



## Effect of Solution Dielectric Constant on the Preparation of Gas Diffusion Electrode Reaction Layer for the Oxygen Reduction Reaction

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### Abstract

This study explored the impact of solvent dielectric constant on the catalyst layer of proton exchange membrane fuel cell (PEMFC) cathodes during the oxygen reduction reaction. Electrochemical analyses were conducted at 25°C in 2.0 M H<sub>2</sub>SO<sub>4</sub> on electrodes that had been prepared with the same Nafion and Pt loadings, but with various solvent dielectric constants for ink preparation of the catalyst layer. A Nafion loading of 0.5 mg cm<sup>-2</sup> and Pt loading of 1 mg cm<sup>-2</sup> were employed for all electrodes. The findings of the research revealed that the dielectric constant of the ink utilized for preparing the gas diffusion electrode reaction layer has an impact on the electrode's performance for the oxygen reduction reaction. This effect was evident in both the kinetics parameters linked to the oxygen reduction reaction and the physical characteristics of the electrode surface. In the preparation of the reaction layer, an optimal electrode performance result of 4.2 was achieved in relation to the dielectric constant.

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## 1. Introduction

Over the past two decades, significant progress has been made in the field of polymer electrolyte membrane fuel cells (PEMFCs) [1-4], with literature addressing various aspects of performance enhancements [5-12]. Both limitations in the reactant transport and undesired Oxygen Reduction Reaction kinetics leads to high importance of cathode catalyst layer in efficiency of PEMFCs. Moreover, the high platinum loading required to sustain adequate reaction rates in cathodes is a significant cost factor impeding the commercialization of PEMFCs. Therefore, research efforts are focused on developing non-precious metal catalysts, improving reactant transport, electro-catalyst preparation modifications, and exploring alternative cathode structures [13-18].

For efficient functioning, at least five essential components are required in the catalyst layer of a PEMFC: an electron conductor, typically carbon; a proton conductor, usually Nafion; platinum catalysts; solvents; and gas pores. In a typical catalyst layer produced using conventional techniques [19-20], these five components are randomly distributed, leading to a significant amount of wasted platinum and low electrochemical performance of the catalyst layer. To address this issue, researchers have been developing novel techniques to improve the distribution of these components and enhance the performance of the catalyst layer [21-22].

Nafion ionomer is commonly used in PEMFC electrodes to facilitate proton conduction from the electrocatalytic metallic surface towards the polymer electrolyte. The variation in ionomer content in the catalyst layer has been extensively studied, with different researchers concluding that the optimal Nafion amount in the electrode catalyst layer typically ranges from 30 to 36 wt. % of the catalyst weight [23-25]. However,

recent studies have demonstrated that the optimal Nafion content depends on various factors, including the Pt metallic loading in the catalyst [26]. Sasikumar et al. [27] found that the optimal value of Nafion content in the electrodes can reach up to 50 wt. % of the catalyst for Pt loadings as low as  $0.1 \text{ mgcm}^{-2}$ , using a catalyst with 20 wt. % of Pt.

When Nafion solution is mixed with various organic solvents, the mixture can undergo one of three stages: (i) solution, (ii) colloid, or (iii) precipitation, depending on the dielectric constant of the solvent [28]. High performance in PEMFCs can be achieved through co-precipitation of Nafion colloid and Pt/C, accompanied by simultaneous cross-linkage of Nafion that covers Pt/C [29].

The role of the dielectric constant of solvent in determining the mixture's stage lies in its ability to affect the solvation of ions and polar molecules in the solution. Solvent molecules with high dielectric constants are shown to be superior in solvating charged species to those with low dielectric constants. In the case of Nafion solution mixed with various kinds of organic solvents, a dielectric constant of the solvent is a crucial factor affecting the solvation of charged species in the Nafion solution. When a low-dielectric-constant solvent is added to the Nafion solution, it cannot effectively solvate the charged species in the solution, leading to the formation of a precipitate. On the other hand, when a high-dielectric-constant solvent is added, it can effectively solvate the charged species, leading to the formation of a solution. The intermediate stage, colloid, occurs when the dielectric constant of the solvent is moderate, and the solvation of charged species is intermediate. Researchers have shown a keen interest in this subject and have conducted extensive investigations across various research activities [30-34].

In the present study, four different solvents, namely Normal butyl acetate, Isopropyl alcohol, Isooctane,

and Ethyl acetate, were selected based on their respective dielectric constants. Catalyst inks were prepared using the selected solvents and a mixture of Normal butyl acetate and Isopropyl alcohol, as well as a mixture of Normal butyl acetate and Isooctane. The prepared inks were then fabricated into gas diffusion electrodes using a transfer-printing technique. After fabrication, the gas diffusion electrodes were studied by using electrochemical techniques. The surface morphology of the electrodes was studied using scanning electron microscopy (SEM).

## 2. Experimental

### 2.1. Fabrication of gas-diffusion electrode (GDE)

A porous gas-diffusion electrode (GDE) was fabricated using a previously described procedure [35]. To prepare the PTFE-bonded porous gas diffusion layer (GDL), the resulting composite structure was dried in air at 80-90°C for 1 hour, then maintained at 250°C for 30 minutes to remove the dispersion agent contained in the PTFE. Finally, the composite structure was sintered in air at 340°C for 15 minutes. The PTFE acted as a binder and provided the necessary hydrophobicity in the GDL. To prepare the catalyst layer, a mixture of a homogeneous suspension of Nafion, Pt/C catalyst, and selected solvents was prepared and homogenized using a sonicator (Misonix model S-3000) for 20 minutes. The resulting ink was then painted onto the GDL. The prepared electrodes were named according to the value of the dielectric constant in the prepared solution from GDE1 to GDE9 (see Table 1). The composite structure was dried in air at 25°C for 1 hour and sintered in air at 140°C for 45 minutes. The amount of Nafion in the GDE was 0.50 mg cm<sup>-2</sup>, and the Pt loading was 1.0 mg cm<sup>-2</sup>.

**Table 1. The dielectric constant of mixed solvents used in the preparation of the catalyst layer**

Name of Electrode	Solvent	Dielectric constant
GDE1	Isopropyl alcohol(IPA)	18.3
GDE2	NBA: IPA(75:25)	8
GDE3	NBA: IPA(90:10)	6.319
GDE4	Ethyl acetate	6
GDE5	Normal butyl acetate(NBA)	5.01
GDE6	NBA: Isooctane(75.75:24.25)	4.3
GDE7	NBA: Isooctane(71.6:28.4)	4.2
GDE8	NBA: Isooctane(68.06:31.9)	4.1
GDE9	NBA: Isooctane(64.77:35.23)	4

### 2.2. Electrochemical Studies

The reduction of oxygen was studied at the porous GDE (geometric exposed area 1.3 cm<sup>2</sup>) in 2 M H<sub>2</sub>SO<sub>4</sub>. All measurements were carried out at 25°C, in a conventional three-electrode cell, with O<sub>2</sub> flowing at 50 mL min<sup>-1</sup>. The GDEs were mounted in a Teflon holder containing a highly pyrolytic graphite disk as a current collector, which had provision for oxygen feeding from the back of the electrode. A large-area platinum flat electrode was used as the counter electrode. An Ag/AgCl reference electrode was placed close to the working electrode surface. The electrochemical cell was connected to a potentiostat-galvanostat (EG&G Princeton Applied Research Model 273A) for cyclic voltammetry (CV), chronoamperometry, linear sweep voltammetry (LSV) and also to a frequency response detector (model 1025) for electrochemical impedance spectroscopy. In this work, the AC potential amplitude was 5 mV, and its frequency range was from 1 mHz to 10 KHz.

### 2.3. SEM Characterization

The surface of the gas diffusion electrode was analyzed using scanning electron microscopy (SEM) (Philips model XL30).

### 3. Results and discussion

#### 3.1. Calculation of dielectric constant

The dielectric constant is a critical parameter in the thermodynamics of electrolyte solutions. Various intermolecular interactions, especially those involving charged particles, give rise to excess thermodynamic properties in electrolyte solutions. Correlations for the dielectric constant in water, the most commonly used solvent, have been extensively studied [36-37], and successful models for the dielectric constant of liquid mixtures have been reported [38-40]. Kirkwood's theory [41] provides a relationship between the dielectric constant and intermolecular interactions in a pure fluid.

$$\frac{(\varepsilon - 1)(2\varepsilon + 1)}{9\varepsilon} = \frac{4\pi N_A}{3v} \left( \alpha + \frac{\mu^2 g}{3kT} \right) \quad (1)$$

Where  $\alpha$  is the molecular polarizability,  $\mu$  is the dipole moment of the molecule,  $N_A$  is Avogadro's constant,  $v$  the molar volume, and  $g$  is a correlation factor that characterizes the relative orientations between neighboring molecules. Equation (2) explicitly relates the polarization per unit volume of the fluid to the dielectric constant.

$$P = \frac{(\varepsilon - 1)(2\varepsilon + 1)}{9\varepsilon} \quad (2)$$

In a fluid mixture, complications arise due to changes in the orientation of various polar species upon mixing. A rigorous extension of Kirkwood's theory to mixtures is not practical due to the complexities of orientational correlations. A commonly used approximation assumes that the orientation  $g$ -factor for each component in the mixture remains unchanged upon mixing at constant temperature and pressure. In this case, Oster's rule [42] applies, and the polarization of

a mixture of  $n$  components can be expressed by equation (3).

$$P_m = \frac{\sum_{i=1}^n x_i v_i p_i}{\sum_{i=1}^n x_i v_i} \quad (3)$$

Where  $P_m$  is the polarization per unit volume of the mixture,  $x_i$  is the mole fraction of component  $i$ , and  $v_i$  and  $p_i$  are the molar volume and polarization of pure component  $i$ . The values of  $v_i$  and  $p_i$  are calculated at the temperature and pressure of interest.

Eq. (3) also assumes a zero-volume change upon mixing. Calculation of the dielectric constant of a fluid mixture becomes equivalent to the calculation of polarization,  $P_m$ , and  $P_i$ . In this study, we used these formulas to predict the dielectric constant of mixed solvents, and the results are shown in Table 1.

#### 3.2. Cyclic Voltammetry study

Cyclic voltammetry studies were conducted to investigate the variation of the electrochemical surface area (ESA) and roughness factor with the solution dielectric constant. Fig.1 shows the voltammograms of electrodes, all of which have a Pt loading of 0.5 mg cm<sup>-2</sup> and a Nafion loading of 1 mg cm<sup>-2</sup>. It is worth mentioning, the electrodes have different solution dielectric constants for the preparation of their catalyst layer. The coulombic charge for hydrogen desorption ( $Q_H$ ) was used to calculate the active platinum surface of the electrodes. The value of  $Q_H$  was calculated as the mean value between the amounts of charge exchanged during the electro-adsorption ( $Q'$ ) and desorption ( $Q''$ ) of H<sub>2</sub> on Pt sites.

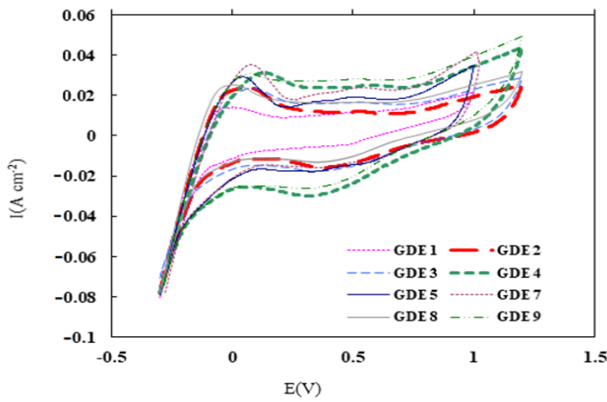


Fig.1. The voltammograms of electrodes (Scan rate 50 mVs-1 and 25°C), each with a Pt loading of 0.5 mg cm-2 and Nafion loading of 1 mg cm-2 but with a different solution dielectric constant for preparation catalyst layer

The contribution of “double layer” charge was also evaluated for each sample, and the charges  $Q_H$  and ESA for the tested electrodes are summarized in Table 2. Figure 2 shows the electrochemical surface area calculated at different dielectric constants for the catalyst layer using Equation (4) [43].

$$EAS = \frac{Q_H}{[Pt] \times 0.21} \quad (4)$$

Where [Pt] represents the Platinum loading ( $\text{mg cm}^{-2}$ ) in the electrode,  $Q_H$  the charge for hydrogen desorption ( $\text{mC cm}^{-2}$ ) and 0.210 represent the charge required to oxidize a monolayer of  $\text{H}_2$  on bright Pt [44-46].

The results presented in Fig. 2 indicate ESA and dielectric constant of the solution are inversely proportional, with the highest ESA value observed at state GDE7. despite the correlation observed, after reaching its maximum value, the rise in the solution dielectric constant is accompanied by decline in ESA. Our findings suggest that the optimum solution dielectric constant is 4.2, which can be achieved benefiting from an NBA: Isooctane (71.6:28.4) mixture. According to previous research, solvents with high dielectric constants (above 10) can form a perfect Nafion solution,

while solvents with dielectric constants below 3 can lead to the formation of precipitates [36]. Ideally, it would be preferable to use solvents with intermediate values to obtain a Nafion colloidal solution, which provides a porous and uniform network without large polymer aggregates.

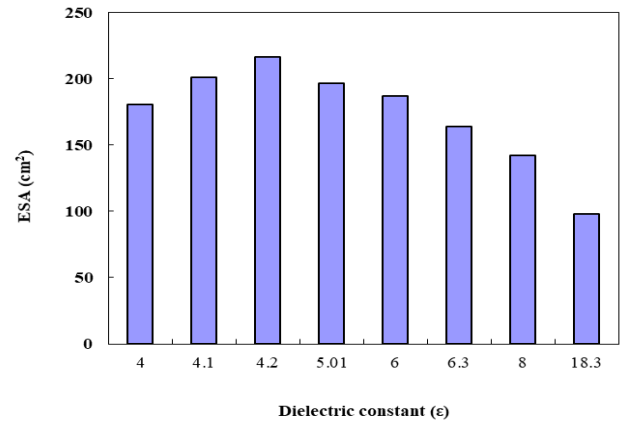


Fig.2. The electrochemical surface area (ESA) calculated at different dielectric constants for the catalyst layer, using Eq. (4)

Table 2. The charges  $Q_H$ , roughness factor, and ESA for the fabricated electrodes.

Name of Electrode	$Q_H$ mC	ESA $\text{m}^2 \text{g}^{-1}$	roughness factor
GDE1	227.516	216.6819	833.3919
GDE2	149.42	142.3048	547.326
GDE3	121.03232	115.2689	443.3418
GDE4	59.9	57.04762	219.4139
GDE5	206.336	196.5105	755.8095
GDE7	172.357	164.1495	631.3443
GDE8	196.5491	187.1896	719.9601
GDE9	102.6339	97.74657	375.9484

### 3.3. Kinetic parameters study

To determine the kinetic parameters of ORR at the fabricated GDEs, a Tafel plot was utilized. As demonstrated in Fig. 3, the Tafel slope values were observed to range between  $-66$  and  $-69.5 \text{ mVdec}^{-1}$ . The observed changes in Tafel slope values can be attributed to the variation in the interphase conditions for ORR that occur as a result of changes in the solvent dielec-

of -60 mVdec<sup>-1</sup> has been explained in previous research [47] as being due to a mechanism of oxygen reduction in which the reaction involves an initial fast charge transfer step followed by a chemical step that is rate-determining under Langmuir conditions.

Fig. 4 demonstrates the influence of the solvent's dielectric constant during the preparation step on the ORR kinetics. Exchange current density reaches its maximum value at GDE7, indicating that the solution dielectric constant plays a critical role in achieving optimal structure in the reaction layer with suitable colloidal Nafion characteristics. This leads to a fast kinetic rate-determining step, as observed in Fig. 4. Counting for the fact that all other effective parameters are held constant, the Sole explanation for observations lies in the preparation solution's dielectric constant.

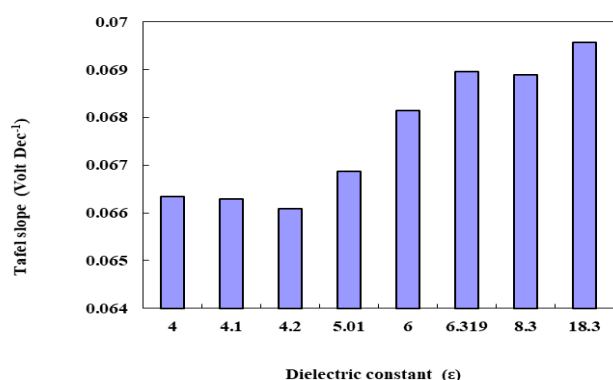


Fig.3. The Tafel slope of the fabricated electrodes prepared using solvents with various dielectric constants.

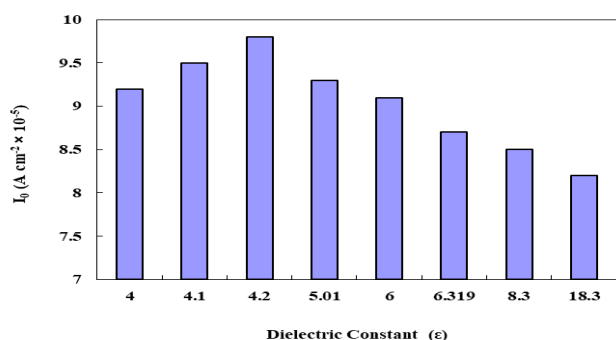


Fig.4. The exchange current density of the fabricated electrodes prepared using solvents with various dielectric constants

### 3.4. Chronoamperometry study

Chronoamperometry is a commonly used method for determining the diffusion coefficient of electroactive species at the electrode surface. In this study, the diffusibility of oxygen in GDEs was quantitatively compared using this method, as described in reference [48].

$$i = nFA(D/\pi t)^{1/2}C^* \quad (5)$$

where  $i$  is the limiting current (mA);  $n$  is the number of electrons;  $F$  is the coulombic charge (96485C mol<sup>-1</sup>);  $A$  is the surface area of the electrode (cm<sup>2</sup>);  $D$  is the diffusion coefficient (cm<sup>2</sup> s<sup>-1</sup>);  $t$  is the time (s);  $C^*$  is the concentration of the reactant (mM).

The term  $D^{1/2}C^*$  can be defined as the permittivity of oxygen at the GDE. A Cottrell plot can be derived from Chronoamperometry data by plotting the current ( $i$ ) versus the inverse square root of time ( $t^{-1/2}$ ). The permittivity values can be determined by calculating the slope of these curves, as presented in Table 3. The highest value of permittivity is observed for GDE7, indicating its greater ability for oxygen diffusion in the reaction layer due to its higher porosity. This finding is consistent with the earlier observation that GDE7 exhibits the highest exchange current density and optimal structure in the reaction layer.

Table 3. The permittivity of the fabricated electrodes was determined by analyzing the data obtained from Chronoamperometry.

Electrode	Permittivity $10^{-7} \times C^* \times D^{1/2}$
	(mol cm <sup>-2</sup> s <sup>-0.5</sup> × 10 <sup>-11</sup> )
GDE1	0.70
GDE2	1.22
GDE3	1.58
GDE4	1.61
GDE5	2.04
GDE7	2.20
GDE8	2.14
GDE9	1.96

### 3.5. Impedance Spectroscopy Study

Impedance spectra were recorded at high overpotential and under oxygen reflux to gain more information on the electrode behavior. Figure 5 shows the impedance data in the Nyquist representation obtained at 300 mV vs. Ag/AgCl (high overpotential). The resulting Nyquist diagram showed two distinct parts: the kinetic control part and the mass transfer control part. The data of these diagrams are shown in Table 4. This data shows that in GDE7, the charge transfer resistance was found to be minimum at a dielectric constant of 4.2.

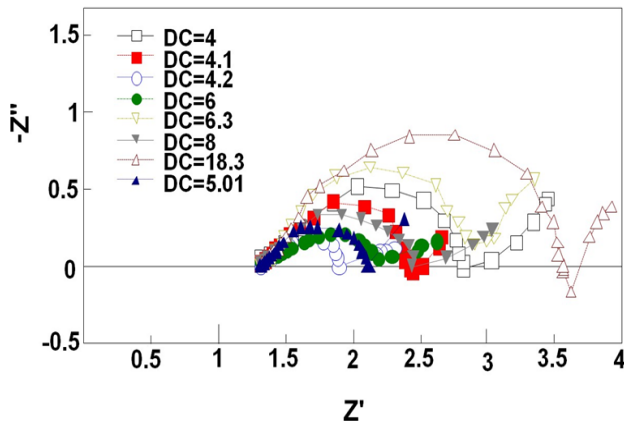


Fig.5. The impedance data in the Nyquist representation obtained at 300 mV vs. Ag/AgCl under oxygen reflux in 25°C

Table 4. The charge transfer resistance of the fabricated electrodes was determined by analyzing the impedance data.

Solvent dielectric constant	Charge transfer resistance ( $\Omega$ )
18.3	2.31
8	1.51
6.3	1.14
6	0.88
5.01	0.81
4.2	0.58
4.1	1.14
4	1.47

### 3.6. Morphology Study

SEM micrographs of prepared electrodes using different solvents, showed that the texture of Nafion varied depending on the solvent used. Fig. 6 displays SEM micrographs of electrodes that were prepared using several solvents listed in Table 1. The electrode produced from isopropyl alcohol (Fig. 6a) exhibited high density and low porosity. In contrast, the electrode formed from the normal butyl acetate: isopropyl alcohol (75:25) mixture in GDE2 (Fig. 6b) was thinner and showed more uniform distribution. In Fig. 6c, the electrode (GDE8), which was prepared using ink dispersed in a mixture of normal butyl acetate and isooctane (68.06:31.94), exhibited an intermediate state. Based on its physical properties, the normal butyl acetate: isooctane mixture was identified as a suitable solvent mixture that can be used as a base component. To reduce dielectric constant value of the ink solvent further, mixtures based on normal butyl acetate and isooctane were tested. The best results based on exchange current density were obtained for a mixture whose volume percentages of the single components were 71.6:28.4, respectively (Table 1). The measured dielectric constant for this solvent was 4.2 at 298 K. Fig. 7a illustrates the structure of the catalyst layer that was deposited on a gas diffusion layer using the mixture mentioned above. A comparison among the Nafion coverage obtained with this mixture and those resulting from its solution in single solvents (Fig. 7b), reveals a significant improvement in the distribution and homogeneity of the catalyst layer. Although the catalyst is uniformly distributed in the layer formed, this structure decreases the mass transfer resistance, makes gas diffusion through the electrode easier, and increases the contact between the catalysts and solvents.

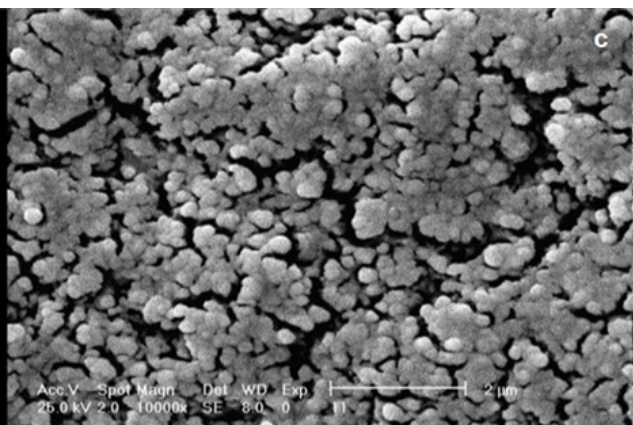
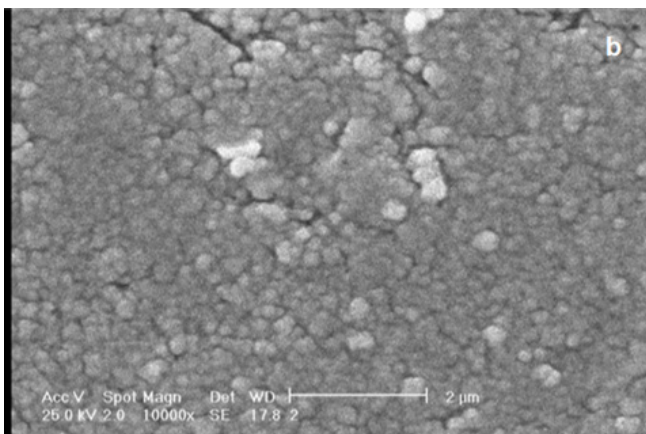
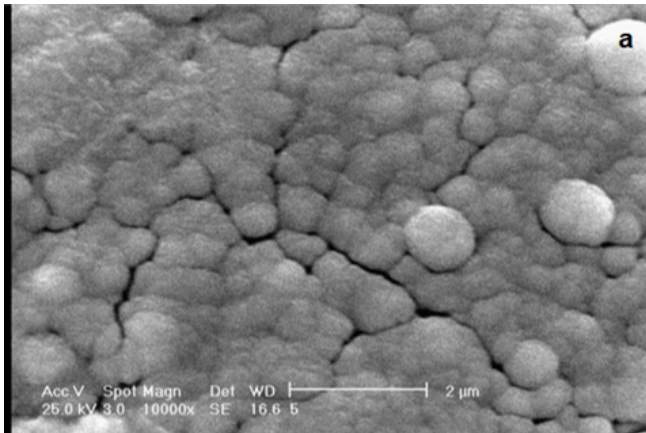


Fig.6. SEM images of GDEs prepared with catalyst ink using different solvent dielectric constant (a) 18.3, (b) 8, (c) 4.1

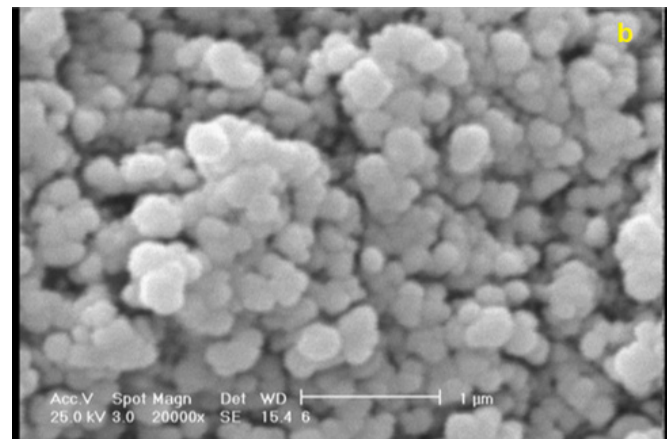
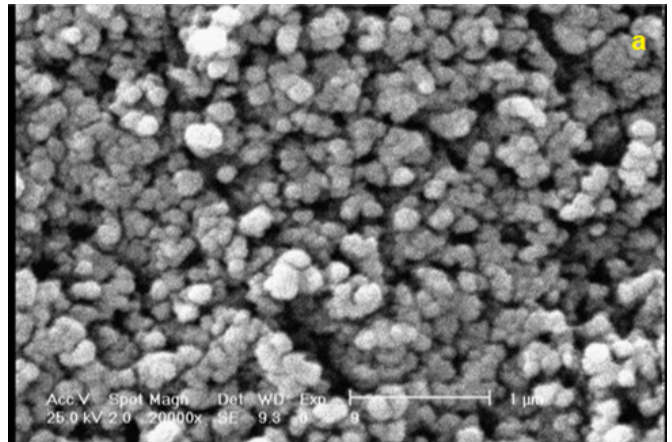


Fig.7. SEM images of GDEs prepared with catalyst ink using different solvent dielectric constant (a) 4.2, (b) 5.01

## Conclusion

As described above catalyst layer plays a crucial role in facilitating the reactions in cathode and anode of fuel cells which is the core foundation for reaching cost-friendly outcomes from fuel cells. The main factors that significantly improved the performance of the prepared electrode for the oxygen reduction reaction were the reduction in pore electrolyte resistance in the catalyst layer and the enlargement of the secondary pores. Pore electrolyte resistance is a measure of the resistance to ion transport through the electrolyte-filled pores of the catalyst layer. Reducing the pore electrolyte resistance is critical for improving the



performance of fuel cells and other electrochemical devices that rely on efficient ion transport through the electrolyte-filled pores of the catalyst layer.

The dielectric constant of the solvent used to prepare the catalyst layer solution can also affect the pore electrolyte resistance of the resulting catalyst layer. Solvents with higher dielectric constant tend to form thicker and more compact catalyst layers, which can lead to higher pore electrolyte resistance. On the contrary, solvents with lower dielectric constants tend to form thinner and more porous catalyst layers, which are able to reduce the pore electrolyte resistance and bring the fuel cells closer to commercial expectations. Moreover, the solvent's dielectric constant can also affect the dispersion of the Nafion ionomer in the solvent and the formation of fine colloidal solutions. This, in turn, can impact the microstructure of the catalyst layer and the resulting pore size and distribution. The microstructure of the catalytic layer is closely related to the ability of the solvent to disperse the Nafion ionomer and form fine colloidal solutions. For a given Pt and Nafion loading in the catalytic layer, the electrode performance was found to be intimately related to its microstructure, which is ultimately defined by the solvent's dielectric constant. In consequence, the choice of solvent and its dielectric constant is an essential factor in the preparation of the catalyst layer for fuel cell electrodes. A solvent with a lower dielectric constant can help achieve a more uniform and porous catalyst layer, reducing the pore electrolyte resistance and enhancing the electrode's performance. In this work, the electrode prepared with a solvent of dielectric constant 4.2 showed the best performance for the oxygen reduction reaction.

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