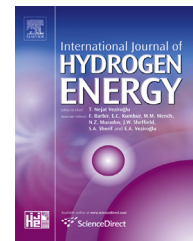




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## Short Communication

# Boosting the performance of formic acid microfluidic fuel cell: Oxygen annealing enhanced Pd@graphene electrocatalyst

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## ABSTRACT

A new oxygen-annealing treatment for Pd supported on graphene was employed to enhance the electro-catalytic performance in formic acid microfluidic fuel cells. Experiments show that both the electro-oxidation reactivity and CO tolerance of the annealed catalyst are significantly improved. When testing the fuel cell, the maximum power density with annealed catalyst is 41% higher than the unannealed Pd@graphene catalyst, and 85% higher than Pd@Vulcan XC-72. This enhancement is attributed to the Pd–O bond formation during the oxygen annealing step, which induces greater CO electro-oxidation reactivity.

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## Introduction

Formic acid microfluidic fuel cells (FAMFC) are promising power sources for portable devices and microelectronics because of their intrinsic non-toxic, high power density, with added suitability for storage and transportation [1–3]. FAMFC employs a membraneless design under laminar flow microfluidics, which conveys additional benefits including lower

cost and improved heat/mass transport. Since FAMFC suffers negligible crossover and mass transfer limitations, their performances strictly depend on the electrode kinetics [4]. Therefore, development of new electro-catalytic materials will be crucial to further FAMFC R&D towards higher power density and stability.

In the past few years, although catalysts for formic acid anode in FAMFCs have been greatly improved, they have yet to reach satisfactory performances. One negative factor relates to

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the fact that poor initial catalytic reactivity remains a challenge. Although many new materials have been applied to improve formic acid oxidation (FAO) activity, such as metal/oxides alloys/carbides [5–7] and alternative supporting materials [8–10], such as activated carbon/CNT/graphene and modification of these carbon materials [11], the reactivities are still far from ideal. Another problem arises from the CO intermediates of FAO cause poisoning of noble-metal electro-catalyst, leading to stability issues during long-term operation of FAMFC [12]. Although many of recent studies have shown to reduce the formation of CO intermediates, the overall progress are still not satisfied [12,13]. Among the different noble metals studied, Pd-based electro-catalysts are regarded to be most suitable for FAO because they can promote the direct pathway of conversion and decrease the generation of CO intermediates [13].

Recently, graphene has been recognized as a promising support material for electro-catalysts. Graphene-based catalysts show great initial performance in FAO, mainly attributed to graphene's two-dimensional structure and ultra-high conductivity [14]. Graphene provides a great surface area favorable for the dispersion of Pd particles, which greatly enhances the desired initial performance [14]. Nevertheless, the performance loss caused by CO poison is still a detrimental factor in Pd@graphene catalysts, which leads to cell degradation over a long-term operation. Some studies have shown that when carbon supports are annealed in different atmospheres, properties of the electro-catalysts could be greatly improved, particularly their tolerance to CO [15,16]. Although various studies on the annealing treatment of carbon-supported materials can be found, to the best of our knowledge, there are no reports on oxygen annealing of graphene-based electro-catalysts available in literature. Due to the unique surface properties of graphene over other carbon materials, developing a suitable oxygen-annealing process is challenging. For example, various functional groups and organic-inorganic bonds on graphene can be readily over-oxidized in an oxygen-rich atmosphere, leading to dramatic performance loss. Therefore, the protocol developed for other carbon materials, e.g. oxygen annealing process for Pd@ Vulcan XC-72 [13], may not be fully suited for graphene-based materials. An optimized and tailored methodology is required for the treatment of graphene-based electro-catalysts, which, this study aims to address.

In this manuscript, and for the first time, an oxygen annealing process is presented for graphene supported Pd electro-catalysts with a set target to boost the FAMFC performance and CO tolerance. The annealing process is tailored and optimized to ensure the enhancement of Pd electro-catalytic activity without weakening graphene's role as a supporting material. According to electrochemical characterization, Pd supported on graphene synthesized via hydrothermal method shows great electro-catalytic activity as well as CO tolerance after oxygen annealing, leading to 85% increase in the FAMFC performance.

## Experimental

Graphene oxide (GO) were made from natural graphite powder via a modified Hummer's method producing a  $1 \text{ mg ml}^{-1}$

solution after washing with deionized water until pH-neutral [17]. Synthesis of Pd supported on graphene was conducted as follows. 3 ml of 10 mM PdCl<sub>2</sub> in HCl was added into 20 ml GO solution, and the pH was adjusted to 10, followed by ultrasonication for 30 min. The mixture was then poured into a 100 ml Teflon autoclave and reacted in an oven under a temperature of 120 °C for 10 h. The resulting solid precipitates were filtered and washed with ethanol and deionized water several times, then dried in a freeze drier before further processing. The catalyst (marked as Pd/G) was then further annealed under an O<sub>2</sub> atmosphere at 100 °C for 12 h. The annealing temperature and duration were determined by optimization studies tailored for graphene-based materials, where thermogravimetric (TG) experiments were adopted. According to the TG results and subsequent electrochemical experiments, the annealing temperature was set at 100 °C. The annealed catalyst was marked as Pd/G-O. Pd supported on VulcanXC-72 carbon powder was also synthesized under the same conditions as a control material (marked as Pd/VulcanXC-72). The Pd loading of all samples were measured to be 3% wt. ( $\pm 0.5\%$ ).

The FAMFC were fabricated following the general procedures as specified in our previous work [18]. The assembly and working principle of the FAMFC are shown in Fig. 1a and b respectively. The poly (methyl methacrylate) and poly (vinyl chloride) layers were machined by a CO<sub>2</sub> laser fabricator (Universal Laser Systems). The sizes of the microchannels were 15 mm × 3 mm × 0.5 mm (L × W × H) with reactive areas at anode and cathode to be 3 mm × 3 mm. The catalyst on cathode gas diffusion electrode (GDE) was 2 mg cm<sup>-2</sup> Pt/C (Hesen), and the catalyst on the anode GDE was 2 mg cm<sup>-2</sup> materials developed in this study (i.e. Pd/G-O, Pd/G and Pd/VulcanXC-72).

All electrochemical measurements were carried out on an electrochemical workstation (CHI660E). Cyclic voltammetry (CV) was performed in 0.5 M HCOOH + 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions with a three-electrode system from -0.2 V to 1.0 V at a scan rate of 50 mV<sup>-1</sup>. The reference electrode was Ag/AgCl in saturated KCl (0.198 V vs. SHE), and the counter electrode was a platinum film electrode (1 cm<sup>2</sup>). Before electrochemical tests, the solutions were deaerated with nitrogen for 15 min. The CO-stripping experiment was conducted in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution with the same setup. Prior to the experiment, CO was purged into the electrolyte for 15 min for CO adsorption onto the catalyst while the working electrode was kept at 0.2 V vs Ag/AgCl. After that, the excess CO was driven out with nitrogen for 15 min [19]. To evaluate the performance of the fuel cells, the anolyte (0.5 M H<sub>2</sub>SO<sub>4</sub> + 0.5 M HCOOH) and catholyte (0.5 M H<sub>2</sub>SO<sub>4</sub>) were pumped at 100 μl min<sup>-1</sup> via a syringe pump (LSP02-1B). A potentiostatic method was performed at different potentials from 0.7 V to 0 V with 0.04 V interval to obtain polarization curve. The electrochemical data was recorded when the potentiostatic current becomes stable after 100 s.

The morphology and structural data of catalysts were determined by transmission electron microscope (TEM, Tecnai G2 F20) operated at an accelerating voltage of 200 kV. The X-ray diffraction (XRD) patterns were carried out on Rigaku D/max-2550 VB + /PC diffractometer using Cu KαD/max-2550. The X-ray photoelectron spectroscopy (XPS) measurements

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