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Tailoring cathode structure of catalyst coated membranes for performance enhancement in direct methanol fuel cells

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ABSTRACT

In this study, we demonstrate how the formulation of colloidal catalyst ink and fabrication conditions affect the cathode microstructure of catalyst coated membranes (CCMs) prepared via decal technique. The CCMs based on conventional and high concentration cathode inks are compared in a direct methanol fuel cell (DMFC). It is found that the cathode catalyst layer made with a high concentration ink possesses superior porosity, leading to an improved DMFC performance. The temperature of roll-press used for preparing CCM is varied ranging from 170 to 210 °C in order to determine the optimal fabrication conditions for high concentration ink-based cathode. The CCM hot-pressed at 200 °C (advanced CCM) retains a significantly higher pore volume and outperforms the conventional CCM by delivering an excellent DMFC performance with a maximum power density of 155 mW cm⁻², which is 20% higher than that of the conventional CCM.

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Introduction

Direct methanol fuel cells (DMFCs) hold considerable promise for powering a variety of small- and medium-range electronic devices for various applications [1]. In order to gain widespread market acceptance, however, DMFC technology must be competitive with other existing technologies in terms of fuel conversion efficiency, operational lifetime, and manufacturing cost. Over the past several years, gradual advances in performance and durability of DMFC systems have been realized by the introduction of either new or modified component

materials and by structural improvements in the membrane electrode assemblies (MEAs) as well as by the optimization of operating conditions [2–7]. MEAs play a key role in determining the performance and operational stability of DMFCs. A standard MEA structure is a multilayer composite mainly consisting of anode and cathode catalyst layers (CLs), a polymer electrolyte membrane (PEM), and gas diffusion layers (GDLs). CLs can either be coated onto GDLs or directly onto the membrane to form a catalyst coated membrane (CCM) configuration.

Generally, CCM-type MEAs, hereafter referred to as CCMs, are preferred in fuel cell operations due to their superior

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performance and stability, because the direct coating of CLs onto the membrane renders an intimate CL-membrane interfacial contact, which enhances catalyst utilization [8,9]. CCMs can either be prepared by spraying catalyst inks directly on both sides of a membrane or by a decal transfer technique. In the decal process, catalyst layers are first coated on inert substrate films (generally inert polymer materials such as PTFE or polyimide films, etc.), which are subsequently transferred onto both sides of a membrane through a hot-pressing step [10,11]. This method is feasible for a roll-to-roll manufacturing process for preparing CCMs in large volume; however, some technical challenges must be resolved for the optimization of this process.

The decal CCMs when used in low-temperature DMFCs generally exhibit inferior performance by comparison with their direct-spray counterparts [5,12,13]. The CCM preparation by decal transfer technique results in the formation of thinner CLs with a lower porosity in contrast with those prepared via direct spray where the catalyst layers are thicker and have superior pore structures [5]. During the operation of DMFCs, there is a large amount of water present in the cathode, a major fraction of which comes from the anode that uses a diluted aqueous methanol solution as fuel [14]. In such a situation, a cathode CL with a dense structure can cause large mass transport resistance to air diffusion to and water removal from the cathode, which decreases the DMFC performance. The issue of ionomer segregation in catalyst layers encountered in the decal process also contributes to their inferior porosity. During the coating of catalyst layers on inert polymer substrates, the ionomer tends to diffuse towards the substrate due to strong hydrophobic interactions between the backbone of the ionomer and the substrate material [15]. As a result, the ionomer content in the outer part of a CL (that faces the flow channel) becomes higher (it can even form a thin ionomer film), which hinders the transport of reactant and product species. Several approaches have been tried to improve the pore structure of decal cathodes: using less hydrophobic materials as decal substrates for avoiding ionomer segregation in a CL; modification of the coating process; and the optimization of hot-pressing conditions and addition of pore forming agents [15–18]. While some of these approaches have proven beneficial in modifying the pore structure of cathode CLs, they can make the overall CCM fabrication process more complicated and time consuming, as in the case of the addition of pore formers.

Another noteworthy point is that nearly all of the reported studies have used very similar compositions of colloidal catalyst inks for fabricating CCMs regardless of whether a decal process or the direct spray method was employed, although these techniques have different characteristic features. However, the potential impact of the concentration of colloidal inks for regulating the pore structure of decal CCMs has largely been ignored. A proper concentration adjustment of colloidal catalyst ink is a crucial parameter as it directs the dispersion of catalyst nanoparticles and ionomer in the colloidal suspension and their interactions with each other, which eventually affects the morphology of catalyst agglomerates and resultant catalyst layers.

In the present work, we have shown that performance of decal CCMs can be upgraded by optimizing the preparation

conditions such as the formulation of colloidal catalyst ink and adjustment of hot-pressing temperature. The concentrated colloidal ink forms large and porous catalyst agglomerates and the resultant cathode CL exhibits a highly porous microstructure. With an optimization of the hot-pressing temperature, the CCM having a modified (advanced) cathode exhibits considerably improved performance compared with the CCM whose cathode was prepared using a conventional dilute ink. Sophisticated electrochemical and physicochemical analysis techniques such as SEM, TEM, mercury porosimetry and DMFC performance tests have been used to characterize the cathode catalyst layers.

Experimental

Preparation of catalyst coated membranes

All the catalyst coated membranes (CCMs) were fabricated via decal transfer [19]. Anode colloidal catalyst ink was prepared by mixing PtRu black catalyst (HiSPEC™ 6000, Johnson-Matthey) with de-ionized water and isopropyl alcohol (IPA) solvents in a catalyst-to-solvent ratio (catalyst:water:IPA) of 1:8:5 by weight. An ionomer content of 10 wt.% (dry ionomer basis with respect to catalyst) was used by adding a 5 wt.% Nafion ionomer solution (DuPont). Anode catalyst layers were prepared by spraying anode catalyst ink on polyimide (Kapton®) substrates that were pre-coated with thin carbon black layers. The total anode PtRu loading was 3.0 mg cm^{-2} . This anode catalyst layer (CL) composition was used for all CCMs tested in this work.

Three colloidal ink compositions with different catalyst-to-solvent ratios were used to prepare the cathode catalyst layers. All cathode inks were prepared by mixing Pt black catalyst (HiSPEC™ 1000, Johnson-Matthey) with 5 wt.% Nafion ionomer solution (DuPont) and solvents (de-ionized water and IPA). The catalyst-to-solvent ratios (catalyst:water:IPA) were 1:8:5, 1:5:5 and 1:2:3 by weight for the conventional (dilute), intermediate concentration, and concentrated colloidal inks, respectively. The same ionomer content of 10 wt.% (dry ionomer basis with respect to catalyst) was used for all ink compositions. The catalyst concentrations in the conventional, intermediate concentration, and concentrated colloidal inks were 6.25, 7.69, and 12.5 wt.%, respectively. The composition of conventional colloidal ink used in this work has been optimized and generally used as a reference in our laboratory for preparing all types of MEAs. A similar ink composition is reported in Ref. [20]. The purpose of reducing the solvent content in the other two ink compositions was to significantly enhance the concentration of cathode colloidal ink. Cathode CLs were prepared by spraying these three types of catalyst inks onto Kapton® substrates. The cathode Pt loading was 2.0 mg cm^{-2} irrespective of the types of inks used.

The geometric area of the anode and cathode electrodes was 10.89 cm^2 ($3.3 \text{ cm} \times 3.3 \text{ cm}$). In preparing the CCMs, the anode and cathode CLs were coated on the decal substrates and then transferred to each side of a Nafion®115 (DuPont) membrane via hot-pressing, which was carried out using a roll-press machine under an applied pressure of 3 MPa at a temperature of 170°C and with a roller speed of 50 mm min^{-1} .

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