

Review on Microfluidic Technology Based Synthesis of Fe-based Nanoparticles for Catalyst in Fuel Cell

Hongyan Liu^{1,*}

¹ Department of Mechanical Engineering, National University of Singapore, 117581, Singapore

* Corresponding author's e-mail: e1011005@u.nus.edu

Abstract: Conventional combustion based energy generations, reliant on fossil fuels, poses significant environmental harm. In contrast, fuel cells offer an efficient and eco-friendly energy conversion method, capable of integrating with renewable sources and contemporary energy carriers to support sustainable development and energy security. Consequently, fuel cells are considered the promising energy conversion devices of the future. However, extensive research reveals that the cost of catalysts constitutes the most substantial portion of the overall fuel cell cost. To tackle this cost constraint, considerable advancements have been achieved in the development of cost-effective, precious metal-free electrocatalysts. Common methods for the preparation of metal nanomaterials (NPs) have more stringent requirements, lower deposition efficiency and higher costs. In addition, conventional preparation methods without precisely control of reagent concentration, mixing and temperature during the preparation process, makes it difficult to obtain the same results with poor reproducibility, restricting the industrial fabrication of high performance nanomaterials. Microfluidic reactors have advantages of efficient mixing, high heat and mass transfer, low reagent consumption, precise control of reactant components, residence time, reaction temperature and other parameters. They can also be coupled with multi-step reactions, greatly reducing the preparation time while obtaining composite nanomaterials with excellent dimensional homogeneity. In this review, we mainly discuss the microfluidic technology-based synthesis of PGM-free catalyst used in fuel cell.

Keywords: Microfluidic synthesis, Metal-based nanoparticle, Fe-based nanoparticle, Catalyst, Fuel cell.

1. Introduction

The existing techniques for generating energy based on combustion bring great harm to ecology system, and also mainly result in some environmental issues (e.g. acidic rains, extreme climate, ozone layer destroy). What's more, the techniques are based on the limited and declining fossil fuels. However, for converting energy, fuel cells demonstrate an environmentally friendly and efficient mechanism. In addition, they show compatibility with currently popular energy fuel and clean sources to develop sustainably and make sure secure energy use. Consequently, fuel cells are viewed as new generation devices for converting energy in the future.

There is a crucial disadvantage of nowadays fuel cell devices and techniques. The drawback is the great dependence on platinum (Pt) group metal (PGM) catalysts in cathode region to accelerate the sluggish Oxygen Reduction Reaction (ORR). As a result, catalysts represent a substantial portion of the total cost of fuel cells. To overcome this obstacle, significant progress has been made in the last few decades to create PGM-free catalysts, like Fe-N-C, which are derived from inexpensive, abundant, and readily available raw materials, leading to reduced costs. The PGM-free catalysts now demonstrate ORR catalytic capability, which is close to catalytic capability of noble-metal catalysts, but the materials cost is lower. Because of these, great total cost reduction of fuel cell techniques becomes possible.

Metal nanomaterials (NPs) are typically developed in reaction conditions which are macroscopic and unlikely to be accurately regulated, causing difficulties of accurately controlling homogeneous and uniform mixture of the raw materials and nucleation and growth of the targeted metal NP.[1] It's a challenge to develop the products with great

reproducibility without precise regulation of concentration of reactants, homogeneous mixture, and surrounding temperature in the synthesis process.[2] This limits the syntheses in industry of nanomaterials with great quality, and is also not feasible to prepare macroscopic materials. In contrary to typical means of synthesis, fluid is treated through the channel in microreactors, that is the conducive to high-efficiency mixture, mass transfer, heat transfer, and small amounts of consumed raw materials and so on, to achieve accurate regulation of parameters of residence time, reaction temperature, concentration of raw materials. They also have the potential to be assembled with multi steps reactions. There is a significant reduction of development duration and great improvement of dimensional uniformity of composite NPs.

2. Background of Microfluidic Technology in Synthesis of Metal Nanoparticle

J M Köhler and group members first studied the development of gold (Au) nanoparticles inside microreactors. They successfully prepared Au nanoparticles in microreactors made of silicon/glass respectively from gold seeds in 2004,[3] and gold salt solution in 2005.[4] Currently, a novel chip was designed with features of 3 zones for mixing process, and gold nanoparticles in two forms (i.e. single and cluster) were prepared.[5] Lin and their group demonstrated the development of silver (Ag) nanoparticles within a continuous-flow microreactor.[6] He and colleagues then investigated development of silver nanoparticles. They demonstrated that there is high affinity between the interior wall and particles, and this could be contributed to dispersed distribution of size and bad yield.[7]

3. Microfluidic Technology-based Synthesis of Iron-based Nanoparticle

3.1. Iron oxide nanoparticle

3.1.1. Continuous flow reactor

There are 2 inlets in continuous flow reactors —an inlet is for the injection of an iron&polymer solution and alkaline solution is entered through another inlet. When the base solution and iron/polymer solution enter the microreactor, iron oxide nanoparticles (IONPs) start to develop at the contact surface of base solution and iron/polymer solution, because it is the only region facilitating nucleation process in the reactor that satisfies the 2 conditions of presence of iron element and the high enough pH value. These IONPs further grow through diffusion effect of free iron&polymer solution toward the surface of laminar flow. Laminar flow plays a crucial role in continuous flow reactors.

3.1.2. Drop-wise flow reactor

Drop-wise flow reactors further decrease the reaction volume by separating the reactant solution into an individual droplet one by one, thus the uniformity and homogeneity of the solution reaction get further improvement. There are typically 3 inlets. 2 of them are used for the main solution while the remaining inlet is used for injecting the liquid as carrier. The 2 inlet channels holding reactant solution have to be at an angle to the primary channel thus droplets are formed in carrier liquids. Because of continuous supply of the carrier liquid into the channel, the droplets can be formed at a desirable rate. Inside one droplet, the advective convection promotes formations of IONPs. Some reactors (e.g. chip and tubular) have been created to synthesize IONPs based on this drop-wise technology.

3.1.3. Gas-segmented flow reactor

Gas-segmented flow reactor is much like drop-wise flow type, while it further decreases the volume required for the reaction. Within the reactor, iron&polymer mixed solution and alkaline solution get blended for the formation of primary solution; After this, the gas is used for separating the primary solution. This division decreases reacting volume of primary solution. The main distinction of drop-wise flow type and gas-segmented flow type lies that latter apply gas for formation and separation of slugs when the main solution is formed, in contrasts to formatin of droplets in the carrier liquid. IONPs are produced through co-precipitation processes governed by diffusion in these reactors.

3.2. Iron-based metal-organic framework (MOF)

Currently, the sedimentation, hydrothermal, and emulsion method, extensively employed in MOF material synthesis, face challenges in achieving nano-sized MOF materials due to limited control over nucleation and growth of particles. The tandem microreactor approach proves to be a more dependable technique for synthesizing high-quality and less stable MOF composites. Furthermore, incorporating multiple parallel channels and enhancing the flow rate within the microreactor enables efficient upscaling of production.[8]

Flow chemistry, a well-established method employed in producing functional nanomaterials, holds significant potential as an approach with bright outlook for large scale preparation of MOFs.[9] Flow chemistry procedure includes 3 main stages: (i) introducing liquid reagents into the blending unit, (ii) undergoing conversion reactions in a temperature-

controlled flow reactor, and (iii) ultimately separating the resulting products. Flow chemistry synthesis is primarily classified into microfluidic reactor plug-flow reactor and stirred-flow reactor approaches.[10]

4. Iron-based Nanoparticles Potentially Synthesized Through the Utilization of Microfluidic Technology

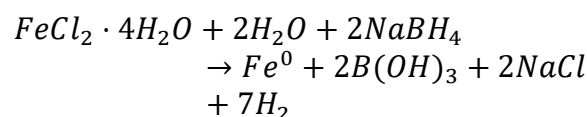
Apart from IONPs and Fe-based MOFs, there are various other iron-based nanoparticles that can serve as catalysts in fuel cells. However, there is limited literature available on the synthesis of these nanoparticles using microfluidic technology.

4.1. Fe-N-C nanoparticle

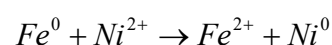
Fe-N-C catalysts have garnered significant attention in research because of their great catalytic capability and stability no matter in either acidic or alkaline environments.[11] The high catalytic activity of Fe-N-C catalysts can be attributed to two primary factors: (1) The substantial electronegativity of nitrogen effectively regulates the electron distribution and charge density of carbon materials, facilitating oxygen adsorption and enhancing the ORR. (2) The unique physical and chemical properties of transition metals lead to alterations in the d-band structure when bonding with neighboring elements. This modification causes the metal's d-band to contract, fundamentally altering the catalytic site's activity and further promoting the ORR catalytic reaction.

4.2. Ni-Fe alloy nanoparticle

Biochar-Ni-Fe (BC-Ni-Fe) composites have been synthesized in a nitrogen-protected environment in a 500 millilitre 3-neck flask. Initially, 70 millilitre of water and 30 millilitre of ethanol are introduced to it, accompanied by a specified quantity of Ferrous Chloride solution. The device is supplied with a mechanical mixing device and a N₂ input. Following thorough mixing, suitable amounts of BC-Ni-Fe chemical is introduced and kept stirring for a specific duration. Once well-dispersed, a proper quantity of polyethylene glycol is introduced, and keep it being stirred for half an hour. Subsequently, with vigorous agitation, 50 millilitre of Sodium borohydride solution was dropwise added to the 3-neck flask using a peristaltic pump. Following the drop-wise addition, the mixture kept stirring for a quarter of an hour to achieve the reaction depicted in the Equation below:[12]



Upon the completion of the aforementioned reaction, the mixture in the three-neck flask was subjected to stirring applying a pump. Subsequently, a drop-wise addition of 10 millilitre of Nickel Chloride solution at a specific concentration initiated a displacement reaction on the surface of Fe⁰, resulting in the formation of elemental Ni⁰ metal, as illustrated in the Equation below:



After 20 minutes of stirring, the resulting suspension was

subjected to magnetic separation and pumping. Subsequently, it underwent multiple washes with anhydrous ethanol and deionized water. The obtained BC-Ni-Fe composite was then vacuum-dried. Throughout the entire process, all operations were carried out within an argon surrounding. The preparation method for Ni-Fe is like the one described above, with the exception of excluding BC and adding polyethylene glycol and biochar. For synthesis of BC-Ni-Fe, the weight ratio of biochar, Ni, and Fe was carefully controlled at 20:1:20.[13]

5. Conclusion

The use of metal nanomaterials, prepared via the microfluidic method, as catalysts in biological and chemical applications, has gained widespread popularity. Improvements in their activity, selectivity, and durability have significantly boosted their economic competitiveness. Microfluidic control offers distinct advantages, enabling precise regulation of kinetic parameters such as reaction temperature, concentration, and flow rate to achieve controllable particle assembly and modification.

In contrast to single-metal nanomaterials, multi-metal composite nanomaterials benefit from the alloy effect and electronic effect, leading to significantly enhanced catalytic performance. However, the synthesis of nanomaterials with complex structures often demands intricate preparation processes involving multiphase mixing and droplet merging. Achieving this in a single homogeneous microreactor or droplet microreactor proves challenging, and the batch method lacks control over composite material surface morphology and interfacial structure, resulting in poor reproducibility and difficulty in obtaining large quantities of composites with consistent structures or modifications.

Consequently, current research primarily centers on designing integrated microfluidic platforms with multiple reactors, facilitating the precise control of processing conditions at the nanoscale and microscale. By regulating the microstructure of different components, these platforms enable the production of composite nanomaterials with optimized properties and reproducible results.

References

- [1] Guo M Y, Li F H, Bao Y, Ma Y Q, Niu L. (2016). Application of microfluidics in nanosynthesis. *Chinese Journal of Applied Chemistry*, 33(010), 1115-1125.
- [2] Kung, C. T., Gao, H., Lee, C. Y., Wang, Y. N., Dong, W., Ko, C. H., ... & Fu, L. M. (2020). Microfluidic synthesis control technology and its application in drug delivery, bioimaging, biosensing, environmental analysis and cell analysis. *Chemical Engineering Journal*, 399, 125748.
- [3] Wagner, J., Kirner, T., Mayer, G., Albert, J., & Köhler, J. M. (2004). Generation of metal nanoparticles in a microchannel reactor. *Chemical Engineering Journal*, 101(1-3), 251-260.
- [4] Wagner, J., & Köhler, J. M. (2005). Continuous synthesis of gold nanoparticles in a microreactor. *Nano letters*, 5(4), 685-691.
- [5] Köhler, J. M., Wagner, J., & Albert, J. (2005). Formation of isolated and clustered Au nanoparticles in the presence of polyelectrolyte molecules using a flow-through Si chip reactor. *Journal of Materials Chemistry*, 15(19), 1924-1930.
- [6] Lin, X. Z., Terepka, A. D., & Yang, H. (2004). Synthesis of silver nanoparticles in a continuous flow tubular microreactor. *Nano letters*, 4(11), 2227-2232.
- [7] He, S., Kohira, T., Uehara, M., Kitamura, T., Nakamura, H., Miyazaki, M., & Maeda, H. (2005). Effects of interior wall on continuous fabrication of silver nanoparticles in microcapillary reactor. *Chemistry letters*, 34(6), 748-749.
- [8] Zhao Y, Xiang Z H. (2020). Advances in microfluidic preparation of functional materials with metal/covalent organic frameworks. *Journal of Chemical Engineering*, 71(6), 2547-2563.
- [9] Dunne, P. W., Lester, E., & Walton, R. I. (2016). Towards scalable and controlled synthesis of metal-organic framework materials using continuous flow reactors. *Reaction Chemistry & Engineering*, 1(4), 352-360.
- [10] Kim, K. J., Li, Y. J., Kreider, P. B., Chang, C. H., Wannemacher, N., Thallapally, P. K., & Ahn, H. G. (2013). High-rate synthesis of Cu-BTC metal-organic frameworks. *Chemical Communications*, 49(98), 11518-11520.
- [11] a) Lefèvre, M., Proietti, E., Jaouen, F., & Dodelet, J. P. (2009). Iron-based catalysts with improved oxygen reduction activity in polymer electrolyte fuel cells. *science*, 324(5923), 71-74.; b) Zhang, J., Chen, G., Müllen, K., & Feng, X. (2018). Carbon-rich nanomaterials: fascinating hydrogen and oxygen electrocatalysts. *Advanced materials*, 30(40), 1800528.; c) Wu, G., More, K. L., Johnston, C. M., & Zelenay, P. (2011). High-performance electrocatalysts for oxygen reduction derived from polyaniline, iron, and cobalt. *Science*, 332(6028), 443-447..
- [12] a) Li, H., Qiu, Y. F., Wang, X. L., Yang, J., Yu, Y. J., & Chen, Y. Q. (2017). Biochar supported Ni/Fe bimetallic nanoparticles to remove 1, 1, 1-trichloroethane under various reaction conditions. *Chemosphere*, 169, 534-541; b) Fang, Z., Qiu, X., Chen, J., & Qiu, X. (2011). Debromination of polybrominated diphenyl ethers by Ni/Fe bimetallic nanoparticles: influencing factors, kinetics, and mechanism. *Journal of Hazardous Materials*, 185(2-3), 958-969.
- [13] Li, Z., Luo, S., Yang, Y., & Chen, J. (2019). Highly efficient degradation of trichloroethylene in groundwater based on peroxymonosulfate activation by bentonite supported Fe/Ni bimetallic nanoparticle. *Chemosphere*, 216, 499-506.