Electrochemical and *in situ* IR characterization of PtRu catalysts for complete oxidation of ethylene glycol and glycerol

Akinbayowa Falase, Kristen Garcia, Carolin Lau, Plamen Atanassov *

University of New Mexico, Department of Chemical and Nuclear Engineering, Albuquerque, NM 87131, USA

ABSTRACT

Unsupported nanostructured PtRu electrocatalysts were synthesized using a spray pyrolysis process with varying atomic compositions. A ruthenium rich and platinum rich PtRu were compared to supported E-Tek PtRu on Vulcan XC-72 at a pH range from 5 to 8 for the oxidation of ethylene glycol and glycerol. Oxalic acid is also evaluated as a fuel because it is a terminal oxidation product of glycerol oxidation that enzymes cannot successfully oxidize electrochemically. The nanostructured catalysts were evaluated by SEM and exhibited a sponge-like morphology that helped to increase the metal utilization despite its low surface area. *In situ* FTIR spectroscopy was used to probe the reaction to determine if complete oxidation occurred by monitoring the production of CO_2. The nanostructured catalyst successfully oxidized each fuel (oxalic acid, ethylene glycol, glycerol) to CO_2 with no indication of CO formation. This presents an interesting opportunity to combine enzymatic catalysts with metallic Pt-based catalysts for oxidation of more complex fuels.

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1. Introduction

Primary alcohols such as methanol and ethanol have been well explored in the literature as anode fuels in fuel cells. The liquid fuels used in direct alcohol fuel cells (DAFCs) have higher volumetric energy density than gaseous fuels such as hydrogen, with methanol being the most well-known and studied alcohol due to its chemical simplicity [1]. Due to higher energy density, low toxicity, and easy integration to existing infrastructure, electrochemical oxidation of polyols is gaining interest.

Various groups interested in sensors for oxalic acid detection, and the reaction mechanism to CO_2 have studied oxidation of oxalic acid, glycerol, and ethylene glycol using various catalysts in both acidic and alkaline electrolytes [2-8]. Binary Pt based catalysts benefit from the addition of ruthenium or tin modifiers to improve catalytic activity and decrease adsorbed oxidation intermediates during oxidation of alcoholic fuels intermediates [9-12]. CO_2 generation from fuel oxidation indicates that all available electrons have been harvested, and oxidation is complete. *In situ* infrared reflection adsorption spectroscopy (IRRAS) is commonly used to monitor oxidation products and verify CO_2 production in solution and on the surface of the electrode [13].

Biological fuel cells use bacteria-derived enzymes for catalysis at room temperature and near-neutral pHs. Utilizing a single enzyme or an enzyme cascade immobilized on an electrode, fuel can be oxidized completely [14]. Combining a traditional metal-based catalyst operating at "mild" operating conditions of near neutral pH and room temperature with an enzyme-based biofuel cell allows for a complimentary relationship that can drive oxidation of fuels further than either catalyst alone.

We present a nanostructured PtRu catalyst produced by spray pyrolysis, an aerosol synthesis technique extensively used to create mesoporous silica [15]. The catalyst is capable of oxidizing oxalic acid, ethylene glycol, and glycerol to CO_2 at neutral pH and room temperature. We compare our synthesized nanostructured catalysts to commercial E-Tek HP precious metal PtRu catalysts. We also present a pH study to determine the efficiency of catalysis in biologically relevant buffer solutions with pHs ranging from pH 5 to 8.

2. Materials and methods

Nanostructured PtRu catalyst synthesis has been reported previously [16], and was used to create nanostructured $Pt_{50}Ru_{50}$ and $Pt_{30}Ru_{70}$ unsupported catalysts. Surface areas were measured by the N_2-BET method using a Micrometrics 2360 Gemini Analyzer. Scanning electron microscopy (SEM) and EDS analyses were performed using a Hitachi S-5200 Nano SEM with an accelerating voltage of 10 keV. Transmission electron microscopy (TEM) was performed on a JEOL 2010 instrument with an accelerating voltage of 200 keV.

Electrochemical studies were performed via cyclic voltammetry using a glassy carbon electrode (5 mm diameter) with a potential sweep from −900 mV to 900 mV vs. Ag/AgCl reference electrode in a conventional three electrode cell with a platinum mesh as a counter electrode. In order to prepare the working electrode, 17 mg of catalyst was dispersed ultrasonically in 1 ml of 5 wt. % Nafion solution. A 3 μl

* Corresponding author. Tel.: +1 505 277 2640.
E-mail address: plamen@unm.edu (P. Atanassov).

aliquot of this mixture was then transferred to a polished glassy carbon disk electrode, which corresponds to a loading of 0.05 mg of catalyst on the working electrode, and allowed to air dry for 30 minutes. The electrochemical measurements were performed at room temperature in nitrogen purged buffer solutions ranging from pH 5 to 8. 30 mM fuel concentrations were used in solutions at a scan rate of 10 mV/s for 4 cycles.

In situ infrared reflection adsorption spectroscopy (IRRAS) experiments using a setup were described previously [17]. The reference spectrum was collected at −600 mV vs. Ag/AgCl in 1.5 ml of 0.1 M respective fuel (oxalic acid, glycerol, or ethylene glycol) and 0.1 M potassium phosphate buffer solution at pH 7, using linear sweep voltammetry with a scan rate of 1 mV/s from −600 mV to +600 mV vs. Ag/AgCl.

3. Results and discussion

The BET surface area of the synthesized nanostructured PtRu catalysts was approximately 32 m^2/g for the Pt$_{50}$Ru$_{50}$, and 30 m^2/g for the Pt$_{30}$Ru$_{70}$ sample. This is in contrast to commercially available E-Tek HP Precious Metal Catalyst 40% PtRu on Vulcan XC-72 1:1 and 60% PtRu on Vulcan XC-72 1:1 which have surface areas of 107 m^2/g and 112 m^2/g, respectively.

SEM (Fig. 1) micrographs show the "sponge-like" nanostructured metal catalyst. EDS analysis of Pt-M and Ru-L lines confirms the presence of Pt$_{30}$Ru$_{70}$ and Pt$_{50}$Ru$_{50}$. TEM observation of the catalyst shows the existence of the [111] platinum and [101] ruthenium faces, correlating to the XRD results.

The electrochemical oxidation of oxalic acid, ethylene glycol and glycerol was tested for all four PtRu catalysts in a neutral pH range (pH 5 to 8). Fig. 2 (A–C) represents the cyclic voltammogram for Pt$_{30}$Ru$_{70}$ (for clarity only that catalyst is shown). The blank PtRu catalyst shows a stable and reversible couple of redox peaks at −500 mV and −300 mV, which is specific to formation of Pt-oxides in phosphate buffer.

The oxidation of oxalic acid exhibits a single peak at approximately −350 mV whereas ethylene glycol and glycerol result in a dual oxidation at −300 mV and 300 mV or −300 mV and 250 mV, respectively. Parallel to the electrochemical scan we employed *in situ* FTIR spectroscopy to monitor the formation of oxidation products (Fig. 2, D–F). The oxidation peak at −350 mV for oxalic acid corresponds to the decreasing bands at 1308 cm^{-1} and 1571 cm^{-1}, both specific wavenumbers for the symmetric and asymmetric oxalate O—C—O stretching vibration mode [18]. The oxalic acid FTIR spectra showa large peak centered at 1626 cm^{-1} and 1723 cm^{-1} due to δ(H—O—H) mode of water and ν(C O) carboxylic stretching of adsorbed oxalate species that can be interpreted as the major contribution to the −350 mV oxidation peak. Finally, the CO$_2$ formation starts at −240 mV, with the appearance of a small perturbation at 2343 cm^{-1}. This absorbance peak grows in intensity as the electrode becomes more positively polarized, reaching a maximum at the end of the sweep.

The oxidation of ethylene glycol and glycerol in neutral media exhibits striking interference peaks due to the absorbance of phosphates to the platinum catalyst from 939 cm^{-1} to 1190 cm^{-1}[19, 20]. Phosphate is a polyprotic molecule that has multiple dissociation constants, resulting in both the [HA$^-$ and HA^{2-}] species present at pH 7. The peak at 1157 cm^{-1} correlates to the asymmetrical PO$_2$ stretch, the peak at 1078 cm^{-1} correlates to the PO$_3$ degenerate stretch and the PO$_2$ symmetrical stretch of H$_2$PO$_4^-$, and the peak at 939 cm^{-1} correlates to the P(OH)$_2$ asymmetric stretch of H$_2$PO$_4^-$. The IR spectrum for oxalic acid oxidation shows none of these phosphate peaks, suggesting stronger adsorption of oxalate anions to the catalyst surface compared to phosphate species. The intensity of the phosphate peaks in the ethylene glycol and glycerol spectra is much stronger than that of a blank spectrum (data not shown) with just the buffer. Therefore it is safe to assume that contributions from C—O stretching
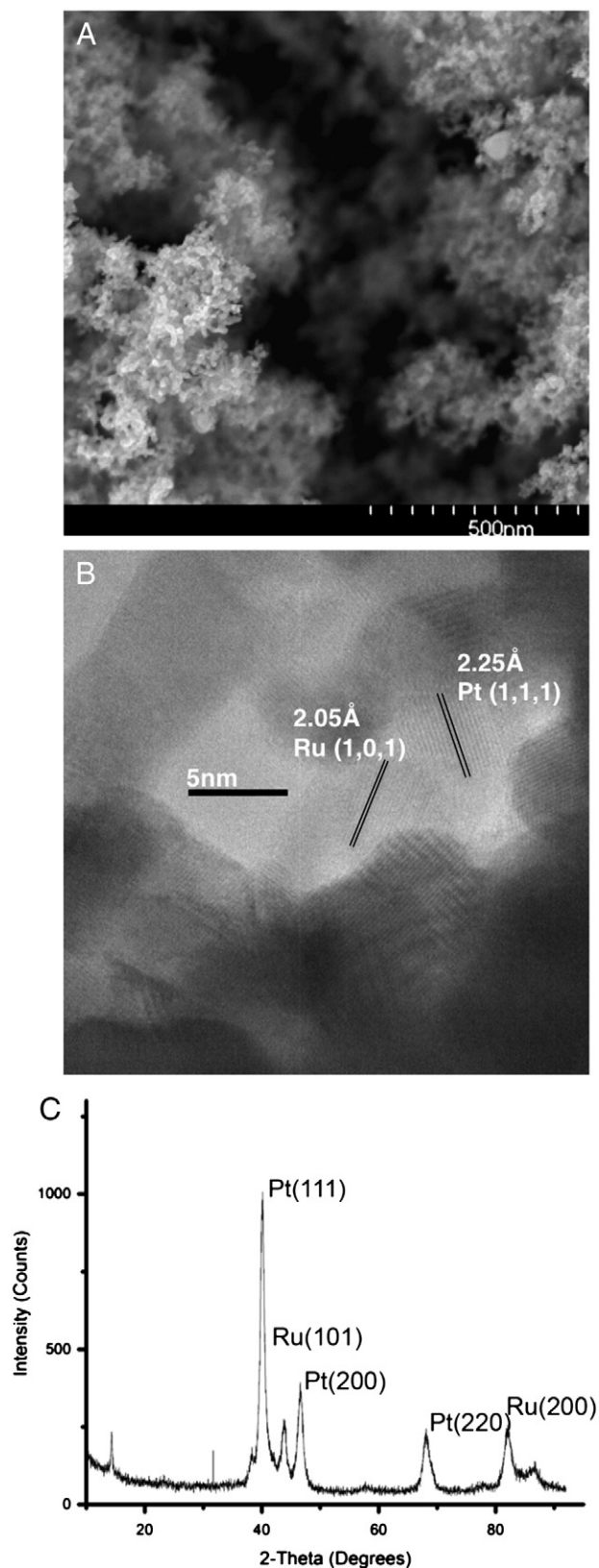

Fig. 1. SEM (A) and TEM (B) micrograph of Pt$_{30}$Ru$_{70}$ sample with XRD pattern (C). The SEM image shows the nanostructured "sponge-like" morphology of the catalyst samples. TEM micrograph shows existence of Pt (111) and Ru (101) faces, correlating to the XRD results. Grain sizes range from 5 to 15 nm.