



Performance of practical-sized membrane-electrode assemblies using titanium nitride-supported platinum catalysts mixed with acetylene black as the cathode catalyst layer



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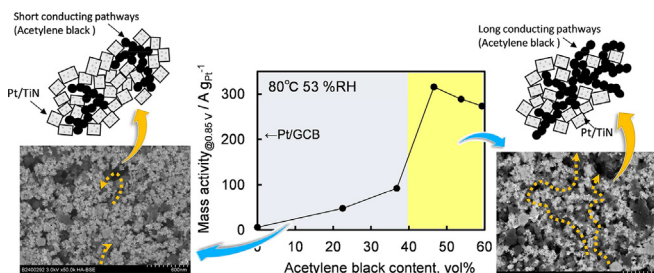
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HIGHLIGHTS

- We fabricated practical-sized MEAs with Pt/TiN + acetylene black (AB) cathodes.
- For AB content over 37 vol%, the electronic percolation threshold was exceeded.
- The cell resistance decreased drastically with percolated AB networks.
- The ORR activity of the MEA using Pt/TiN + 47 vol% AB exceeded that of Pt/GCB.
- The O₂ mass transport overvoltage drastically decreased with percolated AB networks.

GRAPHICAL ABSTRACT



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ABSTRACT

The performance of practical-sized membrane-electrode assemblies (MEAs) using titanium nitride-supported platinum (Pt/TiN) as the cathode catalysts was evaluated with the use of a practical single cell designed for microscale combined heat and power (CHP) applications. The performance can be controlled by adding acetylene black (AB), with the behavior being dominated by the percolation law. The electrical resistance of the MEAs drastically decreased for AB contents greater than 37 vol%. The Pt utilization percentage was close to 100% for Pt/TiN with percolated AB networks. It was also found that the percolated AB networks supplied effective gas transport pathways, which were not flooded by generated water, thus enhancing the oxygen mass transport. The practical-sized MEA using Pt/TiN + 47 vol% AB showed 1.5 times greater mass activity and a comparable performance under a practical operating condition for micro-CHP applications, compared with the MEA using a commercial graphitized carbon black-supported platinum catalyst.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) are attractive electric

power generation systems with low emissions, high energy efficiency and low operating temperature; as such, they are promising for automotive and stationary-power applications. A microscale combined heat and power (micro-CHP) PEFC system, “Ene-Farm,” has been commercialized in 2009 in Japan for residential use, and its popularity has been increasing [1]. However, further cost reductions of the system are required to make it a widespread technology. One of the factors that contributes to increasing the cost is the complicated system for mitigating the degradation of the cathode catalyst in the PEFC stack [2]. Enhancing the durability of the cathode catalyst is a major issue for PEFC micro-CHPs.

Carbon black-supported platinum (Pt/CB) is widely used as a PEFC cathode catalyst material, because CB has many desirable properties as a catalyst support, for example, high electronic conductivity, high surface area, low cost and easy dispersion in slurries. However, carbon has an intrinsic problem in terms of the stability under PEFC cathode operating conditions. It is thermodynamically oxidizable to CO_2 at 0.207 V vs. the standard hydrogen electrode (SHE) [3]. Carbon corrosion is also accelerated by the presence of Pt and high potentials during start/stop cycles or fuel starvation [4–6] and leads to decreasing Pt utilization due to aggregation of Pt particles, as well as detachment of Pt from the support [7–10].

Development of non-carbon cathode support materials is thus necessary; the needed properties are high electrochemical stability at high potentials, high chemical stability at low pH, high electronic conductivity and high surface area. SnO_2 and metal-doped SnO_2 have been widely studied as corrosion-resistant catalyst support materials for PEFC cathodes [11–16]. In our group, Pt/Sb-doped SnO_2 and Pt/Nb-doped SnO_2 with carbon black-like fused aggregate structures, which are beneficial for the lowering of the contact resistance between doped SnO_2 particles, exhibited higher performance than Pt/CB, as well as enhanced stability at high potentials [15,16]. However, slight dissolution of Sn at potentials below 0.4 V has been pointed out in the literature [15,16]. TiO_2 shows excellent chemical and electrochemical stability in acidic media, but the electronic conductivity appears to be insufficient. It is well known that the electronic conductivity of titanium-based ceramics originates from the presence of Ti^{3+} ions [17]. Ti^{3+} ions can be generated by creating oxygen deficiencies or by introducing appropriate donor dopants into the TiO_2 lattice; such materials have been studied as supports for PEFCs [18–20]. Titanium nitride (TiN) is also well known to be a conductive titanium-based ceramic, with more than a factor of ten greater electronic conductivity compared to those of metal oxides or carbons [21], in addition to chemical and electrochemical stability in acidic media [21,22]. Recently, Avsarala et al. demonstrated that a titanium nitride-supported Pt catalyst (Pt/TiN) outperformed a Pt/CB catalyst in catalytic activity for the same Pt particle size and loading [23]. However, they reported that the durability improvement of Pt/TiN compared to Pt/CB was minor, because the increased durability of Pt/TiN, gained from the catalyst support resistance to corrosion, was seen to be offset by an increase in the rate of Pt agglomeration [24]. In our previous study, Pt/TiN catalysts with highly preferred orientation of Pt nanoparticles on the TiN nanoparticles showed higher ORR activity and durability compared to Pt/CB with the thin-film rotating disk electrode (RDE) technique in acidic solutions at room temperature [25,26].

The catalyst layer of membrane-electrode assemblies (MEAs) for PEFCs is essentially the gas diffusion electrode, which needs the practical electrical conductivity and gas diffusivity, besides the catalytic activity of the catalyst itself, in order to realize the high-performance electrode. In the present work, we investigated the performance of practical-sized MEAs using highly oriented Pt nanoparticles supported on TiN, without any aggregated structure, with the use of a practical single cell designed for micro-CHP

applications, controlling the electrically conducting pathways and gas transport pathways in the cathode catalyst layer by adding acetylene black (AB) with a fused aggregate structure.

2. Experimental

2.1. Preparation of Pt/TiN catalysts

Pt/TiN catalysts were prepared with the same method described previously [25,26]. Briefly, TiN nanoparticles with $40 \text{ m}^2 \text{ g}^{-1}$ were synthesized with a radio frequency (RF) plasma method (Nisshin Engineering Co.). Pt nanoparticles were deposited by the colloidal method [27–29]. The powder obtained was heat-treated at $400 \text{ }^\circ\text{C}$ in a 1% H_2 -containing N_2 atmosphere for 2 h and then quickly cooled to room temperature under the same atmosphere.

The morphology of the catalysts was observed by transmission electron microscopy (TEM, H-9500, Hitachi High Technologies Co.). The average particle diameters and size distributions of Pt were confirmed to be $4.6 \pm 1.6 \text{ nm}$ from the TEM images. The Pt loading of the catalyst was measured by use of an inductively coupled plasma-mass spectrometric analyzer (ICP-MS, 7500CX, Agilent Technologies Inc.), after dissolving these Pt catalysts in hot aqua regia and were found to be 10 wt%.

2.2. Preparation of MEAs

Pt/TiN + AB catalyst layer was fabricated by a spray method. The Pt/TiN catalyst was mixed with AB (DENKA BLACK[®], Denki Kagaku Kogyo K. K.), perfluorosulfonic acid (PFSA) solution (equivalent weight = 909 g eq^{-1} , Asahi Glass Co., Ltd.) and solvent (mixture of water and ethanol). The volume ratio of PFSA binder (dry basis) to TiN and AB (PFSA binder/(TiN + AB)) was adjusted to 0.48. The catalyst paste obtained was directly sprayed onto the polymer electrolyte membranes (GORE-SELECT[®], 30 μm , W. L. Gore & Associates Inc.) on a hot plate maintained at $60 \text{ }^\circ\text{C}$ to form the cathode catalyst layers. Graphitized carbon black-supported platinum (Pt/GCB) (TEC10EA50E, Tanaka Kikinokogyo K. K. (TKK)) was evaluated as a reference catalyst, because GCB has been reported to exhibit high stability at high potentials [30]. The cathode catalyst layer, which contained PFSA binder of 0.8 volume ratio to GCB, was prepared in the same manner described above. The volume ratio of the PFSA binder was adjusted considering the difference of the surface area of the materials (TiN: $40 \text{ m}^2 \text{ g}^{-1}$, AB: $68 \text{ m}^2 \text{ g}^{-1}$, GCB: $150 \text{ m}^2 \text{ g}^{-1}$). The anode catalyst layers were fabricated in a similar manner using PtRu/CB (TEC61E54, TKK), PFSA solution and solvent (mixture of water and ethanol). The Pt loadings of the anode and cathode were 0.1 and 0.05 mg cm^{-2} , respectively. The Pt loading of the cathode was about ten times lower than the amount widely used, as a target for the mass-market penetration of fuel cell vehicles [31], whereas the Pt loading of the anode was maintained at the standard 0.1 mg cm^{-2} in order to avoid any effects of low Pt loading for the anode. The catalyst-coated membrane (CCM), having a practical-sized active area (196 cm^2) was heated at $120 \text{ }^\circ\text{C}$ for 30 min and sandwiched between two gas diffusion layers with microporous layers (CARBEL-CL[®], W. L. Gore & Associates, Inc.) to form the MEA. The MEA was mounted in a practical single cell designed for micro-CHP PEFC applications (Fig. 1). The single cell is equipped with carbon plates having a multi-channel serpentine flow field designed such that the pressure drop is lower than 5 kPa at $1 \text{ dm}^3 \text{ min}^{-1}$ (anode) and $2 \text{ dm}^3 \text{ min}^{-1}$ (cathode), because it is necessary for micro-CHP PEFCs to be operated at near-ambient pressure in order to reduce the power consumption of the air blowers.

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