



# Preparation and characterization of carbon-supported PtOs electrocatalysts via polyol reduction method for methanol oxidation reaction



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## HIGHLIGHTS

- A polyol reduction approach was employed to prepare highly active PtOs/C for methanol oxidation.
- The catalysts' physical characteristics correlated with their electrochemical performances.
- Activity improvement was attributed to a mix of nanoparticles, high metallic Os and small sizes.
- The mass and specific activity of PtOs-2/C is 528 mA mg<sup>-1</sup><sub>PtOs</sub> and 0.98 mA cm<sup>-2</sup>, respectively.

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## ABSTRACT

A polyol reduction approach was employed to prepare carbon-supported PtOs/C electrocatalysts (PtOs-1/C was obtained via the co-reduction of H<sub>2</sub>PtCl<sub>6</sub> and K<sub>2</sub>OsCl<sub>6</sub> precursors and PtOs-2/C was obtained via a sequential deposition method in which Pt was deposited on the preformed Os nanoparticles). The home-made electrocatalysts were extensively characterized via transmission electron microscopy, thermogravimetric analysis, X-ray diffraction, and X-ray photoelectron spectroscopy. The evaluation results of the catalytic activities obtained via cyclic voltammetry, CO stripping voltammetry, and chronoamperometry showed that the successively reduced PtOs-2/C out-performed PtOs-1/C in terms of specific/mass activity (528 mA mg<sup>-1</sup><sub>PtOs</sub> and 0.98 mA cm<sup>-2</sup>) and CO tolerance in room temperature methanol electrooxidation reaction. The physical characteristics of the electrocatalysts correlated well with their electrochemical performances. The higher activity of PtOs-2/C was attributed to a combination of factors, such as a mix of nanoparticles (isolated Os, PtOs alloys or bimetallic nanoparticles), higher metallic Os content, and smaller particle sizes.

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## 1. Introduction

Among various types of low-temperature fuel cells, direct methanol fuel cell (DMFC) is the most promising as a power source for portable products that require low power density but high energy density (e.g., 4G phones, iPad, and notebook PCs) [1–3]. Their ability to operate at relatively low temperatures and quick start-up characteristics (considering methanol is used directly without the

need for fuel reforming) is comparable with those of H<sub>2</sub>/O<sub>2</sub> polymer electrolyte membrane fuel cells based on hydrogen oxidation [4–7]. To date, the failure in developing highly efficient electrocatalysts for methanol oxidation has slowed down the development of DMFCs. This obstacle is caused by the slow oxidation kinetics of methanol oxidation at the Pt anode, which involves a complex network of reactions with many possible side products (6-electrons are transferred whereas only 2-electrons are transferred in hydrogen oxidation) especially at low operating temperatures [8]. More active catalysts or a larger quantity of catalyst are required in the case of DMFCs [9,10]. The situation is made worse by the rapid deactivation of the active catalyst surface by CO-like reaction

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intermediates that are formed during the stepwise dehydrogenation of methanol [11]. Pt is therefore often alloyed with an oxophilic metal to increase its CO tolerance. Among bimetallic Pt catalysts, the Pt–Ru system is best known for its activity in the electrochemical methanol oxidation reaction (MOR) [12–15]. However, the efficiency of DMFCs operating on Pt–Ru is still insufficient for most practical purposes. Furthermore, the supply of Ru and the toxicological effect of Ru remain an issue [16]. Therefore, alternative Ru-free DMFC anode catalysts are still being explored [17].

Earlier transition metals are the most oxophilic elements based on their gas-phase dissociation energies. Moreover, Os is more oxophilic than Ru and is known to adsorb water in acidic solutions at potentials that are slightly more negative than Ru [18]. Os and Os-based catalysts (other than Pt) are catalytically inactive for methanol oxidation, as reported by Atwan [19]. Several studies were done on PtOs electrocatalysts for methanol oxidation, CO oxidation, and formic acid oxidation [20–24]. Liu and Huang prepared Pt–Os (3:1)/C catalysts (2.2 nm) via the thermal decomposition of metallic carbonyl cluster, and this catalyst showed a superior electrocatalytic activity to formic acid oxidation compared with Pt/C catalyst because of the fine dispersion of Pt–Os and the bifunctional effect [20]. Carbon-supported Pt–Os electrocatalysts prepared via different methods were compared with Pt/C, and PtOs (9:1)/C heat-treated under H<sub>2</sub> at 500 °C showed the best performance for CO oxidation because of the reduction of inactive Pt and Os surface oxide phases [21]. In a study on PtM<sub>y</sub>O<sub>x</sub> (M = Sn, Mo, Os, or W) electrodes, the Os-added electrode showed dissatisfactory methanol oxidation performance because volatile OsO<sub>4</sub> was formed during the calcination process [22]. Electrochemically co-deposited Pt–Os electrodes have shown enhanced catalytic activity over Pt at potentials beyond 0.2 V versus Ag/AgCl (3 M NaCl) because of more oxophilic behaviors of Os [24]. However, the formation of OsO<sub>2</sub> in high potentials could lead to the loss of active OH species. A carbon-supported Pt–Os bimetallic catalyst (2.2 nm) with a Pt/Os atomic ratio of 3:1 prepared via the carbonyl complexes route has been reported to exhibit enhanced activity for MOR than commercially available Pt/C and Pt–Ru (1:1)/C, and the enhancement has been ascribed to the combination of bifunctional mechanism and the electronic effect [23]. Moore et al. prepared Os/C and Pt–Os/C by thermally treating three types of Os complexes at solely reductive conditions [25]. Although Os/C and Pt–Os/C (5 nm–6 nm) gave open circuit potentials indicative of thermodynamically favorable methanol oxidation, the kinetics of these oxidations are too low to be of practical importance. Therefore, although Os is oxophilic in nature, the reported results on PtOs electrocatalysts for methanol oxidation were by no means consistent. The preparation method has a strong influence on the resulting catalyst performance. The polyol approach, which is often used in fuel cell preparation, has been used to successfully synthesize sub 5 nm nanoparticles with a narrow size distribution [26]. However, to the best of our knowledge, the polyol method has not been applied for the preparation of PtOs electrocatalysts. Studies that focus on the in-depth analysis between comparable preparation methods and the resulting catalyst performances are limited. Thus, in this work, PtOs colloids were synthesized via different deposition sequences (co-deposition versus sequential deposition) and were then harvested using carbon as supported electrocatalysts for methanol oxidation reaction. The Pt/Os atomic ratio was preset at 3:1 because this ratio has been regarded as the optimal one based on published results in literature [20,23]. The catalysts prepared via the polyol method were ~2 nm–2.5 nm in size and behaved quite differently toward MOR. The catalysts prepared in this work need no further post-heat-treatment and the preparative method itself is relatively straightforward (without usage of organic complexes). However,

the addition of Os as PtOs bifunctional catalysts has inherent disadvantages since OsO<sub>4</sub> is a toxic gaseous species.

## 2. Experimental

### 2.1. Chemicals and materials

Potassium hexachloroosmate (K<sub>2</sub>OsCl<sub>6</sub>), chloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>) from Aldrich, ethylene glycol, sodium hydroxide, sulfuric acid (95%–97%), ethanol, and methanol from Merck were used as received without further purification. K<sub>2</sub>OsCl<sub>6</sub> and H<sub>2</sub>PtCl<sub>6</sub> were prepared with 0.05 M aqueous solutions for further use. The carbon support was Vulcan XC-72 (measured BET surface area of 228 m<sup>2</sup> g<sup>-1</sup> and average particle size of 40 nm–50 nm) from Cabot. Filtered deionized water was used throughout the study.

### 2.2. Preparation of PtOs-1/C catalyst

PtOs-1 was prepared by co-depositing the corresponding precursors via a polyol method: 1 mL of 0.05 M K<sub>2</sub>OsCl<sub>6</sub> and 3 mL of 0.05 M H<sub>2</sub>PtCl<sub>6</sub> were added to a 100 mL round-bottom flask containing 50 mL of ethylene glycol, and the pH of the mixture was adjusted to around 9 by using 0.5 M NaOH solution. The mixture was heated at 120 °C in an oil bath under reflux with stirring for 8 h. A calculated amount of XC-72 carbon (254 mg) was added to the reaction mixture after cooling, and stirring was continued overnight. The Pt loading was predetermined to be 10 wt.% assuming a complete reduction of the Pt precursor. The total metal loading (PtOs), assuming a complete reduction of the Pt and Os precursors, is 13.4 wt.%. The suspension was then filtered to recover the solid, which was copiously washed with ethanol before drying in vacuum at 80 °C overnight.

### 2.3. Preparation of PtOs-2/C catalyst

PtOs-2 was prepared via a sequential deposition process, in which Os colloids were first synthesized via a hydrothermal method followed by the subsequent polyol deposition of Pt nanoparticles: 1 mL of 0.05 M K<sub>2</sub>OsCl<sub>6</sub> was mixed with 25 mL of ethylene glycol, and the pH of the mixture was adjusted to around 9 by using 0.5 M NaOH solution. The mixture was then transferred to a Teflon-lined stainless steel autoclave (custom-made cylinder with 4 cm cross-sectional diameter and 50 mL internal volume) and placed inside an electric oven at 120 °C for 4 h. After the synthesis, the colloidal sols were transferred to a 100 mL round-bottom flask. To this flask containing colloidal Os sols, 3 mL of 0.05 M H<sub>2</sub>PtCl<sub>6</sub> and 25 mL of ethylene glycol were added, and the pH of the mixture was again adjusted to around 9 by using 0.5 M NaOH solution. The rest of the preparation procedures followed the same as those in the preparation of PtOs-1/C.

### 2.4. Materials characterizations

The X-ray powder diffraction (XRD) patterns of the catalysts were recorded using a Rigaku D/Max-3B diffractometer (Shimadzu) with CuK<sub>α</sub> radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The  $2\theta$  angles were scanned from 20° to 85° at 2° min<sup>-1</sup>. The diffraction data was curve-fitted using a least square program provided by the equipment manufacturer. Thermogravimetric analysis (TGA) was conducted using a Thermal Analysis Instruments 2050 Analyzer in 100 mL min<sup>-1</sup> continuous airflow to determine the metal loadings in the catalysts. Given that OsO<sub>4</sub> is a volatile and toxic gas [22,25], the analysis was carried out at good ventilation conditions. The elemental compositions of the catalysts were measured using an energy dispersive X-ray (EDX) analyzer, which is attached to a JEOL MP5600LV

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