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Effect of MO_2 (M = Ce, Mo, Ti) layer on activity and stability of PtCo/C catalysts during an oxygen reduction reaction

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ABSTRACT

The performance of PtCo/C catalysts in the presence of a metal oxides layer for an oxygen reduction reaction (ORR) was investigated. Different types of metal oxides (CeO_2, MoO_2 and TiO_2) and metal loadings (0.03–0.45 mg/cm^2) were incorporated on the PtCo/C catalyst layer. Their activity was analyzed in acid solution and proton exchange membrane (PEM) fuel cell under a H_2/O_2 environment at 60 °C and ambient pressure, while the stability was tested in an N_2-saturated H_2SO_4 solution using repetitive potential cycling. It was found that the addition of metal oxides on a catalyst layer had no influence for PtCo/C morphology. However, they significantly affected the electrochemical surface area (ESA), internal contact resistance (ICR) and hydrophilic/hydrophobic properties of the catalysts layer. Furthermore, they significantly affected the ORR activity and stability in acid solution and PEM fuel cell operation. Among all studied metal oxides, the TiO_2 exhibited the best property for use as the catalyst interlayer in PEM fuel cell for both activity and stability enhancement.

1. Introduction

The PEM fuel cell is an electrochemical apparatus that produces electricity effectively and continuously in the presence of continuous reactant feed with zero emission of contaminants [1]. To facilitate the utilization and commercialization of PEM fuel cells, their cost and reliability/durability have to be addressed. Their major cost can be attributed to the utilization of an expensive Pt metal as the catalyst in the electrode layer [2]. Thus, many researchers have been developed the new types of fuel cell catalysts such as non-Pt catalysts [1,3–8], Pt-based catalysts [9–12] and non-precious metal composite electrocatalysts [13–15] as a means to reduce fuel cell cost. Among these, the most promising catalysts are the nanostructured Pt-alloy catalysts because they can enhance activity levels to a high degree when compared with pure Pt catalysts [16]. The Pt–Co alloy catalyst is the most interest because it showed the highest fuel cell performance and more stable than other Pt–M alloys (M = V, Ni, Fe) [17,18]. The loss of fuel cell durability is principally caused by the loss of fuel cell components: catalyst, membrane or bipolar plate [19], which can be alleviated by using appropriate material to fabricate a fuel cell or appropriate operating conditions. Another strategy that can extend the lifttime and activity of fuel cells is the water management strategy [20]. This is because accumulation of excessive water in fuel cells leads to flooding, which causes low accessibility of reactant to the reaction zone, particularly at high current. However, too low water in fuel cells results in dry out of the membrane, which causes sluggishness of proton transfer to the membrane as well as damage of cell components. Thus, various water management strategies have been developed to optimize water content in a fuel cell, particularly in the catalyst layer. The addition of a conductive material plate with perforations between the flow field plate and electrocatalyst substrate can enhance the operational life of a PEM fuel cell for no humid conditions [21]. This then leads to improvement of water management in fuel cells. The mesoporous hydrophobic channels, made as a tubular open-ended mesopores through the catalysts with addition of PTFE nanoparticles, can reduce the concentration loss at high current of the PEM fuel cell owing to its capability for water removal [20]. The incorporation of a double-layer cathode gas diffusion media (GDM) with high PTFE content in the fuel cell can improve the ability of water management as it can reduce the overall saturation level and voltage fluctuations [22]. The addition of a GDL coated with hydrophilic carbon in microporous layer exhibited an ability to conserve membrane humidity under low humidity conditions due to its ability to expel

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Nomenclature

j_k	kinetic current density (mA/cm^2)
j	current density (mA/cm^2)
ω	rotation rate (rpm)
n_e	number of involved electrons
F	Faraday's constant (96,485 C/mol)
D	diffusion coefficient of oxygen in solution (1.9×10^{-5} cm^2/s)
v	kinematics viscosity (0.01 cm^2/s)
C	oxygen concentration in the bulk solution (1.1×10^{-6} mol/cm^3)

water and maintain oxygen on electrocatalyst electrode [23]. In previous work of Chaisubanan et al. [24], the PtCo/C catalyst with TiO_2 in mixed phase of anatase and rutile could improve the hydrophilic property of PtCo/C catalyst layer and had significant effect on the PEM fuel cell performance in middle to high voltage than that of PtCo/C catalyst with TiO_2 in rutile phase.

In the present study, the various types and loadings of the MO_2/PtCo/C catalyst (M = Ce, Mo, Ti) were investigated to determine their effect on water management in the PEM fuel cell. The ORR activity and stability of all prepared catalysts were also explored. This is because they have different hydrophilic/hydrophobic properties and, as mentioned previously, the interface of Pt and metal oxide are the ORR active sites [25]. It was then expected that these properties of metal oxides would facilitate a high ORR activity as truly as the stability of PEM fuel cell.

2. Experimental

2.1. Preparation of catalyst-coated membrane

The PtCo/C catalyst was produced by $H_2PtCl_6 \cdot 6H_2O$ (Sigma–Aldrich) and $CoCl_2 \cdot 6H_2O$ (Kanto Chemical) as the precursors and $NaBH_4$ (Labchem) as the reducing agent. The method of the preparation was same as research of Chaisubanan et al. [24] as shown in Fig. 1.

To prepare the catalyst-coated membrane, the mixture of PtCo/C catalyst and distilled H_2O was sonicated at approximate 30 °C for 30 min. Sequentially, Nafion solution (5 wt%, Fluka) and *i*-propanol (99.99%, Fisher) were added and sonicated for 1 h to obtain catalyst ink with a catalyst to Nafion weight ratio of 67:33 [26]. Afterward, the ink was sprayed slowly onto the Nafion membrane 115 at 80 °C by a spray gun (Crescendo, Model 175-7™) and left at room temperature to dry the catalyst layer for a few minute. This method was repeated to obtain a metal of 0.15 mg/cm^2 and dried at the same temperature for 10 min. For an anode side, the commercial 20 wt% Pt/C (ETEK) was applied by the same method at identical Nafion content and catalyst loading (0.15 mg/cm^2).

2.2. Preparation of metal oxide-coated PtCo/C catalyst

Three types of commercial metal oxides, including TiO_2 (P25 Degussa, Sigma–Aldrich), MoO_2 (Sigma–Aldrich) and the as-prepared CeO_2, prepared by the calcination of $Ce[NO_3]_3 \cdot 6H_2O$ (Sigma–Aldrich) at 600 °C for 90 min [27] were used in this study. To incorporate commercial TiO_2 and CeO_2 on the catalyst layer at different loadings of 0.03, 0.06, 0.15, 0.30 and 0.45 mg/cm^2, 0.4, 0.8, 1.5, 3.0 and 5.0 mg of either TiO_2 or CeO_2 were mixed with 6 mL of *i*-propanol and sonicated 15 min at ambient temperature. For MoO_2, a similar quantity of MoO_2 as TiO_2 and CeO_2 were dispersed in 6 mL of ethanol (Merck) and resonicated for 30–60 min. Sequentially, the metal oxide slurry was applied on the PtCo/C catalyst layer by direct spray. Finally, the ready-to-use metal oxide-coated PtCo/C catalyst (MO_2/PtCo/C) was obtained after drying at 80 °C for 30 min.

2.3. Preparation of membrane electrode assembly (MEA)

The MEA was fabricated by a conventional process, and described in Chaisubanan et al. [24]. In brief, the sublayer ink-coated GDL was formulated by mixing of deionized water, 60%

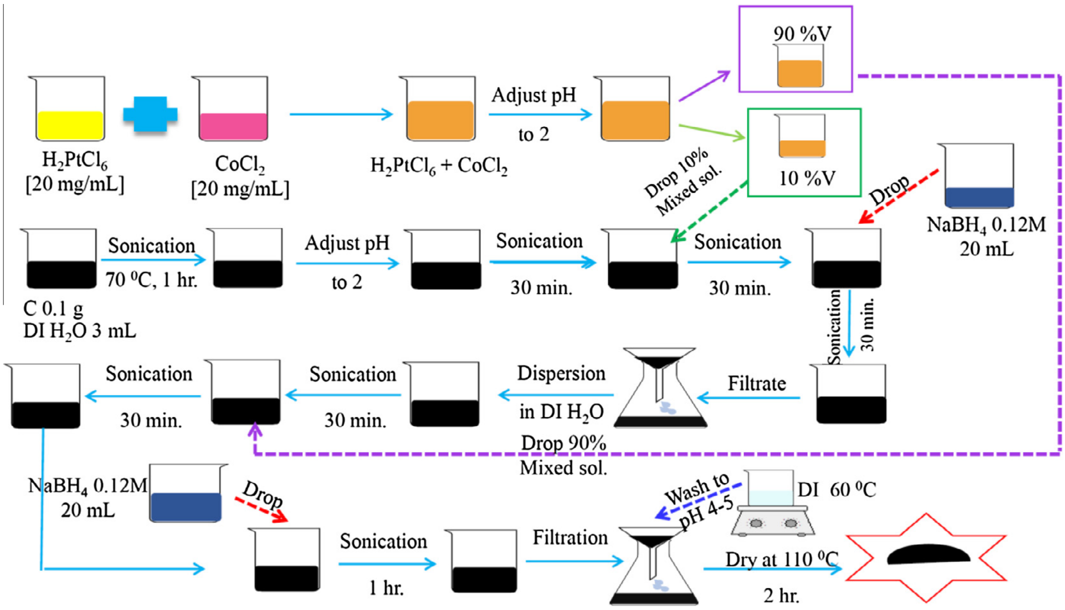

Fig. 1. Schematic representation of 30 wt% PtCo/C catalyst preparation by the seeding and impregnation method.