



Sol–gel synthesis of Pt–Ru–Os–Ir based anode electro-catalysts for direct methanol fuel cells

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ABSTRACT

A high specific surface area ($\sim 95 \text{ m}^2/\text{g}$) $\text{Pt}_{44}\text{Ru}_{41}\text{Os}_{10}\text{Ir}_5$ based anode electro-catalysts for direct methanol fuel cell, synthesized by a novel complexed sol–gel (CSG) process, shows better catalytic activity in comparison to pure equi-atomic compositions of Pt–50 at.% Ru anode catalysts synthesized by similar sol–gel processes. A homogeneous amorphous gel was successfully synthesized by complexing platinum(II) acetylacetonate, ruthenium(III) acetylacetonate, iridium(III) acetylacetonate and osmium(III) chloride with tetramethylammonium hydroxide (TMAH) used as a complexing agent. Phase-pure Pt(Ru,Os,Ir) and Pt(Ru) solid solutions possessing high specific surface area (SSA) ($\sim 90\text{--}120 \text{ m}^2/\text{g}$) were successfully synthesized by thermal decomposition of the amorphous gel followed by controlled removal of carbonaceous species present in the thermally treated powders. The controlled removal of carbon, present in the thermally treated Pt–Ru–Os–Ir powder, has been successfully achieved by conducting precise thermal treatments of the thermally treated powders using controlled oxidizing atmospheres. Results indicate that the nano-crystalline pure Pt(Ru,Os,Ir) solid solution of nominal composition Pt–41 at.% Ru–10 at.% Os–5 at.% Ir possessing good chemical homogeneity exhibit excellent catalytic activity, demonstrating the potential of the novel complexed sol–gel process for synthesizing high-performance Pt–Ru–Os–Ir based catalysts for direct methanol fuel cells.

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1. Introduction

Direct methanol fuel cells (DMFC) are of interest as suitable power sources for several portable electronic devices such as cellular phones, PDA, camcorder and notebook PC [1–4] as well as remote and auxiliary power units for transportation [5,6]. The main advantage of DMFC is the use of liquid methanol rather than gaseous hydrogen as the operating fuel and its operation at low working temperatures. The theoretical energy density afforded by methanol which is in essence, the amount of energy contained in a given volume of methanol is an order of magnitude greater than even highly compressed hydrogen [6] and five to ten times greater than rechargeable lithium ion batteries [1,2]. However, the currently achieved power densities of DMFC are still significantly below that of hydrogen fueled PEM and other fuel cell types which severely limits its use for commercial application. This mainly arises due to the relatively sluggish kinetics of the electrochemical

reactions occurring on the catalyst layers at the electrode surface combined with the methanol crossover to the cathode compartment [1,3,6–9]. There is therefore a critical need to conduct research and develop new and improved electro-catalysts with higher catalytic activity at both the anode and cathode regions in order to enhance the efficiency and power density of DMFC, while lowering the precious metal loadings necessary to realize the much-desired cost savings to match the performance. Currently, Pt–Ru alloy of nominal composition Pt–50 at.% Ru is considered the most suitable electro-oxidation catalyst composition for oxidation of methanol yielding the best catalytic activity and is hence widely recognized as the effective anode catalyst for use in DMFCs to date [3,6,7,10–14].

Improved anode catalysts can be obtained by synthesizing high surface area Pt–Ru based alloy catalysts combined with engineered proper alloy design by modifying the chemical composition of the alloy, and doping or alloying with other elements onto the catalyst structure [3,7,10–18]. Several researchers have reported significantly improved performance in ternary and quaternary alloys of Pt–Ru–Os, Pt–Ru–Ir, Pt–Ru–Sn, Pt–Ru–Ni, Pt–Ru–P, Pr–Ru–Ni–Zr, Pt–Ru–Os–Ir etc. when compared to pure Pt–Ru alloys [14–20]. Out of the different multi-component systems, it has been reported that Pt–Ru–Os and Pt–Ru–Os–Ir exhibit superior catalytic activity

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in comparison to other systems [14–16,22,23]. Reddington et al. [15,22] and Chu and Jiang [14] have reported that Pt–Ru–Os and Pt–Ru–Os–Ir based catalysts of specific surface area $\sim 31 \text{ m}^2/\text{g}$ show better catalytic activity in comparison to Pt–Ru alloy despite the higher specific surface area of the latter ($\sim 65 \text{ m}^2/\text{g}$). In recent years, we have also reported the improved catalytic activity of phase-pure Pt–Ru–Os alloy with respect to Pt–50 at.% Ru alloy of comparable specific surface area [16]. Using combinatorial electrochemistry of five elements (Pt, Ru, Os, Ir and Rh), Reddington et al. [15] has reported that the electro-catalyst of nominal composition $\text{Pt}_{44}\text{Ru}_{41}\text{Os}_{10}\text{Ir}_5$ is more active than $\text{Pt}_{50}\text{Ru}_{50}$ in a direct methanol fuel cell operating at 60°C , even though the latter catalyst has about twice the surface area of the former. Synthesis of nano-crystalline $\text{Pt}_{44}\text{Ru}_{41}\text{Os}_{10}\text{Ir}_5$ catalyst of high specific surface area as reported herein can therefore be expected to enhance the catalytic activity in comparison to high surface area $\text{Pt}_{50}\text{Ru}_{50}$ alloy. Furthermore, an SEM–EDAX analysis of commercially obtained Pt–Ru based Johnson–Matthey (JM) catalyst showed presence of Os which also served as a motivation for the incorporation of Os and Ir in the present work. In addition to alloy development, considerable efforts have also been devoted to synthesize high surface area binary or ternary Pt–Ru based alloy catalysts to achieve higher methanol oxidation activity [7,10–13,20–25]. Hence, several approaches have been reported for synthesizing high surface area Pt–Ru based binary or ternary alloy nano-particles anode catalysts primarily using halide precursors of the respective components, which inevitably require several follow-up washing treatments to remove the undesired halide secondary residues [7,10–21]. As a result, these processes are cumbersome and cost-inefficient leading to significant loss of the starting noble metal precursors. In addition, the use of Vulcan carbon and other high surface area electronic conductors (e.g. carbon nanotube and metal oxide) have been reported as supports to synthesize high surface area Pt–Ru based anode catalyst to obtain better performance than pure Pt–Ru catalyst [7,11,12,18,20,24–26]. However, the relatively low density of carbon leads to a build-up of thick catalyst layers that impede the mass transport of methanol to the catalytic sites.

We have demonstrated that the novel sol–gel complexation based chemical process, aptly termed complexed sol–gel (CSG) process, is an attractive alternative route for synthesizing unsupported phase-pure Pt(Ru) and Pt(Ru,Os) solid solution catalyst possessing a high specific surface area ($>100 \text{ m}^2/\text{g}$) with excellent catalytic activity [13,16,27]. In the present work, the CSG process has been further exploited to synthesize $\text{Pt}_{44}\text{Ru}_{41}\text{Os}_{10}\text{Ir}_5$ based complexes, which were thermally treated at various conditions to synthesize phase-pure Pt(Ru,Os,Ir) solid solution catalysts possessing a high specific surface area (SSA) with good catalytic activity. The synthesis, phase analysis, thermal characteristics, and electrochemical performance of the high specific surface area $\text{Pt}_{44}\text{Ru}_{41}\text{Os}_{10}\text{Ir}_5$ catalyst is presented and described in the present manuscript.

2. Experimental details

2.1. Materials synthesis

Phase-pure and high specific surface area (SSA) Pt–Ru–Os–Ir based catalyst powders were synthesized using the CSG process. Platinum(II) acetylacetonate [Pt-acac: $\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2$, Alfa Aesar], ruthenium(III) acetylacetonate [Ru-acac, $\text{Ru}(\text{C}_5\text{H}_7\text{O}_2)_3$, Alfa Aesar], iridium(III) acetylacetonate [Ir-acac, $\text{Ir}(\text{C}_5\text{H}_7\text{O}_2)_3$, Alfa Aesar] and osmium(III) chloride [OsCl₃, Sigma–Aldrich] were used as the sources for Pt, Ru, Ir and Os. Pt-acac, Ru-acac, Ir-acac and OsCl₃ of the desired composition (e.g. Pt-41 at.%Ru-10 at.%Os-5 at.%Ir) were dissolved at 50°C in 100 ml of acetone. Tetramethylammonium hydroxide [TMAH, $(\text{CH}_3)_4\text{NOH}$, 25% in methanol, Alfa Aesar], set at TMAH:(Pt + Ru + Os) = 1.75:1, was then added to the solution to serve both as a high molecular weight organic complexing as well as a hydrolyzing agent. Since Pt-acac, Ru-acac, Ir-acac and OsCl₃ tend to phase separate during drying and evaporation of the solvent, the addition of the high molecular weight organic reagent, tetramethylammonium hydroxide (TMAH), and its intended dual role to complex and induce hydrolysis of the starting noble metal precursors was found to be ben-

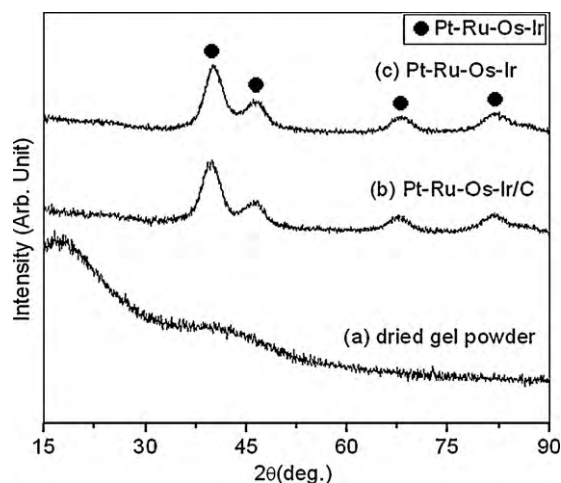


Fig. 1. X-ray diffraction traces of the Pt–Ru–Os–Ir based alloy powders derived using tetramethylammonium hydroxide (TMAH) acting as a hydrolysis and a complexing agent; (a) dried gel powder obtained after drying the gel precursor at 120°C for 10 h in air, (b) Pt–Ru–Os–Ir/C obtained after thermal treatment of the dried gel powder in UHP–Ar at 450°C for 4 h, (c) Pt–Ru–Os–Ir alloy obtained after two sequential thermal treatment cycles of Pt–Ru–Os–Ir/C at 300°C in Ar–1% O₂ atmosphere for 3 h.

eficial in yielding homogeneous amorphous gels containing Pt, Ru, Ir and Os. After stirring for 10 min, the solvent was evaporated until the solution became viscous, transforming into a thixotropic gel. The viscous gel was dried in air at 120°C for 10 h. The dried gels were then heat-treated in various conditions based on our earlier published results [13,16,27] to generate high surface area Pt–Ru–Os–Ir catalysts. In order to compare the electrochemical performance of the Pt–Ru–Os–Ir catalyst with Pt–Ru catalyst, the CSG process has also been used to synthesize high specific surface area Pt–50 at.% Ru alloy as reported by us previously [13,16,27].

2.2. Materials characterization

In order to identify the presence of phase/phases, X-ray diffraction (XRD, Philips XPERT PRO system with $\text{CuK}\alpha$ radiation) study has been conducted on the as-prepared precursors as well as the heat-treated powders. The effective crystallite sizes of the Pt–Ru and Pt–Ru–Os–Ir catalysts were calculated from the most intense peak by Voigt function using the single line approximation method [28]. Specific surface area of the catalyst has been measured using the Brunauer–Emmett–Teller (BET) technique (ASAP 2020 Accelerated Surface Area and Porosimetry System, Micromeritics). In order to understand the phase formation and decomposition temperature, thermogravimetric and differential scanning calorimetry (TGA/DSC) has been conducted on the as-prepared precursors as well as the thermally treated powders using a simultaneous TGA/DSC machine (STA 409PC Luxx, Netzsch). The TGA/DSC analysis has been carried out employing a heating rate of $10^\circ\text{C}/\text{min}$ from room temperature to 500°C in various atmospheres using $\sim 10 \text{ mg}$ sample mentioned in the sections to follow. To investigate the particle size and particle morphology, transmission electron microscopy (TEM) analysis was conducted. JEOL 4000EX operating at 400 kV was employed for conducting the TEM analysis.

Electrochemical characterization was conducted on selected samples using a three-electrode cell. The working electrodes for electrochemical characterization were prepared by spreading the catalyst ink of the respective powders on teflonized carbon papers (applied on 1.5 cm^2 area). The ink consists of 88 wt% catalysts, and 12 wt% Nafion (5 wt% solution in mixed alcohols, Aldrich). The Pt loading on the electrode was $0.2 \text{ mg}/1.5 \text{ cm}^2$. The working electrodes were electrochemically tested using a Potentiostat/Galvanostat (VersaSTAT 3, Princeton Applied Research). A solution containing 1 M methanol and 0.5 M sulfuric acid was used as an electrolyte while also serving as a source of the fuel. A Mercury/Mercurous sulfate electrode that has a potential of $+0.65 \text{ V}$ with respect to standard hydrogen electrode (SHE) was used as the reference electrode.

3. Results and discussion

The XRD patterns of the dried gel precursor (Fig. 1a) obtained after drying the as prepared gel, derived using a molar ratio of TMAH:(Pt-acac + Ru-acac + Ir-acac + OsCl₃) = 1.75:1 of nominal composition Pt-acac:Ru-acac:OsCl₃:Ir-acac = 4.4:4.1:1.0:0.5, at 120°C for 10 h in air exhibit an amorphous structure devoid of any peaks corresponding to the crystalline starting precursors which indicate the expected good chemical homogeneity of the dried gel

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