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High CO tolerance of $Pt/Fe/Fe_2O_3$ nanohybrid thin film suitable for methanol oxidation in alkaline medium

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The toluene–water interface has traditionally been employed to prepare particle assemblies and films of metals and semiconductors. The interface between water and an organic liquid, however, has not been investigated sufficiently for possible use in preparing nanocrystals and thin films of magnetic alloys. In this article, we demonstrate the use of the liquid–liquid interface as a medium for preparing ultrathin films of magnetic Pt/Fe/Fe₂O₃ nanohybrid catalysts for methanol electrooxidation in NaOH medium. The resulting Pt/Fe/Fe₂O₃ hybrid catalyst shows the highest activity and CO tolerance ($j_f/j_p = 8.09$) among all other catalysts that were tested up to now toward methanol electrooxidation. The results reported in this article demonstrate the versatility and potential of the liquid–liquid interface for preparing nanomaterials and ultrathin films and encourage further research in this area.

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Introduction

Direct alcohol fuel cells (DAFCs) are considered a promising alternative power source, due to their unique advantages, such as high energy conversion efficiency and being environmentally benign.1-3 However, large-scale applications of DAFCs are seriously hampered, due not only to high loading of expensive Pt catalysts (*i.e.* >0.4 mg_{Pt} cm_{electrode}⁻²),^{4,5} but also to poor catalyst CO tolerance.⁶⁻⁸ Bimetallic alloy catalysts were found to improve the CO tolerance of Pt catalysts.9-12 Bimetallic nanoparticles (NPs) composed of a noble metal and a non-noble metal have attracted increasing interest among researchers because of the high possibility of tailoring the electronic and geometric structures, which in turn can enhance the catalytic activity and selectivity.¹³⁻¹⁷ Besides, reducing the consumption of precious metals such as Pt by bimetallization with a low-cost metal is a popular approach to accelerate the practical application of noble metal-based catalysts in new areas of energy technology, such as fuel cells.18 The improvements derived from the combination of two metal elements into bimetallic particles can arise from an ensemble effect, a modified electronic structure, or the formation of new catalytic sites.19,20

Although alloy particles such as Pt/Ru are very useful in the anodic oxidation of methanol, high costs limit their practical application. Therefore, economical and effective alternative catalysts are required, and cost-effective routes are being sought to make more efficient Pt catalysts. One approach is to use Pt alloys with low-cost metals. Among these alloy catalysts, Pt/Fe alloy NPs have been demonstrated as an attractive candidate for direct methanol fuel cells (DMFCs). Nanoscale magnetic particles are of interest for developing a more complete methanol electrooxidation.21 However, in spite of the significant enhancement in the methanol oxidation reaction (MOR) activity, Pt/Fe nanostructured electrocatalysts can hardly be used in electrode assembly due to difficulties in their synthesis. Previously, many researchers have attempted to chemically synthesize monodisperse Pt/Fe NPs which occur at high temperature annealing, however this leads to particle aggregation, and wider size distributions.22-24 To prevent particle agglomeration, many methods have been developed such as doping with Ag, Au and Cu in the Pt/Fe phase to lower the onset temperature,²⁵⁻²⁷ coating Pt/Fe with iron oxide,^{28,29} SiO₂,³⁰ or MgO,³¹ and annealing with salt (*i.e.* NaCl).³² Nevertheless, a definitive technique for magnetic recording fabrication has not been achieved vet.

Toluene–water interface has been employed to prepare metal nanocrystals by the reduction of the metal salts.³³ The liquid–liquid interface itself has been exploited to form nanocrystals and their assemblies to a limited extent, such as Au, Ag, Pt, Pd and Cu NPs, chalcogenides such as CdS, CdSe, ZnS, CoS, NiS, CuS, PbS, oxides such as γ -Fe₂O₃, ZnO, CuO and nanostructured peptide fibrils.^{34–43} The initial experiments carried out by Rao and coworkers,^{37–47} yielded ultrathin nanocrystalline films of metals, semiconducting chalcogenides, metal oxides, metal sulfides and other materials at the liquid–liquid interface and indicated that the method may have greater potential than at first imagined. Thin films are of great importance for many chemical and electrochemical applications such as electronic devices, sensors, catalysts and electrodes. The method involves

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dissolving an organic precursor of the relevant metal in the organic layer and the appropriate reducing reagent in the aqueous layer. The product formed by the reaction at the interface contains ultrathin nanocrystalline films of the relevant material formed by closely packed nanocrystals. Under controlled conditions, ultrathin nanocrystalline films of metals with interesting properties have been obtained.48 It has been possible to prepare single crystalline 2D sheets of metal chalcogenides and oxides. The liquid-liquid interface appears to provide a general method of producing a variety of nanomaterials in the form of 2D films, the important adjustable parameters being the reactant concentrations, temperature, area of the interface and viscosity of the aqueous medium. Previously, we have investigated the effect of different stabilizers on the structure and catalytic activity of Pt NPs thin films at oil-water interface.39 Also, we have reported the effect of different organoplatinum(II) and organopalladium(II) complexes on the morphology and size of Pt NPs and Pt-Pd NPs alloys at oil-water interface in the absence of stabilizer and their electro-oxidation activity was investigated in the MOR.47,49 Recently, we fabricated Pd NPs/reduced-graphene oxide thin films as effective catalysts for Suzuki-Miyaura reaction in water.50

To the best of our knowledge, there is no report concerning application of $Pt/Fe/Fe_2O_3$ alloy thin film obtained from a liquid–liquid interface in producing chemically modified electrodes and using it as an electrocatalyst in the oxidation of small organic molecules. To date, the effective method to control the size, shape, and composition of Pt/Fe NPs alloy by using low toxic precursors remains a challenge that must be overcome before their potential applications will be fulfilled.

We describe herein, for the first time, synthesis and characterization of magnetic bimetallic Pt/Fe/Fe₂O₃ NPs alloy thin film *via* a simple reduction of $[PtCl_2(cod)]$, (cod = cis, cis-1, 5cyclooctadiene) and $[Fe(acac)_3]$, (acac = acetylacetonate)complexes at toluene-water interface in the absence of stabilizer. We also present the catalytic properties of the alloy thin film in the MOR and investigate its tolerance toward CO adsorption. This method provides a novel, simple and cheap strategy to produce different bimetallic thin films, suitable for application in DMFCs.

Experimental

All of the chemical compounds were purchased from Merck Company. The complexes $[PtCl_2(cod)]^{51}$ and $[Fe(acac)_3]$,⁵² were synthesized using reported procedures. X-ray diffraction (XRD) patterns of the as-prepared electrocatalyst were recorded using a Bruker AXS (D8, Avance) instrument equipped with Cu-K α radiation ($\lambda = 1.54184$ Å). Transmission electron microscopy (TEM) images of the electrocatalyst were recorded using a Philips CM-10 TEM microscope operated at 100 kV.

Preparation of PtFe bimetallic thin film at the toluene-water interface

An equimolar solution of $[PtCl_2(cod)]$ (0.5 mM, 12.5 ml) and $[Fe(acac)_3]$ (0.5 mM, 12.5 ml) in toluene was sonicated for 5 min

to prepare an orange color solution. This solution was stand in contact with double distilled water (25 ml) in a beaker (100 ml). Once the two layers were stabilized, an appropriate volume of aqueous NaBH₄ (10 ml, 0.1 M) was injected into the aqueous layer using a syringe with minimal disturbance to the toluene layer. The onset of reduction was marked by a coloration of the liquid–liquid interface. With the passage of time, the color became more vivid, finally resulting in a film at the liquid–liquid interface. The aqueous and organic layers below and above the film were, however, transparent.

Electrode preparation

To transfer thin films from liquid–liquid interface to the surface of glassy carbon electrode, the toluene phase (top phase) was removed slowly by a syringe and then a solid substrate was inserted into the liquid phase and pulled out.

Electrochemical measurements

The catalyst was characterized using an Autolab Potentiostat/ Galvanostat PGSTAT12 (Eco Chemie, Switzerland). All characterizations were conducted at room temperature in a standard three-electrode system using an Ag/AgCl (sat. KCl) reference electrode, a platinum wire counter electrode and glassy carbon coated with prepared electrocatalysts as a working electrode. However, all potentials in the manuscript were converted to values with reference to a normal hydrogen electrode (NHE). The glassy carbon electrode area diameter was 2 mm. All cyclic voltammograms (CVs) were recorded under the same conditions.

Results and discussion

In this study, Pt/Fe/Fe₂O₃ alloy NPs thin film was synthesized by the reduction of $[PtCl_2(cod)]$ and $[Fe(acac)_3]$ complexes as platinum and iron precursors at the toluene–water interface, shown in Scheme 1. $[PtCl_2(cod)]$ and $[Fe(acac)_3]$ complexes were dissolved in toluene at room temperature and then contacted with water. The aqua solution of NaBH₄ was injected into the aqueous layer with minimal disturbance to initiate the reduction and thin film formation was indicated by the interface color change from orange to black.

The results of XRD spectrum indicate that the catalyst is well synthesized. Fig. 1 shows the XRD pattern of the as-prepared Pt/Fe/Fe₂O₃ from the typical experiment. It can be observed from the XRD pattern that it has five peaks at $2\theta = 40^{\circ}$, 47° , 68° , 83° and 86° corresponded to planes (111), (200), (220), (311) and (222) of face-centered cubic (fcc) crystalline Pt, respectively.⁵³ Besides, Fig. 1 exhibits other seven weak diffraction peaks at $2\theta = 36^{\circ}$, 51° , 53° , 57° , 61° , 67° and 78° corresponded to planes (110), (113), (024), (116), (018), (214) and (300) which could be assigned to α -Fe₂O₃ with rhombohedral structure.⁵⁴ Weak diffraction peaks at $2\theta = 44^{\circ}$, 65° and 83° corresponded to planes (110), (200) and (211) belongs to Fe(0).⁵⁵ The XRD results show that nanohybrid catalyst from the typical experiment consists of crystalline Pt, Fe, and Fe₂O₃.



Scheme 1 Schematic illustration of the $Pt/Fe/Fe_2O_3$ bimetallic NPs thin film formation at toluene–water interface, (a) addition of Pt and Fe complexes solution into water, (b) stabilized mixture of $[PtCl_2(cod)]$ and $[Fe(acac)_3]$ in toluene (orange colour) and water, (c) addition of NaBH₄ to the aqueous layer, (d) the thin film of $Pt/Fe/Fe_2O_3$ NPs appeared at the toluene–water interface after adding NaBH₄, and (e) remove the toluene (top) phase by a syringe.



Fig. 1 XRD pattern of Pt/Fe/Fe₂O₃ NPs thin film on a glass.

The chemical composition of these NPs was determined by energy dispersive X-ray analysis (EDX) (Fig. 2), confirming the existence of Pt (52.89%), Fe (24.80%) and O (22.31%) elements.

TEM images (Fig. 3a–c) show that $Pt/Fe/Fe_2O_3$ NPs have spherical, connected chain-like structure with a mean diameter of 20 nm (Fig. 3d).

Magnetic hysteresis loop (M/H plot) measured at 298 K for the Pt/Fe/Fe₂O₃ nanohybrid thin film as a powder is shown in



Fig. 2 EDX spectrum of the magnetic Pt/Fe/Fe₂O₃ NPs thin film.

Fig. 4. Superparamagnetic behavior with coercivity (H_c) of 0 Oe and remanent magnetization (M_r) of 0 emu g⁻¹ is observed. Saturation of magnetization is not observed at this temperature. At 298 K, typical behavior expected for a superparamagnet with zero coercivity is observed.⁵⁶ It is known that bulk α -Fe₂O₃ behaves as an antiferromagnet with a Neel temperature (T_N) of about 960 K. α -Fe₂O₃ exhibits a first-order magnetic transition called a Morin transition at about 263 K. The magnetic sublattices are antiparallel below the Morin transition and the material behaves like an antiferromagnet. Above the Morin transition temperature, α -Fe₂O₃ exhibits a small net magnetic moment due to spin canting, thereby resulting in weak ferromagnetism.⁵⁷ The superparamagnetic property of Pt/Fe/Fe₂O₃ alloy thin film decreased compared to Fe-free NPs.⁵⁸

It is reported that metal oxides had significant promotion effect on the alcohol electrooxidation for Pt-based catalysts.⁵⁹⁻⁶²



Fig. 3 (a–c) TEM images of the spherical, chain-like $Pt/Fe/Fe_2O_3$ nanostructures and (d) histogram of particle size distribution.



Fig. 4 Magnetic hysteresis loop of Pt/Fe/Fe₂O₃ thin film.

Therefore, the introduction of Fe_2O_3 might be conducive to improving the electrocatalytic performance of Pt/Fe/Fe₂O₃ toward methanol oxidation, which was demonstrated by the following electrochemical measurements.

Electrocatalytic activity for methanol oxidation

To investigate the catalytic activity of this electrocatalyst, we have studied hydrogen adsorption and methanol oxidation on the Pt/Fe/Fe₂O₃ thin film. The cyclic voltammograms demonstrate that the Pt/Fe/Fe₂O₃ catalyst reveals high activity for methanol electrooxidation. As Fe₂O₃ is acid soluble oxide, the electrooxidation of methanol was investigated in alkaline medium.⁵⁴ Cyclic voltammogram of Pt/Fe/Fe₂O₃ NPs thin film in 0.5 M NaOH at a scan rate of 50 mV s⁻¹ is shown in Fig. 5. The humps on Pt/Fe/Fe₂O₃ diagram are associated with atomic hydrogen desorption and adsorption (I and III regions in Fig. 5). Metal oxides formation was also observed (region II in Fig. 5).

If the maximum peak current density in the forward direction is designated as j_f and the maximum peak current density in the backward is designated as j_b , the ratio of j_f/j_b is generally used to evaluate the tolerance of the catalysts to incompletely



Fig. 5 Cyclic voltammogram of Pt/Fe/Fe₂O₃ thin film in the presence of NaOH (0.5 M) with a scan rate of 50 mV s⁻¹.

oxidized species accumulated on the surface of the electrode.^{63,64} A larger ratio of j_f/j_b represents more complete methanol oxidation, less accumulation of CO or CO-like species on the catalyst surface.⁶⁵ The efficiencies of the Pt and Pt-alloys nanostructures on methanol oxidation were compared with regard to oxidation potential, forward oxidation peak current density, and the ratio of the j_f/j_b .

From Fig. 6, the j_f/j_b ratio for the Pt/Fe/Fe₂O₃ synthesized thin film is about 8.09 that is larger than 0.99 for ETEK Pt (ref. 66) or 0.58 for other type of commercial Pt/C.⁶⁷ Therefore, Pt/Fe/ Fe₂O₃ thin film electrode can lead to more complete methanol oxidation and less accumulation of CO or CO-like species than commercial Pt and Pt NPs thin film. This may put down to Fe₂O₃ that promotes the adsorbed intermediate species removal by supplying active oxygen species like other metal oxides during the electrooxidation process.⁵⁴ The results reveal that Pt/Fe/Fe₂O₃ hybrid catalyst not only decreases the Pt dosage but also enhances the performance of MOR in comparison with commercial Pt and Pt NPs thin film. j_f/j_b data are summarized in Table 1.

The bifunctional mechanism suggested by Liu and Norskov implies that the Ru sites provide the OH groups, which react with CO adsorbed on Pt sites to form CO₂.⁷² Apart from Ru, several other elements including Sn, W and Mo showed enhancement of methanol oxidation and specifically CO oxidation due to co-catalytic effects when used as Pt based alloys or layers adsorbed on Pt.^{73,74} A similar mechanism for methanol oxidation catalyzed by Pt–Fe catalyst summarized as follows:

 $Pt + CH_3OH_{(sol)} \rightarrow Pt-CH_3OH_{ad} \rightarrow Pt-CO_{ad} + 4H^+ + 4e^- (1)$

$$Fe + OH^- \rightarrow Fe - OH_{ad} + e^-$$
 (2)

$$Pt + OH^{-} \rightarrow Pt - OH_{ad} + e^{-}$$
(3)

$$Pt-CO_{ad} + Fe-OH_{ad} \rightarrow Pt-COOH_{ad} + Fe$$
(4)

$$Pt-CO_{ad} + Pt-OH_{ad} \rightarrow Pt-COOH_{ad} + Pt$$
(5)

$$Pt-COOH_{ad} + Pt-OH_{ad} \rightarrow 2Pt + CO_2 + H_2O$$
(6)



Fig. 6 Cyclic voltammogram of Pt/Fe/Fe₂O₃ thin film in 0.5 M NaOH electrolyte containing 0.5 M CH₃OH with a scan rate of 50 mV s⁻¹.

Table 1 Comparison of electrocatalytic activity of methanol oxidation

Electrode	$j_{ m f}/j_{ m b}$ ratio	Reference
Comm-Pt/C	0.57	68
Pt/C	0.605	69
Pt-Ru/C	0.629	69
Pt-Ru-Co/C	0.868	69
Pt/C	1.18	54
Pt-Pd	1.19	49
Pt-CeO ₂	1.20	70
Pt-Au	1.23	71
Pt thin film	1.28	47
Pt-Fe ₃ O ₄ -CeO ₂	1.32	70
Pt-Pd/RGO	1.50	49
Pd/XC-72	1.73	54
Pd-Fe ₂ O ₃	1.98	54
Hexa-Pt/C	2.13	68
Pt/Fe/Fe ₂ O ₃	8.09	This work

The strongly adsorbed CO intermediate $(CO)_{ads}$ is produced during electrooxidation of methanol on the catalyst, which could be a serious problem for both catalytic activity and stability. Step (5) was proposed to be the rate-determining step, in which the adsorbed hydroxyl ions removed the adsorbed CO intermediate to form carboxylate and released free active catalytic sites of Pt.

The methanol electrooxidation was also investigated at lower methanol concentration in order to see the oxidation peak more obviously. Cyclic voltammogram of Pt/Fe/Fe₂O₃ NPs thin film in 0.1 M NaOH and 0.1 M CH₃OH at a scan rate of 50 mV s⁻¹ is shown in Fig. 7. The electrocatalytic activity of this thin film for the oxidation of methanol was investigated by the appearance of an oxidation current in the positive potential region. The oxidation current for this electrocatalyst in 0.1 M CH₃OH became lower than in 0.5 M CH₃OH. There is not distinguishable hump for determination of j_b in Pt/Fe/Fe₂O₃ cyclic voltammogram in this methanol concentration (see Fig. 7). Not seeing the MOR peak clearly is due to the fact that Pt/Fe/Fe₂O₃ nanohybrid is a thin film with a low metal loading.



Fig. 7 Cyclic voltammogram of Pt/Fe/Fe₂O₃ thin film in 0.1 M NaOH electrolyte containing 0.1 M CH₃OH with a scan rate of 50 mV s⁻¹.

Typical cyclic voltammograms recorded for the Pt/Fe/Fe₂O₃ thin film in 0.1 M NaOH and 0.1 M CH₃OH at different scan rates ranging from 20 to 100 mV s⁻¹ are shown in Fig. 8a. The increase in the current density with the scan rate is observed and the peak potentials almost show no change. Fig. 8b shows that peak current densities are linearly proportional to the square root of the scan rates. Following equations were used to find out the number of exchanged electrons for an irreversible electrochemical reaction during MOR:^{75,76}

$$E_{\rm p} - E_{\rm p/2} = 47.7 \ ({\rm mV})/\alpha n_{\alpha}$$
 (7)

$$I_{\rm p} = (2.99 \times 10^5) n A C_{\rm O}^* D_{\rm O}^{1/2} (\alpha n_{\alpha})^{1/2} \nu^{1/2}$$
(8)

 $E_{p/2}$ is the potential where the current is half the peak value, E_p is a function of scan rate, shifting (for oxidation) in a positive direction by an amount in $1.15RT/(1 - \alpha)F$ for each tenfold increase in ν , α is an electron transfer coefficient and n_{α} is the number of electrons involved in the rate-determining step (eqn (7)).^{75,76} In eqn (8), I_p is the peak current observed in amperes, n is the number of electrons transfer during the electrochemical process, A is the surface area of working electrode in cm², D_O is the diffusion coefficient for the oxidized species in cm² s⁻¹, ν is the rate at which the potential is swept (V s⁻¹), C_O^* is the concentration of the oxidized species before the electrochemical perturbation is applied in mol cm⁻³, α is an electron transfer coefficient and n_{α} is the number of electrons involved in the rate-determining step.⁷⁵⁻⁷⁷

From Fig. 8a, E_p and $E_{p/2}$ are 2100 and 1925 (mV), respectively and are taken for the scan rate of 100 mV s⁻¹:

$$E_{\rm p} - E_{\rm p/2} = 47.7 \text{ (mV)}/\alpha n_{\alpha}, 2100 - 1925 \text{ (mV)} = 47.7 \text{ (mV)}/\alpha n_{\alpha}$$

From eqn (7), αn_{α} value is 0.27. Also, eqn (7) is used for all scan rates and have obtained the same value for αn_{α} . In eqn (8), *A* value is 0.0314 cm², αn_{α} value is 0.27 (from eqn (7)), $C_{\rm O}^*$ value is 0.0001 mol cm⁻³, $D_{\rm O}$ is a diffusion coefficient of methanol and its value is 1.3×10^{-5} cm² s⁻¹. $I_{\rm p}/A\nu^{1/2}$ can obtain from the slope of Fig. 8b and its value is 0.27332. By these data deposition in eqn (8) we have:

$$n = [(0.27332)]/[2.99 \times 10^5 \times 0.0001 \times (1.3 \times 10^{-5})^{1/2} \times (0.27)^{1/2}]$$

= 5.97 \approx 6

From this equation the number of exchanged electrons is 6 and confirm that the MOR is an overall 6 electron process:^{76,78}

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$$
 (9)

Pt/Fe/Fe₂O₃ electrocatalyst is a very thin layer that stick strongly to the surface of the electrode. This nanohybrid has no change during MOR due to its stability in alkaline media. The electrocatalyst was analyzed by XRD after catalytic cycle. It can be observed from the XRD pattern that it has five peaks at $2\theta = 40^{\circ}$, 47° , 68° , 83° and 86° corresponded to planes (111), (200), (220), (311) and (222) of fcc crystalline Pt, respectively.⁵³



Fig. 8 (a) Cyclic voltammograms of the $Pt/Fe/Fe_2O_3$ thin film at different scan rates in 0.1 M NaOH + 0.1 M CH₃OH. (b) Dependence of the peak currents on the square root of the scan rates.



Fig. 9 XRD pattern of $\text{Pt/Fe/Fe}_2\text{O}_3$ NPs thin film on a glass after catalytic cycle.

Besides, Fig. 9 exhibits other seven diffraction peaks at $2\theta = 36^{\circ}$, 51°, 53°, 57°, 61°, 67° and 78° corresponded to planes (110), (113), (024), (116), (018), (214) and (300) which could be assigned to α -Fe₂O₃ with rhombohedral structure.⁵⁴ Diffraction peaks at $2\theta = 44^{\circ}$, 65° and 83° corresponded to planes (110), (200) and (211) belongs to Fe(0).⁵⁵ The XRD results show that nanohybrid catalyst consists of crystalline Pt, Fe, and Fe₂O₃.

In our previous study,⁴⁷ platinum thin film was formed using [PtCl₂(cod)] complex and its electrocatalytic activity was investigated in a 0.5 M H₂SO₄ solution containing 0.5 M methanol. But in this paper, we used previous strategy to synthesize Pt/Fe/Fe₂O₃ metal alloy for the electro-catalytic oxidation of methanol in alkaline medium. On the other hand, using of metal binary alloy strategy can lead to a lower amount of Pt catalysts and in turn, can decrease the price of the electrocatalysts for MOR. Also, the *j*_f/*j*_b ratio for Pt/Fe/Fe₂O₃ thin film was about 8.09, that was larger than 1.28 for Pt thin film. Therefore, Pt/Fe/Fe₂O₃ thin film electrode can lead to more complete methanol oxidation and less accumulation of CO or CO-like species than Pt NPs thin film.

Conclusions

The current study introduces a novel preparation method for metal oxide modified Pt NPs for the electro-catalytic oxidation

of methanol in alkaline medium via a simple toluene-water interface strategy. Presence of iron oxides NPs resulted in a significant enhancement of methanol oxidation as evident from the increase in the anodic peak current. The presence of iron oxides is believed to provide oxygen to the adsorbed methanol residues (e.g., CO) thus facilitating its oxidation to CO_2 and leads eventually to the retrieval of the Pt active surface site. Therefore, iron oxide has a promoting effect on oxidizing and removing the adsorbed CO-like intermediate species during electrooxidation of methanol. These results indicate that due to the low cost and enhanced performance, the Pt/Fe/Fe₂O₃ hybrid catalyst may be a superior candidate for DMFCs. Reducing the consumption of precious metals such as Pt by bimetallization with a low-cost metal or completely replacing Pt by other nonnoble metals is a popular approach. One of the most attractive advantages of alkaline fuel cells is the possibility of using non-precious and low cost metal catalysts. Among different metals, nickel is the most investigated Pt alternative anode catalyst for methanol oxidation in alkaline media. Since nickel placed in contact with a solution of aqueous alkali has been shown to become covered with a layer of NiOOH, but it has some disadvantages. The accumulation of NiOOH had an inhibiting effect on activity and can be counteracted by a period of re-activation. Also, activity of the Ni electrodes towards methanol oxidation was found to vary with the amount of deposited Ni and high metal loading is needed.79 The MOR activity of Ni can be enhanced by alloying with Ru and Cu in alkaline solutions and is higher than that of Ni and Ru alone.⁸⁰ In some cases, MOR activity of non-noble metals can be enhanced by using stabilizers. For example gold films deposited on the surface of ultrafine PAni fibers,⁸¹ Ni dispersed on graphite,⁸² a Ni zeolite,⁸³ or by using polymer templates like polymer template coordination with metal-ions loaded with a carbon-reduction method (P-M-C complexes), P stands for polymer, M = Fe, Co and Ni and C is carbon.⁸⁴ Some of the nonnoble electrocatalysts need heat treatment. Heat treatment was shown to improve oxidation performance for Co-W alloy.⁸⁵ Pd, Au, Ni, ... are active for methanol oxidation in alkaline media, but their activity is remarkably lower than that of platinum.86-89 In this study, using liquid-liquid self-assembly (a facile strategy to prepare metal alloys), can decrease the cost of the Pt-based

alloy electrocatalysts with a low metal loading. Here, the Pt amount is too low and all the metal atoms of the alloy are on the surface of the electrocatalyst. Synthesizing Pt-based alloys thin films *via* the liquid–liquid interface have lower cost even compare to non-noble metal catalysts with high metal loading.

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