior electrochemical testing in alkaline solution to evaluate their catalytic performances.

2. Results and Discussion

The electrode fabrication approach is summarized in Figure 1. Electrode design is firstly obtained using largely available CAD software. The corresponding .STL file is then used by the metal 3D-printer control software to create a sliced configuration of the printed part which dictates the sequential creation in a layer by layer fashion of the electrode. Here selective laser melting is employed with stainless steel powder to generate a solid and robust electrode. This electrode is highly conductive but possesses poor catalytic properties toward the hydrogen and oxygen electrogeneration. Such properties can be easily conferred and/or tuned by means of electrochemical procedures which can modify the electrode surface by depositing thin films of additional materials (catalyst) with desired catalytic properties. By selecting within a wide range of electrodeposition compounds the resulting catalytic properties of the 3D-printed electrode can be efficiently and controllably tuned. Here we selected, as proof-of-concept, Ni, Pt, and IrO₂ as possible electrodeposited catalysts for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER).

Different electrodeposition procedures are available and viable for the modification of conductive electrodes. Here we employed cyclic voltammetry to electrodeposit IrO₂,[12,23,24] a galvanostatic time-controlled method to deposit Pt,[25] by applying a fixed current and a potentiostatic time-controlled method to deposit Ni[26] by applying a fixed potential. More details on the electrodeposition of these materials are provided in the Experimental Section. Figure 2 shows the variation of the electrochemical parameters corresponding to each procedure during the electrodeposition.

To facilitate the investigation of the deposition conditions and the electrocatalytic performances, preliminary tests have been carried out using only small 3D printed steel ribbons. IrO₂ was electrodeposited onto 3D printed steel electrodes using an established procedure based on cyclic voltammetry which allows a precise control over the deposition process which can be monitored by variation of the current during multiple potential scans.[12,23,24] A typical growing trend can be seen in Figure 2A, which indicates the successive deposition of multiple layers of the oxide on the electrode surface. Film thickness can be controlled by varying the number of CV scans. Figure 2B shows the variation of the potential during the deposition of Pt from a commercially available Pt plating solution (used as received) with the application of a fixed current of 2 mA cm⁻². Deposition of Pt alter the steel electrode surface and consequently its open circuit potential which varies from the value of 0.2 V (vs Ag/AgCl) reaching the saturation value of 0 V during 30 min deposition. Similar trend can be seen during the deposition of Ni (Figure 2C) which is performed for a period of 1 h. In this case the current passing through the steel electrode (working electrode) varies over time with the application of a fixed reductive potential of –1 V.

We employed SEM with energy dispersive X-ray (EDX) detector to confirm the successful deposition of the catalysts onto the steel electrodes. Figure 3 summarizes SEM images of a small section of the steel electrode without any deposition (3D-S) and after deposition of Pt (3D-S-Pt), IrO₂ (3D-S-IrO₂), or Ni (3D-S-Ni). EDX microanalysis provides the chemical composition of the electrode surface. It can be seen in the EDX mapping analysis in Figure 3 (right panel) that the bare steel electrode is characterized by the presence of Fe as major component accompanied by a lower amount of Ni. These elements are normally the major components of steel. As expected no
Pt or Ir are detected. The electrode with deposited Pt presents less intense signals from Fe and Ni because of the presence of a homogeneous layer of Pt on the electrode surface indicated in red. No Ir was detected. Similarly, the electrode with electrodeposited IrO$_2$ presents less intense Fe and Ni signals due to the presence of a surface layer of IrO$_2$ as indicated by the presence of Ir (yellow). Finally, the electrode with deposited Ni presents an enhanced signal from Ni and the absence of Pt and Ir. EDX spectra confirm this trend (see Figure S1, Supporting Information). Additional SEM images at higher magnification are provided in Figure S2 of the Supporting Information. Particularly for the electrodes modified with Pt and IrO$_2$, it can be clearly seen that a thin film of the catalyst is deposited onto the steel electrode surface. Ni film deposition is less evident from the SEM characterization although the performance improvement as well as the EDX analysis confirmed its presence. From SEM/EDX analysis we can conclude that catalyst materials were homogeneously and efficiently deposited onto the steel electrodes.

We then moved on testing the electrodes for HER and OER using linear sweep voltammetry in the presence of 1 m KOH electrolyte. It can be seen in Figure 4A that the different electrodes possess different electrocatalytic properties toward HER and OER. The bare steel electrodes possess indeed catalytic properties but which cannot be considered sufficient for possible application in water splitting devices. The HER occur at potential more negative than –0.5 V (vs reversible hydrogen electrode, RHE) while the oxygen generation requires potential
more positive than 1.7 V. This means that water splitting would occur only with cell potential difference of about 2.2 V. The deposition of Ni confer an enhanced performance since HER and OER occur at potential more positive than –0.4 V and lower than 1.6 V, respectively, which translates into a cell voltage difference of about 1.9–2.0 V required to generate water electrolysis. A significant improvement is obtained depositing Pt as catalyst for HER and IrO₂ as catalyst for OER. Polarization curves recorded with 3D-steel-Pt and 3D-steel-IrO₂ show that hydrogen can be produced at potential close to 0 V and OER occur at potential close to 1.5 V (vs RHE). This means that a cell voltage of 1.5 V could be sufficient to obtain water splitting. A simple water splitting setup was then used to test all the electrodes. Figure 4B collects a series of video snapshots taken during operation (videos are available in the Supporting Information) applying two different cell potentials between cathode and anode (1.6 and 2.0 V) in order to visualize the bubble formation as confirmation of hydrogen and oxygen evolution. It can be seen that using steel electrodes as anode and cathode, very little bubbling is obtained only using a high cell voltage of 2 V (see Video-16-a and Video-20-a, Supporting Information). Using Ni modified steel electrodes both as cathode and anode a little bubbling is visible also using the low cell voltage of 1.6 V (see Video-16-b, Supporting Information). Using Pt and IrO₂ modified steel electrodes as cathode and anode, respectively, significant bubbling is observed from both electrodes at the lowest cell voltage of 1.6 V (see Video-16-c, Supporting Information). Increasing the cell voltage to 2 V generates an intense flow of gas bubbles from both electrodes (see Video-20-c, Supporting Information). Clearly modifying the steel electrode surface with Ni or Pt and IrO₂ infers enhanced catalytic properties enabling steel electrodes to be used for such electrocatalytic applications. The advantage of this approach resides in the fact that standard 3D-printing procedures can be adopted to fabricate...
Conductive electrodes with the desired size and design, and then simple electrochemical deposition can infer the desired catalytic properties by modifying only the electrode surface choosing from a wide range of possible catalytic materials. Since only a thin layer is generated onto the electrode surface, a significantly reduced amount of catalytic material is required.

The catalytic performance of Pt-modified and IrO$_2$-modified steel electrodes for HER and OER, respectively, is clearly superior to Ni-modified electrodes or bare electrodes. We then opted to modify the surface of the desired gauze-shaped 3D-printed steel electrodes fabricated by SLM according to our design, using Pt and IrO$_2$. Metal 3D printing can be used to fabricate almost infinite shape and geometries of electrodes enabling the possibility for fast prototyping, so that different shapes and assembling can then be easily tested to determine the highest efficiencies. Gauze-shaped electrodes were chosen here only as proof-of-concept example of an electrode with high surface area as advisable for higher catalytic performances. This shape is also chosen as example of complex design which cannot be easily produced with standard fabrication methods.

We first characterized these electrodes using electrochemical measurements and then tested them in a water splitting setup to evaluate their performance. Figure 5A shows images of the electrodes before and after the electrochemical surface modification with Pt and IrO$_2$. Polarization curves were recorded in 1 m KOH solution and which indicate again the enhanced catalytic ability of the electrode modified with Pt for HER (Figure 5B) and with IrO$_2$ for OER (Figure 5C) compared to the bare steel electrode as printed. Corresponding Tafel plots are presented in Figure S3 of the Supporting Information. In relation to HER, bare steel and Pt modified showed Tafel slope of 121 and 112 mV dec$^{-1}$, respectively, which are similar to other values available in literature.$^{[27]}$ It is known that HER kinetic on Pt electrode in alkaline solution are orders of magnitude lower than in acidic media.$^{[28]}$ Mechanism of oxygen evolution reaction in alkaline solution is more complex than hydrogen evolution since involves more intermediate steps.$^{[29]}$ In this work bare steel and IrO$_2$-modified electrodes showed Tafel slope of 53 and 92 mV dec$^{-1}$, respectively. It seems clear that while the onset potential for IrO$_2$ modified electrode is smaller than for the unmodified electrode, the overall reaction rate appears lower. Stability tests were also performed for both Pt and IrO$_2$ modified electrodes (Figure S3C,D, Supporting Information). Polarization curves were recorded using as-fabricated electrodes and after the application of a constant potential (=0.1 V for Pt-modified; +1.6 V for IrO$_2$-modified electrode) for the period of 1 h. Both electrodes showed good stability presenting almost overlapping polarization curves.

A cell voltage of only 1.5 V should be sufficient to generate hydrogen from the cathode and oxygen from the anode in a water splitting setup. Video snapshots were taken during water splitting operations in which the cell voltage was applied by using a common alkaline AA battery with nominal voltage of 1.5 V (videos are available in the Supporting Information). It can be seen in Figure 5D that using the bare steel electrodes no gas was generated from neither the anode nor the cathode (see Video-15-Gauze-a, Supporting Information). On the contrary, the gauze electrodes modified with Pt and IrO$_2$ generated significant bubbling applying the same cell voltage of 1.5 V (Figure 5E) (see Video-15-Gauze-b, Supporting Information).

A fully 3D-printed water electrolyzer can be fabricated combining different 3D-printing technologies and materials. A common fused deposition modeling (FDM) printer can be used to fabricate a polymeric electrolyzer body while a metal...
Electrochemical surface modification represents an extremely useful tool to infer and/or tune specific properties to conductive 3D-printed parts. We have shown here that stainless steel electrodes printed by SLM can undergo surface modification by simple electrodeposition which enhances their electrocatalytic properties toward hydrogen and oxygen evolution. A controlled electrodeposition of thin films of IrO₂, Ni, or Pt onto the electrode surface can significantly enhance the catalytic properties of the steel electrodes offering a viable solution to the material limitations suffered by additive manufacturing technologies. In addition, since only the surface of the printed electrode is modified, a considerably reduced amount of catalytic material is required. As proof-of-concept, a fully 3D-printed water electrolyzer was fabricated using selective laser melting (SLM) and poly lactic acid (PLA) based microelectrochemical cells obtained by fused deposition modeling (FDM).

3D-printer in combination with electrodeposition procedures can be employed to fabricate the electrocatalysts. Both enable great versatility in terms of materials and design (Figure 6).

3. Conclusions

Electrochemical surface modification represents an extremely useful tool to infer and/or tune specific properties to conductive 3D-printed parts. We have shown here that stainless steel electrodes printed by SLM can undergo surface modification by simple electrodeposition which enhances their electrocatalytic properties toward hydrogen and oxygen evolution. A controlled electrodeposition of thin films of IrO₂, Ni, or Pt onto the electrode surface can significantly enhance the catalytic properties of the steel electrodes offering a viable solution to the material limitations suffered by additive manufacturing technologies. In addition, since only the surface of the printed electrode is modified, a considerably reduced amount of catalytic material is required. As proof-of-concept, a fully 3D-printed water electrolyzer was fabricated using selective laser melting (SLM) and poly lactic acid (PLA) based microelectrochemical cells obtained by fused deposition modeling (FDM).

4. Experimental Section

Materials: Commercial platinum plating solution was purchased from Technic Inc., USA. Iridium chloride, hydrogen peroxide (35%), oxalic acid, sodium carbonate, nickel chloride, sodium citrate, and potassium hydroxide were purchased from Sigma-Aldrich, Singapore.

Apparatus: Voltammetric experiments were performed using a three-electrode configuration. A platinum foil served as an auxiliary electrode, while an Ag/AgCl wire served as a reference electrode. All voltammetric experiments were performed on an Autolab PGSTAT101 electrochemical analyzer (Methrom Autolab B. V., The Netherlands) connected to a personal computer and controlled by NOVA software Version 1.8 (Methrom Autolab B. V.). SEM images and EDS mapping were obtained by using Jeol 7600F SEM (Jeol, Japan) operating at 5 kV.

Procedures: Fabrication of 3D-Printed Stainless Steel Electrodes: Electrode design was first drawn using sketch-up 3D modeling open-source software. Metal 3D printing was carried out with a Concept Laser printer (Concept Laser GmbH, Germany) which uses an SLM technique. A focused, high-energy laser beam fuses and links metallic particles deposited in powder form on a printing stage according to the established design in a layer by layer fashion. Stainless steel particles (CL 20ES, Concept Laser, GmBH) were employed to produce stainless steel electrodes.

Fabrication of 3D-Printed Electrochemical Polymeric Cells: Cell design was first drawn using sketch-up 3D modeling open-source software. FDM was employed to fabricate the electrochemical cells with poly lactic acid thermo plastic filaments. FlashForge Dreamer desktop 3D printer was used for the printing process upon the slicing of the STL design by Simplify 3D software.

Deposition of Pt Film on Stainless Steel 3D-Printed Electrodes: A commercial platinum plating solution was used directly for the Pt deposition onto the electrodes. A galvanostatic electrodeposition was performed applying a fixed current of −2 mA cm⁻² for a period of 30 min to the metal 3D-printed electrode immersed in the plating solution in the presence of Ag/AgCl and Pt foil as reference and auxiliary electrodes, respectively. After the deposition the electrode was carefully washed with ultrapure water and let drying at room temperature.

Deposition of Ni Film on Stainless Steel 3D-Printed Electrodes: Nickel plating solution consisted of 0.3 M NiCl₂·6H₂O and 0.2 M sodium citrate with an excess of sodium carbonate giving a final pH of 9.2. Ni deposition onto the stainless steel electrodes was performed using a potentiostatic method applying a fixed potential of −1 V for a period of 1 h to the metal electrode in the presence of Ag/AgCl and Pt foil as reference and auxiliary electrodes, respectively. After the deposition the electrode was carefully washed with ultrapure water and let drying at room temperature.

Deposition of IrO₂ Film on Stainless Steel 3D-Printed Electrodes: IrO₂ deposition solution was prepared by dissolving 75 mg of IrCl₃·xH₂O in 50 mL of distilled water in a 100 mL glass beaker, and then followed by the addition of 180 mg of oxalic acid. After complete dissolution, 450 µL of 35% hydrogen peroxide were added. The solution was stirred for further 15 min before adjusting the pH to 10.5 by using sodium carbonate. The light yellow-green solution turned dark blue after heating for 2 h at 65 °C and which indicates the completion of the reaction. The solution was let to cool down naturally to room temperature and then stored in the fridge before each use. The IrO₂ film was deposited by immersing the stainless steel electrode (connected to the electrochemical analyzer by means of a copper wire) into the deposition solution and then applying potential scans between −0.6 and +0.6 V (vs Ag/AgCl) at scan rate of 0.05 V s⁻¹.

Electrochemical Measurements: HER was evaluated using linear sweep voltammetry scanning from 0.6 to −0.6 V (vs RHE) at 5 mV s⁻¹ scan rate in 1 M KOH solution. OER was tested by linear sweep voltammetry scanning from 1 to 1.8 V (vs RHE) at 5 mV s⁻¹ scan rate in 1 M KOH solution. Both HER and OER were tested in a three-electrode setup using Ag/AgCl and Pt foil as reference and auxiliary electrode, respectively. Water splitting tests were carried out in a two-electrode setup with the stainless steel electrodes as printed and after modification as cathode and anode electrodes. A fixed voltage was applied between the electrodes using Autolab PGSTAT101 or a commercial AA type alkaline battery of 1.5 V.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.
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Conflict of Interest

The authors declare no conflict of interest.

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3D printing, electrochemistry, hydrogen evolution reaction, oxygen evolution reaction, water splitting

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