

# Optimizing Electrospinning Parameters for Enhanced Diameter Control of Composite Nanofibers in Direct Methanol Fuel Cells (DMFCs)

Norulsamani Abdullah<sup>1,2\*</sup>, R. Saidur<sup>1,2,3</sup>, Siti Kartom Kamarudin<sup>4</sup>, and Nabila A. Karim<sup>4</sup>

<sup>1</sup>Research Center for Nano-Materials and Energy Technology (RCNMET), School of Engineering and Technology, Sunway University, Bandar Sunway, Petaling Jaya, 47500, Selangor Darul Ehsan, Malaysia

<sup>2</sup>Sunway Materials Smart Science & Engineering (SMS2E) Cluster, Sunway University, Petaling Jaya, Selangor, 47500, Malaysia

<sup>3</sup>School of Engineering, Lancaster University, Lancaster, LA1 4YW, UK

<sup>4</sup>Fuel Cell Institute, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

**Abstract.** This study investigates the impact of electrospinning parameters, particularly focusing on the applied voltage parameter, on the diameter of TCNFs composite nanofibers for application in direct methanol fuel cells (DMFCs). The electrospun nanofibers are comprehensively characterized using fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM), Brunauer–Emmett–Teller (BET) analysis and electrochemical techniques of cyclic voltammetry (CV). The results revealed that the optimal applied voltage is 16 kV for TCNFs nanofiber, resulting in an average nanofiber diameter of 161.18 nm. Furthermore, the electrochemically characterized composite nanofibers of PtRu/TCNFs demonstrate exceptional performance, achieving a peak current density of 265.33 mA/mg<sub>PtRu</sub><sup>-1</sup>, surpassing PtRu/C by 3.35 times. The comprehensive analysis contributes valuable insights for tailoring nanofiber design to enhance electrocatalytic performance, paving the way for advancements in DMFC technology.

## 1 Introduction

Nanostructured materials or known as nanomaterials are one of the attractive materials to be chosen in the research field. This fascinating material have a wide range of potential in applications includes energy, electronic, optical and mechanical devices, medicine, consumer product and many more [1]. Nanomaterials is the structured components produced with dimension in the range of 1 to 100 nm [2]. This quickly expanding materials can be divided into several type of structure such as nanofibers, nanotubes, nanoparticles, nanorods, nanowire and others. Each structure has their own potential and benefit in certain application. One of the most shining nanostructures is nanofibers form due to the amazing properties and

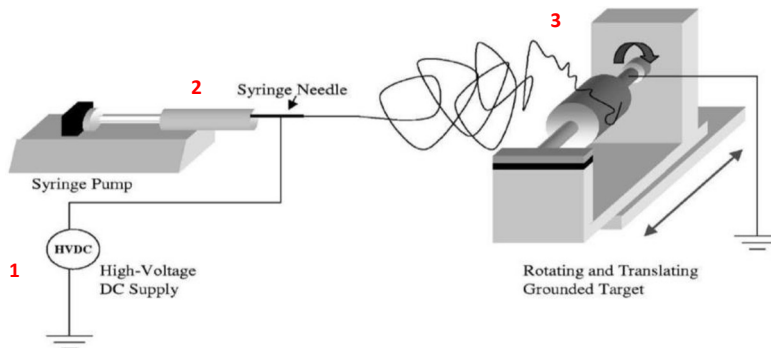
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\* Corresponding author: [nabdullah@sunway.edu.my](mailto:nabdullah@sunway.edu.my)

the potential towards many importance applications. The nanofibers can produce a very large surface area to volume ratio, flexibility in surface functionalities and having the superior mechanical performance [3].

There are different processing techniques to produce the nanofibers such as several type of electrospinning (basic, melt, gas-jacket, bubble, magneto, etc.), centrifugal, phase separation, drawing, self-assembly, template synthesis and electroblowing [4]. In the recent years, electrospinning process become the most popular technique to be used in nanofibers production [5]. This is because the electrospinning technique providing the simplicity, versatility, economical and able to produce fine nanofiber with the small diameter. The electrospinning technique involved three main components, which is the high voltage source, syringe pump with capillaries or tubes, and the grounded collector (various shape) [6].

This technique mainly using the high electric field to convert the polymer solution into the fine nanofibers. The processing of nanofiber is begun with the provided polymer solution is injected towards the grounded collector. During the injection process, the polymer solution at the needle tip is subjected to an electric field and the charge is induced on the solution surface that make the polymer solution deforms and form the Taylor cone. When the electric field reach the critical value, the jet experiencing the bending instability mechanism, which is the injected solution in unstable rapid whipping towards the grounded collector [5]. The overall illustration of electrospinning technique is shown in Fig. 1.



**Fig. 1.** Illustration of electrospinning technique.

Electrospinning has various parameter to be adjusted in order to produce the best nanofiber, that can divide into three main parameter, solution, process and ambient parameter. Flowrate, applied voltage and distance between tip and collector is included as process parameter, where one of these parameters have a major factor to control the fiber diameter which is applied voltage [7]. The uniform, smaller and fine diameter, which lead towards high surface area is a critical need in resulting the better result in various industry, including in direct methanol fuel cell (DMFC). DMFC is one of the promising energy technologies for the next generation. However, this technology facing a few problems that hindering the commercialization, such as low oxidation kinetics, high methanol crossover, and costly [8]. By introducing nanofiber to this technology, it can help to increase catalytic activity and the overall performance of DMFC. To increase the potential of DMFC as the future alternative energy, the new composite nanofiber is chosen, which is combination between titanium dioxide ( $\text{TiO}_2$ ) and carbon nanofiber (CNF), known as TCNFs. This composite nanofiber will act as a catalyst support, and automatically can reduce the catalyst manufacturing cost of DMFC. Material selection is carried out based on their special characteristic, the crystal structure of  $\text{TiO}_2$  can increase the stabilization of thermodynamic, thermal, and electrochemical in composite material [9].

The catalyst support, TCNFs, and nanofiber structure is seen to be one of the most potential material and structure selection for DMFC. This article aims to address DMFC challenges by investigating the impact of the electrospinning process parameter, specifically the applied voltage, on nanofiber diameter. The fabrication involves incorporating  $\text{TiO}_2$  precursor into the polymer solution, which is then electrospun through a syringe. Following electrospinning, the nanofibers undergo stabilization and carbonization processes before characterization, including fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM), Brunauer–Emmett–Teller (BET) analysis. The nanofiber is then deposited onto the catalyst, and the electrocatalyst is undergo the electrochemical measurement of cyclic voltammetry (CV) to identify the potential in anodic DMFC system.

## **2 Experimental**

### **2.1 Preparation of the TCNFs nanofiber**

The polymer solution is prepared by adding poly(vinyl acetate), PVAc (11.5 wt.%), into a solvent, dimethylformamide, DMF. The polymer is dissolved in the solvent by stirring for 1 hr at 60 °C, and then continue stirring for 12 hours at room temperature. After that, a proper amount of polymer solution is isolated and a few drops of titanium isopropoxide, TiPP, is added and continued with a drop of ethanol and acetic acid. The mixture is stirred for another 2 hours to ensure the solution is homogenized. The solution is transferred into the syringe for undergo the electrospinning technique using Nfiber electrospinning unit. The electrospinning technique is applied with the range of 13 to 19 kV of voltage, 16 cm of tip and collector distance, and  $0.1 \text{ mlhr}^{-1}$  of flowrate. The electrospun nanofiber is left at room temperature for 5 hours, and continued with stabilization at 130 °C for 8 hr. The carbonization takes place for 2 hours at 600 °C in nitrogen atmosphere by tube furnace. The carbonized nanofiber is crushed for 5 min by mortar and pestle before further used in this study.

### **2.2 Deposition of TCNFs nanofiber onto PtRu catalyst**

The TCNFs nanofiber is added into the mixture of isopropyl alcohol (IPA) and deionized water (DI water) and sonicated in ultrasonic bath for 20 min. The precursor of platinum, and ruthenium is mixed into the solution and stirred for 20 min. Then, pH value for the mixed solution is adjusted with NaOH solution until reaches pH 8. The temperature is raised to 80 °C and 25 ml of 0.2 M  $\text{NaBH}_4$  is added drop by drop into the mixed solution. The solution is stirred for another 1 hour. The mixture was then cooled, filtered, and washed repeatedly. The catalyst powder was dried at 120 °C for 3 hour and finally crushed using mortar and pestle to obtain the fine catalyst powder and ready to be used for performance test.

### **2.3 Characterization of the catalyst**

The chemical composition of the catalyst support nanofiber was characterized through FTIR (PerkinElmer). Surface morphology analysis of the catalyst support nanofiber and the prepared catalyst was conducted using FESEM (SUPRA 55 VP). The specific surface area of catalyst support nanofibers was measured with BET analysis (Micromeritics ASAP 2020).

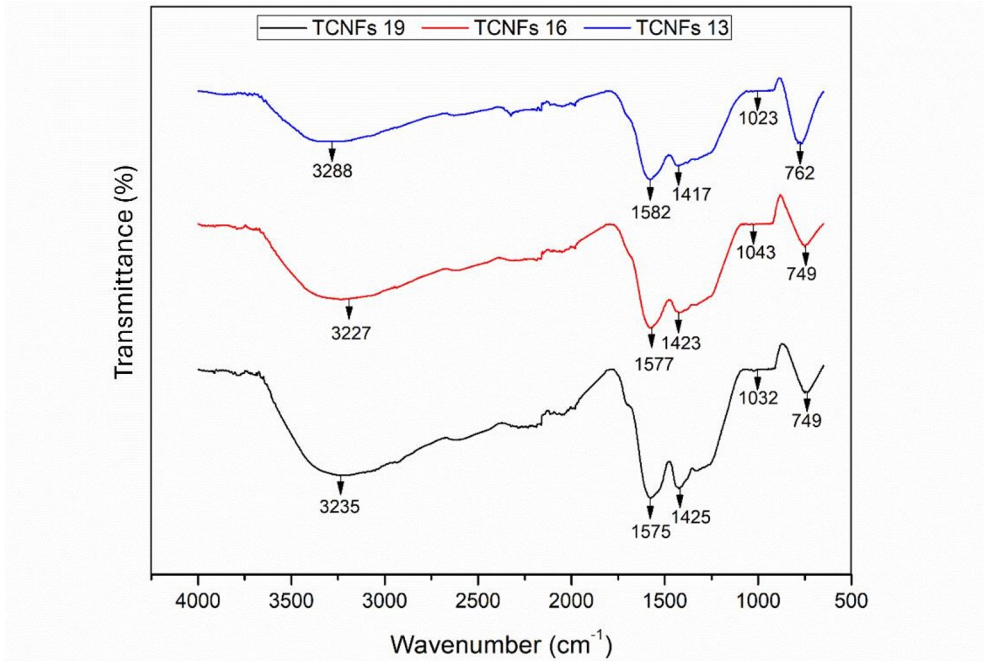
## 2.4 Evaluation of the electrochemical measurement

The evaluation of performance focused on identifying the optimal parameter among those investigated in this study. The PtRu catalyst was applied onto the TCNFs catalyst support for assessment through electrochemical measurements. These measurements were conducted using a three-electrode cell system, involving ECSA and CV to assess the electrochemical active surface area and catalytic activity of methanol oxidation reaction (MOR) using an electrochemical workstation (Autolab PGSTAT 204). The three-electrode cell system, operating at room temperature, comprised a Pt counter electrode, a silver/silver chloride (Ag/AgCl) reference electrode, and a glassy carbon electrode (GCE) with a diameter of 3 mm, serving as the working electrode. Before each measurement, the GCE underwent cleaning with alumina and polishing paper. The catalyst ink for the GCE was prepared by dispersing 5 mg of catalyst in a mixture of 80  $\mu$ L DI water, 80  $\mu$ L IPA, and 25  $\mu$ L Nafion solution (5 wt.%) for 30 min. A micropipette dispensed 2.5  $\mu$ L of the catalyst ink onto the GCE, which was then dried for 1 hr at room temperature and heated at 80  $^{\circ}$ C for an additional 30 min. The electrolyte, a solution of 0.5 M H<sub>2</sub>SO<sub>4</sub> in 2 M methanol, was purged with nitrogen gas for 20 min to remove oxygen content. The measurement was conducted in a potential range of -0.1 – 1.0 V vs. Ag/AgCl with a scan rate of 20 mVs<sup>-1</sup>.

## 3 Result and Discussion

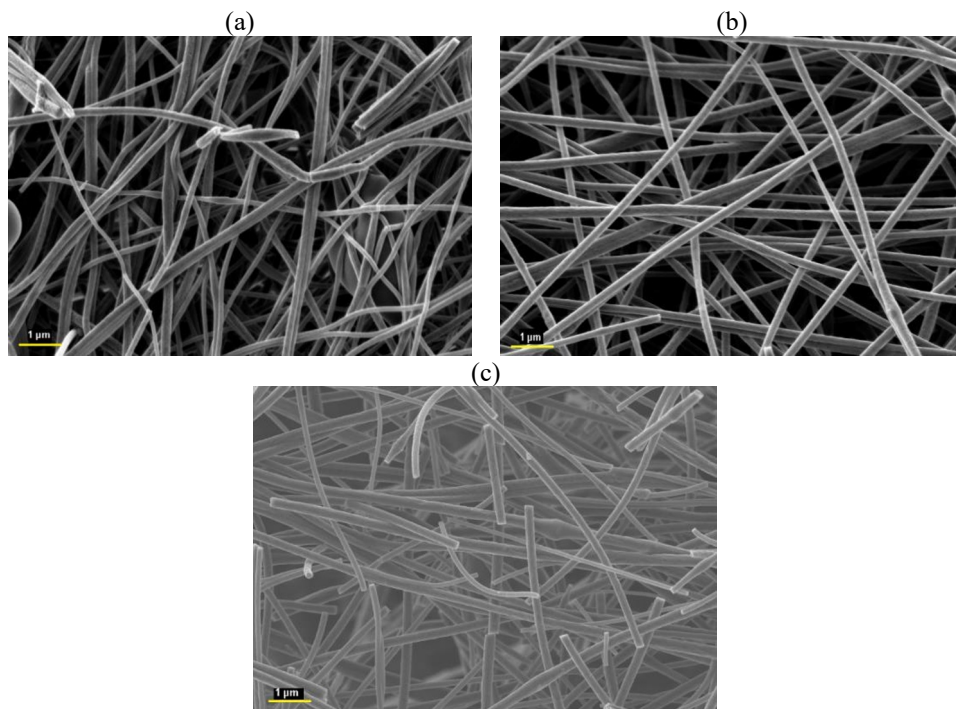
### 3.1 Structural Characterization

The electrospinning fabrication of TCNFs nanofibers at different applied voltage is denoted as TCNFs 13, TCNFs 16, and TCNFs 19, represent the voltage parameter value of 13, 16 and 19 kV, respectively. The identification of chemical compounds or bonding within the sample is achievable through FTIR. Fig. 2 displays the FTIR spectrum for the samples, with wavenumbers ranging from 650 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>. The peaks and wavenumbers for all samples are nearly identical, suggesting that the electrospinning parameter of voltage does not significantly impact the chemical compound of the samples. The O-H functional groups were represented by medium and broad peaks in the range of 3200 to 3600 cm<sup>-1</sup>, while a distinct and intense C=O absorption band appeared between 1550 to 1850 cm<sup>-1</sup> [10]. Weak and broad peaks corresponding to C-H groups were observed in the 1300 to 1450 cm<sup>-1</sup> range. Notably, C-C groups, expected at very low wavenumbers below 500 cm<sup>-1</sup>, were not visible in the spectra due to the limited wavenumber range covered by the spectrum. The medium and sharp bands between 650 to 900 cm<sup>-1</sup> were attributed to Ti-O groups, as proposed by Ding et al. [11]. The spectra exhibited signals indicative of chemical bonds associated with TiO<sub>2</sub> and carbon, which are present in TCNFs samples.



**Fig. 2.** FTIR spectroscopy for TCNFs samples at 400 to 1000  $\text{cm}^{-1}$  wavenumber.

This study specifically targets the generation of the smallest nanofiber size, emphasizing diameter variation. Nanofiber mean diameters are determined through FESEM analysis and data distribution technique with 100 samples of measured diameter sizes. The FESEM images of catalyst support with different flowrate is presented in Fig. 3 and mean diameter results is tabulated in Table 1. The images affirm the presence of nanofiber structures for all flowrates. TCNFs 13 showcases intertwined nanofibers with a substantial diameter, accompanied by the formation of droplets between the fibers. At lower applied voltages, the Coulombic forces prove insufficient to overcome the surface tension of the polymer solution, leading to the generation of droplets instead of continuous fibers [12]. Conversely, TCNFs 16 display the smooth and finer nanofibers morphology compared to the TCNFs 13 and 19. This is attributed to its moderate strength of electric field, allowing for controlled stretching of the polymer solution, resulting in thinner and more evenly distributed nanofibers. The electrospun nanofibers also producing the uniform diameter of nanofibers with low beading morphology. This result can be seen in the Table 1, where the range diameter of TCNFs 16 is between 140 to 190 nm, the smallest range compared to other samples. This voltage also produces the smallest mean diameter of nanofibers with 161.18 nm. TCNFs 19, with a higher voltage, exhibits non-uniform diameter, and the presence of beads on the nanofiber morphology. As the voltage increases, the initially spherical shape of the jet transforms back into a cylindrical shape due to charge repulsion, which leads to the creation of beads along the elongated fibers. Comparable results have been documented in studies involving the electrospinning of polycaprolactone nanofibers [13] and microporous polyimides nanofibers [14].



**Fig. 3** FESEM Image of (a) TCNFs 13, (b) TCNFs 16, and (c) TCNFs 19 at 10K X magnification.

**Table 1.** The mean diameter and BET surface area of TCNFs sample with different voltage.

Experiment	Voltage (kV)	DTC (cm)	Flowrate (mlhr <sup>-1</sup> )	Range of Diameter (nm)	Mean Diameter (nm)	BET Surface Area (m <sup>2</sup> g <sup>-1</sup> )
TCNFs 13	13	16	0.1	180 – 270	225.19	29.04
TCNFs 16	16	16	0.1	140 – 190	161.18	73.09
TCNFs 19	19	16	0.1	100 – 250	178.51	55.92

The surface area of TCNFs samples was assessed through BET analysis, with nitrogen absorption/desorption isotherms conducted at 77 K. Table 1 presents the BET surface area values for TCNFs 13, TCNFs 16, and TCNFs 19 nanofibers. Among these, TCNFs 16 exhibits the highest BET surface area at 73.09 m<sup>2</sup>g<sup>-1</sup>, followed by TCNFs 19 and TCNFs 13 in decreasing order. The observed correlation between BET surface area and nanofiber mean diameter suggests that a smaller nanofiber diameter corresponds to an increased surface area. This heightened surface area is particularly desirable in the catalytic system of DMFC, as it enhances the distribution and homogeneity of the immobilized catalyst, thereby improving stability and catalytic activity [8].

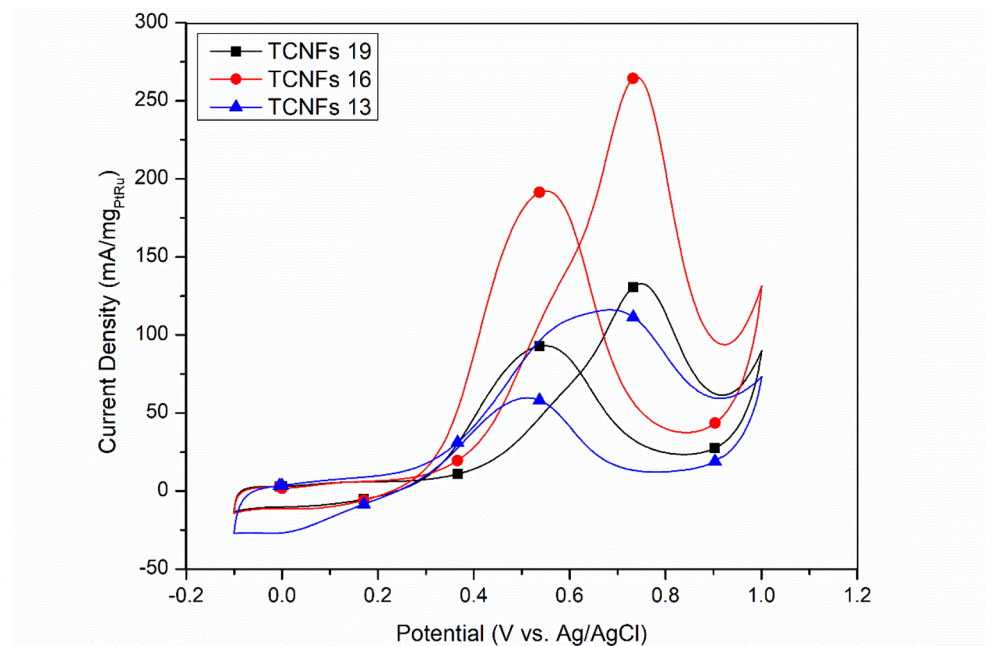
### 3.2 Electrochemical Measurement

The electrocatalytic potential of PtRu/TCNFs (13, 16, 19) samples was explored by depositing PtRu catalyst onto the TCNFs nanofibers. This investigation aimed to evaluate the electrocatalyst's performance in anodic DMFC systems. CV analysis, illustrated in Fig. 4,



was employed to assess the electrocatalytic performance under conditions of 2 M methanol and 0.5 M H<sub>2</sub>SO<sub>4</sub>, saturated with nitrogen gas at room temperature. Multiple CV curves were recorded within the potential range of -0.1 to 1.0 V vs. Ag/AgCl. Comparative analysis of the CV results for TCNFs nanofibers and the conventional PtRu/C electrocatalyst, as per Abdullah et al.'s previous study [15], is presented in Table 2.

The findings reveal a hierarchy in peak current density: PtRu/TCNFs 16 > PtRu/TCNFs 19 > PtRu/TCNFs 13 > PtRu/C. Notably, PtRu/TCNFs 16 achieves a peak current density of 265.33 mA/mg<sub>PtRu</sub> at a peak potential of approximately 0.74 V vs. Ag/AgCl. This superior performance is attributed to the small diameter and large surface area of TCNFs 16, as confirmed by FESEM and BET analyses. The results underscore that smaller diameters and larger surface areas of nanofibers creates a favorable environment for methanol oxidation reactions by increasing the number of active sites, improving mass transport, enhancing electrocatalytic activity, facilitating electron transfer, and optimizing accessibility to catalytic sites. These factors collectively contribute to the improved efficiency and performance of methanol oxidation reactions in electrochemical systems of DMFCs. Overall, all TCNFs-supported catalyst samples exhibit significantly higher peak current density compared to the carbon black-supported catalyst. This emphasizes the superior suitability of TCNFs as a catalyst support over carbon black. The positive metal-support interaction further reinforces this, with the PtRu and TCNFs combination proving to be a successful electrocatalyst in DMFC applications.



**Fig. 4.** CV result for PtRu/TCNFs samples in a solution of 2 M methanol and 0.5 M H<sub>2</sub>SO<sub>4</sub>, with a scan rate set at 20 mVs<sup>-1</sup>.

**Table 2.** CV results for PtRu/TCNFs samples and comparison with PtRu/C electrocatalyst.

Electrocatalyst	Peak Potential (V vs. Ag/AgCl)	Peak Current Density (mA <sub>mg<sub>PtRu</sub></sub> <sup>-1</sup> )
PtRu/C	0.72	79.32
PtRu/TCNFs 13	0.68	116.06
PtRu/TCNFs 16	0.74	265.33
PtRu/TCNFs 19	0.75	132.75

## 4 Conclusion

In summary, this study focused on crafting TCNFs nanofibers, primarily for potential applications in DMFCs. By optimizing electrospinning parameters, specifically adjusting the voltage, the morphology and diameter of the nanofibers were successfully customized. Among the samples, TCNFs 16 demonstrated a significant surface area, positioning it as a promising catalyst support. Deposition of PtRu onto these nanofibers showcased superior electrocatalytic performance, especially in PtRu/TCNFs 16, which outperformed the conventional PtRu/C catalyst. The small diameter and extensive surface area of TCNFs 16 contributed to heightened catalytic activity for methanol oxidation. This project lays a foundation for future innovations in nanofiber-based electrocatalysts, offering insights into advancing DMFC performance through electrospinning techniques.

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