Review on Polymer-supported Metal Particles as Catalysts in Microfluidic Fuel Cell

Hongyan Liu*

Department of Mechanical Engineering, National University of Singapore, Singapore, 117581

ABSTRACT

In modern society, electrical energy is commonly converted by chemical energy, which is essential for various applications. Over time, several techniques involved in converting energy have been investigated, including electricity generator, battery, and fuel cell. Conventional electric generators powered by fossil fuel face challenges related to efficiency because of multiple steps within its energy converting process. On the other hand, batteries also have their limitations, primarily related to density of energies, which is limited by their volume for storing reactants. In contrast, fuel cells represent an anticipated technique for supplying power in the future. This innovative technique takes the strengths of both electricity generator and battery, offering great efficiency of converting energies process and impressive density of energies simultaneously. By directly converting the chemical energy from fuels into electrical energy through an electrochemical process, fuel cells overcome the efficiency and storage limitations associated with traditional generators and batteries. Microfluidic fuel cells (MFFCs) are a category of fuel cells with structure sizes ranging from 1 to 1000 μm. The choice of catalyst material has been demonstrated to affect the efficiency of MFFCs. In recent years, there has been growing interest in utilizing metal nanoparticle/conductive polymer nanocomposites as catalysts in fuel cells. Conductive polymers have emerged as promising substitutes for traditional carbon-supported catalysts. Thanks to properties of large specific areas, satisfying electrically conductive capabilities, and chemically stable ability in their porous surfaces, it makes polymers attractive for supporting catalysts in fuel cells. When metal nanoparticles (NPs) are incorporated into these conductive polymers in a highly dispersed manner, it maximizes the active surface area available for oxidation and reduction reactions, thereby allowing for low catalyst loading in fuel cell applications. In this study, we aim to explore and discuss recent developments in the field of polymer-supported metal nanoparticles as catalysts for fuel cells. By examining the synergistic effects of conductive polymers and metal NPs, we hope to gain insights into their possibility to improve the efficiency and performance of fuel cell. This research could be an advancement and reference for developing more efficient and sustainable energy conversion technologies.

KEYWORDS

Microfluidic fuel cell; Catalyst; Metal particle; Polymer support

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*Corresponding Author: Hongyan Liu.

1 Introduction

Converting chemical energy into electrical energy is widespread nowadays, powering a wide range of applications. In order to achieve the conversion, various techniques used for conversion of energies were created and investigated, including electricity generator, battery, and fuel cell. Conventional electricity generator driven by fossil fuel suffers from inefficiency because of their multiple steps process for converting energy. However, they have the potential to operate for a very long time if fuel can be continuously provided, resulting in large density of energies. On the other hand, batteries achieve much higher energy efficiency thanks to their one-step energy conversion process. However, their energy density is significantly limited by the capacity to store reactants. Fuel cells, an innovative technology, combine strengths of both electricity generator and battery. They achieve satisfying efficiency for converting energies and impressive density of energies simultaneously, making them an anticipated choice for supplication of power in the future. Unlike general batteries, fuel cells can work continuously without the need for recharging, as long as they receive a steady supply of fuel. Microfluidic fuel cells (MFFCs) are a specific category of them whose structure sizes are less than 1000 μm but greater than 1 μm. Unlike conventional fuel cells, MFFCs typically do not need a proton exchange membrane (PEM) and operate in the principle of laminar flow. These MFFCs can be classified into 3 types: microfluidic photocatalytic fuel cell (MFPFC), microfluidic biofuel cell (MFBFC), and microfluidic electrochemical fuel cell (MFEFC), each distinguished by catalysts used. Among these, MFEFC offers a great number of strengths in contrast to MFBFC and MFPFC. Catalyst plays an important role in influencing efficiency in operation process of MFEFCs. In recent years, there has been significant interest in using metal nanoparticle/conductive polymer nanocomposites as catalysts in fuel cells. Conductive polymers have gained attention as promising substitutes for traditional carbon-based supports. Due to properties of large specific areas, satisfying electrically conductive capabilities, and chemically stable ability in their porous surfaces, it makes them well-suited for fuel cell applications. Incorporating highly-dispersed metal nanoparticles (NPs) in the conductive polymer further expands the surface areas for the electrochemical reaction, enabling little catalyst loadings for applications in fuel cells. In this study, we focus on recent developments in polymer-supported metal nanoparticles as catalysts, specifically exploring their potential applications in MFEFCs. By examining the synergistic effects of these nanocomposites, we hope to shed light on their ability to enhance fuel cell performance and contribute to the advancement of efficient and sustainable energy conversion technologies.

2 Background of Microfluidic Fuel Cell

An MFFC operates by utilizing two distinct laminar flows within a microchannel: one containing utilized fuel and the rest containing utilized oxidant. Both flows are supplemented with a support of acidic or alkaline electrolyte to enhance their ionic conductivity, which is essential for efficient electrochemical reactions. The microfluidic flow in MFFCs offers a significant advantage due to its low Reynolds number, resulting in a unique behavior. The anolyte and catholyte coexist in the microchannel without experiencing intense mixing, creating a stable surface at the midpoint within this microchannel. In this surface, liquid diffuses slowly, and it exhibits significantly slower compared to the advective flow of electrolyte in the channels. This controlled diffusion at the interface greatly minimizes reactant crossover, a crucial aspect in ensuring the normal operation of the fuel cell. [1-5] Microfluidic fuel cell systems offer a promising solution to address the challenges associated with traditional fuel cells that rely on PEM. In contrast, microfluidic fuel cells operate without the necessity of a membrane, thanks to their utilization of micro laminar flow, which occurs in 3 primary

configuration types:[6] (i) In the first configuration, a single flow of electrolyte replaces the membrane, creating a thin microchannel. This setup is particularly suitable for fuel cell utilizing gas reactants like H2 and O2, separated in different microchannels; (ii) The second configuration involves 2 parallel flows, where fuels and oxidants or fuels and electrolyte flows in a format of separated layers and co-lamination. This arrangement ensures the elimination of the source of convection or turbulence from cross-stream mixing. Every flow containing an electrolyte to facilitate ion conducting from an electrode to another, but the fuels and oxidants are contained within separated streams; (iii) The third configuration features 3 parallel flows of fuels, electrolytes, and oxidants, operating in the approximate co-laminar manner. Similar to the second type, this setup also relies on low Reynolds numbers to minimize cross-stream mixing. The mixing between fuels and oxidants flows diffuses at a slow rate, and may be regulated by changing stream rates of every flow or by an introduction of the third electrolyte flow. These co-laminar flow configurations enable precise control over reactant delivery and ionic conduction without requirements for traditional membranes. Through optimizing the laminar-flow conditions, microfluidic fuel cells demonstrate great potential for efficient and reliable energy conversion, offering a promising alternative to conventional fuel cell technology. Figure 1 illustrates a typical MFFC.

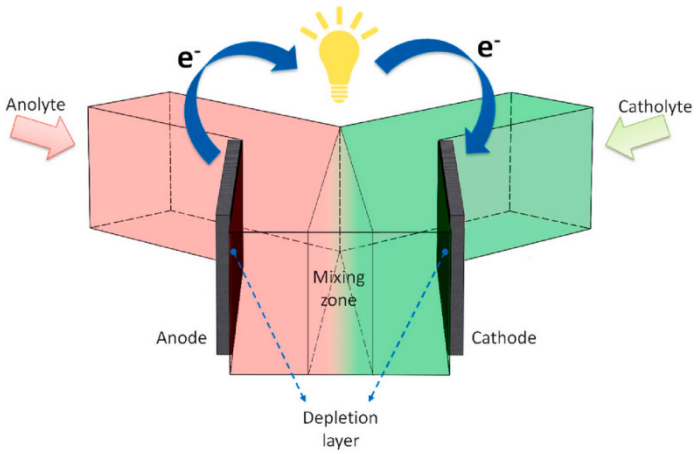

Figure 1. An illustration of a common MFFC featuring Y-shape structure.[7]

3 Common Types of Fuels in Microfluidic Fuel Cell

Extensive efforts have been dedicated to advancing the MFFC technology, focusing on reduced cost, enhanced power productivity, efficient fuel employment, and seamless integration. In initial stages, MFFCs utilized vanadium redox species, similar to vanadium redox flow batteries (RFB), but without the need for a membrane. However, due to high toxicity of vanadium, this approach was not suitable for portable electronics. Subsequently, hydrogen fuel was explored, initially dissolving in the anolyte but encountering issues with weak concentrating of fuels, then was provided as gas forms from external sources. To address the challenge posed by storage of hydrogen, liquid hydrocarbon fuel like methanol, ethanol and formic acid were investigated due to great densities of energies and convenient storing manners. While the fuels demonstrated highly soluble within the electrolyte, the slow and inefficient oxidation reactions necessitated noble metal-based catalyst at large cost, that are susceptible to carbon monoxide poisonously from the intermediate of reactions. Moreover, toxicity of methanol raised safety concerns, while C–C bond in ethanol proved challenging to break, leading to the formation of harmful intermediates. Formic acid, on the other hand, produced CO_2 bubbles vigorously, leading to disruption at the interfacial of the anolyte and catholyte and unstable

discharge. Besides the aforementioned fuel types, recent literature has explored other liquid fuels like H_2O_2, glucose and glycerol. H_2O_2 fuel has gained interest as it can function as both a fuel and oxidant, eliminating the crossover issue by realizing a stream of electrolyte. However, H_2O_2 is likely to decompose on electrodes and generates large O_2 bubbles that disrupt operations of fuels. Glucose fuel, primarily applied in implantable technique, utilize the bioglucose fluids to realize long-lasting operation, but its complex molecule limits power output. Glycerol, benefited from its non-flammable and non-volatile properties in contrast to ethanol and methanol, faces challenges with highly viscous property, restricting its concentrating within anolytes. What's more, MFFCs have been studied with other fuel types like ethylene glycol (EG), hydrazine, urea, ammonia and borohydride, showcasing the versatility and efficiency of technology in generation of electricity using various fuels. With nearly two decades of development, MFFCs have demonstrated adaptability and proficiency in electricity generation, highlighting their potential as a flexible and efficient energy conversion technology. Continuous research and advancements in MFFC systems hold promise for revolutionizing the way we generate electrical power in a diverse range of applications.

4 Common Types of Polymer-based Metal Particles

The synthesis of polymer-supported metal particles can be achieved through two main approaches: ex-situ and in-situ methods.

(1) Polypyrrole-supported Pd particles (PPy-supported Pd particles)

PPy-supported Pd particles demonstrate several advantageous features in contrast to the Pd particles without PPy supports. The incorporation of PPy in the support leads to an enlarged electrochemically active surface area and improved electron transport, contributing to improved electrocatalytic capabilities and superior stabilities in methanol oxidation reaction. In particular, the PPy-supported Pd particles exhibit significantly larger electrochemically active surface areas, specific activities, and overall stabilities for methanol oxidation reaction when compared with Pd particles without PPy supports. These clearly indicate polymer-supported material exerts an important effect of the catalytic performance and stable capability of the methanol oxidation reaction process. The study offers a convenient and efficient way for preparing the 3-dimensional structure, and presents a catalyst showing greatly improved catalytic performances for microfluidic fuel cell. Figure 2 shows and compares some densities of peak current of different catalysts. [8]

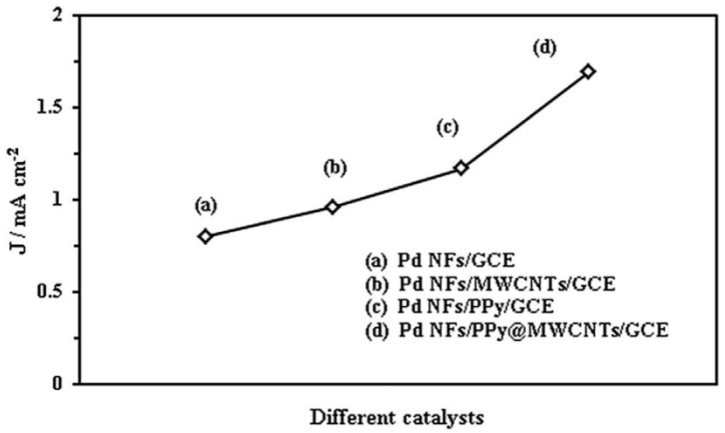

Figure 2. Peak current densities of some catalysts on methanol electrooxidation. (NF: nanoflower; GCE: glassy carbon electrode; MWCNT: multi-walled carbon nanotube) [8]

(2) Polymer-supported Pt-based particles

In their study, Jia et al. developed an innovative support material by combining Poly (triazine imide) (PTI) to enhance their performances of Pt-based catalyst. Additionally, they introduced tin (Sn) as the supplement catalyst, recognizing its ability to diminish the poison effects commonly observed in Pt catalysts. The PTI nanosheet in PTI hybrids played a crucial role in facilitating the production of well uniform Pt-Sn particles. As a result, PTI-supported Pt-Sn particle catalysts exhibited outstanding catalytic capability. The outcomes are illustrated in Figure 3.[9] Choi et al. conducted a study on synthesis of Pt-Ru alloy particles, utilizing two conductive polymers, namely poly (N-vinyl carbazole) and poly (9-(4-vinyl-phenyl) carbazole). Similarly, Kim group and Choi group synthesized polyaniline (PANi) to be the supports for Pt-Ru catalysts in a direct methanol fuel cell system. They performed investigations to make comparison between the PANi-supported Pt-Ru particles and carbon-supported Pt-Ru particles. Amani et al. focused on synthesizing PANi-supported Pt-Sn particles, utilizing a series of atom ratios of Pt and Sn through the impregnation method. Yaldagard and colleagues investigated catalytic performances of PANi-supported Pt particles for methanol oxidation reaction and oxygen reduction reaction. Wu et al. proposed the use of polypyrrole nanowire networks (PPNNs) in passive direct methanol fuel cell. Furthermore, Selvaraj et al. prepared polypyrrole-supported Pt-Ru particles. This was then the depositing of Pt particles on the PPy composite membranes, leading to the formation of PPy-supported Pt particles.[10-16]

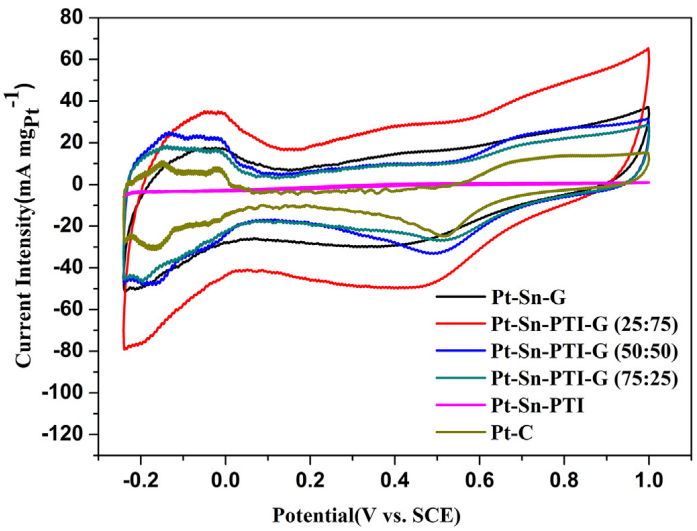

Figure 3. Comparison of current intensity of different catalysts. (G: graphene)[9]

(3) Polydopamine-supported metal particles

Polydopamine (PDA) has shown great promise as a highly useful preparation in combination with electrocatalysts. Additionally, the results obtained with carbon nanotube-supported metal particles for catalysts in methanol oxidation have been thoroughly studied and compared.

1) In alcohol oxidation

Liu and colleagues developed a support material using a multi-step process, starting with the oxidation of carbon nanotube (CNT) using KMnO4, followed by the creation of the PDA membrane, and finally forming ultra-dispersed Pt particles. The resulting PDA-supported Pt particles catalyst exhibited excellent catalytic capability in methanol oxidation. Qiu et al. reported a series of related catalysts with H_2 [$PtCl_6$] to PDA contents. Du and colleagues made treatments within dopamine

solution and then deposited Pd particles. They was further reacted with $H[AuCl_4]/NaBH_4$ to synthesize 3 electrocatalysts with different Pd-Au ratios. The Pd-Au, Pd particles were in uniform distribution over the supports. Kim and colleagues investigated the development and utilization of a PDA-supported Pt particle syntheses. Recently, the group studied the synthesis of PDA-supported Pt particles. Pd particles were formed on PDA sphere surfaces through Na_2 $[PdCl_4]$ with Lascorbic acid. By using PDA, well dispersed homogeneous Pd particles were generated. The shifts in Pd-binding energy provided evidence of the modifying structures of Pd induced by PDA.[17-22]

2) In oxygen reduction reaction

In fuel cells, the common cathode reaction is the oxygen reduction reaction. While platinum-based materials are known for their high oxygen reduction reaction activity, their widespread use is limited due to the high cost of platinum. To address this, researchers have been working on developing alternative catalysts with excellent oxygen reduction reaction activity. One such promising catalyst is coated by PDA This nanocomposite has demonstrated remarkable electrocatalytic activity for oxygen reduction. Additionally, a cost-effective electrocatalyst was prepared through mixing process of $CoCl_2$ and $FeCl_3$ solutions with PDA. Zheng and colleagues successfully developed composite membranes with PDA and then decorating them with silver particles. This membrane showed potential for various applications, including fuel cells. Another effective gas diffusion electrode catalyst was prepared using a simple method. Graphene Oxide (GO) was treated with dopamine, and then with H_2 $[PtCl_6]$ was introduced to form PDA-supported Pt particles.[23-26]

3) Other electrochemical reaction

Kim and colleagues successfully synthesized membranes using a combination of polytetrafluoroethylene, PDA, and ceria particles. These membranes were investigated for their potential application in alcohol oxidation. Additionally, the Saipanya group conducted a study on their performance of catalysts when formic acid undergoes oxidation, with a particular interest in their application indirect formic acid fuel cell. In a recent research, they investigated the preparation of PDA composites with Pt-Pd metals, with three ratios of 1:1, 1:3, and 3:1. The preparation involved mixing PDA/rGO with H_2 $[PtCl_6]$ and $PdCl_2$ and subsequently reducing the mixture using $NaBH_4$.[27-28]

5 Conclusion

In recent years, significant strides have been made in the developing and optimizing novel catalyst materials for microfluidic fuel cell. Pt-based catalysts have long been recognized for their excellent catalytic capabilities in fuel cells. But the expensive price of Pt necessitates efforts to reduce its usage and overall cost in electrocatalysts. To address this challenge, researchers have explored various strategies, including alloying Pt with transition metals, leading to catalysts with greater catalytic capability. Incorporating transition materials into Pt-based catalysts has not only improved their catalytic performance but also facilitated better dispersion on the polymer supports. Consequently, these composite catalysts have demonstrated higher efficiency compared to using Pt metal alone. This approach opens up exciting avenues for further research, especially in the development of novel polymer and polymer-supported metal particle materials.

About the Author

Hongyan Liu is postgraduate of Department of Mechanical Engineering, National University of Singapore, and his

research field is development of nanoparticle.

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