Short communication

# Methanol electro-oxidation by a ternary Pt–Ru–Cu catalyst identified by a combinatorial approach

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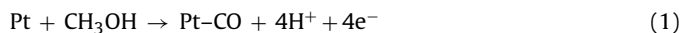
### A R T I C L E   I N F O

### A B S T R A C T

Composition optimization of the ternary Pt–Ru–Cu system for the methanol electro-oxidation reaction (MOR) was performed by combinatorial synthesis and high-throughput screening methods. A thin film library of the Pt–Ru–Cu system was prepared by a sputtering system to generate 63 different compositions. The compositions were characterized in parallel by a multichannel multielectrode analyzer. The highest MOR activity was observed for the $Pt_{66}Ru_{17}Cu_{17}$ composition. The $Pt_{66}Ru_{17}Cu_{17}$/C composition was synthesized and characterized as a powder catalyst to verify the performance of this new composition. During cyclic voltammetry tests, the $Pt_{66}Ru_{17}Cu_{17}$/C catalyst showed less dissolution and irreversible oxidation of Ru than a $Pt_{50}Ru_{50}$/C catalyst, with increasing number of cycles. In MOR activity measurement experiments, the $Pt_{66}Ru_{17}Cu_{17}$/C catalyst exhibited 26 and 86% higher activities in cyclic and chronoamperometric tests, respectively, than those of the $Pt_{50}Ru_{50}$/C catalyst.

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## 1. Introduction

Direct methanol fuel cells (DMFCs) are under intensive research, primarily because of their ability to utilize a liquid fuel. This feature makes DMFCs the most promising alternative to lithium ion batteries for application in portable power sources. Present lithium ion batteries suffer from long recharge times, while DMFCs can be easily refueled in a short time. However, the use of methanol in fuel cells suffers from obstacles, such as low catalytic activity at the anode electrode and cross-over of methanol from the anode to the cathode electrode [1]. There have been many efforts to develop highly active catalysts for the methanol electro-oxidation reaction (MOR) [2].

Pt was the first catalyst used for the MOR, but a rapid drop of performance was observed because of poisoning by adsorbed CO ($CO_{ads}$), which is an intermediate of the MOR. This problem was significantly reduced by incorporating Ru into the Pt catalyst [3] through the "bi-functional mechanism" as shown below [4]:

$$Pt + CH_3OH \rightarrow Pt–CO + 4H^+ + 4e^- \qquad (1)$$

$$Ru + H_2O \rightarrow Ru–OH + H^+ + e^- \qquad (2)$$

$$Pt–CO + Ru–OH \rightarrow Pt + Ru + CO_2 + H^+ + e^- \qquad (3)$$

Ru discharges water at a lower potential than the pure Pt to produce Ru–OH. But, the state-of-the-art PtRu catalyst needs further improvement due to relatively low catalytic activity and the high cost of noble Pt and Ru. The most successful way to achieve the both goals has been to add transition metals to the PtRu catalyst. Ternary PtRuFe [5,6], PtRuNi [7–9], PtRuCo [10,11], PtRuW [10,12,13], and PtRuIr [14] were reported as highly active MOR catalysts. In a recent review [15], Demirci used theoretical calculations and agreed that incorporation of a third metal might be the best way to improve MOR activity [16,17]. In this study, we investigated the Pt–Ru–Cu system for MOR catalytic activity, with the hope of achieving higher activity and reduced catalyst cost. Addition of Cu was reported in cathode applications as a Pt–Cu alloy for oxygen electro-reduction [18–21], but there are no reports of MOR anode applications. For efficient examination of the PtRuCu system, we applied combinatorial synthesis and high-throughput screening to accelerate our research on the PtRuCu system.

Reddington et al. [22] first introduced combinatorial synthesis and parallel screening to the field of electrocatalysts. Since that study, various techniques have been reported for synthesis and characterization of combinatorial libraries [23]. Various deposition methods for synthesizing combinatorial libraries have been developed including physical vapor deposition [11,24], electro-deposition [25], and solution dispensing [26]. Additionally, many high-throughput electrocatalyst screening methods have been reported including optical screening [22,26], scanning

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electrochemical microscopy [27], multielectrode half cell [28,29], and multielectrode full cell [30]. In this study, thin film sputtering and a multielectrode half cell were used for synthesizing and characterizing the Pt–Ru–Cu library, respectively. The sputtering system can produce discrete composition thin film libraries reproducibly [30], while the multielectrode half cell system can characterize the library pads quickly and quantitatively in parallel [10]. In the present work thin film combinatorial synthesis and parallel screening was used to identify the most active MOR catalyst composition in a Pt–Ru–Cu library. This composition was further studied by synthesizing and characterizing in powder form catalyst to verify the feasibility of the composition as a MOR catalyst.

## 2. Experimental

### 2.1. Library synthesis and characterization

Preparation and characterization methods are described in detail elsewhere [10,31]. Briefly, Pt, Ru, and Cu targets were sequentially sputtered through a series of shadow masks onto a 50 mm diameter silicon wafer to generate 63 discrete pads of different compositions. The deposited library was rapidly annealed (5 min) at 900 °C to form homogeneous alloys from the as-deposited library of multilayers of Pt, Ru, and Cu. A commercial multielectrode potentiostat system (Scribner Associates model 900B Multichannel Microelectrode Analyzer (MMA)) was used to test the MOR activity of the library. The annealed library was aligned in a specially designed cell equipped with spring-loaded "pogo" probes and connected to the MMA to measure potentiostatic response of the pads simultaneously. MOR activity was tested by cycling potential from $-0.06$ to $1.34$ V vs. reference hydrogen electrode (RHE) in $0.5$ M $H_2SO_4$ solution without and with $0.5$ M methanol at a scan rate of $10$ mV s$^{-1}$. Comparison of potentiostatic curves without and with methanol revealed compositions with MOR activity.

### 2.2. Powder catalyst synthesis and characterization

After having been identified as a promising composition in the thin film library, carbon supported $Pt_{66}Ru_{17}Cu_{17}/C$ catalyst, ("PtRuCu/C"), was synthesized by a conventional NaBH$_4$ reduction method [32]. Vulcan XC72R (Cabot Co., Ltd.) was used as the carbon support. $H_2PtCl_6 \cdot 6H_2O$, $RuCl_3 \cdot H_2O$, and $Cu(NO_3)_2 \cdot 3H_2O$ were used as precursors of Pt, Ru, and Cu, respectively. The precursors were dissolved in a mixture of de-ionized (DI) water and methanol and then the carbon support were added to the solution. The total amount of metal was adjusted to be 20 wt.% of the total catalyst. The mixture was sonicated and stirred for 30 min to achieve homogeneous mixing. $0.2$ M NaBH$_4$ solution was added to the mixture and then the mixture was further stirred for 1 h to complete the reduction reaction. The resulting mixture was filtered and washed with DI water. The filtered powder was dried in an oven at 100 °C overnight. Carbon supported $Pt_{50}Ru_{50}/C$ catalyst, ("PtRu/C"), was also prepared by the same way.

X-ray diffraction (XRD) was performed on the powder catalysts in a step scan mode with a step size of $0.02°$ and duration time of $0.5$ s for each step from 20 to 80° $2\theta$. Electrochemical characterization was performed in a beaker-type three-electrode cell. A glassy carbon electrode (3 mm dia., BAS Co., Ltd., MF-2012) was used as a working electrode. Catalyst layers were deposited by using the thin-film method [33]. Platinum mesh and standard calomel electrodes were used as the counter and reference electrodes, respectively. Cyclic voltammetry (CV) tests were performed by cycling the potential between 0 and 1.2 V (vs. RHE) at a scan rate of 50 mV s$^{-1}$. For the
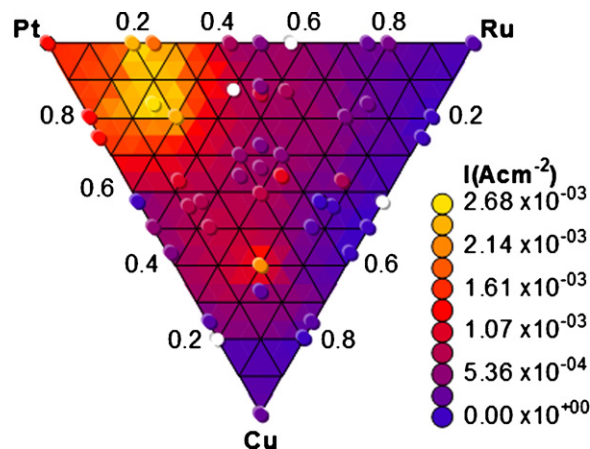


**Fig. 1.** Peak current densities of the Pt–Ru–Cu library during potential cycling between $-0.06$ and $1.34$ V at a scan rate of $10$ mV s$^{-1}$.

CV tests, nitrogen purged $0.5$ M $H_2SO_4$ solution was the electrolyte. MOR activity measurement by CV in the presence of methanol was performed by cycling potential between 0 and $0.8$ V (vs. RHE) at a scan rate of $50$ mV s$^{-1}$. Chronoamperometric activity for MOR was measured by keeping the electrode at $0.6$ V (vs. RHE). For both of the MOR activity measurement tests, nitrogen purged $1$ M $H_2SO_4 + 1$ M methanol solution was used as the electrolyte. All potentials in this paper were converted to RHE scale.

## 3. Results and discussion

Fig. 1 shows the compositional map of MOR activity from measurements of the PtRuCu thin film library. The highest activity was observed for $Pt_{66}Ru_{17}Cu_{17}$ with a current density of $2.7 \times 10^{-3}$ A cm$^{-2}$, which exceeded the $2.41 \times 10^{-3}$ A cm$^{-2}$ value for binary $Pt_{80}Ru_{20}$ composition. Compositions around $Pt_{80}Ru_{20}$ show the highest values in the thin film library system, rather than $Pt_{50}Ru_{50}$ as seen in bulk due to the (1 1 1) texture [10,11,34]. When the amount of Pt was less than 60 at.%, the compositions showed relatively poor performance, indicating that incorporation of Ru and Cu should be limited to less than 40 at.%. Binary Pt–Cu compositions also did not show any signs of activity improvement, which likely explains why there are no reports on Pt–Cu alloys for MOR application. Even the ternary compositions showed only a very narrow region of compositions that are more active than PtRu. This result illustrates that it is easy to miss active compositions if insufficient number are explored. Because there have been no reports
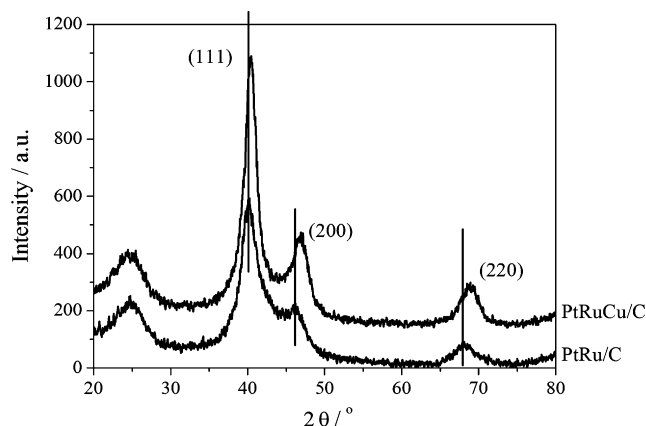


**Fig. 2.** Powder XRD patterns of the PtRuCu/C and PtRu/C catalysts.

**Table 1**
Structural and electrochemical properties of the $Pt_{66}Ru_{17}Cu_{17}/C$ and $Pt_{50}Ru_{50}/C$ catalysts

| Catalysts | (2 2 0) peak position (°) | $d$ (Å) | Lattice parameter (Å) | Crystallite size (nm) | Current density at 0.6 V during CV for MOR ($A\,g_{cat.}^{-1}$) | Current density at 600 s during chronoamperometry ($A\,g_{cat.}^{-1}$) |
|---|---|---|---|---|---|---|
| PtRuCu/C | 68.96 | 1.361 | 3.848 | 3.4 | 7.99 | 6.96 |
| PtRu/C | 67.90 | 1.379 | 3.901 | 2.8 | 6.35 | 3.75 |

on the activity of the PtRuCu catalysts, further investigation was warranted to confirm the performance of a powder version of the most active composition ($Pt_{66}Ru_{17}Cu_{17}$, at.%).

The XRD patterns of the powder samples are shown in Fig. 2. The broad peak at 25° is from the carbon support. We could not observe any peaks from Cu or Cu oxides, indicating alloying was relatively complete. In the PtRuCu/C catalyst, all peaks were shifted to higher 2θ values than those of PtRu/C due to the incorporation of Cu. The (2 2 0) peak moved from 67.90° in PtRu/C to 68.96° in PtRuCu/C. Because the Cu atom is much smaller than Pt, the incorporation of Cu causes shrinkage of the lattice parameter, which results in the peak shift to the higher 2θ values. Lattice parameters calculated from the (2 2 0) peaks were 3.848 and 3.901 Å for the PtRuCu/C and PtRu/C catalysts, respectively. Crystallite sizes, calculated from the (2 2 0) peaks by using the Scherrer equation [35], were 3.4 and 2.8 nm for the PtRuCu/C and PtRu/C catalysts, respectively. A summary of the XRD results is listed in Table 1.

Fig. 3 shows the CV test results of the (a) PtRuCu/C and (b) PtRu/C catalysts performed for 50 cycles. During the CV tests, more significant changes were observed in PtRu/C than in PtRuCu/C. First, the current density along the positive scan direction decreased with an increasing number of CV cycles. This current density originated from oxidation of Ru hydrous oxide ($RuO_xH_y$) and metallic Ru [36]. The reduction in the current density in the high potential region implies that the $RuO_xH_y$ and metallic Ru were dissolved or oxidized to $RuO_2$ irreversibly during the CV tests. These $RuO_xH_y$ and metallic Ru species play an important role in methanol oxidation, as the contribution of Ru species for MOR follows the order of $RuO_xH_y$ > Ru (metal) $\gg RuO_2$ [37–39]. Therefore, the dissolution or irreversible oxidation of $RuO_xH_y$ and metallic Ru is not preferred for MOR. The differing behavior between the PtRuCu/C and PtRu/C catalysts is clear in the region between 0.25 and 0.6 V of the positive scan direction. Here, the PtRu/C catalyst showed a decrease of current density, while the PtRuCu/C did not, indicating that the incorporation of Cu may inhibit the dissolution or irreversible oxidation of Ru. In the negative scan direction, the PtRu/C catalyst showed a significant change of reduction peak of PtO in both the potential and current density, while the PtRuCu/C catalyst did not. This behavior in the PtRu/C catalyst also shows that dissolution of Ru or $RuO_2$ formation occurred during the CV tests, while it was inhibited in the PtRuCu/C catalyst.

Fig. 4(a) shows the CV results of MOR activity measured in 1 M $H_2SO_4$ + 1 M methanol electrolyte. The PtRuCu/C catalyst showed higher activity than the PtRu/C catalyst. At 0.6 V, current densities of the catalysts were 7.99 and 6.35 $A\,g_{cat.}^{-1}$ for the PtRuCu/C and PtRu/C catalysts, respectively. The current density of PtRuCu/C was 26% higher than that of PtRu/C although we reduced the amount of noble metals by 17%. Chronoamperometry tests were also performed, and the results are shown in Fig. 4(b) and (c). A notable feature is the slight increase in current density of the PtRuCu catalyst during the first 25 s of testing. Such behavior has been reported in other catalysts [40], but at higher potential (0.7 V) than the 0.6 V used in this study. The current increase has been attributed to the oxidation of adsorbed carbon monoxide being faster than methanol decomposition. The current increases because of a slow increase in CO coverage. This reaction is thought to slow down due to increased poisoning of the surface. More work is required to determine if this

mechanism is applicable here, or if some other adsorbed species are responsible for the observed behavior. After testing for 600 s, the current densities of the catalysts were 6.96 and 3.75 $A\,g_{cat.}^{-1}$ for the PtRuCu/C and PtRu/C catalysts, respectively. The current density of PtRuCu/C was 86% higher than that of PtRu/C, indicating significant improvement in MOR activity. Also, the current densities were reduced to 83 and 60% of their peak current density during the chronoamperometry tests for the PtRuCu/C and PtRu/C catalysts, respectively. This result shows that the PtRuCu/C catalyst exhibited less poisoning by reaction intermediates. The electrochemical properties are summarized in Table 1. The MOR activity measurement results prove that PtRuCu/C is a promising catalyst, which agrees with the results of the thin film combinatorial library characterization. This result clearly shows the value of the combinatorial method as a fast and efficient way to identify promising catalyst compositions.
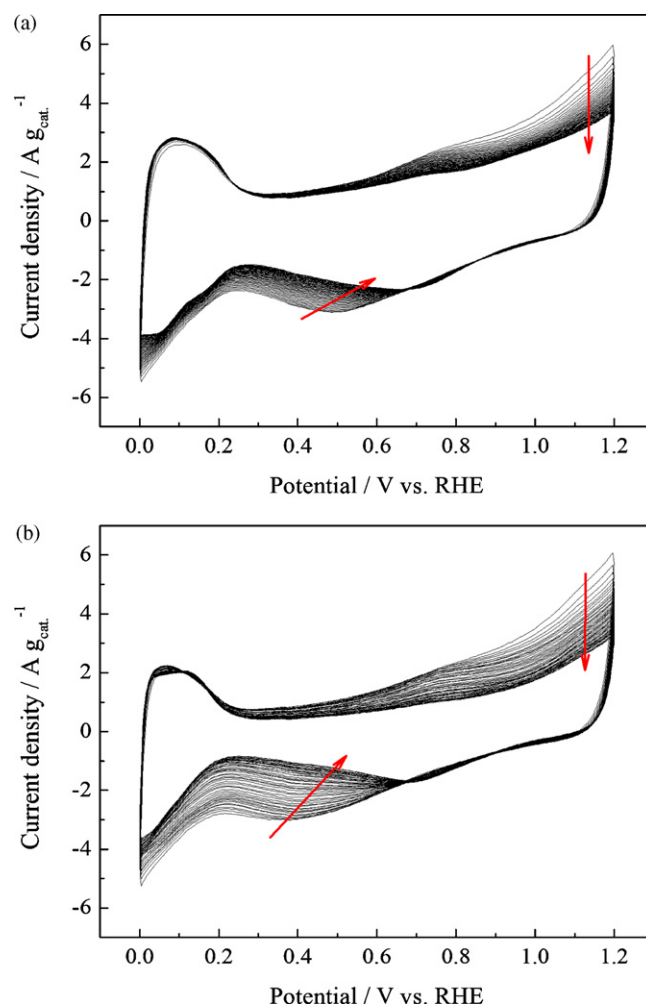


**Fig. 3.** CV test results of the (a) PtRuCu/C and (b) PtRu/C catalysts measured by potential cycling between 0 and 1.2 V at a scan rate of 50 mV s⁻¹. Nitrogen purged 0.5 M $H_2SO_4$ solution was used as the electrolyte.
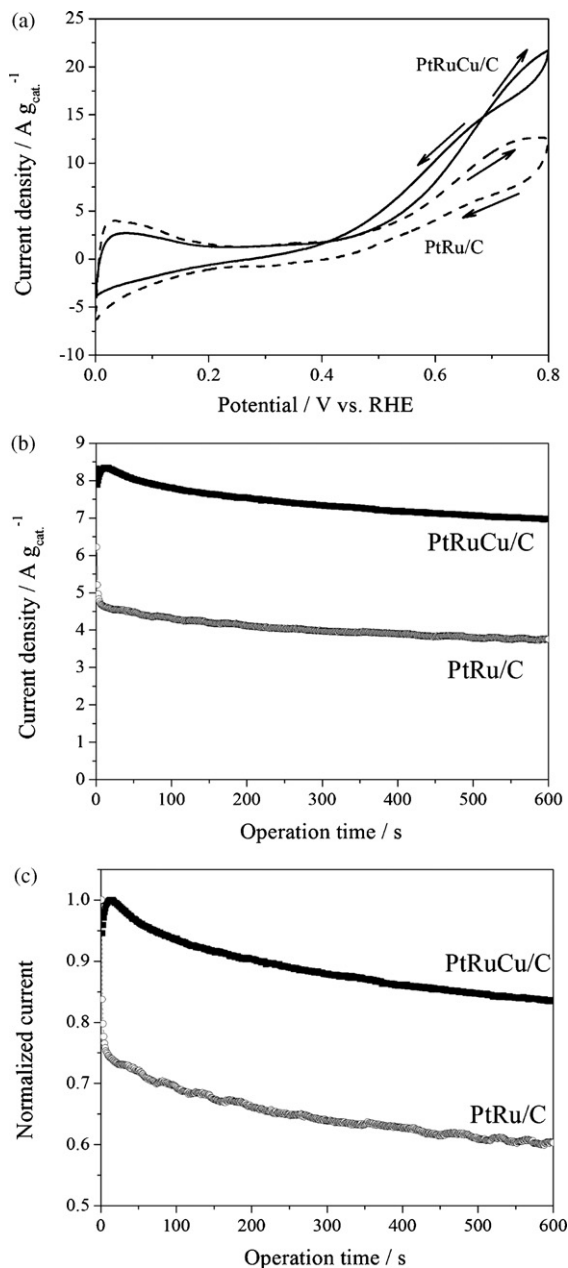
**Fig. 4.** (a) MOR activity measurement results during potential cycling between 0 and 0.8 V at a scan rate of 50 mV s$^{-1}$. (b) Chronoamperometry test results obtained by keeping the working electrode at 0.6 V for 600 s. Nitrogen purged 1 M H$_2$SO$_4$ + 1 M methanol solution was used as the electrolyte for both of the tests. (c) Normalized current–time curves of (b).

## 4. Conclusions

Ternary Pt–Ru–Cu compositions in thin film combinatorial library were explored by parallel synthesis and characterization. The composition Pt$_{66}$Ru$_{17}$Cu$_{17}$ exhibited the highest MOR activity among the 63 different compositions in the combinatorial library. In CV tests, the powder form of the Pt$_{66}$Ru$_{17}$Cu$_{17}$/C catalyst showed that dissolution and irreversible oxidation of Ru was inhibited by Cu incorporation. In MOR activity measurement experiments, the PtRuCu/C catalyst showed 26 and 86% higher activities than those of the PtRu/C catalyst during cyclic and chronoamperometric tests, respectively.

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