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Oxygen partial pressures on gas-diffusion layer surface and gas-flow channel wall in polymer electrolyte fuel cell during power generation studied by visualization technique combined with numerical simulation

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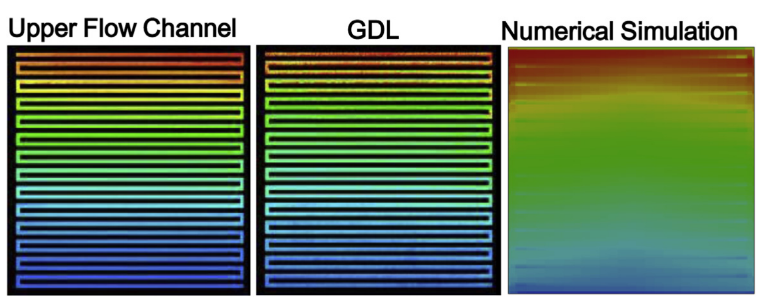
HIGHLIGHTS

- $p(O_2)$ was visualized at the GDL and the upper channel wall of a running PEFC.
- Two different oxygen-sensitive luminescent dye films were used.
- Different distributions of $p(O_2)$ were seen at the two locations inside a PEFC.
- A numerical calculation was carried out to understand the reactions inside the MEA.
- Water distribution influenced the current density and $p(O_2)$ in the MEA.

GRAPHICAL ABSTRACT



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ABSTRACT

Visualization of the oxygen partial pressures was carried out at the surface of a gas diffusion layer (GDL) for the first time together with the upper part of the gas-flow channel of the cathode of a running polymer electrolyte fuel cell (PEFC) using two different oxygen-sensitive luminescent dye films. The visualized distributions of the oxygen partial pressures at the GDL and the upper gas-flow channel during the PEFC operation were very different in a conventional test cell. The change in the distribution of the oxygen partial pressures was observed by changing the oxygen utilization, which should be connected with the reactive locations in the membrane-electrode assembly (MEA). A numerical calculation was carried out to understand the distributions of water and current density inside the MEA. The water

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Gas diffusion layer
Gas-flow channel
Oxygen reduction reaction
Numerical modeling

distribution inside the MEA was confirmed to strongly affect the distributions of the current density and the oxygen /partial pressure.

1. Introduction

Polymer electrolyte fuel cell (PEFC) is a new energy source expected to be widely used with its high power density and cleanliness. Although PEFCs have many advantages compared with current internal-combustion engines, the cost reduction and the improvement of durability/reliability are still needed. The development of new materials for the cell components and suitable cell designs are required. Adequate operation modes also need to be researched. For the improvement of PEFCs via the issues pointed out above, it is important to reveal the distribution of chemical species (O_2, H_2, H_2O, CO_2, H_2O_2, etc.) and physical parameters (temperature, current density, etc.) in a PEFC under the operating conditions and to feedback the so-obtained data into the designs of the membrane electrode assembly (MEA) and the PEFC itself. The visualization inside the PEFC, therefore, is essential.

Recently, visualization studies inside PEFCs have been focused mainly on liquid water to understand the flooding and plugging, which could occur in the catalyst layer, gas diffusion layer (GDL), and gas-flow channels to block supply gases. The water visualizations have been carried out by using various technologies: direct optical visualization [1–6], neutron radiography imaging [7–14], X-ray imaging [15–18], and magnetic resonance imaging (MRI) [19–21]. Those studies revealed that the generated water plays a key role in the performance and stability of the PEFCs. Now, the visualization of other chemical species, such as oxygen, is expected.

Our research group has developed a nondestructive, real-time/space visualization system for oxygen partial pressure ($p(O_2)$) at the cathode of PEFCs [5,6,22–24] and a direct methanol fuel cell (DMFC) [25] under the operating conditions using a chemical probe for $p(O_2)$, "platinum-tetrakis(pentafluorophenyl)porphyrine (PtPP)" (Fig. 1(a)) [26]. In the previous papers, $p(O_2)$ was visualized only on the upper channel walls. In this paper, the distributions of $p(O_2)$ at the GDL surfaces, together with that on the upper channel walls, at the cathode were visualized for the first time using two different dyes: regularly-used PtPP and a new probe "platinum-tetrakis(pentafluorophenyl)porpholactone (PtPL)" (Fig. 1(b)) [27,28]. Experimentally, by using those dyes, different $p(O_2)$ distributions were visualized between at the GDL surface and at the upper position of a gas-flow channel.

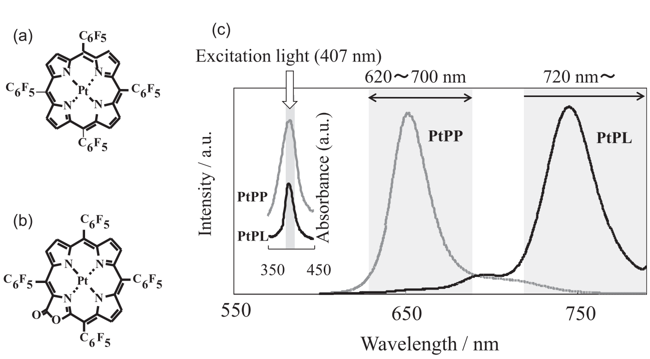

Fig. 1. (a) Chemical structure of platinum-tetrakis(pentafluorophenyl)porphyrine (PtPP). (b) Chemical structure of platinum-tetrakis(pentafluorophenyl)porpholactone (PtPL). (c) Absorption spectrum and luminescence spectra of PtPP and PtPL.

For understanding the oxygen reduction reaction (ORR) in the MEA, or the reaction current distribution, we also carried out numerical and simulation inside the PEFC. To evaluate the performance of PEFCs speedily and accurately, our research group has developed a simulation tool including the macroscopic parameters of gas and heat transport in flow field and MEA characteristics such as electrochemical kinetics in the catalyst layer and proton/water transport in the electrolyte membrane [29]. In this paper, experimental and simulation data are carefully compared to demonstrate a new evaluation strategy for understanding the reaction distributions inside a PEFC. The simulation results gave clear explanations for the change of the $p(O_2)$ distributions under different cell-operation conditions.

2. Experimental

2.1. Oxygen sensitive dye films and see-through PEFC

Toluene solutions of PtPP (Fig. 1(a)) and PtPL (Fig. 1(b)) were mixed with an oxygen-permeable polymer, poly(1-trimethylsilyl-1-propyne) (PMSP) at room temperature as previously reported [27,28]. Absorption and emission spectra of PtPP and PtPL are shown in Fig. 1(c). Both PtPP and PtPL have the absorption peaks approximately at 400 nm, but have different emission peaks at 650 and 750 nm, respectively. Therefore, $p(O_2)$ at two positions inside a cell can be visualized by using a single light source (407 nm).

Commercial MEAs with the Pt loadings of 0.4 mg cm^{-2} both on the anode and the cathode were used. The catalyst area was 52 mm × 52 mm. For the electrolyte membrane with a thickness of 30 μm, perfluorosulfonic acid ionomers were employed. On a gas diffusion layer with a thickness of approximately 200 μm, a microporous layer (MPL) with a thickness of several micrometers was attached.

A see-through cell with a transparent window was used for visualizing $p(O_2)$ in the PEFC under the operating condition. The endplate of a "Standard Cell of Japan Automobile Research Institute (JARI standard cell)" [30], a commonly-used cell employed for the development of PEFCs, at the cathode side was replaced by an acrylic plate to visualize inside the cell (Fig. 2(a)) [24,31]. PtPL was sprayed on a perfluoroalkoxy (PFA) film (film thickness = 2 μm), and the film was inserted between the endplate and the current collecting ribs. In this way, $p(O_2)$ on the upper wall of the gas-flow channel was visualized. On the other hand, PtPP was sprayed uniformly on the GDL surface at the cathode with the average thickness of 4 μm. The

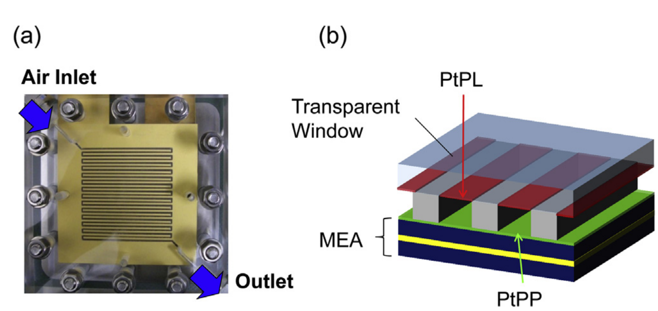

Fig. 2. (a) Photograph of a see-through cell. (b) Schematic drawing of a flow field with two dye films.