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The durability of carbon supported Pt nanowire as novel cathode catalyst for a 1.5 kW PEMFC stack

Bing Li[a,b,*], Drew C. Higgins[c], Qiangfeng Xiao[d], Daijun Yang[a,b], Cunman Zhng[a,b], Mei Cai[d], Zhongwei Chen[c], Jianxin Ma[a,b]

[a] School of Automotive Studies, 4800 Caoan Road, Tongji University (Jiading Campus), Shanghai 201804, China
[b] Clean Energy Automotive Engineering Center, Tongji University, Shanghai 201804, China
[c] Department of Chemical Engineering, University of Waterloo, Waterloo, ON, Canada N2L 3G1
[d] Research & Development Center, General Motors, Warren, MI 48090, United States

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ABSTRACT

Carbon supported platinum nanowires (PtNW/C) synthesized by a simple and inexpensive template-free methodology has been used for the first time as a cathode catalyst in a 15 cell with an active area of 250 cm^2, 1.5 kW proton exchange membrane fuel cell (PEMFC) stack. Drive cycle testing along with in-situ and ex-situ accelerated degradation testing (ADT) showed that the PtNW/C catalyst exhibited better durability than commercial Pt/C. After a 420 h dynamic drive cycle durability testing, the PEMFC stacks exhibited a performance degradation rate of 14.4% and 17.9% for PtNW/C and commercial Pt/C based cathodes, respectively. It was found that the majority of performance loss was due to degradation of the commercial Pt/C anode materials, resulting from the rapidly changing load frequencies used in the testing protocol, ultimately leading to harsh fuel/air starvation conditions and subsequent Pt nanoparticle growth and agglomeration. Notably, based on post-testing characterization, the structure, electrochemically active surface area (ECSA) and oxygen reduction activity of the PtNW/C cathode catalyst remained unchanged during the drive cycling, indicating its excellent stability under these practical conditions. Conversely, when using commercial Pt/C as a cathode catalyst, significant Pt nanoparticle growth and agglomeration were observed, resulting in the reduced PEMFC stack durability. Therefore, PtNW/C materials are presented as promising replacements to conventional Pt/C as cathode electrocatalysts for PEMFCs, and particularly demonstrate improved stability under the practical conditions encountered for automotive applications.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are considered promising sustainable energy technologies due to their high efficiency, quick startup, relatively low operating temperature, simple construction, good dynamic performance, and environmental benignity [1]. For these reasons, the major application potential has been focused on the transportation sector. At present, the major barrier preventing the successful commercialization of PEMFCs is its performance and insufficient durability [2]. State of the art carbon-supported platinum nanoparticles (Pt/C) are the most widely used catalysts due to their high catalytic activity toward the sluggish oxygen reduction reaction (ORR). However, reducing the overall expensive platinum loading at the cathode, along with improving the long-term operational durability of the cathode catalysts remain two key technical challenges that need to be addressed. Nanostructure control strategies have been effective in improving electrocatalyst stability, whereby extended surface Pt and Pt-alloy structures have been demonstrated to result in increased resistance to Pt rearrangement or dissolution [3–5]. Particularly, Pt-based nanowires (NWs) [6,7], nanowire networks (NWNs) [8] and nanoarrays (NA) [9] have recently been shown capable of significantly improving upon the ORR activity and/or durability of commercial Pt/C catalyst. Recently, Sun et al. [10–13] reported that Pt-based NWs synthesized by template-free methods can provide significantly improved specific and mass based activities, coupled with improved operational durability in

* Corresponding author at: Clean Energy Automotive Engineering Center, Tongji University, Shanghai 201804, China. Tel.: +86 21 6958 3891/+86 21 6958 3796; fax: +86 21 6958 3850.
E-mail addresses: libing210@tongji.edu.cn (B. Li), yangdaijun@tongji.edu.cn (D. Yang).

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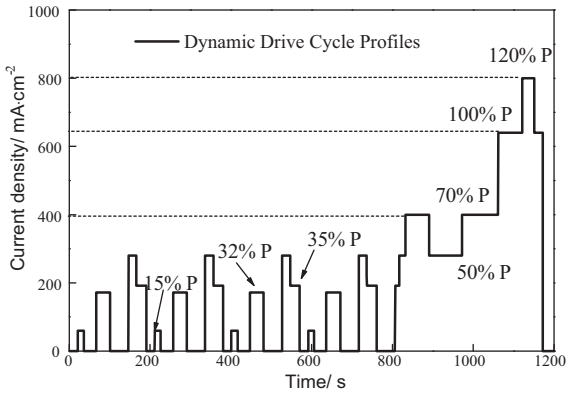

Fig. 1. Profile of dynamic load cycle used for durability testing.

comparison to commercial Pt/C. However, the aforementioned studies have relied on half-cell investigations in order to evaluate the ORR activity and stability. No reports currently exist reporting electrode and cell preparation, stack integration, along with performance and drive cycle durability testing of PtNW based catalysts. These evaluations are highly necessary in order to evaluate the practical application potential of this unique catalyst technology.

In the present work, we prepare carbon-supported platinum nanowires (PtNW/C) using this simplistic and inexpensive template-free methodology. In-situ and ex-situ accelerated degradation testing (ADT) was employed to evaluate the durability of these materials. Furthermore, as-prepared PtNW/C was used as a cathode catalyst for a 1.5 kW FC stack, and a 420 h durability testing based on simulated drive cycles was conducted in order to elucidate the practical performance and evaluate the feasibility of PtNW/C catalyst for automotive applications. Finally, several post-drive cycle characterization techniques were applied to analyze the mechanistic pathways of stack performance degradation, providing fundamental insight that will aid in the design of engineered cathode structures with improved durability.

Table 1
Parameter of JM Pt/C and PtNW/C catalysts.

Catalyst	Initial ECSA ($m^2\ g^{-1}$)	ECSA after 1500 cycles ($m^2\ g^{-1}$)	Maintenance rate (%)
JM Pt/C	50	38.35	76.7
PtNW/C	41	39.73	96.9

2. Experimental

2.1. Materials and catalyst synthesis

PtNW/C were prepared by modifying a procedure reported previously [10]. In a typical synthesis, a mixed aqueous solution of $H_2PtCl_6{\cdot}6H_2O$ and 98% pure HCOOH, as well as an appropriate amount of carbon black (Vulcan XC72) was placed in a 100 mL glass beaker at room temperature. To control the loading of Pt on the carbon support at 40 wt.% Pt, 0.15 g $H_2PtCl_6{\cdot}6H_2O$ and 30 mL HCOOH were dissolved in 50 mL ultrapure water. 75 mg of carbon black (Vulcan XC72) was the dispersed in the above solution by ultrasonication (Model B25, BRT) for 60 min. This solution was left stagnant and allowed to react for 72 h, after which the product was collected, washed and dried completely. The final catalyst

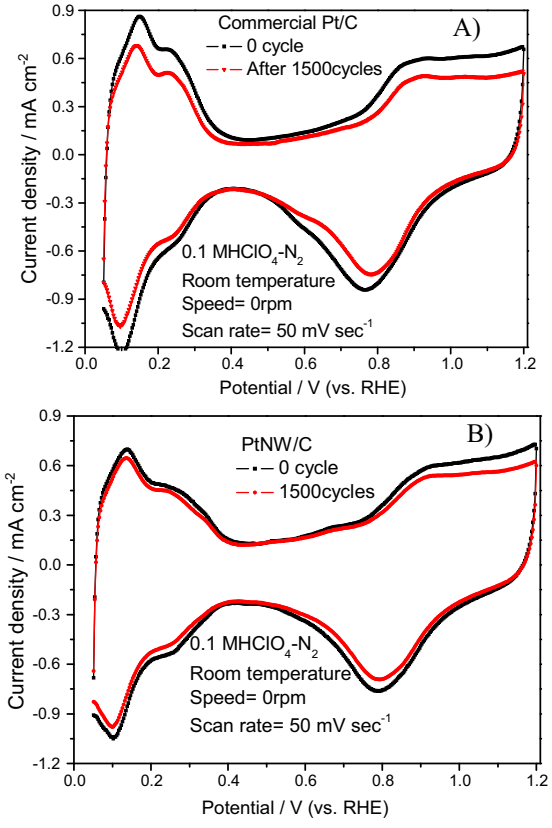

Fig. 2. CV curves of before and after 1500 cycles for (A) commercial Pt/C and (B) PtNW/C in 0.1 M $HClO_4$ at the ambient solution temperature in N_2, Scan rate: 50 mV s^{-1}, electrode area: 0.283 cm^2; catalyst loading: 28 μg cm^{-2}.

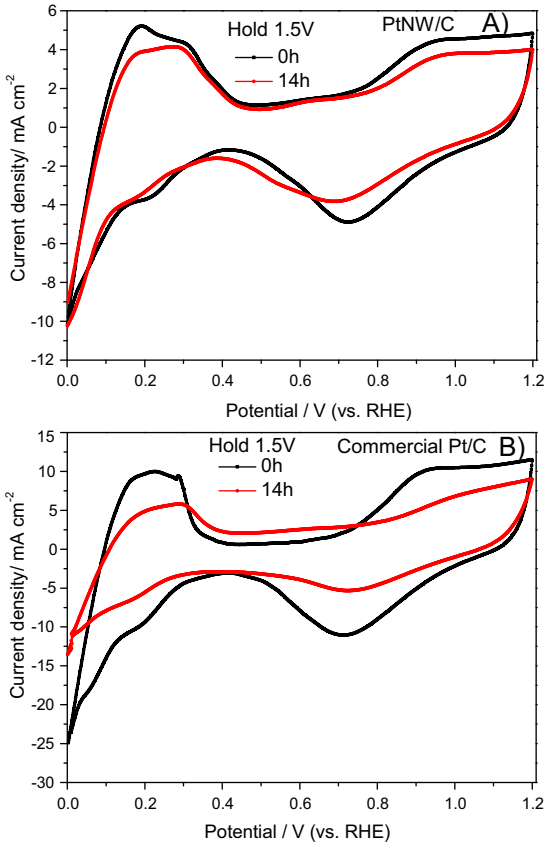

Fig. 3. CV curves of before and after 14 h ADT (hold 1.5 V) for MEA prepared with (A) PtNW/C and (B) commercial Pt/C, respectively. CE: 400 mL min^{-1} H_2, WE: 400 mL min^{-1} N_2.