

Overview of the development of CO-tolerant anode electrocatalysts for proton-exchange membrane fuel cells

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Abstract

Poisoning of Pt anode electrocatalysts by carbon monoxide (CO) is deemed to be one of the most significant barriers to be overcome in the development of proton-exchange membrane fuel cell systems (PEMFCs). The use of CO-tolerant electrocatalysts serves as the most hopeful way to solve this problem. It is well established that Pt-based alloy systems of CO-tolerant electrocatalysts can substantially withstand the presence of CO in the fuel stream. Based on literature starting in 2000, a few efforts have still been conducted at developing a more CO-tolerant anode electrocatalyst than the traditional Pt/C or PtRu/C systems. This review introduces and discusses these efforts.

Pt-based electrocatalysts, including PtSn/C, PtMo/C (atomic ratio = 5:1), PtRuMo/C (Mo = 10 wt.%), PtRu-H_xMoO₃/C and PtRu/(C nanotubes), appear to be poisoned by CO at the same, or a lower, level than traditional Pt/C or PtRu/C electrocatalysts. Platinum-free electrocatalysts, such as PdAu/C, have proven to be less strongly poisoned by CO than PtRu/C counterparts at temperatures of 60 °C.

A greater tolerance to CO can be achieved by modifying the structure of the electrocatalyst. This involves the use of a composite or double-layer that is designed to make the CO react with one of the electrocatalyst in advance while the main hydrogen reacts at another layer with a traditional Pt/C electrocatalyst.

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1. Introduction

Among the various types of fuel cell, the proton-exchange membrane fuel cell (PEMFC) possess several highly advantageous features such as a low-operating temperature, sustained operation at high current density, low weight, compactness, potential for low cost and volume, long stack life, fast start-up and suitability for discontinuous operation [1–4]. These features currently make PEMFC the most promising and attractive candidate for wide variety of power applications that range from portable/micro-power and transportation uses to large-scale stationary power for buildings and distributed generation. For these reasons, over the past few years, fuel cell and automotive companies have announced new technologies or prototype vehicles based on PEMFCs [5–10]. In addition, numerous fuel cells are under development for different applications [2,11]

and expected to enter the market in large numbers world-wide [12,13].

Recently, PEMFCs have passed the demonstration phase and have partly reached the commercialization stage due to an impressive research effort. Nevertheless, there are still some technological challenges to be solved, as follows [4]:

- (i) Choice of fuel (gasoline, methanol or hydrogen).
- (ii) Efficient fuel processing, with reduction of weight, volume and carbon monoxide (CO) residuals.
- (iii) Development of anode electrocatalysts tolerant to CO at levels of 50 ppm (with a noble metal loading lower than 0.1 mg cm⁻² or less).
- (iv) Development of a cathode electrocatalyst to reduce the overpotential encountered at open circuit and to significantly enhance the exchange current density.
- (v) Development of alternative proton-conducting membranes with a lower cost but with the same proton conductivity as state-of-the-art perfluorosulfonic acid membranes.

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- (vi) Development of new proton-conducting membranes that do not depend on water for high-temperature operations between 150 and 200 °C.
- (vii) Manufacture of low-cost bipolar plates.
- (viii) Development of an air-compressor/turbine with improved performance and reduced size and cost.
- (ix) Optimization of thermal and water management.

Among these challenges, problems (i)–(iii) are deemed to be most significant barriers that PEMFCs must overcome to achieve complete commercialization. The first and second challenges are closely related to the source and purity of hydrogen as the fuel. This is very important with respect to presence and composition of poisonous CO. Many workers have investigated other available fuels such as gasoline, natural gas and methanol [14] instead of pure hydrogen. Hydrogen is generated by the consecutive reforming and cleaning of these carbon-based fuels and the resulting gas mixture contains hydrogen at a concentration of 30–75%. Numerous efforts [14–16] have been made to determine the optimum conditions, which depend on the type of primary fuel and the reforming process. The importance of these challenges is attributed to the nature of the Pt/C anode electrocatalyst, which is susceptible to CO poisons. When pure hydrogen is used as a fuel, it is well known that the Pt/C electrocatalyst exhibits its best performance. On the other hand, when the hydrogen is produced from other available fuels, CO levels of over 10 ppm severely poison the Pt/C and cause a substantial degradation in PEMFC performance due to the severe anode polarization that results from CO adsorption on the electrocatalyst [17]. Therefore, reduction of the concentration of CO in the fuel and development of CO-tolerant electrocatalysts are regarded as the most important factors to improve the performance of PEMFCs.

There are several ways to overcome the CO poisoning of electrocatalysts [18,19], namely: (i) oxidant bleeding into the fuel feed stream; (ii) advanced reformer design; (iii) use of CO-tolerant catalysts; (iv) membranes for CO separation. In addition to these methods, others such as the employment of a double-layer (composite) anode electrocatalyst, have been examined in recent years.

This review introduces and discusses a few of the latest research projects (i.e., those conducted since 2000) into potential methods for overcoming the CO poisoning of anode electrocatalysts in PEMFCs. Useful information is also provided on the development of anode electrocatalysts that are more resistant to CO poisons. The development of Pt-based binary/ternary metallic electrocatalysts and Pt-free electrocatalysts as well as reconfiguration of the anode layer structure, is discussed.

2. Proton-exchange membrane fuel cell

In a PEMFC, hydrogen gas is electrocatalytically oxidized to hydrogen ions (as shown in Eq. (1)) at the anode electrocatalyst that is composed of Pt deposited on a conductive carbon. The cell operates at approximately 70–80 °C. The protons released during the oxidation of hydrogen are conducted through the proton-exchange membrane to the cathode [20]. The latter is

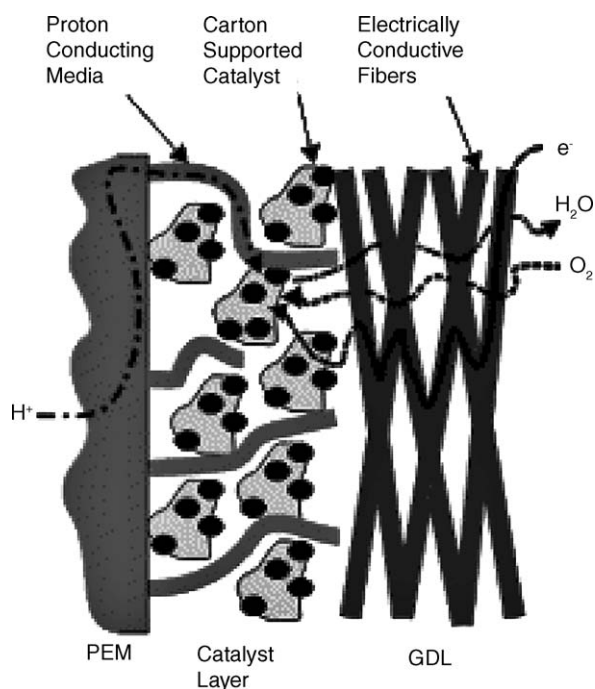
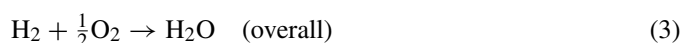
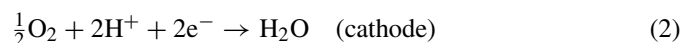


Fig. 1. Transport of gases, protons and electrons in PEMFC electrode [21].

comprised of Pt on carbon and electrocatalytically reduces oxygen in the air to combine with the protons and, thereby, produce water and heat, as represented by Eq. (2). Therefore, the overall reaction can be expressed by Eq. (3). The open-circuit voltage or theoretical maximum voltage is $E_o = 1.16$ V. The electrons flow through the external circuit and do the work.



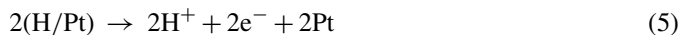
The heart of the PEMFC is the membrane–electrode assembly (MEA), a schematic of which is given in Fig. 1 [21]. The MEA consists of a proton-exchange membrane (i.e., perfluoro-sulfonic acid, Nafion), the catalyst layers of both electrodes and gas-diffusion layers (GDLs) that are constructed from porous carbon paper or carbon cloth. Typically, these components are fabricated individually and then pressed together at high temperature and pressure [21].

The catalyst layer is applied to the membrane or to the gas-diffusion layer. In either case, the objective is to place the catalyst particles of platinum or platinum alloys within close proximity of the membrane. The interface between the membrane and the electrode is critical. The MEA is sandwiched between two flow-fields to form a single cell and many cells are stacked in series to produce a greater voltage [21].

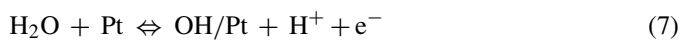
2.1. CO poisoning of Pt catalyst

The mechanism by which a Pt catalyst is poisoned by CO is well established. As shown below (Eqs. (4)–(6)), the CO competes with the adsorption of hydrogen on the active sites of

platinum at normal anode operating potentials [18]. Recently, Papageorgopoulos and de Bruijn [22] investigated CO poisoning quantitatively. For a 1% CO/hydrogen mixture, it was found that CO blocks 98% of the active sites at 25 °C.



The adsorbed CO on a catalytic site can be removed by raising the anode potential to about 700 mV versus the reversible hydrogen electrode (RHE). At this potential, as shown in Eqs. (7) and (8), CO reacts with the hydroxyl species that are adsorbed on the platinum surface to form CO₂. In addition, the CO is removed by oxidation to CO₂ at an anode potential above 700 mV. Both cases result, however, in a serious loss of efficiency and are not practical [18].



2.2. General approaches to decreasing CO poisons

The following methods are commonly employed to decrease the poisoning of Pt anode electrocatalysts [18].

2.2.1. Oxidant bleeding into the fuel feed

Low levels of oxygen or oxygen-evolving compounds [23–25] are bled into the fuel feed to decrease CO poisoning. With this procedure, the levels of CO produced in the reforming reaction can be reduced by reactions such as the water–gas shift (WGS) reaction and the selective oxidation of CO. (Note: CO can also be diminished by the methanation reaction with hydrogen but this is not efficient because it consumes the hydrogen.) Many working groups have reported that oxidant bleeding can be effective. In addition, the use of hydrogen peroxide (H₂O₂) [24,25] in an anode humidifier has been successfully used to mitigate the level of CO in H₂-rich feed [24,25]. In this case, however, the utilization of the fuel will certainly be decreased and safety issues must also be considered [26].

2.2.2. Advanced reformer design

Most of the reformers, including auxiliary processors that are currently available, are capable of producing a CO content of 50 ppm or less after a warm-up period of up to 2 h. To acquire the bleeding oxidant effect by modifying the reformer, many researchers have considered the possibility of designing a new reformer to which auxiliary processors for clean-up steps, e.g., as shift converters and a selective oxidizer, are fitted [27–29]. These methods would, however, increase the complexity and cost of the fuel cell system. Even when these additional stages are used, it is difficult to maintain low CO levels during start-up and transient operations without the addition of an air bleed into the fuel stream [18,30–35].

Table 1
Oxidation potentials of CO at Pt and Pt/Ru surfaces [19]

Fuel	Catalyst	Fuel cell voltage	η_v (%)	$\Delta\eta_v$ (%)
Hydrogen	Pt	0.682	55.4	–
100 ppm CO	Pt	0.231	18.8	–66.1
100 ppm CO	Pt/Ru	0.482	39.2	–29.2

2.2.3. Use of CO-tolerant catalysts

Because the use of CO-tolerant electrocatalysts would be more efficient and cause less associated problems, it is generally considered that this is the most promising way for solving the CO poisoning problem in PEMFCs.

It is well established that binary systems of CO-tolerant electrocatalysts, with Pt as one of the components, can exhibit a substantial resistance to the presence of CO in the fuel stream. It has been found that the use of a second element with Pt, such as Ru, Sn, Co, Cr, Fe, Ni, Pd, Os, Mo, Mn, etc., in the form of an alloy or a co-deposit yields significant improvement in the CO-tolerance relative to pure Pt [36–45].

Among these various Pt-based binary systems, the most commonly used catalyst is the PtRu/C. This material is known to enhance CO tolerance, which can be ascribed to electronic modification of Pt–Ru in PtRu alloys that decreases the CO binding energy on Pt (Eq. (6)) and also binds OH strongly on the Ru active sites in the PtRu alloys [46]. Within this system, the performance of PEMFCs has been improved for fuel streams containing CO [47–49].

A PEMFC with a PtRu/C alloy does not perform as actively as Pt when pure hydrogen is employed as the fuel [11]. In fact, the use of PtRu results in a substantial loss in cell potential [18,19], as shown in Table 1 [19]. The results show that the potential of a cell with PtRu is about 250 mV compared with that of a cell with pure Pt. When there is 100 ppm of CO, there is still a loss of about 200 mV (30% of voltage efficiency) compared with the use of pure hydrogen as a fuel [18].

Ternary catalyst systems, typically based on a PtRu alloy, have also been investigated and their performance has been compared with that of pure Pt/C or PtRu/C [50–55]. Specifically, PtRu alloys with Ni, Pd, Co, Rh, Ir, Mn, Cr, W, Zr and Nb have been investigated. Nevertheless, there remain associated problems over the preparation method and the enhancement of electrochemical performance.

2.2.4. Membranes

There is also considerable interest at the present time in the development of membranes designed for purification and separation. One approach has been the development of high-temperature (140 °C) membranes [56]. The CO tolerance of PEMFCs increases with increasing temperature [57]. Therefore, to decrease CO poisoning, it is desirable to develop high-temperature membranes. On the other hand, increasing temperature decreases the life of the membrane and renders in maintenance of membrane hydration more difficult. Work [58] on phosphoric acid-doped polybenzimidazole revealed long-term chemical and mechanical stability at high temperature. Nevertheless, there were still problems with membrane cycle-life and hydration.

Other membrane approaches can be used for separating hydrogen from gas mixtures. For example, the palladium membrane has been studied extensively, but is still very expensive for use in fuel cells [59].

2.3. Recent approaches to decreasing CO poisoning of anode electrocatalysts

2.3.1. Development of CO-tolerant catalysts

When using fuel (containing over 10 ppm of CO) from the reformat, PtRu binary systems are still regarded as the most efficient anode electrocatalysts due to their electronic or bifunctional effects in reducing CO poisoning [60,61]. Therefore, the development of CO-tolerant electrocatalysts is still concentrated on Pt or PtRu-based bimetallic or ternary catalyst systems. In fact, many papers in recent years have presented details of new preparation methods and the performance of Pt-based electrocatalysts such as PtSn/C, PtMo/C, PtRuMo/C, PtRu- H_x MoO₃/C and PtRu/(C nanotubes). In addition, efforts to develop Pt-free electrocatalysts such as PdAu/C have been undertaken. A summary of the research in this area is given in Table 2.

2.3.1.1. PtSn/C binary system. Evaluation of CO oxidation on PtSn electrocatalyst systems has been investigated in earlier work [45,62]. It was demonstrated that bimetallic PtSn catalysts with an oxide support display superior catalytic activity for CO oxidation [63–68]. In 2000, Crabb et al. [69] applied a PtSn/C, anode electrocatalyst, prepared by a surface organometallic chemistry method, in a PEMFC. Their preparation method involved a selective means of adding a second metal to the surface of another. This produced a controlled surface reaction between an organometallic species of the second metal (tetrabutyl- or tetraethyl-tin) with a pre-reduced monometallic platinum metal catalyst. The PtSn/C prepared by this method gave enhanced activity that resulted in large decrease in the onset potential of CO oxidation compared with that for Pt/C. It was claimed that this enhancement was caused by the addition of Sn

to the Pt/C-suppressed chemisorption of both the hydrogen and the carbon monoxide. Furthermore, in using this method, only a small amount of Sn is required to decrease the onset potential of CO oxidation. Analysis with TEM, EDX and XPS provided evidence of a bimetallic effect as the Pt and Sn appeared together on the support and the catalysts consisted mainly of metallic platinum in close association with tin oxide after exposure to air.

2.3.1.2. PdAu/C binary system. In 2001, Schmidt et al. [70] produced a paper on the CO tolerance of PdAu/C (Vulcan XC-72) that was prepared via bimetallic colloidal precursors. This work was based on an earlier study by Fishman [71] in which PdAu-black alloys provided a highly active medium for the hydrogen oxidation reaction and a second metal (Au) produced surfaces that did not adsorb CO under the operating conditions of a phosphoric acid fuel cell (PAFC). In addition, much lower CO adsorption energies on different poly- and single-crystalline PdAu surfaces, compared with pure Pd or pure Pt surfaces, were found from ultrahigh vacuum (UHV) studies [72]. Schmidt et al. [73] prepared colloidal PdAu precursors by the co-reduction of Pd- and Au-salts with NOct₄[BET₃H] (tetraoctylammoniumtriethylhydroborate) in dry THF under argon. Three types of PdAu/C were prepared, all with different compositions. The oxidation reactions of H₂, CO and CO/H₂ were used as probes to determine the CO tolerance of these electrocatalysts. At low overpotentials, these were more free active surface sites for hydrogen oxidation on PdAu than on PtRu at room temperature. Furthermore, at an elevated temperature of 60 °C, the surface of the PdAu/C appears to be less strongly poisoned by CO than that of PtRu/C, which gives rise to a larger concentration of free active Pd sites for H₂ oxidation. The superior activity of PdAu compared with PtRu/C was shown by CO/H₂ oxidation measurements at fuel-cell-relevant anode potentials (0.50–0.10 V). These results, however, were acquired at temperatures below 60 °C and further improvements such as optimizing the PdAu/C with respect to particle size, alloy homogeneity and stoichiometry are required.

Table 2
Various CO-tolerant anode electrocatalyst reported since 2000

Composition of anode electrocatalyst	Preparation method	Comments	Reference	Referred earlier papers
PtSn/C	Surface organometallic chemistry	Enhanced activity with a larger decrease in the onset potential of CO oxidation compared with Pt/C	[69]	[45,62]
PdAu/C	Deposition of bimetallic colloidal precursors	PdAu/C seems to be less strongly poisoned by CO than PtRu/C at 60 °C	[70]	[71–73]
PtM/C, PtRuM/C (M = Mo, Nb and Ta)	Precipitation	PtRuMo (10 wt.% Mo) gives higher activity than PtRu/C	[60]	[51,52,74–76]
PtMo/C	–	PtMo (5:1 atomic ratio)/C shows lowest overpotential losses for 5–100 ppm CO	[77]	[74,75]
PtRu- H_x MeO ₃ /C (Me = Mo and W)	Dispersion of PtRu particle in a composite support (colloidal H_x MeO ₃ and C)	Cell performance of PtRu- H_x MoO ₃ /C better than that of PtRu/C	[82]	[42,78–81]
PtRu/carbon nanotubes	PtRu; precipitation of carbon nanotubes; arc-discharge method	Performance similar to that of PtRu/C in PEMFC but better in DMFC	[83]	[84–86]
Double-layer; outer: PtRu/C inner: Pt/C	Composite electrocatalyst structure	Exhibits less performance drop in H ₂ /CO fuel than the PtRu/C	[87]	[88–90]

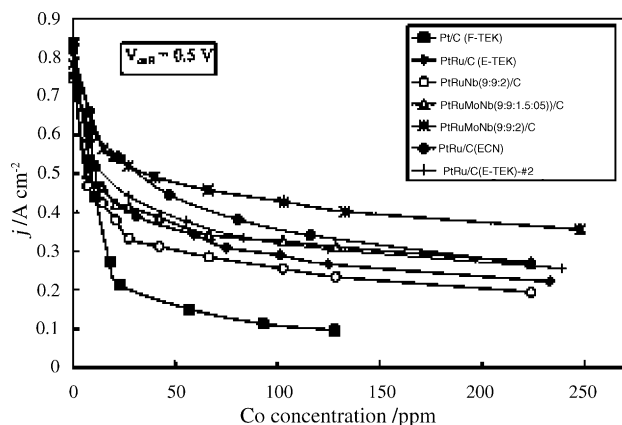


Fig. 2. Current density vs. CO concentration for cells operated with anode catalysts of: carbon-supported Pt (E-TEK), PtRu (E-TEK), PtRuNb (9:9:2), PtRuMoNb (9:9:1.5:0.5) and PtRuMo (9:9:20) at pressure of 1.5 bar and cell voltage of 0.5 V. $T_{\text{cell}} = T_{\text{hum}} = 80^\circ\text{C}$ [60].

2.3.1.3. PtM/C, PtRuM/C ($M = \text{Mo}$, Nb and Ta) systems. In 2002, Papageorgopoulos et al. [60] investigated the effect on CO tolerance of including a metal M ($M = \text{Mo}$, Nb and Ta) in Pt/C and PtRu/C. This was undertaken by comparing the cyclic voltammetry data and cell performance of the modified catalysts with those of traditional Pt/C and PtRu/C catalysts [60]. The new catalysts were binary PtM/C and ternary PtRuM/C (Vulcan XC-72) systems, with a 20 wt.% metal loading. The results (Fig. 2) showed that the inclusion of 10 at.% Mo in PtRu, produced an electrocatalyst with higher activity in the presence of CO than PtRu/C. Two earlier sets of studies prompted these experiments. One was work [74–76] that demonstrated that PtMo/C gave up to a three-fold enhancement in performance with H_2 (100 ppm CO)/ O_2 compared with PtRu/C in the absence of CO_2 in the fuel. The other research [51,52] had reported the improved behaviour of PtRu binary catalysts with the incorporation of a third metal, such as Cr, Zr or Nb.

The evaluation of PtMo/C continued in 2003 with the investigations of Urian et al. [77], who investigated the CO and CO_2 tolerance of four types of PtMo/C (Pt:Mo atomic ratio = 1:1, 3:1, 4:1 or 5:1) anode electrocatalyst by comparison with Pt and Pt:Ru (atomic ratio = 1:1) in fuel in which CO_2 was present. It was observed that PtMo/C exhibited at least a three-fold increase in CO tolerance with respect to PtRu/C and a four-fold increase with respect to Pt/C. Pt:Mo atomic ratios had a negligible influence on the anode polarization of the CO tolerance at 100 ppm of CO. Variation of the CO content in H_2 (in the range of 5–100 ppm) exhibited the least influence on the overpotential losses for PtMo (atomic ratio = 5:1) electrocatalysts.

2.3.1.4. PtRu- $\text{H}_x\text{MO}_3/\text{C}$ ($M = \text{Mo}$ and W) system. In 2003, based on the results of previous papers [42,78–81] that showed that the addition of Mo or W (especially, for PtRu/ WO_3/C [80]) could enhance the CO tolerance of catalysts, Hou et al. [82] prepared new composite catalysts of PtRu- $\text{H}_x\text{MO}_3/\text{C}$ ($M = \text{Mo}$ and W) by dispersing PtRu particles in a composite support composed of colloidal H_xMO_3 ($M = \text{W}$ or Mo) and Vulcan XC-72. These authors investigated the performance of the cat-

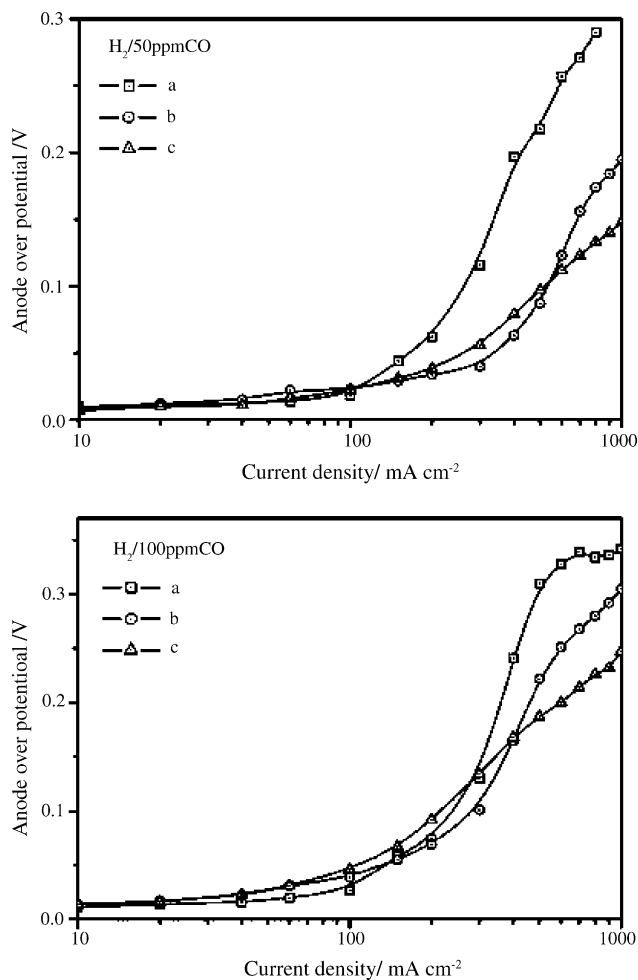


Fig. 3. Anode polarization curves for PEMFCs with: (a) PtRu/C, (b) PtRu- $\text{H}_x\text{WO}_3/\text{C}$ and (c) PtRu- $\text{H}_x\text{MoO}_3/\text{C}$ anodes. Cell temperature of 80°C ; both humidifiers at 80°C ; operating pressure of 0.2 MPa [80].

alyst by comparing its electrochemical behaviour with that of PtRu/C. The contents of the noble metals in all the catalysts were 20 wt.% Pt and 10 wt.% Ru, and the content of H_xMO_3 in PtRu- $\text{H}_x\text{MO}_3/\text{C}$ was 20 wt.%. It was found that the noble metals in both PtRu/C and PtRu- $\text{H}_x\text{MO}_3/\text{C}$ were uniformly and highly dispersed on the supports, and there were no obvious differences when a composite support was used instead of the carbon support. Both H_xWO_3 and H_xMoO_3 existed in an amorphous form and provided sufficient interfaces between the noble metals and the transition metal oxides in the catalysts. Such a structure promises a better CO tolerance than PtRu/C by lowering the starting potential for CO oxidation and by improving the H_2 oxidation when active sites on the noble metals are blocked by CO. In single-cell performance tests of all the catalysts operated with $\text{H}_2/50\text{ppmCO}$ and $\text{H}_2/100\text{ppmCO}$, those with PtRu- $\text{H}_x\text{MO}_3/\text{C}$ electrodes were better than those of PtRu/C, as shown in Fig. 3. These results were attributed to the presence of sufficient interfaces between the noble metals and transition metal oxides in the catalysts and to the bifunctional effects of CO electrooxidation reactions strengthened by the existence of active water that is bonded on the transition metal oxides.

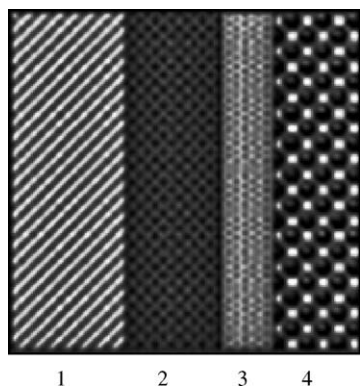


Fig. 4. Schematic structure of composite anode: (1) gas-diffusion layer; (2) outer catalyst layer; (3) inner catalyst layer; (4) Nafion membrane [87].

2.3.1.5. PtRu on carbon nanotube systems. In 2005, Gonzalez and co-workers [83] reported the performance of PtRu catalysts supported on carbon nanotubes [84–86] for $H_2 + 100$ ppm CO. Their results were similar to those for PtRu on Vulcan XC-72 with an overpotential of 100 mV at $1 A cm^{-2}$ in a PEMFC. By contrast, a direct methanol fuel cell gave power densities and the activity levels that exceeded those obtained with PtRu/Vulcan XC.

2.3.2. Double-layer anode electrocatalysts

Although many attempts have been made in the last few decades to develop Pt-based binary or ternary electrocatalyst for replacing or reducing the platinum in the catalysts of PEMFCs, there has been less effort towards developing CO-tolerant electrodes by modifying their structure. The electrode structure relates to the diffusion process and reaction dynamics. In other words, because the diffusion coefficients of H_2 and CO are different, it is possible to design a special composite electrode structure according to the fuel components. In doing so, the anodes can be made with different electrocatalyst components, contents and pore distributions. Therefore, this is considered to be a promising alternative approach to decreasing the poisoning of PEMFC anodes [87–90].

In 2003, Yu et al. [87] investigated the CO tolerance of composite electrodes with a structure designed to make poisonous CO react with CO-active electrocatalysts in advance at a separate layer, and to have the main hydrogen react at another layer with a traditional platinum electrocatalyst [87]. This composite anode structure is shown in Fig. 4; PtRu is used to electrocatalyze the oxidation of CO and Pt to catalyze the hydrogen oxidation reaction. As hydrogen diffuses faster than CO in the gas-diffusion layer, the inner catalyst layer should have a higher platinum loading, and the outer catalyst layer should be rich in PtRu. The electrode structures and electrocatalyst components employed by Yu et al. in [87] are listed in Table 3. The inner catalysts of E2 and E4 were prepared by a transfer method that involved a very thin layer. For a H_2/CO fuel, it was found that PEMFCs with the new composite electrodes exhibited a smaller drop in performance than traditional PtRu electrodes. When pure hydrogen was used, the fuel cell exhibited almost the same performance as the traditional Pt electrode.

Table 3
Several electrode structures and electrocatalyst loading [87]

Anode	Inner catalyst layer	Outer catalyst layer
E1	–	Traditional method; Pt/C, $0.3 mg cm^{-2}$ Pt
E2	–	Traditional method; PtRu/C, $0.3 mg cm^{-2}$ PtRu
E3	Transfer method; Pt/C, $0.02 mg cm^{-2}$ Pt	–
E4	Traditional method; Pt/C, $0.1 mg cm^{-2}$ Pt	Traditional method; PtRu/C, $0.2 mg cm^{-2}$ PtRu
E5	Transfer method; Pt/C, $0.02 mg cm^{-2}$ Pt	Traditional method; PtRu/C, $0.28 mg cm^{-2}$ PtRu

3. Conclusions

The most commonly used anode electrocatalyst in PEMFCs is the binary catalyst, PtRu/C. This system evidently enhances CO tolerance and decreases the CO binding energy on platinum due to its electronic or bimetallic effects.

The Pt-based binary anode electrocatalyst, PtSn/C, prepared by a surface organometallic chemistry method, enhances the performance of PEMFCs by causing a larger decrease in the onset potential of CO oxidation compared with Pt/C.

The PtMo (atomic ratio = 5:1) electrocatalyst displays a lower variation in overpotential losses than the PtRu counterpart. Furthermore, Pt-based ternary electrocatalysts, such as PtRuMo (Mo 10 wt.%), give better performance than those of PtRu/C in the presence of CO. The cell performance of PtRu- H_x MoO₃/C electrodes is superior to that of PtRu/C in the presence of 50–100 ppm of CO.

The performance of PtRu catalysts supported on carbon nanotubes in 100 ppm of CO in a PEMFC is similar to that of PtRu on Vulcan XC-72. By contrast, the power densities and activity of the anodes in a DMFC exceeded those of PtRu/Vulcan XC.

In Pt-free electrocatalysts, the surfaces of PdAu/C electrocatalysts to be less strongly poisoned by CO than those of PtRu at temperatures of 60 °C.

According to the fuel selection, a more effective tolerance of CO in a PEMFC can be achieved by modifying the structure of the catalyst, i.e., with a composite or a double-layer. For example, the structure is designed to make the CO react at a separate layer with the CO active electrocatalyst in advance and have the main hydrogen react at another layer with the traditional Pt electrocatalyst. There is still scope to optimize this type of structure and thus make the method even more effective for the suppression of CO poisoning.

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