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Effect of MO₂ (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 (CeO₂, MoO₂, and TiO₂) and metal loadings (0.03–0.45 mg/cm²) were incorporated on the PtCo/C catalyst layer. Their activity was analyzed in acid solution and proton exchange membrane (PEM) fuel cell under a H₂/O₂ environment at 60 °C and ambient pressure, while the stability was tested in an N₂-saturated H₂SO₄ 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 TiO₂ exhibited the best property for use as the catalyst interlayer in PEM fuel cell for both activity and stability enhancement.

Keywords:
PtCo/C catalyst
PEM fuel cell
Metal oxide
Titanium dioxide

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 lifetime 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...
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$_2$PtCl$_6$·6H$_2$O (Sigma–Aldrich) and CoCl$_2$·6H$_2$O (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$_2$O 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 TM) 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$_3$)$_3$·6H$_2$O (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%

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**Nomenclature**

- {$j_k$} kinetic current density (mA/cm$^2$)
- {$j$} current density (mA/cm$^2$)
- {$\omega$} 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$^3$)

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**Fig. 1.** Schematic representation of 30 wt% PtCo/C catalyst preparation by the seeding and impregnation method.
(w/w) polytetrafluoroethylene, i-propanol and treated carbon in ultrasonic bath at the ambient temperature for 30 min. The ink was brushed on a GDL (carbon cloth, ETEK) several times to get the loading of carbon of ~2.0 mg/cm². After that, it was dried 1 h at 300 °C to remove an excess solvent. Afterward, the catalyst coated membrane (Section 2.1) was pressed between coated GDL sheets by a compression mold at 65 kg/cm² and 137 °C for 2.5 min and cool pressed at ambient temperature for 2.5 min.

2.4. ORR activity test

The ORR activities of all catalysts were tested by a rotating disk electrode (RDE) in H₂SO₄ solution saturated with oxygen and in the PEM fuel cell with H₂/O₂ environment. The other test was carried out in the fuel cell environment by mounting the MEA obtained from Section 2.3 on commercial hardware and testing in a test station at 60 °C and ambient pressure. The 100 scm of humidified H₂ and O₂ were fed into the anode and cathode, respectively. Prior to drawing the current, the cell was run at high current density (>700 mA/cm²) for a certain period. Subsequently, the current was drawn between the open circuit potential (OCP) to 0.1 V and demonstrated in terms of a performance curve or current-density-potential curves. For the activity test in H₂SO₄ solution, the catalyst ink prepared was coated on the circular GDL with 1 cm diameter, assembled with the RDE using as a working electrode. A Pt gauze and the saturated calomel electrode (SCE) were used as the counter and reference electrodes respectively. The 0.5 M H₂SO₄ in the potential range of −0.58 to 0.02 V with scan rate of 1 mV/s using the LSV program connected with the Potentiostat/Galvanostat (PGSTAT 30, Autolab). The as-prepared catalysts were used as working electrode, a Pt gauze was used as counter electrode and saturated calomel electrode (SCE) was used as reference electrode.

In this work, all experimental data were obtained from 3 experiments with the accepted error of less than 3%.

3. Results and discussion

3.1. Physical and chemical characterizations of metal oxides (MO₂) and MO₂/PtCo/C catalysts

The SEM images of all metal oxides used in this work are demonstrated in Fig. 2. At identical magnification, both CeO₂ and MoO₃ demonstrated their structure as a large flat sheet. A smoother surface was observed for MoO₃ than for CeO₂, probably because the former metal oxide had a higher crystallinity than that of the latter metal oxide. TiO₂ demonstrated an almost spherical shape with a smaller particle size than other metal oxides. Regarding their crystal structures, the XRD pattern of CeO₂ demonstrated peaks at 28.59°, 33.03°, 47.31° and 56.03°, assigned to [111], [200], [220] and [311] crystalline planes, respectively, indicating a face-centered cubic of CeO₂ (Fig. 3). Sharp XRD peaks were observed for MoO₃ at 26.1°, 37.1°, 53.6° and 60.1°, corresponding respectively to the [011], [211], [022] and [031] lattice planes of the monoclinic MoO₃ crystal, suggesting a greater crystallinity than that of CeO₂. The XRD peaks of TiO₂ demonstrated the main characteristic peaks of a mixed phase of the anatase phase (A) at a 2θ of 25.65°, 37.60°, 48.38°, 54.23°, and 55.65° and the rutile phase (R) at a 2θ of 27.51° and 62.26°, corresponding to the A[101], A[004], A[200], A[105], A[211], R[110], and R[002] planes, respectively. The particle sizes, calculated by the Scherrer equation, of CeO₂, MoO₃ and TiO₂ were 44.21, 41.61, and 11.59 nm, respectively.

When all metal oxides were incorporated on PtCo/C catalyst surface, they distributed uniformly along the catalyst surface (Fig. 4) and had an insignificant effect on either crystalline size or d-spacing of the catalysts as well as the weight ratio of Pt:Co (1:1). The crystalline size or d-spacing of the PtCo/C and MO₂/PtCo/C catalysts were still between 0.222–0.223 nm and 7.41–7.67 nm, respectively (Data not shown).

The ESA was then determined from the H₂ desorption peak, obtained from the CV experiment carried out in the potentials range of −0.35 to 1.2 V/SCE, 20 mV/s scan rate under N₂ saturated with N₂ with the potential range of −0.24 to +1.00V and 20 mV/s of scan rate by potentiostat/galvanostat (DEA332, Radiometer) [28]. A Pt gauze and the saturated calomel electrode (SCE) were used as the counter and reference electrodes respectively. The corrosion of all MO₂/PtCo/C catalysts was tested in 0.5 M H₂SO₄ in the potential range of −0.58 to 0.02 V with scan rate of 1 mV/s using the LSV program connected with the Potentiostat/Galvanostat (PGSTAT 30, Autolab). The as-prepared catalysts were used as working electrode, a Pt gauze was used as counter electrode and saturated calomel electrode (SCE) was used as reference electrode.

![Fig. 2. SEM images of commercial metal oxides at 10,000× magnification.](image-url)
atmosphere. As demonstrated in Fig. 5, the presence of CeO$_2$ affected negatively the ESA of the PtCo/C catalyst. Namely, the ESA was reduced almost 50% in the presence of CeO$_2$ at all investigated loadings in the range of 0.03–0.45 mg/cm$^2$. In addition, the presence of MoO$_2$ at any loadings in the range of 0.03–0.45 mg/cm$^2$ affected negatively the PtCo/C catalyst ESA. More amount of MoO$_2$ loading led to the decreasing catalyst ESA. The decreasing ESA with increasing CeO$_2$ and MoO$_2$ loading is probably attributed to their large particle size compared with that of the PtCo/C, which could decrease an available Pt active site to precede the reaction. Interestingly, the addition of TiO$_2$ on the layer of PtCo/C catalysts gave both positive and negative influences on their ESA. Increasing the TiO$_2$ from 0.03 to 0.06 mg/cm$^2$ gave an increasing ESA. Then, greater than 0.15 mg/cm$^2$ of TiO$_2$ content led to decreasing ESA. The augmentation of ESA at low TiO$_2$ content could be involved to the growth of electrode roughness. However, over content of TiO$_2$, especially more than 0.30 mg/cm$^2$, might induce the blockage of active catalyst surface as well as the disconnection of the electron-conducting network through the catalyst layer, resulting of a decreasing ESA.

With regard to the effect of metal oxides on the conductivity of the catalyst, the result showed that the incorporation of metal oxides at all loadings in the range of 0.03–0.45 mg/cm$^2$ led to an increase of ICR of catalyst layer (Fig. 6). In other words, the conductivity of catalyst decreased with the increase of metal oxide loading. This is because the oxygen molecule on the metal oxide structure can reduce the electron mobility along a carbon surface and other elements [29]. Among all MO$_2$/PtCo/C catalysts, the TiO$_2$/PtCo/C catalyst exhibited the lowest ICR, probably due to the fact that TiO$_2$ can form a more percolating electron-conducting network in the catalyst layer than that of CeO$_2$ and MoO$_2$.
MoO$_2$. The conductivity of CeO$_2$, MoO$_2$, and TiO$_2$ were measured at 25 °C as 0.071, 0.167, and 9.432 S/m, respectively.

The influence of MO$_2$ on the hydrophilic/hydrophobic properties of the PtCo/C catalyst was then analyzed in terms of water contact angle. Theoretically, the material having a contact angle greater than 150° exhibits the superhydrophobic property, while the material having a contact angle between 65° and 150° demonstrates the hydrophobic property. The hydrophilic material usually has a contact angle between 0° and 65°, and the superhydrophobic material exhibits a contact angle of around 0° [30]. As demonstrated in Fig. 7, the original PtCo/C catalyst had a contact angle of 90.6°, exhibiting the hydrophobic property. The incorporation of both CeO$_2$ and MoO$_2$ on the PtCo/C catalyst layer induced an increase of the contact angle of such a catalyst, suggesting an increase of hydrophobic properties of the PtCo/C catalyst. Increasing the CeO$_2$ and MoO$_2$ loading in the catalyst layer led to an increase of hydrophobic properties of the catalyst. For the TiO$_2$/PtCo/C catalyst, it exhibited the hydrophilic property at low TiO$_2$ loading (0.03–0.15 mg/cm$^2$) and hydrophobic property at high TiO$_2$ loading (0.30–0.45 mg/cm$^2$). Theoretically, the TiO$_2$ has the hydrophilic properties [31]. Thus, the PtCo/C catalyst exhibited the hydrophilic property at low TiO$_2$ content. However, in the presence of high TiO$_2$ content, the PtCo/C catalyst exhibited the hydrophobic property; this is probably due to the effect of its high roughness. As mentioned previously, the hydrophobic property of TiO$_2$ increases as the increase of TiO$_2$ layer roughness [32,33], which is usually found in the presence of thick TiO$_2$ layer. In this work, different loadings of TiO$_2$ were loaded on identical area of catalyst layer, thus the thickness of TiO$_2$ increased as the increase of TiO$_2$, which is consequently induced an increase of surface roughness as well as the hydrophobic property of catalyst layer.

### 3.2. ORR activity of MO$_2$/PtCo/C catalysts

The ORR activity of MO$_2$/PtCo/C catalysts was first analyzed in H$_2$SO$_4$ solution saturated by oxygen. The operating condition was at RDE rates of 500–2000 rpm, potential range of ~0.05 to 0.65 V and 10 mV/s of scan rate. Fig. 8(a) showed the same pattern of the current density–potential curve for all MO$_2$/PtCo/C catalysts. From this pattern, it can be explained in three parts as kinetic control region, mixed control region and mass transfer region. The first region was observed during the potential of 0.65–0.45 V where mass transfer and rotation ($\omega$) rates had not affect the current density. The second region appeared at 0.45–0.30 V. The current was uncompletely controlled by electron and mass transfers. The current increased with increasing of rotating rate in nonlinear function of square root of rotation rate ($\omega^{1/2}$). The last region

![Fig. 5. ESA of PtCo/C catalysts with and without metal oxides loading.](image5)

![Fig. 6. Internal contact resistance (ICR) of PtCo/C catalysts with and without metal oxides loading.](image6)

![Fig. 7. Contact angle of PtCo/C catalysts with and without of metal oxides loading.](image7)

![Fig. 8. (a) Voltammogram for the ORR of TiO$_2$/PtCo/C catalyst (at loading of 0.06 mg/cm$^2$) and (b) kinetic current of MO$_2$/PtCo/C catalysts at different metal oxide loadings in H$_2$SO$_4$ solution saturated with O$_2$ at 0.385 V with 10 mV/s of scan rate.](image8)
appeared at 0.3–0.05 V, showed a plateau of limiting current that increased linearly with square root of rotation rate \( \omega^{1/2} \) [24].

The current density was as a first order function of the rotating rate expressing by the Koutecky–Levich equation, which is valid for the diffusion species as demonstrated by [34]:

\[
\frac{1}{j} = \frac{1}{j_0} + \frac{1}{B_0 \omega^{1/2}}
\]

and where \( B \) is determined by Eq. (2).

\[
B = 0.62n_F D^{2/3} \gamma^{-1/6} C
\]

The function of \( j^{-1} \) vs. \( \omega^{-1/2} \) at particular potentials (the insert of Fig. 8(a)) provided straight lines, allowing the calculation of the kinetic current density \( j_k \) from intercept and number of electrons involved in the ORR reaction from slope. The summary of kinetic plot of all \( \text{MO}_2/\text{PtCo}/C \) catalysts at different metal oxide loadings is shown in Fig. 8(b). The kinetic current density, or \( j_k \), was found to depend on the loading of metal oxide.

The \( \text{MO}_2/\text{PtCo}/C \) catalysts in the presence of either CeO\(_2\) or MoO\(_2\) at all loadings in the range of 0.03–0.45 mg/cm\(^2\) exhibited ORR activity less than that of the \( \text{PtCo}/C \) catalysts, probably because of their low ESA, high ICR as well as their hydrophobic property. The presence of TiO\(_2\) at appropriate loading (0.06 mg/cm\(^2\)) can promote an increase of ORR activity of the \( \text{PtCo}/C \) catalyst, which might be attributed to their high ESA, low ICR and appropriate hydrophobic/ hydrophilic properties.

To obtain the actual ORR activity of all prepared catalysts, all catalysts were analyzed in a PEM fuel cell using \( \text{H}_2/\text{O}_2 \) gases at 60 °C at atmospheric pressure. The inclusion of MoO\(_2\) in the \( \text{PtCo}/C \) catalyst layer affected insignificantly the OCP (Fig. 9). The presence of CeO\(_2\) or MoO\(_2\) affected negatively the performance of the \( \text{PtCo}/C \) catalyst at low current density, which could be ascribed to their low active surface area. The addition of TiO\(_2\) onto the \( \text{PtCo}/C \) catalyst surface had not affect the performance of the catalyst under this region. The performance loss of the MoO\(_2/\text{PtCo}/C \) catalyst was more pronounced at ohmic region, which was initiated by the sluggishness of electron transfer through the electrodes and the sluggishness of protons (H\(^+\)) flowing through the membrane. The addition of CeO\(_2\) and MoO\(_2\) at all loadings influenced negatively the current density at 0.6 V as displayed in Fig. 10, due to their high ICR as well as their hydrophobic property of the catalyst layer. From the plot, the water contact angles of CeO\(_2/\text{PtCo}/C\) and MoO\(_2/\text{PtCo}/C\) were close to 150°, indicating extremely high hydrophobicity of the catalyst layer, and their hydrophobicity increased with the increase of CeO\(_2\) and MoO\(_2\) loading. This behavior caused the rapid water removal from the catalyst layer and membrane, resulting in the loss of proton conductivity, which consequently deteriorated the cell performance.

For the TiO\(_2/\text{PtCo}/C \) catalyst, incorporation of TiO\(_2\) at low loading between 0.03 and 0.06 mg/cm\(^2\) induced an increase of current at 0.6 V of the fuel cell. This is because low TiO\(_2\) content can ameliorate the hydrophilic property of the catalyst electrode to obstruct its fast dry out, which is confirmed obviously by their
low value of water contact angle. Otherwise, the loading of TiO$_2$ greater than 0.15 mg/cm$^2$ induced a significant decreased fuel cell performance, probably due to a high mass transport limitation. Namely, an excess amount of TiO$_2$ particles could adsorb an enormous quantity of water and consequently block the fuel/oxidant to react at catalyst site. One more possible reason, oxygen molecules could be adsorbed by TiO$_2$. It could capture electrons and donate O$_2$ and also decrease dark conductivity [35,36]. So, the electrical conductivity was reduced 1.09- to 1.59-fold by the presence of 0.03–0.45 mg/cm$^2$ TiO$_2$ on PtCo/C catalyst. The cell performances were 1.14- to 1.36-fold more than that of the PtCo/C catalyst at 0.6 V. This is an effect of the hydrophilic property of TiO$_2$ [24].

3.3. Stability of MO$_2$/PtCo/C catalyst

The stability of all MO$_2$/PtCo/C catalysts was finally monitored by the change of ESA during the repetitive potential cycling experiment of these catalysts in H$_2$-saturated 0.5 M H$_2$SO$_4$. The example cyclic voltammogram of MO$_2$/PtCo/C catalysts was exhibits in Fig. 11(a). The similar pattern of cyclic voltammogram of all as-prepared catalyst was observed. Namely, the H$_2$ adsorption peak appeared as a broad shoulder, not in a sharp peak, probably due to the partial overlapping with the oxygen atom reduction peaks (Pt–O reduction). The H$_2$ desorption peak appeared as a clear sharp peak. Increasing the potential cycling to the 10th cycle resulted in the increase of peak intensity because of the humid Nafion membrane coating the catalyst [37]. Further increasing the repetitive potential cycling led to the decrease of peak intensity, indicating the decrease of ESA of the catalyst. As summarized in Fig. 11(b), the loss of normalized ESA of catalysts after 200 cycles was observed as the order of CeO$_2$/PtCo/C > MoO$_2$/PtCo/C > PtCo/C > TiO$_2$/PtCo/C. Approximately 78%, 43%, 28% and 20% were observed for CeO$_2$/PtCo/C, MoO$_2$/PtCo/C, PtCo/C and TiO$_2$/PtCo/C, respectively. This suggests that the TiO$_2$/PtCo/C catalyst had the most stability compared with the other catalysts. This is probably due to a strong resistance of TiO$_2$ in acid media. According to the results of corrosion test as demonstrated in Fig. 12, the magnitude of corrosion current density was changed as the order of CeO$_2$/PtCo/C > MoO$_2$/PtCo/C > PtCo/C > TiO$_2$/PtCo/C as 14.17, 9.37, 6.71 and 5.68 mA/cm$^2$, respectively. This confirms that the TiO$_2$/PtCo/C exhibited the highest corrosion resistance compared to other MO$_2$/PtCo/C catalysts.

4. Conclusion

Three types of metal oxides, including CeO$_2$, MoO$_2$ and TiO$_2$, were incorporated as the interlayer of PtCo/C catalysts at different loadings. The results demonstrated that incorporation of those metal oxides had insignificant effect on either crystalline size or d-spacing of the PtCo/C catalyst. However, they have a significant effect on the ESA and ICR. Addition of CeO$_2$ and MoO$_2$ affected negatively the ESA and ICR as well as the hydrophilic/hydrophobic properties of the PtCo/C catalyst. The addition, TiO$_2$ at appropriate loading can enhance an increase of ESA as well as the decrease of ICR of the PtCo/C catalyst. Moreover, it can assist to manage the water in the catalyst layer. The PtCo/C catalyst with TiO$_2$ of 0.06–0.15 mg/cm$^2$ can produce a maximum power density of 305 mW/cm$^2$ with a loss of around 20% of ESA after the repetitive potential cycling of 200 cycles.

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