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Flame aerosol synthesis of carbon-supported Pt–Ru catalysts for a fuel cell electrode

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ABSTRACT

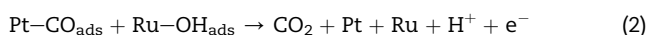
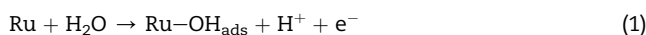
This study describes how a flame spray pyrolysis method was successfully used to synthesize PtRu catalysts supported by carbon agglomerates. Nearly spherical catalysts composed of metallic Pt and Ru with molar ratio of 1:1 were produced in the flame and their size was about 1.9 nm. X-ray diffraction measurements revealed that amorphous-like Ru was well mixed into the Pt crystalline lattices. Through cyclic voltammetry for methanol oxidation reaction and CO stripping, it was found that the electrochemical activities of the catalysts produced from this process are comparable to or slightly better than those of an equivalent commercial sample with the same composition.

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1. Introduction

Platinum (Pt) is widely used as an electrochemical catalyst for low-temperature fuel cells due to its excellent catalytic performance; however, Pt catalysts are often degraded by trace levels of CO produced during the reforming process of fossil fuels. The adverse effect of CO, well known as CO poisoning, is the result of CO molecules binding with the Pt surface stronger than the hydrogen. This CO binding inhibits the catalytic reaction of hydrogen. Platinum-ruthenium (Pt–Ru) composite nanoparticles are generally considered as one of the most promising catalysts to circumvent the CO poisoning [1].

Excellent CO tolerance of Pt–Ru catalyst was described by the bifunctional mechanism [2–4] of Ru as:



Eqs (1) and (2) explain how hydroxyl groups adsorbed on the surface of Ru regenerate the CO-contaminated Pt surface. For maximizing performance, the Ru must be exposed to the surrounding H₂O vapor and be in contact with the surface Pt. On the other hand, Pt-encapsulated Ru core–shell nanostructures

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are expected to be least active because the Ru has no chance to contact the atmosphere. Thus, microstructure control of Pt and Ru is of particular interest in order to improve the catalytic performance while maintaining the CO tolerance. Moreover, the Pt–Ru catalyst provides another benefit in reducing the cost of the precious electrode catalyst, as the price of ruthenium is about one eleventh the price of platinum [5].

Many researchers have proposed various methods such as chemical reduction method¹, chemical vapor deposition [6], and thermal reduction [7] for synthesis of the catalysts. However these methods require a long time and multistep processes. Here, we recently proposed a novel method using flame which offers great benefits relative to the other methods: a continuous single-step production [8] of such catalysts and easy scale up. In the process, the flame was used not only as a precursor for carbon agglomerates but also as a heat source to pyrolyze Pt precursor vapor toward metallic Pt spheres in a size range of 1–10 nm. The key was to make carbon agglomerates form prior to the inception of Pt particles in flame. As a result, the size and surface coverage of Pt particles on carbon agglomerates were both controllable and the Pt/C catalysts had a similar electrochemical activity to a commercial (E-TEK) Pt/C sample [8].

In this study, we attempted to extend this flame method to a continuous production of well-designed Pt–Ru/C catalysts with a single step. However, there is another big challenge as compared to the synthesis of Pt/C catalysts. Ru species should be well mixed with Pt in a scale of 1–10 nm so as to maximize the function of Ru to relieve CO poisoning. Another requirement is that such tiny Pt–Ru nanoparticles are made to form on surface of carbon agglomerates with good dispersion conditions. Hence, the purpose of this study is to resolve the issues using the flame method.

As-produced carbon-supported Pt–Ru (PtRu/C) particles are characterized by transmission electron microscopy, energy-dispersive spectroscopy, thermogravimetric analysis, X-ray diffraction and X-ray photoelectron spectroscopy. The electrocatalytic properties of the PtRu/C particles are examined by cyclic voltammetry and CO-stripping, and compared to an equivalent commercial catalyst.

2. Experimental section

As aforementioned, there would be two important timings: one is the formation of carbon agglomerates prior to the formation of Pt or Ru [8]; the other is the simultaneous nucleation of Pt and Ru in flame for better mixing of them. As the nucleation of the Pt or Ru is initiated by the pyrolysis of the precursor in flame, it is of great importance to find a good pair of precursors of Pt and Ru which have a similar pyrolysis reaction kinetics. For this purpose, the reaction temperatures of platinum and ruthenium precursors were estimated running a thermogravimetric analyzer (TGA; Z50, TA Instruments) with a dynamic mode: a constant ramplng rate of 10 °C min⁻¹ in air. After a series of preliminary TGA experiments for several types of those precursors, platinum(II) acetylacetonate (Pt(acac)₂, Aldrich, 97%) powder and ruthenium(III) acetylacetonate (Ru(acac)₃, Aldrich, 97%) powder were finally chosen for the catalyst precursors. In Fig. 1, the two precursors

denoted very similar kinetics of decomposition reaction which was ended at ~250 °C starting from 170 °C. A 1:1 mole ratio mixture of Pt(acac)₂: Ru(acac)₃ was dissolved in xylene with a concentration of 0.12 wt %. After mixing, the solution was ultrasonicated for 10 min at 10 °C. The Pt–Ru/xylene precursor was sprayed as droplets from an ultrasonic atomizer by compressed air at 50 psi, and then fed to the center of the burner through a heated tube as shown in Fig. 2. The carrier gas (air) containing the solution droplets flowed at 1.33 L min⁻¹. Next to the center tube, a shield gas of Argon flowed at a rate of 0.36 L min⁻¹. As a carbon source, acetylene (C₂H₂) and dry air were injected through the third and fourth concentric annuli at 0.105 and 1.35 L min⁻¹, respectively, forming a coflow diffusion flame. On the edge of the burner, argon gas was injected at 30 L min⁻¹ to stabilize the flame. The injection speed of the shield gas was 10 times larger than that of the C₂H₂, so as to retard the decomposition of both the Pt(acac)₂ and Ru(acac)₃ precursors to after carbon inception. More details of material preparation and instrumentation are described in our previous work [8].

As such, carbon-supported Pt–Ru composite particles were thermophoretically deposited to a water-cooled quartz tube as depicted in Fig. 2, then collected and dried for further characterization of the samples. Mass fraction of Pt–Ru metallic species in the dried sample was determined by measuring the mass difference before and after burning the carbon species in TGA machine. This experiment was repeated upon changing the stoichiometry ratio of the flame until the mass fraction of Pt–Ru in the sample denoted 20 wt%. It should be noted that the gas flow rates described above were the final result from these preliminary experiments. As-deposited PtRu/C particles were then dispersed in ethanol with an ultrasonicator. A few milliliters of PtRu/C-ethanol suspension were dropped onto a carbon-coated grid and then dried at room temperature. Morphology and size of PtRu/C particles were characterized with a transmission electron microscopy (TEM; JEOL 2010, JEOL). The Pt and Ru mole ratio was confirmed through the energy dispersive spectroscopy (EDS; JEM 2100F, JEOL). Crystalline phases of the dried powder samples were verified by X-ray diffraction (XRD; D/Max-2400, Rigaku). The XRD measurement was performed by scanning the angle of 2θ in a range of 30–90° with 0.1° min⁻¹, while irradiating Cu Kα X-ray (30 kV, 40 mA, 0.15218 nm). The PtRu/C particle size was

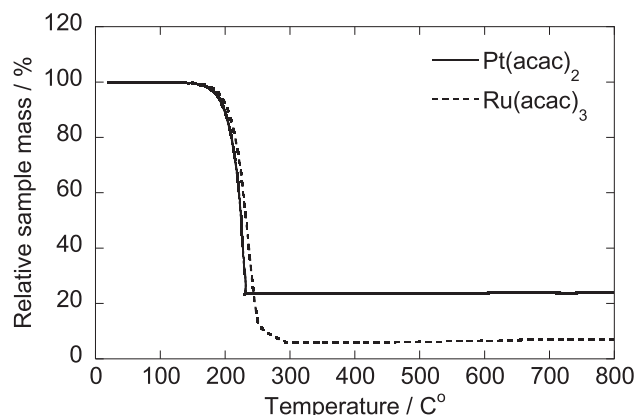


Fig. 1 – TGA profiles of Pt and Ru precursors.

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