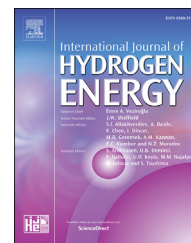


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Mechanism of improving oxygen transport resistance of polytetrafluoroethylene in catalyst layer for polymer electrolyte fuel cells

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ARTICLE INFO

Article history:

Received 14 November 2017

Received in revised form

8 January 2018

Accepted 12 January 2018

Available online 20 March 2018

Keywords:

Polytetrafluoroethylene

Catalyst layer

Oxygen transport resistance

Limiting current

Knudsen diffusion

Pore size distribution

ABSTRACT

Oxygen transport resistance of catalyst layer (CL) has significant impact on the performance for polymer electrolyte fuel cells (PEFCs). Nano-Polytetrafluoroethylene (PTFE) particles are added into CL to improve the oxygen transport resistance. The CV curves indicate that PTFE do not reduce the utilization of Pt. The I–V polarization curves suggest that the performance incorporated PTFE in CL gradually improve at high current densities and the output is 0.57 V at 1.8 A cm⁻², 70 mV higher than that without PTFE. The water contact angle for CL with 20 wt% PTFE shows that continuous hydrophobic network may not be formed at 150 °C heat treatment temperature. The total transport resistance of CL with PTFE decreases about 2.5% at 70 °C and 250 kPa, mainly caused by the reduction of pressure-independent resistance (R_{other}). In the R_{other} reduction, the Knudsen diffusion resistance reduction in CL account for 74%. The pore size distributions reveal that the porosity increases 29% and the proportion of pores at around 100 nm increases for primary pores in CL with PTFE. This finding indicates that not the hydrophobicity of PTFE but the porous structure conducive to Knudsen diffusion for CL plays the predominant role in improving the performance.

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Introduction

High performance polymer electrolyte fuel cells (PEFCs) for automotive propulsions have been regarded as an ideal and the most promising alternative to replace fossil fuel based internal combustion engines. Over the last two decades, the performance of PEFCs has been improved significantly [1–4].

However, barriers for the wide use of PEFCs are still present. Cost and durability are supposed as the main challenges or bottlenecks to the development and commercialization of PEFCs. Pt is commonly used as electrocatalytic material, while its scarcity-induced high cost is one of the obstacles for widespread application of PEFCs [5–7]. Reducing Pt loading and improving operating current density are two effective

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<https://doi.org/10.1016/j.ijhydene.2018.01.091>

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solutions. However, both of them suffer from a serious voltage loss at high current density. At high current densities, the formation of liquid water inside catalyst layer (CL) can substantially reduce oxygen transport to Pt surface and cause a significant voltage drop due to oxygen transport limitations. This phenomenon has been confirmed by Toyota, Nissan, and General [8–12]. Therefore, it is very important to improve oxygen transport at high current density to realize PEFCs commercial application.

The oxygen transport pathway in PEFCs is complicated, involving various transport mechanisms including convection in flow field, molecular diffusion and Knudsen diffusion in gas diffusion layer (GDL), Knudsen diffusion and diffusion through ionomer film in CL [13]. Previous research works have shown that limiting current method can be applied to quantitatively analyze oxygen transport in PEFCs and the GDL accounts for 50% of the total resistance [14]. In the few last years, considerable efforts have focused on modifying GDL to improve oxygen transport [15,16]. For examples, Wang et al. have investigated that the double-layer gas diffusion media with different PTFE loading can mitigate liquid water saturation and further improve oxygen supply to the CL [17]. Lu et al. have reported that the microporous layer (MPL) modified by laser perforation can significantly reduce oxygen transport resistance when water condenses in electrode [13]. However, the oxygen transport resistance in CL is close to 50% [18] and even becomes more and more prominent with decreasing Pt loading [19]. The related studies about optimized CL to improve oxygen transport are relatively few. Gasteiger et al. have confirmed that the CL can be optimized by introducing surface groups containing nitrogen to decrease oxygen transport resistance at high current density [20]. Many researchers have proved that polytetrafluoroethylene (PTFE) [21–23] and fluorinated ethylene propylene (FEP) [24] added into CL can improve the performance, which ascribes to the hydrophobicity of hydrophobic materials at ca. 150 °C heat treatment temperature. Because the melting temperature of PTFE is ca. 327 °C, PTFE is commonly used to bind the catalyst particles and form a hydrophobic structure at 340–370 °C heat treatment temperature [25–27]. While the degree of crystallinity in ionomer is generally less than ca. 10 wt% and the glass transition temperature of ionomer is ca. 140 °C [28,29]. The sulphonate functionality on the ionomer can be lost in the temperature range of 275–380 °C [30]. Thus, the heat treatment temperature is controlled at ca. 150 °C when the ionomer is used to bind the catalyst particles. Taking above factors into consideration, the hydrophobic materials added into CL may improve the CL hydrophobicity slightly, but the continuous hydrophobic network of PTFE may not be formed when the CL modified by PTFE is treated at low temperature (ca. 150 °C). Therefore, the hydrophobic improvement of CL by PTFE may not be the main reason for performance improvement.

In this work, the nano-PTFE particles are added into cathode CL to improve the oxygen transport resistance. And limiting current method is applied to analyze the mechanism of improving oxygen transport resistance of PTFE in CL for PEFCs. Moreover, the contact angle is applied to study the hydrophobicity and the pore size distributions are characterized to further clarify the structural change.

Experimental

Preparation of membrane electrode assembly (MEA)

Nano-PTFE particles were first dispersed in isopropyl alcohol to form PTFE solution. Then, ionomer solution (20 wt%, EW 750, Asahi Kasei) was slowly dropped into PTFE solution under ultrasonication and the mixtures actually displayed sticky colloid. The final mixtures of catalyst (60 wt% Pt/C, Tanaka, TKK), water and the sticky colloid were fully mixed to form a homogeneous slurry, which was spread on Teflon membrane and dried out as cathode. The proportion of Pt/C, ionomer and PTFE in dried catalyst layer were 60, 20 and 20%, respectively. Then the cathode and anode catalyst layers were transferred from Teflon membranes onto proton exchange membrane (PEM) using decal technology to form the catalyst coated membrane (CCM) by hot pressure at 150 °C, 1.5 MPa and 150 s. After the Teflon supports were peeled away, CCM was sandwiched between two GDLs to form the MEA finally. As comparison, MEAs which cathode without PTFE had the same Pt loading and ratio of Pt/C and ionomer were also prepared as cathode, The CLs of anode were same for all MEAs. The GDL was consisted of carbon paper and MPL. The specifications of MEAs are shown in Table 1.

Physical characterization

The morphologies of the samples were performed on field-emission scanning electron microscope (FESEM, Nova Nano-SEM 450). The contact angle was tested by OCA35 Automatic contact angle measure device. The pore size distributions of CCM were acquired on autopore 9500.

Electrochemical characterization

Rotating disk electrode technique was used to analyze the electrochemical performance of the catalyst on an electrochemical workstation (CHI660E) with a rotating system (Pine Research Instruments, USA). First, Pt/C catalyst (60 wt%, TKK) and PTFE were dispersed in a mixed solvents of ultra-pure water (18 M Ω cm), isopropyl alcohol and ionomer solution (5 wt%, Asahi Kasei) to form a homogeneous slurry by ultrasonication. The proportion of dry matter for Pt/C, ionomer and PTFE in slurry were 60, 20 and 20%, respectively. Then the slurry was dropped uniformly onto a 5 mm diameter glassy carbon electrode, which was used as working electrode. Pt piece and reversible hydrogen electrode (RHE) were applied as counter electrode and reference electrode, respectively. Cyclic voltammetry (CV) was performed from 0.05 to 1.2 V with a scan rate 50 mV s⁻¹ in 0.1 M N₂-saturated HClO₄ solution and oxygen reduction reaction (ORR) polarization curves were obtained in O₂-saturated electrolyte from 0.1 to 1.1 V with a scan rate of 5 mV s⁻¹ and rotation rate of 1600 rpm.

Fuel cell performance tests were conducted on the HTS-125 fuel cell test station (HEPHAS, Scribner Associates 890e Fuel Cell Test System). All MEAs were conditioned by scanning current until the constant performance were reached. The current densities were added from zero to 1.2 A cm⁻² in 0.1 A cm⁻² steps and each step remained 2 min. When the

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