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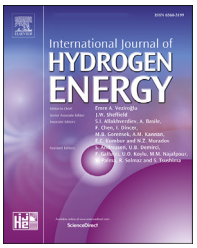

Developing titanium micro/nano porous layers on planar thin/tunable LGDLs for high-efficiency hydrogen production

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ABSTRACT

Proton exchange membrane electrolyzer cells (PEMECs) have been considered one of the most promising devices for hydrogen generation and energy storage from water splitting, especially when coupled with sustainable energy resources. Microporous layers (MPLs), which have been widely used in fuel cells for better catalyst access and product/reactant removal, have limited investigations in PEMECs due to harsh environments and carbon corrosion. In this study, the MPLs with both irregular micro (~5 μm) and spherical nano (30–50 nm) titanium particles are developed on novel thin/tunable liquid/gas diffusion layers (TT-LGDLs) and are investigated comprehensively both *in-situ* and *ex-situ* for the first time. The MPLs change the wettability of the TT-LGDLs and show super hydrophobic property. The results reveal that micro particle MPLs exhibit improved catalytic activity but increased ohmic resistances, and that nano particle MPLs do not impact catalytic activity meaningfully but exhibit even greater increases in ohmic resistance. The effects of the thickness of the MPLs are also investigated and the typical MPL is also studied by *in-situ* visualization in a transparent PEMEC with a high-speed and micro-scale visualization system (HMVS). The results indicate the strong feasibility of the TT-LGDLs with small pore size and large porosity for high-efficiency and low-cost PEMEC practical applications.

Introduction

Hydrogen is regarded as an ideal energy carrier, due to its high energy density and zero emission, either greenhouse gas or criteria pollutant during its usage [1–6]. Therefore, the high-efficiency and robust hydrogen production devices for energy storage or conversion are strongly desired. The proton exchange membrane electrolyzer cell (PEMEC), which works

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in reverse of proton exchange membrane fuel cells (PEMFCs), is considered as one of the most promising methods to store the sustainably-produced energy, especially for the electricity generated from intermittent energy sources, such as solar, wind, tide, or hydro [7–15]. PEMECs can mitigate the impact of electricity fluctuations from the intermittent sources and consumers' needs, and alleviate the energy waste within the current grid by storing the excess electricity during low demand and release the energy during high demand period. More importantly, it can be used to generate very high purity hydrogen/oxygen gas in an environmentally friendly way with high efficiency, which is beneficial for future storage and applications [2,16–21].

PEMECs mainly consist of a proton exchange membrane (PEM) that is sandwiched by two electrodes. At each electrode, there is a catalyst layer (CL), a liquid/gas diffusion layer (LGDL), a bipolar plate (BP) with flow channels, and a current distributor [7,22,23]. The heart of a PEMEC is the membrane electrode assembly (MEA), which consists of the PEM, CLs and LGDLs, and it has a great impact on the PEMEC performance [24]. The LGDLs, located between the CLs and BP, control the flow of reactants and products to and from the catalyst layer, and have to meet certain requirements, such as high corrosion resistance, good electrical conductivity, and small mass transport losses [18,25,26]. Due to the high potential seen at the anode (~2 V), the most widely used LGDLs are titanium (Ti) based materials, such as Ti felt, Ti mesh, or sintered Ti particles [26–30]. These LGDLs share similar properties, including random pore size and pore shape, large thickness, complex water/gas transport path, uneven surface, etc., which lead to large ohmic resistances, poor interfacial contact, large two-phase transport losses, all of which ultimately limit PEMEC performance. Much attention has been paid to reduce the interfacial contact resistance between the CLs and LGDLs, and different methods have been proposed and studied in both PEMFCs and PEMECs [31–34]. It is well known that introducing a micro-porous layer (MPL) between the nano-structured CLs and macro-structured gas diffusion layers (GDLs) at the cathode of PEMFCs can greatly improve its performance, durability, and stability. The MPL serves to decrease the interfacial contact resistance, protect the membrane from being punctured by GDL fibers, and promote water/gas transport [35–42].

Nam et al. have proposed two effects of MPLs in water management in PEMFCs. They found that the MPLs can reduce the size and saturation level of the interfacial water droplets on CL surface, and reduce the number of water breakthroughs toward GDL in PEMFCs [33]. Chen et al. developed MPLs in PEMFCs to examine its effects and mechanisms of water management under a wide range of operating conditions. They found that the effects and mechanisms of MPLs were closely related to humidity and temperature [36]. Su et al., on the contrary, eliminated the MPLs from the GDL in PEMFCs to achieve high performance under high temperature [31]. Zhang et al. firstly fabricated a metallic gas diffusion layer with well-controllable pore morphologies and a thin MPL on it. They showed the PEMFC performance improvement mainly due to the in-plane transport enhancement [43–45]. Kumbur et al. and LaManna et al. studied two-phase transport through the microporous layer, catalyst layer, thin diffusion media, and their interfaces, and found more hydrophobicity in MPLs will result in less flooding [46,47]. LaManna et al. further investigated DM|MPL|CL interfacial effects thoroughly. While very little has been reported on the role of MPLs in PEMECs [48]. P. Lettenmeier et al. developed a MPL for PEMECs by thermally spraying Ti particles on sintered Ti filters. They found that the MPL has a moderate impact on the PEMEC performance when the current density was below 1.2 A/cm^2, while the MPL can greatly improve the performance under high current density ranges by reducing the interfacial contact resistance and mass transport limitations [32]. P. Lettenmeier et al. also developed a novel pore-graded GDL for water electrolyzers, which has similar MPL effects in PEMECs. They found that proper novel GDL structures developed by vacuum plasma spraying method could significantly decrease the mass transport limitation which provided a new direction for LGDL structure design and fabrication [49]. J. Polonsky et al. developed an MPL on Ti felt with antimony-doped tin oxide (ATO) mixed with Nafion solution, and improved performance was achieved in the voltage range dominated by charge transfer kinetics. They also concluded that a more conductive MPL could greatly enhance the PEMEC performance [50]. C. Lee et al. investigated the behavior or oxygen bubble growth during PEMEC operation by using a PTL-on-Chip. They found the importance of the throat sizes of the PTL during bubble growth and suggested a modified PTL structure for reducing the average gas saturation in PTL, which provided a deep understanding for the relation between the PTL microstructure and oxygen bubble behavior [51]. Grigoriev et al. conducted an optimization of porous current collectors. The optimum porosity and mean pore size value were investigated of porous titanium plates formed by thermal sintering of spherically particles. According to his research, the mean pore size of the particles and the thickness of the titanium plates have a significant effect on performances. They pointed out that the optimum spherical particle sizes are 50–75 μm and the optimum pore size value is 12–13 μm [52].

Recently, we reported a novel thin/tunable LGDLs (TT-LGDLs), which has a thickness of only 25 μm, well controlled pore morphologies (including pore shape, pore size, and porosity), and planar surface with straight-through pores, as shown in Fig. 1(A) [53,54]. These TT-LGDLs can achieve superior PEMEC performance compared to the current state-of-the-art, and the cell voltage can be as low as 1.63 V at 2.0 A/cm^2 and 80 °C with a commercial Nafion 115 CCM (3.0 mg/cm^2 IrRuOx at anode and 3.0 mg/cm^2 Pt black at cathode and 5 cm^2 active area), and the performance of TT-LGDLs can be further enhanced by thin film surface modifications (the cell voltage can be reduced from 1.685 V to 1.633 V by introducing a 180 nm Au thin film on TT-LGDL surface) [54,55].

Based on our previous discoveries, the oxygen evolution reaction (OER) sites can be identified by the formation of oxygen bubble nucleation sites, which were found to occur at the rim of the TT-LGDL pores due to the large in-plane electrical resistance of the CL and the difficult two-phase transport under the TT-LGDL land area [24,53,56]. Therefore, it seems that large amounts of catalyst located in the pore area and under the TT-LGDL land area is inactive or underutilized to some extent. By introducing the MPLs between the CLs and TT-LGDLs, as shown in Fig. 1(B), it is anticipated that more OER

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