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# Electrocatalyst composed of platinum nanoparticles deposited on doubly polymer-coated carbon nanotubes shows a high CO-tolerance in methanol oxidation reaction

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## ABSTRACT

High CO-tolerance and durability of anodic fuel cell electrocatalysts is one of the important factors for commercialization of direct methanol fuel cells (DMFCs). In this study, we describe the preparation of an electrocatalyst composed of poly[2,2'-(2,6-pyridine)-5,5'-bibenzimidazole] (PyPBI) and poly(vinylphosphonic acid) (PVPA) coated multi-walled carbon nanotubes (MWNTs) on which ~3 nm Pt nanoparticles (Pt-NPs) are deposited. The fabricated electrocatalyst shows 1.5-times higher CO tolerance compared to the commercial CB/Pt, which would be due to the wrapping of the CNTs with PVPA by the aid of PyPBI. Meanwhile, the electrocatalyst almost maintains its initial electrochemical surface area (ECSA) and mass activity of the methanol oxidation reaction (MOR) after 10,000 potential cycling in the range of 1–1.5 V vs. RHE. In contrast, the commercial CB/Pt shows almost a 50% loss in its ECSA and mass activity. These results indicate that the durability of the newly fabricated electrocatalyst is quite high and the obtained high CO-tolerance and durability are important for the design of an electrocatalyst for DMFC applications.

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## Introduction

The global energy crisis has forced us to develop sustainable energy sources and polymer electrolyte fuel cells (PEFCs) that have attracted much attention due to their higher energy

conversion efficiency, environmental friendliness and lower operating temperature [1–3]. Based on the different phase in the fuel, PEFCs are classified as hydrogen PEFCs and direct liquid fuel cells, which feed hydrogen and liquid fuels to the anode, respectively. Liquid fuels, such as borohydride [4–9]

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and methanol, received considerable attention because of easy storage and transportation compared to hydrogen. In Direct methanol fuel cells (DMFCs), the single cell offers an almost comparable cell voltage (1.19 V) to that of the hydrogen fuel cell (1.23 V) [10,11]. The DMFCs can be used as portable energy sources for electronic products due to their easy storage and high energy density ( $5.04 \text{ kWh L}^{-1}$ ) [12–14], while the DMFCs face three serious anodic problems; namely, i) CO poisoning of the electrocatalysts that is induced by the incomplete methanol oxidation reaction (MOR) [15–17] ii) low durability in the electrocatalysts due to the use of carbon black as the platinum (Pt) support in the commercial CB/Pt [18], and iii) a sluggish MOR [19].

Many researchers have tried to separately solve three problems. Alloying Pt with some transition metals (Ru [20–22], Au [23,24], Sn, [16,25]) was found to enhance the CO tolerance of the electrocatalysts due to their lower potential for forming the M–OH species, which react with the Pt–CO to remove CO from the Pt surfaces, while the transition metals are easily dissolved in the acidic medium, which is the practical environment in the real DMFC operation due to the use of Nafion membranes. Changing the Pt support to carbon nanotubes (CNTs) [7,26,27], graphene [28–30] or metal oxides [20,31,32] has proved to provide a higher durability. Also, we reported that the CO tolerance and durability of the electrocatalyst are simultaneously enhanced after coating with poly(vinylphosphonic acid) (PVPA) assisted by the poly[2,2'-(2,6-pyridine)-5,5'-bibenzimidazole] (PyPBI) due to the acid–base interaction between the –OH groups of PVPA and –NH groups on PyPBI [18,33,34]. The enhanced CO tolerance and durability are considered to be that the phosphorus on the PVPA weakened the binding energy between the Pt and CO species and the Pt–NPs sandwich structures, respectively. Nevertheless, the mass activity of the coated electrocatalyst decreased by 35% due to the coverage of the Pt–NPs by the PVPA, which negatively affected the methanol adsorption on the Pt surfaces [33]. Thus, coating the Pt–NPs with PVPA did not enhance the sluggish MOR.

In this study, we synthesized a Pt electrocatalyst that was deposited on doubly-polymer-coated multi-walled carbon nanotubes (MWNTs) as shown in Fig. 1, in which the MWNTs are coated with PyPBI and then with PVPA. Briefly, the MWNTs were dispersed in a solvent by the aid of PyPBI due to the  $\pi$ – $\pi$  interaction between the MWNTs and the PyPBI [35,36], then coated with the PVPA based on the acid–base interaction. Finally, the Pt–NPs were deposited onto the surfaces of the doubly polymer-coated MWNTs. Importantly, the Pt–NPs are not covered by any polymers in this structure and the PVPA in the electrocatalyst is expected to enhance the CO tolerance of

the electrocatalyst. The CO tolerance during the MOR of the synthesized electrocatalyst was compared with that of the commercial CB/Pt and the previously reported MWNT/PyPBI/Pt/PVPA [37].

## Experimental section

### Materials and reagents

2-Propanol, hydrogen hexachloroplatinatehexahydrate ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ), ethylene glycol (EG), *N,N*-dimethylacetamide (DMAc) and PVPA (30 wt%) were purchased from Wako Pure Chemical Co., Ltd. The MWNTs with ~an 20 nm diameter were provided by the Nikkiso Corp. The Pt–NPs-deposited CB (CB/Pt) catalyst was purchased from Tanaka Kikinzoku Kogyo K. K., in which the Pt loading on the CB was 37.5 wt%. A Nafion solution (5 wt%), perchloric acid ( $\text{HClO}_4$ , 70%) and methanol were purchased from Sigma–Aldrich, EMD Millipore Chemical Co., Ltd., and Kanto Chemical Co., Inc., respectively. Poly[2,2'-(2,6-pyridine)-5,5'-bibenzimidazole] (PyPBI) was synthesized according to a previous report [38]. The Milli-Q water ( $18.2 \text{ M}\Omega \text{ cm}$ ) was used to prepare the solutions during all the experiments and all the chemicals were used as received without any further purification.

### Synthesis of MWNT/PyPBI/PVPA/Pt

Briefly, the MWNTs (10 mg) were dispersed in DMAc (20 mL) to which 10 mg of the PyPBI dissolved in 10 mL of DMAc was added at room temperature, then sonicated for 1 h to obtain a solution of the composite, MWNT/PyPBI, which was then collected by filtration followed by rinsing with DMAc. The obtained black powder was dried under vacuum overnight at  $60^\circ\text{C}$  to completely remove the solvent. MWNT/PyPBI (10 mg) was dispersed in an EG aqueous solution ( $v/v = 3:2$ ) to which 1 mL of the PVPA (30 wt%) was added and stirred for 10 min. The mixture was filtered and dried under vacuum overnight at  $60^\circ\text{C}$ . Finally, the Pt loading was carried out by the reduction of the  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  in an EG aqueous solution ( $v/v = 3:2$ ) at  $140^\circ\text{C}$  for 30 min under an  $\text{N}_2$  atmosphere. The obtained product was filtered, washed, then dried overnight under vacuum at  $60^\circ\text{C}$  to obtain the MWNT/PyPBI/PVPA/Pt.

### Materials characterization

The X-ray photoelectron spectroscopy (XPS) was carried out using an AXIS-ULTRA<sup>DL</sup> (Shimadzu) instrument. The pressure in the XPS analysis chamber was maintained at  $10^{-9}$  Pa. For the

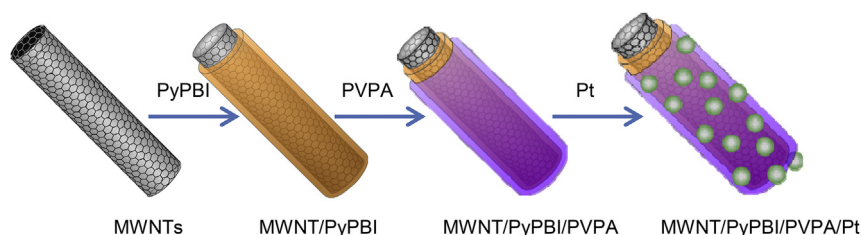


Fig. 1 – Schematic illustration for the preparation of the MWNT/PyPBI/PVPA/Pt electrocatalyst.

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