Development of Ru-substituted Pt@Nitrogen-doped carbon catalyst for highly durable PEMFC with high chemical and structural tolerance

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ABSTRACT

This study explores the development of advanced Pt-based catalysts for Polymer Electrolyte Membrane Fuel Cells (PEMFCs), critical for carbon neutrality and clean energy systems. To address the high cost and limited durability of platinum, two strategies were investigated: partial substitution of Pt with Ru to improve CO tolerance, and the use of nitrogen-doped carbon (N-doped carbon) as a support to prevent agglomeration and degradation. Ru substitution enhances CO resistance by facilitating CO oxidation, while the N-doped carbon support strengthens metal-support bonding for improved durability. These approaches offer a viable path to reduce PEMFC costs and increase performance.

KEY WORDS

Polymer Electrolyte Membrane Fuel Cell, Platinum Catalyst, Ruthenium Substitution, Nitrogen-Doped Carbon, CO Tolerance

1. INTRODUCTION

To Achieving carbon neutrality by 2050 and developing clean energy systems are essential steps to address climate change, with fuel cells, particularly Polymer Electrolyte Membrane Fuel Cells (PEMFCs), playing a key role. PEMFCs generate electricity from hydrogen and oxygen reactions, emitting only water, and operate efficiently at low temperatures, making them attractive for hydrogen vehicles.

However, commercial platinum-based catalysts (40 wt.% Pt/C) account for around 40% of PEMFC costs, with platinum’s high expense and limited durability hindering widespread adoption [1]. PEMFC durability suffers from platinum agglomeration and dissolution, along with CO poisoning from trace CO impurities in fuel, leading to performance degradation [2-3].

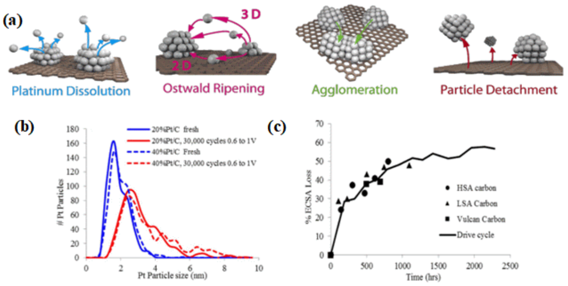

Figure 1. (a) Degradation mechanism of platinum catalyst [4], according to the long-term durability test, (b) Changes in PtC catalytic particles, (c) electrochemically active surface area loss [5]

To address these issues, this study explores two main strategies: enhancing CO resistance and durability by partially substituting Pt with Ru, a metal known for CO tolerance, which helps oxidize CO to CO_2 in the presence of Pt, improving chemical stability [6-7]. Additionally, nitrogen-doped carbon support is used to strengthen metal-support bonding, reducing agglomeration and particle detachment. Nitrogen doping has shown to improve the stability and durability of platinum nanoparticles on carbon supports, making the catalyst more robust under prolonged operational conditions [8].

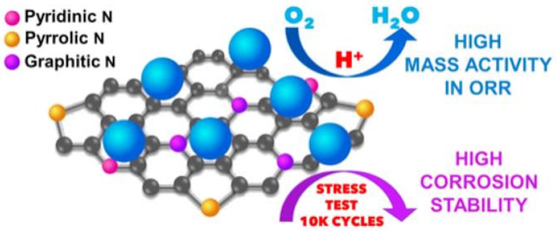

Figure 2. A schematic diagram of a nitrogen-doped carbon [9]

2. EXPERIMENTAL

In this study, a plasma synthesis device available in our laboratory was used for catalyst synthesis. For catalyst preparation, 50 ml of NMP, 30 ml of toluene, 20 ml of pyridine, and 8 mmol of DDAP were mixed with varying molar amounts of Carish to create the precursor solution, which was dispersed at 800 rpm for 1 hour. A total of three catalysts were synthesized in this study: Pt/NC, PtRu2/NC, and PtRu3/NC, with Carish molar amounts of 0 mmol, 6 mmol, and 9 mmol, respectively.

Subsequently, the well-dispersed precursor underwent plasma engineering under the conditions of 60 kHz frequency, 0.6 μs pulse width, and 10 kV voltage for 30 minutes. The plasma conditions were carefully selected to apply minimal energy while ensuring stable plasma maintenance.

After completing the solution plasma process, the solution was centrifuged at 8000 rpm for 30 minutes to separate the solid samples from the organic solvents. The separated samples were then filtered and washed with ethanol and water to remove any residual organic solvents from the sample surfaces.

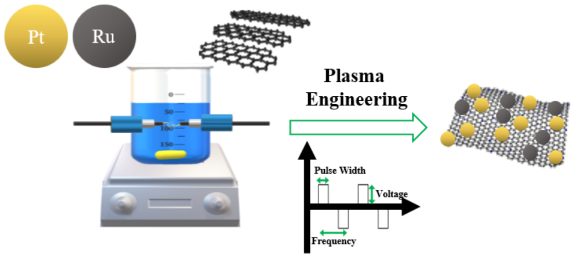

Figure 3. Schematic diagram of plasma engineering synthesis process

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction (XRD) analysis

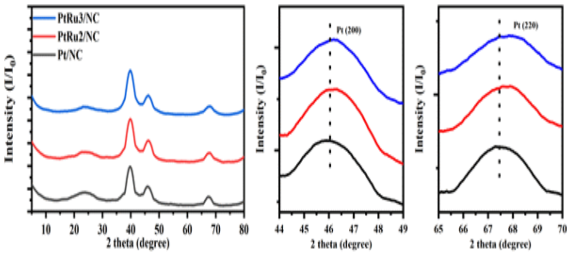

Figure 4. XRD diffractograms of the catalysts

Figure 4 presents the X-ray diffraction patterns of Pt/NC, PtRu2/NC, and PtRu3/NC catalysts. Three distinct peaks are observed around 40°, 46°, and 67.5°, corresponding to the (111), (200), and (220) planes of metallic Pt, respectively [6]. Notably, the diffraction peaks at the (200) and (220) planes for PtRu2/NC and PtRu3/NC exhibit a slight rightward shift compared to Pt/NC. This shift suggests structural changes due to the addition of Ru, which may influence the catalyst's performance, to be evaluated in subsequent testing.

3.2 Inductively Coupled Plasma Spectrometry (ICP) analysis

Table 1: Table of ICP Analysis Results for catalysts

ICP (wt.%)	Pt/NC	PtRu2/NC	PtRu3/NC
Platinum	15.7	14.8	15.5
Ruthnium	0	0.73	0.91

Due to the absence of observable Ru peaks in the XRD analysis, further elemental quantification of the catalysts was conducted using ICP analysis. Table 1 displays the ICP results for Pt/NC, PtRu2/NC, and PtRu3/NC, indicating an increase in Ru content with the increasing molar ratio of Ru, consistent with the synthesis design targeting low Ru inclusion.

3.3 TEM analysis

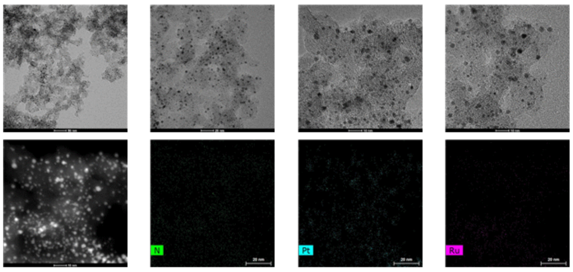

Figure 5. TEM images of PtRu3/NC

Figure 5 shows TEM images and TEM-EDS mapping for PtRu3/NC. Across all three catalysts, including PtRu3/NC, nitrogen doping in the carbon support and uniform metal particle dispersion were confirmed. The average metal particle size was approximately 2 nm, which is expected to contribute to an increased reactive surface area.

4. CONCLUSION

The Pt-based catalysts with Ru substitution and nitrogen-doped carbon support demonstrated enhanced CO resistance and structural stability, addressing key durability challenges in PEMFCs. Ru substitution improved CO oxidation, while the N-doped carbon support prevented agglomeration and detachment, preserving catalyst integrity. These modifications show promise for reducing costs and enhancing PEMFC performance, supporting their wider adoption in sustainable energy systems.

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