Electrochimica Acta 56 (2011) 9064–9073

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Fabrication of microstructure controlled cathode catalyst layers and their effect on water management in polymer electrolyte fuel cells

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ARTICLE INFO

Article history:
Received 8 February 2011
Received in revised form 30 May 2011
Accepted 31 May 2011
Available online 13 June 2011

Keywords:
Polymer electrolyte fuel cells
Membrane electrode assembly
Cathode catalyst layer
Water management
Microstructure

ABSTRACT

Although cathode catalyst layers (CCLs) are at the center of water management in polymer electrolyte fuel cells (PEFCs), the understanding of water movement in CCLs and their roll on fuel cell performance is still limited. In this present study, several CCLs with controlled microstructure, including main pore size, pore volume and porosity ranging from 30 to 70 nm, 0.443 to 0.962 $cm^3/g_{Pt/C}$, and 45.4 to 64.4%, respectively, were prepared by changing the hot-pressing pressure in a decal process, and their water management ability and cell performance were evaluated. The electrochemical analyses reveal that, as the pore size and pore volume of CCLs increase, the diffusion resistance mainly arising from water accumulation in the pores is evidently reduced by capillary water equilibrium, which leads to better cell performance. Water balancing between accumulation and discharging in the pores also depends on the CCL pore structure, and the CCLs with greater pore sizes and larger pore volumes reveal more stable cell performance by better water management in steady state operation, even under extremely humid conditions. Based on these MEA technologies such as fabrication of CCLs, further study will be performed to understand microscopic phenomena in nano pores of CCLs by combining the experimental approach with CCL numerical modeling.

1. Introduction

Hydrogen has been regarded as a promising future energy that can substitute for fossil fuels; hence, much attention has been paid to polymer electrolyte fuel cells (PEFCs) utilizing hydrogen energy due to their unique advantages and potential as energy conversion devices for portable, mobile and stationary applications [1]. However, the PEFC technology has suffered from several technical barriers, such as high cost, material durability and water and heat management [2,3]. Particularly, the water management in PEFCs is a difficult process that significantly impacts the overall system performance and reliability. Too much water in the cell hinders gas transport to the electrode catalyst, leading to significant performance loss; however, too little water in the cell produces significant ohmic resistance due to membrane dehydration, resulting in low cell performance [4]. Hence, a large number of studies for the water transport and balance in PEFCs have been performed for a gas diffusion layer/microporous layer (GDL/MPL) [5–11], a gas flow channel [12–14], and water visualization [15–26], but many controversial issues still remain, mainly due to complex water phase changes and movements in a PEFC. Recently, the water management problems have focused on cathode catalyst layers (CCLs), where the oxygen reduction reaction (ORR) occurs. Although the CCLs have similar microstructure with MPL, the studies on the CCLs have been scarce, accordingly, the understanding on the water behavior in the CCL microstructure has been limited, mainly due to the difficulty in investigating the water movements occurring together with complex physicochemical reactions relating to ORR such as proton and electron transfer, gas diffusion, and water and heat generation in nano-scale CCL pores. However this means the understanding of the CCL microstructure and its role on water management is critical to enhance the cell performance.

Recent approaches to understand the CCL microstructures and their role in water behavior have begun with numerical modeling studies [27–34]. Eikerling's CCL model focused on the CCL pore characteristics, such as pore size distribution (PSD), porosity and wetting properties, to explain water movements and their effect on PEFC performance [27,28]. The studies reported that different wetting states of the CCL can be made by different liquid water accumulation driven by capillary water equilibrium in nano-scale CCL pores, depending on the pore characteristics and fuel cell operating conditions, which is critical for cell performance by affecting oxygen transport in the CCLs. A mesoscopic, two-phase model has also been developed by Mukherjee et al. to describe the

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doi:10.1016/j.electacta.2011.05.123

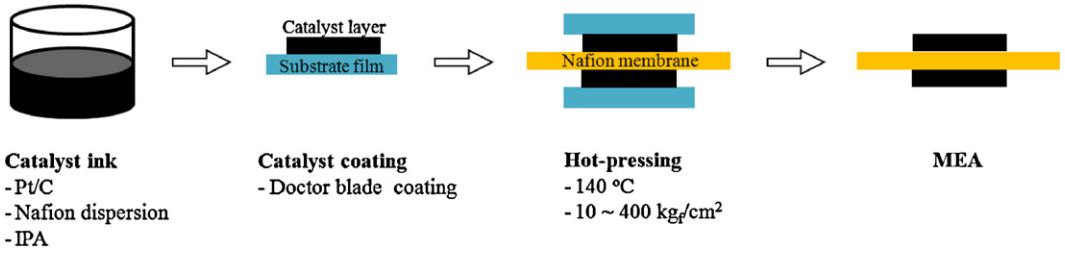

Fig. 1. Schematic procedure of MEA preparation by decal transfer process.

structure-wettability influence on the liquid water transport and flooding dynamics in the CCL [29]. The model proposed that liquid water flooding be processed as a transition from capillary fingering to a stable displacement pattern in CCLs. The same group also reported a direct numerical simulation (DNS) model to describe the proton transport through a random catalyst layer microstructure and predicted the optimal composition of catalyst layer as 0.4 of porosity and as 0.26 of ionomer volume fraction [30]. Similarly, Siddique and Liu developed 3D mathematical model including the Knudsen diffusion of oxygen in nano-pores and proton transport in thin-film electrolytes and proposed that there is a threshold in both porosity and ionomer weight fractions that affects the electrochemically active area (ECA) and species transport in CCLs [31]. Agglomerate cathode models have also been developed to optimize catalyst layer structure parameters, such as ionomer film thickness and agglomerate size, focusing on proton transport in catalyst layers, without considering liquid water accumulation in the catalyst layer [32–34].

These recent studies of CCL models, however, do not have experimental verification, mainly because of the difficulty in fabricating microstructure-controlled CCLs and monitoring complex physicochemical phenomena occurring in the CCLs. Some recent experimental approaches have tried to measure the liquid water content [35] and oxygen partial pressure [36] in CCLs for better understanding of oxygen and proton transport. However, those studies mainly focused on the experimental measurement of water content and oxygen concentration in a specially designed gas diffusion electrode (GDE), hence, having some limitations to represent real phenomena in MEAs.

In the present study, microstructure-controlled CCLs were prepared by the decal transfer process [37–42]. The decal process is useful for continuous fabrication of a membrane electrode assembly (MEA), leading to uniform and reproducible catalyst layers [43]. The decal method requires a hot-pressing process to transfer the catalyst layer to the membrane in a wide range of temperatures (130–210 °C) and pressures (100–450 kg_f/cm^2) [37–42]. It was expected that the CCL microstructure can be controlled by changing the hot-pressing conditions, and a hot-pressing process that covers wide ranges of pressures (10–400 kg_f/cm^2) can be useful. Actually, by changing the hot-pressing pressure, microstructures of the CCLs, such as porosity, PSD, pore volume and catalyst layer thickness, are controlled based on the same carbon materials and constant CCL compositions such as Pt loading and ionomer content. The prepared CCLs were tested with respect to their fuel cell performance and water management ability, and the experimental results for better understanding of the water behavior in the CCLs and its role in cell performance were explained based on several previous studies on CCL numerical models.

2. Experimental

2.1. Preparation of MEAs

A decal process [37–42] was used to prepare all MEAs used in this study as depicted in Fig. 1. Catalyst inks were prepared by mixing catalyst powder (40 wt.% Pt/C, Johnson Matthey Fuel Cells), Nafion dispersion (Dupont Fuel Cells), and isopropyl alcohol. The ink was coated onto a decal substrate by a doctor blade film applicator, producing a coating with a thickness of about 100 μm. The decal was fully dried in an oven and hot-pressed onto a Nafion 212 membrane at 10–400 kg_f/cm^2 and 140 °C. During the hot pressing process, the catalyst on the decal was transferred to a Nafion 212 membrane surface, forming a MEA. The Pt content was controlled in the range of 0.3–0.4 mg/cm^2, which was calculated by weighting the decal before and after catalyst transfer. All the catalyst layers contain 70 wt.% Pt/C and 30 wt.% Nafion, which is the optimized content in the present decal-MEA. Specifications of the prepared MEAs are summarized in Table 1.

2.2. Electrochemical measurements

2.2.1. Cell operation

Polarization characteristics of the MEAs with microstructure controlled CCLs were evaluated in a single fuel cell, consisting of an MEA with an active area of 25 cm^2, flow field plates made of graphite, gas diffusion layers (GDL, SGL 10BC), gaskets, and current collectors derived from gold coated copper blocks. The cell temperature was set to 70 °C, and humidified H_2 and air with 100% RH were fed into the cell under ambient pressure. The RH value was controlled by changing the humidifier temperature, and the dew points of the gases were confirmed by a humidity sensor (Viasensor HS-1000).

Table 1
Specifications of MEAs prepared at different hot-pressing pressures.

MEA	Hot-pressing pressure (kg_f/cm)	Hot-pressing temperature (°C)	Pt content (mg/cm^2)		Ionomer content (wt.%)
			Cathode	Anode	
MEA-10	10	140	0.42	0.30	30
MEA-100	100	140	0.38	0.28	30
MEA-200	200	140	0.39	0.28	30
MEA-400	400	140	0.41	0.30	30
MEA-10-L	10	140	0.30	0.29	30
MEA-100-L	100	140	0.31	0.28	30
MEA-200-L	200	140	0.31	0.30	30
MEA-400-L	400	140	0.32	0.30	30