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Performance comparison of low-temperature direct alcohol fuel cells with different anode catalysts

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Abstract

Low-temperature polymer electrolyte membrane fuel cells directly fed by methanol and ethanol were investigated employing carbon supported Pt, PtSn and PtRu as anode catalysts, respectively. Employing Pt/C as anode catalyst, both direct methanol fuel cell (DMFC) and direct ethanol fuel cell (DEFC) showed poor performances even in presence of high Pt loading on anode. It was found that the addition of Ru or Sn to the Pt dramatically enhances the electro-oxidation of both methanol and ethanol. It was also found that the single cell adopting PtRu/C as anode shows better DMFC performance, while PtSn/C catalyst shows better DEFC performance. The single fuel cell using PtSn/C as anode catalyst at 90 °C shows similar power densities whenever fueled by methanol or ethanol. The cyclic voltammetry (CV) and single fuel cell tests indicated that PtRu is more suitable for DMFC while PtSn is more suitable for DEFC.
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1. Introduction

Low-temperature polymer electrolyte membrane fuel cells (PEMFCs) fueled directly by liquid fuels are gaining more and more attention for their large potential application for fuel cell vehicles, stationary applications and portable power sources. Operation on liquid fuels without the external bulky fuel-reforming system could greatly simplify the fuel cell system, therefore would result in its rapid commercialization. At present direct methanol fuel cells (DMFCs) are being actively investigated and during the past 10 years great progress has been made in this field [1–6]. Yet, it is still desirable to increase the number of liquid fuels that can be employed in these systems in order to extend the practical application of low-temperature fuel cells and to facilitate their penetration into energy market. Besides methanol, other small organic compounds such as formic acid [7–11], formaldehyde [9,11], ethanol [12], ethylene glycol [12,13],

n-propanol [12] and so on have been investigated and demonstrated appropriate for this type fuel cell, because they are reasonably inexpensive, nontoxic and largely available and have suitable electrochemical reactivity at relatively low temperatures. Furthermore, they have comparable energy density and reversible energy efficiency compared to H_2. Among these fuels, ethanol is of particular interest because it is a green fuel and can be readily and easily produced in great quantity by fermentation of sugar-containing raw materials. However, the present development of direct ethanol fuel cells (DEFCs) is not so satisfying as DMFCs (both are jointly called as direct alcohol fuel cells (DAFCs)), and fewer papers about DEFCs are obtained. There are several obstacles for DAFCs to overcome before their commercialization. The main problems [5,6,12] of DAFCs concern with the poor performance of electrocatalysts, especially anode catalysts at lower temperatures, and the severe fuel crossover from anode to cathode, which leads to serious poisoning of cathode catalysts in addition to the lower consumption efficiency of fuels. The activity improvement of anode catalysts is helpful to reduce fuel permeation through electrolyte, because the fuel concentration on the interface between anode and proton electrolyte is lowered as the

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fuel is consumed more exhaustively, consequently reducing the alcohol crossover pressure. Either increasing reaction temperature or adopting more active electrocatalysts can enhance the alcohol electro-oxidation reaction rate. However, upon increasing reaction temperature commercial perfluosulfonic-based polymer membranes dehydrate resulting in the intrinsic impedance increase and consequently deteriorate the fuel cell performance. Such problems may be addressed by using composite membranes [14,15]. The development of highly active anode catalysts is also of the primary importance [5]. Pt [16] has been demonstrated the only active and stable noble metal for alcohol oxidation, particularly in acid medium. However, it is well known [16] that pure platinum is readily poisoned by CO-like intermediates of methanol or ethanol electro-oxidations. Making alloys with a second or a third metal is a convenient way to modify electrocatalytic properties of Pt in order to overcome poisoning effects. Several metals have been found to enhance the activity for methanol oxidation definitely, among them Ru [1,5] is the favorite metal which can greatly increase the methanol electro-oxidation rate. Sn is another addictive investigated extensively, but controversial results on its effect on methanol electro-oxidation and CO tolerance have been reported in recent literature [17]. Most results of previous literatures about PtSn catalysts for methanol or ethanol electro-oxidation were carried out in half-cell devices [18], and as far as authors know, a few are directly concerned with single DMFCs or DEFCs [19]. Here we adopted carbon supported Pt, PtRu and PtSn as anode catalysts and compared the performances of single cells fed by methanol and ethanol, respectively.

2. Experiments

All the carbon supported Pt-based anode catalysts were homemade (20 wt.% Pt and the atomic ratio of Pt to Ru or Sn is 1) [20,21] and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The cyclic voltammetry (CV) tests for Pt/C, PtRu/C and PtSn/C were carried out on the potentiostat/galvanostat (EG&G Model 273A) at 25 °C [20]. The electrolytes were 0.5 M H_2SO_4 solution containing 1.0 M methanol or 1.0 M ethanol, respectively. The reference electrode and counter electrode were a saturated calomel electrode (SCE) and a platinum wire. The scan rate was 10 mV/s.

The membrane-electrode assemblies (MEAs) were prepared according to the literature [22,23]. Commercial Pt/C (20 wt.%, Johnson Matthey Co.) was used as cathode catalyst and Pt loading was 1.0 mgPt/cm². Nafion®-115 (125 μm thick) from Du Pont was employed as solid electrolyte. Anode catalysts were in-house Pt/C (2.0 mgPt/cm² loading), PtRu/C (2.0 mgPtRu/cm²) and PtSn/C (2.1 mgPtSn/cm²), respectively. Every single fuel cell has been operated at least 3 days after fixed. On the first day, the anode was fed by deionized water at 75 °C for about 4 h in order to fully hydrate the MEAs. At the same time the cell was short-circuited several times to oxidatively remove the slight amount of organic impurity on the anode. Then, the anode was fed by alcohol aqueous solution and the effluent solution was not used again. The polarization data were collected at 90 °C on the second day. Oxygen was directly fed into cathode without humidification and methanol or ethanol aqueous solution of 1.0 mole/l was fed into anode at a rate of 1.0 ml/min.

3. Results and discussion

The characterization results of catalysts are listed in Table 1. It is found from Table 1 that all catalysts have similar nanosized particles. The addition of Ru and Sn to Pt leads to obvious but opposite change of Pt lattice parameter, indicating the different interaction between Pt and Ru or Sn. No reflection signals for Ru and Sn or their oxides were found in the XRD patterns of these catalysts. XRD results showed that all in-house catalysts only had Pt fcc crystalline structures. The XPS results [20] showed that most of Pt and Ru in homemade catalysts were in metallic state, while most of Sn was in oxidized state.

From the CV results of methanol (Fig. 1), it is observed that methanol electro-oxidation on Pt/C starts at 250 mV (versus SCE), and the positive scan oxidation peak is at about 700 mV (versus SCE). On the PtRu/C catalyst, the onset potential of methanol electro-oxidation is 110 mV (versus SCE), and the positive scan oxidation peak is at about 500 mV (versus SCE), shifting negatively by about 200 mV compared to Pt/C. The methanol electro-oxidation on PtSn/C starts at a more negative value of about 20 mV (versus SCE), but its positive scan peak appears at a higher potential of about 640 mV (versus SCE) compared to PtRu/C. It is clear that the addition of either Ru or Sn improves the electro-oxidation of methanol on Pt. It is also found that methanol electro-oxidation on PtSn starts at more negative values than on PtRu/C. The positive scan peak current density of methanol electro-oxidation on PtSn/C is close to that on PtRu, but appears at higher potential. From the point of view of current and peak position, PtRu is thought to be more active for methanol electro-oxidation than PtSn/C.

Table 1
Results of XRD and TEM of Pt/C, PtRu/C and PtSn/C catalysts

Catalyst	Mean particle size (nm)		Lattice parameter (Å)[a]
	TEM	XRD[b]	
Pt/C	2.7	2.6	3.9156
PtRu/C	2.2	2.0	3.8837
PtSn/C	2.5	2.2	3.9866

[a] Calculated from Gauss-fitted Pt(2 2 0) peak 2θ position according to Fragg formula.
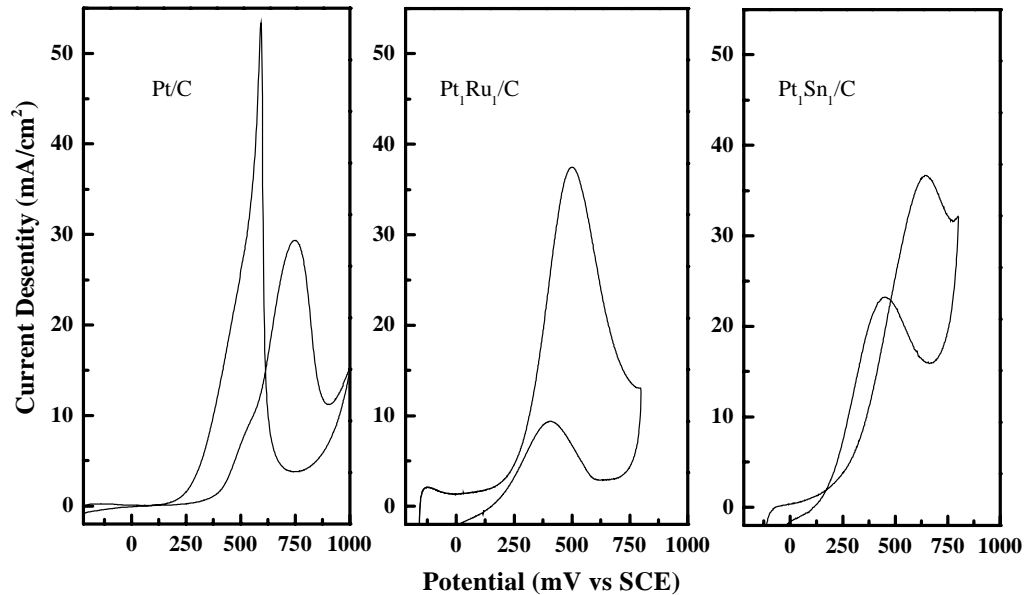[b] Calculated from Gauss-fitted Pt(2 2 0) peak according to Sherrer formula.

Fig. 1. The cyclic voltammetry spectra of Pt/C, PtRu/C and PtSn/C catalysts at 25 °C. Electrolyte is 0.5 M H_2SO_4 solution containing 1.0 M methanol. The scan rate was 10 mV/s.

The ethanol CV results on the three catalysts are reported in Fig. 2. As one can observe in Fig. 2, Pt shows the most positive onset and peak potentials for ethanol electro-oxidation. The onset potentials of ethanol electro-oxidation on Pt/C, PtSn/C and PtRu/C are 240, 90 and 60 mV (versus SCE), respectively. The positive sweep peak potentials of ethanol on Pt, PtRu and PtSn are 770, 550 and 710 mV (versus SCE), respectively. It is noticeable in Fig. 2 that the PtSn shows the highest positive scan peak current density for ethanol electro-oxidation among the catalysts investigated here. As found for methanol electro-oxidation, both Ru and Sn en-

hance ethanol electro-oxidation on Pt. It is also found from Figs. 1 and 2 that the positive scan peak position of methanol electro-oxidation is always less positive than that of ethanol at the same catalysts, indicating that methanol is more active than ethanol at low-temperatures.

It was found from the experiments that the power output of all single fuel cells was constant at least for 3 days. More precisely, the performance of single cells with different anode on the second day was comparable to that on the third day and both were relatively improved compared to the single cell performance on the first day. Here
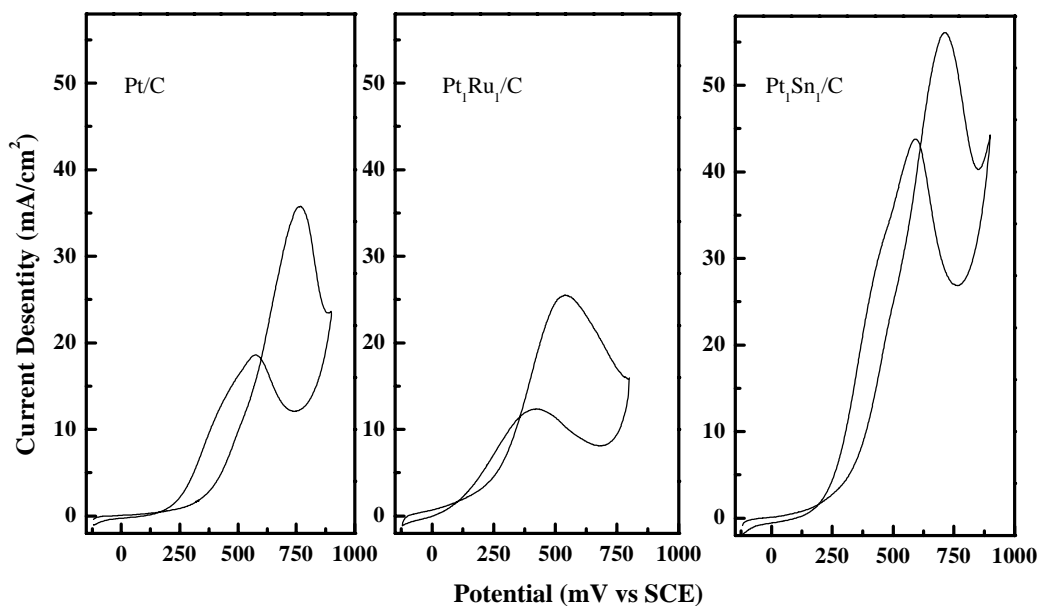

Fig. 2. The cyclic voltammetry spectra of Pt/C, PtRu/C and PtSn/C catalysts at 25 °C. Electrolyte is 0.5 M H_2SO_4 solution containing 1.0 M ethanol. The scan rate was 10 mV/s.
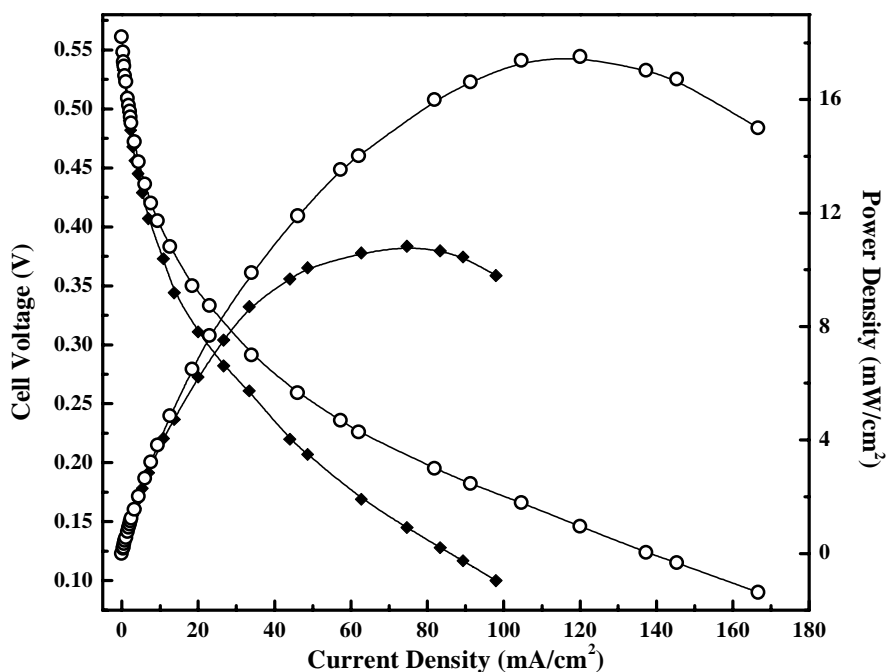
Fig. 3. The performance of single direct alcohol fuel cells with Pt/C as anode catalysts. Cathode: 1.0 mgPt/cm^2 (20 wt.% Pt/C, J.M.). P_{O_2}: 0.2 MPa (abs.); 90 °C; MeOH (or EtOH): 1 M and 1.0 ml/min. (○) DMFC (◆) DEFC (J.M. denotes the Johnson Matthey Co.).

the results for every single fuel cell were recorded on the second day. The cell performances of DMFCs and DEFCs with Pt/C, PtRu/C and PtSn/C employed as anode catalyst are depicted in Figs. 3–5, respectively. It is found that the performances of single cells (Figs. 3–5) are greatly different when anode catalyst is the unique variable parameter to be considered and other factors such as electrolyte, cathode catalyst and MEA preparation procedure are defined. Therefore single cell test can be used to evaluate anode catalysts, and the differences of single cell performances with different anode catalysts embody the activities of anode catalysts to some extent. On the other hand, from the practical point of view, the single cell test is the ultimate evaluation criterion for novel materials such as electrocatalysts and electrolyte.

As one can observe in Fig. 3, although the Pt loading on anode catalyst layer is higher than that of other bimetallic anode catalysts (2.0 mgPt/cm^2 for Pt/C versus 1.3 mg Pt/cm^2 for PtRu/C and PtSn/C), the performance of the respective single cells is still poor. The open-circuit voltage of single cells adopting Pt/C as anode catalyst were similar, only 0.56 V for methanol and 0.55 V for ethanol, respectively, far from their standard electromotive forces (1.213 V for methanol and 1.145 V for ethanol). The large gap between the open-circuit potential and standard electromotive force is mainly attributed to the low anode catalytic activity for alcohol oxidation and severe fuel crossover. The single cell peak power densities, the maximum product of cell voltage and corresponding current density at 90 °C, are only 17.5 mW/cm^2 for DMFC and 10.8 mW/cm^2 for DEFC. The performance of single DMFC with Pt/C as anode catalyst is

found better than that of single DEFC, which is due to that methanol is more reactive than ethanol on pure Pt catalyst as mentioned above. The inferior performances of DAFCs clearly indicate that pure Pt is not practically appropriate anode catalyst for methanol or ethanol direct oxidation.

By comparing the single cell performances depicted in Figs. 3 and 4, it is evidently demonstrated that employing PtRu/C as anode catalyst improves the performances of both DMFC and DEFC, although there is a great difference between them. The open-circuit potential of DMFC approaches 0.7 V, and the peak power density is 136 mW/cm^2 at 420 mA/cm^2. The open-circuit voltage of DEFC is 0.68 V and its peak power densities at 90 °C is only 28 mW/cm^2 from 100 to 130 mA/cm^2, which is only equivalent to the DMFCs performance with PtRu/C as anode catalysts at 25 °C [24]. Therefore, the performance of DMFC is superior to that of DEFC when PtRu was used as anode catalyst. Ethanol is less reactive on PtRu/C catalyst than methanol, as reported in previous literature [14,15] even at higher temperature, which is the main reason for their difference in performances.

Different from Ru, the addition of which enhances indubitably methanol electro-oxidation on Pt regardless of the preparation mode [5,25–28], the effect of Sn on Pt activity for methanol electro-oxidation is controversial in previous papers, from huge enhancement [29–32] to lower activity than pure Pt even inhibition [33–35], depending greatly on PtSn catalyst preparation procedure. As shown in Fig. 5, both performances of DMFC and DEFC demonstrate that PtSn/C is active for electro-oxidation of methanol and ethanol, as found in CV results. It can be observed in Fig. 5 that the
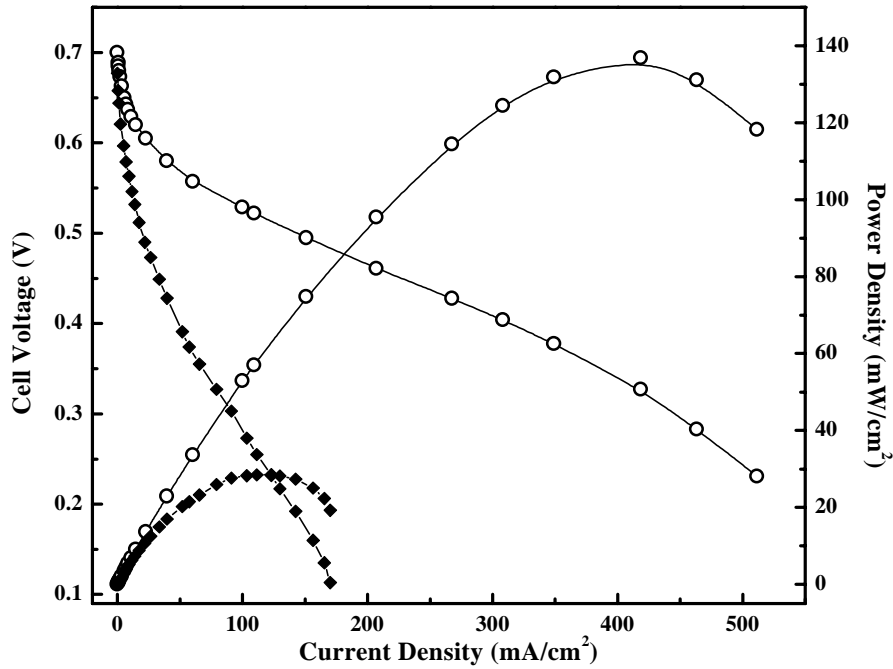
Fig. 4. The performance of single direct alcohol fuel cells with PtRu/C as anode catalysts. Anode: PtRu/C (20–10%), 1.33 mgPt/cm². Cathode: Pt/C (20%, J.M.), 1.0 mgPt/cm². P_{O_2}: 0.2 MPa (abs.); 90 °C; MeOH (or EtOH): 1 M and 1.0 ml/min; Nafion®-115 was used as electrolyte. (○) DMFC (◆) DEFC (J.M. denotes the Johnson Matthey Co.).

open-circuit potentials of DMFC and DEFC with PtSn/C are 0.71 and 0.81 V, respectively. The performance of DEFC is better than that of DMFC in the current density range from 0 to 168 mA/cm², which covers the activation-controlled region and internal resistance-controlled region. Both the

DEFC and DMFC have the same cell voltage of 0.3 V at the current density of 168 mA/cm², after which DMFC shows a better performance than DEFC. Another remarkable point is that the peak power density of DEFC is comparable to that of DMFC employing PtSn/C as anode catalyst with the
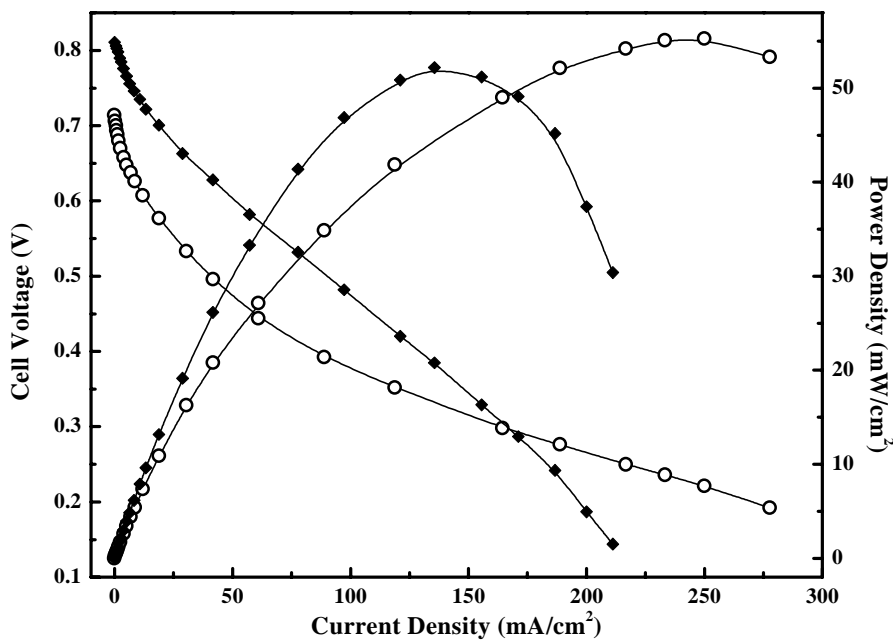

Fig. 5. The performance comparison of DMFC and DEFC employing PtSn/C as anode catalyst. Anode: PtSn/C, 1.33 mgPt/cm². Cathode: Pt/C (J.M.), 1.0 mgPt/cm². Fuel: 1 M and 1.0 ml/min; P_{O_2}: 0.2 MPa (abs.); 90 °C; Nafion®-115 was used as electrolyte. (○) DMFC (◆) DEFC (J.M. denotes the Johnson Matthey Co.).

same Pt loading at 90 °C, namely 52 mW/cm^2 for DEFC and 55 mW/cm^2 for DMFC.

From the comparison of results shown in Figs. 4 and 5, according to the open-circuit voltage and peak power density, the DEFC employing PtSn/C as anode catalyst shows a superior performance to that employing PtRu/C, contrary to the DMFCs experimental results. Thus, given the ethanol CV results, it is inferred that ethanol is more reactive than methanol on PtSn/C catalyst and PtSn/C is more active for ethanol electro-oxidation than PtRu/C at 90 °C, while PtRu/C is more suitable for methanol electro-oxidation than PtSn/C, as demonstrated in previous literature.

A relatively high ethanol conversion percent, which will be presented more detailed in the next paper, was found in the DEFC employing PtSn/C as anode. CO_2 and acetic acid were the main products of both DEFCs with PtSn/C and PtRu/C. CO_2 and acetic acid productivity of the DEFC with PtSn/C were higher than those of the DEFC with PtRu/C. More acetaldehyde was detected in the effluent solution of the DEFC with PtRu/C than that of the DEFC with PtSn/C. A very small amount of acetic ester was also detected in both effluents. The product distribution and ethanol conversion also indicated PtSn is more suitable for ethanol electro-oxidation than PtRu.

According to literature [18,36–44], Sn favors the low potential oxidation of CO and CO-like intermediates formed during the chemical adsorption of methanol and ethanol. Therefore, tin improves the electro-oxidation of methanol and ethanol at lower potentials and increases the reaction rate. Ru also favors the CO_{ads} species oxidative removal and methanol electro-oxidation at more negative potentials according to the bifunction mechanism [17,25,45]. Consequently, both DMFCs and DEFCs with PtRu/C or PtSn/C here show improved performances compared to Pt/C. It was reported that Ru promotes the bifuntional mechanism whereas Sn determines a ligand effect on Pt [5]. However, the above discussion is not enough to explain why PtRu/C is suitable for DMFC while PtSn/C is suitable to DEFC as reported here. It was also mentioned [34,46,47] that alloying Pt with Sn changes its structure electronically and structurally, which was not advantageous to dissociative adsorption of methanol. It is thought that both the positive effect that improves oxidative removal of CO_{ads} intermediates and negative effect resulting from alloying of Pt and Sn, which does not favor methanol chemical adsorption on PtSn catalyst to a certain extent, are present for the in-house PtSn/C catalyst. On the other hand, dehydrogenation of methanol occurs not only on Pt sites but also on Ru sites at high temperature. This effect and synergetic effect of Ru favor methanol electro-oxidation on PtRu catalyst. Another possible explanation is that CO_{ads} removal is mainly via the weakening of the CO_{ads} adsorption on PtSn/C catalyst although there are also surface oxygen-containing species taking part in the oxidative removal of intermediates. The PtRu/C catalyst, which has been investigated thoroughly, improves methanol electro-oxidation mainly via the oxida-

tive removal of CO-like intermediates [44]. The different interaction between Pt and Ru (or Sn) determines the CO_{ads} removal and dissociative adsorption of methanol. Furthermore, methanol electro-oxidation is relatively fast and the current of DMFC is relatively large. As mentioned above, there are more oxides in PtSn/C catalyst, which inevitably reduces its conductivity and increases the intrinsic resistance of fuel cell. Therefore, the intrinsic resistance effect on performance of DMFC with PtSn/C is more obvious in high current region, resulting in relatively low output cell voltage and cell performance.

For ethanol electro-oxidation, in addition to the low potential oxidation of CO_{ads} species, the cleavage of C–C bond is another important task and a possible precondition of CO_{ads} species formation. Especially at higher temperature and higher current, the cleavage of C–C bond would influence the ethanol utilization. It was observed from XRD and TEM results [20] that both the in-house PtRu/C and PtSn/C catalysts have similar nanoparticle sizes, and the distinct difference between them was that lattice parameter of PtSn/C was larger while that of PtRu/C was smaller in comparison with Pt/C. Thus, a possible explanation could be that the extended lattice parameter of PtSn/C catalyst favors the C–C bond cleavage, and CO_{ads} intermediates formed during the breaking of C–C bond are oxidatively removed by the surface oxygen-containing species. The primary analysis of product distribution of the DEFC, as mentioned above there was more CO_2 produced in the DEFC with PtSn/C, would also be used to support this explanation, which needs more experimental work to prove. Besides, the different internal resistances of cell, including that of anode catalyst, influences the cell performance of the internal resistance-controlled region, which also explains that the DMFC with PtRu/C shows a better performance than that with PtSn/C because metallic PtRu/C is a better conductor than PtSn/C that contains more oxides. The above explanations are also validated by the following experiment results. The PtRuSn/C with metal atomic ratio of 1/1/1, which was synthesized by the same method, has a lattice parameter between those of PtRu/C and PtSn/C, which means Ru and Sn have opposite effect on the Pt crystalline structure. When PtRuSn/C was used as anode catalyst for DMFC, the performance was better than with PtSn/C, but inferior to that with PtRu/C. For DEFC, the single ethanol cell with PtRuSn/C exhibited a performance superior to that for PtRu/C while inferior to that for PtSn/C.

In summary, the CV results and single fuel cell performances jointly show that the Pt/C is not suitable anode catalyst for both methanol and ethanol. The addition of either Ru or Sn to Pt enhances methanol or ethanol electro-oxidation activity on Pt, and consequently improves their single cell performances. It is also found the PtRu/C catalyst is more suitable for DMFC, and PtSn/C is more suitable for DEFC. At 90 °C, the DMFC employing PtRu as anode shows much better performance than the cell employing PtSn. The single cell adopting PtSn as anode catalyst exhibits a similar

peak power density, whenever it is fed directly by methanol or ethanol.

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