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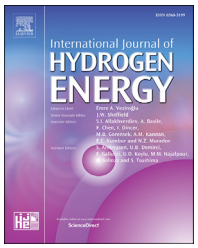

Short Communication

Correlation between the carbon structures and their tolerance to carbon corrosion as catalyst supports for polymer electrolyte fuel cells

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ABSTRACT

The tolerance to corrosion of cathode catalyst supports comprising carbon nanofibers with differing alignments of graphene layers was evaluated, and its correlation with structural parameters obtained from Raman spectra was discussed. The carbon nanofibers employed in this study were platelet-type carbon nanofibers (PCNF) and tubular carbon nanofibers (TCNF). The tolerance to carbon corrosion was evaluated in a membrane electrode assembly using a start-stop durability testing protocol. While the ratio of the D band peak intensity to that of the G band (I_D/I_G) does not show any correlation with tolerance to carbon corrosion, full width at half maximum of the G band (FWHM(G)) correlates well with tolerance to carbon corrosion. The results suggest that carbon materials with low FWHM(G) values are promising as cathode catalyst supports in PEFCs.

Introduction

Polymer electrolyte fuel cells (PEFCs) exhibit high energy conversion efficiency, even at low temperatures, and thus attract considerable research attention as energy devices for residential and automotive applications. However, the wider application of PEFCs has been hindered partly due to the low durability of the catalysts in the cathode where the oxygen reduction reaction occurs. The current state-of-the-art

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catalysts employed in PEFC cathodes are Pt nanoparticles supported on high-surface-area carbon black (Pt/C). However, this catalyst support suffers from severe carbon corrosion, especially during start-stop operation where hydrogen and oxygen co-exist in the anode [1,2]. The cathode potential can increase to around 1.5 V [1–4], due to the reverse-current mechanism, which results in destruction of the cathode [1,2,4–6]. Thus, the problem of carbon corrosion has become a critical issue for PEFCs.

One approach to addressing carbon corrosion is to employ carbon-free electrodes. Several recent reports have presented promising results using unsupported nanostructured catalysts [7,8] and alternative supports [9–14]. Another approach is to improve the durability of carbon materials. Tolerance to carbon corrosion has been reported to be increased by heat treatment (graphitization) of carbon materials [15–19] or by the use of graphitized carbon [20–25], carbon nanotubes [15,26–31], carbon nanofibers [17,31–33], and other carbon nanomaterials [15,30,33,34]. Most commonly accepted reason for the improved tolerance to carbon corrosion is an increase in the degree of graphitization. Evaluating the degree of graphitization is commonly achieved using X-ray powder diffraction (XRD) [17–20,26,33,34], or Raman spectroscopy [20,23,31]. Several structural parameters obtained from these techniques have been discussed in relation to tolerance to carbon corrosion. However, there is currently no general consensus regarding which parameter is an appropriate index for tolerance to carbon corrosion.

In the present study, we have evaluated the tolerance to carbon corrosion of carbon nanofibers with differently aligned graphene layers as catalyst supports in PEFC cathodes, and discussed the correlation of this tolerance with structural parameters obtained from Raman spectra. The carbon nanofibers employed in this study were platelet-type carbon nanofibers (PCNF) and tubular carbon nanofibers (TCNF). PCNF and TCNF have a high degree of graphitization and differ in the alignment of their graphene layers; the graphene layers align perpendicularly to the fiber axis in PCNF and align parallel to the axis in TCNF, as shown in Fig. 1(a-1) and (b-1). Two characteristic peaks in the Raman spectra of the carbon materials were used for evaluation of structural parameters; the G band at ~1580 cm^{-1}, which corresponds to an ideal graphitic lattice vibration mode, and the D band at ~1350 cm^{-1}, which appears due to discontinuity of the graphite planes [35,36].

The degree of graphitization is generally discussed using the ratio of the D band peak intensity to that of the G band (I_D/I_G). In previous studies discussing the carbon corrosion of cathode catalyst support in PEFCs with employing Raman spectroscopy to evaluate the carbon structures, the parameters used for the discussion are I_D/I_G [20,31], and peak area ratio of D band to that of G band [23]. These parameters differentiate well-graphitized materials such as reinforced-graphite [20], graphitized carbon black [23], and carbon nanofiber [31], from other carbon materials (e.g. commercial carbon black), and are effective in clarifying the degradation mechanism of carbon materials [20,23]. However, there exists a difficulty when using I_D/I_G as an index for tolerance to carbon corrosion: carbon materials with similar I_D/I_G, high-surface area carbon and Vulcan XC-72, shows different degradation behaviors [20]. One reason for this difficulty may be because the D band inevitably appears when edges are present, and therefore does not necessarily indicate the presence of defects or a low degree of graphitization [35,36]. Thus, in this study, another parameter, the full width at half maximum of the G band (FWHM(G)) [35–37], was also employed to evaluate the degree of graphitization. Although FWHM(G), peak width, and the sharpness of the peaks are known to be related to the degree of graphitization [35–38], the correlation of FWHM(G) with tolerance to carbon corrosion in PEFCs has not been discussed in detail previously. Evaluating degradation behaviors of two CNFs, PCNF and TCNF, both of which have a high degree of graphitization helps to identify an appropriate index for tolerance to carbon corrosion. The tolerance to carbon corrosion was evaluated in a membrane electrode assembly (MEA) using a start-stop durability testing protocol recommended by the Fuel Cell Commercialization Conference of Japan (FCCJ), which applies a triangular wave between 1.0 and 1.5 V vs. a reversible hydrogen electrode at a scan rate of 0.5 V s^{-1} [4,5]. Using results from these analyses, correlation of the tolerance to carbon corrosion with the structural parameters obtained from Raman spectra, I_D/I_G and FWHM(G), was discussed in order to identify an index parameter.

Materials and methods

PCNFs and TCNFs were synthesized as reported previously [39,40]. Pt nanoparticles were synthesized on PCNF (Pt/PCNF) and TCNF (Pt/TCNF) via a polyol method using ethylene glycol as a reducing reagent. A commercial Pt/C, TEC10E50E with 45.8 wt% Pt from Tanaka Kikinzoku Kogyo (TKK Pt/C), was used for comparison. Structural analyses of the catalysts were performed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), transmission electron microscopy (TEM), X-ray powder diffraction (XRD), and Raman spectroscopy. Curve fitting of the Raman spectra for the determination of spectral parameters was performed by considering a combination of five bands [20,23,37] as shown in Table S1 in Supplementary data, and performed with a software Fityk [41]. The catalysts were fabricated into cathode catalyst layers, and then into MEAs, which were used for the evaluation of the tolerance to carbon corrosion. The start-stop durability test of the MEAs followed the revised FCCJ protocol [4,5] that applied a triangular wave between 1.0 and 1.5 V vs. an RHE at a scan rate of 0.5 V s^{-1}, and was performed at 80 °C and 100% relative humidity. The details are described in Supplementary data.

Results and discussion

Fig. 1 shows TEM images of (a-2) PCNF, (b-2) TCNF, (a-3) Pt/PCNF and (b-3) Pt/TCNF. Pt nanoparticles with a particle size of ~3 nm are homogeneously dispersed on both the PCNF and TCNF.

Raman spectra of Pt/PCNF, Pt/TCNF, and TKK Pt/C are shown in Fig. 2a–c. The spectra show G bands at ~1580 cm^{-1}, and D (D1) bands at ~1350 cm^{-1}. The results of curve fits are shown in Fig. S1 and Table S2 in Supplementary data. I_D/I_G (I_{D1}/I_G) calculated from the fitted curves is 1.19 ± 0.05 for Pt/PCNF,