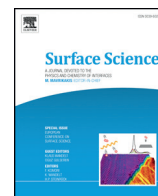




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 2 Pd@Pt(2 ML)/C Cathode Catalysts in Polymer Electrolyte Fuel Cells  
 3 during Potential-step Operating Processes Characterized by In-situ  
 4 Time-resolved XAFS

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## ABSTRACT

The dynamic structural and electronic transformations of Pt/C, Pd@Pt(1 ML)/C, Pd@Pt(2 ML)/C cathode catalysts 23  
 in polymer electrolyte fuel cells (PEFCs) during the potential-step operating processes between 0.4 and 1.4 V<sub>RHE</sub> 24  
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 of the Pt/C, Pd@Pt(1 ML)/C and Pd@Pt(2 ML)/C cathode catalysts. 32

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## 1. Introduction

At Berkeley in 1964 Prof. Gabor A. Somorjai started working with platinum in the hope of learning how and why it is so good at carrying out so many chemical surface reactions. It was first used in 1823 to produce flames, instantly aiding the combustion of hydrogen in air (H<sub>2</sub> + ½O<sub>2</sub> → H<sub>2</sub>O). Today, platinum is at the heart of the catalytic converter that cleans the exhaust gases from automobiles, and the metal produces high-octane gasoline from naphtha. Surface science and catalysis developed by the tremendous achievements of Prof. Somorjai on Pt single crystal surfaces and nanoparticles have been applied to the systems with more complex surfaces including electrochemistry, biointerfaces corrosion, etc. To probe real catalysts more fully, studies advanced from work on single crystal surfaces of metals to work on nanoparticles, Prof. Somorjai says this is the ongoing third phase of his research. The outstanding and highly suggestive

achievements of Prof. Gabor A. Somorjai have had great effect and big impact on both academic and industrial researches in the world.

In autumn 2014 Toyota Motor Corporation launched the world's first commercially available hydrogen fuel-cell vehicle, "Toyota Mirai" by using Pt/C nanoparticle catalysis. Polymer electrolyte fuel cells (PEFCs) (converter of the chemical reaction energy, H<sub>2</sub> + ½O<sub>2</sub> → H<sub>2</sub>O, to electrochemical energy (electric power)) have the potential to provide clean energy for powering vehicles, but improved performance and durability are needed for wide-spread commercialization [1–15]. There is still a lot of fundamental research required in order to benefit from the ultimate potential of PEFCs. In particular, our understanding of the chemical reactions and structural behaviors of cathode nanoparticle surfaces governing the generation of electricity from PEFCs and the long-term durability of cathode catalysts under the harsh PEFC conditions is still incomplete [1–15]. Specifically, the active structures, reactions mechanisms, and degradation mechanisms of PEFC cathode catalysts in-situ under the PEFC operations are still "a black box", which must be understood more thoroughly for development of next-generation PEFCs for automobiles.

However, there are few suitable in-situ spectroscopic techniques to elucidate the structures and chemical states of cathode catalysts with

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nanometer dimensions inside membrane electrode assembly (MEA) of PEFC under the operating conditions, where the wet, heterogeneous and multiphase reaction field involving catalyst nanoparticles, carbons, ionomers, water and fuel gases prevents in situ measurements of the MEA cathode catalysts by spectroscopic techniques. X-ray absorption fine structure (XAFS) is an element-selective powerful tool for in-situ investigation of the local coordination structures and oxidation states of supported metal nanoparticle catalysts under the reaction conditions [16–36]. In-situ potential-dependent XAFS analysis at Pt L<sub>III</sub>-edge can provide atomic-scale information on the structure and composition and their transformations of Pt surface layers in MEA cathode catalysts [29–33]. In-situ time-resolved XAFS for PEFCs has recently been developed to elucidate the dynamic transformations of structures and electronic states of Pt/C, Pt<sub>3</sub>Co/C and Pt<sub>3</sub>Ni/C cathode catalysts and to decide elementary steps and their rate constants for the chemical events at the catalyst surfaces [20,28,30,34–36]. The cathode degradation mechanism has also been studied to improve the MEA durability [37–40]. To image the spatially-heterogeneous cathode degradation, recently, two-dimensional and three-dimensional micro and nano-scale observations of PEFCs [41–44] and functional materials [45–51] using X-rays have also received much attention.

In comparison to the constant potential hold process, Pt dissolution in MEA Pt/C cathode catalysts is 3–4 times higher in voltage cycling, which is a major problem because automobiles require continual repetition of the power-on/off processes with rapid changes in cell voltages for driving cars [52]. Although the operation potential of PEFCs is usually 0.6–1.0 V<sub>RHE</sub> (potential vs. RHE), ramping of the potential to open circuit voltage (OCV) around 1.0 V<sub>RHE</sub> during the power-on/off drive, steep ramping to the higher potentials (>1.4V<sub>RHE</sub>) by start-up and shut-down processes and possible undesirable ramping to the higher potentials (>1.1 V) at unidentified places of MEA cathode catalysts with ill-defined heterogeneous environments may promote the Pt leaching and detachment, resulting in degradation of catalyst performances.

Among a variety of approaches to reduce Pt loadings and to improve performance and durability of cathode catalysts, a promising approach is deposition of thin Pt overlayers on less or non-noble metal substrates to make Pt surface-enriched nanoparticles called as skin, skeleton and core-shell structures, where Pt can be sufficiently used and hence catalyst cost can be reduced [53–60]. Among examined metal core substrates (Ru, Ir, Rh, Au and Pd) for Pt monolayer shell, Pd showed the highest oxygen reduction reaction (ORR) activity. However, the Pt surface-specific ORR activity in the bimetallic systems has been demonstrated to depend on a variety of key issues, such as nanoparticle size and shape (plane), surface roughness, compressive strain effect (bond distance), downward Pt d-band center, ligand effect (electron transfer), metal-oxygen bond strength, etc. [28,30,34] Although many investigations on electrochemical surface events have been performed for both model systems and practical PEFCs, the genesis and fundamental issues for the ORR activity and durability of Pt-based cathode catalysts such as the potential-dependent structures and electronic states of cathode catalyst surfaces, the structural kinetics of the dynamic transformations of catalysts in transient potential operating processes, and the kinetic factors for the Pt dissolution are not clearly understood yet.

In this paper, we report the results of in-situ time-resolved Pt L<sub>III</sub>-edge XAFS analysis for Pt/C, Pd(core)-Pt(1 ML shell)/C (denoted as Pd@Pt(1 ML)/C) and Pd(core)-Pt(2 ML shell)/C (denoted as Pd@Pt(2 ML)/C) cathode catalysts in PEFC MEAs during potential-step operating processes between 0.4 V<sub>RHE</sub> and 1.4 V<sub>RHE</sub>. Their performances depend on the number of Pt shell layers, but there are controversy reports on the activity and the activity order for Pt monolayer shell, Pt two monolayers, and Pt three monolayers compared to a standard Pt/C. It is still difficult to calculate and simulate theoretically the property and reactivity of the shell surfaces. Thus, direct spectroscopic characterization of the core-shell cathode catalysts has been needed. The in-situ time-resolved XANES and EXAFS spectra revealed the transient response transformations of structures and electronic states of the Pt/C, Pd@

Pt(1 ML)/C and Pd@Pt(2 ML)/C in the potential-step operations. The in-situ XAFS analysis also revealed the potential-dependent restructuring of the catalyst surfaces. The rate constants for the electronic and structural transformations of the Pt/C, Pd@Pt(1 ML)/C and Pd@Pt(2 ML)/C in the potential-step operating processes were determined and compared in relation to the origin of the ORR activity and durability.

## 2. Material and methods

### 2.1. Catalyst fabrications

The Pd core-Pt shell (1 ML and 2 ML) catalysts were prepared by a similar method to that reported by Zhang et al. [57], where Pt skin layers were deposited on Pd/C by the galvanic displacement of Cu monolayer underpotentially deposited on Pd core surfaces by Pt.

#### 2.1.1. Preparation of Pd@Pt(1 ML)/C (Pt 15wt%, Pd 25wt%)

0.1 M CuSO<sub>4</sub> was dissolved into 0.1 M H<sub>2</sub>SO<sub>4</sub> (100 mL), to which solution 1.00 g of 30wt% Pd/C purchased from N. E. CHEMCAT was dispersed under stirring for 30 min. The solution was applied to current until the whole quantity of 175 Coulomb(C) at 0.32 V vs RHE. The slurry solution was filtered and the precipitates were washed with deionized water 10 times to remove Cu<sup>2+</sup> ions from the solution. The obtained sample was added to 0.1 mM H<sub>2</sub>PtCl<sub>4</sub> in H<sub>2</sub>SO<sub>4</sub> and stirred for 1 h in a N<sub>2</sub> atmosphere to replace the Cu monolayer by Pt monolayer. The slurry solution was filtered and washed with deionized water 10 times. The obtained catalyst was dried at 313 K for 1 day.

#### 2.1.2. Preparation of Pd@Pt(2 ML)/C (Pt 20wt%, Pd 20wt%)

1.00 g of 25wt% Pd/C purchased from N. E. CHEMCAT was dispersed into 100 mL of 0.1 M CuSO<sub>4</sub>/0.1 M H<sub>2</sub>SO<sub>4</sub> under stirring for 30 min. The slurry solution was applied to current until the whole quantity of 100 C at 0.32 V vs RHE and filtered in a N<sub>2</sub> atmosphere. The obtained precipitates were washed with deionized water 10 times. The obtained sample was added to 0.1 mM H<sub>2</sub>PtCl<sub>4</sub> in H<sub>2</sub>SO<sub>4</sub> and stirred for 1 h in a N<sub>2</sub> atmosphere to replace the Cu monolayer by Pt monolayer. The slurry solution was filtered and washed with deionized water 10 times. The obtained sample was dispersed into 100 mL of 0.1 M CuSO<sub>4</sub>/0.1 M H<sub>2</sub>SO<sub>4</sub> under stirring for 30 min. The slurry solution was applied to current until the whole quantity of 150 C at 0.32 V vs RHE and filtered in a N<sub>2</sub> atmosphere. The obtained precipitates were washed with deionized water 10 times. The obtained sample was added to 0.1 mM H<sub>2</sub>PtCl<sub>4</sub> in H<sub>2</sub>SO<sub>4</sub> and stirred for 1 h in a N<sub>2</sub> atmosphere to replace the Cu monolayer by Pt monolayer again. The slurry solution was filtered and washed with deionized water 10 times. The obtained catalyst was dried at 413 K for 1 day.

### 2.2. Cyclic voltammetry measurements

The cyclic voltammograms (CVs) were recorded in H<sub>2</sub> (anode) and N<sub>2</sub> (cathode) flows at 5 mV/s in the range 0.05–0.9 V at 353 K. The electrochemical surface areas (ECSAs) of the cathode catalysts were calculated by charge density of hydrogen adsorption on a Pt surface (210 μC/cm<sup>2</sup><sub>Pt</sub>) in the hydrogen underpotential deposition region (0.05 V– ca. 0.35 V of the onset of the double-layer region).

### 2.3. MEA and RDE operations

We used KB(Ketchenblack)-supported Ru (0.6 mg cm<sup>-2</sup>) anode (Ru/C (43.1 wt%)) to avoid interference against XAFS measurements of Pt/C and Pd@Pt/C cathodes. Nafion NR-212 was used as electrolyte membrane in MEAs. The electrode catalyst areas in the MEAs were 3 × 3 cm<sup>2</sup>. The MEAs were conditioned by 150 aging cycles of galvanostatic current steps every 6 s from open circuit voltage (OCV) to a potential near 0.3 V<sub>RHE</sub> in H<sub>2</sub> and air operating atmospheres. CV measurements

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