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Study on durability of Pt supported on graphitized carbon under simulated start-up/shut-down conditions for polymer electrolyte membrane fuel cells

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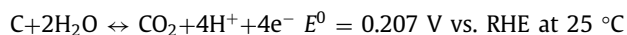
ABSTRACT

The primary issue for the commercialization of proton exchange membrane fuel cell (PEMFC) is the carbon corrosion of support under start-up/shut-down conditions. In this study, we employ the nanostructured graphitized carbon induced by heat-treatment. The degree of graphitization starts to increase between 900 and 1300 °C as evidenced by the change of specific surface area, interlayer spacing, and I_D/I_G value. Pt nanoparticles are deposited on fresh carbon black (Pt/CB) and carbon heat-treated at 1700 °C (Pt/HCB17) with similar particle size and distribution. Electrochemical characterization demonstrates that the Pt/HCB17 shows higher activity than the Pt/CB due to the inefficient microporous structure of amorphous carbon for the oxygen reduction reaction. An accelerating potential cycle between 1.0 and 1.5 V for the carbon corrosion is applied to examine durability at a single cell under the practical start-up/shut-down conditions. The Pt/HCB17 catalyst shows remarkable durability after 3000 potential cycles. The Pt/HCB17 catalyst exhibits a peak power density gain of 3%, while the Pt/CB catalyst shows 65% loss of the initial peak power density. As well, electrochemical surface area and mass activity of Pt/HCB17 catalyst are even more stable than those of the Pt/CB catalyst. Consequently, the high degree of graphitization is essential for the durability of fuel cells in practical start-up/shut-down conditions due to enhancing the strong interaction of Pt and π -bonds in graphitized carbon.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have been attracted huge attention for mobile, automotive and stationary applications as a new power source, due to their unique advantages such as low emission, high energy density, and high efficiency. However, there are still some problems to solve like the high activity and durability of catalysts in order to advance toward the commercialization stage. In general, the carbon supported Pt or Pt-based alloy is used as catalysts. Degradation mechanisms for catalysts involve the dissolution of Pt [1–6], migration of Pt [7,8] and carbon corrosion [9–13]. Especially, since the standard electrode potential of carbon is as low as 0.207 V vs. reversible hydrogen electrode (RHE) as shown in the following equation, the carbon support is electrochemically oxidized under high temperature and humidity employed in normal operating conditions.



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It is believed that there are two parallel pathways for carbon degradation [14,15]. One is the direct carbon oxidation reaction in the presence of water and the other is the indirect carbon oxidation via surface oxides. Secondly, the Pt accelerates the formation of CO-like species, which is further oxidized to produce CO₂ in the presence of water [11].

Reiser et al. proposed the reverse-current mechanism related to the local hydrogen starvation [16]. During transient conditions of the cell operation such as start-up and shut-down, a high interfacial potential difference causes carbon corrosion. When hydrogen is introduced into the anode during startup, a condition is created where hydrogen occupies only part of the anode. At this moment, the carbon corrosion occurs at the cathode. During the shutdown procedure, a similar phenomenon can occur, when the air from the outside or through the membrane, replaces the hydrogen causing carbon corrosion at the anode [15–19]. Moreover, according to a reverse-current decay mechanism, after the shut-down or during start-up, the cathode in PEMFC can experience a higher potential than the OCV. Such a high potential rapidly oxidizes the carbon support [15,16].

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36 Roen et al. detected CO₂ in the cathode exhaust gas during CV
37 with varying Pt mass fraction, catalyst type, and temperature [11].
38 An Arrhenius plot indicated higher apparent activation energy
39 for CO₂ production at the positive potential limit of the CV on
40 0% Pt (carbon-only) electrode than on 39% Pt/C electrode. It was
41 concluded that platinum accelerated the corrosion rate of the
42 carbon support. DEMS shows that pure carbon is oxidized only
43 at potentials higher than 0.9 V (RHE) and that Pt catalyzes the
44 oxidation of a CO_{surf} surface layer to CO₂ at potentials between 0.6
45 and 0.8 mV (RHE) in the sulfuric acid solution. The result indicates
46 that the carbon corrosion by Pt occurs in the neighborhood of
47 Pt-sites, thus damaging the Pt to carbon contact [20]. As a result,
48 the formation of carbon oxidation products like CO₂, CO and
49 HCOOH is observed [21] and the in-situ EQCM study shows mass
50 changes of a variety of carbon supports during the CV in deaerated
51 0.5 M H₂SO₄ solution [22]. High surface area CBs ECP 600 and
52 ECP 300 have a carbon loss of 0.0245 ng cm⁻² s⁻¹ and 0.0144 ng
53 cm⁻² s⁻¹ and as compared to 0.0115 ng cm⁻² s⁻¹ for low surface
54 area support XC-72.

55 Despite the critical disadvantage, it is still required to employ
56 the high surface area carbon as a support for cathode catalysts
57 in PEMFCs due to a wide range of its intrinsic benefits. First, the
58 specific activity of catalyst without supporting on proper materials
59 decreases with decreasing the particle size of catalyst [23,24].
60 Moreover, its high electrical conductivity, mesopores, and stability
61 in an acidic environment are appropriate as a supporting material
62 for the PEMFCs. However, the carbon-supported Pt nanoparticles
63 under the carbon oxidation conditions readily migrate, detach and
64 aggregate to larger particles, and the porosity of catalyst layer is
65 changed [25,26]. These results bring about the reduction of elec-
66 trochemical surface area (ECSA) and exhibit a huge performance
67 loss. Therefore the stability of carbon materials has to be further
68 enhanced under practical start-up/shut-down conditions.

69 Much attention is to be paid to the research on heat-treated
70 high surface area carbon since it is already commercialized, easy
71 to obtain, cheap, impurity-free and not necessary to apply compli-
72 cated steps and expensive chemical in preparation. Also, it showed
73 reasonable corrosion resistance as conducted in 3 electrode system
74 [27–30]. In the present study, we demonstrate that the nanostruc-
75 tured carbon supports obtained by heat-treating amorphous high
76 surface area carbon improve the corrosion resistance in a single
77 cell under practical start-up/shut-down conditions in fuel cell ve-
78 hicles. We have systematically synthesized carbon nanostructures
79 at various temperatures, deposited Pt nanoparticles using polyol
80 method, and evaluated the durability of the synthesized catalysts
81 using an electrochemical potential cycle protocol between 1.0 and
82 1.5 V. The activity has been evaluated by the kinetic current and
83 half-wave potential in a rotating disk electrode (RDE), while the
84 durability has been estimated by ECSA, potential loss, and current
85 density loss in 25 cm² MEAs.

86 2. Experimental

87 2.1. Preparation of support and catalyst

88 For the treatment of carbon supports, the as-received carbon
89 black (CB, Ketjen Black EC-300J) was heat-treated at different
90 temperatures in order to obtain carbon supports having different
91 graphitization degrees. Before the heat-treatment, nitrogen gas
92 was flown to purge the quartz tube furnace (OTF-1200X-SNT-110,
93 MTI corp.) for 30 min. The nitrogen gas was fed to the tubular
94 furnace during the heat-treatment and treated at respective tem-
95 peratures for 1 h. The temperatures of 900, 1300, and 1700 °C
96 are used in this study. Supports thus prepared are denoted as
97 HCB9, HCB13, and HCB17, while the un-heat-treated sample is
98 denoted as CB. The supports were non-covalently activated by the

pyrenecarboxylic acid before the Pt deposition due to their high
hydrophobicity deposition [31,32].

Pt deposition was accomplished by a polyol reduction method
for the preparation of 30% Pt/C catalyst. First, each support was
dispersed in 25 mL of ethylene glycol in a round bottom flask us-
ing an ultrasonication bath (Branson ultrasonic cleaner). A desired
amount of PtCl₄ was added and the pH was adjusted to 11 by the
addition of 0.5 M NaOH solution. The resulting solution was re-
fluxed at 160 °C for 3 h and allowed to cool to room temperature.
Then, the solution was filtered, washed with DI water, and dried
at 160 °C for 30 min under air atmosphere.

2.2. Physical characterization

The nitrogen adsorption/desorption isotherms were obtained
at –196 °C using a Quantachrome NOVA 2000. Specific surface
area was determined by a multipoint Brunauer–Emmett–Teller
(BET) analysis. Pore size distribution (PSD) curves were calculated
by the Barrett–Joyner–Halenda (BJH) method using the adsorp-
tion/desorption branch. X-ray diffraction (XRD) analysis was per-
formed using a Rigaku D/Max 2500 V/ PC with a Cu K α radiation. A
tube voltage of 30 kV and a current of 15 mA were used during the
scanning. To estimate the Pt nanoparticle size of the synthesized
catalysts, we employed the following Scherrer equation [33]:

$$D = \frac{k\lambda}{10B \cos \theta}$$

where D is the crystallite size in nm, k is a coefficient (0.9), λ is
the wavelength of X-ray (0.15404 nm), B is the line broadening
at half the maximum intensity in radians, and θ is the angle at
the position of the maximum peak known as Bragg angle. Raman
spectroscopy was used to evaluate the degree of graphitization
of the carbon supports using HORIBA "LABRAM 1B" (He–Ne 20
mW laser, wavelength 632.817 nm). High-resolution transmission
electron microscopy (HR-TEM) was used to study the morphology
and particles size distribution of the catalysts using Hitachi 9500
HR-TEM operated at 300 kV accelerating voltage. X-ray fluores-
cence (XRF) (Fischer XDAL) was used to determine the Pt loading
in the catalyst coated membrane.

2.3. Electrochemical characterization

Electrochemical characterization was performed in an RDE
setup using a Pine bi-potentiostat (Model AFCBP1). A glassy car-
bon disk electrode (0.247 cm²) was acted as a working electrode.
The Ag/AgCl electrode and platinum mesh were used as a ref-
erence and counter electrodes. RDE tests were performed in 0.1
M HClO₄ solution as an electrolyte at room temperature. All the
potentials are reported against RHE. In a typical experiment, Pt
catalyst was mixed with isopropyl alcohol (IPA) and deionized
water (DI) water ultrasonically. The catalyst ink was deposited
onto the glassy carbon electrode, leading to a catalyst loading of
20 μg_{Pt} cm⁻². For all RDE tests, 5 μL of 0.25 wt% ionomer (Alfa
Aesar) was additionally deposited on the catalyst layer to ensure
good adhesion of the catalyst onto the glassy carbon electrode.
Linear sweep voltammetry (LSV) was measured at a scan rate
of 5 mV s⁻¹ by sweeping the potential between 0.2 V and 1.05
V under oxygen purging. The LSV curves presented in this work
were properly corrected using the background capacitance current
that was measured in the nitrogen atmosphere at a scan rate of 5
mV s⁻¹. The ECSA was calculated at a scan rate of 50 mV s⁻¹ from
0.005 to 1.0 V in deaerated electrolyte under N₂ atmosphere. The
ECSA was calculated from the integrated charge in the hydrogen
desorption peak using the following equation:

$$\text{ECSA} = \frac{Q_{\text{H}}}{0.21 \times L_{\text{Pt}}}$$

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