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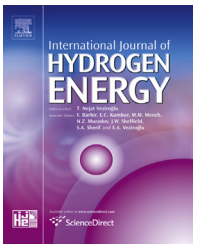

Engineered catalyst layer design with graphene-carbon black hybrid supports for enhanced platinum utilization in PEM fuel cell

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ABSTRACT

In this study, a new approach was applied to prepare platinum/reduced graphene oxide/carbon black (Pt/rGO/CB) hybrid electrocatalysts. Unlike literature firstly GO and CB in varying ratios are homogeneously mixed with a high shear mixer and then Pt was impregnated onto the hybrid support structure according to the polyol method. According to our approach CB was used as a spacer and intercalating agent in both Pt impregnation and electrode preparation to avoid restacking and increase the Pt utilization. Thus rGO/CB based hybrid support can ease the diffusion while it is promoting to the use of high electrical connectivity and surface area of graphene. The maximum power density of 645 mW cm^{-2} with Pt utilization efficiency of 2.58 kW/gPt was achieved with the hybrid containing the smallest amount of CB. It seems that this small amount of CB effectively modifies the electrode structure. The enhanced fuel cell performance can be attributed to synergistic effects from graphene and CB providing better mass transport and Pt utilization in the catalyst layer.

Introduction

Polymer electrolyte membrane (PEM) fuel cell is one of the most promising alternative energy sources especially for transportation applications due to its high energy density, compact structure, quick refill and start-up time. Even the PEM fuel cell can overcome the commercialization barrier, its cost, mainly comes from platinum (Pt) catalyst and durability issues still remains as unsolved.

In this study we mainly focused on using most of the precious Pt by increasing its utilization and reducing the cost of PEM fuel cell. In this approach, Pt can usually be loaded on high surface area support materials, such as graphene [1,2]. Graphene with its superior properties is perfectly suited to be used as the support for the electrocatalyst, since graphene is a unique two dimensional (2D) material with high electrical conductivity, high surface area, and high mechanical strength, has all requirements of a good electrocatalyst support. However, during the electrode fabrication (spraying or blading of catalyst ink) and cell assembly graphene layers even loaded with Pt nanoparticles tend to horizontally stacked to establish a catalyst layer [3]. These stacking causes a

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significant loss in the Pt catalytic sides and higher diffusion resistance to the reactant molecules especially at higher current density region during the operation [1–4]. Thus, graphene/carbon black (CB) based hybrid Pt supports can be a potential to mitigate the diffusion resistance when benefit the high electrical connectivity and surface area of graphene at the same time.

In literature, in the study of Park et al. CB was added as a spacer between Pt supported graphene sheets in the catalyst layer by mechanical mixing. The authors showed a 200 mW cm^{-1} maximum power density for 0.2 mg cm^{-1} Pt loading on both anode and cathode with Nafion® 117 membrane and SGL10 CC carbon paper containing MEA at 80 °C cell temperature and 150 kPa cell pressure [5]. Woo et al. demonstrated graphene-CB hybrids to prepare PtRu electrocatalysts. Similar to Park's study, they used CB as a spacer between PtRu supported graphene sheets [6]. Li et al. also prepared hybrid composite materials by mechanical mixing of CB with Pt-loaded reduced graphene oxide (Pt/rGO). With the insertion of CB, the particles inserted between Pt/rGO sheets and stacking of rGO can be effectively prevented [7]. However, there was no fuel cell test result reported in the study. In another study, three dimensional (3D) Pt/rGO/CB was synthesized by hydrothermal assembly of GO and Pt/CB followed by freeze drying to obtain foam like structures [8]. Even though Pt/rGO/CB electrocatalyst showed promising ex-situ characterization results, no fuel cell performance was reported in their results [8]. Another approach was conducted by Jung et al. [9]. In their study, commercial Pt/CB (HiSPEC 4000, Johnson Matthey) electrocatalyst was used as the anode catalyst and the hybrid catalyst composed of mechanically mixed commercial Pt/CB and synthesized Pt/rGO hybrid was used as the cathode catalysts to prepare MEAs. Their hybrids exhibited higher durability (24.7% activity loss) than pristine catalyst (43.15% activity loss) according to the half cell reaction [9]. Jung et al. [10] also mechanically mixed the commercial Pt/C catalyst with micro graphite (MG) to enhance the performance of the MEA in which anode was standard Pt/CB (HiSPEC 4000, Johnson Matthey) and cathode was Pt/CB/MG. Moreover, Yang et al. [11] firstly synthesized Pt/boron doped graphene, then by mechanical mixing authors used the CB as the intercalation agent and reported the enhanced the fuel cell performance by the combined effect of boron and CB intercalation.

To the best of our knowledge, the maximum power density that was reported in literature for the rGO containing hybrid studies is about 400 mW cm^{-2} with MEA, consisting of two electrodes using as-prepared electrocatalysts at 0.2 mg cm^{-2} Pt loading and Nafion® NR212 as the membrane, operated at 80 °C in ambient pressure [12]. In this study of Cho et al. [12] synthesized Pt/graphene electrocatalysts via polyol process (using ethylene glycol) and mechanically mixed Pt/graphene with CB to have Pt/graphene/CB electrocatalysts same as Park et al. [5].

As a summary, most of the hybrid studies in literature so far had the approach of mechanical mixing of commercial CB or commercial Pt/CB with synthesized Pt/rGO. Moreover, only a few of the studies could report a PEM fuel cell performance with both anode and cathode electrodes fabricated from the synthesized hybrid electrocatalysts [5,12].

Apart from literature, we have firstly mechanically mixed GO and CB by high shear mechanical mixing so that CB can also act as a spacer or intercalating agent for GO layers during the Pt impregnation. Thus, both of the high surface graphene sides meet with Pt and CB can also prevent restacking of these Pt impregnated graphene layers. Since, restacking is also severe during hot pressing of membrane electrode assembly (MEA). By our approach, most of the high surface area of GO can be benefited during the impregnation of Pt nanoparticles and enhanced the fuel cell performance and power density since CB would not block Pt active sides (Fig. 1).

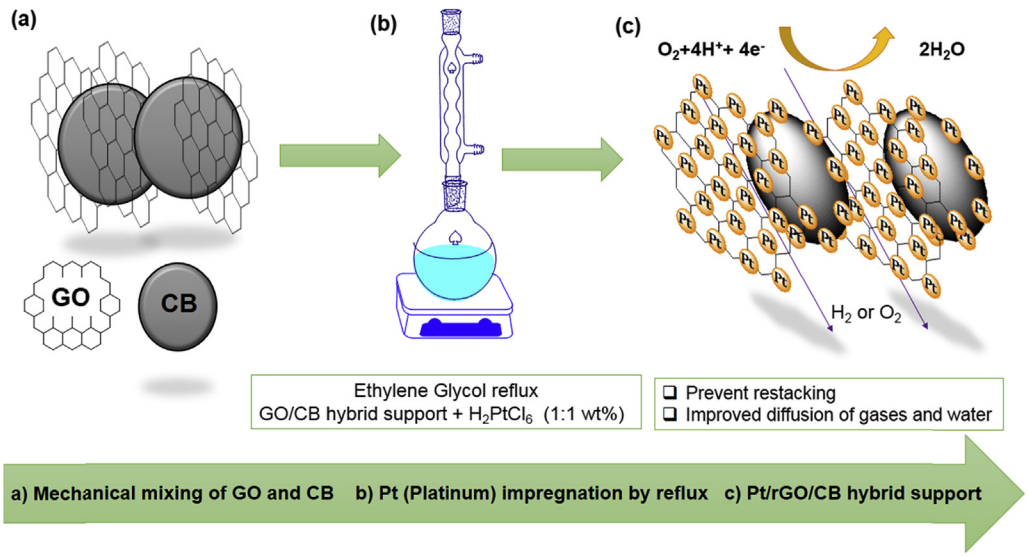

Fig. 1 – Schematic of graphene-CB hybrid support synthesis and structure.

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