



# Performance of the electrode based on silicon carbide supported platinum catalyst for proton exchange membrane fuel cells



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## ABSTRACT

To promote fuel cell commercialization, various catalyst supports have been explored to provide more durable performance of proton exchange membrane fuel cells. In this work, we continue our efforts on silicon carbide (SiC), with a focus on electrode structure and single cell performance. Nafion® ionomer was found of good affinity to the SiC supported catalyst. Based on both ex-situ and in-situ electrochemical evaluation and accelerated stress test (AST), SiC supported platinum catalyst (Pt/SiC) electrode showed superior stable performance, less particle size increment and durable interface composition in comparison to traditional carbon supported catalyst (Pt/C), though not apparently favorable for Pt redeposition. Single cells of area 50, 6.25 and 5.0 cm<sup>2</sup> for both long-term test and support focused AST were prepared. The best single-cell performance results were obtained with low catalyst loading, which is likely due to lower electrode thickness and easier mass transport. Considering the low Pt content and large Pt-particle size, the Pt/SiC catalyst shows rather promising Pt utilization, especially with low loaded electrode. The specific performance is actually superior to that of a conventional MEA, though the electrode interface structure should be optimized.

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## 1. Introduction

Stable performance of proton exchange membrane fuel cells (PEMFCs) is one of the key factors [1] influencing fuel cell commercialization and integration into both stationary and mobile devices. In the last two decades, explorations of robust, active and economic catalyst components have been extensively carried out. During cell operation, platinum (Pt) nanoparticles suffer from poor durability because of the rapid and significant loss of the active Pt electrochemical surface area (ECSA) over time. The well-known degradation mechanisms include corrosion of the carbon support, Pt dissolution, Ostwald ripening, and Pt aggregation. The corrosion of carbon support and Pt dissolution are believed to be the major primary degradation mechanisms [2]. Thus, increasing the stability of the catalyst support, enhancing the oxidation resistance of the Pt catalyst, and increasing the interaction between the Pt catalyst and the supports are all effective strategies to improve the durability of a fuel cell.

Moreover, in a fuel cell electrode, the three-phase boundary, where the catalyst has simultaneous access to protons, electrons and mass/gas, is another critical issue to develop [3,4,5,6]. Sound transports for all three species are equally important. In real PEMFCs, solid state proton

conductive polymers, rather than liquid electrolyte, are responsible for proton transport. Their interaction with the catalyst components, the electrode interface structure and the stability of the total structure are of great influence to the performance of the catalyst and the fuel cell. Due to the vast surface property differences among catalysts (e.g. surface area, porosity, hydrophobicity), the adsorption between the ionomer and the catalyst can vary massively [7]. Therefore, individual investigation on the electrode depending on the catalyst type is inevitable.

Catalyst support development can greatly benefit cell life and efficiency [8]. A lot of efforts have been devoted to this area: nanocarbons e.g. carbon nanotube [9,10], carbon nanofiber [11,12] and graphene [13,14,15]; non-carbon catalyst supports including transition metal oxides [16,17,18], nitrides [19,20] and carbides [21,22]. Our group has been working intensively on silicon carbide (SiC) with various synthesis techniques leading to different morphologies [23,24]. Its application as Pt catalyst support for fuel cells has shown improved activity [25,26] and durability [27]. However, the catalyst electrochemical performance was only examined with rotating disc electrode; the material property and compatibility were not reported on the electrode and single cell level so far.

In this work, SiC-supported Pt catalyst (Pt/SiC) was used to prepare fuel cell electrode for the first time. Its primary performance and durability were characterized with both three-electrode cell and single fuel

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cell setup. The electrode structure and the degradation mechanism were studied. Parallel work on catalyst ink and electrode structure optimization according to component content and preparation conditions is going on and will be reported separately.

## 2. Experimental

Silicon carbide was prepared according to the shape memory synthesis method as reported in the earlier work [23,25,27]. In short, a wood sample was dried at 70 °C for 2 h and then heated at a slow rate of 1 °C min<sup>-1</sup> up to 500 °C. Then, it was heated to 1200 °C at a heating rate of 5 °C min<sup>-1</sup> and kept for 6 h for further crystallization and purification. Silicon and silicon dioxide (99.5%, Sigma-Aldrich) were mixed in a 1:1 M mixture and placed in an alumina crucible next to the pyrolyzed wood. Then, this was heated to 1450 °C at 5 °C min<sup>-1</sup> and dwelled for 16 h under a 300 mL min<sup>-1</sup> argon flow. All the processes were carried out in an argon flow to prevent carbon oxidation. The obtained material contained a carbon (C) and silicon carbide (SiC) mixture. This was placed in a funnel containing a 1:1 mixture of chloroform (99.9%, Sigma-Aldrich) and toluene (99.9%, Sigma-Aldrich). A two-phase solution was obtained after mechanical stirring, which allowed the separation of SiC from unreacted carbon. This procedure was repeated 10 times, and the resulting material was dried at 80 °C for 12 h to obtain SiC. The SiC substrate was treated with concentrated acid [28] to increase the conductivity and the concentration of anchoring points on the surface. Pt loading of SiC was carried out by a modified polyol method with potassium tetrachloroplatinate (K<sub>2</sub>PtCl<sub>4</sub>) as the metal precursor according to a procedure derived from previous works [25,27]. From four batches of platinization a total of about 1 g of the Pt/SiC material was obtained. The Pt content was about 22 wt%, and the size of the Pt nanoparticles was around 8 nm. Morphological characterization of the catalyst using transmission electron microscopy can be found in the earlier work [25,27]. The reference catalyst is commercially available Pt on Vulcan® carbon black (Pt/C) with 20 wt% Pt loading (BASF).

A detailed procedure for Nafion® ionomer adsorption on different carbon substrates can be found in our previous publication [7,29,30]. This procedure was applied for adsorption studies with SiC, carbon and their platinized equivalents. Briefly, a thorough mixing/adsorption between the powder sample and Nafion solution (Sigma Aldrich) was achieved by 15 min ultra-sonication with an ultrasonic bath (Bandelin Sonorex Super of frequency 35 kHz, the transmitted power is estimated to be below 2 W and the final temperature of the bath is around 50 °C); followed by 24 h mechanical shaking of the sample. These are a rather mild homogenization conditions, which should not lead to damage on the organic component in the mixture as reported by others [31,32,33]. The samples were afterwards centrifuged for 1 h at 12,000 rpm and 4 °C. Finally 600 µL of the well-separated clean solution was carefully transferred into a 5 mm NMR glass tube. 20 µL heavy water (99.9%, Sigma Aldrich) was added to provide a deuterium lock, and 20 µL 1% trifluoroacetic acid (99.9%, Aldrich) was added for internal reference. All NMR experiments were performed in a Bruker 400 MHz spectrometer with an auto-sampler. Signal analysis was done using Mestre Nova®. Data fitting was assisted by OriginPro® 9.1.

Catalyst ionomer electrode (CIE) microstructures containing around 30 wt% Nafion ionomer (w/w) were prepared by applying a catalyst/Nafion/water/alcohol suspension on a gas diffusion layer (GDL), SIGRACET® 35 DC (SGL Group), by screen printing. The Pt/SiC-containing CIEs were prepared with high loading (HL) of about 0.5 mg<sub>Pt</sub> cm<sup>-2</sup> and with low loading (LL) of about 0.2 mg<sub>Pt</sub> cm<sup>-2</sup>, respectively.

The CIEs were used as working electrode to perform cyclic voltammetry (CV) in a conventional three-electrode wet cell. A Radiometer® Hg/Hg<sub>2</sub>SO<sub>4</sub> electrode was used as the reference electrode. All potential values are reported versus (vs.) the reversible hydrogen electrode (RHE). A glassy carbon rod was used as the counter electrode. The liquid electrolyte was 1 M H<sub>2</sub>SO<sub>4</sub> (Sigma Aldrich). Electrochemical accelerated stress test (AST) was performed by potential cycling as a simulated

start/stop test [34]. The AST was carried out between 0.4 and 1.6 V with a scan rate of 1 V s<sup>-1</sup> up to 2500 cycles. The CV evaluation was performed between 0 and 1.2 V, with a scan rate of 10 mV s<sup>-1</sup>, after 1, 20, 100, 500 and 2500 AST cycle(s). The first cycle was abandoned, while the second cycle is reported in this work. Ar purging was maintained during the measurements with a constant flow of 0.2 mL s<sup>-1</sup>. The experiments were carried out with an electrochemical workstation (Zahner® IM6). The connection between the sample and the device was established with a 0.2 mm thick gold wire. Deviation of the measurements is within 5%.

The electrochemical surface area is calculated based on coulombic charge transfer of monolayer atomic hydrogen adsorption, as shown in Eq. (1)

$$ECSA = \frac{Q}{[Pt] \times A \times C} \quad (1)$$

where, ECSA presents electrochemical surface area [cm<sup>2</sup> mg<sup>-1</sup>]; Q presents the charge for hydrogen desorption [mC]; [Pt] presents platinum loading, [mg cm<sup>-2</sup>]; A presents geometric area [cm<sup>2</sup>]; C presents the charge required to oxidize a monolayer of atomic hydrogen on Pt catalyst, C = 0.22 [mC cm<sup>-2</sup>].

Utilization is the percentage of platinum surface area contributing in the electrochemical reaction in relation to its real geometric area. It is calculated according to Eq. (2)

$$U = \frac{ECSA \times \left(\frac{4}{3}\pi r^3 \rho\right)}{4\pi r^2} \times 100 = \frac{1}{3} \times ECSA \times r \times \rho \times 100 \quad (2)$$

where, U presents utilization [%]; r presents average radius of the platinum catalyst [m]; ρ presents density of platinum, 2.145 × 10<sup>7</sup> [g m<sup>-3</sup>].

X-ray diffraction (XRD) patterns were achieved by direct measurement on the electrodes using a Panalytical X'Pert diffractometer. Data treatment was assisted by X'Pert HighScope Plus. Dissolved Pt in the aqueous electrolyte was analyzed with a Varian® Atomic Absorption Spectrometer (AAS) equipped with a graphite furnace providing high sensitivity. X-ray photoelectron spectroscopy (XPS) analysis was performed using a SPECS® system with Mg Kα (1253.6 eV) as the X-ray source. The data was analyzed using CasaXPS™ and presented with Origin® Pro 9.1.

Membrane electrode assemblies (MEAs) of different sizes were prepared from the Pt/SiC-containing CIEs, standard CIEs and Nafion membrane by hot-pressing for 3 min at 140 or 150 °C and with a pressure depending on the MEA size and the applied equipment. Details on the MEA composition and manufacture are given in Table 1.

The MEAs with an active area of 50 cm<sup>2</sup> were characterized by electrode CV, polarization (IV) experiments, and electrochemical impedance spectroscopy (EIS) in a homemade single-cell setup. The operation temperature was 70 °C, and the feed gases were humidified to approximately 80% relative humidity (RH). The MEAs were conditioned by gentle operation until reaching a steady state. For the CV, the compartment of the investigated electrode was filled by N<sub>2</sub>, while the opposite compartment was filled by H<sub>2</sub>. The voltammograms were recorded from 0.05 to 0.6 V with a scan rate of 20 mV s<sup>-1</sup> using a Bio-Logic SP-150 potentiostat. The polarization experiments were done with ambient-pressure H<sub>2</sub> (anode) and air (cathode), where the IV curves were produced at increasing current steps with a hold time of at least 10 s per step. EIS was performed from 10 kHz to 100 mHz with approximately 70 recorded points.

The 6.25-cm<sup>2</sup> MEAs were subjected to single-cell polarization and continuous-operation testing in a 15-cell screening test plant based on MACCOR hardware. The operation temperature was 70 °C, and the gases (H<sub>2</sub> and air) were humidified at 69 °C and supplied at ambient pressure in stoichiometric values of 2 and 4 for λ<sub>H2</sub> and λ<sub>air</sub>, respectively. IV curves were recorded using increasing current steps, with each point

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