

Effect of Nafion loading and the novel flow field designs on Innovative anode electrocatalyst for improved DMFCs performance

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Abstract

Efficiency of a Direct methanol fuel cells (DMFCs) not just merely depends on the catalyst, but also on the flow channels, physical/electrochemical kinetics, Membrane Electrode Assembly (MEA) preparation and other operating parameters. This article is focused on the influence of novel flow field design and the effect of Nafion loading during MEA preparation on the performance of DMFC. A novel Pt/NiTiO₃ was used as the anode electrocatalyst in the DMFC. The results show a 27.8 % & 5.1 % increment in cell performance due to changes in Nafion loading and flow field designs, respectively. A Nafion loading of 0.5mg/cm² and the sinuous flow field gave the highest performance. Thus, Pt-NiTiO₃/C performed to be an encouraging anode catalyst with the new sinuous flow field.

Keywords: Direct Methanol Fuel cell; Electrocatalyst; Nafion Binder; Flow Fields;

1. Introduction

DMFC are labelled as high-power transition density system, green energy source for futuristic pollution free environment and easy power generator with readily available low-cost methanol fuel among the listed fuel cell types [1]. The reduced usage of Pt electrocatalyst, alloying with group

VIII (2) transition metals supported on Vulcan carbon for methanol oxidation reaction (MOR) is the best pathway for maximizing the electrocatalytic efficiency [3]. Our group has investigated the newly formulated Pt and PtRu metals on NiTiO₃/C supported electrocatalysts and the effect of synthesis conditions, particle size, surface morphology and electrochemical behavior on the DMFC performance [4,5]. It is observed that the anode electrocatalyst exhibits good stability and higher MOR activity for the half cell reaction. Recently, intensive research has been carried out on improving the performance of 5 cm² single cell DMFCs using Pt-NiTiO₃/C anode electrocatalyst with conventional serpentine flow field with various operating parameters like temperature, methanol concentration and flow rates for the development scalable DMFC stack system [6]. However, this article is chiefly aimed at the improvement of single cell performance by targeting the Nafion binder loading (MEA preparation), different flow field designs and stability.

2. Experimental aspects

Fig. S1 and S2 shows the process flow methodology of the present work and synthesis procedure for preparation of Pt-NiTiO₃/C electrocatalyst. Our previous results [4] show that the synthesized material has homogenous dispersion of quasi spherical morphology with diameter ranging from ~3.5 nm to ~36 nm and has higher current density of about 98 mA cm⁻² with good short term durability. The MEA fabrication, cell assembly, various flow fields for fabrication of 5 cm² DMFC cell with respective operating parameters are given in the supplementary information.

3. Results and Discussion

3.1 Effect of Nafion Loading

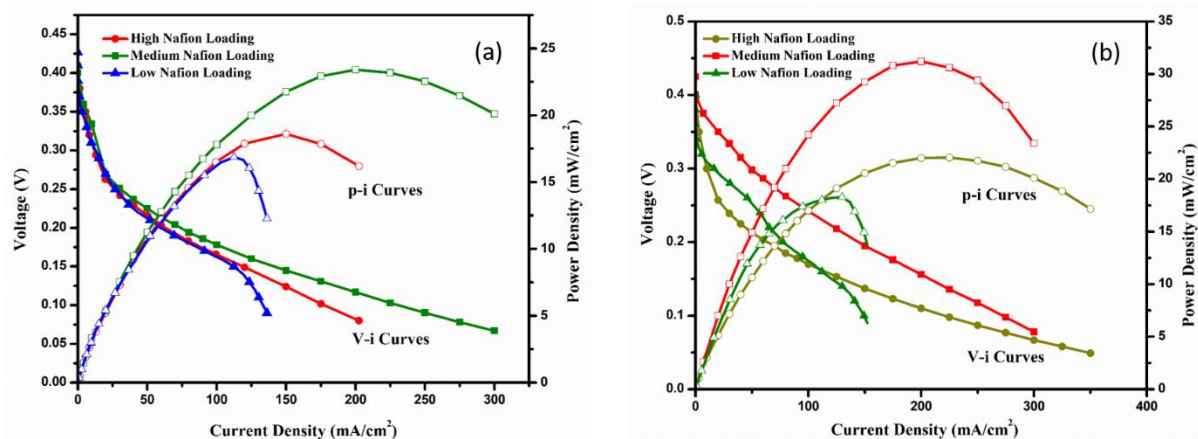


Fig. 1 (a) & (b) Polarization (V-i) and Power Density (P-i) curves of DMFCs based on Pt/C and Pt-NiTiO₃/C anode catalyst at different Nafion loading with 5 cm² active area.

In order to study the influence of Nafion loading in anode catalyst layer on the performance of DMFC, three different MEAs with low (0.3mg/cm²), medium (0.5mg/cm²) and high (2.5mg/cm²) concentrations of Nafion were prepared. Also, two different catalyst layers namely the commercial Pt/C and the homemade Pt-NiTiO₃/C were used for testing. The performance analysis was carried out accordingly for different Nafion loadings in two different catalyst layers at their optimum operating conditions. With a low Nafion loading, visible cracks were seen on the catalyst layer due to lower binding of Nafion with catalyst. However, when the Nafion concentration was increased, more smooth catalyst surfaces were obtained. Fig. 1 (a) and (b) shows the performance analysis comparison of different ionomer loadings on Pt/C and Pt-NiTiO₃/C respectively. It is clearly evident that fuel cell power output is affected by the Nafion content. In both the analysis, the performance curve for a medium Nafion loading gave the highest performance output compared to low and high loadings. However, Pt-NiTiO₃/C showed better performances than the commercial Pt/C. The various performance output parameters for different Nafion content and catalyst layer are given in Table 1.

From the table it is inferred that low Nafion loading gave the lowermost performance which is attributed to the cracks. Due to binder insufficiency, cracks were developed on the catalyst surface. This led to discontinuities in flow of charge within the catalyst layer. Since Nafion being a membrane that allows only protons to pass through, a lower concentration of it affected the overall performance of the cell. With increase in Nafion content, the performance showed marked change reaching highest power density and current density for medium Nafion loading. The above observation is due to the fact that, when binder content increases there is significant increase in proton transport and hence the overall performance. Nevertheless, with very high binder concentration, catalyst layer becomes thick which limits the mass transport and ionic conductivity in the catalyst layer. Thus, leading to a performance deterioration with high Nafion loading. Therefore, an optimum concentration of Nafion is necessary to generate high performance output from a DMFC. In our case, both Pt/C and Pt-NiTiO₃/C catalysts require 0.5mg/cm² loading of Nafion for efficient binding and performance.

Table 1: Performance output for different Nafion loading

S. No	Catalyst	Nafion loading (10 wt.%)	Voltage (V)	Current density (mA/cm ²)	Power density (mW/cm ²)
1	Pt/C	Low	0.15	112.37	16.86
2		Medium	0.117	199.89	23.39
3		High	0.124	150.17	19.12
4	Pt-NiTiO ₃ /C	Low	0.14	129.95	18.19
5		Medium	0.156	200.06	31.21
6		High	0.10	225.3	22.53

3.2 Performance studies

3.2.1 Effect of anode catalysts

To study the catalytic activity and efficacy of the home-made anode catalyst with 40 wt.% of Pt on Pt-NiTiO₃/C, a comparative investigation of the performance was made with two other pure noble metal catalysts: Pt/C and PtRu/C. All the MEAs were prepared with constant Nafion loading of 0.5mg/cm². A conventional serpentine flow field (Fig S3 (a)) was used in both cathode and anode side for this purpose. The experiments were performed with constant operating conditions: 1 molar methanol concentration, flow rate of 3 & 100 ml/min for anode and cathode and the cell temperature as 80 °C. Fig 2 (a) describes the performance studies of three different catalysts with serpentine flow field. From the graph, it is observed that Pt-NiTiO₃/C marks the highest power density (31.2 mW/cm²) at a cell potential of 0.156 V and current density of 200.06 mA/cm² followed by PtRu/C and Pt/C. There is almost 1.5 times increase in the performance output of Pt-NiTiO₃/C compared to commercially available Pt/C. The enhanced performance is attributed to the increase in methanol adsorption sites and the synergistic effect between the various metals. A detailed study on the catalyst has been made in our previous work [4-6].

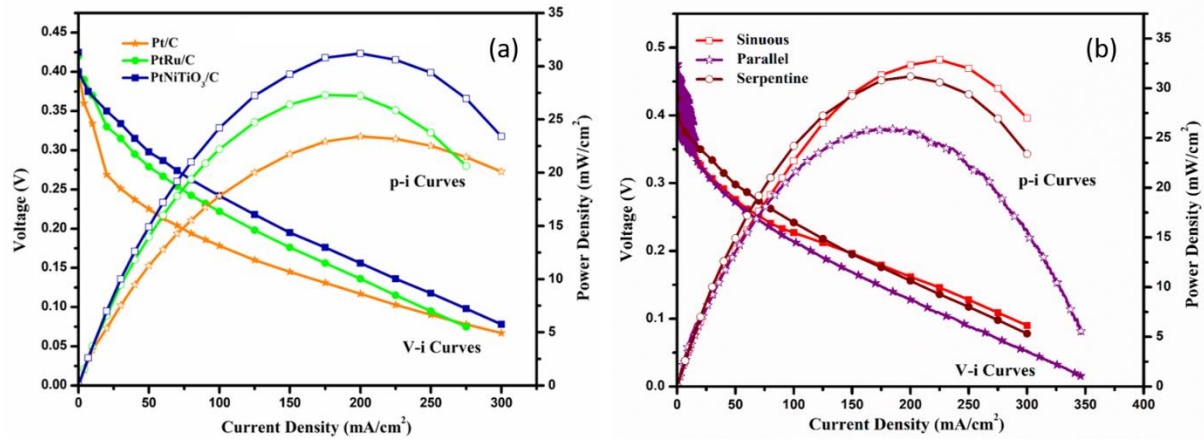


Fig. 2 (a) & (b) Polarization (V-i) and Power Density (P-i) curves of DMFCs based on different anode catalysts and different cathodic flow fields with Pt-NiTiO₃/C catalyst on 5 cm² active area.

3.2.2 Effect of flow field design

A new flow field design of sinuous structure to the cathode of a DMFC was tested and compared to the conventional serpentine flow field and parallel flow field. A conventional Pt/C was used as a catalyst for the oxygen reduction reaction (ORR).

Fig. 2 (b) shows the performance polarization curves of the various flow fields. It is clear that sinuous flow field (Fig S3 (c)) gives the highest power density (32.85 mW/cm²) at a cell potential of 0.146 V and current density of 224.96 mA/cm². Serpentine marks a slightly lower power density (31.2 mW/cm²) at a cell potential of 0.156 V and current density of 200.11 mA/cm². The lowest performance of the three was observed in parallel flow field (Fig S3 (b)) which could be due to the lower pressure drop and flow velocity within the channel which limits the diffusion of oxygen into the GDL and hence a non-uniform O₂ distribution which makes for poor water removal. However, in serpentine flow field, there is a higher pressure drop due to the friction of the wall and turning channel. This in turn gives O₂ enough time to react which aids in uniform distribution of O₂ to the GDL and higher reaction rate between the flow channel and catalyst layer, improving diffusion, but higher pressure drop requires more energy. In case of sinuous flow field, the design incorporates inclinations of about 10° which allows relatively lower pressure drop than serpentine but higher than parallel flow fields. The inclinations reduce the lateral diffusion distance for O₂ resulting in uniform distribution of O₂. In addition, there is an increased water removal which enhances the overall performance of the sinuous flow field.

3.3 Short term Durability test

Real time performance of a DMFC is evaluated based on its stability under constant power and constant current operations over a period of time. The stability tests were performed for both serpentine and sinuous flow fields at the cathode side with Pt-NiTiO₃/C as catalyst at a power of 100 mW for a period of 5 hours. Fig 3 depicts the stability curves for both the flow fields. It is evident that sinuous flow field shows a higher stability with only a 1% decline in power density. Also, it gives a steady power output of 100 mW for the entire duration exhibiting the superiority of the flow channel to provide uniform reactant distribution and water removal. Serpentine on the other hand showed a 22% decline in power at the end of 5 hours which could be possibly due to water flooding in the channel.

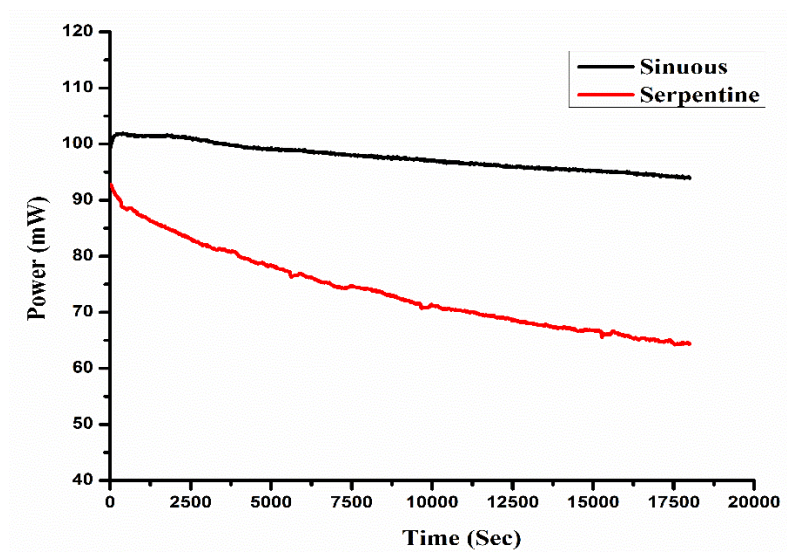


Fig 3. Short term stability test of DMFC based on Pt-NiTiO₃/C catalyst for serpentine and sinuous cathode flow fields.

4. Conclusion

In this work, the performance of various anode catalysts such as Pt-NiTiO₃/C, PtRu/c and Pt/C were investigated for a typical DMFC. Pt-NiTiO₃/C exhibited the highest performance compared to other precious catalysts due to its increased methanol adsorption sites contributed by the synergistic effect of the various metals. The effect of Nafion loading for the preparation of MEA was studied which showed the importance of Nafion content in determining DMFCs performance. A very low concentration of Nafion developed cracks in the MEA and high concentration limited

the mass transport of protons due to increased MEA thickness. An optimum Nafion concentration of 0.5 mg/cm^2 gave the highest performance. Further on, the effect of flow field design at cathode side was studied with three flow fields; parallel, serpentine and sinuous. Sinuous flow field showed enhanced performance output due to its efficient reactant distribution and water removal provided by relatively lower pressure drop than serpentine flow field. Finally, the stability of DMFC for different flow fields at cathode side was evaluated which gave higher stability for sinuous flow field.

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References:

- [1] X. Zhao, M. Yin, L. Ma, L. Liang, C. Liu, J. Liao, T. Lu, W. Xing, *Energy Environ. Sci.* 4 (2011) 2736–2753.
- [2] V.R. Stamenkovic, B.S. Mun, M. Arenz, K.J. Mayrhofer, C.A. Lucas, G. Wang, P.N. Ross, N.M. Markovic, *Nat. Mater.* 6 (2007) 241–247.
- [3] M. Vorokhta, I. Khalakhan, I. Matolínová, J. Nováková, S. Haviar, J. Lanc̃ok, et al., *Appl. Surf. Sci.* 396 (2017) 278–283.
- [5] Thiagarajan V, Karthikeyan P, Thanarajan K, Neelakrishnan S, Manoharan R, Chen R, et al., *Int J Hydrogen Energy* 44 (2019) 13415–13423.
- [6] Thiagarajan, V, Manoharan, R, Karthikeyan, P, Nikhila, E, Hernández- Ramírez, A & Rodríguez-Varela, FJ, *Int. J. Hydrog. Energy* 42 (2017) 9795- 9805.
- [7] Thiagarajan, V, Karthikeyan, P, Manoharan, R, Sampath, S, Hernández- Ramírez, A, Sánchez-Castro, ME, Alonso-Lemus, IL & Rodríguez-Varela, FJ, *Electrocatalysis* 9 (2018) 582-592.