

# Enhanced Activity and Stability of Pt/C Fuel Cell Anodes by the Modification with Ruthenium-Oxide Nanosheets

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## Abstract

Ruthenium oxide nanosheet (RuO<sub>2</sub>ns) crystallites with thickness less than 1 nm were prepared via chemical exfoliation of a layered potassium ruthenate and deposited onto carbon supported platinum (Pt/C) as a potential co-catalyst for fuel cell anode catalysts. The electrocatalytic activity towards carbon monoxide and methanol oxidation was studied at various temperatures with for different RuO<sub>2</sub>ns loadings. An increase in electrocatalytic activity was evidenced at temperatures above 40°C, while little enhancement in activity was observed at room temperature. The RuO<sub>2</sub>ns modified Pt/C catalyst with composition of RuO<sub>2</sub>:Pt= 0.5:1 (molar ratio) exhibited the highest methanol oxidation activity. CO-stripping voltammetry revealed that RuO<sub>2</sub>ns promotes oxidation of adsorbed CO on Pt. In addition to the enhanced initial activity, the RuO<sub>2</sub>ns modified Pt/C catalyst exhibited improved stability compared to pristine Pt/C against consecutive potential cycling tests.

Keywords: Direct methanol fuel cell; CO oxidation; Platinum; Ruthenium oxide; Electrocatalyst; Nanosheet

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## 1. Introduction

Development of anode catalysts with higher tolerance to catalyst poison and better stability are major issues that must be resolved for wide-spread commercialization of direct methanol fuel cells for portable electronics and polymer electrolyte fuel cells operating on reformed fuel for residential applications. The carbon supported platinum-ruthenium system is considered as one of the most promising anode catalysts for such fuel cells [1]. Metallic Ru in the alloy catalyst is known to promote the oxidation of the carbon monoxide. Carbon monoxide strongly adsorbs on the active Pt sites, inhibiting successive reaction of the fuel. The promotional effect of Ru has been mainly discussed based on the so-called “bi-functional mechanism” [2] and/or “ligand effect” [3]. The bi-functional mechanism is based on the assumption that Ru supplies an oxygen source ( $\text{Ru-OH}_{\text{ad}}$ ) promoting the oxidation of CO on adjacent Pt sites. The ligand effect assumes that the energy level of the metal catalyst is modified so that the binding strength with the metal and adsorbed CO is weakened, resulting in a reduction in overpotential for CO oxidation. The possibility that some nanostructured ruthenium oxides (expressed as  $\text{RuO}_x\text{H}_y$  or  $\text{RuO}_2 \cdot x\text{H}_2\text{O}$  in the literature) may act as co-catalysts has attracted interest and debate [4-18]. Several studies have suggested that the binary PtRu alloy structure is not a prerequisite for obtaining the highest activity, and partially oxidized ruthenium species ( $\text{RuO}_x$ ) that are present in the PtRu/C catalysts may contribute to the anodic activity [4-6]. Enhancement in methanol oxidation activity has been reported for Pt- $\text{RuO}_2$  composite catalysts although the activity of such material is in general lower than that of PtRu alloy [7-14]. On the contrary, other studies have reported that ruthenium oxide is inactive for CO oxidation [15-18]. One reason for the apparent inconsistency in the reported literature may be due to the various forms of ruthenium oxide with different oxidation states and hydrous states having different electrochemical characteristics.

In terms of catalyst stability, Ru has been reported to be vulnerable to dissolution under long-term fuel cell operation, especially by voltage fluctuation due to repeated start up and shut down [19-22]. It is well known that crystalline  $\text{RuO}_2$  has high electrochemical stability within the hydrogen and oxygen evolution region [23-30]. However, it has also been reported that hydrous ruthenium oxide containing  $\text{Ru}^{3+}$  is not stable in acidic electrolyte [30].

We have studied the electrochemical behavior of crystalline  $\text{RuO}_2$  nanosheet ( $\text{RuO}_2\text{ns}$ ) electrodes derived by chemical exfoliation of layered  $\text{K}_{0.2}\text{RuO}_{2.1}$ . The negatively charged  $\text{RuO}_2$  nanosheets with sub-nanometer thickness are stabilized as a colloid by tetrabutylammonium counter ions [25]. Earlier, we communicated that the modification of Pt/C with  $\text{RuO}_2$  nanosheets decreases the potential for CO and  $\text{CH}_3\text{OH}$  electro-oxidation at  $60^\circ\text{C}$  [31]. In the case of alloy catalysts, it has been reported that the optimal alloy composition changes as a function of temperature; Ru-rich catalysts (Pt:Ru=1:1) are more active at  $60^\circ\text{C}$  while Pt-rich catalysts (Pt:Ru=3:1) are more active at  $25^\circ\text{C}$  [32-34]. Thus, it is essential that the activity at different temperatures with different co-catalyst loadings is studied. In this work, a systematic investigation of the CO and  $\text{CH}_3\text{OH}$  oxidation activity on  $\text{RuO}_2\text{ns}$  modified Pt/C ( $\text{RuO}_2\text{ns-Pt/C}$ ) was conducted with various  $\text{RuO}_2$  nanosheet content at temperatures ranging from 25 to  $60^\circ\text{C}$  in order to further understand the effect of the  $\text{RuO}_2$  nanosheet modification. In addition, the stability of  $\text{RuO}_2\text{ns-Pt/C}$  was compared with pristine Pt/C.

## 2. Experimental

An aqueous colloid containing exfoliated RuO<sub>2</sub> nanosheet crystallites was prepared following a procedure reported earlier [25]. First, layered K<sub>0.2</sub>RuO<sub>2.1</sub> was obtained by solid-state reaction. The interlayer K<sup>+</sup> was exchanged with H<sup>+</sup> by acid treatment to obtain layered H<sub>0.2</sub>RuO<sub>2.1</sub> (residual potassium K/Ru <0.05:1 [25]). Layered H<sub>0.2</sub>RuO<sub>2.1</sub> was then reacted with 50% aqueous ethylamine to obtain an ethylammonium-ruthenate intercalation compound, (C<sub>2</sub>H<sub>5</sub>NH<sub>3</sub>)<sub>0.2</sub>RuO<sub>2.1</sub>. The interlayer ethylammonium was subsequently ion-exchanged with tetrabutylammonium by reaction of the ethylammonium-ruthenate intercalation compound with 10% aqueous tetrabutylammonium hydroxide, yielding a tetrabutylammonium-ruthenate intercalation compound, ((C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N)<sub>0.2</sub>RuO<sub>2.1</sub>. The solid product was centrifugally collected (15,000 rpm). The tetrabutylammonium-ruthenate intercalation compound in a powder form was dispersed in distilled water and subjected to ultrasonication for 30 min and centrifuged at 2,000 rpm. The colloidal supernatant, which contains the exfoliated RuO<sub>2</sub> nanosheets (RuO<sub>2</sub>ns), was used for further investigation.

Carbon supported Pt (30 mass% Pt) was prepared by an impregnation method reported previously [35, 36]. Vulcan XC-72R was mixed with Pt(NO<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub> dissolved in ethanol, and then allowed to dry at 60°C to a powder state. The dried precursor was reduced in a tube furnace under flowing H<sub>2</sub>(10%)-N<sub>2</sub>(90%) gas for 2 hours at 200°C. Pt/C was suspended in distilled water and added into the RuO<sub>2</sub>ns colloid and thoroughly mixed. The amount of Pt/C added to the RuO<sub>2</sub>ns colloid was controlled so that the molar ratio of the additive was RuO<sub>2</sub>:Pt = 1:1, 0.5:1 and 0.2:1. Reaction of Pt/C with the RuO<sub>2</sub>ns could be realized by sedimentation. The final product, RuO<sub>2</sub>ns modified Pt/C, was obtained by drying the mixture at 80°C. The samples will be denoted as RuO<sub>2</sub>ns(1.0)-Pt/C, RuO<sub>2</sub>ns(0.5)-Pt/C, and RuO<sub>2</sub>ns(0.2)-Pt/C, according to the amount of RuO<sub>2</sub> in the composite. For comparative reasons, RuO<sub>2</sub>ns supported on carbon, RuO<sub>2</sub>ns/C (10 mass% RuO<sub>2</sub>), and PtRu/C (20 mass% Pt and 10 mass% Ru; Ru source Ru(NO<sub>3</sub>)<sub>3</sub> dissolved in ethanol) were also prepared. **The prepared PtRu/C catalyst shows activity comparable to values reported in literature [18, 32, 37].** The metal ratio in the samples was analyzed by energy-dispersive X-ray spectroscopy (EDX) (EMAX-7000; Noran Instruments Voyager). The structure of the catalysts was characterized by X-ray diffraction (XRD, Rigaku RINT-2550 with monochromated CuKα radiation at 40 kV and 50 mA).

The working electrode was prepared by depositing 20 μL of a 2 g L<sup>-1</sup> electrocatalyst ink dispersed in distilled water on a mirror-polished glassy carbon rod (40 μg-catalyst per 0.196 cm<sup>2</sup> exposed surface) with a micropipette. For electrochemical studies, the overall amount of catalyst was kept constant, giving metal loadings for the non-modified electrodes as 12 μg-metal for Pt/C and PtRu/C. For the RuO<sub>2</sub> nanosheet modified electrodes, the Pt loadings are 11.5, 10.9, and 10 μg-Pt cm<sup>-2</sup> for RuO<sub>2</sub>ns:Pt with 0.2, 0.5, and 1.0. 20 μL of a 1 wt% Nafion ionomer (resulting in a calculated Nafion thickness of ~4.5 μm) was dropped onto the electrode surface to immobilize the electrocatalysts. A beaker-type electrochemical cell equipped with the working electrode, a platinum mesh counter electrode and an Ag/AgCl/KCl(sat.) reference electrode, connected with a salt bridge, was used. A Luggin capillary faced the working electrode at a distance of 2 mm. Electrochemical measurements were conducted at 25, 30, 40, 50 and 60°C. All electrode

potentials throughout the paper will be referred to the reversible hydrogen electrode (RHE) scale corrected for the temperature effect (RHE(*t*)) according to the following equation:

$$E \text{ vs RHE}(t) = E \text{ vs Ag/AgCl} + (224 - T) \times \frac{\partial T}{\partial E} - \frac{RT}{nF} \times \text{pH} \times 2.303$$

where *R* is the gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>), *T* is the temperature, *n* is the number of electrons involved in the reaction (in this case, *n*=1), *F* is the Faraday constant (96,485 C mol<sup>-1</sup>) and  $\partial T/\partial E$  is 0.0010 K V<sup>-1</sup>.

Oxidation of pre-adsorbed carbon monoxide (CO<sub>ad</sub>) was measured by CO<sub>ad</sub> stripping voltammetry in 0.5 M H<sub>2</sub>SO<sub>4</sub> at a scan rate of 10 mV s<sup>-1</sup>. Gaseous CO(10%)-N<sub>2</sub>(90%) was purged into the 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte for 90 min to allow complete adsorption of CO onto the catalyst surface while maintaining a constant voltage of 50 mV vs. RHE(*t*). Excess CO in the electrolyte was then purged out by bubbling N<sub>2</sub> gas for 40 min. The electrochemical surface area (ECSA) of the catalysts was calculated from the CO-stripping voltammograms. The amount of CO<sub>ad</sub> was measured by integration of the CO<sub>ad</sub> stripping peak, corrected for the electrical double-layer capacitance, assuming a monolayer of linearly adsorbed CO on metal surface and the Coulombic charge necessary for oxidation as 420 μC cm<sup>-2</sup>. Electro-oxidation of CH<sub>3</sub>OH was characterized by chronoamperometry at 500 mV in 0.5 M H<sub>2</sub>SO<sub>4</sub> containing 1 M CH<sub>3</sub>OH at various temperatures. The ECSA obtained from CO-stripping voltammetry was used to calculate the specific activity, i.e., the quasi-steady state current for methanol electro-oxidation obtained by chronoamperometry after 30 min of polarization normalized by the ECSA. The mass activity was obtained by normalizing to the amount of Pt coated onto the glassy carbon surface. Catalyst stability was characterized by measuring the methanol oxidation activity after the catalysts were subjected to potential cycling. After the initial methanol oxidation activity was measured, the electrolyte was changed to a fresh 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte free of methanol. The potential was then cycled between 0.05 and 1.2 V at 50 mV s<sup>-1</sup> for 1,000 cycles at 60°C. Methanol was then added into the electrolyte and the methanol oxidation activity was again measured by chronoamperometry.

### 3. Results and Discussion

#### 3.1 Structural characterization

Figure 1(a) shows the XRD pattern of a film obtained by casting the RuO<sub>2</sub>ns colloid. A series of (00*l*) diffraction peaks typical of a well-ordered layered structure with an interlayer spacing of ~1.7 nm is observed. Thus, by casting the RuO<sub>2</sub>ns colloid, re-stacking and re-organization of the exfoliated RuO<sub>2</sub>ns occurs resulting in a tetrabutylammonium intercalation compound. The lack of such two-dimensional ordering for RuO<sub>2</sub>ns(0.5)-Pt/C (Fig. 1(b)) is evidence that RuO<sub>2</sub>ns is deposited onto the carbon surface with negligible re-stacking. Weak diffraction peaks at 2θ=10 and 35° are observed, which is attributed to partial ordering of the RuO<sub>2</sub>ns. The XRD peaks attributed to metallic Pt in RuO<sub>2</sub>ns(0.5)-Pt/C are identical in peak position and width with Pt/C. Thus, the Pt particle size is not affected by the RuO<sub>2</sub>ns modification and there is no atomic alloying of Ru into the Pt structure. This is anticipated since the RuO<sub>2</sub>ns-Pt/C composite is not exposed to any heat treatment other than the drying process. The observed Ru:Pt ratio of the prepared catalyst as determined by energy dispersive X-ray measurements was Ru:Pt=0.92:1,

0.52:1, 0.15:1 for RuO<sub>2</sub>ns(1.0)-Pt/C, RuO<sub>2</sub>ns(0.5)-Pt/C, and RuO<sub>2</sub>ns(0.2)-Pt/C, in agreement with the nominal content.

### 3.2 Electrochemical properties of RuO<sub>2</sub>ns/C

The electrochemical properties of RuO<sub>2</sub>ns/C (10 mass%) in the absence of Pt nanoparticles were first evaluated to understand the electrocatalytic activity of RuO<sub>2</sub>ns alone. The cyclic voltammograms of RuO<sub>2</sub>ns/C in 0.5 M H<sub>2</sub>SO<sub>4</sub> at various temperatures are shown Fig. 2. These voltammograms represent the background for the RuO<sub>2</sub>ns-Pt/C composite. Three characteristic redox pairs are observed at ~0.1, 0.65 and 0.8 V (hereafter denoted A1/C1, A2/C2, A3/C3). A2/C2 and A3/C3 are attributed to electrosorption of anionic and cationic species, respectively [27, 28]. A1/C1 is uncommon for polycrystalline RuO<sub>2</sub> systems but bears similarity to peaks observed in high quality RuO<sub>2</sub> (100) single crystal surfaces [38]. The A1/C1 pair is tentatively ascribed as adsorption/desorption of hydronium ions on the surface of the RuO<sub>2</sub>ns, similar to that observed on RuO<sub>2</sub> (100) [38]. The specific capacitance of RuO<sub>2</sub>ns/C, calculated by averaging the charge of the anodic and cathodic portion of the voltammograms, at 60°C was ~73 F (g-catalyst)<sup>-1</sup> which translates to ~732 F (g-RuO<sub>2</sub>)<sup>-1</sup> at 10 mV s<sup>-1</sup>, comparable to the value of unsupported RuO<sub>2</sub>ns.

Figure 3 shows the CO<sub>ad</sub> stripping voltammograms for RuO<sub>2</sub>ns/C at various temperatures. It is clear that RuO<sub>2</sub>ns behaves as a poor electrocatalyst for CO oxidation. The poor CO oxidation behavior of RuO<sub>2</sub>ns can be attributed to the lack of CO adsorption sites on the RuO<sub>2</sub>ns surface. Note that the A1/C1 peak is still evident after the CO adsorption procedure. If the A1/C1 peak was due to hydrogen desorption/adsorption similar to many metal surfaces, this peak is anticipated to disappear by the replacement of hydrogen with CO. As this is not the case, the A1/C1 peak is probably not due to hydrogen desorption/adsorption.

Voltammograms in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M CH<sub>3</sub>OH of RuO<sub>2</sub>ns/C at various temperatures are shown in Fig. 4. There is essentially no difference between the voltammograms with and without CH<sub>3</sub>OH in the electrolyte below ~1.0 V. Evidently, CH<sub>3</sub>OH adsorption does not occur on the surface of RuO<sub>2</sub> nanosheets in the region of practical meaning to anode catalysts for fuel cells. The above results show that RuO<sub>2</sub>ns single-handedly is a poor electrocatalyst for CO and CH<sub>3</sub>OH oxidation.

### 3.3 CO tolerance of RuO<sub>2</sub>ns-Pt/C with different RuO<sub>2</sub>ns loading

Cyclic voltammograms of RuO<sub>2</sub>ns-Pt/C with various RuO<sub>2</sub>ns content in 0.5 M H<sub>2</sub>SO<sub>4</sub> (60°C) are shown Fig. 5. The CVs of RuO<sub>2</sub>ns-Pt/C are characterized by features of both RuO<sub>2</sub>ns/C and Pt/C. The A1/C1, A2/C2 and A3/C3 redox peaks distinctive of RuO<sub>2</sub>ns can be clearly observed for all catalysts with different RuO<sub>2</sub>ns loading. The charge related with these redox peaks increases with increasing RuO<sub>2</sub>ns content. The gravimetric capacitance also increases linearly with the RuO<sub>2</sub>ns content (Table I). The CO<sub>ad</sub> stripping voltammograms of RuO<sub>2</sub>ns-Pt/C with different RuO<sub>2</sub>ns loading at 60°C are shown Fig. 6. The onset and peak potential of CO<sub>ad</sub> oxidation for RuO<sub>2</sub>ns-Pt/C shows a negative shift compared to pure Pt/C. Although the CO tolerance of RuO<sub>2</sub>ns-Pt/C is not as good compared to PtRu/C, a gain of ~180 mV in the onset for CO<sub>ad</sub> oxidation is observed by the modification of Pt/C with RuO<sub>2</sub>ns. Since RuO<sub>2</sub>ns itself is a poor CO oxidation catalyst, the

enhanced  $\text{CO}_{\text{ad}}$  oxidation activity of  $\text{RuO}_2\text{ns-Pt/C}$  must be due to the ability of the  $\text{RuO}_2\text{ns}$  surface to supply an oxygen source ( $-\text{OH}$ ) for the oxidation of  $\text{CO}_{\text{ad}}$  on the Pt surface. For  $\text{RuO}_2\text{ns}(0.2)\text{-Pt/C}$ , the promotional effect is seen only as a small shoulder peak on the negative potential side, and the potential for the main peak is more or less the same as Pt/C. For  $\text{RuO}_2\text{ns}(0.5)\text{-Pt/C}$  and  $\text{RuO}_2\text{ns}(1.0)\text{-Pt/C}$ , the shift in the onset potential of  $\text{CO}_{\text{ad}}$  oxidation is more clear. It should be emphasized that the main  $\text{CO}_{\text{ad}}$  oxidation peak is also shifted with regards to pure Pt ( $E=0.7$  V) for the catalysts with higher  $\text{RuO}_2\text{ns}$  content, i.e.  $\text{RuO}_2\text{ns}(0.5)\text{-Pt/C}$  and  $\text{RuO}_2\text{ns}(1.0)\text{-Pt/C}$ . The peak broadening and the shift in onset and peak potential observed for the higher loadings can be explained by the OH nucleation and diffusion on the  $\text{RuO}_2\text{ns}$  surface to nearby Pt sites. The reactions sites for  $\text{CO}_{\text{ad}}$  oxidation should be confined to sites where the  $\text{RuO}_2\text{ns}$  surface is in contact with the Pt surface. The broad and multiplex  $\text{CO}_{\text{ad}}$  oxidation peak can be interpreted as a result of the heterogeneous interface between  $\text{RuO}_2$  nanosheets and Pt. Surface diffusion of OH groups on the  $\text{RuO}_2$  nanosheet surface should be the main cause for the sluggish kinetics. The limited co-catalytic effect of  $\text{RuO}_2\text{ns}$  at low loading can be rationalized as insufficient contact between Pt nanoparticles and  $\text{RuO}_2\text{ns}$ . The sluggish CO oxidation kinetics of the  $\text{RuO}_2\text{ns-Pt/C}$  is similar to the behavior observed for Pt/ $\text{RuO}_2$  catalysts. Surface diffusion of  $\text{CO}_{\text{ad}}$  has been shown to play a significant role in the CO oxidation reaction for Pt-Ru as well as Pt/ $\text{RuO}_2$  catalysts [39]. As the Pt particle size for the  $\text{RuO}_2\text{ns-Pt/C}$  catalysts are all the same in this study, the CO oxidation kinetics most likely is governed by the OH nucleation and diffusion rate on the  $\text{RuO}_2\text{ns}$  surface.

Quantitative evaluation of the Pt surface area from the hydrogen adsorption/desorption peaks was not possible due to the overlapping of the A1/C1 redox peaks from  $\text{RuO}_2\text{ns}$ . The effective Pt surface area was thus estimated from the  $\text{CO}_{\text{ad}}$  oxidation charge. The electrochemically active Pt surface area ( $S_{\text{ECA}}$ ) obtained from CO stripping is summarized in Table I. Note that the  $S_{\text{ECA}}$  is a measure of only the electrochemically active Pt surface sites as CO does not adsorb on  $\text{RuO}_2\text{ns}$ . The modification with  $\text{RuO}_2\text{ns}$  induces an increase in  $S_{\text{ECA}}$ .  $\text{RuO}_2\text{ns}$  has a hydrophilic surface which may result in an increase in the interphase between the electrolyte and Pt nanoparticles.

Figure 7 shows the effect of temperature on the  $\text{CO}_{\text{ad}}$  stripping voltammograms for  $\text{RuO}_2\text{ns}(0.5)\text{-Pt/C}$ , Pt/C and PtRu/C. The shape of the  $\text{CO}_{\text{ad}}$  oxidation peak for  $\text{RuO}_2\text{ns}(0.5)\text{-Pt/C}$  is strongly affected by the temperature. At  $25^\circ\text{C}$ , the  $\text{CO}_{\text{ad}}$  stripping voltammogram of  $\text{RuO}_2\text{ns}(0.5)\text{-Pt/C}$  is similar to that of Pt/C, indicating that  $\text{RuO}_2\text{ns}$  does not promote  $\text{CO}_{\text{ad}}$  oxidation. The co-catalytic effect of  $\text{RuO}_2\text{ns}$  becomes obvious as the reaction temperature is increased, as evidenced by the gradual broadening and splitting of the  $\text{CO}_{\text{ad}}$  oxidation peak with increasing temperature. Although  $\text{RuO}_2\text{ns}$  acts as a promoting additive, it is not as effective as Ru in the PtRu alloy. Obviously, the Pt nanoparticles and  $\text{RuO}_2\text{ns}$  have limited contact compared to an intimately mixed PtRu alloy and an electronic effect is rather unlikely. However, the CO tolerance of  $\text{RuO}_2\text{ns}(1.0)\text{-Pt/C}$  is comparable to PtRu/C at elevated temperatures, where PtRu/C stability may become a major issue. The instability of Ru under the fuel cell operation conditions has been reported [20-22]. The amount of Ru loss due to dissolution should increase with increasing cell temperature.

### 3.4 $\text{CH}_3\text{OH}$ oxidation activity of $\text{RuO}_2\text{ns-Pt/C}$

Chronoamperograms of RuO<sub>2</sub>ns-Pt/C, Pt/C and PtRu/C catalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M CH<sub>3</sub>OH (60°C) are shown in Fig. 8. The mass and specific activities of methanol oxidation calculated from the quasi-steady state current after 30 min. are summarized in Table II. The specific activity (the current density normalized by the  $S_{ECA}$  of Pt obtained from CO-stripping voltammetry) for RuO<sub>2</sub>(0.5)-Pt/C was almost as high as PtRu/C, and roughly 8 times higher than that of Pt/C. The mass activity for CH<sub>3</sub>OH oxidation for RuO<sub>2</sub>(0.5)-Pt/C and RuO<sub>2</sub>(1.0)-Pt/C showed an enhancement of approximately 10 times compared to Pt/C. It is obvious that RuO<sub>2</sub>ns acts as a co-catalyst for CH<sub>3</sub>OH oxidation due to the enhanced CO<sub>ad</sub> oxidation activity.

The temperature dependence of the CH<sub>3</sub>OH oxidation activity was studied for the RuO<sub>2</sub>ns(0.5)-Pt/C catalyst. The voltammograms measured at various temperatures for RuO<sub>2</sub>ns(0.5)-Pt/C are compared with Pt/C and PtRu/C in Fig. 9. The temperature dependence of CH<sub>3</sub>OH oxidation follows a similar tendency to the CO<sub>ad</sub> oxidation behavior, which is not surprising since CO poisoning occurs only on Pt sites as mentioned earlier. At elevated temperatures, the CH<sub>3</sub>OH oxidation activity of RuO<sub>2</sub>ns(0.5)-Pt/C catalyst is higher compared to Pt/C, but is slightly lower than that of PtRu/C. At ambient temperature, CH<sub>3</sub>OH oxidation on RuO<sub>2</sub>ns(0.5)-Pt/C is similar to that of Pt/C, since diffusion of OH<sub>ad</sub> on RuO<sub>2</sub>ns is not sufficient for the RuO<sub>2</sub>ns to participate in the oxidation of the intermediate products. The temperature dependence of the mass activity obtained from chronoamperometry in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M CH<sub>3</sub>OH for RuO<sub>2</sub>ns(0.5)-Pt/C, Pt/C and PtRu/C are shown in Fig. 10. The slope in the  $\log j - T^{-1}$  curve for RuO<sub>2</sub>ns-Pt/C was larger compared to Pt/C and PtRu/C, showing the strong temperature dependence of the co-catalytic effect of RuO<sub>2</sub>ns. The apparent activation energy  $E_a$  estimated from the slope in the  $\log j - T^{-1}$  curve for RuO<sub>2</sub>ns(0.5)-Pt/C was  $\sim 102$  kJ mol<sup>-1</sup>, while for Pt/C and PtRu/C  $E_a$  was  $\sim 53$  and  $\sim 33$  kJ mol<sup>-1</sup>, respectively.

### 3.6 Stability of RuO<sub>2</sub>ns(0.5)-Pt/C and Pt/C

It has been reported that metallic Ru in the PtRu alloy catalyst dissolves as Ru<sup>n+</sup> and deposits at the cathode under fuel cell operating conditions, leading to catalyst degradation [20-22]. Thus, the stability of RuO<sub>2</sub>ns(0.5)-Pt/C was considered by an accelerated stability test (potential cycling between 0.05-1.2 V vs. RHE in 0.5 M H<sub>2</sub>SO<sub>4</sub>(60°C) at 50 mV s<sup>-1</sup> for 1,000 cycles). Figure 11 compares cyclic voltammograms in 0.5 M H<sub>2</sub>SO<sub>4</sub>(60°C) for RuO<sub>2</sub>ns(0.5)-Pt/C, Pt/C, and PtRu/C before and after the stability test. The results show that RuO<sub>2</sub>ns is stable under conditions that PtRu would be drastically de-activated due to irreversible oxidation of Ru. The  $S_{ECA}$  obtained from the hydrogen adsorption current for Pt/C decreased drastically from  $S_{ECA}=57$  to 14 m<sup>2</sup> (g-Pt)<sup>-1</sup> after the stability test. In the case of RuO<sub>2</sub>ns(0.5)-Pt/C, the  $S_{ECA}$  decreased only 55% in comparison with initial state, showing that the presence of RuO<sub>2</sub>ns increases the stability of Pt nanoparticles. After the accelerated potential cycling test, the methanol oxidation activity of Pt/C retained only  $\sim 14\%$  of its initial activity, decreasing from 7 to 1 A (g-Pt)<sup>-1</sup>. Under the same stability test conditions, the methanol oxidation activity of RuO<sub>2</sub>ns(0.5)-Pt/C was 20 A (g-Pt)<sup>-1</sup>. Thus  $\sim 70\%$  of the initial mass activity was maintained. The accelerated test conducted in this study is considerably intense bearing in mind that the anode potential of a fuel cell will not exceed 0.5 V in general. However, the results show that both activity and stability of Pt/C were dramatically increased by modification with RuO<sub>2</sub>ns under the present experimental conditions. The role of RuO<sub>2</sub>ns towards the enhanced stability must be studied in more detail in order to reach

a sound conclusion. A tentative explanation is given on the basis of the strong acidic nature of RuO<sub>2</sub>ns. RuO<sub>2</sub>ns is intrinsically negatively charged ([RuO<sub>2.1</sub>]<sup>0.2-</sup>) and behaves as a solid acid, as indicated by the intercalation behavior of layered H<sub>0.2</sub>RuO<sub>2.1</sub>. Thus RuO<sub>2</sub>ns should attract dissolved cationic Pt<sup>n+</sup>, thereby acting as a protective layer inhibiting the diffusion of Pt<sup>n+</sup> into the electrolyte.

#### 4. Conclusions

We have shown that high methanol oxidation activity is achieved by modifying conventional Pt/C with crystalline RuO<sub>2</sub> nanosheets (RuO<sub>2</sub>ns). The highest activity was obtained for RuO<sub>2</sub>ns-Pt/C with RuO<sub>2</sub>:Pt=0.5:1 (molar ratio) with a 10 fold increase in activity for methanol oxidation at 500 mV vs. RHE(60°C). The increased activity is attributed to the co-catalytic effect of RuO<sub>2</sub>ns towards CO<sub>ad</sub> oxidation. The promotional effect is evident at temperatures above 40°C, exhibiting a merit of ~180 mV for CO<sub>ad</sub> oxidation. At room temperature, RuO<sub>2</sub>ns does not promote CO<sub>ad</sub> oxidation, most likely due to the poor kinetics of OH surface diffusion on RuO<sub>2</sub>ns. Accelerated potential cycling tests indicated that the stability of RuO<sub>2</sub>ns-Pt/C is drastically enhanced compared to Pt/C, which has been tentatively attributed to the solid acid characteristic of RuO<sub>2</sub>ns, restraining the diffusion of Pt<sup>n+</sup> into the electrolyte. RuO<sub>2</sub>ns is an efficient co-catalyst exhibiting enhanced CO tolerance and improved catalyst stability.

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## Figure captions

Figure 1. The XRD patterns of (a) cast RuO<sub>2</sub>ns film, (b) RuO<sub>2</sub>ns(0.5)-Pt/C (c) and Pt/C.

Figure 2. Cyclic voltammograms of RuO<sub>2</sub>ns/C at various temperatures in 0.5 M H<sub>2</sub>SO<sub>4</sub> at  $\nu=10$  mV s<sup>-1</sup>.

Figure 3. CO<sub>ad</sub> stripping voltammograms for RuO<sub>2</sub>ns/C at various temperatures in 0.5 M H<sub>2</sub>SO<sub>4</sub> at  $\nu=10$  mV s<sup>-1</sup>. Solid line: 1<sup>st</sup> cycle after CO adsorption, broken line: 2<sup>nd</sup> cycle. Current normalized with respect to the geometric surface.

Figure 4. Voltammograms of RuO<sub>2</sub>ns/C at (a) 25, (b) 30, (c) 40, (d) 50 and (e) 60°C at  $\nu=10$  mV s<sup>-1</sup>. Solid line: 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M CH<sub>3</sub>OH, broken line: 0.5 M H<sub>2</sub>SO<sub>4</sub>. Current normalized with respect to the geometric surface.

Figure 5. Cyclic voltammograms of (a) RuO<sub>2</sub>ns(1.0)-Pt/C, (b) RuO<sub>2</sub>ns(0.5)-Pt/C, (c) RuO<sub>2</sub>ns(0.2)-Pt/C, (d) and Pt/C in 0.5 M H<sub>2</sub>SO<sub>4</sub> (60°C) at  $\nu=10$  mV s<sup>-1</sup>. Current normalized with respect to the Pt mass.

Figure 6. CO<sub>ad</sub> stripping voltammograms of (a) RuO<sub>2</sub>ns(1.0)-Pt/C, (b) RuO<sub>2</sub>ns(0.5)-Pt/C, (c) RuO<sub>2</sub>ns(0.2)-Pt/C, (d) Pt/C and (e) PtRu/C in 0.5 M H<sub>2</sub>SO<sub>4</sub> (60°C) at  $\nu=10$  mV s<sup>-1</sup>. Solid line: 1<sup>st</sup> cycle after CO adsorption, broken line: 2<sup>nd</sup> cycle. Current normalized with respect to the Pt mass.

Figure 7. CO<sub>ad</sub> stripping voltammograms (difference spectra) for RuO<sub>2</sub>ns(0.5)-Pt/C (solid line), Pt/C (broken line) and PtRu/C (dotted line) at various temperatures in 0.5 M H<sub>2</sub>SO<sub>4</sub> at  $\nu=10$  mV s<sup>-1</sup>. Current normalized with respect to the Pt mass.

Figure 8. Chronoamperometry curves for (a) RuO<sub>2</sub>ns(1.0)-Pt/C, (b) RuO<sub>2</sub>ns(0.5)-Pt/C, (c) RuO<sub>2</sub>ns(0.2)-Pt/C, (d) Pt/C, and (e) and PtRu/C in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M CH<sub>3</sub>OH (60°C) at  $E=0.5$  V vs. RHE. Current normalized with respect to the Pt mass.

Figure 9. Voltammograms of RuO<sub>2</sub>ns(0.5)-Pt/C (solid line), Pt/C (dotted line) and PtRu/C (broken line) at (a) 25, (b) 30, (c) 40, (d) 50 and (e) 60°C in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M CH<sub>3</sub>OH at  $\nu=10$  mV s<sup>-1</sup>. Current normalized with respect to the Pt mass.

Figure 10. The mass activities of RuO<sub>2</sub>ns(0.5)-Pt/C (circles), Pt/C (triangles) and PtRu/C (squares) at 30 min after the potential step to 0.5 V vs. RHE in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M CH<sub>3</sub>OH at various temperatures. Current normalized with respect to the Pt mass.

Figure 11. Cyclic voltammograms of (a, a') RuO<sub>2</sub>ns(0.5)-Pt/C, (b, b') Pt/C and (c, c') PtRu/C before and after the stability test: (a) initial state of RuO<sub>2</sub>ns(0.5)-Pt/C, (a') after stability test of RuO<sub>2</sub>ns(0.5)-Pt/C, (b) initial state of Pt/C, (b') after stability test of Pt/C, (c) initial state of PtRu/C, (c') after stability test of PtRu/C. Consecutive cycling test conditions: potential cycling between 0.05 to 1.2 V vs. RHE for 1,000 cycles at 50 mV s<sup>-1</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub> (60°C). Current normalized with respect to the Pt mass.

Table I. Specific capacitance and electrochemically active Pt surface area ( $S_{ECA}$ ) of RuO<sub>2</sub>ns-Pt/C measured at 60°C.

sample	Specific capacitance / F (g-composite) <sup>-1</sup>	$S_{ECA}$ / m <sup>2</sup> (g-Pt) <sup>-1</sup>
RuO <sub>2</sub> ns(1.0)-Pt/C	199	83
RuO <sub>2</sub> ns(0.5)-Pt/C	166	64
RuO <sub>2</sub> ns(0.2)-Pt/C	147	71
Pt/C	97	52

Table II. Methanol oxidation activity of RuO<sub>2</sub>ns-Pt/C, Pt/C and PtRu/C.

sample	Mass activity / A (g-Pt) <sup>-1</sup>	Specific activity / A m <sup>-2</sup>
RuO <sub>2</sub> ns(1.0)-Pt/C	42	0.50
RuO <sub>2</sub> ns(0.5)-Pt/C	47	0.73
RuO <sub>2</sub> ns(0.2)-Pt/C	5	0.11
Pt/C	4	0.08
PtRu/C	83	0.78

polarization potential :500 mV vs. RHE, electrolyte : 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M CH<sub>3</sub>OH (60°C)