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Load cycle durability of a graphitized carbon black-supported platinum catalyst in polymer electrolyte fuel cell cathodes

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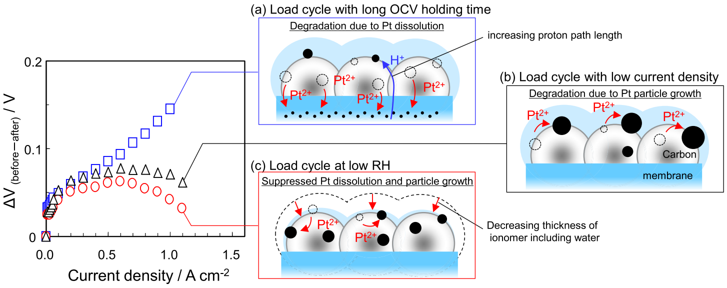
HIGHLIGHTS

- The degradation of Pt is suppressed by FCV drive cycles with short OCV holding times.
- The oxidation of Pt depends on the OCV holding time and RH.
- Load cycles with long OCV accelerate Pt dissolution in the CL near the membrane.
- Load cycles with low current density accelerate the Pt particle growth.
- Load cycles at low RH suppress the dissolution and particle growth of Pt.

GRAPHICAL ABSTRACT



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ABSTRACT

We focus on Pt degradation occurring during fuel cell vehicle (FCV) combined drive cycles involving load and open circuit voltage (OCV) just after startup and during idling. Load cycle durability is evaluated as a function of OCV/load holding time, load rate and relative humidity (RH) with a graphitized carbon black-supported platinum catalyst (Pt/GCB) in the cathode. The degradation of Pt/GCB is suppressed for shorter OCV holding times, lower load rates and lower RH. Scanning ion microscopy (SIM) images of membrane cross-sections indicate that the amount of Pt deposited in the membrane decreases during drive cycles involving load with short OCV holding times. Investigations of the Pt distribution in the cathode catalyst layer (CL) by using scanning TEM-EDX show that the dissolution of Pt is suppressed on the membrane side in the CL. The Pt dissolution is accelerated by the high Pt oxidation due to the long OCV holding time. A load cycle with both long OCV holding time and low load inhibits the Pt^{2+} migration into the membrane but accelerates the Pt particle growth due to electrochemical Ostwald ripening; meanwhile, a load cycle with long OCV holding time at lower RH prevents both the Pt dissolution and particle growth.

1. Introduction

Polymer electrolyte fuel cells (PEFCs) used in fuel cell vehicles (FCV) are power generation devices with low environmental impact, having features such as high theoretical efficiency and zero CO_2 emissions. One of the main impediments to the expansion of the FCV market is the high cost of the FC engine system as compared to the internal-combustion engine, e.g., because the PEFC electrodes still require a large amount of Pt as the electrocatalyst. In addition, it is known that both the carbon-supported Pt

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electrocatalyst and the membrane are degraded under various types of FCV operating conditions such as startup/shutdown [1–4], load cycling [5,6], and idling [7,8]. It is important to increase the durability of the electrocatalyst under these operating conditions in terms of decreasing the FCV life cycle cost. Therefore, we particularly focused on load cycling, which accelerates the degradation of the Pt nanoparticles (NPs). Since load cycling leads to the degradation of Pt NPs due to dissolution [9–11] and particle growth [12,13], many researchers have been trying to resolve this issue. It is well known that the degradation of Pt NPs is evaluated by potential cycling, which simulates load cycling, using a potentiostat. The degradation of Pt has been intensively investigated under various potential cycling conditions by Mitsushima et al. [14–17]. According to these papers, the degradation of Pt under potential cycling is accelerated by a high positive-going rate and a low negative-going rate [15], increasing temperature and decreasing pH [16]. Moreover, other researchers have also reported the degradation of Pt under various potential cycling regimes [18–20]. Uchimura et al. have reported that the degradation of Pt was accelerated to a greater extent under potential cycling involving asymmetric triangular profiles with lower negative-going rates compared with those with low positive-going rates [18]. Yasuda et al. found that Pt deposition in the membrane was accelerated by the presence of hydrogen transported through the membrane from the anode. This deposition was also affected by the presence of oxygen in the cathode [20]. Kongkanand et al. also concluded that the electrooxidation of Pt is accelerated more by the presence of oxygen than the presence of nitrogen at lower potentials [21]. The degradation of Pt NPs under potential cycling is primarily caused by Ostwald ripening and place exchange. Ostwald ripening leads to increased Pt particle size, because the smaller particles have a higher surface energy and thus are less stable than the larger particles [5,17,20,22]. Oxygen atoms adsorbed on the Pt surface can enter the Pt lattice by place exchange at potentials greater than 1.1 V [23–26]. These studies have revealed that the degradation of Pt during potential cycling is correlated strongly with the oxidation of Pt NPs. However, it has been suspected that the actual degradation of Pt is different from that observed with potential cycling with H_2/N_2, because the FCV operating condition includes load cycling with H_2/air.

In this research, we investigated the degradation of the electrocatalyst in terms of Pt dissolution, Pt deposition, and Pt particle growth in both the catalyst layer (CL) and membrane under various load cycle conditions, as a function of the open circut voltage (OCV)/load holding time, current density range, and RH. Electrochemical evaluation was carried out with cyclic voltammetry (CV) and current–potential (*I–E*) polarization curve measurements. The electrodes were analyzed by transmission electron microscopy (TEM), scanning ion microscopy (SIM) and scanning transmission electron microscopy–energy dispersive X-ray spectroscopy (STEM-EDX) before and after the load cycling evaluations. These results provide information on the degradation of Pt under realistic FCV operating conditions.

2. Experimental

2.1. Preparation of membrane-electrode assembly (MEA)

Uniformly catalyst-coated membranes (CCM) were prepared in the same manner as in our previous research [3,4]. The catalyst pastes were prepared with 30 wt% Pt-loaded graphitized carbon black for the cathode (Pt/GCB, TEC10EA30E, Tanaka Kikinzoku Kogyo K. K.) or 46 wt% Pt-loaded carbon black for the anode (Pt/CB, TEC10E50E, Tanaka Kikinzoku Kogyo K. K.), mixed with ionomer (ion exchange capacity, IEC $= 0.99$ meq g^{-1}, Nafion ionomer DE521, E. I. Du Pont de Nemours & Co., Inc.), ethanol, and pure water by use of a planetary ball mill (P-6, Fritsch GmbH) for 30 min. The mass ratio of Nafion binder (dry basis) to carbon black (Nafion binder/carbon) was adjusted to 0.7. To prepare the uniform CCM, the catalyst pastes were directly sprayed onto a Nafion membrane maintained at 55 °C (NRE 211, 25 μm thickness, E. I. Du Pont de Nemours & Co., Inc.) with the pulse-swirl-spray technique (PSS, Nordson Co. Ltd.), and then dried at 60 °C in an electric oven. The CCMs were annealed by hot-pressing at 140 °C and 1.0 MPa for 3 min, and then they were assembled with two gas diffusion layers (GDLs, 25BCH, SGL Carbon Group Co., Ltd.) and a single serpentine pattern cell (Japan Automobile Research Institute (JARI) standard cell) with an active geometric area of 29.2 cm^2. The Pt loading of the cathode CLs was 0.10 ± 0.006 mg-Pt cm^{-2}, and the Pt loading of the anode CLs was 0.50 ± 0.025 mg-Pt cm^{-2}.

2.2. MEA characterization

The cell was operated with hydrogen and oxygen/air at 80 °C under ambient pressure (1 atm). Hydrogen gas was supplied to the anode and oxygen/air to the cathode. The flow rates of all gases were controlled by mass flow controllers. The utilizations of the reactant gases were 70% for H_2, 40% for O_2 and 40% for air. These gases were humidified at various levels of humidification by bubbling through a heated water reservoir. The cell potential (E) was measured as a function of current density by use of an electronic load (PLZ-664WA, Kikusui Electronics Co.) operated in the constant current mode, controlled by a measurement system (AB-3520AS001, Panasonic Production Technology Co., Ltd.). The cell resistance was measured at 1 kHz under load by use of a digital ac milliohmmeter (Model 3566, Tsuruga Electric Co.). The *I–E* curves were measured during quasi-steady-state operation achieved after 5 min at each potential step. For experimental convenience, the hydrogen anode was used as the reference electrode for both MEA polarization and CV measurements, since the polarization of the hydrogen anode was relatively small, even at high current density. To evaluate the electrochemically active surface area (ECSA) of the Pt catalyst in the cathode layer, CV measurements were performed at 80 °C and 100% RH by use of a potentiostat (HZ-5000, Automatic Polarization System, Hokuto Denko Co.). The cathode compartment was purged with N_2 (100 mL min^{-1}, 100% RH), while H_2 gas (100 mL min^{-1}, 100%-RH) was supplied to the anode. Prior to the sweep, the potential was maintained at 0.075 V for 3 s to ensure that the Pt was in a reproducibly reduced state. Then, the potential was swept from 0.075 V to 1.000 V at 20 mV s^{-1} and reversed back to 0.075 V. The electrical charge for H^+ reduction to adsorbed H was calculated from the current flowing in the negative-going potential sweep in the range from ca. 0.4 V vs. RHE to 0.075 V at the cathode, with subtraction of the estimated double layer charging current [3,4]. The entire CV was measured without N_2 flow to avoid perturbing the H_2 partial pressure [27]. The value of ECSA was determined from the hydrogen adsorption charge referred to $Q_H^o = 0.21$ mC cm^{-2}, the conventional value for a monolayer of adsorbed hydrogen on polycrystalline platinum [28].

2.3. Durability evaluations in load cycles

Fig. 1(a) shows the protocol for the evaluation of the durability of the Pt/GCB cathode catalysts in the current-load mode. Table 1 shows the details of the protocols employing various load cycling conditions involving OCV and load holding times at a high current density (sample names A1, A2 and A3), at a lower current density (A5) and at OCV (A4) under 100% RH and a lower RH (A6). These durability evaluation protocols can be characterized as follows: A1, with the OCV/load holding times of 3 s/3 s, simulates a normal acceleration/deceleration drive cycle; A2, with the OCV/load