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

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This manuscript has been co-authored by UT-Battelle, LLC, under Contract No. DE-AC0500OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for the United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (<http://energy.gov/downloads/doe-public-access-plan>).

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/cm² 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.

Keywords: proton exchange membrane fuel cells/ electrolyzer cells, liquid/gas diffusion layers, hydrogen production, water splitting, performance and efficiency

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 [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 Figure 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.

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

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.

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 minute in Microposit® MF® CD-26 Developer (Shipley Company, Marlborough, MA), rinsed with DI water and dried with N₂. Masks were then submerged in chrome etchant for 2 minutes, rinsed with DI water and dried with N₂. 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 N₂. As shown in Figure 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 by coating the substrate with adhesion promoter, waiting for 10 seconds and spin-drying the samples at 3000 RPM for 45 seconds. Subsequently Microposit SPR220 photoresist (Rohm and Haas, Marlborough, MA) was spin-coated onto samples at 3000 RPM for 45 seconds. The titanium film was then placed on the resist coated silicon wafer with special care due to its delicate features, and soft baked at 115 °C for 90 s. A second layer of P20 and SPR 220 photoresist was applied to the titanium foil under identical conditions, and after heating to 115 °C for 90 s, exposed to UV light using conventional contact photolithography. They were then developed in Microposit® MF® CD-26 Developer (Shipley Company, Marlborough, MA), rinsed with DI water and dried with N₂. Finally, after patterning the photoresist mask on the foil, the patterned material was etched in HF.

Figure 2. Typical fabrication process for titanium thin LGDLs

2.2. Test system and *in-situ* characterizations

A standard PEMEC was used for conducting the designed experiments. It has two endplates, which are made from commercial grade aluminum to provide even compression on the cell. In order to apply a current to the cell, a copper plate was inserted at the cathode as a current distributor. The bipolar plate was manufactured from graphite with a parallel flow field to distribute the flow over the active area of the cell. The catalyst-coated membrane is comprised of Nafion 115, a perfluorosulfonic polymer with a thickness of 125 μm , an anode catalyst layer with an IrRuOx catalyst loading of 3 mg/cm^2 , and a cathode layer with a platinum black (PtB) catalyst loading of 3 mg/cm^2 . The cell was compressed by eight evenly distributed bolts, which were tightened to 40 in-lb. of torque during assembly. The electrolyzer had an active area of 5 cm^2 and was operated at a temperature of 80 $^{\circ}\text{C}$.

The PEMEC was connected to a modular potentiostat system with a current booster, which can operate under a current range of up to 100A and a voltage range of up to 5V. The hardware was connected to Bio-Logic software, EC-Lab, which was used to conduct performance testing and electrochemical impedance spectroscopy (EIS). While the cathode tubing was employed to safely exhaust hydrogen gas that formed during electrolysis, water was circulated through the anode of the PEMEC at a constant volumetric flow rate of 20 ml/min by a diaphragm liquid pump from KNF Neuberger.

For the performance evaluation, a constant current was applied to the PEMEC, while the required voltage was measured. The current density was increased from 0 A/cm^2 to 2 A/cm^2 in steps. At each current density, the potential of the cell was measured for five minutes before incrementing the current density again. Five minutes was chosen as an acceptable amount of time, after which the cell potential remained stable.

Electrochemical impedance spectroscopy (EIS) was used for measuring the impedance of the PEMEC at different operating conditions. In this method, the current is controlled as opposed to the potential. It can run under an operating current of -100A to +100A and a voltage of 0V – 5V. The current precision was 100 fA. The scanning frequency was varied from 15 kHz to 10 mHz, and we recorded 15 points of data per decade. For analyzing impedance data, a Nyquist plot is normally used.

2.3. *Ex-situ* characterizations

The ex-situ characterizations of LGDLs were performed with a Hitachi S-4800 FEG Scanning electron microscopy (SEM) equipped with a cold cathode field emission column emitter. Ultra-high resolution and high image quality was obtained at low operating voltage ~1.4 nm at 1 KV (1 nm at 15 KV). It can be operated under a wide voltage range of 100V to 30 KV. It was employed to observe uncoated samples by a beam deceleration option and used In-lens SE and BSE detection at low voltages. Samples were loaded on AGAR scientific conductive carbon tabs and put into the vacuumed instrument. Images were captured under acceleration voltages of 15 kV and were collected by built in Quartz PCI image acquisition and processing software.

3. Results and Discussion

3.1. *Ex-situ* characterization of titanium conventional and novel thin LGDLs

The morphological characteristics of the liquid/gas diffusion layers used in testing were characterized using a field emission SEM. Figure 3 details SEM images of conventional titanium felt and newly designed titanium thin LGDLs, respectively. The surface structures and pore morphologies between titanium felt LGDL and thin LGDL are obviously different. The titanium felt LGDL has a thickness of 350 μm with a fiber diameter of about 20 μm . Its average pore size and porosity are around 100 μm and 0.78, respectively. The felt LGDL shows random pore shapes

and pore distributions. The new thin LGDL is manufactured from a titanium thin foil with a thickness of about 25 μm . Its pore size, pore shape, and pore distribution are well controlled. With flat surface feature, its pore size and porosity are 100 μm and 0.3, respectively.

Figure 3. SEM Images of titanium conventional and thin LGDLs with similar pore size (a) titanium felt LGDL with average pore size of 100 μm and porosity of 0.78; (b) titanium thin LGDL with a pore size of 100 μm and porosity of 0.30.

3.2. PEMEC performance and efficiency

Both the new thin LGDL with well-tunable micro-pores and the conventional felt LGDL were evaluated in a standard PEMEC. They were applied as anode LGDLs, while the Toray – 090 carbon papers were used on the cathode sides in the PEMEC tests. The relationship between current density and voltage is a critical measure of the performance of the PEMEC, with lower voltage for a given current density indicating better performance. Figure 4 shows the PEMEC performance curves with both the thin/well tunable LGDL (red color), and conventional felt LGDL (black color) under the same operating conditions. The operating voltages needed for both LGDLs are increased with the current densities, while much lower voltages were needed for new thin LGDLs. At a current density of 2 A/cm^2 , the needed voltage is reduced from 1.88V with

conventional titanium felt LGDL to 1.69V with new thin LGDL, which reaches the new-low among the recent publications[9, 27, 46-48].

The efficiency of the PEMEC, η , can be calculated as following,

$$\eta = \frac{V_{thermal}}{V_{cell}} \quad (1)$$

where V_{cell} and $V_{thermal}$ are the PEMEC operating voltage and theoretical thermal voltage, respectively. Under the operating conditions with a temperature of 80°C and a pressure of 1 atm, $V_{thermal}$ is about 1.4841V [49, 50]. As shown in Figure 4, at a current density of 2 A/cm², the PEMEC efficiency is increased from 79% with the titanium conventional felt LGDL to 88% with titanium thin/well tunable LGDL. The efficiency is much better than a recent report with a best efficiency of 82% [7].

Figure 4. Performance comparisons of PEMEC with titanium thin LGDL and conventional LGDL (red colour: titanium thin/ well tunable LGDL with thickness of 25 μ m, pore size of 100 μ m and porosity of 0.30; black color: titanium felt LGDL with thickness of 350 μ m, average pore size of 100 μ m and porosity of 0.78)

3.3. Electrochemical impedance spectroscopy results

The *in-situ* EIS testing was conducted with both titanium conventional felt and new thin LGDLs. Figure 5 shows their EIS results at a fixed current density of 0.2 A/cm². Over the frequency range from 15 kHz to 10 mHz, there is one big arc. The high-frequency resistance, which mainly represents total ohmic resistance, is the leftmost intersection point of the arc with the real axis at the high-frequency end. It includes the ohmic resistances of all electrolyzer components, including bipolar plates, diffusion media, electrodes and membranes, and the associated interfacial resistances between them. As shown in Figure 5, the impedance representing total ohmic resistances significantly decrease from 0.18 $\Omega \cdot \text{cm}^2$ with a conventional titanium felt LGDL of 350 μm thickness to 0.076 $\Omega \cdot \text{cm}^2$ with a titanium thin LGDL of 25 μm thickness. These results show that a thicker titanium felt LGDL with complicated surface structures have higher total ohmic losses, thus degrading the PEMEC performance, as shown in Figure 4. Between these two results, only anode LGDLs have been changed in the experiments. So the differences of total ohmic resistances are only due to the change from the bulk titanium felt to nanomanufactured thin titanium film. The new thin LGDL with simple flat surface results in great reduction of its associated ohmic resistances and interfacial resistances. It has been indicated that the LGDL thickness and interfacial structures at a fixed material dominate the total ohmic resistance, thus playing crucial roles on PEMEC performance.

The thickness of novel designed titanium thin LGDL is much less than the conventional titanium felt LGDL, which definitely will reduce the ohmic resistance. More importantly, the surface structure of titanium thin LGDL and titanium felt LGDL are quite distinct. The titanium felt LGDL is made of titanium fibers, and its interfacial contacts with the catalyst layer and the bipolar plate (BP) is mainly due to curved surfaces of titanium fibers with plane surfaces of CLs and BPs. On

the other hand, since the novel titanium thin LGDL is etched from a flat thin foil, its interfacial contacts with the catalyst layer and the bipolar plate have been improved due to the planar surfaces. Those plane-surface contacts significantly reduce the CL/LGDL/BP interfacial resistances, which dominate the total ohmic resistances in a PEMEC[10, 50]. This is the main reason that the total ohmic resistance with titanium thin LGDL is significantly lower compared to the titanium felt LGDL, which agrees with the result of EIS test as shown in Figure 5.

Figure 5. EIS comparisons of PEMEC with titanium thin etched LGDL and conventional LGDL (red colour: titanium thin/ well tunable LGDL with thickness of 25 μm , pore size of 100 μm and porosity of 0.30; black color: titanium felt LGDL with thickness of 350 μm , average pore size of 100 μm and porosity of 0.78)

With the nanomanufactured thin LGDLs, the true electrochemical reactions in both micro spatial and time scales are revealed by introducing a high-speed and microscale characterization system and innovative design of electrochemical PEM electrolyzer cells in our group[51]. The functions of LGDL essentially consist of (1) conducting electrons between electrodes and current

distributors, (2) transport liquid water from micro channels to reaction sites, and (3) allow diffusion of gaseous oxygen to the flow channel. So the LGDL can be developed and optimized after considering those critical functions. With optimal designs of thickness, porosity and pore size/shape, a better PEMEC performance can be achieved with thin structured LGDLs by taking advantage of well-tunable and straight-through micropores, while maintaining excellent properties for two phase flow in LGDLs. For conventional LGDLs of titanium felts with interconnect pore structure at a thickness of 350 μm and a mean pore size of about 100 μm , liquid water needs large capillary pressure to get through the titanium felt LGDL and reach the interfaces of LGDL and the catalyst layer -the reaction sites , which has been demonstrated with two-phase modeling in our group [50]. In addition, the thickness reduction of the felt-based LGDLs has been limited by felt diameters, felt loading quantities, and required LGDL electrical/mechanical/interfacial properties, as addressed previously. To meet the fundamental requirements of multifunction, conventional LGDLs have been challenged to be thinner than 200 μm [52]. On the other hand, with nanomanufactured thin titanium LGDLs, even under the same pore size of 100 μm , the two-phase transport resistances are significantly reduced because of their straight-through micropore features and a thickness of about 25 μm . As shown in Figures 4 and 5, a total resistance reduction of LGDL will make it possible to decrease the PEMEC operating voltage and enhance its performance. In addition, with LGDL straight-through micropore features, precise controls of pore size, pore shape, pore distribution, and therefore porosity and permeability, can be easily obtained with advanced manufacturing technologies, including 3D printing, which has been successful demonstrated [24]. The plane-surface features of LGDLs allow the easy integration with other components, and will make it possible for one single part to act as LGDL, bipolar plate, flow field, and current distributor/collector simultaneously. Therefore, this development of thin titanium LGDLs will lead

to reducing the cost, volume, and weight of the LGDL and the system as a whole. Its well-tunable features, including pore size, pore shape, pore distribution, and thus porosity and permeability, will be very valuable for developing PEMEC models and to validating simulations of PEMECs with optimal and repeatable performance as well. The thin and well-tunable LGDL with straight-pore features, which results in less two-phase transport resistances across the LGDL, could also be applied in PEMFC to alleviate the floodings for better water management. Coupled with micro-porous layers at CL sides and in-plane transport layers at BP sides, outstanding PEMFC performance could be achieved.

4. Conclusion

Titanium thin and well-tunable liquid/gas diffusion layers (LGDLs) with flat interfacial surfaces are developed and applied into a PEMEC for the first time, and exhibit superior multifunctional performance over conventional LGDLs. The operating voltages at a current density of 2.0 A/cm^2 were as low as 1.69 V with an efficiency of up to 88%. In order to gain better understanding the mechanisms, both the *ex-situ* and *in-situ* characterizations were conducted and they showed the thin and well-tunable LGDL with flat surface features remarkably reduced its total resistances, and significantly promoted the PEMEC performance and efficiency by over 9%. Additionally, the LGDL thickness reduction from 350 μm of conventional LGDLs to 25 μm will greatly decrease the weight and volume of PEMEC stacks, which can lead to new directions for future developments of low-cost PEMECs with higher performance. Its well-tunable features, including pore size, pore shape, pore distribution, and thus porosity and permeability, will be very valuable for developing PEMEC models and to validating simulations of PEMECs with optimal and repeatable performance. The comprehensive investigation of the thin LGDL optimization on pore

morphologies, including pore sizes, pore shapes, pore distributions and porosities, and their associated modeling are under way.

Acknowledgments

The authors greatly appreciate the support from U.S. Department of Energy's National Energy Technology Laboratory under Award DE-FE0011585. The research was partially performed at ORNL's Center for Nanophase Materials Sciences (CNMS), which is sponsored by DOE Office of Basic Energy Sciences. The authors also wish to express their appreciations to Dr. Bo Han, Stuart Steen, Alexander Terekhov, Douglas Warnberg, Kate Lansford, Andrew Mays, and Rong Chen for their help.

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