# Synthesis of mesopours PtCu film modified with Ru submonolayer as catalyst for methanol electrooxidation<sup>†</sup>

## Satoshi Tominaka, Mayumi Shigeto, Hiroshi Nishizeko and Tetsuya Osaka\*

Department of Applied Chemistry, Graduate School of Advanced Science and Engineering, Waseda University, Tokyo 169-8555, Japan. <sup>10</sup> ‡Current affiliation: World Premier International Research Center for Materials Nanoarchitectonics, National Institute for Materials Science, Ibaraki 305-0044, Japan. E-mail: TOMINAKA.Satoshi@nims.go.jp \* E-mail: osakatets@waseda.jp

# **Eletronic supplementary information**

#### A. Additional information on the synthesis of mesoporous Pt

Since the oxidation current appeared to become negligible, the time, 1 min, was judged to be <sup>25</sup> sufficient for the dissolution of Cu. When we tested one cycle of 30-min deposition and 30-min dealloying, the deposited layer was peeled off from the Si substrate by the strong stress caused during dealloying process. This peeling off was solved by the method above described. In addition, a longer time was applied, the crack became larger as shown in the following figures (Figs. S1 and S2).

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**Fig. S1** SEM images of a mesoporous PtCu film synthesized by applying 3-min deposition/3-min dealloying cycles (10 cycles). The top two are plan-view images and the bottom ones are cross-sectional images.



**Fig. S2** SEM images of a mesoporous PtCu film synthesized by applying 5-min deposition/5-min dealloying cycles (6 cycles). The top two are plan-view images and the bottom ones are cross-sectional images.

#### **B.** Experimental details 1: Evaluation

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The surface composition was analyzed using X-ray photoelectron spectroscopy by applying a Mg-K $\alpha$  radiation at 14 kV, 400 W. The charge collection was conducted by setting the C 1s peak to be at 284.5 eV. Ru content was determined by using Ru 3p<sub>3/2</sub> peak, because the Ru 3d<sub>5/2</sub> peak was overlapped with <sup>5</sup> C 1s peak.

The crystal structure was determined by X-ray diffractometry using Bruker D8 Discover with a 2D detector of Hi-Star by applying a Cu-K $\alpha$  radiation at 40 kV, 40 mA. To determine the peak positions superimposed with substrate peaks, the spots on the 2D detector attributed to the substrate, *i.e.*, the Si (100) wafer and the (111)-oriented Au film deposited on the wafer by electron beam <sup>10</sup> evaporation) were excluded from the data analysis.

The electrochemical response was measured by cyclic voltammetry (CV) scanned in a nitrogen-saturated 0.5 M  $H_2SO_4$ . The methanol oxidation properties were analyzed by scanning a CV in 2 M methanol solution containing 0.5 M  $H_2SO_4$  (air-saturated as a test for use in our on-chip fuel cell system<sup>1, 2</sup>).

#### C. Experimental details 2: Synthesis of Pt black and PtRu alloy

All the electrodeposition procedures were carried out at room temperature in a conventional three electrode cell. Pt black was deposited by applying pulse currents (on:  $-50 \text{ mA cm}^{-2}$ , 0.1 s; off: 0.5 s; 1  $_{20} \text{ C cm}^{-2}$ ) in a solution containing 20 mM H<sub>2</sub>PtCl<sub>6</sub>, 2 M HCl and 0.002% (CH3COO)<sub>2</sub>Pb.

Pt-Ru alloy was deposited by applying pulse current (on:  $-50 \text{ mA cm}^{-2}$ , 0.1 s; off: 0.5 s) to deposit 1 C cm<sup>-2</sup> of Pt-Ru in a solution containing 10 mM H<sub>2</sub>PtCl<sub>6</sub>, 10 mM RuCl<sub>3</sub> and 0.002% (CH<sub>3</sub>COO)<sub>2</sub>Pb on the Pt black layer to increase the surface area.

#### 25 D. Cyclic voltammograms for underpotential codeposition of Pt-Cu alloy

For the better understanding of the synthesis, the underpotential codeposition of Pt-Cu alloy was confirmed by cyclic voltammetry. In a solution containing Cu ions or  $PtCl_4^{2-}$  ions, stable CVs were obtained as shown in Fig. S3. In the case of Cu deposition, the onset potential of large reduction current is *ca*. 50 mV with an oxidation peak at 0.1 V (Figs. S3a and S3b). These redox <sup>30</sup> reactions simply resulted from the overpotential deposition of Cu.

$$\operatorname{Cu}^{2+} + 2e^{-} \rightleftharpoons \operatorname{Cu} \qquad (E^{\circ} = 0.143 \text{ V})$$
 (1)

Where  $E^{\circ}$  is the standard potential referring to the Ag/AgCl electrode at 25 °C. Looking closely, <sup>35</sup> the reduction has a prepeak at 0.15 V (Fig. S3b), which is attributed to Cu underpotential deposition on the Au electrode.<sup>3</sup> This behavior is repeatedly obtained.

In the case of Pt deposition, the onset potential of the reduction current was *ca*. 0.15 V at the 1<sup>st</sup> cycle, and during the positive scan, the onset potential was found to be shifted up to 0.5 V, *i.e.*, Nernst potential of the Pt complex (10 mM  $PtCl_4^{2-}$ ). This is simply due to the large

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overpotential for nucleation of Pt on Au electrode, and once Pt was deposited, the overpotential was decreased. Then, from the  $2^{nd}$  cycle, the same behaviors were obtained. The net reaction is a two-electron reduction reaction of  $PtCl_4^{2-}$  complex.

$$PtCl_4^{2-} + 2e^- \rightleftharpoons Pt + 4Cl^- \quad (E^\circ = 0.559 \text{ V})$$
(2)

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These behaviors were dramatically changed in the case of Pt-Cu deposition. The onset potential for reduction current was similar to that of Pt at the 1<sup>st</sup> cycle. The reduction current increased about two times, resulting from codeposition of Cu with Pt. During the positive scan, <sup>10</sup> oxidation current was observed above 0.2 V, which can be attributed to dealloying of Cu from the deposited Pt-Cu layer. The three oxidative peaks at 0.15, 0.3 and 0.5 V are attributed to the dealloying of Cu from Pt-Cu alloy with different phases, *i.e.*, Cu, Pt<sub>1</sub>Cu<sub>1</sub> and Pt<sub>3</sub>Cu<sub>1</sub>, respectively. From 2<sup>nd</sup> cycle, Pt deposition current peak around 0.2 V (compare Figs. S3d with S3e) with a prepeak at 0.4 V, which can be attributed to Cu underpotential deposition onto Pt electrode. The <sup>15</sup> prepeak was increased with cycles, this representing the increase in the Pt surface area. Huang used this potential cycling to prepare nanoporous Pt electrode with a large surface area.<sup>4</sup> We consider such a gradual potential change indicates Cu dissolusion from each phases, resulting in the almost complete leaching of Cu.



$$Pt-Cu \rightarrow Pt + Cu^{2+} + 2e^{-}$$
(3)

**Fig. S3** Cyclic voltammograms of a Au electrode in the Pt-Cu deposition solution containing 20 mM K<sub>2</sub>PtCl<sub>4</sub>, 20 mM CuSO<sub>4</sub> and 0.5 M H<sub>2</sub>SO<sub>4</sub> (blue lines), a Pt solution containing 20 mM K<sub>2</sub>PtCl<sub>4</sub> and 0.5 M H<sub>2</sub>SO<sub>4</sub> (red <sup>25</sup> lines) and a Cu solution containing 20 mM CuSO<sub>4</sub> and 0.5 M H<sub>2</sub>SO<sub>4</sub> (green lines). (a) 1<sup>st</sup> cycles. (b) Magnified view of the 1<sup>st</sup> cycle in the Cu solution. (c) 5<sup>th</sup> cycles.

#### E. XRD pattern for the mesoporous Pt film

Compared with the diffraction angles for the pure fcc-Pt lattices, which are located at 39.76° for (111), 46.25° for (200), 67.47° for (220), 81.27° for (311) and 85.71° for (222) (PDF No. 01-070-2057, lattice constant is 3.922 Å), the angles for the synthesized mesoporous PtCu film, *i.e.*, <sup>5</sup> 40.54°, 47.12°, 68.84°, 82.98° and 87.14°, are similar but shifted to higher angles.



**Fig. S4** (a) XRD patterns of the mesoporous PtCu film synthesized by applying 30 cycles of 1-min deposition and 1-min dealloying (blue line) compared with that of the sample synthesized by 30-min deposition (red line). <sup>10</sup> (b) Raw data detected on the 2D detector.

### F. Cyclic voltammogram of the mesoporous Pt film and the Ru-modified one

The electrochemical response of the mesoporous PtCu electrode was evaluated by cyclic voltammetry in a nitrogen-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution (Fig. S5). The CV had a small oxidative current peak at 0.57 V attributable to the dissolution of Cu atoms underpotentially deposited on the Pt surface. Since <sup>5</sup> the dissolution peak was observed only at the first scan, such dissolved Cu atoms are not from the bulk but from the surface, *i.e.*, residual or re-adsorbed ones. XRF results confirm that the composition was not changed by this voltammetric treatment.

The CV of the mesoporous PtCu electrode was compared with that of the Ru-modified one in Fig. S6.



**Fig. S5** CVs of the mesoporous PtCu film at  $10 \text{ mV s}^{-1}$ .



Fig. S6 Comparison of CVs of the mesoporous PtCu films with and without the Ru-modification. 50 mV  $s^{-1}$ .

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### G. XRD pattern of the PtRu alloy synthesized by electrodeposition on a Pt black electrode

The electrodeposited PtRu, which was synthesized on the Pt black electrode, exibited a XRD pattern similar to pure Pt. Moreover, the XRD pattern shows a strong (111) orientation.





## H. Stability of the Ru-modified mesoporous PtCu catalyst

Stability of the Ru-modified mesoporous PtCu catalyst was evaluated by cyclic voltammetry scanned <sup>5</sup> for 100 cycles (the experimental conditions were the same as Fig. 3). As shown in Fig. S8, even after 100 cycles, the activity of the catalyst was still higher than that of the as-synthesized mesoporous PtCu catalyst. The decrease in current around 0.6 V is probably attributed to the decrease in methanol concentration, but further detailed analyses are needed for concluding the stability of the Ru-modified mesoporous PtCu catalyst.



Fig. S8 Anodic scans of cyclic voltammograms for the methanol oxidation reaction at 50 mV s<sup>-1</sup>.

#### I. Activity of the catalysts for the methanol oxidation reaction

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<sup>15</sup> **Table S1** Methanol oxidation properties of mesoporous PtCu electrode, compared with those of electrochemically synthesized Pt catalysts.

	Current density at 0.3 V / mA cm <sup>-2</sup>	Tafel slope / mV decade <sup>-1</sup>	Roughness factor / -	Specific activity at 0.3 V / µA cm <sup>-2</sup>
Mesoporous PtCu	0.73	88	450	1.6
Mesoporous PtCu	1.0	170	_	_
(Ru-modified)				
Pt black	0.085	95	18	4.8
Pt black (Ru-modified)	0.46	75	_	_
PtRu alloy	1.7	120	—	—



## J. X-ray photoelectron spectra of the Ru-modified Pt-black and the PtRu alloy

**Fig. S9** Core-level XPS of a Ru-modified Pt black and a PtRu alloy: Pt  $4f_{7/2}$  and Ru  $3d_{5/2}$ . The dotted lines show the peak position in the metallic state.

#### References

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