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Fabrication of catalyst coated membrane with screen printing method in a proton exchange membrane fuel cell

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ABSTRACT

A new proton exchange membrane fuel cell catalyst paste based on direct screen printing was developed to fabricate membrane electrode assembly (MEA) with catalyst coated membrane (CCM) technique. A mixture of cyclohexanol and ethylene glycol was found to be the best solvent for the screen printing catalyst paste in terms of avoiding the swelling of K⁺ form Nafion[®] membrane and mud-cracking in the catalyst layer during the CCM-MEA fabrication process and improving adhesion between the Nafion[®] membrane and catalyst layers. The CCM-MEAs fabricated with this new catalyst paste with the direct screen printing method showed better or comparable performance with the same or much less catalyst loading compared with that of MEA fabricated with a gas diffusion electrode (GDE) technique. An empirical relationship was provided to determine the amount of solvents used for the catalyst paste. Criteria were also proposed to choose the potentially suitable solvents. The other factors which might affect the performance of the screen printed CCM-MEAs were also examined. The low cell voltage decay rate and the relatively high performance of the screen printed CCM-MEAs demonstrated that the direct screen printing method with the proposed new catalyst paste could be a beneficial complement to the conventional CCM fabrication technique.

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Introduction

Proton exchange membrane fuel cells (PEMFCs) have long been considered most promising for vehicular, backup power and portable applications due to their unique features like quick start-up, low operation temperature, high efficiency,

high power density, and zero emission. However, there are still many challenges to meet before PEMFCs can be commercialized. High cost is one of the issues which hinder the commercialization of PEMFCs. Typically, about 80% of the total cost of a 50-kWe fuel cell stack comes from membrane electrode assemblies (MEAs), which are an essential part of a proton exchange membrane fuel cell [1]. Fabrication methods

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that can make MEAs perform well with relatively low catalyst loading are critical for the commercialization of PEMFCs. MEAs can be categorized as two types: three-layer MEA without gas diffusion layers (GDLs), which is fabricated with catalyst coated membrane (CCM) technique; five-layer MEA with GDLs, which is prepared with gas diffusion electrode (GDE) technique. The two types of MEAs are called CCM-MEA (or just CCM) and GDE-MEA, respectively. In the early days, MEAs were fabricated with a Pt black/Teflon[®] or carbon supported Pt/Teflon[®] mixture [2–5]. Srinivasan et al. drastically reduced the catalyst loadings of MEAs from 4 mg cm⁻² to 0.35–0.5 mg cm⁻² by impregnating the catalyst sides of GDEs with a 5 wt% Nafion[®] solution before hot pressing the GDEs to H⁺ form Nafion[®] membrane [6], in which method Nafion[®] served as an ionic conductor while Teflon[®] served as a binder. Srinivasan et al.'s seminal work demonstrated the importance of Nafion[®] content in the catalyst layer. Therefore new catalyst layer structures were developed by Wilson and Gottesfeld to maximize the Pt catalyst utilization by using H⁺, Na⁺, or tetrabutylammonium solubilized ionomer/catalyst suspension to form a thin catalyst layer on H⁺, Na⁺, K⁺ form Nafion[®] membrane, thin Teflon[®] film [7–9], or Kapton polyimide film [10]. Wilson and Gottesfeld's method of MEA preparation eliminated the use of Teflon[®] binder in the catalyst layer. The solubilized Nafion[®] in the catalyst layer worked both as a binder and as an ionic conductor. In Wilson and Gottesfeld's "ink" or "suspension", the solubilized Nafion[®] could also be changed to "colloid" Nafion[®] by adding organic solvents which had an intermediate dielectric constant of $3 < \epsilon < 10$. It was reported by Uchida et al. that a good network and uniformity of Nafion[®] on Pt particles could be achieved by using "colloid" form of Nafion[®] in the catalyst "ink" [11]. Kim et al. presented a new CCM-MEA fabrication method by hot pressing Pt/C catalyst layer into a pre-formed sheet made from perfluorosulfonyl fluoride powder (a precursor for perfluorosulfonate polymer) [12]. Usually the Wilson and Gottesfeld's "ink" is either sprayed, inkjet-printed onto a membrane or a decal, which is referred to as a CCM technique, or sprayed onto a gas diffusion layer (carbon paper, carbon cloth, etc), which is otherwise referred to as a GDE technique. Wilson and Gottesfeld's creative idea of using solubilized Nafion[®] in the catalyst ink has been widely accepted and used for the fabrication of high-performance MEAs with both CCM technique and GDE technique by researchers in the fuel cell community [12–39]. Sputter deposition technique [40–45], pulse electrodeposition technique [46], dry preparation method [47,48], and electrophoretic deposition technique [49,50] were also investigated for the fabrication of MEAs earlier. However, nowadays the direct spraying method and the decal transfer method based on the conventional ink/suspension with low aliphatic alcohols as solvents have been used predominantly for the fabrication of CCM-MEAs [51–80]. It has been reported that MEA fabricated with decal transfer or thin film decal process demonstrated better performance compared with that fabricated with GDE technique [81]. Since the CCM technique based on decal transfer process requires a hot pressing step, which may degrade the Nafion[®] membrane, especially when the Nafion[®] membrane is very thin ($\leq 50 \mu\text{m}$). It could be better and more convenient to apply the catalyst ink directly onto the Nafion[®] membrane instead of onto the

decal and transferring the catalyst ink on the Nafion[®] membrane. Since a CCM technique based on a slurry or paste tends to be efficient and fast and only a doctor blade method based on catalyst slurry has been reported recently [82], more research needs to be done on it. In this work, a direct application process involving both a catalyst paste and a screen printing kit was first reported. Criteria for choosing right solvents and determining appropriate amount of solvents for the catalyst paste were proposed. The effects of paste composition on catalyst loading and post-treatment on transient behavior of CCMs were also investigated.

Experimental

The screen printing paste was prepared by mixing the carbon supported Pt (40 wt% Pt/C, E-TEK, Inc.), Nafion[®] solution, organic solvent(s) together. The paste was first ball-milled for 24 h and then was put into a small plastic vial with a cap. The small vial with the paste was then put into a high-speed mixer (FlackTek Speedmixer™) for 1 min to form a homogeneous screen printing paste. The weight ratio of carbon supported Pt to Nafion[®] was kept at 1:0.35 [77]. The amount of organic solvent(s) used for 1.0 g E-TEK 40 wt% Pt/C catalyst was found to be less than 12 mL to form a paste. Otherwise, the paste would be too "dilute" to stay on the mesh of a screen printer. Usually the mixing of catalyst and organic solvent(s) is done in N₂ environment to avoid the undesirable "ignition" of Pt/C catalyst. Some air or N₂ may be entrapped in the catalyst paste during the mixing. The entrapped air and N₂ may form bubbles and cause some defects in the resultant catalyst layer when the catalyst paste was applied to the Nafion[®] membrane with the screen printer. An ultrasonic sonication process can help break and remove the air or N₂ bubbles in the catalyst paste. In this work, the sonication time for the screen printing catalyst paste was 15 min.

Cracks or crevices are often seen on the surface of catalyst layers of CCM-MEAs fabricated with conventional direct application process. Mud-cracking is usually caused by shrinkage taking place on the surface of the catalyst layers during the drying process. Inks or paste with fast-evaporating solvents (water, lower aliphatic alcohols, etc) are more prone to mud-cracking. Slow-evaporating solvents with high dielectric constant ($\epsilon > 10$) would be used to make Nafion[®] to stay in solution form [11]. Conventional Nafion[®] solution (5 wt %, EW = 1000, Ion Power, Inc.) always contains water and lower aliphatic alcohols. To remove the fast-evaporating solvents in the conventional Nafion[®] solution, the as-received Nafion[®] solution was put in a glass beaker and heated on a hot plate (Schott Instruments GmbH) at 80 °C till it was reduced to 30% of the original volume, then a slow-evaporating solvent would be added to the glass beaker till the original volume was attained and would be heated at 80 °C till the new Nafion[®] solution was reduced to 30% of the original volume. The slow-evaporating solvent would be added to the glass beaker again and reheated under the same condition. After this step, no water and lower aliphatic alcohols were assumed to be present in the new Nafion[®] solution except the slow-evaporating organic solvent. A series of slow-evaporating organic solvents had been investigated for the

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