

# Pt and Pt-Ru/Carbon Nanotube Nanocomposites Synthesized in Supercritical Fluid as Electrocatalysts for Low-Temperature Fuel Cells

Yuehe Lin<sup>1\*</sup>, Xiaoli Cui<sup>1</sup>, Jun Wang<sup>1</sup>, Clive. H. Yen<sup>2</sup> and C. M. Wai<sup>2</sup>

<sup>1</sup>Pacific Northwest National Laboratory, 902 Battelle Blvd, P. O. Richland, WA 99352, Tel: 1-509-376-0529, Email: [yuehe.lin@pnl.gov](mailto:yuehe.lin@pnl.gov)

<sup>2</sup>University of Idaho, Moscow, ID 83844, USA

## ABSTRACT

In recent years, the use of supercritical fluids (SCFs) for the synthesis and processing of nanomaterials has proven to be a rapid, direct, and clean approach to develop nanomaterials and nanocomposites. The application of supercritical fluid technology can result in products (and processes) that are cleaner, less expensive, and of higher quality than those that are produced using conventional technologies and solvents. In this work, carbon nanotube (CNT)-supported Pt and Pt-Ru nanoparticles catalysts have been synthesized in supercritical carbon dioxide (scCO<sub>2</sub>). The experimental results demonstrate that Pt, Pt-Ru/CNT nanocomposites synthesized in supercritical carbon dioxide are effective electrocatalysts for low-temperature fuel cells.

**Keywords:** carbon nanotubes, fuel cell, supercritical fluid

## 1 INTRODUCTION

Direct methanol fuel cells (DMFC) is considered as one of the most promising options to solve the future energy problem because of its high energy conversion efficiency, low pollutant emission, low operating temperature, and simplicity of handling and processing of liquid fuel.[1-7] Electrocatalysts with higher activity for methanol oxidation at room temperature are critically needed to enhance its performance for commercial device applications. It is well known that platinum is the only single-component catalyst that shows a significant activity for methanol oxidation. Considerable efforts have been devoted to design and synthesize Pt-based alloy catalysts with higher poison tolerance and greater methanol oxidation activity. PtRu is a promising catalyst for methanol oxidation in DMFC. It is well known that the preparation technique is one of the key factors to determine its catalytic activity. Numerous approaches including impregnation and chemical reduction electrodeposition sputtering method have been developed in order to generate clusters on the nanoscale and with greater uniformity on the carbon supports. The PtRu nanoparticles can be prepared by chemical reduction with formic acid or impregnation method, a microwave-assisted polyol process using metal precursors H<sub>2</sub>PtCl<sub>6</sub> and RuCl<sub>3</sub>. Chemical methods are the most widely used in the synthesis of metal or mixed metal nanoparticles. However, conventional preparation techniques based on wet impregnation and chemical

reduction of the metal precursors are often time-consuming and labor-intensive. In addition, these procedures often do not provide adequate control of particle shape and size. The physical methods mainly proceed in a vacuum through atomization of metals by thermal evaporation or sputtering.

The use of supercritical fluids (SCF) for the synthesis and processing of nanomaterials has gained considerable interest in recent years. SCF exhibits an attractive combination of the solvent properties of a gas and a liquid. It can dissolve solutes like a liquid, and yet possess low viscosity, high diffusivity, and zero surface extension like a gas. Furthermore, the solvent strength of SCF can be varied by manipulating fluid temperature and pressure, thus allowing a degree of control and rapid separation of products, which is impossible using conventional solvents. It provides a rapid, direct and clean approach to preparing nanomaterials and nanocomposites. These special and unique features make SCF an attractive medium for delivering reactant molecules to areas with high aspect ratios, complicated surfaces, and poorly wettable substrates. The supercritical carbon dioxide (scCO<sub>2</sub>) allows reactive components to penetrate inside the porous materials themselves, partitioning into the inner regions of the porous supports. Through hydrogen reduction of metal-β-diketone complexes in scCO<sub>2</sub>, multiwalled carbon nanotubes can be decorated by metal nanoparticles with uniformity to achieve nanocomposites. In previously papers, we have demonstrated high activity for oxygen reduction reactions of Pd/CNT and Pt/CNT processed in SCF. Recently, platinum and ruthenium nanoparticles were successfully loaded on carbon aerogel in scCO<sub>2</sub>. In principle, a number of metal precursors can be used as starting materials in SCF and metal alloys can be coated on CNT to form nanocomposites. Cu-Pd alloy nanoparticles attached to SiC nanowires through hydrogen reduction of a mixture of Cu(hfa)<sub>2</sub>·xH<sub>2</sub>O and Pd(hfa)<sub>2</sub>·xH<sub>2</sub>O [hfa=hexafluoroacetylacetonate] in scCO<sub>2</sub> have been obtained. In this paper, platinum/ruthenium alloy nanoparticles were decorated on carbon nanotubes in scCO<sub>2</sub> and the nanocomposites were characterized by transmission electron microscopy (TEM) and X-ray diffraction (XRD). The PtRu/CNT powder was loaded on the glassy carbon electrode through a casting process, and the electrocatalytic activity for methanol oxidation was investigated in 1 M H<sub>2</sub>SO<sub>4</sub> at room temperature using electrochemical methods such as cyclic voltammetry (CV), linear sweep voltammetry (LSV), chronoamperometry (CA), and

electrochemical impedance spectroscopy (EIS). Its catalytic performance was compared with that of Pt/CNT synthesized in scCO<sub>2</sub>.

## Experiments

### 2.1 Decorating PtRu Nanoparticles on Carbon Nanotubes

The PtRu/CNT catalyst was synthesized by using the following procedures: The CNT (20 mg) and the metal precursors Pt(acac)<sub>2</sub> (20 mg) and Ru(acac)<sub>2</sub> (20 mg) [acac = acetylacetonate] with a small amount of methanol (3 mL) as a modifier were all loaded in a high pressure reaction cell (10 mL) located in an oven at 200°C. Pt(acac)<sub>2</sub> and Ru(acac)<sub>2</sub> have a low solubility in supercritical CO<sub>2</sub>. Addition of methanol modifies the polarity of CO<sub>2</sub> and enables dissolution of the Pt and Ru precursors in the fluid phase. Carbon dioxide gas was introduced into the reaction cell and was pressurized to 80 bar in order to make the gas become a supercritical fluid. Hydrogen gas at 10 bar was initially filled in the H<sub>2</sub>+CO<sub>2</sub> mixer cell and CO<sub>2</sub> gas of 120 bar was then added to the cell. After one hour of waiting for the precursors to completely dissolve in the supercritical CO<sub>2</sub>, the H<sub>2</sub>+CO<sub>2</sub> gas was introduced into the reaction cell by pressurizing it to 160 bar. The reductions (Pt<sup>2+</sup> to Pt<sup>0</sup> and Ru<sup>2+</sup> to Ru<sup>0</sup>) were fast and took 15 min only. After depressurizing the reaction cell, PtRu/CNT powder could be recovered and then was washed 5 times using methanol and ultrasonication for 30 minutes each time. The detailed procedures for the preparation of Pt/CNT were described in our previous report.

### 2.2 Electrode preparation and modification

A 0.5 wt% Nafion solution was prepared by diluting the 5 wt% Nafion solution with water. Catalyst powder was dispersed ultrasonically in 0.5% Nafion solution to obtain a homogeneous black suspension solution with 1 mg/mL PtRu/CNT or Pt/CNT, and a 5 μL aliquot of this solution was pipetted onto glassy carbon (GC, 3 mm in diameter, BAS, West Lafayette, IN) electrode surface. Before the surface modification, the GC electrode was polished with 0.3 μm and 0.05 μm alumina slurries, washed with water and acetone, and finally subjected to ultrasonic agitation for 1 minute in ultrapure water and dried under an air stream. The coating was dried at room temperature in the air for 1 hour. The catalyst should be homogeneously dispersed and the same procedures for experiments should be controlled in order to obtain reproducible results. The modified electrode surface was then washed carefully with ultra pure water before measurement.

### 2.4 Apparatus

Cyclic voltammetry, linear sweep voltammetry, and chronoamperometry experiments were performed with a CHI 660 electrochemical workstation (CH Instruments Inc, Austin, Texas). All electrochemical experiments were carried out with a conventional three-electrode system. The working electrode was glassy carbon coated with Pt/CNT

or PtRu/CNT composite films. An Ag/AgCl (saturated by KCl solution) reference electrode was used for all electrochemical measurements, and all the potentials were reported versus this reference electrode. A platinum wire was used as a counter electrode. In order to obtain reproducible and reliable results, a fresh methanol solution was used for every measurement. All the electrochemical experiments were carried out at room temperature.

## RESULTS AND DISCUSSION

Figure 1 (left) shows a typical TEM image of the carbon nanotube-supported platinum nanoparticles. The little dark spots which represent the Pt nanoparticles are closely attached to the CNT surfaces. The Pt nanoparticles have a size distribution range of approximately 5 to 15 nm. This size distribution of Pt nanoparticles is considered suitable for fuel cell applications since Peuckert et al. showed that once the Pt particle size was below 4 nm, the oxygen reduction peak would drop significantly.

It has been suggested that the curvature of the carbon nanotubes was a controlling factor for attachment of a certain range of metal nanoparticles to the nanotube surfaces during the supercritical fluid deposition.<sup>1,5</sup> Larger particles probably would fall off from the nanotube surfaces during the deposition process. There are two possible mechanisms for the formation of

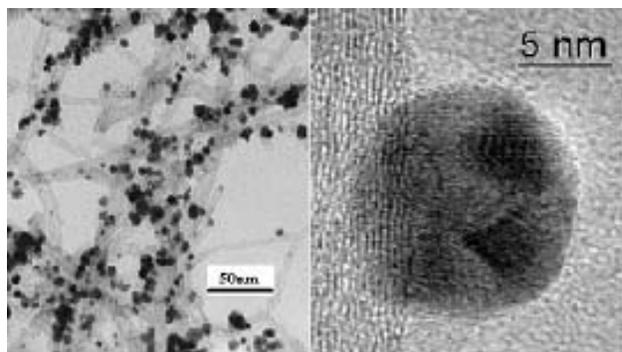


Figure 1. TEM (left) and HRTEM (right) images of a Pt-CNT sample prepared by the supercritical fluid deposition method

nanoparticles on CNT surfaces. The first one is that if the metal precursor molecules are close to the CNT surface when hydrogen is introduced, reduced metal atoms may grow directly on the functional groups of the substrate surface to develop uniformly distributed metal nanoparticles that strongly adhere to the surface of the CNT. The second mechanism is the aggregation of the reduced metal, forming nanoparticles in the fluid phase far away from the CNT surface, followed by attachment of the particles to the functional groups of the substrate surface by collision. If the size of the metal nanoparticles is too large for attachment to the CNT surface, these nanoparticles will fall off because of the

curvature limitation. If the size of the metal nanoparticles is moderate and suitable for attachment to the curved surface, they may still adhere to the CNT surfaces. The second mechanism probably is a main cause of the variation in particle size distribution of the metal particles observed on CNT surfaces after washing and sonication. A HRTEM micrograph shown in Figure 1 (right) indicates that Pt nanoparticles are crystallites with visible lattice fringes. The Pt-CNT sample was washed and ultrasonicated several times to remove the metal particles that are not attached or adhered to the CNT' surfaces before characterization. The remaining platinum nanoparticles were attached strongly to the surfaces of CNT and showed no obvious changes from TEM images taken after catalysis experiments. Methanol Oxidation Reaction is also a very important indication of the electrocatalytic activity of a catalyst especially for direct methanol fuel cell.

The Oxygen Reduction Reaction (ORR) is especially important for the realization of highly efficient fuel cells, batteries, and many other electrode applications. Platinum particles on a variety of carbon supports are the most widely used and efficient catalysts for the cathode of fuel cells. For the ORR experiments at the GC/Pt-CNT electrode, a solution of 0.1 M H<sub>2</sub>SO<sub>4</sub> was purged with ultrapure oxygen for 15 min. The solution became completely saturated with oxygen. The electrode was scanned over a potential range from 0.7 V to 0 V for 5 cycles to ensure reproducibility and the last cycle is shown in Figure 2. Figure 2 illustrates the cyclic voltammograms of GC/CNT (a) and GC/Pt-CNT (b) electrodes for the reduction of oxygen reaction. For the

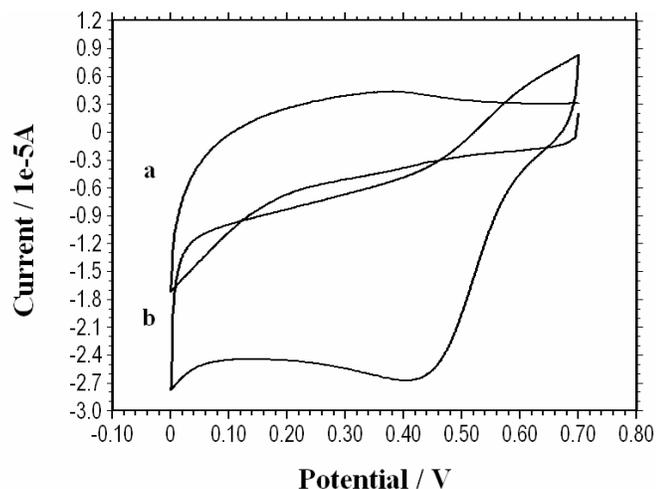


Figure 2. Cyclic voltammograms at GC/CNT (a) and GC/Pt-CNT (b) electrodes for oxygen reduction reaction at scan rate of 0.02 V/s. The electrolyte is 0.1 M H<sub>2</sub>SO<sub>4</sub> saturated with oxygen. The scan involves 5 cycles and the fifth cycle (last cycle) is shown here.

electrode of GC/CNT, oxygen reduction current increased with the potential decrease, suggesting that the catalytic reduction of oxygen at GC/CNT is a kinetics-controlled process. For the electrode of GC/Pt-CNT

oxygen reduction proceeded in a relatively positive potential region. A cathodic catalytic peak current occurred at about 0.42 V. The oxygen-reduction potential showed a significant shift anodically in the presence of platinum on the carbon nanotubes. The peak current increases linearly with the square root of the scan rates which indicates that the ORR process on Pt-CNT is controlled by the diffusion of oxygen to the electrode surface. This observation reveals a high activity to oxygen reduction by Pt-CNT synthesized in supercritical CO<sub>2</sub>.

The electrocatalytic activity for methanol oxidation of Pt-CNT prepared in supercritical CO<sub>2</sub> was characterized by cyclic voltammetry in an electrolyte of 1 M H<sub>2</sub>SO<sub>4</sub> and 2 M CH<sub>3</sub>OH at 50 mV/s. Figure 3 shows the cyclic voltammograms of GC/CNT (a) and GC/Pt-CNT (b) electrodes for the oxidation of methanol reaction. This feature of CV curve is in agreement with the literature report for Pt/C catalysts. The ratio of  $I_f$  to  $I_b$  can be used to describe the catalyst tolerance to carbonaceous species accumulation. High  $I_f/I_b$  value implies good oxidation of methanol to carbon dioxide. In our experiments, the ratio was estimated to be 1.4 for the Pt-CNT electrode. Such a high value indicates that most of intermediate carbonaceous species were oxidized to carbon dioxide in the forward scan. For comparison, a ratio of 0.87 was reported with a nanosized Pt on XC-72 synthesized by a microwave-assisted polyol process. The experimental results highlighted the high activity of the Pt-CNT prepared from supercritical CO<sub>2</sub> for methanol oxidation. The high activity may result from the high surface area of CNT and the nanostructure of the platinum particles.

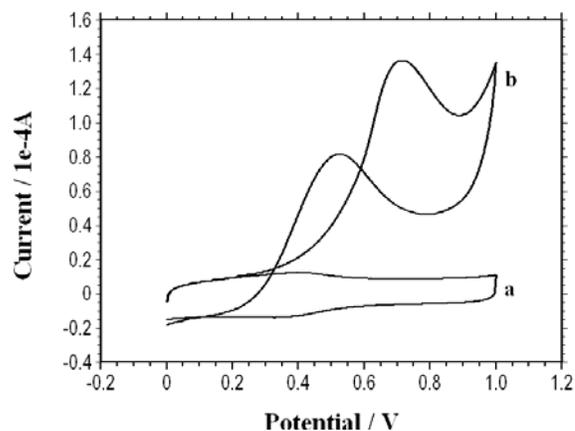


Figure 3. Cyclic voltammograms of room-temperature methanol oxidation on GC/CNT (a) and GC/Pt-CNT (b) electrodes cycled from 0 V to 1.0 V vs Ag/AgCl at 50 mV/s in 1 M H<sub>2</sub>SO<sub>4</sub>, 2 M CH<sub>3</sub>OH.

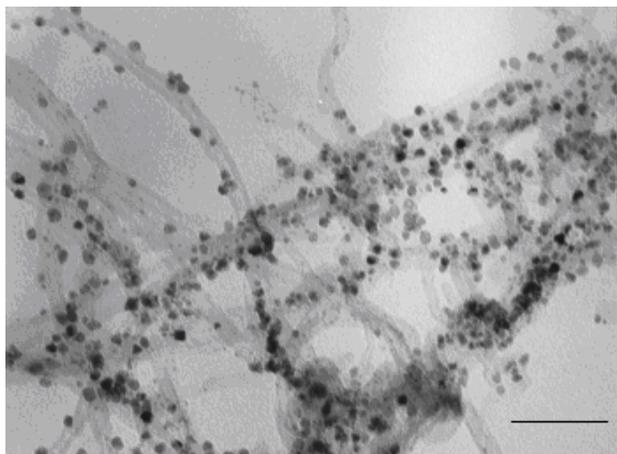


Figure 4. A typical TEM image of CNT decorated by platinum/ruthenium nanoparticles synthesized in supercritical carbon dioxide. The scale bar is 50 nm.

Figure 4 shows the typical transmission electron microscopy micrograph of PtRu/CNT electrocatalysts prepared in  $scCO_2$ . The nanoparticles show a good distribution on the surface of CNT and the particles with an average size of 5~10 nm. The EDS results indicates that the Pt and Ru content in the nanocomposite is 4.1% and 2.3 % by weight and molar ratio approximately Pt:Ru = 45:55, respectively.

The electrocatalytic activity for methanol oxidation of PtRu/CNT prepared in  $scCO_2$  was characterized by cyclic voltammetry in an electrolyte of 1 M  $H_2SO_4$  and 2 M  $CH_3OH$  at 50mV/s, and the resulting voltammograms are shown in Figure 5. Figure 5 shows the results of Pt/CNT electrodes for the electrooxidation of methanol. Before recording cyclic voltammograms, the electrode was soaked in the test solution for 10 minutes to allow the system reaching a stable state. The potential scan starts from its open circuit potential positively to 1.0 V then to -0.1 V and then it cycles between -0.1 V and 1.0 V for PtRu/CNT electrode. The cyclic voltammograms of PtRu/CNT are different from those obtained on Pt/CNT electrode. The onset of methanol oxidation occurs at about 0.05 V at the electrode of PtRu/CNT. The lower onset potential indicates clear evidence for superior electrocatalytic activity for methanol oxidation. There are large changes in the potential cycles over time. The early cycles exhibit a low peak current and lower peak potential in the forward scan and there is almost no peak during the reverse potential scan. As the number of cycles increases, the potential for the peak current in the forward scan shifts to higher values and the peak potential increases greatly. The forward anodic peak potential shifts more positively from cycle to cycle. By the sixth cycle, the forward peak potential is located at about

0.57 V and a broadened peak centered at 0.45 V appeared in the reverse scan. Then, anodic peaks appeared in both the forward and backward scans. Significant changes can be observed between the sixth and twenty-five cycles as shown in Figure 4. The peak potential in the reverse scan moves to higher voltages and the peak current increases. This phenomenon may result from the leaching of ruthenium during the cycling of the electrode between oxidizing and reducing potentials. At last, the cyclic voltammogram of the catalyst was found to have become similar to that of pure Pt/CNT, indicating excessive loss of Ru. Previous results have been shown that similar performance was observed on a commercial E-TEK catalyst PtRu/C on carbon paper as reported in a recent paper. The loss of ruthenium was confirmed by TEM and X-ray microanalysis in the commercial catalyst.

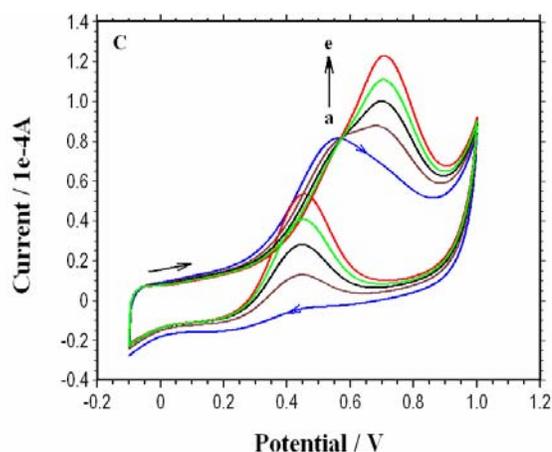


Figure 5. Cyclic voltammograms of room-temperature methanol oxidation on PtRu/CNT (C) electrodes cycle cycles 5, 10, 15, 20, 25 from a to e (C) respectively at 50 mV/s in 1 M  $H_2SO_4$ , 2 M  $CH_3OH$ .

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