

出國報告（出國類別：國際研討會）

出席第三十三屆「國際溶液化學研討會 （ICSC-33）」會議心得報告

服務機關：國防大學理工學院化學及材料工程學系
姓名職稱：文職教授 汪成斌
派赴國家：日本
出國期間：102 年 7 月 7 日至 7 月 13 日
報告日期：102 年 7 月 22 日

摘要

第三十三屆「國際溶液化學研討會 (ICSC-33)」是由日本溶液化學協會 (JASC)、日本分析化學學會 (JSAC) 和國際純粹與應用化學聯合會 (IUPAC) 共同主辦，於 2013 年 7 月 7 - 12 在日本京都 Terrsa 舉行。會議內容包含大會專題演講，並邀請各相關主題(離子液體、配位化學、膠體與界面、分析化學與光譜、電化學、熱力學與熱化學等)之講座，提供口頭和海報論文之發表。另為鼓勵年輕學者從事溶液化學研究，提升科學與技術水準之發展，特別安排「年輕學者」之口頭發表競賽。參加人員來自世界各地，包括德國、葡萄牙、奧地利、瑞典、美國、加拿大、匈牙利、英國、法國、以色列、科威特、俄國、捷克、烏克蘭、巴西、西班牙、澳大利亞、印尼、印度、新加坡、韓國、日本、中國、台灣等多國之專家學者，此研討會投稿論文分口頭報告及壁報展示，共計 350 餘篇。在會議中聆聽各國學者之學術演講，其中以日本學者 Hiroyuki Ohno 針對離子液體與分子液體混合液之物性與化性之分析做一完整的回顧性報導；另一日本學者 Kazuaki Ninomiya 探討以離子液體精煉生質能的應用研究對我們現階段的研發受益最大。本次會議提供一個相當好的知識交流平台，世界各國學者齊聚一堂討論不同領域的研究成果與應用，藉此學術交流進而瞭解國際未來研究發展方向及趨勢，真是獲益匪淺。另藉由參與大會各國專家學者之交換研究心得及吸取他人寶貴之研究經驗，將可做為本實驗室日後精進之參考。

筆者此次感謝獲國科會研究計畫之補助成行，發表題目共計乙篇：“Electro-oxidation of ethanol over Pt(Sn)/TiO₂-C anodic catalysts”，達到與各國學者切磋交流的機會，真是獲益匪淺。

目次

	頁碼
壹、 會議目的.....	4
貳、 會議過程.....	4
參、 會議心得.....	6
肆、 建議事項.....	7

壹、 會議目的

第三十三屆「國際溶液化學研討會 (ICSC-33)」是由日本溶液化學協會 (JASC)、日本分析化學學會 (JSAC) 和國際純粹與應用化學聯合會 (IUPAC) 共同主辦，為國際純粹與應用化學聯合會籌辦每二年舉辦一次之國際學術會議。其會議宗旨在於結合世界各國從事有關溶液化學之研究：離子液體、配位化學、膠體與界面、分析化學與光譜、理論計算、電化學、熱力學與熱化學、生命科學等領域之學者專家，就專長領域進行一系列學術研究成果發表及新知討論，以便交流最新進展和技術信息，歷年來所主辦之學術研究年會、研討會及專題討論會，皆對該學術領域有深遠的影響及貢獻。因此，藉由此學術交流進而瞭解國際未來研究發展方向及趨勢，並與各國專家學者交換研究心得及吸取他人寶貴研究經驗，將可做為日後研究之參考。

貳、 會議過程

(一)本會議屬於一大型國際研討會，參加人員約600員，分別來自世界各國之民間機構、專家學者及研究人員參與為期五天之學術論文發表討論會及旅遊。第三十三屆「國際溶液化學研討會 (ICSC-33)」是由日本溶液化學協會 (JASC)、日本分析化學學會 (JSAC) 和國際純粹與應用化學聯合會 (IUPAC) 共同主辦，於2013年7月7 - 12在日本京都Terrsa舉行。此為溶液化學領域非常重要的研討會之一，因領域涵蓋範圍較廣，吸引與會者包含化學、物理、生物學、工程學科、醫藥及醫療科學各領域學有專精之教授與學者，本次台灣參與之教授及研究生多達二十餘人(包含中研院、成大、清大、交大、中興、明志及國防大學等)。於此與各國學者相互交流之下獲益良多。

(二)本次研討會為一大型研討會，安排於京都Terrsa中之大型演講廳、展示廳及研討室，分為邀請演講(INV)、口頭發表(OP)、「年輕學者」之口頭發表競賽及壁報發表(PO)。大會針對不同議題討論，前三天(7月8-10日)由早上09:00開始至下午18:00結束，另於7月9日晚上安排一公開的市民講座，由京都大學及崇城大學教授以「生命科學」為演講之主題，吸引了眾多市民的參與聆聽，此公開性之學術活動與市民之結

合、接觸是值得參考的一項活動。後二天(7月10-11日)則由早上09:00開始至中午12:00結束，議程內容相當豐富緊湊。本人五天與會期間過程十分順利，由於每天議程都有不同主題分開在不同的場地同時進行，因而無法全面顧及，故謹將本人出席參與的部分簡要介紹如下。

7月8日

大會第一天針對「離子液體」主題即有相當精采的演講，印象最深刻的是日本學者Hiroyuki Ohno針對離子液體與分子液體混合液之物性與化性之分析做一完整的回顧性報導，讓在座的學者提出了許多問題請教，迴響最熱烈。目前本實驗室相關之研究係以離子液體為橋梁，試圖將磷鎢酸嫁接至中孔矽材，唯摸索過程中遭遇一些瓶頸，嫁接率太低。趁中場休息時間請教Hiroyuki Ohno教授，建議我們可以改變溶劑並控制溫度，另亦可嘗試以微波系統進行，回國後已依建議修正，初步已可將嫁接率由30%提升至50%以上。

7月9日

大會第二天針對「離子液體」主題仍安排許多精采的演講，印象最深刻的是日本學者Kazuaki Ninomiya探討以離子液體精煉生質能的應用研究。由於生質能是目前很熱門的研究主題，在座的學者提出了許多不同的論點與質疑，Kazuaki Ninomiya教授均能詳細一一辯解，真令人佩服，具有大師風範。目前本實驗室相關之研究嘗試以固體超酸為催化劑，欲由棕櫚酸合成生質柴油，因尚在起步階段，聆聽這場演講收穫頗多，有好多影響因子起初並未納入考量，正好可以重新設計，以免走冤枉路。今天下午時段大會安排第一次的"壁報論文討論時間"，所有發表論文學者站在壁報旁邊，詳細解說討論與互換研究心得，效果非常好。當天本人發表乙篇論文：“Electro-oxidation of ethanol over Pt(Sn)/TiO₂-C anodic catalysts”，達到與各國學者切磋交流的機會，真是獲益匪淺。綜整各學者提供之建議如下：合金相之鑑定需再確認、乙醇電氧化機制需做修正、金屬含量需精確量測、TiO₂所扮演之角色需詳述。感謝各學者之建議，擬於暑假期間將文章撰寫完成，投稿至“Journal of Solution Chemistry”。另

晚上安排一公開的市民講座，由京都大學及崇城大學教授以「生命科學」為演講之主題，吸引了眾多市民的參與聆聽。

7月10日

大會第三天在「配位化學」主題安排了一系列精采的演講，印象最深刻的是匈牙利學者T. Kiss針對抗癌藥物： Ru(II, III) 化合物之合成、鑑定、生物轉化機理做一完整的報導，獲得熱烈迴響。目前本實驗室無相關之研究進行，唯 Ru(II, III) 化合物之合成為配位化學之領域，此化合物為有效的抗腫瘤劑，合成技術應沒問題，若能與國防醫學院的教授合作是可行的。今天下午時段大會安排第二次的"壁報論文討論時間"，亦引起熱烈討論。

7月11日

大會第四天針對「配位化學」主題仍安排了許多精采的演講，印象最深刻的是瑞典學者D. Lundberg針對鐳系及錒系元素在核研究領域之應用做一完整的報導，獲得熱烈迴響。目前本實驗室並無進行核研究領域之相關應用，唯我們在合成乙醇重組催化劑，有使用到鐳系及錒系元素修飾催化劑，且對整體活性有提升效果，將我們的觀點與D. Lundberg教授分享，雖然D. Lundberg教授未涉及到這方面的應用，不過，確認同我們的成果，感到欣慰，只是仍需更深入探討。

7月12日

大會第五天安排「年輕學者」之口頭發表競賽，展現出青春活力，印象最深刻的是印尼學者M.L. Rinting將混成的雙硫脲天然沸石吸附劑應用於溶液中重金屬離子之吸附，台風穩健，答辯有條理，獲得與會者認同。

參、 會議心得

本研討會宗旨在於結合世界各國從事有關溶液化學研究之學者專家，就專長領域進行一系列學術研究成果發表及新知討論，以新理論、分析方法、新技術應用於工業上之挑戰為主軸，會議是由日本溶液化學協會(JASC)、日本分析化學學會(JSAC)和國際純粹與應用化學聯合會(IUPAC)共同主辦，為該領域中相當重要之研討會。

參加人員為世界各國之專家學者，此研討會投稿論文分口頭報告及壁報展示，共計350餘篇。大會所討論之範圍很廣，包含離子液體、配位化學、膠體與界面、分析化學與光譜、理論計算、電化學、熱力學與熱化學、生命科學等。部份足以為我國所參考之依據，另相關論述主題亦十分具參考價值。

本人計有壁報展示乙篇，透過各國學者不同領域的經驗，於問答間各取所需，達到智識精進功效，並積極與各國學者交換演講意見達到學術交流目的。經過此次研討會歷練，使本人對未來之研究更具信心，將持續於此領域探討研析，並且對於後續之研究將會秉持精益求精的精神戮力完成。本次會議提供一個相當好的知識交流平台，藉由此學術交流進而瞭解國際未來研究發展方向及趨勢，真是獲益匪淺。

肆、 建議事項

本研討會為溶液化學領域非常重要的研討會之一，因領域涵蓋範圍較廣，吸引與會者包含化學、物理、生物學、工程學科、醫藥及醫療科學各領域學有專精之教授與學者，為一大型國際會議，探討範圍包含離子液體、配位化學、膠體與界面、分析化學與光譜、理論計算、電化學、熱力學與熱化學、生命科學等，值得相關研究人員與學者參與。建議未來可鼓勵並增加國內專家學者參與機會，藉以吸收國際新知並分享研究成果，相信對國內各方面研究及學術工作的提昇，必定有所助益。願以此次的與會心得與大家分享共勉之，本次研討會攜回會議論文集乙本。



Electro-oxidation of Ethanol over Pt(Sn)/TiO₂-C Anodic Catalysts

Ying-Huei Liou^{1,2}, Yi-Ping Tsai^{1,2}, Josh Y.Z. Chiou¹, Shu-Hua Chien^{2,3*} and Chen-Bin Wang^{1*}

¹Department of Chemical and Materials Engineering, Chung Cheng Institute of Technology, National Defense University, Tahsi, Taoyuan, 33509, Taiwan, R.O.C.

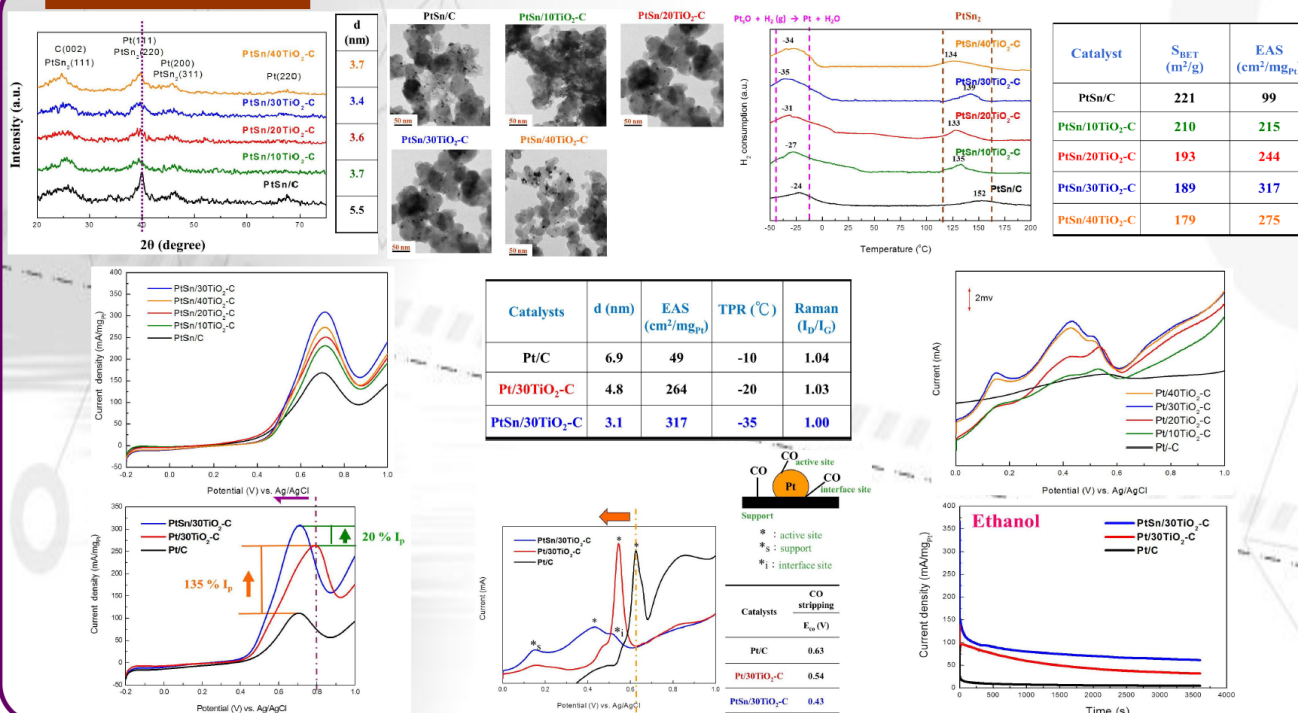
²Institute of Chemistry, Academia Sinica, Taipei, 11529, Taiwan, R.O.C.

³Department of Chemistry, National Taiwan University, Taipei, 10764, Taiwan, R.O.C.
Email address: chenbinwang@gmail.com

Abstract

This research focused on the modified Pt/C anodic catalyst with titania (30 wt% TiO₂) and tin (5 wt% Sn) to improve the utilization and efficiency of direct ethanol fuel cell. The TiO₂-doped on active carbon support was prepared by impregnation method. Then, the Pt(Sn)/TiO₂-C (10 wt% Pt) anodic catalyst was synthesized by formic acid reduction method using platinum chloride (PtCl₄) and tin dichloride dihydrate (SnCl₂ · 2H₂O) as precursors. The carbon paper coated with Pt(Sn)/TiO₂-C catalyst was used as the working electrode. Evaluation of the catalytic activity for the electro-oxidation of ethanol on working electrodes was performed with cyclic voltammetry (CV) in 0.5 M H₂SO₄ and 1 M ethanol electrolyte at room temperature. The results of XRD and TEM show that all the prepared Pt(Sn)/TiO₂-C anodic catalysts present uniform dispersion of platinum with a diameter around 3 - 6 nm. The activity for electro-oxidation of ethanol was affected remarkably by the content of TiO₂ and Sn in the anodic catalyst. The addition of TiO₂ can promote the CO stripping by the surface oxygen functional groups to reduce CO oxidizing potential. Also, the formation of PtSn alloy can enhance the CO stripping at lower oxidizing potential.

Results



Conclusions

The results presented in this study indicated that the activity for electro-oxidation of ethanol was affected remarkably by the addition of TiO₂ and Sn in the anodic catalyst. Modification of Pt/C anodic catalyst with TiO₂ and Sn can get well-dispersed and higher EAS of active species that improve the electro-catalytic activity and lower potential. The addition of TiO₂ can promote the CO stripping by the surface oxygen functional groups to reduce CO oxidizing potential. Also, the formation of PtSn alloy can enhance the CO stripping at lower oxidizing potential. Among the prepared Pt(Sn)/TiO₂-C anodic catalysts, the PtSn/30TiO₂-C exhibits the best catalytic performance.

作者發表之論文

Electro-oxidation of ethanol over Pt(Sn)/TiO₂-C anodic catalysts

Electro-oxidation of ethanol over Pt(Sn)/TiO₂-C anodic catalysts

Ying-Huei Liou^{1,2}, Yi-Ping Tsai^{1,2}, Wen-Kai Tu², Josh Y.Z. Chiou¹,
Chen-Bin Wang^{1*} and Shu-Hua Chien^{2,3} *

¹Department of Chemical and Materials Engineering, Chung Cheng Institute of Technology, National Defense University, Tahsi, Taoyuan, 33509, Taiwan, ROC

²Institute of Chemistry, Academia Sinica, Taipei, 11529 Taiwan, ROC

³Department of Chemistry, National Taiwan University, Taipei, 10764, Taiwan, ROC

Abstract

This research focused on the modified Pt/C anodic catalyst with titania (30 wt% TiO₂) and tin (5 wt% Sn) to improve the utilization and efficiency of direct ethanol fuel cell. The TiO₂-doped on active carbon support was prepared by impregnation method. Then, the Pt(Sn)/TiO₂-C (10 wt% Pt) anodic catalyst was synthesized by formic acid reduction method using platinum chloride (PtCl₄) and tin dichloride dihydrate (SnCl₂·2H₂O) as precursors. The carbon paper coated with Pt(Sn)/TiO₂-C catalyst was used as the working electrode. Evaluation of the catalytic activity for the electro-oxidation of ethanol on working electrodes was performed with cyclic voltammetry (CV) in 0.5 M H₂SO₄ and 1 M ethanol electrolyte at room temperature. The results of XRD and TEM show that all the prepared anodic catalysts present uniform dispersion of platinum with a diameter around 3 - 6 nm. The activity for electro-oxidation of ethanol was affected remarkably by the content of TiO₂ and Sn in the anodic catalyst. The addition of TiO₂ can promote the CO stripping by the surface oxygen functional groups to reduce CO oxidizing potential. Also, the formation of PtSn alloy can enhance the CO stripping at lower oxidizing potential.

Keywords: Pt(Sn)/TiO₂-C anodic catalyst; Electro-oxidation; Cyclic voltammetry.

*Corresponding authors

E-mail address: chenbinwang@gmail.com chiensh@gate.sinica.edu.tw

1. Introduction

In the past 20 years, the direct alcohol fuel cells (DAFCs) have been widely studied and considered as possible power sources for the portable electric apparatus and electric vehicles [1-8]. Among the alcohols, methanol (MeOH) [1–3], ethanol (EtOH) [4–6] and ethylene glycol (EG) [7, 8] are popular energy resource due to their non-toxicity and high energy density.

Titanium dioxide possesses a high activity and stability of catalytic in acidic solutions [9, 10]. It has been used as photocatalyst to execute the oxidation of alcohol under UV irradiation [9]. It has been proposed that the TiO₂-support Pt has high catalytic activity for ethanol electro-oxidation [10]. Reaction intermediate of CO easily poisoned platinum to become inactive of electro-oxidation for anodic catalysts. Recently, Kokoh *et al* [11] showed that the addition of Sn to Pt catalysts could mitigate the poisoning effect of CO for ethanol electro-oxidation.

Based on the approaches, a comparative study on three Pt(Sn)/TiO₂-C anodic catalysts by the formic acid reduction method and evaluated the activity for electro-oxidation of alcohols by using cyclic voltammetry (CV) have been studied.

2. Experimental

The support of TiO₂-doped (30 wt%) active carbon (S.A. 240 m²·g⁻¹, Cabot) was prepared by impregnation method (assigned as TiO₂-C). The active carbon was added into a 250 mL flask with 2-propanol-TBOT-HNO₃ mixture for 24 h stirring at room temperature, and then the suspension was filtered and washed by distilled water. The precipitate was dried at 110 °C overnight. Three anodic catalysts (Pt/C, Pt/TiO₂-C and PtSn/TiO₂-C) were prepared by formic acid reduction method [12] using platinum chloride (PtCl₄) and tin dichloride dihydrate (SnCl₂·2H₂O) as precursors. An appropriate mass of support (C or TiO₂-C) powder was suspended in formic acid solution. Precursor salt solutions of chloroplatinic acid (PtCl₄, Strem Chemicals) and/or (SnCl₂·2H₂O, Acros Organics) were slowly added to the suspension of support for 6 h stirring at 60 °C in water bath. As the mixture was cooled to room temperature, filtered and washed by distilled water until the washing water showed pH = 7. Then, the precipitates were dried at 110 °C overnight. The nominal loading of Pt and Sn was 10 wt% and 5 wt%, respectively.

The microstructure and particle size of the anodic catalysts was observed, using transmission electron microscopy (TEM) with a JEM-2010 microscope (JEOL), at an acceleration voltage of 200 kV. X-ray diffraction (XRD) analysis was performed using the MAC Science MXP18 X-ray diffractometer with CuK α -source. The 2 θ angular regions between 20° and 80° were explored at a scan rate of 6°·min⁻¹ with step of 0.02°.

Electrochemical measurements were carried out in a three electrode cell with

electrochemical analyzer (CH Instruments Model 611C) at 25 °C. The gold patch coated with catalyst ink was used as the working electrode. The loading of catalyst on the work electrode was 4 mg·cm⁻². A saturated calomel electrode (SCE) and Pt foil were used as reference and counter electrodes, respectively. All electrode potentials in this paper were referred to the SCE. The cyclic voltammetry test of electro-oxidation of ethanol was conducted in the potential range of -0.2 to 1.0 V vs. SCE with a scan rate of 10 mV·s⁻¹ in a solution of 0.5 M H₂SO₄ with 1 M ethanol. Electrolyte solution was purged with nitrogen gas before each experiment. The electrochemical active surface area (EAS) of anodic catalysts is measured on the hydrogen adsorption by cyclic voltammograms in the potential range of -0.2 to 1.0 V with a scan rate of 50 mV·s⁻¹ in 1.0 M HClO₄ solution. EAS is obtained from:

$$\text{EAS} = Q_{\text{H}}/M_{\text{Pt}} \cdot Q_{\text{Href}} \quad (1)$$

Q_{H} is the charge of hydrogen atoms on the Pt surface by the electro-adsorption, M_{Pt} is the mass of Pt, and Q_{Href} is the charge of hydrogen atoms (assumed to be 0.21mC/cm²). The chronoamperometric measurement was performed at 0.45 V for 3600 s. The carbon monoxide (CO) stripping was measured by voltammetry in the potential range of - 0.2 to 1.0 V at a scan rate of 10 mV·s⁻¹ by 0.5 M H₂SO₄ solution.

3. Results and discussion

XRD patterns of anodic catalysts are shown in Fig. 1. It is found that there is no

diffraction peaks of TiO_2 in the XRD patterns of $\text{Pt/TiO}_2\text{-C}$ and $\text{PtSn/TiO}_2\text{-C}$. It is indicated that the prepared TiO_2 -modified support is amorphous. The diffraction peaks around 39° 、 46° and 68° are attributed to Pt (111)、(200) and (220) crystalline planes according to the JCPDS, which represent the typical character of a crystalline of Pt with a face-centered cubic (fcc) structure. Comparing the diffraction patterns of platinum, broadening of peaks and contracting of 2θ on both $\text{Pt/TiO}_2\text{-C}$ and $\text{PtSn/TiO}_2\text{-C}$ catalysts are observed. These results indicate that the modification of active carbon with TiO_2 can well-dispersed active species and the addition of tin can form alloy with platinum. In order to evaluate the particle size of platinum, the Pt (111) diffraction peak is selected to calculate the particle size by Scherrer formula. Three anodic catalysts are calculated that the mean particle size of platinum (d_{Pt}) are 6.0, 5.2 and 3.4 nm for Pt/C , $\text{Pt/TiO}_2\text{-C}$ and $\text{PtSn/TiO}_2\text{-C}$, respectively. In the same, TEM micrographs of Pt/C , $\text{Pt/TiO}_2\text{-C}$ and $\text{PtSn/TiO}_2\text{-C}$ catalysts are shown in Fig. 2. The observed mean particle size is about 6 ~ 3 nm, which is close to the calculated values from XRD.

The TPR profiles of anodic catalysts are shown in Fig. 3. As shown, we can find two type reduction signals. The signal at lower ($-45^\circ\text{C} \sim -5^\circ\text{C}$) is attributed to the reduction of $\text{Pt}^{\text{s}}\text{O}$ and/or $\text{PtSn}^{\text{s}}\text{O}$ (Pt^{s} and/or PtSn^{s} is the species of Pt metal or PtSn alloy on the surface of catalyst) reduced to metal.



Comparison of the three anodic catalysts, the temperature of PtSn^sO alloy oxide is lower than the Pt^sO. Also, the modification of active carbon with TiO₂ could well-dispersed active species to depress the reduction temperature of catalyst. The signal at higher (95 °C ~ 125 °C) comes from the interaction of Pt and/or PtSn with TiO₂.

The as-prepared Pt(Sn)/TiO₂-C catalysts were tested for their catalytic activity in the oxidation of ethanol. In order to further investigate the role played by the Pt/C, Pt/TiO₂-C and PtSn/TiO₂-C catalyst were also tested in the same condition for comparison. Fig. 4 shows cyclic voltammetry curves recorded for the prepared catalysts in the supporting electrolyte of 0.5 M H₂SO₄ with 1 M ethanol. As shown, it can be seen that the trend for ethanol electro-oxidation of activity is: PtSn/TiO₂-C > Pt/TiO₂-C > Pt/C. This fact indicated that PtSn/TiO₂-C catalysts have highest catalytic activity for ethanol oxidation than Pt/C and Pt/TiO₂-C catalysts.

Fig. 5 is the chronoamperometric curves by PtSn/TiO₂-C, Pt/TiO₂-C and Pt/C electrodes in 1M C₂H₅OH and 0.5 M H₂SO₄ electrolyte for 3600 s. As shown, the ethanol oxidation current density at PtSn/TiO₂-C electrode for 3600 s is 60 mA/mg_{Pt}, and the current density is 30 mA/mg_{Pt} and 10 mA/mg_{Pt}, respectively for Pt/TiO₂-C and Pt/C electrodes. This result indicating the PtSn/TiO₂-C anodic catalyst have better stability and activity than Pt/TiO₂-C and Pt/C catalysts for ethanol electro-oxidation.

Fig. 6 shows the Cyclic voltammogram curves in 1 M HClO₄ solutions with a scan rate of 50 mVs⁻¹. It can understand the reason why TiO₂ and Sn can promote the catalytic

activity of Pt/C greatly. The electrochemical active surface (EAS) was measured from the charge of hydrogen desorption. The calculated data were recorded in Table 1. From Table 1, we can be seen the EAS for PtSn/TiO₂-C catalyst were 1.2 times bigger than Pt/TiO₂-C catalyst and 6 times bigger than Pt/C catalyst. The results were showed the both TiO₂ and Sn that can enhance the true surface area of Pt. It was inferred that adding the TiO₂ and Sn can enhance dispersed for Pt/C anodic catalysts. So, it can be explained that ethanol electro-oxidation of activity is: PtSn/TiO₂-C > Pt/TiO₂-C > Pt/C.

The CO stripping curves for PtSn/TiO₂-C, Pt/TiO₂-C and Pt/C anodic catalysts are shown on Fig. 7. The peak potentials of CO oxidation are 0.43, 0.54 and 0.63 V, respectively for PtSn/TiO₂-C, Pt/TiO₂-C and Pt/C anodic catalysts. We suppose that the reaction of TiO₂ with water will product Ti-OH functional groups, and Sn with Pt generate PtSn₂ alloy, they can effectively reduce the oxidation of CO to CO₂ oxidation potential. This result implies that adding TiO₂ and Sn can promote the ability of oxidize CO to CO₂ at lower potential, which was helpful for adding the active sites to promote the electro-oxidation of ethanol.

4. Conclusions

The results presented in this study indicated that the activity for electro-oxidation of ethanol was affected remarkably by the addition of TiO₂ and Sn in the anodic catalyst. Modification of Pt/C anodic catalyst with TiO₂ and Sn can get well-dispersed and higher

EAS of active species that improve the electro-catalytic activity and lower potential. The addition of TiO_2 can promote the CO stripping by the surface oxygen functional groups to reduce CO oxidizing potential. Also, the formation of PtSn alloy can enhance the CO stripping at lower oxidizing potential. Among the prepared Pt(Sn)/ TiO_2 -C anodic catalysts, the PtSn/ TiO_2 -C exhibits the best catalytic performance.

Acknowledgement

We are pleased to acknowledge financial supports for this study from Academia Sinica and the National Science Council of the Republic of China.

References:

- [1] A. Demirbas, Prog., "Progress and recent trends in biofuels," Energy Combust. Sci., Vol. 33, pp. 1-18, 2007.
- [2] Jiang, L., Zhou, Z., Li, W., Zhou, W., Song, S., Li, H., xSun, G., and Xin, Q., "Effects of treatment in different atmosphere on $\text{Pt}_3\text{Sn}/\text{C}$ electrocatalysts for ethanol electro-oxidation," Energy & Fuels, Vol. 18, pp. 866-871, 2004.
- [3] Lamy, C., Belgsir, E.M., Hahn, F., Coutanceau, C., Vigier, F., "On the mechanism of ethanol electro-oxidation on Pt and PtSn catalysts: electrochemical and in situ IR reflectance spectroscopy studies," Journal of Applied Electrochemistry, Vol. 563, pp. 81-89, 2004.
- [4] Lai, S. C. S., Kleyn, S. E. F., Rosca, V. and Koper, M. T. M., "Mechanism of the

- dissociation and electro-oxidation of ethanol and acetaldehyde on platinum as studied by SERS,” *J. Phys. Chem. C*, Vol. 112, pp. 19080-19087, 2008.
- [5] Wang, H., Jusys, Z., Behm, R.J., “Ethanol electro-oxidation on carbon-supported Pt, PtRu and Pt₃Sn catalysts: A quantitative DEMS study,” *Journal of Power Sources*, Vol. 154, pp. 351–359, 2006.
- [6] Derek R. Lycke, Elod L. Gyenge, “Electro-chemically assisted organosol method for Pt-Sn nanoparticle synthesis and in situ deposition on graphite felt support: Extended reaction zone anodes for direct ethanol fuel cells,” *Electrochimica Acta*, Vol. 52, pp. 4287–4298, 2007.
- [7] Wang H., Zhao Y., Jusys Z., Behm R. J., “Ethylene glycol electrooxidation on carbon supported Pt, PtRu and Pt₃Sn catalysts—A comparative DEMS study,” *Journal of Power Sources* Vol. 155 pp. 33–46, 2006.
- [8] de Lima R.B., Paganin V., Iwasita T., Vielstich W., “On the electrocatalysis of ethylene glycol oxidation,” *Electrochimica Acta*, Vol. 49, pp. 85–91, 2003.
- [9] Javier Marugan, Dirk Hufschmidt, Maria-Jose Lopez-Munoz, Volker Selzer, Detlef Bahnemann, “Photonic efficiency for methanol photooxidation and hydroxyl radical generation on silica-supported TiO₂ photocatalyst,” *Applied Catalysis B: Environmental*, Vol. 62, pp. 201–207, 2006.
- [10] Brian E. Hayden, Dzmitry V. Malevich, Derek Pletcher, “Platinum catalysed nanoporous titanium dioxide electrodes in H₂SO₄ solutions,” *Electrochemistry Communications*, Vol. 3, pp. 395–399, 2001.

- [11] Simoes F. C., dos Anjos D. M., Vigier F., L'éger J. M., Hahna F., Coutanceau C., Gonzalez E.R., Tremiliosi-Filho G., de Andrade A.R., Olivi P., and Kokoh K.B., "Electroactivity of tin modified platinum electrodes for ethanol electrooxidation," *Journal of Power Sources*, Vol. 167, pp. 1-10, 2007.
- [12] Moitrayee Chatterjee, Abhik Chatterjee, Susanta Ghosh, I. Basumallick, "Electro-oxidation of ethanol and ethylene glycol on carbon-supported nano-Pt and -PtRu catalyst in acid solution," *Electrochimica Acta*, Vol. 54, pp. 7299–7304, 2009.

Figure Captions

1. XRD patterns of Pt(Sn)/TiO₂-C anodic catalysts.
2. TEM images of anodic catalysts: (a) Pt/C (b) Pt/TiO₂-C (c) PtSn/TiO₂-C.
3. TPR profiles of Pt(Sn)/TiO₂-C anodic catalysts.
4. Cyclic voltammograms of 1 M ethanol in 0.5 M H₂SO₄ with scan rate 10 mV/s at 298 K for ethanol electro-oxidation.
5. Current density–time curves at 0.45 V for 3600 s at Pt/C, Pt/TiO₂-C and PtSn/TiO₂-C electrode in ethanol solutions.
6. Cyclic voltammogram curves in 1M HClO₄ solutions with a scan rate of 50mV·s⁻¹.
7. CO stripping voltammograms in 0.5M H₂SO₄ solution under room temperature (scan rate = 10 mV·s⁻¹).

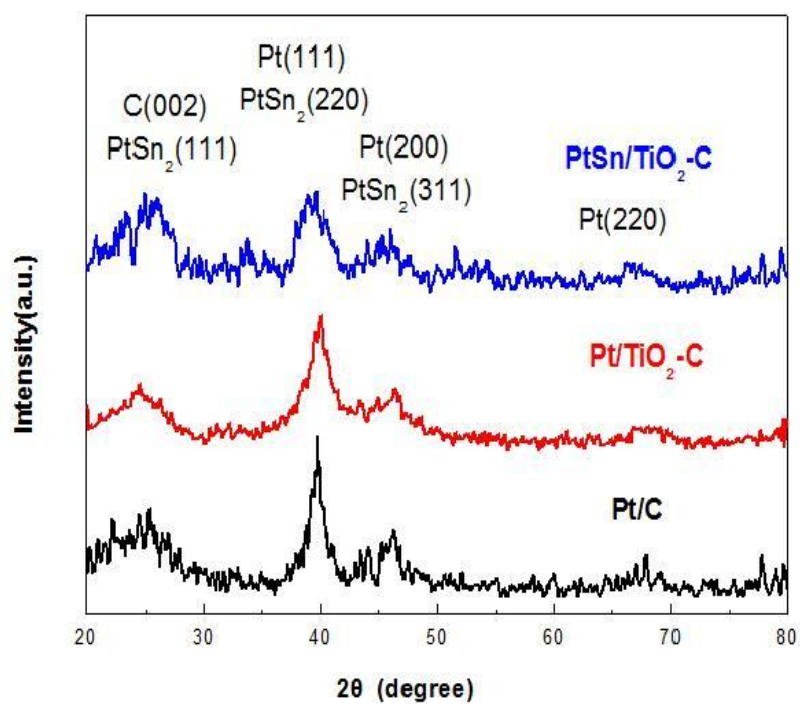


Fig. 1 XRD patterns of Pt(Sn)/TiO₂-C anodic catalysts.

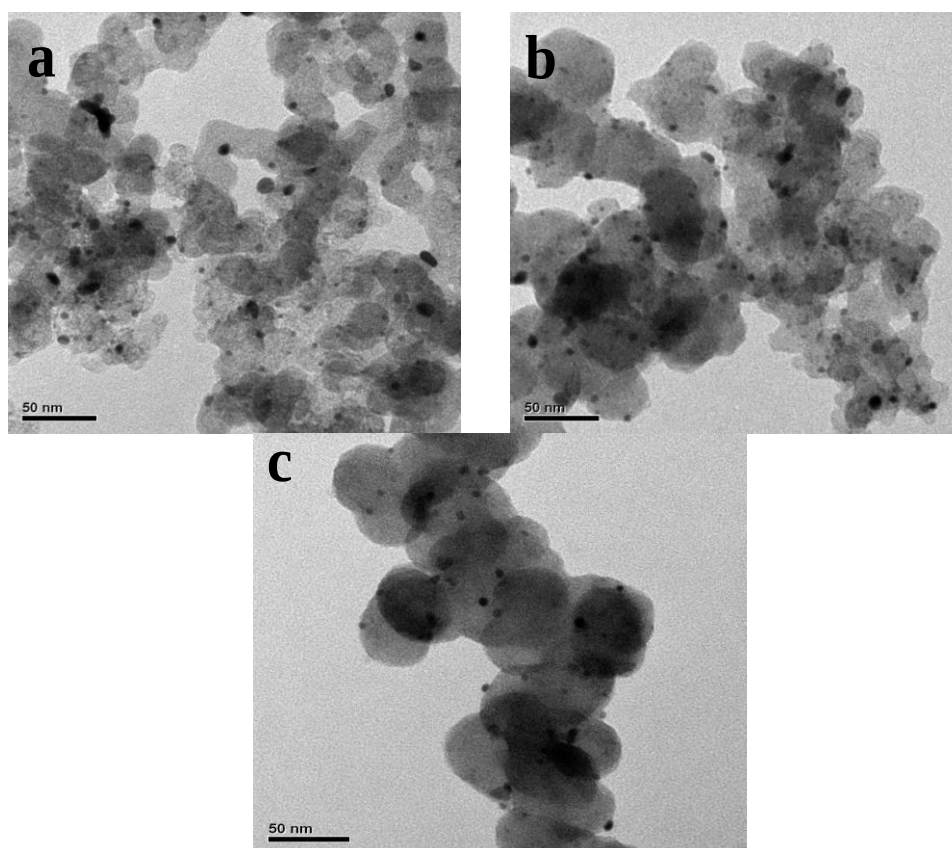


Fig. 2 TEM images of Pt/C (a), Pt/TiO₂-C (b) and PtSn/TiO₂-C (c) anodic catalysts.

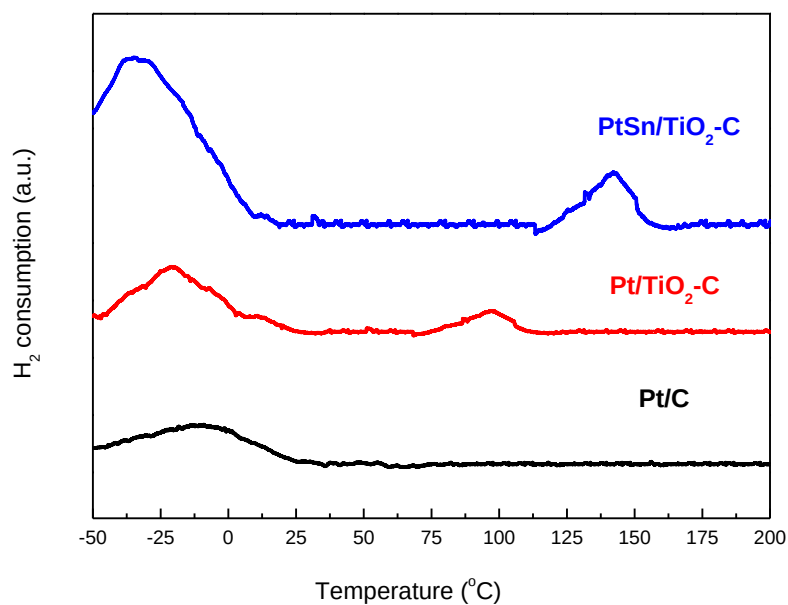


Fig. 3 TPR profiles of $Pt(Sn)/TiO_2-C$ anodic catalysts

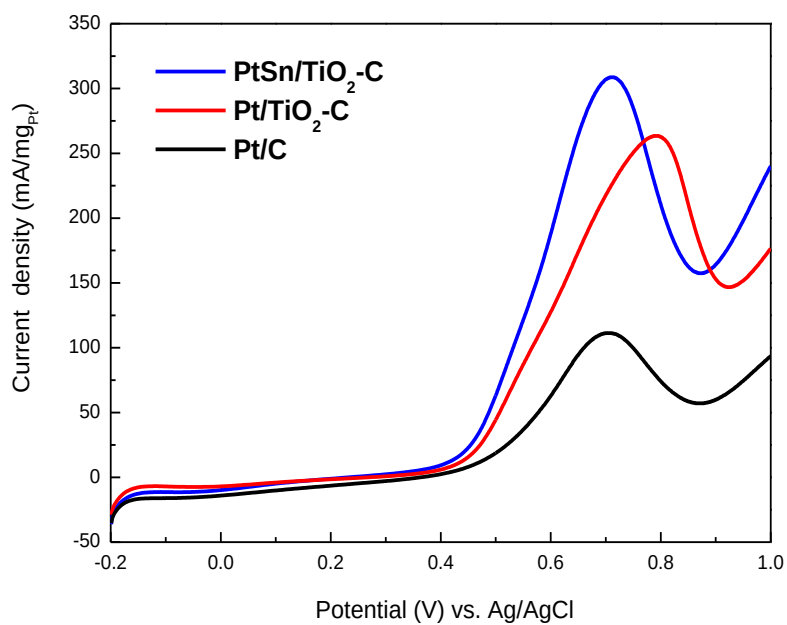


Fig. 4 Cyclic voltammograms of 1 M ethanol in 0.5 M H_2SO_4 with scan rate 10 mV/s at 298 K for ethanol electro-oxidation.

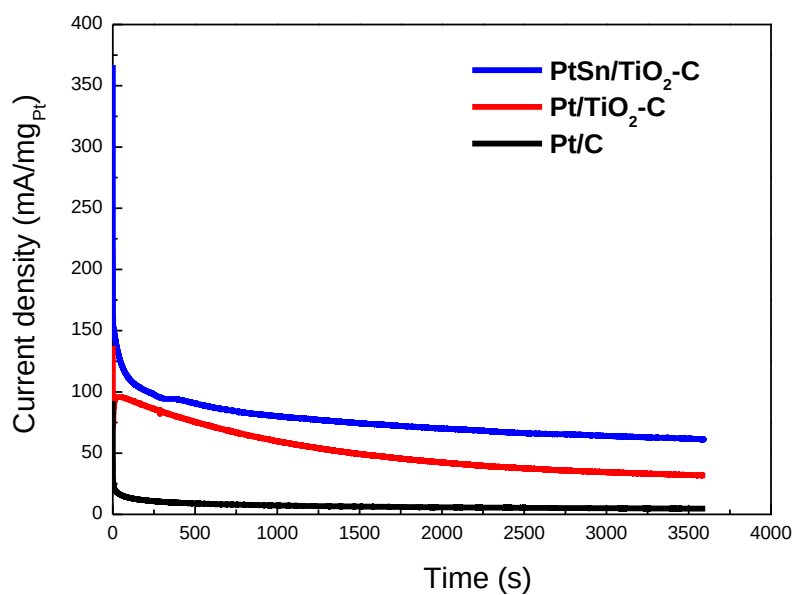


Fig. 5 Current density–time curves at 0.45 V for 3600 s at Pt/C, Pt/TiO₂-C and PtSn/TiO₂-C electrode in ethanol solutions.

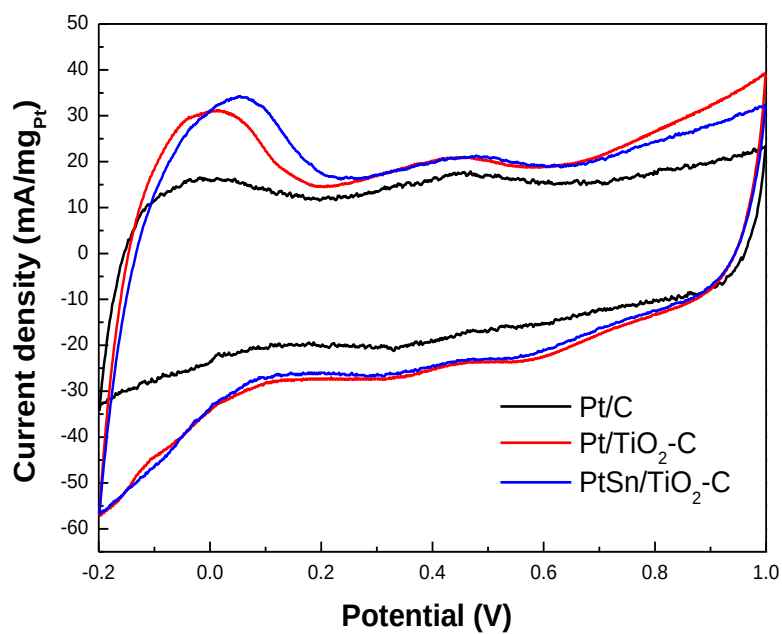


Fig. 6 Cyclic voltammogram curves in 1M HClO₄ solutions with a scan rate of 50mV·s⁻¹.

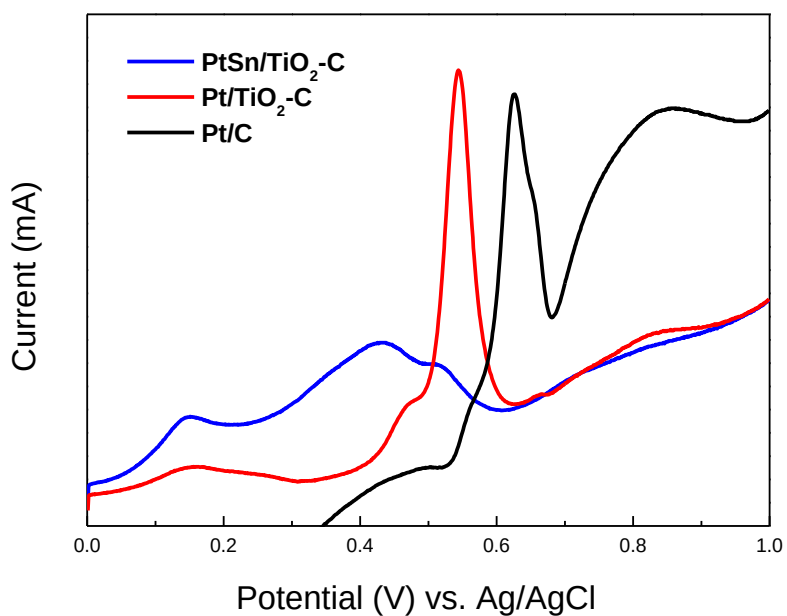


Fig. 7 CO stripping voltammograms in 0.5M H₂SO₄ solution under room temperature (scan rate = 10 mV·s⁻¹).

Table 1 Comparison the electro-oxidation active surface of ethanol over Pt(Sn)/TiO₂-C anodic catalysts.

Catalysts	EAS (cm ² /mg _{Pt})
Pt/C	49
Pt/TiO₂-C	264
PtSn/TiO₂-C	317