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Thin liquid/gas diffusion layers for high-efficiency hydrogen production from water splitting ☆

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HIGHLIGHTS

- A novel thin titanium LGDL is developed based on nanomanufacturing.
- Superior multifunctional performance for hydrogen production is obtained.
- Thin, flat, and straight-pore features significantly reduce the total resistance.
- Thin LGDLs provide new directions for reducing weight/volume, and lowering cost.
- Well-tunable pore morphologies will be very valuable for developing PEMEC models.

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ABSTRACT

In this study, a novel titanium thin LGDL with well-tunable pore morphologies was developed by employing nano-manufacturing and was applied in a standard PEMEC. The LGDL tests show significant performance improvements. The operating voltages required at a current density of 2.0 A/cm^2 were as low as 1.69 V, and its efficiency reached a report high of up to 88%. The new thin and flat LGDL with well-tunable straight pores has been demonstrated to remarkably reduce the ohmic, interfacial and transport losses. In addition, well-tunable features, including pore size, pore shape, pore distribution, and thus porosity and permeability, will be very valuable for developing PEMEC models and for validation of its simulations with optimal and repeatable performance. The LGDL thickness reduction from greater than 350 μm of conventional LGDLs to 25 μm will greatly decrease the weight and volume of PEMEC stacks, and represents a new direction for future developments of low-cost PEMECs with high performance.

1. Introduction

Hydrogen, as a proven energy carrier, is becoming increasingly attractive and is currently undergoing rapid advancement, since it can be generated from clean and sustainable energy sources at low-temperature water electrolysis. A proton exchange membrane electrolyzer cell (PEMEC) is an advanced, reverse PEM fuel cell (PEMFC), and is a key element of an effective energy storage solution that produces both hydrogen and oxygen from water. This is mainly due to its quick response, high energy density and efficiency, easy to scale up and scale down, large capacity, and ability to use the energy from sustainable and renewable energy sources [1–13]. PEMECs are robust and may be coupled with PEMFCs in order to create highly efficient regenerative energy systems [5,14–19]. A PEMEC mainly consists of two electrodes separated by a catalyst-coated membrane (CCM). At the anode, deionized water is circulated through microchannels to the membrane electrode assembly (MEA) where oxygen evolution reaction occurs and the deionized water is split into oxygen, protons and electrons

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[4,20,21]. The protons are then transported through the membrane, react with electrons from an external electrical load, and form hydrogen gas at the cathode, which exits through the microchannel. Meanwhile, the oxygen is transported out of the anode along with the deionized water.

In the PEMEC, as shown in Fig. 1, a liquid/gas diffusion layer (LGDL) is one of key components, and is sandwiched by the catalyst layer and the current distributor/flow field, similar to one in PEMFC [5,19,22,23]. Its major functions are to conduct electrons and heat, and transport reactants/products to and from the reaction site with minimal activation, thermal, ohmic, interfacial, and fluidic losses [5,24–36]. To meet these requirements, the LGDL has to provide:

- Simultaneous liquid/gas permeabilities: reactants (liquid water) access the reaction sites from flow fields, and products of H_2/O_2 from reaction sites move into flow channels, which reduce their local concentration to improve the performance;
- Electrical and thermal conductivities: conduct electrons away from the reaction sites at anode and meanwhile supply electrons to all reaction sites at cathode, and maintain efficient heat transport and uniform heat distribution;
- Interfacial and mechanical properties: high-corrosion resistance and excellent contacts with the adjacent parts (bipolar plate and catalyst layer), also maintain small effect on pressure drops in the flow channel.

Carbon-based materials (carbon paper, or carbon cloth), which are typically used for LGDLs in PEMFCs [8,37–43], are unsuitable for PEMECs due to the high operating potential and the highly oxidative environment of the oxygen-rich electrode [7,44]. The corrosion and consumption of the carbon will degrade the LGDL and result in bad conductivity and poor interfacial contacts, consequently decrease the performance and efficiency of PEMECs. In order to counteract this impact, materials with high-corrosion resistance have been explored. One such material with desirable properties for use as the LGDL in the anode of a PEMEC is titanium [6,44], which is a highly promising structural/functional material in aerospace, marine, nuclear, electronics, medical implements, implants and instruments due to its high corrosion resistance even at high positive overpotential, highly acidic and humid conditions. In addition, it has good thermal/electrical conductivities and excellent mechanical properties. Currently, titanium meshes/felts/foams are mainly utilized as LGDLs at the PEMEC anode side. Its thickness is larger than 300 μm with significant electrical conductive path and fluidic resistance. In addition, their random structures make it impossible to control the water/electron/thermal distribution and their complicated pore morphology results in unusual interfacial contact resistance.

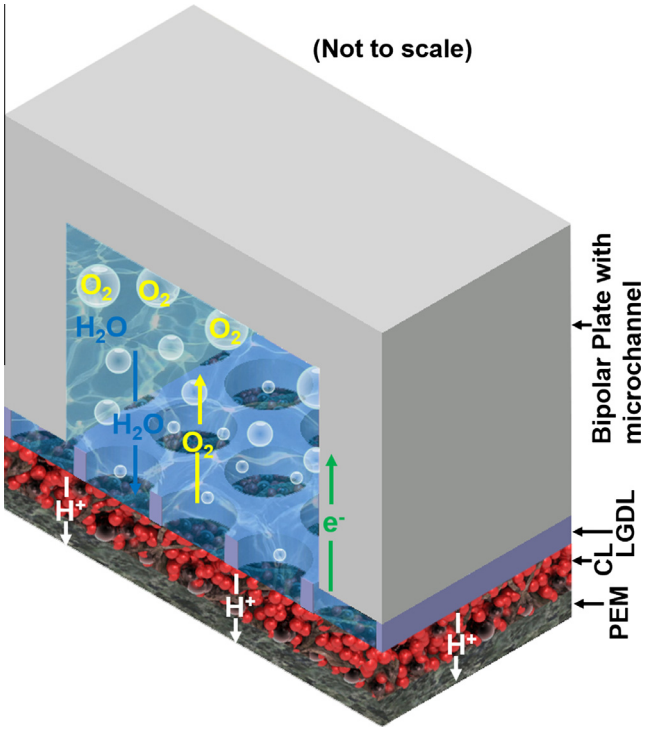

Fig. 1. Schematic of LGDL functions at the anode of PEMECs.

With the development of micro/nanotechnology, which has the advantages of high precision, good repeatability, and less raw material, several solutions for improved thermal and electrical conductivity, mass transport, and permeability will become possible. In this study, a new titanium, thin, LGDL with well-tunable pore morphologies is developed by using micro/nano-manufacturing. Both experimental evaluations of the electropotential performance and electrochemical impedance in an applied PEMEC are conducted with this new LGDL, and the test results are compared with a conventional LGDL. It has been demonstrated that thin/well tunable LGDLs remarkably reduce the ohmic, interfacial and transport losses, and achieve a superior multifunctional performance. Prospects for future LGDL development and optimization in PEMEC are also discussed.

2. Experimental details

2.1. Nano-manufacturing of titanium thin/well-tunable LGDLs

Although titanium has a lot of advantages to be chosen as a promising raw material for LGDLs, such as high corrosion resistance, excellent electric conductivity and good mechanical properties, the material itself is difficult to fabricate with the conventional methods. Currently, with the developments of additive manufacturing, 3D printing is capable to fabricate LGDLs with relatively plane surfaces in prototypes, however, it is still expensive and time-consuming for large-volume commercial application. In addition, it has great challenges for precise manufacturing with micro and submicro features. Photochemical machining of thin titanium foils seems the most efficient way to massproduce the titanium thin/well-tunable LGDLs, since it has the advantages of high precision, good repeatability, and less raw material. The titanium thin/well-tunable LGDLs are manufactured from thin foils by using lithographically patterned masks and chemical wet etching method with nanofabrication facilities [45]. A typical fabrication procedure for titanium thin LGDL begins with the design and fabrication of the photomasks, which is the most important step to control the pore size, pore shape and porosity. A mask pattern was designed using commercially available CAD/VLSI software (LayoutEditor, layouteditor.net). The design pattern was imported into a Heidelberg DWL 66 laser lithography system and patterned on a soda-lime glass mask plate that is pre-coated with chromium and photoresist. After patterning, the masks were developed for 1 min in Microposit® MF® CD-26 Developer (Shipley Company, Marlborough, MA), rinsed with DI water and dried with N_2. Masks were then submerged in chrome etchant for 2 min, rinsed with DI water and dried with N_2. The remaining resist was subsequently removed in a heated bath (70 °C) of N-Methyl Pyrolidone (NMP). Masks were rinsed with DI water and dried with N_2. As shown in Fig. 2, in order to provide structural integrity of the extremely thin titanium foil, foils were affixed to a silicon wafer during processing. Substrate were treated with Microprime P20 Primer (Shin-Etsu MicroSi, Inc., Phoenix, AZ) adhesion promoter