

## On-line electrochemical mass spectrometry system to study mechanism of the ethanol oxidation reaction

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**ABSTRACT:** In this work, we have developed the system of the on-line electrochemical mass spectrometry to detect volatile intermediates / products of the ethanol oxidation reaction (EOR). In order to verify the accuracy of measurement of the developed system, we were first synthesized the Pt/C catalyst using polyol method. The catalyst was physically characterized by X-Ray Diffraction (XRD) and Transmission Electron Microscopy (TEM). Next, we have considered the behavior of EOR on the Pt/C electrocatalyst by using the system. The CO<sub>2</sub> current efficiency (~7%) and CH<sub>3</sub>CHO current efficiency (~27%) were determined on the Pt/C catalyst, and the fact that incomplete ethanol oxidation reaction to acetaldehyde and acetic acid prevails for Pt/C electrocatalyst was found.

**KEYWORDS:** Mass spectrometry, Ethanol oxidation, Electrocatalyst, CO<sub>2</sub> current efficiency, Polyol method.

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### I. INTRODUCTION

In the development of electrochemical science, modern electrochemical analysis techniques for the study of products or intermediates of electrochemical reactions play a very important role. Especially, in recent years, many improvements have been made in the field of in-situ spectroscopic analysis techniques (such as infrared spectrophotometry, Raman spectroscopy), surface analysis techniques (such as XPS, Auger photoelectron spectroscopy) and gas and liquid chromatography coupled with electrochemical systems [1-4].

Among these numerous electrochemical spectroscopy techniques, differential electrochemical mass spectrometry [5-7] is a combination technique of electrochemical measurement and mass spectrometry for real-time quantitative detection of reaction products. In modern electrochemical analysis methods, although DEMS analysis technology is a very effective in-situ analysis method because it can analyze dynamic products or intermediates, it has a short history of development. The standard structure has not yet been formed, and stereotyped products have not yet been produced, so DEMS is not as widely used as analytical techniques such as infrared spectroscopy, Raman spectroscopy, and XPS.

An important application of DEMS is to predict the electrooxidation mechanism of the fuel in the field of electrocatalyst, especially fuel cells, and provide effective tools for design of the high-efficiency catalysts.

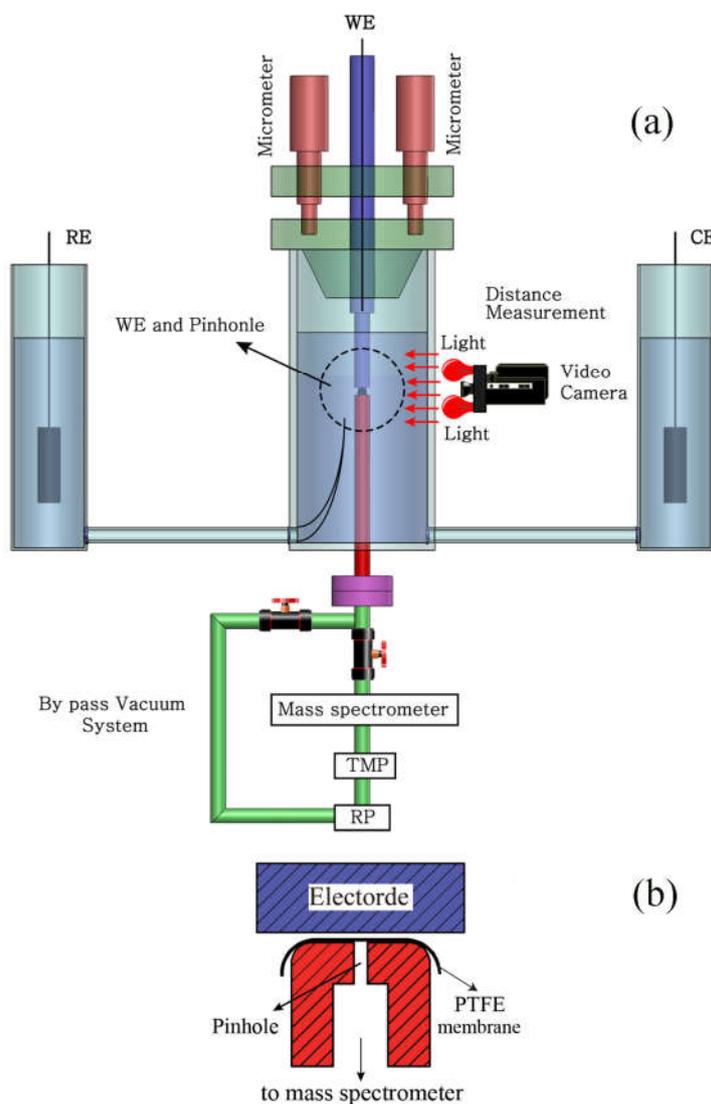
In the past, some research on the electrochemical mass spectrometry system have been performed. Balt et al. [8-10] have verified the double-channel electrooxidation mechanism of methanol on PtRu catalyst by using in-situ DEMS system with two-layer electrolytic cell structure. Abruna et al. [11] have combined the DEMS system with infrared spectroscopy to study the electrocatalytic mechanism and electrochemical kinetics of PtPb and PtBi intermetallic compounds on small organic molecules such as formic acid, formaldehyde and methanol. Moreover, by using DEMS system, the electrocatalytic oxidation of methanol was studied quantitatively and the efficiency of electrooxidation of methanol to CO<sub>2</sub> on the PtRu catalyst was monitored

[12]. Behm et. al have published more than 30 electrooxidation mechanisms for small organic molecules on the different catalysts using DEMS real-time monitoring technology [1, 13, 14]. This technique is now a routine technique utilized by many groups worldwide [15-17].

This study aims at establishing the system of Pinhole On-line Electrochemical Mass Spectrometry (POEMS), and verifying the accuracy of measurement of the analytical system through the electrochemical considering of the EOR on Pt/C electrocatalyst in acid medium at room temperature by POEMS. In this work, quantification of the CO<sub>2</sub> current efficiency (CCE) after calibration of the signal  $m/z=44$  and CH<sub>3</sub>CHO current efficiency were performed.

## II. ELECTROCHEMICAL MASS SPECTROMETRY SETUP

Fig.1 shows the system of developed on-line pinhole electrochemical mass spectrometry. As illustrated schematically in Fig 1(a), the on-line pinhole electrochemical mass spectrometer (MS) setup consists of a MS system, measuring pinhole, homemade micro-controlled system, video camera, and electrochemical cell. The mass spectrometer is a Qulee BGM-202 mass spectrometer with Qulee QCS software. During measurement, the inside pressure of the MS must be smaller than  $6 \times 10^{-5}$  mbar using combination of rotary pump and turbo molecular pump. The glass pinhole (Fig. 1(b)) covered with a thin Gore-Tex PTFE membrane with 20  $\mu\text{m}$  thickness was used as the gas inlet of the mass spectrometer. The inner diameter of pinhole inlet for MS is 9.5  $\mu\text{m}$ .



**Fig. 1. (a) Schematic drawing of the pinhole on-line electrochemical MS setup. WE – Working Electrode, RE – Reference Electrode, CE – Counter Electrode, TMP-turbo molecular pump, RP- rotary pump. (b) Schematic drawing of the on-line electrochemical MS inlet.**

The electrode-MS tip (MS inlet) assembly is positioned with the aid of “micro-controlled device” mounted on Teflon block, which can be placed on the cell. During positioning, the distance between the MS tip and the electrode is monitored using color camera with magnifying lenses and a periscope. It is adjustable in all directions over a range of a few cm, and which can overturn somewhat to place the camera view in the same plane as the plane of the electrode. The magnification is 50 times and is imaged on a computer display. The working electrode is dropped into solution and is placed at ca. 15 $\mu\text{m}$  distance from the MS tip with the help of “micro-controlled device” and the video camera, without touching the MS tip surface. The “micro-controlled device” not only ensured the short responsive time of mass spectra but also reduce the effect of concentration polarization. Finally, the electrode and MS tip are fixed and are placed simultaneously in hanging meniscus configuration.

The electrochemical cell is made of glass, and the working electrode mounted above PTFE membrane is close to the side of the cell such that the positioning can be followed by the video camera.

Fig. 2 shows some photographs of the system as currently developed in our laboratory.

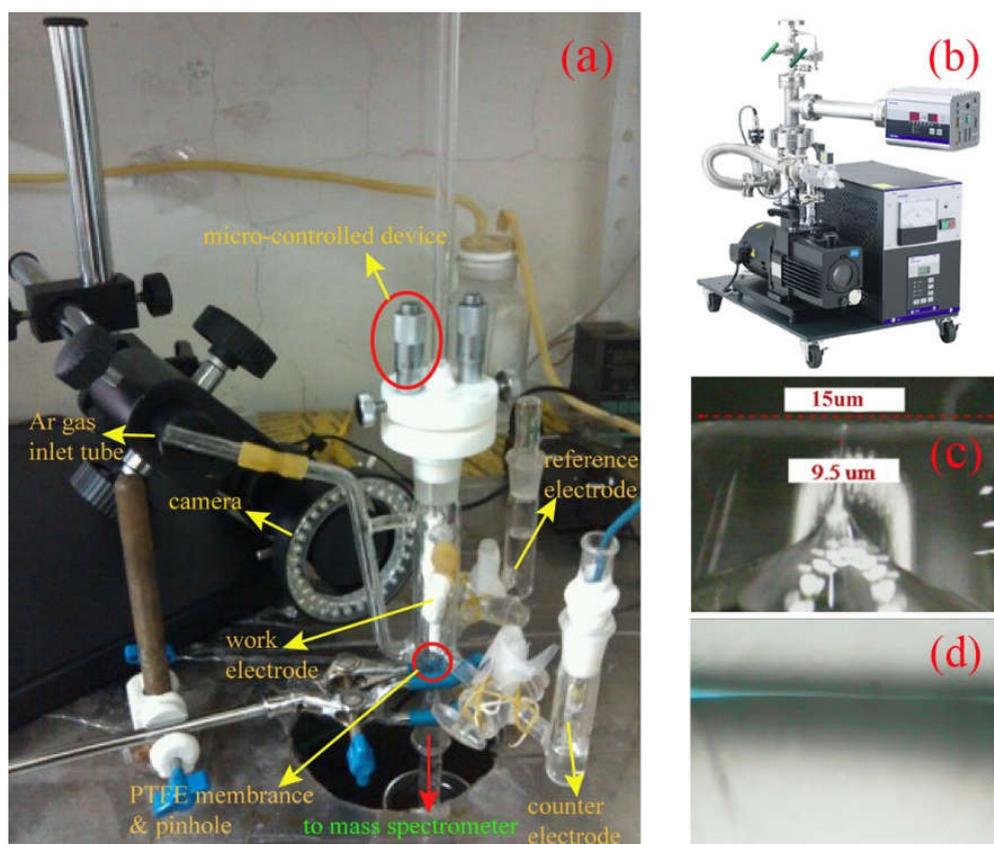


Fig. 2. Photographs of (a) electrochemical cell with the inlet configuration and connection to the MS, (b) Qulee BGM-202 mass spectrometer, (c) MS pinhole, (d) view of the tip-electrode configuration on the camera screen.

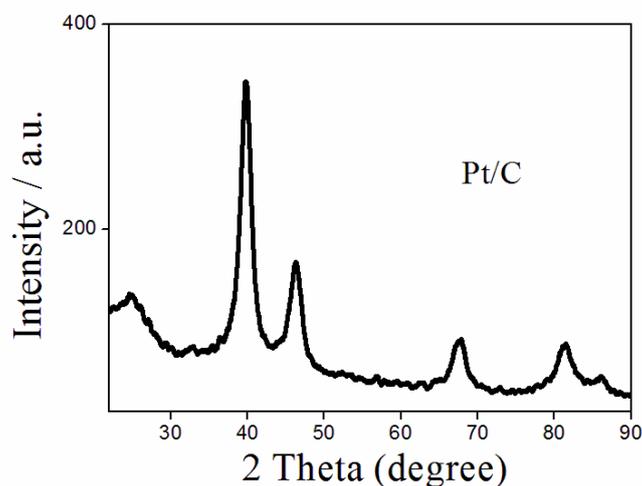
### III. PREPARATION OF PT/C CATALYST AND ELECTROCHEMICAL MEASUREMENTS

#### Preparation of Catalyst

All materials are purchased from the indicated suppliers and used without any further pretreatment. All the solutions were prepared with ultrapure water (Millipore, 18.2  $\text{M}\Omega\text{ cm}^{-1}$ ). Pt/C catalyst with a Pt loading of 20 wt.% was synthesized by a microwave-assisted polyol process. Briefly, 40 mg Vulcan XC-72 carbon black was dispersed into 60 mL ethylene glycol and isopropyl alcohol (v/v=4:1) under ultrasonic treatment for 1 h. Then 1.33 mL 0.03855  $\text{mol L}^{-1}$   $\text{H}_2\text{PtCl}_6\text{-EG}$  solution was added into the uniform carbon ink with urgent agitation for 3 h. The pH value of the mixture was then adjusted to 12.0 by adding dropwise 1  $\text{mol L}^{-1}$  NaOH-EG solution. After being saturated with argon for 20 min, the mixture was heated using a microwave oven for 60 s. When the mixture cooled down to room temperature, dilute  $\text{HNO}_3$  was added dropwise to adjust the pH value of the mixture to 2.0–3.0. The mixture was kept stirring for 12 h and then suspension was filtered and washed with ultrapure water (18.2  $\text{M}\Omega\text{ cm}^{-1}$ ) thoroughly, and finally dried in a vacuum oven at 80 $^\circ\text{C}$  for 6h.

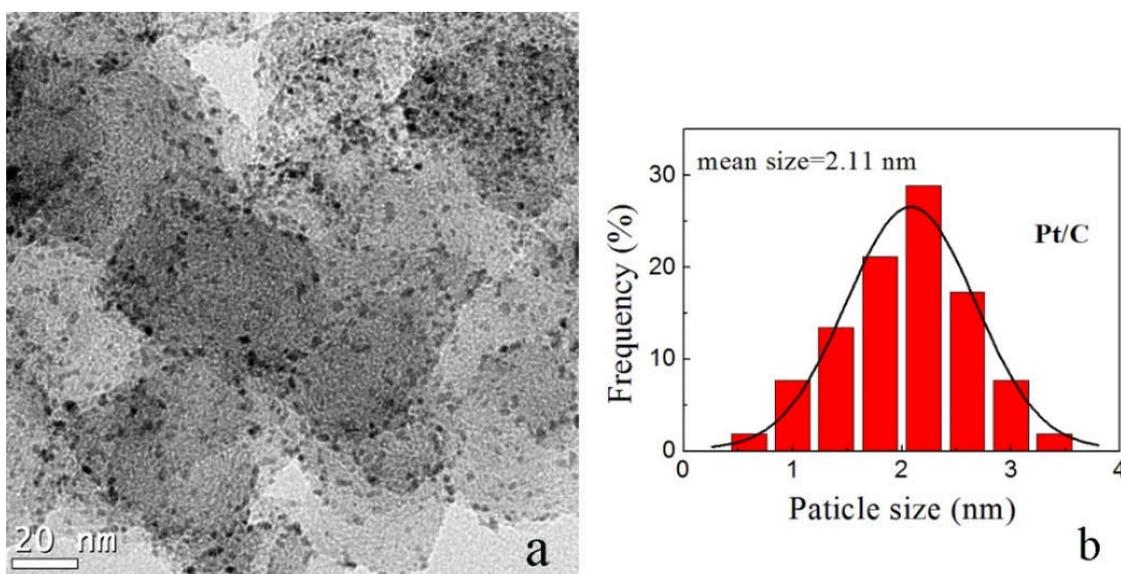
### Physical characterization

The prepared catalyst was characterized by D/max-RB X-ray diffractometer (Japan) with the Cu  $K\alpha$  X-ray source at 40 kV and 100 mA. Fig. 3 shows X-ray diffraction (XRD) patterns of the carbon-supported Pt electrocatalyst. The diffraction peak at about  $2\theta = 24.7^\circ$  is attributed to the amorphous phase of the Vulcan XC-72R carbon support and the Pt peak corresponding to the (111), (200), (220) and (311) planes appear at  $2\theta = 39.9^\circ$ ,  $46.6^\circ$ ,  $67.5^\circ$  and  $81.8^\circ$ , respectively.



**Fig.3. X-ray diffraction pattern of the carbon-supported Pt electrocatalyst.**

Transmission electron microscopy (TEM) experiments was performed with a TECNAI G2 F30 field emission transmission electron microscope. Fig.4 shows TEM image and particle size distribution histogram for the investigated electrocatalyst.



**Fig. 4. TEM image (a) of Pt/C and corresponding particle size distribution histogram (b).**

As shown in Fig.4a, the metal nanoparticles are uniformly distributed on the carbon for the Pt/C. The corresponding rough histogram in Fig. 4b reveal a particle size distribution with 2.11nm for Pt/C, which is in good agreement with the XRD result.

### Electrochemical measurements

Fig. 5 displays the cyclic voltammogram on Pt/C performed at 10 mV s<sup>-1</sup> in 0.1 M HClO<sub>4</sub>. The usual features of the so-called hydrogen and oxygen regions can be observed. Fig. 6a display CO-stripping

voltammogram recorded on Pt/C, and Fig. 6b the corresponding MSCV for the  $m/z=44$  mass signal. The CO stripping onset potential on Pt/C is placed at 0.6 V. Furthermore, the CO stripping peak potential on Pt/C appear at 7.6 V. Fig. 7 shows reality spectra of  $m/z=29$  and  $m/z=44$  for the ethanol oxidation on Pt/C in 0.1 M HClO<sub>4</sub> + 0.1 M EtOH solution measured by the developed MS system. Fig. 8 presents simultaneously recorded CVs and  $m/z=29$ ,  $m/z=44$  MSCVs for the ethanol oxidation on Pt/C in 0.1 M HClO<sub>4</sub> + 0.1 M EtOH solution. In order to get complete EOR current, the Faradaic signal for EOR has subtracted the background signal in 0.1 M HClO<sub>4</sub> (Fig. 8a). The mass signals of  $m/z=29$  and  $m/z=44$  represent acetaldehyde and CO<sub>2</sub>, respectively. Moreover, Fig. 8b demonstrate a simultaneous increase of the Faraday and ionic currents of the mass to charge signal  $m/z=29$  ([CHO]<sup>+</sup>), corresponding to CH<sub>3</sub>CHO ionization and to defragmentation in [CHO]<sup>+</sup>. Especially, since the  $m/z=44$  corresponds to the ion current for [CO<sub>2</sub><sup>+</sup>] and [CH<sub>3</sub>CHO<sup>+</sup>], the initial signal of  $m/z=44$  have removed the interference of [CH<sub>3</sub>CHO<sup>+</sup>] fragment signal to acquire pure [CO<sub>2</sub><sup>+</sup>] signal (Fig. 8c). Based on the assumption that acetic acid, as well as CO<sub>2</sub> and acetaldehyde, are the main products during ethanol oxidation, they are determined by calculating the difference between the measured Faradaic current and the acquired partial currents for ethanol oxidation to CO<sub>2</sub> and CH<sub>3</sub>CHO.

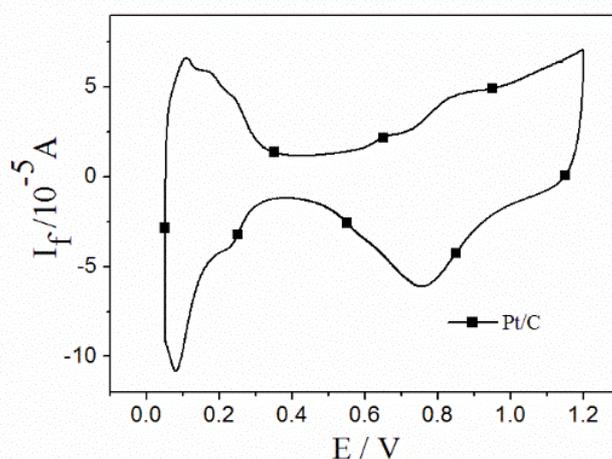


Fig. 5. CV in 0.5 M HClO<sub>4</sub> on Pt/C; scan rate=10 mV s<sup>-1</sup>, T = 25°C.

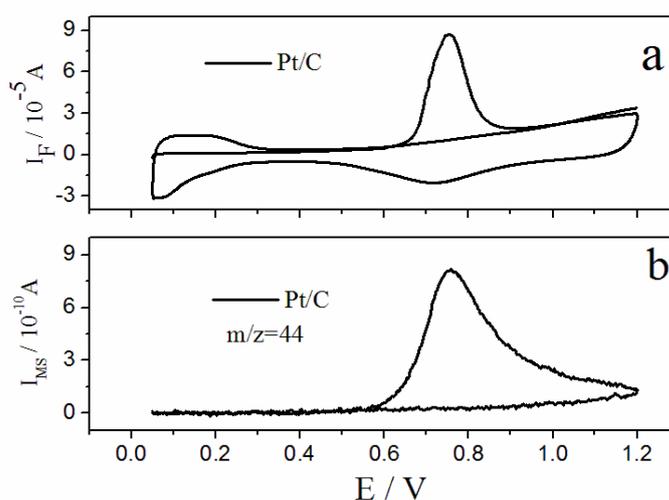


Fig. 6. CO-stripping CVs in 0.1 M HClO<sub>4</sub> and corresponding MSCVs for  $m/z = 44$  of the CO stripping on Pt/C; scan rate=10 mV s<sup>-1</sup>.



Fig. 7. Reality spectra of  $m/z=29$  and  $m/z=44$  for the ethanol oxidation on Pt/C.

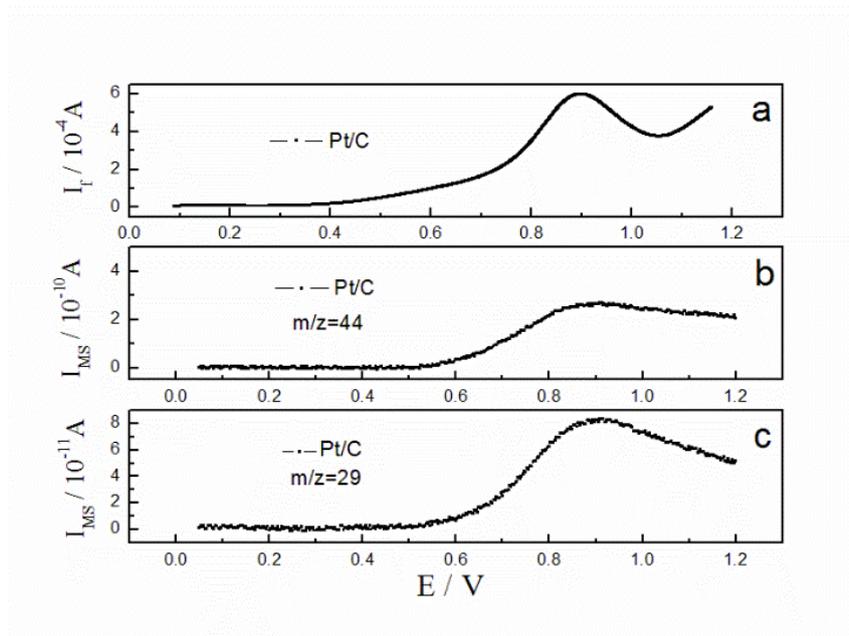


Fig. 8. Simultaneously recorded CV and MSCV for  $m/z = 29$  and  $m/z=44$  for the oxidation of ethanol on Pt/C in 0.1 M  $\text{HClO}_4$  + 0.1 M EtOH solution; scan rate =  $10 \text{ mV s}^{-1}$ .

The following table shows the current efficiencies of above three products calculated by the equations mentioned in the previous literature, which are in good agreement with the previous results [18, 19].

Table. Average current efficiencies for  $\text{CO}_2$ , acetaldehyde and acetic acid formation on Pt/C (0.1 M  $\text{HClO}_4$  + 0.1 M EtOH solution).

Sample	$A_q(\text{CO}_2)$ (%)	$A_q(\text{CH}_3\text{CHO})$ (%)	$A_q(\text{CH}_3\text{COOH})$ (%)
Pt/C	6.9	26.9	66.1

These results above further prove that the incomplete ethanol oxidation reaction to acetaldehyde and acetic acid prevails for Pt/C electrocatalyst. Therefore, the system developed can be said to be very suitable for studies on electrooxidation reaction mechanism of the fuel on the electrocatalyst.

#### IV. CONCLUSION

In this study, we have developed the on-line electrochemical mass spectrometry system to predict the electrooxidation mechanism of the fuel such as ethanol and methanol on the electrocatalyst. We were designed and manufactured the system in our own, and Pt catalyst was synthesized by a microwave-assisted polyol process to evaluate the measurement accuracy of the system.

The current efficiencies for CO<sub>2</sub> and CH<sub>3</sub>CHO were determined on the Pt/C electrocatalyst at 25°C by the electrochemical potentiodynamic experiment, which agree with the results of previous paper. Therefore, the measurement accuracy of the developed system was confirmed again on the basis of experimental result that the incomplete ethanol oxidation reaction to acetaldehyde and acetic acid prevails for Pt/C electrocatalyst.

We will use the developed system in the future to carry out a study on mechanism of ethanol oxidation reaction on the various catalysts.

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