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Bipolar plate development with additive manufacturing and protective coating for durable and high-efficiency hydrogen production

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ABSTRACT

Additive manufacturing (AM) of the complex devices for energy application remains an almost unexplored area, and the harsh acidic environment also limits the application of AM parts in water splitting for hydrogen production. Here, bipolar plates (BPs), which are used to transport reactants/products and conduct electrons in proton exchange membrane electrolyzer cells (PEMECs), are printed from stainless steel (SS) with selective laser melting (SLM). Then surface treatments are employed on those BPs by thin film electroplating with Au, and the protective thin layer enables the utilization of AM SS parts to both cathode and anode sides of water electrolyzer cells and exhibits superior corrosion resistances and electronic conductivities. The Au-coated AM SS BPs deliver a low interfacial contact resistance (6.4 $m\Omega\,cm^2$ under 1.45 MPa) and an excellent performance in PEMECs (1.71 V at 2 A/cm^2), and maintain a remarkable durability in the simulated anode environment compared with the uncoated AM SS BPs and conventional graphite BPs. This approach demonstrates the possibility of 3-dimensional printing fully integrated water electrolyzer cells at both anode and cathode sides.

1. Introduction

Due to the requirement for a cleaner environment, renewable and green energy, such as wind and solar, is considered a promising alternative to fossil fuels for electricity production [1–13]. Because these energy sources are intermittent and unpredictable, a highly efficient and quickly responsive energy conversion system needs to be developed to store the energy as electricity. With the capability of handling the fluctuations of intermitted energy, proton exchange membrane electrolyzer cells (PEMECs) are attracting significant attentions [2,4,14–18]. But the relatively low performance and high cost limit their wide commercialization [4,5,15,19–25].

In a single conventional PEMEC, a catalyst coated membrane (CCM) is sandwiched by two liquid/gas diffusion layers (LGDLs), two bipolar plates (BPs), and two current distributors (CDs), as shown in Fig. 1a. At the anode side, water is split into oxygen, electrons, and protons, as in equation (1), then the protons transport from the anode to the cathode through the proton exchange membrane, and react with electrons to form hydrogen at the cathode catalyst layer (CL), as shown in equation (2) [26],:

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \quad (1)$$

$$4H^+ + 4e^- \rightarrow 2H_2 \quad (2)$$

At the cathode side, there is a reducing environment full of hydrogen with a low potential, so BPs and LGDLs are seldom corroded [27]. For the anode side, the thermo-neutral voltage of the PEMECs at room temperature is ~1.48 V, while the operating voltage could be over 2.00 V at a high current density and hydrogen producing rate, and the fluorinated polymer with sulfonic acid side chains in the CCMs will cause a strong acidic environment [28–32]. Thus, the components in an oxygen rich anodic ambient, where the pH is low and the potential is high, will be easily corroded.

Most recent researches on PEMECs have focused on catalyst developments for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) [33–40]. Few improvements have been realized for other components, such as the LGDLs and BPs [41–44]. The BPs distribute mass and electron and should provide good mechanical support for the PEMECs. They are expensive components, which account for ~48% of the cost of the PEMEC stacks [5,6,45–47]. Stainless steel (SS), titanium (Ti) and graphite are the most widely used materials for BPs [48–52]. Ti has good electrical conductivity, corrosion

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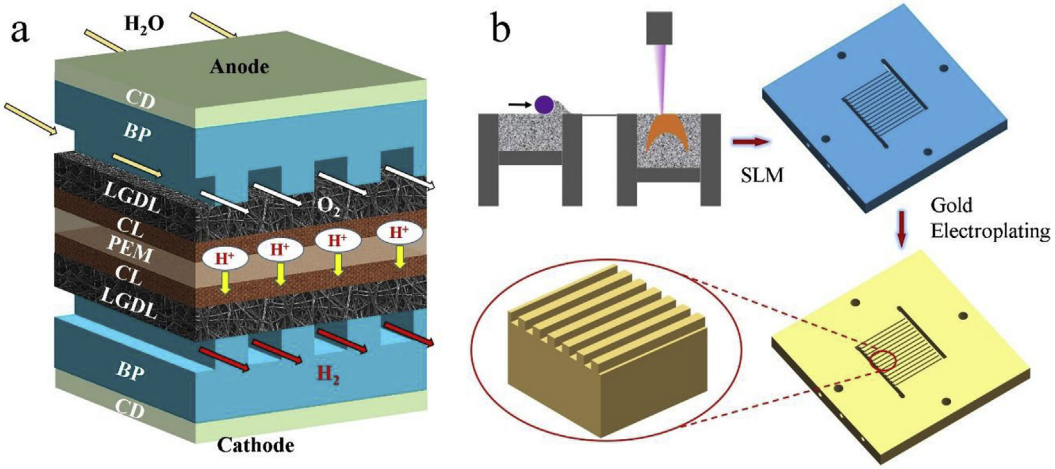

Fig. 1. Schematic of a) the internal structure of a PEMEC, b) manufacturing processes of Au-coated AM SS BPs.

resistance and mechanical strength, but it is very expensive and difficult to machine due to its hardness [5,27,28,52–54]. Even graphite is widely used due to its high electrical conductivity, but its brittleness leads to high machining cost. For SS, the electrical conductivity and mechanical strength are good, but it can easily corrode at the anode where there is an acidic environment and a high electrical potential.

To improve the efficiency and reduce the cost of PEMECs, either simplifying the manufacturing process, or using cheap materials like SS and plastic materials could be effective [27,55–57]. However, traditional moulding and cutting processes cannot provide many improvements due to material waste and challenging machining to produce complex flow channels. As an alternative to traditional manufacturing, additive manufacturing (AM) technology is a revolutionary approach to fabricate complex structures with nearly zero waste of material. Several researchers have tried to print bipolar plates with plastic and SS materials using AM to improve the performance and reduce the cost of PEMECs or proton exchange membrane fuel cells (PEMFCs). Scotti et al. tried to print SS micro flow field plates for fuel cell, but measurements of corrosion resistance and durability were not provided [55]. Conductive polylactic acid (PLA) was also used to print BPs for water electrolysis, but the performance of the cells was neither acceptable nor practical [20,57]. Our group used the AM SS BPs at the cathode side where a reducing environment occurs. Some of those AM SS plates served as integrated parts in the PEMEC, which reduced the weight and cost and improved the performance. But the SS bipolar plates have never been incorporated into the anode side due to the high potential and acidic environment, and the using of AM SS plates at the anode side of PEMECs needs to be explored [21,58].

The corrosion of BPs at an acidic environment in PEMECs can not only lead to the damage of the plate structure, but also result in the increase of contact resistance and contamination of the CCMs, especially for SS materials [5,49,59–61]. Meanwhile, SS typically contains Cr which will be oxidized into a passive layer of Cr_2O_3, particularly at the anode of PEMECs; then the passive layer will lead to a higher interfacial contact resistance (ICR). ICR is of great importance for the performance of PEMECs or PEMFCs, and the target of US Department of Energy is 20 mΩ cm^2 [59,62,63]. A higher ICR will lead to a faster increasing in working voltage with the increment of working current density, and the efficiency will be reduced, and the electricity costs will be increased [53].

Herein, in order to use AM parts at both the anode and cathode sides in PEMECs, we proposed a protective coating on AM SS BPs for high-efficiency and low-cost PEMECs. The BPs were firstly printed using selective laser melting (SLM) technologies, then the BPs were coated with gold by electroplating to form a protecting layer, as shown in Fig. 1b. Compared with traditional BPs, the AM plates not only have a greatly simplified fabrication processes, but also help to lower the cost and provide a rapid prototyping process. In *ex-situ* tests, the Au-coated AM SS BPs show a very low ICR, 6.4 mΩ cm^2 under 1.4 MPa, compared with the bare AM SS BPs and graphite BPs. In *in-situ* tests, those AM SS BPs are incorporated into both the anode and cathode sides in PEMECs, and an excellent performance is achieved even at a high current density. The durability test also indicates the Au-coated AM SS BPs are suitable for highly corrosive environment. The results suggest that AM technologies combined with protective coatings have a potential to rapidly produce high-efficiency and low-cost integrated energy conversion devices with better performance, and will facilitate the design and improvement of those devices.

2. Experimental details

2.1. Additive manufacturing of BPs

The BPs were designed using SOLIDWORKS 2016, and exported as *.STL files that were sliced for printing by Materialise Magics 20. The printing process was conducted in a laser powder bed Renishaw AM250 printer with SS 316L powder. During printing, a roller or wiper spread the SS powder uniformly over the build platform to form a powder bed, then the laser will selectively irradiate and melt the powder layer by layer (Fig. 1b). This process took approximate only 1.4 h for 5 BPs. Conditions used during printing include laser power (200 W), focus offset (0 mm), layer thickness (50 μm), point spacing (60 μm), exposure time (80 μs), and hatch spacing (110 μm). The average beam velocity was 0.64 m/s, and a stripe melting mode (5 mm) was used. The BP surface was rough right after printing, and needed to be ground with grinding papers (SiC grindings paper #150–2400, BUEHLER).

2.2. Gold protective coating

For the gold electroplating on stainless steels, there are 3 steps, including electro-cleaning, electro-striking, and electro-plating. And the AM SS BPs received the negative charges during all the steps. During electro-cleaning, 4% solution of sodium hydroxide was heated to 60 °C to remove the contamination and oxide, and the SS BPs were immersed in the solution as a cathode at 6 V and 60 °C for 30 s. The surfaces of SS plates were totally hydrophilic with no water beads or breaks after the first step.

For electro-striking, TriVal - 24K Acid Gold Strike solution (TV128, Gold Plating Services) was used to pre-treat the SS surface at 7 V and 25 °C for 45 s, shown in Fig. 2a. In the solution, the pH was lower than 1, and the effective component was $KAu(CN)_4$, which allowed the electroreduction of gold occurred directly on the bare AM SS BP