



# Modeling and optimization of Scaffold-like macroporous electrodes for highly efficient direct methanol fuel cells



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## HIGHLIGHTS

- Advanced electrode design with ordered macro-porous structure is proposed.
- Mass transport is greatly enhanced by theoretical and experimental analysis.
- Energy production and efficiency of DMFC stack is remarkably enhanced.

## ARTICLE INFO

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## ABSTRACT

Construction of advanced electrode architecture, and understanding the electrochemical and mass transport phenomena within its structures are core issues that determine the development of fuel cells and other electrochemical energy technologies. Here in this work, we propose a new scaffold-like electrode with controllable porous volume and size via facile freeze-drying process. Deriving from the delicate surface unevenness and the well-defined macro-pores constructed by the ice template, the electrochemical surfaces and mass transport for methanol and oxygen are greatly enhanced by adapting this electrode structure as anode and cathode for direct methanol fuel cells, respectively. Computational fluid dynamics simulation and mathematic model is adopted to elucidate and predict the intrinsic improvement of mass transport within the newly designed electrode structure. Further practical application of such design is validated in a 10-cell short stack of direct methanol fuel cell systems equipped with this novel electrode.

## 1. Introduction

As one of the most promising substitutes for the energy conversion devices, such as portable batteries, combustion engines, and stationary electric power supplies, direct methanol fuel cells (DMFCs) have attracted intensive interest in the past decades for the advanced composite materials and efficient manufacturing techniques [1–6]. To achieve the crucial requirements of commercialization in wide public, reinforcing electrochemical and mass transport processes within the electrodes is a determinative approach for the development of DMFCs. Membrane electrode assembly (MEA) plays a core role as the micro-chemical reactors with multiple electrochemical reactions confined in their micro/nano-scaled spaces. These spatial confined structures, namely porous electrode, involving catalytically active surfaces, mass transport channels, and conductive pathways for charges, would be critical to the performance, durability, and cost of a fuel cell system [7–9]. However, the complexity of the electrochemical nature renders the electrode of

fuel cells a complicated composite structure. Firstly, the migration of ions and electrons should occur within the effective conductors, while the boundaries formed by the two kinds of conductors should be evenly distributed through the electrode [10–12]. Secondly, mass (including gas and liquid) transport should take place in suitable channels with macro-porous structure, and hydrophobic and hydrophilic pathways for gas and liquid phase respectively [13–16]. Hence, to construct well defined electrode architecture to meet these requirements is a promising strategy but still remains in challenges. The related electrochemical processes within these structures also lack further discussion.

Delicately structural design of catalyst in meso/micro-scale to improve mass transport and reaction kinetics has led to great development in chemical engineering and catalysis [17–19]. For fuel cell and battery techniques, significant progresses in the advanced electrode architecture have been made to boost the mass transport and electrochemical processes based on new fabrication methods or new materials [20]. Ordered nano-arrays with effective mass transport channels were

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proved as a kind of excellent electrode structures for fuel cell applications. Carbon nano-tubes, conductive polymers, and metal materials could be used as bricks to construct the ordered electrodes by adapting chemical vapor deposition, electrochemical polymerization, or hydrothermal approaches [21–27]. Furthermore, pores in micro- and nano-scales with ordered structures have also achieved enhanced electrochemical and mass transport properties [28–30]. However, due to the mature fabrication techniques and good catalytic properties, carbon supported platinum group metal (PGM) catalysts are still recognized as the most promising electrode materials in the commercialization of fuel cells [31–35].

Based on the carbon supported PGM catalysts, electrode fabrication techniques are crucial issue to achieve well-defined electrode design. Ink-coating process, including brush painting, silk-screen printing, spraying, and blade coating, etc., is the major preparation method for fuel cell electrodes. Some advanced fabrication routes have been proposed in recent years, such as electrospinning, magnetic assisted coating, electrohydrodynamic deposition [36–38]. However, the active sites for electrochemical reactions and pores for mass transport within the electrode are usually randomly distributed [39]. As a result, the blind spots and pores constructed in the electrode could dramatically reduce the utilization of the catalyst and increase the voltage loss caused by mass transport.

Theoretical studies of mass transport in electrochemical systems could further validate the phenomena in the alternative electrode designs [13,32,40]. Mathematic models and simulations are powerful approaches to analyze and predict the transport and reaction processes, especially for the new designs of electrode structures [20,41]. To demonstrate the fuel cells based on polymer electrolyte membranes, empirical and semi-empirical models have been developed based on the Butler-Volmer expression [42,43]. However, the intrinsic relationships between mass transport and electrochemical behaviors, and the electrode structures could be hardly illustrated by such models. One-dimensional and multi-dimensional models have been further proposed to understand the effects brought by the micro-structures within the MEAs [44–47]. Besides, single-phase models have been widely adopted for their simplicity, whereas two-phase models could further describe the details of gas phase (carbon dioxide) behaviors in anodes [48,49].

Herein this work, we propose the new electrode architecture with scaffold-like macroporous structure based on commercialized carbon supported catalysts for fuel cells by adapting a simple freeze-drying approach. The tailored channels for gas/liquid transport and the delicate surface structures could lead to the enhanced performance in the application of direct methanol fuel cells (DMFCs). A one-dimensional single-phase model, associating with computational fluid dynamic (CFD) approach, is further developed to validate, predict, and optimize such improvement brought by the new electrode architecture.

## 2. Material and methods

### 2.1. Fabrication of the electrodes

The scaffold-like macroporous electrode was fabricated based on the freeze-drying method [50,51]. Firstly, the commercial catalyst of amorphous carbon loaded platinum (Pt/C, 60 wt%, Johnson Matthey Co.) or platinum/ruthenium alloy (PtRu/C, 75 wt%, Johnson Matthey Co.) was mixed with PFSA ionomer (Nafion, water dispersion, 10 wt%, DuPont Co.) and a certain amount of de-ionized water. The weight ratio of catalyst to ionomer is 4:1, and to DI water is 1:10. The mixture was then constantly blended under the protection of nitrogen gas flow to form the homogenous slurry. After that, the as-prepared slurry is kept at 60 °C with constant stirring to evaporate the water until the water content is 40, 65, and 90%. The condensed catalyst slurry was then painted on the substrate of a gas diffusion layer (GDL), and the catalyst loading was fixed as 3.05 mg cm<sup>-2</sup> (1.80 mg<sub>Pt</sub> cm<sup>-2</sup> for cathodes, 2.25 mg<sub>PtRu</sub> cm<sup>-2</sup> for anodes). The as-prepared slurry-coated GDL was

quickly transferred to the liquid nitrogen bath to form the solidified ice layer. The drying process was then performed in a freeze-drier under the temperature of -51 °C and the pressure of 7–10 Pa for 24 h. The dried electrode samples were denoted as SMPE-1 (scaffold-like macroporous electrode), SMPE-2, and SMPE-3, corresponding to the different DI-water (or ice) content of 40, 65, and 90 wt%, respectively. The control electrode sample with the traditional drying process of ambient evaporation was prepared with the same catalyst loading and Nafion content.

### 2.2. Physical characterizations

The as-prepared samples were characterized by a field emission scanning electron microscope (FESEM, JSM-6360LV, JOEL). The wetting behavior was measured by a contact-angle meter (JC2000C1, Shanghai Powereach). The pressure differences of gas pass through the samples were measured by a homemade instrument.

### 2.3. Fabrication of DMFCs and electrochemical characterizations

The MEA (membrane electrode assembly) used for DMFC single cell tests was equipped with the as-prepared electrode samples as cathodes (Pt/C electrodes) or anodes (PtRu/C electrodes) by sandwiching a piece of Nafion 115 membrane with another piece of additional anodes or cathodes, respectively. The MEA with an active area of 4 cm<sup>2</sup> (2 × 2 cm<sup>2</sup>) was inserted into steel end plates with serpentine gas flow channels to assemble single cell units. The single cell tests on DMFC were carried out by using a fuel cell test system (FCTS, Arbin Co.) and an electrochemical workstation (SI1287 and SI1260, Solartron Co.). The methanol stripping tests were carried out following these procedures: 1, the anode was fed with 1 M methanol solution at the flow rate of 1 mL min<sup>-1</sup> for 1800 s under the constant polarization potential of 0.1 V vs. DHE; 2, then the methanol solution was replaced by DI water for another 1800 s under the same potential; 3, CV test with a scan rate of 50 mV s<sup>-1</sup> was then applied to the anode for 5 cycles. The anode polarization curves were obtained by linear scanning applied to anodes with a scan rate of 1 mV s<sup>-1</sup>. Short stacks with 10 cells were fabricated by using graphite serpentine end plates. The active area of a single MEA is 25 cm<sup>2</sup> (5 × 5 cm<sup>2</sup>). The lifetime tests of the DMFC short stacks were carried out by a fuel cell test system (G20, Green Light Co.).

## 3. Mathematic model and simulation

### 3.1. Cathode simulation

The mass transport behavior of oxygen through the catalyst layer is simulated by Autodesk CFD 2016. The catalyst layer models for different SMPE samples are constructed based on the structural parameters acquired from the physical and electrochemical characterizations. To simplify the simulation processes from the complicated real electrode environment, we construct interconnected cubic pores with 1–3 layers as illustrated in Fig. 6a. The chamber with tens of times in size below the porous layer is set as the relatively huge flow area of gas diffusion layer and bipolar plate channels. The initial and boundary conditions of simulation are set based on the experimental details listed in Table 1. The mass transport of oxygen in the catalyst layer obeys Fick's Law of diffusion:

$$J_{O,cc} = \rho_O D_{O,cc} \nabla y_{O,cc} \quad (1)$$

For the case of oxygen transport within the cathode catalyst layer under mass transport dominated situation, the boundary condition of oxygen mass fraction at the boundary of catalyst layer and gas diffusion layer could be set as  $y_{O,cc} = 1$ , whereas at the inner surface of the catalyst, the oxygen mass fraction could be set as  $y_{O,cc} = 0$ . The consumption rate of oxygen via ORR on the catalyst surface could be calculated by:

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