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# Methanol-tolerant cathode electrode structure composed of heterogeneous composites to overcome methanol crossover effects for direct methanol fuel cell

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## ABSTRACT

A methanol-tolerant cathode electrode composed of heterogeneous composites was developed to overcome CO poisoning and large O<sub>2</sub> mass transfer overpotential generated by methanol crossover as well as the limitation of a single alloy catalyst with methanol-tolerance in direct methanol fuel cells (DMFCs). Two additives, PtRu black and PTFE particles, were well distributed in the Pt/C matrix of the cathode electrode, and had significant effects upon open circuit voltage (OCV) and performance. A small amount of PtRu black protected the Pt surface during the oxygen reduction reaction (ORR) by decreasing CO poisoning. In addition, hydrophobic PTFE particles reduced the O<sub>2</sub> mass transfer overpotential induced by water and permeated methanol in the cathode. Despite only 0.5 mg cm<sup>-2</sup> of metal catalysts in the cathode, the membrane electrode assembly (MEA) with 3 M methanol showed high performance (0.117 W cm<sup>-2</sup>), which was larger than that of the traditional MEA (0.067 W cm<sup>-2</sup>).

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## 1. Introduction

Direct methanol fuel cell (DMFC) has been developed as a small power device due to its large energy density and usage of methanol solution as a fuel [1]. Methanol solution is more convenient than H<sub>2</sub> gas since it can be easily handled without a high-pressure container [2]. However, when used as a small power device, DMFC requires highly concentrated methanol solution for convenience. It causes severe methanol crossover in the membrane electrode assembly (MEA) and heavy damage to the cathode, which results in mixed potential in the cathode and low performance [3]. There are various techniques to overcome the effects of methanol crossover in the

cathode such as the prevention of methanol crossover by a membrane modification, the enhancement of catalytic activity for the methanol oxidation reaction (MOR) in the anode, the developments of methanol-tolerant cathode catalysts, and so on [4–6]. Up to now, however, new electrode structures for the DMFC performance enhancement have been hardly developed. Therefore, to get a new point of view, changing catalyst layer structures such as layered electrode have been recently studied for the DMFC performance enhancement [7]. Especially, new concepts for the cathode electrode structure have been very important since a certain amount of methanol can be transferred to the cathode although methanol is efficiently oxidized in the well-

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structured anode electrode or is blocked by new types of membrane [8,9].

When many researchers have studied the DMFC cathode, most of them have concentrated on methanol-tolerant cathode catalysts such as Pt-based bi- or tri-metal alloy catalysts to inhibit the MOR in the cathode [10–16]. The oxygen reduction reaction (ORR) performance of Pt-based metal alloy catalysts such as PtPd, PtNi, PtAu, PtFe, PtCoSe, and PtCoRu generally was similar to or higher than that of bare Pt catalyst when only pure O<sub>2</sub> was saturated in an acid electrolyte. In addition, in the presence of methanol with oxygen in the electrolyte, they showed higher ORR performance than bare Pt catalyst, which indicated that they had the methanol-tolerance. However, Pt-based metal alloy catalysts were too expensive to be used in the cathode which needed much precious metal catalyst loading (more than 2.0 mg cm<sup>-2</sup>) for real DMFC operation [17]. Therefore, recently, Pt-free metal alloy catalysts such as RuSe, PdCo, CoSe, and PdNi have been investigated [17–21]. However, due to the absence of Pt, they showed even lower ORR activity compared to bare Pt catalyst in pure O<sub>2</sub> condition, and poor stability in an acid electrolyte although they had methanol-tolerant property in the presence of methanol. Unfortunately, in the development of methanol-tolerant catalysts, most of researchers had to choose only one thing between the ORR activity and catalyst cost since the electronic structures of the metal alloy could not have been easily changed after alloying metal elements were selected in Pt-based or Pt-free metal alloy catalyst synthesis.

Therefore, in order to solve the dilemma in DMFC cathode, we propose an idea that is the use of heterogeneous catalysts, which had two catalyst compositions in the cathode, not a single alloy catalyst with methanol-tolerance. It may achieve a cathode cost down as well as high ORR activity of the cathode. In heterogeneous catalysts, one is the main catalyst showing high ORR performance such as Pt, PtNi, and PtCo, and the other one is the additional catalyst suppressing methanol effects (CO poisoning) such as PtRu and PtSn in the cathode. For the realization of the cathode electrode with heterogeneous catalysts, there are various combinations of heterogeneous catalysts. However, in this work, we chose two catalysts, Pt/C (carbon-supported Pt) and PtRu black, to distinctly manifest the effects of heterogeneous catalysts. Pt/C was selected for high ORR kinetic in the cathode, but didn't have any methanol-tolerant property. PtRu black were used as a protector to suppress the effect of methanol on Pt/C by helping the oxidation of CO-like species by adsorption of oxygen-containing species nearby the poisoned Pt surfaces [22–24], but had even lower ORR activity than Pt/C. PtRu/C (carbon-supported PtRu) may not be suitable in this electrode structure since nano-sized PtRu particles as a protector should be located nearby Pt particles on carbon. However, when small PtRu black was mixed with Pt/C, it might have made the electrode structure dense, and blocked the gas pores for the O<sub>2</sub> diffusion. Therefore, the introduction of particles with large size was needed to make gas pores enough, but should not have inhibited the catalytic activity of catalysts. Accordingly, PTFE particle as additional binder was together added to the electrode, which resulted in a decrease in the O<sub>2</sub> mass transfer overpotential by an increase in the secondary pores and its hydrophobic property.

We could have identified that the effects of methanol on Pt/C were reduced by simply mixing two catalysts together with small amount of binders, and Pt/C itself could have high ORR selectivity despite the presence of methanol in the cathode. Accordingly, using heterogeneous catalysts may make the cathode methanol-tolerant, and simultaneously keep the high ORR activity of bare Pt or metal alloy catalysts despite small total metal loading in the DMFC cathode. The heterogeneous composite electrode had not a general layered-structure but a 3-D structure composed of well-dispersed heterogeneous materials. The additional protector and binder enhanced Pt catalyst utilization during the ORR in the cathode despite methanol crossover, and the newly developed MEA showed high performance, especially at high methanol concentrations, although the total metal loading was reduced up to 0.5 mg cm<sup>-2</sup> in the cathode.

## 2. Experimental

Cathode catalyst ink for the heterogeneous composite structure was prepared from 60 wt.% Pt/C (Johnson Matthey), PtRu black (Johnson Matthey), 5 wt.% Nafion ionomer solution (Aldrich), 60 wt.% PTFE solution (Aldrich), and isopropyl alcohol (IPA) (Aldrich). The ink contained heterogeneous catalysts (Pt/C and PtRu black) and binders (Nafion ionomer and PTFE), and the weight ratio of Pt: PtRu was 3: 1. The first step in the new ink preparation method was the same as the traditional preparation method which involved mixing together 60 wt.% Pt/C, IPA, and Nafion ionomer solution. However, in the second step, PtRu black and PTFE (10 wt.% of PtRu black weight) were added to the catalyst ink prepared in the first step. All anode catalyst inks were made with 75 wt.% PtRu/C (Johnson Matthey), water, IPA, and Nafion ionomer solution. The prepared catalyst inks were then blended by ultrasonic treatment. Two MEAs (the MEA composed of heterogeneous composites and the traditional MEA) were fabricated by spraying the anode and cathode catalyst inks directly onto Nafion 115 membranes (DuPont). Nafion 115 membranes were used after the pretreatment in which the membranes were boiled in 3% hydrogen peroxide solution, 0.5 M H<sub>2</sub>SO<sub>4</sub>, and D.I. water at 80 °C in order. While the traditional MEA cathode had only Pt/C and Nafion ionomer, the MEA cathode composed of well-mixed Pt/C, Nafion ionomer, and the two additives (PtRu black and PTFE particles) formed a heterogeneous composite. To clearly manifest the effects of methanol crossover, total metal loading were only 0.5 mg cm<sup>-2</sup>, instead of excessive metal catalysts of 2 mg cm<sup>-2</sup>, for the all cathode electrodes. All anode electrodes had PtRu loadings of 2 mg cm<sup>-2</sup>.

(a) Traditional MEA (anode = PtRu of 2 mg cm<sup>-2</sup>)

Cathode = Pt of 0.5 mg cm<sup>-2</sup>

(b) MEA composed of heterogeneous composites (anode = PtRu of 2 mg cm<sup>-2</sup>)

Cathode = heterogeneous metal (Pt: PtRu = 3: 1) of 0.5 mg cm<sup>-2</sup>

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