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Advances of Phosphide Promoter Assisted Pt Based Catalyst for Electrooxidation of Methanol

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Abstract: Transition metal phosphide (TMP), as an ideal catalytic promoter in methanol fuel oxidation, has received increased attention because of its multifunctional active sites, tunable structure and composition, as well as unique physical and chemical properties and efficient multi-composition synergistic effect. Some advances have been made for this catalyst system recently. In the current review, the research progresses of transition metal phosphides (TMPs) in the assisted electrooxidation of methanol including the catalysts fabrication and their performance evaluation for methanol oxidation are reviewed. The promotion effect of TMPs has been firstly presented and the catalyst systems based on the different metal centers of TMPs are then mainly discussed. It is concluded that the TMPs can greatly promote methanol oxidation through the electronic effect and the oxyphilic property based on the bi-functional catalytic mechanism. The problems and challenges in methanol fuel oxidation by using TMPs are also described at the end with the attention being paid to the precise catalyst design. The catalytic mechanism probing and application of the fuel cells device are proposed. The current effort might be helpful to the community for novel catalyst system design and fabrication.

Key words: transition metal phosphide; methanol oxidation reaction; promoter; electrocatalysis

1 Introduction

Direct methanol fuel cells (DMFCs) that use liquid methanol as fuel are kind of promising energy conversion technique because they can overcome the unsafe problems involving the application of hydrogen fuel; the advantages of small size, high theoretical energy, clean and pro-environment make it a promising portable power source[1-3]. Moreover, as a carbon-neutral fuel, the sustainable carbon cycle can be realized by combining the CO_2 reduction to methanol fuel and direct methanol fuel cells technique[4]; therefore, attention has been given to the green cycle of methanol production and consummation. In the fuel cells technique, the slow kinetics of methanol oxidation, as well as the high cost of the Pt based catalyst, is more challenging for their commercial applications[5,6]. The initial commercialization of DFMCs has been tried by some companies like UltraCell (United States) and Smart Fuel Cells (Germany) with the system ranging from 25 to 1000 W; meanwhile, a series of DMFCs systems with a power output range of 25 ~ 1000 W for portable applications have been done by Sun's research group of Dalian Institute of Chemical Physics, Chinese Academy of Sciences[7]. The vigorous development of the fuel cell system requires highly efficient catalysts, and the common anode catalyst is based on the precious Pt metals[8-10]. The high cost and rareness of Pt are insufficient to the large scale application, and from the fundamental study, the poisoning effect induced by the intermediates adsorption during the methanol oxidation is a tricky problem[11, 12]. Moreover, the weak interaction between the noble metal active sites and carbon support re-

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Received: 2021-06-21, Revised: 2021-08-03. *Corresponding author, E-mail: ligang.feng@yzu.edu.cn sults in the particles agglomeration, migration and leaching during the methanol oxidation reaction (MOR) process, leading to the rapid catalytic performance degradation. The commercialization of DMFCs relies on the highly efficient catalyst for methanol oxidation. In order to solve the above problems, novel carbon supports with a high specific surface area have been developed to enhance the interaction between the support and active metal nanoparticles; besides, catalyst promoter modified carbon support as anchoring sites have also been done to increase the interaction.

Pt-Ru catalyst is currently the best catalyst system for methanol oxidation, while in light of the high cost and instability of Ru, attention has been given to the alternatives[13, 14]. One of the effective approaches is introducing the catalyst promoter that can assist the active sites in promoting methanol oxidation. The catalyst promoter must have some good characters like high stability, good conductivity as well as the electronic structure tunning ability in promoting the intermediates ad/desorption[15, 16]. Transition metal phosphides (TMPs) have received wide attention in the water-splitting reaction because of their unique electronic and catalytic properties[17-19]. They have also been considered as ideal catalyst promoters in enhancing the noble active sites for methanol oxidation[20, 21]. Compared with metal oxides[22], nitrides[23], sulfides[24], TMPs have an electron-rich metal surface, good electrical conductivity and water activation ability; in addition, the synergistic effect of effective contact between TMPs and precious metals is conducive to improving the performance of MOR. The first study reported by Xing et.al. demonstrated the promotion effect of Ni_2P on Pt for methanol oxidation and a performance improvement of 7 times to that on Pt/C catalyst[25]. Moreover, when measured in the real fuel cell devices, the power density of a direct methanol fuel cell using an optimized Pt-Ni_2P/C anode catalyst was twice that of a similar fuel cell using Pt based reference catalysts. Following that report, the family members of TMP including Ni_2P, Fe_2P, CoP, MoP, WP and Cu_3P, have been reported as catalytic promoters for methanol fuel oxidation. For example, either Ni_2P or Fe_2P coupled with Pt was shown to largely improve catalytic performance for methanol oxidation, and the high catalytic performance was attributed to the hydrophilic property of TMP induced electronic effect and the ligand effect[26,27]; The physically mixed carbon black and Cu_3P as a mixed support of Pt nanoparticles were found to have high catalytic activity for the electrooxidations of methanol and ethanol[28].

Since the promotion effect of TMP is efficient for methanol oxidation, and some significant works have been done to develop this kind of catalyst system, the review on these advances would be helpful to understand the catalysis mechanism and the development of novel catalyst systems. While to our knowledge, the summary report about TMPs system has not been provided. Considering their application in the fuel cells technology as well as the promoting effect in the fundamental catalysis, we have tried to review the advances in the application of TMP as a catalytic promoter for methanol oxidation. The promotion principle of the promoter is firstly described in this review, including the electronic effect and the ligand effect on the bifunctional catalysis mechanism; and then, typical examples of TMPs classified into nickel phosphides, iron phosphides, cobalt phosphides, etc. are discussed in terms of the hybrid catalyst fabrication and their catalysis application for methanol oxidation. Finally, the problems and challenges for this hybrid catalysts system are also presented, and hopefully, this effort can shed light on the new catalytic promoter development as well as their application in fuel cell catalysis.

2 Promotion Effect of The Catalytic Promoter

There are two recognized ways of methanol oxidation, namely, direct and indirect partways. In the direct mechanism, methanol is directly oxidized to CO_2; in the indirect mechanism, CO-like intermediates are usually formed at the beginning of the oxidation reaction when methanol is rapidly decomposed (Eqns (1)-(4))[29]. During the methanol oxidation, because of the indirect pathway involved, the intermediates of CO-like species will be adsorbed over the active sites of the Pt surface, and the strong affinity makes it not easy for further desorption. Thus, the occupied active sites will prevent the reaction from further going on, and the largely reduced catalytic performance happens resulted from the poisoning effect[12, 30]. Bagotzky et al. found that the CO intermediates are very stable at low potentials (< 0.5 V) and can be continuously oxidized to CO_2 between 0.5 V and 0.7 V, but there is almost no CO intermediate on the surface of Pt when the potential is higher than 0.7 V because they will be removed according to the following reactions (Eqns (5)-(6))[19].

$$CH_3OH + Pt \rightarrow Pt\text{-}CH_2OH_{ads} + H^+ + e^- \quad (1)$$

$$Pt\text{-}CH_2OH_{ads} + Pt \rightarrow Pt_2\text{-}CHOH_{ads} + H^+ + e^- \quad (2)$$

$$Pt_2\text{-}CHOH_{ads} + Pt \rightarrow Pt_3\text{-}COH_{ads} + H^+ + e^- \quad (3)$$

$$Pt_3\text{-}COH_{ads} \rightarrow 2Pt + Pt\text{-}CO_{ads} + H^+ + e^- \quad (4)$$

$$Pt + H_2O \rightarrow Pt\text{-}OH_{ads} + H^+ + e^- \quad (5)$$

$$Pt\text{-}CO_{ads} + Pt\text{-}OH_{ads} \rightarrow 2Pt + CO_2 + H^+ + e^- \quad (6)$$

$$M + H_2O \rightarrow M\text{-}OH_{ads} + H^+ + e^- \quad (7)$$

$$Pt\text{-}CO_{ads} + M\text{-}OH_{ads} \rightarrow Pt + M^+ CO_2 + H^+ + e^- \quad (8)$$

At present, there are two main fundamental principles for efficient catalyst construction, namely, bifunctional catalytic mechanism and electronic effect. The bifunctional catalytic mechanism was proposed by Watanabe[31, 32] to explain the catalytic performance of Pt-Ru catalysts system for methanol oxidation; during the methanol oxidation, two active centers on the catalyst surface functionalize synergistically for methanol oxidation. Methanol is catalytically dehydrogenated on the Pt surface firstly to form the intermediate species CO_{ads} (Eqns (1)-(4)); meanwhile, the adjacent component can offer OH_{ads} by water dissociation at lower potentials (Eqn (7)), and then, the CO_{ads} adsorbed on the Pt surface will be oxidized to CO_2 with the help of OH_{ads} (Eqn (8)); the cycle of this process promotes methanol oxidation efficiently. On the other hand, the d-band theory proposes that the d-orbital center of the transition metal is linearly related to the adsorption free energy of the reactive species on the metal surface, and the electronic configuration of the d-band center can be correlated with the catalytic activity, the catalytic activity of the catalyst, thus, can be modified by adjusting the electronic structure to change the adsorption strength of the species[33, 34]. Based on the electronic effect, the introduced second component can modulate the adsorption of CO_{ads} by Pt, which is dependent on the center position of the d-band of Pt. The interaction between the promoter and d-band of Pt changes the electronic structure of Pt surface, making the center of the d-band of Pt lower relative to the Fermi level, and decreases the electron back-donation from the adsorbate to Pt, which reduces the binding energy of the Pt and CO intermediate[27]. Therefore, the adsorption strength of CO_{ads} on the Pt surface is weakened because of the easy filling of the antibonding orbits, and the oxidation potential of CO_{ads} is decreased[20, 26]. In the TMPs, the metal is regarded as a hydride-acceptor center and P is the proton-acceptor center resulting from electron cloud deviation of metal M induced by the lower electronegativity of P atoms. TMP demonstrates strong application ability for water splitting reaction because of the robust water activation ability; and formation of the oxygen-containing species can thus be helpful to the intermediates of CO-like species oxidation based on the above mechanism (Eqns (7)-(8)). Moreover, the metallic properties of TMPs can change the electronic structure of adjacent Pt metals, which is generally observed that the binding energy positions of Pt 4f shift to low binding energy positions resulting from partial electron transfer from TMP to Pt[20, 35]. The electron transfer is due to the formation of a delocalized bond in M-P where M has a partially positive charge and P has a partially negative charge. Thus, the d-band center of Pt is lowered relative to the Fermi level, which makes it easier to fill the antibonding orbits and reduces the binding energy of the Pt and CO intermediate[27]. Therefore, the methanol oxidation performance is increased with the assist of TMPs in the catalyst system. In the following section, we will show the fabrication and application of TMP as a promoter in assisting the active phase of Pt for methanol oxidation. Considering the different active metal centers in the promoter and their contribution to the catalytic reaction, the corresponding phosphide promoter is classified by the metal center and some examples of their application for methanol oxidation are discussed. It is concluded that the TMPs can promote the Pt-based catalyst for methanol oxidation, while the real catalytic mechanism is still not clear, and more effort is required toward the precise interaction tunning and the understanding in their catalytic mechanism.

3 Nickel Phosphide

Nickel phosphide (Ni_2P) is the first catalyst promoter in the TMPs family used for methanol oxidation. It has a hexagonal crystal structure with high physical and chemical stability for water splitting reaction due to its excellent Pt-like properties and corrosion resistance[36]. The effects of Ni_2P amounts and the interaction between Pt and Ni_2P on Pt/C catalyst for methanol oxidation were reported[25]. The Ni_2P nanoparticles anchored over the carbon support were employed to support the Pt nanoparticle by an impregnation method and a microwave-assisted ethylene glycol reduction method, and the fine distribution of the Pt nanoparticles with the average particle size of 2.5 nm was obtained (Figure 1(A)). The optimized Pt-Ni_2P/C-30% catalyst showed significantly higher performance than Pt/C, Ni-Pt/C and P-Pt/C catalysts (Figure 1(B)). The improved performance was attributed to the strong interaction between Pt and Ni_2P, resulting in the partial electron transfer from Ni_2P to Pt and the water activating ability of Ni_2P. When applied in the real fuel cell, the power density of 65 $mW \cdot cm^{-2}$ was achieved, much higher than that of the most advanced Pt/C catalyst (Figure 1 (C)). The promotion effect on PtRu catalyst was also realized previously[37]. By depositing PtRu over the support of Ni_2P/C, the hybrid catalyst showed good catalytic activity and stability for methanol oxidation. Specifically, the maximum power density achieved at 30 °C was 69.9 $mW \cdot cm^{-2}$ for PtRu-Ni_2P/C, which was still higher than that of the commercial PtRu catalyst for 63.1 $mW\ cm^{-2}$ at 70 °C (Figure 1(D-F)). To enhance the interaction between Ni_2P and Pt, graphene was selected as a conductive carrier and a Pt-Ni_2P/graphene catalyst was prepared[38]. Electrochemical test results showed that Pt-Ni_2P/graphene catalyst exhibited much higher catalytic activity and stability for methanol oxidation than Pt/C alone, and the authors attributed the high catalytic performance to the improved electron transfer among Pt, Ni_2P and graphene, thus, promoting the electrooxidation kinetics of CO_{ads}. Our group[26] simplified the experimental process and successfully prepared ultrafine Pt-Ni_2P-graphene nanoparticles by a simple one-step hydrothermal method, and further studied the co-catalysis of Ni_2P on the Pt catalyst. Spectral analysis showed that the Pt-Ni_2P-graphene nanoparticles exhibited a hybrid crystal structure with slightly reduced lattice parameters. XPS data revealed that the Pt 4f peak of 20% Pt-Ni_2P-graphene significantly shifted about 0.4 eV to the low binding energy direction (Figure 1(G)), indicating a strong electron interaction resulting from some electrons transfer from Ni_2P to Pt. In addition, the strong electron interaction between Pt and Ni_2P nanoparticles was influenced by the content of Ni_2P in the system. When the content of Ni_2P was 20%, the catalyst had the best anti-CO poisoning ability and the electrooxidation performance of alcohol fuel (Figure 1(H-I)). By performing the physical characterizations and the electrochemical measurements, it was suggested that the high catalytic performance can be attributed to the Pt and Ni_2P hybridization encountered during the one-step hydrothermal process that enhanced the anti-poisoning ability and electronic interaction.

4 Iron Phosphide

Iron phosphide (FeP) with special active sites of $Fe^{\delta+}$ and $P^{\delta-}$ is facile to the mass and charge transfers, and high catalytic performance in assisting Pt for methanol oxidation was also demonstrated due to the hydroxyl groups generation[39]. FeP nanosheet was employed to support Pt nanoparticles for methanol oxidation[39], and the as-prepared Pt/FeP hybrid catalyst exhibited superior performance for methanol oxidation that was 2.74-fold greater than that of commercial Pt/C catalyst; and meanwhile, a better CO tolerance of Pt/FeP nanosheet was found, that had the CO oxidation peak potential of 100 mV lower than Pt/C.

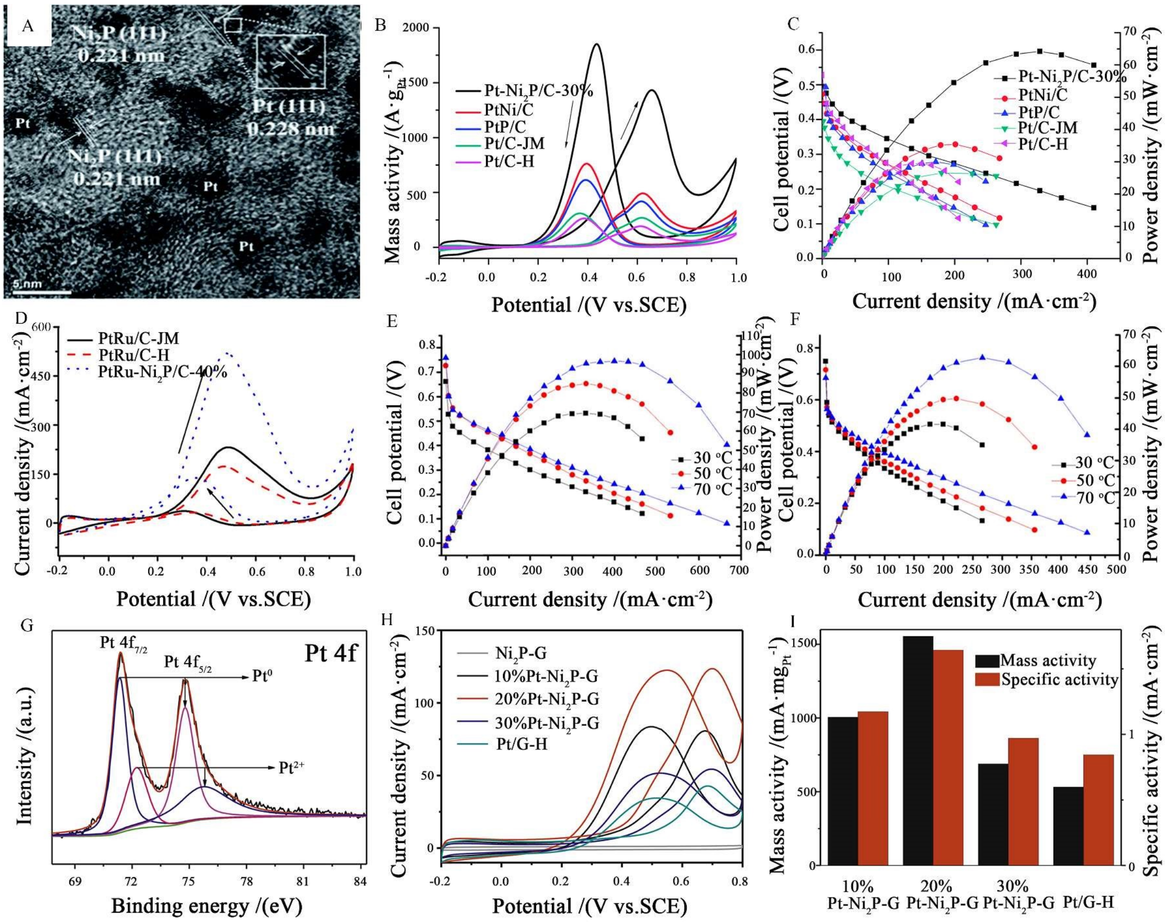

Figure 1 (A) High-resolution transmission electron microscopic image of a Pt-Ni_2P/C-30% sample, (B) cyclic voltammograms and (C) power-density curves for fuel cells employing Pt-Ni_2P/C-30%, Pt-Ni/C, Pt-P/C, Pt/C-JM and Pt/C-H as anode catalysts[25]. Steady-state polarization curves (D) and power-density curves for fuel cells employing (E) PtRu-Ni_2P/C-40%, (F) commercial PtRu/C-JM as anode catalysts[37]. (G) High-resolution XPS spectra of Pt 4f, (H) CV curves of the prepared catalysts measured in 0.5 mol·L^{-1} H_2SO_4 containing 1 mol·L^{-1} CH_3OH at a scan rate of 50 mV·s^{-1} and (I) specific activity and mass activity at the peak potential for methanol oxidation[26]. (color on line)

The better resistance to CO poisoning was proposed due to the downshifting of the d-band center of Pt and hydroxyl groups formation in Pt/FeP. In light of the significant interface formed between the promoter and the active Pt phase, our group[27] developed a new catalyst system consisting of ultrafine Pt nanocrystals coupled over the petal-like Fe_2P surface for the efficient methanol oxidation reaction (MOR). Ultrafine Pt nanoparticles with an average particle size of 2.2 ± 1 nm were anchored over the petal-like Fe_2P surface that had a large surface area and a lot of defects (Figure 2(A-B)). Some good catalytic features like the strong electronic effect and more defects, and the increased surface area of the petaloid Fe_2P made the Pt-Fe_2P catalyst system have high catalytic activity and the anti-poisoning ability for methanol electro-oxidation compared with a controlled Pt/C catalyst (Figure 2(C)). We further found that the catalytic performance of PtRu catalyst, which is the best catalyst system for methanol oxidation, can be largely promoted by forming core-shell structured catalyst (PtRu@FeP) with FeP as the core and active PtRu as the shell[20]. The catalytic performance for methanol oxidation catalyzed by this system was influenced by the amount of the FeP, and the molar ratio of PtRu shell and FeP core with 1:1 showed the best catalyst performance with its peak current density being about 2 times and 3 times higher than those of the commercial

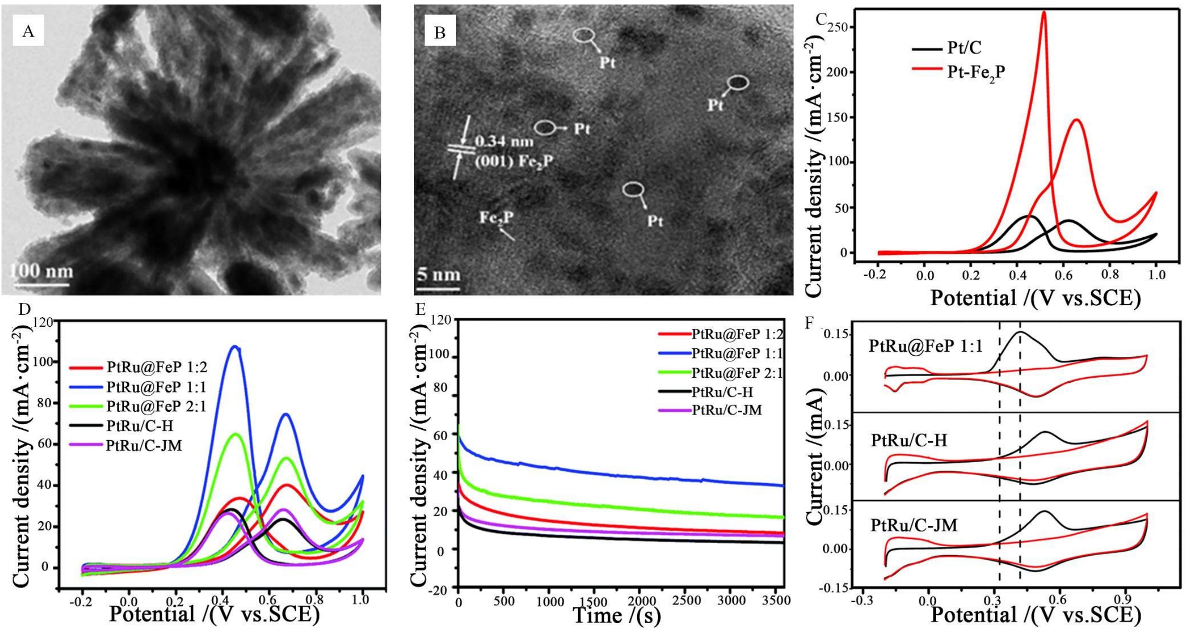

Figure 2 (A-B) TEM images of Pt-Fe_2P sample, (C) cyclic voltammograms of Pt-Fe_2P and Pt/C catalysts for methanol oxidation[27]. (D)The electrocatalytic performance of different PtRu catalysts for methanol electro-oxidation; (E) Chronoamperometric curves of different PtRu catalysts in 0.5 mol·L^{-1} H_2SO_4/1 mol·L^{-1} CH_3OH solution at 0.6 V for 3600 s; (F) CO_{ads} stripping voltammograms of PtRu@FeP 1:1, PtRu/C-H and PtRu/C-JM catalysts in 0.5 mol·L^{-1} H_2SO_4 solution[20]. (color on line)

PtRu/C catalyst and home-made PtRu/C catalyst, respecetively (Figure 2(D)). The largely improved catalyst stability compared to the PtRu/C reference catalysts was observed by chronoamperometric test for 3600 s (Figure 2(E)). The CO stripping voltammograms showed that the prepared PtRu@FeP catalyst had excellent tolerance to CO poisoning effect with the peak potential and the onset potential of CO oxidation being 110 mV and 60 mV, respectively, lower than those of the benchmark commercial PtRu/C catalyst (Figure 2(F)). This core-shell structure was found to have an efficient ligand effect of PtRu active sites and adjacent FeP as well as an electron-enriched surface of strong electronic effect. Thus, the close contact of the nano-interface, the ligand effect based on the bifunctional mechanism, and the electronic effect generated by the interaction between the active sites and the adjacent promoters are significant to the catalytic performance improvement.

5 Cobalt Phosphide

Cobalt phosphide has moderate binding energy to hydrogen when activating water molecular, and such modest binding energy is beneficial to the adsorption and desorption of intermediates, thus, it has received large attention for water splitting reaction[40, 41]. Such characters make it be a suitable platform for assisting the Pt based catalysts for methanol oxidation, and it has a variety of stoichiometry such as CoP and Co_2P. For example, Co_2P supported on graphitized carbon fabricated by an ion-exchange method was employed to anchor the Pt nanoparticles[42]; compared to the commercial Pt/C catalyst, Pt-Co_2P/C catalyst showed much better performance for methanol electrooxidation including the catalytic activity and onset potentials; and specifically, the peak current density was 1236.8 mA·mg_{Pt}^{-1}, that was nearly four times of that of Pt/C catalyst (Figure 3(A)). The CoP was introduced into the nanostructured PtRu catalyst for methanol oxidation in the fuel cell application, which significantly improved the catalytic performance[43]. Specifically, the maximum power density offered by PtRu-CoP/C-40% catalyst was 85.7 mW·cm^{-2} achieved at 30 ℃ and the performance could be further increased by increasing temperature (Figure 3(B)); this

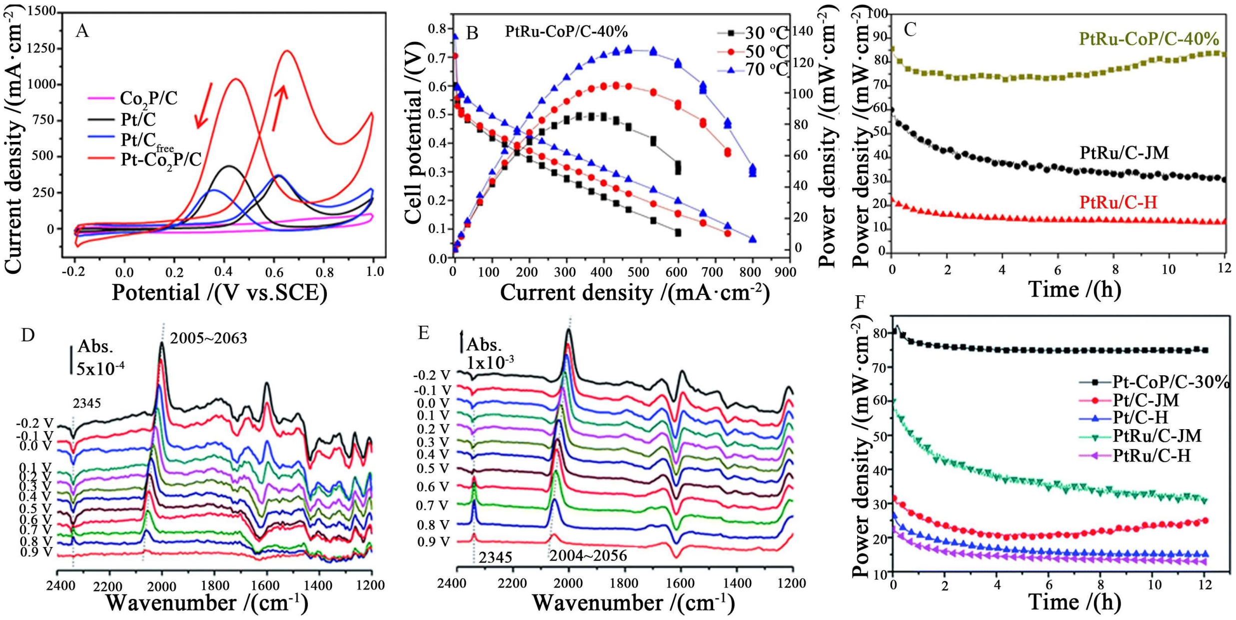

Figure 3 (A) Cyclic voltammetric curves of Co_2P/C, commercial Pt/C, Pt/Cfree, and Pt-Co_2P/C catalysts at 50 mV·s^{-1} in acidic electrolytes[42]. (B) Power-density curves for fuel cells employing PtRu-CoP/C-40% and (C) discharge curves at 0.3 V (50 °C) for fuel cells employing PtRu-CoP/C-40%, commercial PtRu/C-JM and PtRu/C-H as anode catalysts[43]. The multi-step attenuated total reflectance surface-enhanced infrared absorption spectroscopic curves on (D) the Pt/C-JM and (E) the Pt-CoP/C electrodes, and discharge curves (F) at 0.3 V (70 °C) for fuel cells employing different catalysts[35]. (color on line)

performance was even higher than the power density offered by the state-of-the-art commercial PtRu/C catalyst at 70 °C (63.1 mW·cm^{-2}). The stability of the catalyst was evaluated when discharged at 0.3 V for 12 h at 50 °C by comparing it to the PtRu based catalysts (Figure 3(C)). It was found that the power density of the PtRu based catalysts decreased significantly in the first 2 h, but PtRu-CoP/C-40 % catalysts showed a highly stable discharge performance. By further physical characterizations of the degraded catalysts, the authors did not observe the obvious structural changes on PtRu-CoP/C-40% catalyst, but serious agglomeration and increased particle size were found on other PtRu based catalysts. The physical stability of PtRu-CoP/C-40 % catalyst exposed to 0.5 mol·L^{-1} H_2SO_4 solution was examined by inductively coupled plasma-atomic emission spectrometer-mass spectrometry. After exposure to the electrolyte for 1 h, elements of Co, Pt and Ru were detected probably because of the loss of the oxidized surface. After that, all concentrations of the elements increased very slowly and became stable. Moreover, it was found that the presence of CoP mitigated the losses of Pt and Ru during the fuel cells operation compared to the PtRu/C catalyst; the Co element was not found in the cycled methanol solution with the detection limit of 0.001 ppb. This further confirmed the excellent stability of PtRu-CoP/C-40% catalyst and showed great application prospects in DMFC. The largely improved anti-CO poisoning ability with the presence of CoP in the Pt-CoP/C catalyst was previously observed by *in-situ* attenuated total reflection surface-enhanced infrared spectroscopy compared to Pt/C catalyst[35]. They noted that less CO_2 was formed on Pt/C but more CO_2 on the Pt-CoP/C catalyst, therefore CoP in the Pt based catalyst promoted the methanol oxidation to final CO_2 products (Figure 3 (D-E)). Compared with commercial Pt/C-JM (JM means Johnson Matthey company) and PtRu/C-JM, Pt-CoP/C-30% catalyst not only showed the highest initial power density, but also exhibited good catalytic stability for continuous discharge for 12 h at 0.3 V and 70 °C (Figure 3(F)). In order to enhance the interaction between CoP and carbon support, the CoP nanoparticles over carbon nanotubes were fabricated and further used as a support to grow the Pt nanoparticles[44], and the high catalytic activity and stability were found as compared to the Pt/CNTs without CoP.

6 Other Phosphide Promoters

Besides the above-mentioned TMPs promoters, there are some reports using MoP, WP, Cu_3P as co-catalysts to improve the catalytic activity of Pt in methanol oxidation. MoP was found both active in hydrodesulfurization and electrochemical hydrogen evolution[45-47]. It was also promising in assisting methanol oxidation due to the facile dehydrogenation performance. Molybdenum phosphating (MoP) nanocrystals anchored on graphitized carbon were also developed by an ion-exchange method, and they were employed to support the Pt nanoparticles for methanol oxidation[48]. Compared with commercial Pt/C, Pt-MoP/C catalysts showed high CO poisoning resistance and catalytic ability. The theoretical calculation indicates that Pt-MoP had neither strong nor weak methanol adsorption energy, which facilitated the charge transfer and electrooxidation of methanol. Meanwhile, molybdenum phosphide/multi-walled carbon nanotubes supported Pt nanoparticles showed high catalytic activity due to the interaction between Pt and MoP, and the uniform dispersion of Pt nanoparticles[49]. Molybdenum phosphide/porous carbon (MoP/C) composites as Pt-supports and co-catalysts for the MOR were also found to have higher electro-catalytic activity and durability than commercial Pt/C[50]. The authors attributed the high performance to the close integration between MoP and carbon, and the ligand effect of Mo-P bonds. The authors also fabricated the tungsten phosphide-embedded carbon-thin-layer/acid-treated expanded graphite composites as Pt-supports/co-catalysts for methanol oxidation. The Pt nanoparticles

Table. 1 Transition metal phosphide promoters reported for methanol oxidation.

Catalyst	Mass activity/(mA·mg_{Pt}^{-1})	Specific activity/(mA·cm^{-2})	Reference
Pt-WP/C	1559.3	/	[17]
Pt-$FeNi_2P$/C	1125	1.24	[19]
PtRu@FeP 1:1	700 mA·mg_{PtRu}^{-1}	1	[20]
Pt-Ni_2P/C-30%	1432	4.049	[25]
20%Pt-Ni_2P-G	1554.6	1.643	[26]
Pt-Fe_2P	1039	1.29	[27]
Pt/C-Cu_3P 50%	578.02	2.02	[28]
PtRu-Ni_2P/C-40%	518.8 mA·mg_{PtRu}^{-1}	0.459	[37]
Pt/FeP	/	0.994	[39]
Pt-Co_2P/C	1236.8	/	[42]
PtRu-CoP/C-40%	670.5 mA·mg_{PtRu}^{-1}	0.577	[43]
Pt-CoP/C-30%	1706.41	2.09	[35]
Pt-4% CoP/CNTs	1600	2.15	[44]
Pt-MoP/C	1860.7	/	[48]
Pt-MoP/MWCNTs-3	1063	/	[49]
Pt-MoP/C-2	680.7	/	[50]
Pt-WP-CL/AEG	2234	/	[51]
Ni_2P-NiP_2-Pt/ CNTs	435.2	1.14	[52]
Pt-Ni HSNs	2170	/	[53]

were uniformly dispersed over the support, which efficiently increased the Pt active site utilization, and the lowest onset potential was observed both in methanol oxidation and CO stripping voltammogram[51]. Besides, the Cu_3P was also reported as an effective promoter of Pt for methanol oxidation[28]; the amount of Cu_3P in the composite catalysts was probed and high catalytic performance was observed for Pt/C-Cu_3P 50% catalyst due to the ideal composition ratio and the electronic effect, and bifunctional mechanism induced between Cu_3P and Pt.

7 Conclusions and Perspectives

In conclusion, the largely improved catalytic performance for methanol oxidation by adding TMPs in the Pt catalyst was evidenced by the examples aummarized in Table 1. All the TMPs promoted catalyst system showed much better catalytic activity and anti-CO poisoning ability compared to the catalyst system without the presence of TMPs. The roles of the TMPs in the catalysts system can be described in terms of the electronic structure modification of the active Pt centers, the absorbing sites for Pt active sites growth and dispersion, the water activation induced by the oxyphilic property as well as the bifunctional catalytic mechanisms synergistically catalyzing the reaction. To increase the synergistic interaction between the TMPs promoter and Pt based active sites, some fabrication approaches by increasing the coupling ability of Pt sites and the TMPs promoters can be employed, such as the surface engineering, morphology tunning and the hybrid fabrication methodology.

While based on the current reports and the advanced progresses, there are still lots of unknown issues, such as the exact promoting effect and designing principles for such catalysts, that will strongly hinder the development of their applications in methanol fuel cells. Therefore, some effort is still required to understand the catalytic mechanism and to make these catalysts systems more robust in real fuel cell applications. Currently, the fabrication of the TMPs promoted catalysts system was mainly based on two separated steps, namely the fabrication of the TMPs and the deposition of Pt active phase over their surface; and the carbon support was mixed with the TMPs by increasing the conductivity and dispersion. Therefore, the interaction and electronic effect of Pt active sites and TMPs will be reduced, which might not fully make use of the promotion effect of TMPs. Attention thus might be directed to the microstructure construction with the efficient interfaces of Pt active sites and TMPs promoters. Moreover, to clearly understand the promotion effect of TMPs in the system, some in situ spectroscopic studies might be helpful to probe the catalytic intermediates during the catalytic process, and the catalytic mechanisms might be further understood with the help of electrochemical measurements. Furthermore, the hybrid catalyst rational design and fabrication by precisely tuning the structure and morphology would be helpful to maximize the catalytic ability. Finally, the newly developed catalysts should be tested in the real fuel cells. Though some catalysts were tested in the fuel cell devices with excellent catalytic performance compared to the commercial state-of-the-art catalysts, some effort is still required towards the membrane electrode fabrication, catalyst layer optimization, etc. Therefore, future attention can be directly paid to the understanding of catalytic mechanism with novel techniques, and precise catalyst structure design and fabrication, as well as their application in the real fuel cell devices.

Declaration of Competing Interest:

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Note:

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磷化物助力铂基催化剂甲醇电氧化的研究进展

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摘要: 过渡金属磷化物(TMP)作为一种理想的甲醇电氧化助催化剂,因其具有多功能活性位点、结构和组成可调、独特的物理化学性质和高效的多组分协同效应等优势而受到越来越多的关注。本文综述了过渡金属磷化物促进甲醇电氧化的研究进展,包括催化剂的制备及其催化甲醇电氧化的性能评估。首先,介绍了TMP对催化甲醇氧化反应的促进作用,然后在正文中讨论了基于不同金属中心的TMP催化剂体系的制备与性能研究。从电子效应和基于双功能催化机制的亲氧性来看,TMPs对催化甲醇氧化有明显的促进作用。最后,我们讨论了在催化剂理性设计及其催化机理探索和燃料电池装置应用中应注意的问题和挑战,希望对新型催化剂体系的设计和制备有一定的指导意义。

关键词: 过渡金属磷化物;甲醇氧化反应;促进剂;电催化