



Enhanced carbon monoxide tolerance of platinum nanoparticles synthesized through the Flash Joule Heating Method

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ABSTRACT

Was employ the Flash Joule Heating Method (FJHM) to synthesize carbon-supported Pt nanoparticles. In this method, an aqueous solution of the Pt precursor $\text{H}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$ is introduced into a reactor containing Vulcan XC 72 carbon. Subsequently, the mixture undergoes 50 cycles of discharges at 100 coulombs per discharge. Comparative XRD analysis with a commercially prepared Pt/C BASF, utilizing a reduction deposition method, reveals an expansion in the interplanar spacing of the platinum crystal lattice in the FJHM-prepared Pt/C catalyst (FJHM-Pt/C). This expansion suggests the emergence of structural defects, a finding confirmed by TEM images displaying distinct step-like features on the FJHM-Pt/C surface. Cyclic voltammogram analysis demonstrates a noteworthy increase in the oxidation pre-peak at 0.5 V for FJHM-Pt/C compared to Pt/C BASF. When employing pure H_2 as fuel, the single proton exchange membrane fuel cell (PEMFC) utilizing Pt/C BASF as the anode catalyst exhibits a higher maximum power density (MPD) than its FJHM-Pt/C counterpart. Conversely, in the presence of CO, the PEMFC with FJHM-Pt/C as the catalyst demonstrates a superior MPD compared to the cell equipped with commercial Pt/C as the anode. These findings underscore enhanced CO tolerance, highlighting the potential advantages of the FJHM preparation method.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are suitable device for energy conversion, thanks to their high-power density, efficiency, and operational viability even at low temperatures. However, the introduction should delve deeper into the needs and challenges surrounding these fuel cells. Notably, extensive research has been conducted on the development of electrocatalysts rich in defects, signifying a significant area of advancement in this field [1].

Platinum serves as a common catalyst at both the anode and cathode, facilitating the oxidation of hydrogen and the reduction of oxygen, respectively. However, the presence of impurities like carbon monoxide (CO), primarily derived from the catalytic reforming of hydrocarbons to obtain hydrogen, poses a challenge. CO adsorption on the platinum catalyst's active sites reduces the performance of the fuel cell at the anode [2].

In the 1990 s, studies on platinum single crystals [3–5] highlighted Pt (111) as the most active plane for CO oxidation, suggesting potential

strategies for enhancing catalytic processes. However, the application of such strategies, such as introducing steps and terraces to favor CO oxidation at less positive potentials [6], proved impractical for nanoparticle synthesis. This underscores the need for alternative approaches to mitigate CO adsorption on platinum surfaces.

A strategy to mitigate the issue of CO adsorption on platinum nanoparticles surfaces involves the development of binary and ternary Pt-based catalysts, such as PtRu, PtMo, and PtRuMo [7–12]. The presence of a second/third metal modifies the CO adsorption characteristics of Pt nanoparticles, with this effect attributed to reaction with surface oxy-hydroxyl species formed at less positive potentials than pure platinum [13], and/or by modifying the d-band of the noble metal, altering its affinity for CO adsorption [14]. In addition to Pt, other metals such as Ir, Te, Cu, Fe, and Rh have been studied for this purpose [15–18].

A common method to prepare these electrocatalysts involves the utilization of sodium borohydride as a reducing agent for both Pt and the second/third metal precursors [19,20]. Other method involves the process of spontaneous deposition of the second metal by immersing the

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platinum electrode within a solution that contains a ruthenium salt, leading to the irreversible adsorption of Ru onto the Pt surface [21]. In contrast, the forced deposition approach involves submerging the Pt electrode in an electrolyte under the presence of hydrogen bubbling or exposing the wet sample to a stream of H₂ gas [22]. This leads to the creation of a suitably reducing potential that promotes the direct deposition of Ru species onto the electrode. Both techniques predominantly employ Pt single-crystal surfaces as the preferred substrate [23]. Another approach entails the use of transition metal oxides, nitrides, carbides, or phosphides as co-catalysts. These co-catalysts serve to enhance the overall catalytic activity and selectivity of the Pt-based catalysts, particularly by influencing the adsorption properties of CO and other relevant species [24,25].

Ramos et al. [18] reported a novel approach involving the utilization of a sodium borohydride reducing agent in conjunction with a magnetic field and radiofrequency pulse. This study revealed a compression of lattice strain within the Pt crystallographic structure. As a result, the adsorption energy of CO on Pt/C was potentially attenuated. This outcome might be attributed to the introduction of structural defects, suggesting a correlation between lattice strain manipulation and CO adsorption behavior. Li et al. [26] showed that a Joule heating technique could induce the fragmentation of metal precursors, thereby facilitating the uniform blending of constituent elements. This is followed by a swift cooling phase, which facilitates the creation of precisely defined crystalline nanoparticles.

Qiu et al. [27] synthesized an Ag/Co/C electrocatalyst using the flash Joule heating method for the oxygen reduction reaction within an alkaline environment. This hybrid catalyst delivered a specific activity that exceeded that of the pristine Ag/C by 40 times, and its mass activity surpassed the reference material by 52 times at 0.8 V vs. RHE in alkaline media. Additionally, the hybrid catalyst showed enhanced tolerance to methanol and ethanol compared to commercially available Pt/C electrocatalysts. In the present work, for the first time a Pt/C electrocatalyst was prepared using the Flash Joule Heating process in a device developed within our research group. The aim is to synthesize a catalyst with defects, thereby enhancing the activity for the oxidation of the H₂+CO mixture originating from catalytic reforming.

2. Experimental

The Pt/C 20 % electrocatalyst was prepared using a Flash Joule Heating Method, a technique involving the placement of appropriate amounts of the metal precursor H₂PtCl₆·6H₂O (Aldrich) and water in a 1:1 (w/w) ratio onto a quantity of Vulcan XC-72 carbon to obtain a catalyst with a 20 % loading in a graphite crucible. The crucible is then sealed and subjected to 50 discharge cycles at 100 coulombs per discharge at 65 V, for a total time of 60 seconds [28]. The charge-to-electron ratio required for the metal reduction is 2 per discharge. Subsequently, the obtained FJHM - Pt/C catalyst was subjected to characterization.

The platinum load on carbon was determined by thermogravimetric analysis performed on a SETARAM LABSYS. The samples were heated from 25 to 900 °C at a constant rate of 10 °C per minute. The electrocatalysts were characterized through X-ray diffraction (XRD) utilizing a Rigaku Miniflex II diffractometer equipped with a Cu K α source ($\lambda = 1.54056 \text{ \AA}$) at a 2θ range spanning from 20° to 90°, employing a step size of 0.02° and a scan duration of 2 seconds per step. Transmission Electron Microscopy (TEM) analysis was carried out employing a JEOL electron microscope model JEM-2100.

Cyclic voltammetry measurements were carried out at a temperature of 25°C, employing an Autolab PGSTAT 302 potentiostat/galvanostat. The working electrode comprised a vitreous carbon (0.2 cm²) material with a deposited porous ultrathin layer [29] in an aliquot of 20 μl . The reference electrode employed was the reversible hydrogen electrode (RHE), while the counter electrode took the form of a platinum (Pt) plate. These electrochemical analyses were performed within

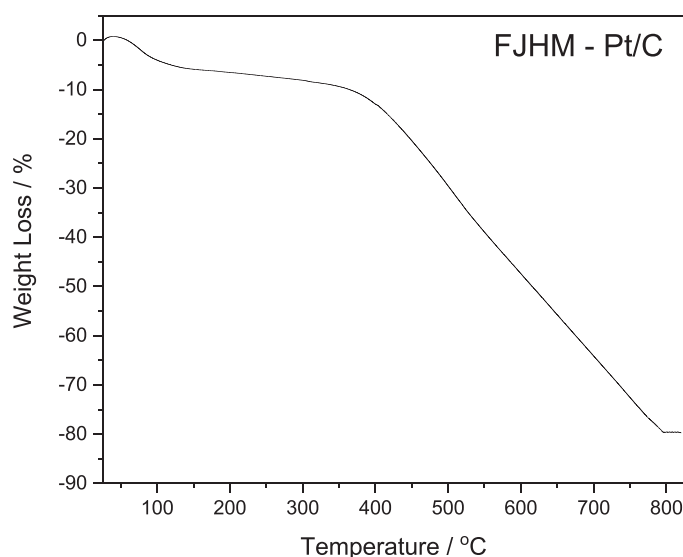


Fig. 1. Thermogravimetric analysis of FJHM-Pt/C.

0.5 mol L⁻¹ H₂SO₄ solutions saturated with nitrogen (N₂). For CO-stripping experiments, the working electrode was purged with N₂ for 30 minutes, then exposed to purified CO gas for an additional 30 minutes, with the working electrode potential set at 0.2 V vs. RHE. Following the adsorption process, CO was purged from the electrolyte solution, subsequently submitted to 15 minutes of N₂ bubbling. The CO-stripping voltammograms were recorded using a scan rate of 10 mV s⁻¹.

The fuel cell experiments were performed utilizing Pt/C materials synthesized by Flash Joule Heating Method for the anode and commercial Pt/C (BASF) for the cathode. A hydrogen flux of 300 mL min⁻¹ was employed for the anode, while the cathode utilized an oxygen flux of 200 mL min⁻¹. Tests were carried out in a single PEMFC, featuring electrodes with an active geometric surface area of 5.0 cm². The gas diffusion layer comprised PTFE-treated carbon cloth, and the electrolyte involved a Nafion® 117 membrane.

For the fuel cell investigations, both the anode and cathode utilized electrodes loaded with 1.0 mg_{Pt} cm⁻² of electrocatalyst. In experiments involving the synthesis gas (H₂+CO), atmospheric pressure was

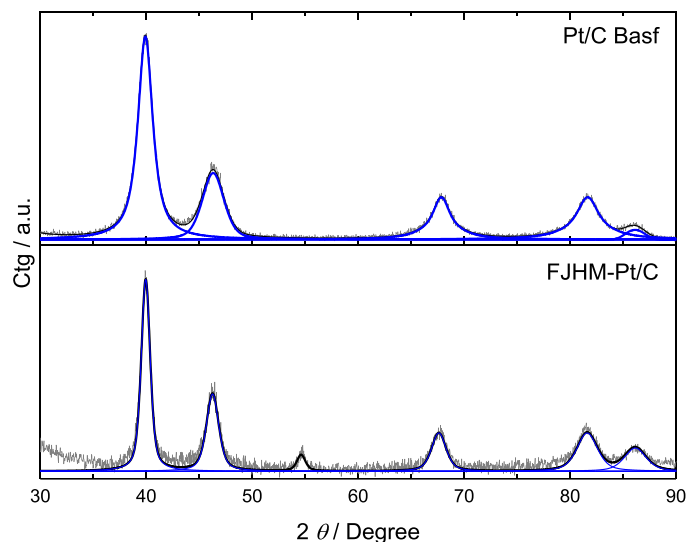


Fig. 2. X-ray diffractions pattern of Pt/C BASF and FJHM-Pt/C. In grey measured data, in black fitted data, and in blue the function corresponding to each platinum peak.

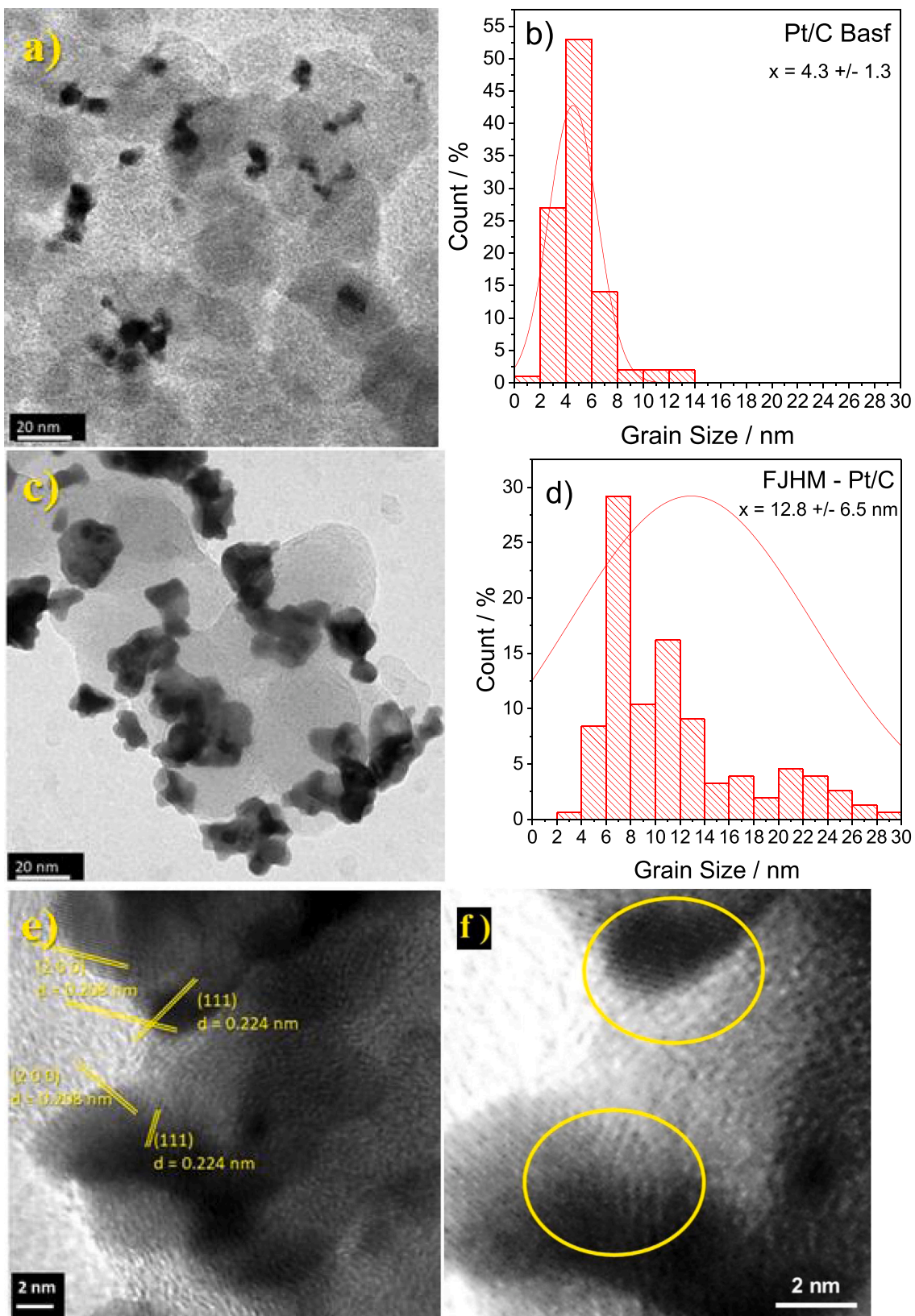


Fig. 3. a) TEM of Pt/C BASF, b) histogram of size distribution of Pt/C BASF, c) TEM of FJHM-Pt/C, d) histogram of size distribution of FJHM-Pt/C, e) TEM image of FJHM-Pt/C with d-space and plane highlighted, f) marking of interplanar crossings in the TEM image of FJHM-Pt/C.

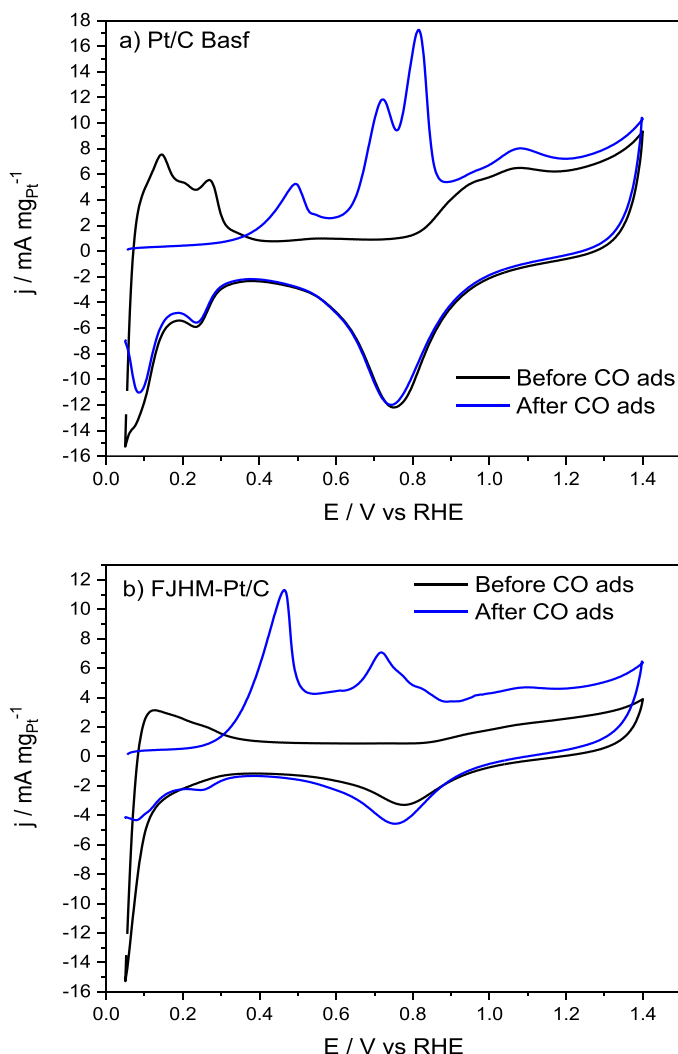


Fig. 4. Cyclic voltammetry of Pt/C BASF and FJHM-Pt/C in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$, $v = 10 \text{ mV s}^{-1}$.

maintained at the anode and cathode. The operating temperature of the fuel cell was set at 80°C , with the flux of H_2+CO (with CO at 100 ppm) regulated at 300 mL min^{-1} for the anode, and O_2 flux set at 200 mL min^{-1} for the cathode. Pt/C was prepared in triplicate, and these distinct batches were characterized simultaneously with an error margin of less than 10 %.

3. Results and discussion

As a novel synthesis method, the FJHM-Pt/C material was submitted to a thermogravimetric analysis to verify the metal-to-carbon ratio. The weight loss of the electrocatalyst (Fig. 1) initiates below 100°C as a result of the desorption of adsorbed water [30]. Noticeably, substantial mass reductions occur at approximately 230°C due to the decomposition and evolution of CO and CO_2 from the carbon support. After the depletion of carbon, the mass remained constant at 79.5 %, indicating a platinum content of $\sim 20 \%$, and that during the synthesis there is no loss of carbon or platinum.

The XRD patterns of FJHM-Pt/C and, for comparison, of a commercial Pt/C (BASF), prepared by a reduction-deposition method [30] are shown in Fig. 2. The diffraction patterns revealed distinct peaks at 2θ angles of approximately 40° , 47° , 67° , 82° , and 86° , corresponding to the (111), (200), (220), and (311) planes of a face-centered cubic (FCC) structure. The Pt/C BASF sample aligned with the reference parameters

JCPDS #87–647, featuring d-spacing values of 0.230, 0.194, 0.138, 0.117, and 0.112 nm for the (111), (200), (220), (311), and (222) planes, respectively.

In contrast, FJHM-Pt/C exhibited noticeable shifts toward more negative values in the 2θ angles for the (200), (220), (311), and (222) planes, while the (111) plane displays a shift towards more positive angles when compared to Pt/C BASF. This shift strongly suggests alterations in the lattice parameters of the crystal structure, with FJHM-Pt/C featuring d-spacing values of 0.224, 0.208, 0.142, 0.125, and 0.115 nm. It is valid to add that in the diffractogram of the FJHM material, a peak appears at $\sim 54^\circ$ corresponding to the 101 plane of graphitized carbon.

An additional significant observation was the prominence of the (222) plane peak, which appears considerably larger than that observed for the commercial Pt/C. To elucidate this, the relative intensities of the (111), (200), (220), (311), and (222) planes was calculated. In the case of commercial Pt/C, these planes showed relative intensities of 100, 42, 30, 28, and 5 %, respectively, while for FJHM-Pt/C, the corresponding values were 100, 56, 32, 45, and 29 %. This discrepancy indicates that the particle production method employed here discourages the formation of the (111) plane while favoring the high-index planes such as (311) and (222). These changes in the lattice parameters and relative plane intensities strongly suggest that the Flash Joule Heating method induced structural modifications in the platinum nanoparticles. Such structural alterations may lead to the emergence of structural defects, a phenomenon well-documented in the literature, which has the potential to influence the catalytic properties of the material [31,32].

Fig. 3 displays transmission electron microscopy (TEM) images for both Pt/C BASF and FJHM-Pt/C. Both materials showed a well-dispersed distribution on the support. However, the particles in the FJHM-Pt/C catalyst were significantly larger in size and feature prominent corners, whereas the Pt/C BASF nanoparticles presented rounded shapes. The pronounced corners in the FJHM-Pt/C nanoparticles could be attributed to a rapid and forced reduction process induced by the electron cascade resulting from the discharges during synthesis.

Additionally, intriguingly, the TEM images of the FJHM-Pt/C catalyst revealed the presence of distinctive step-like features (Fig. 3f), which can be interpreted as indicative of defects within the crystal structure of the electrocatalyst. These findings prompt a more in-depth exploration of the impact of these structural differences on the electrocatalytic properties and performance of Pt/C in various applications.

Fig. 4 shows the cyclic voltammetry of Pt/C BASF and FJHM-Pt/C nanoparticles during CO adsorption and desorption in a $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ aqueous solution. In the absence of CO (depicted by the black line), a well-defined hydrogen adsorption and desorption region ranging from 0.05 to 0.4 V was clearly observed [18,30]. In the case of the FJHM-Pt/C catalyst, a reduction in the sharpness of the hydrogen adsorption and desorption peaks can be observed. This modification can be attributed to changes in the relative abundance of crystallographic facets or to defects generated during the particle formation process.

In the case of the commercial Pt/C and its CO oxidation behavior, it is possible to observe the typical pre-peak centered at 0.5 V, along with two additional higher peaks at 0.75 V and 0.85 V. However, when examining FJHM-Pt/C, a notably strong peak emerges at 0.45 V, which is significantly larger than that observed for Pt/C. Additionally, there are two less intense peaks at approximately 0.72 V and 0.82 V, corresponding to those observed for commercial Pt/C. This heightened peak at 0.45 V in FJHM-Pt/C, when compared to Pt/C BASF, suggests that a substantial portion of the adsorbed intermediates has been oxidized at lower potential values. Cudero et al. [33,34] have shown that the pre-peak corresponds to the oxidation of adsorbed CO, primarily resulting from its reaction with oxygenated species that initially nucleate at step sites. The appearance of the main peak coincides with the nucleation of oxygenated species not only at step sites but also on the terrace regions [34]. The presence of the pre-peak may also indicate an increase in structural defects within the electrocatalyst.

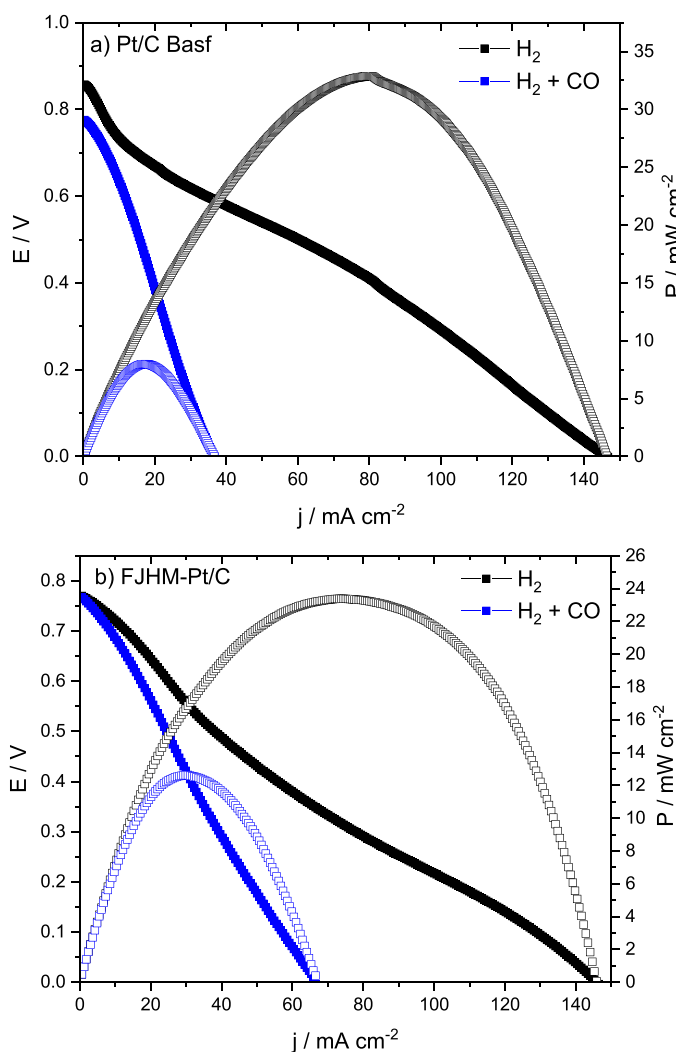


Fig. 5. Polarization and power density curves for PEMFCs with Pt/C BASF and FJHM-Pt/C as the anode catalyst. The black lines represent the H₂ experiment and the blue lines H₂+CO experiment.

Fig. 5 presents the polarization and power density curves for PEMFCs with both Pt/C BASF and FJHM-Pt/C as anode catalysts. In the case of pure H₂, the cell with the commercial Pt/C electrocatalyst showed a remarkable maximum power density (MPD) of approximately 32 mW cm⁻² and an open-circuit potential of 0.85 V. Conversely, the cell with FJHM-Pt/C catalyst delivered a lower MPD of 22 mW cm⁻², about 31 % smaller than that of the cell with Pt/C BASF, and a reduced open-circuit potential to 0.75 V. These results emphasize the superior performance of the Pt BASF electrocatalyst for pure hydrogen oxidation, which can likely be attributed to its considerably smaller average particle size compared to FJHM-Pt/C.

However, when the oxidation of an H₂+CO mixture in a single PEMFC was evaluated, an opposite result was observed. The FJHM-Pt/C electrocatalyst delivered a higher MPD (13.0 mW cm⁻²) compared to the commercial Pt/C electrocatalyst (8.0 mW cm⁻²). The reduction in maximum power density for the Pt/C BASF was approximately 75 %, whereas for FJHM-Pt/C was 46 %. This suggests an improved tolerance to CO. This intriguing observation aligns with the cyclic voltammetry results. Several factors may contribute to this phenomenon, including the presence of surface defects, adlayers with varying crystallographic orientations, and/or strong metal/support interactions [18,35–38]. These factors likely play a role in a complex, multi-step CO oxidation process on the Pt catalyst surface.

4. Conclusion

The Flash Joule Heating Method enabled the preparation of an effective platinum electrocatalyst for the oxidation of the H₂+CO mixture. The thermographic analysis confirmed the metal load of 20 %. X-ray diffraction revealed significant shifts in the diffraction angles for specific crystallographic planes in FJHM-Pt/C compared to Pt/C BASF. Notably, the (222) plane exhibited a more prominent peak in FJHM-Pt/C, suggesting a preference for high-index planes. TEM images further demonstrated that the FJHM-Pt/C particles were larger and featured prominent corners, while the commercial Pt/C particles had rounded shapes. Regarding CO oxidation behavior, FJHM-Pt/C exhibited a stronger peak at 0.45 V, indicating a higher ability for CO oxidation compared to Pt/C BASF. In single PEMFC tests with pure H₂, the commercial Pt/C outperformed FJHM-Pt/C, likely due to its smaller average particle size. However, in the presence of CO, the cell with the FJHM-Pt/C catalyst displayed a higher power density, indicating an enhanced CO tolerance. This result can be attributed to various factors, including Pt structural defects and metal-support interactions.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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