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Experimental Studies of Graphene-Coated Polymer Electrolyte Membranes for Direct Methanol Fuel Cells

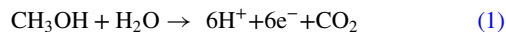
The two main technical limitations of direct methanol fuel cells (DMFCs) are the slow kinetic reactions of the methanol oxidation reaction (MOR) in the anode and the crossing over of unreacted methanol through the proton exchange membrane (PEM). It is a common practice to use Nafion membranes as PEMs, which have high ion exchange capacity. However, Nafion-based membranes also have high fuel permeability, decreasing fuel utilization, and reducing the potential power density. This article focuses on using graphene-coated (Gr-coated) PEMs to reduce fuel crossover. Protons can permeate across graphene, and thus, it can be employed in various devices as a proton conductive membrane. Here, we report the efficiency of Gr-coated Nafions. We tested performance and crossover at three different temperatures with four different fuel concentrations and compared it to a Nafion PEM that underwent the same test conditions. We found that the adhesion of Gr on to PEMs is insufficient for prolonging fuel cell operation, resulting in Gr delamination at high temperatures and higher fuel crossover values compared to lower temperature testing. The results for 7.5M methanol fuel show a reduction of up to 25% in methanol crossover, translating to a peak power density that increases from 3.9 to 9.5 mW/cm² when using a Gr-coated PEM compared to a Nafion PEM at 30 °C.

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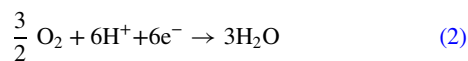
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1 Introduction

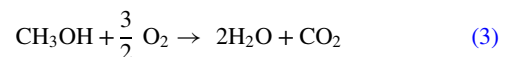
Direct methanol fuel cells (DMFCs) are a subset of a larger group of fuel cells called proton exchange membrane fuel cells (PEMFCs). Liquid methanol solution is supplied to the anode, and air is supplied to the cathode of DMFCs. DMFCs use platinum–ruthenium (PtRu) alloy on the anode as the catalyst for the methanol oxidation reaction (MOR):



Once the hydrogen ions reach the cathode, they react with air with the help of the Pt catalyst through the oxygen reduction reaction (ORR):



The overall reaction in DMFCs is expressed as follows:



As the hydrogen ions transfer across the proton exchange membrane (PEM), electrons are transferred through an external circuit, allowing power to be provided to connected systems. This process is detailed visually in Fig. 1(a), where the anode and

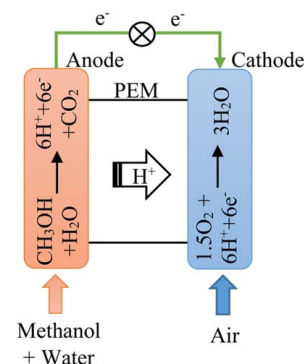


Fig. 1 A DMFC under ideal fuel consumption conditions

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MOR are shown in red and the cathode and ORR are shown in blue. The air supplied to the cathode is typically humidified to relative humidity (RH) of 100%. The typical structure of a membrane electrode assembly (MEA) consists of a gas diffusion layer (GDL) on the anode with an applied catalyst, a PEM, and the structure mirrored on the cathode side, as shown in Fig. 1(b). To make the MEA, catalyst solutions are fabricated using a variety of components that will be detailed further later. These solutions are then applied to the GDLs by a variety of methods.

1.1 Benefits of DMFCs as an Alternative Power Source.

There are many potential benefits to DMFCs over other energy sources. The benefit most focused on is the reduction of CO₂ emissions. Even though DMFCs produce CO₂ as a product of the reaction, methanol is a biofuel and can be produced in a variety of ways. While it is flammable and slightly toxic, it is easy to store, refuel, and handle. On the other hand, pure hydrogen gas is extremely volatile posing risks of explosions and requires specialized personnel to store and transport [1]. Furthermore, the process of producing hydrogen is cost intensive in terms of personnel and practice. Methanol has a high volumetric energy density in a liquid state compared to other fuels like hydrogen, which generally needs to be compressed to high pressure. For example, methanol's energy density is 8.3 times higher than that of hydrogen compressed at 200 bar and approximately 2.6 times higher than that of lithium-ion batteries [2]. In addition, all PEMFCs, including DMFCs, operate at relatively low temperatures, between 30 °C and 130 °C, with a typical operating temperature of 80 °C. These cells are also quick to reach full operating capacity and operate quietly. This makes DMFCs ideal for small and portable power applications requiring lower power input [1]. DMFCs can also be ideal for material handling applications such as deploying DMFC-powered forklifts for warehouses.

1.2 Current Limitations of DMFCs.

While methanol boasts many advantages as a fuel, several limitations prevent DMFCs from meeting similar performance standards to hydrogen-fueled PEMFCs. The two main technical limitations of the broader use of DMFCs have been identified as the slow reaction kinetics of the MOR on the anode and the crossing over of unreacted methanol fuel through the PEM [3]. Many of the other drawbacks of DMFCs stem from these two fundamental problems. For example, the slow MOR on the anode results in lower catalyst utilization than that of PEMFCs [3]. As a result, DMFCs require much higher platinum group metal loadings, with the typical anode catalyst loading being 4.5 mg_{PtRu}/cm² and the cathode loading at approximately 1.5 mg_{Pt}/cm². In addition, the crossing over of concentrated fuel from the anode to the cathode results in an unstable stack voltage, reduced cell potential, and limited overall power density. It is important to note that power density refers to the amount of power generated per unit area of the MEA and is the most common quantification of performance. To alleviate the methanol crossover, dilute methanol solutions (<10 wt% or <3 mol/L) are used as fuel. There are two main reasons for using dilute methanol solutions: (1) water is required for the MOR to occur and (2) unreacted methanol in the anode will crossover through the PEM and deteriorate the fuel cell performance. However, dilute methanol solutions have low energy density. Different fuel cell structures and fuel delivery systems have been proposed to decrease the methanol crossover through the PEM so that more concentrated methanol solutions or even pure methanol could be applied as fuel [4–6]. Meanwhile, studies have been carried out to develop modified PEMs with low methanol crossover rates.

Zhou et al. [7] provided a review of strategies to develop methanol-permeation-resistant PEMs. The review focused not only on the modification of Nafion-based (sulfonated tetrafluoroethylene) membranes using nanomaterial, polymers, and composite structures but also covered non-Nafion membranes.

1.3 Application of Graphene in Fuel Cells.

Extensive research on graphene (Gr) has been done in recent years. Since Gr was reported to have high proton conductivities and superior proton selectivity, it has the potential for many applications in the electrochemical sector [8–12]. Gr's proton conductivity can be further increased by the introduction of defects into graphene crystal lattice by various treatments (plasma, ion bombardment) at the expense of proton selectivity [13–15]. Other properties include a large specific surface area of 2630 m² g⁻¹, high charge mobility, good mechanical durability, and high chemical stability. In addition, it is known for its high thermal conductivity and electron transfer properties [16]. Su et al. [16] recently published a comprehensive analysis of recent findings on various Gr materials used in fuel cell applications. The review covers not only Gr's applications to modify PEM but also other applications in the current collectors and catalysts [16]. Meanwhile, some studies applied Gr or Gr oxide (GO) to modify the PEM for reduced methanol crossover.

Tseng et al. dispersed a monolayer of Gr oxide flakes in a sulfonated polyimide membrane [17]. The GO dispersion prevents methanol from migrating through the membrane while maintaining high ionic conductivity. The composite membrane achieved lower methanol permeability than commercial Nafion 117. Meanwhile, it obtained higher ionic conductivity (6.67 × 10⁻¹ S/cm) than Nafion 117 (2.31 × 10⁻¹ S/cm) at 90 °C. The composite membrane also has promoted internal self-humidification and increased water retention.

Yogarathinam et al. used GO and conductive polyaniline decorated GO (PANI-GO) as additives in sulfonated poly(ether etherketone) (SPEEK) membranes to reduce methanol crossover [18]. The acidic and hydrophilic groups in PANI and GO enhanced the proton conductivity of the modified SPEEK membranes. The PANI-GO-modified SPEEK membrane obtained reduced methanol permeability from 6.16 × 10⁻⁷ to 4.33 × 10⁻⁷ cm² s⁻¹ than neat SPEEK. The modified SPEEK membrane showed significantly increased proton conductivity (from 8.4 × 10⁻³ S/cm to 2.28 × 10⁻³ S/cm) than neat SPEEK at ambient temperature.

Wang et al. deposited GO nanosheets layer by layer onto Nafion117 composite membranes [19]. The composite membrane with 20-layered GO nanosheets showed two orders of magnitude lower methanol permeability (6.7 × 10⁻⁸ cm² s⁻¹ at 30 °C) than the recast Nafion 117 membrane. However, the ionic conductivity of the composite membrane with GO nanosheets (0.041 S/cm at 30 °C) was slightly lower than that of the recast Nafion 117 membrane (0.077 S/cm at 30 °C). Overall, the composite membranes showed better selectivity, which is defined as the ratio of proton conductivity to methanol permeability. As a result, the composite membrane with 50-layered GO nanosheets obtained higher open circuit voltage (OCV; 0.67 V) and higher peak power density (64.4 mW/cm²) than Nafion 117 (41.6 mW/cm²) with 5M methanol at 60 °C.

Xianglin et al. prepared a monolayer Gr sheet using chemical vapor deposition (CVD) and sandwiched it between two Nafion212 membranes [20]. The sandwiched membrane took advantage of monolayer Gr's selective permeability to only protons. The composite membrane showed a 68.6% decrease in methanol permeability than the pristine Nafion membrane while maintaining similar (only 7% lower) ionic conductivity. The composite membrane obtained a similar peak power density (24.9 mW/cm²) with pristine Nafion membrane (25.2 mW/cm²) tested with 5M methanol in passive DMFCs. However, the peak power density of the composite membrane (23.0 mW/cm²) was much higher than that tested with pristine Nafion membrane (14 mW/cm²) using 10M methanol.

The aforementioned publications lack performance tests under well-controlled temperature and flow conditions using more concentrated methanol solutions (>5M) to evaluate the benefit of the Gr and GO coatings. This study focuses on the cost-effective fabrication of Gr-enhanced PEMs. We carried out detailed experiments at different temperatures and methanol concentrations to quantify

the effect of the Gr coating on both the methanol crossover rate and cell performance.

2 Experimental Setup

2.1 Membrane Electrode Assembly Fabrication. We use a Scribner 890e Fuel Cell Tester connected to a 5-cm² MEA cell to test all MEAs. The standard fabrication procedure is as follows. Catalyst solution for the anode is fabricated by mixing appropriate amounts of deionized (DI) water, isopropyl alcohol, anode catalyst, and Nafion[®] 10% ionomer so that the ionomer-to-PtRu ratio is 0.4. The solution is then sonicated for 2 h in a Branson 1800 sonicator to adequately disperse the solution. The catalyst ink is then dripped into an Iwata Ninja Jet airbrush and spray-coated onto the GDL to achieve the desired catalyst loading (4.5 mg_{PtRu}/cm²) in the gas diffusion electrode (GDE). The cathode is fabricated similarly except that the ionomer-to-Pt ratio is 0.2. For baseline tests, Sigracet 29BC (with a hydrophobic MPL) and Toray Carbon Paper (without MPL) are used for the anode and cathode, respectively. An anode GDE, a Nafion[®] membrane, and a cathode GDE were hot pressed using a Dulytek DE10K at 135 °C and 345 kPa for 5 min.

2.2 Membrane Electrode Assembly Activation. Before testing, MEA was activated using the standard activation procedure where the MEA is inserted into the Scribner 890e fuel cell test system and heated to 80 °C. The fuel cell was supplied with 0.25 M aqueous methanol solution at 0.1 mL/min flowrate and 0.1 L/min of air at 80 °C with 100% RH. Once the fuel cell reached the target temperature, the MEA was allowed to rest at the OCV for 3 min. A polarization scan was then performed, followed by holding the voltage at 0.4 V for 1 h. This process was repeated four times until the performance and resistance appeared stable.

2.3 Membrane Electrode Assembly Performance Tests. In standard tests, the air was supplied to the cathode at the rate of 0.1 L/min, fully humidified to 100% RH. The methanol solution was supplied to the anode with the same fuel stoichiometric ratio. For example, the flowrate of 1 mL/min using 1M methanol solution was reduced to 0.33 mL/min for 3M methanol solution. The cathode was pressurized to 50 kPa backpressure using a Scribner manual backpressure regulating module. This setup also allows for anode and cathode supply lines to be changed to desired gas, such as N₂, H₂, or vapor, depending on the desired testing parameters. The cell was allowed to rest at the OCV for 3 min for standard methanol tests. A polarization scan is then performed by scanning from the OCV to 0.2 V. This process was repeated three times for each concentration to ensure performance was stable.

2.4 Methanol Crossover Tests. We measured the crossover of unreacted methanol through PEM from the anode to the cathode of MEAs following the method developed by the Los Alamos National Laboratory [16] (Fig. 2). An Arbin MSTAT4 battery tester was connected to the fuel cell using the standard two-electrode configuration. Nitrogen was supplied to the cathode as an inert gas to prevent ORR from occurring. Methanol at

0.25M, 1M, 3M, or 7.5 M (25 wt%) was supplied to the anode to analyze its reaction at the cathode side. The flux of methanol across the membrane was then determined by measuring the current required to raise the voltage of the cell to approximately 1.2 V. The highest current, i_{\max} , was recorded and converted to methanol flux, N_{MeOH} :

$$N_{\text{MeOH}} = \frac{i_{\max}}{6F} \quad (4)$$

A high methanol flux in this geometry is equivalent to a high methanol crossover rate, leading to a power loss in the fuel cell configuration. The PEM made from Nafion has a high methanol crossover, and the goal of the Gr coating is to reduce it.

2.5 Gr Synthesis and Transfer. Gr was synthesized and transferred as described previously [21–23]. In brief, electropolished copper foils (75 mm thick) were loaded into an atmospheric pressure CVD reactor and annealed at 1065 °C. Foil annealing was done under a flow of 2.5% H₂ in Ar for 30 min. Gr growth was performed by adding methane with a gradual increase of its concentration from 14 to 20, 40, and 100 ppm for 30 min in each step. As was shown before [20,21], such a procedure leads to a high-quality Gr with a domain size over 100 μm and less than 5% of second-layer coverage [21,23,24]. Figure 3 shows the characteristic Raman spectrum (a) and scanning transmission electron microscopy (STEM) image (b) of the grown Gr. A large 2D/G ratio in the Raman spectra and small D peak suggest that synthesized Gr is a single-layer with a low defect density. The STEM image with atomic resolution further unambiguously confirms the single-layer Gr.

The prepared Gr on copper of a typical size ~6 × 6 cm² was hot pressed onto Nafion at 150 °C using 2000 kg for 1 min. Subsequently, the copper was dissolved in 15 wt% of ammonium persulfate in DI water. An additional fresh piece of Nafion was again hotpressed on the prepared Nafion/Gr sandwich under the same conditions, thus forming Nafion/Gr/Nafion structure [25,26]. For the preparation of double-layer Gr, Gr on copper foil was covered with Microchem PMMA 495A4 solution via spin coating at 1500 rpm. The copper was dissolved by 1 M FeCl₃ in 3% HCl. The Gr/PMMA sandwich floating on the surface of water was washed by DI water and transferred on the neat Gr/Cu substrate to form 2Gr/Cu structure.

3 Results and Discussion

3.1 Baseline Tests. The fabricated MEAs were tested using methanol solutions of three concentrations, 1M, 3M, and 7.5M. Figure 4 details the results of a baseline test, i.e., PEM without Gr. The power density, represented by the solid points, first increases and then decreases with the current density. The voltage, shown in empty points, decreases with the increase in current density.

It can be clearly seen that increasing the methanol concentration from 1M to 3M, and 7.5M, shows a significant reduction of the peak power density (from 92.9 to 74.7 and to 33.0 mW/cm²) and the limiting current density. The performance reduction is mainly caused by the increased methanol crossover. Figure 4(b) shows the crossover current densities at various voltages tested with different concentrations of methanol solutions. The corresponding calculated methanol crossover rates are 2.5×10^{-7} , 3.5×10^{-7} , and 4.0×10^{-7} mol/cm²/s with 1M, 3M, and 7.5M methanol solutions, respectively. Increasing methanol crossover rates correlates decline of the operating voltage and power density shown in Fig. 4(a).

3.2 Gr-Coated Proton Exchange Membrane. To study the effect of Gr-coated PEMs, modified PEMs were fabricated. The

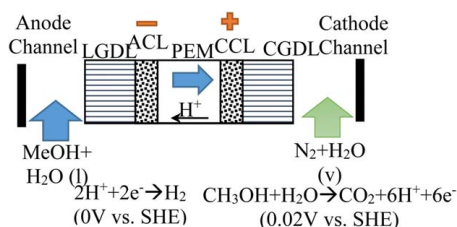


Fig. 2 Sketch of the methanol crossover testing mechanism

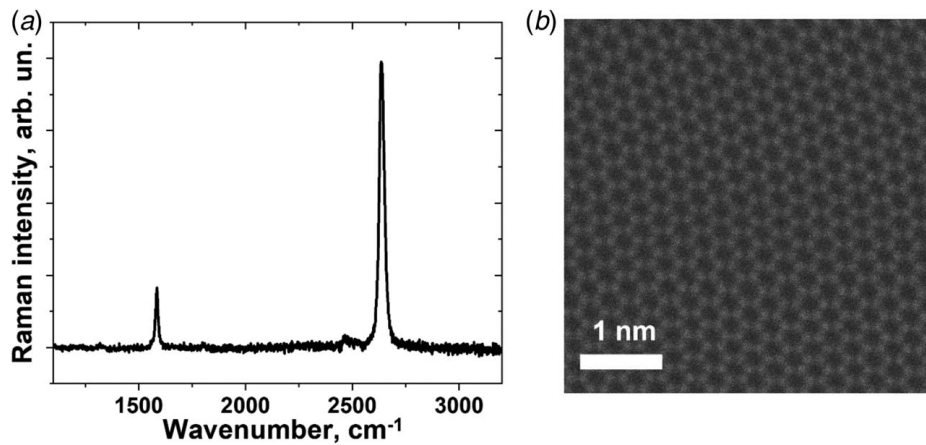


Fig. 3 (a) Characteristic Raman spectra and (b) STEM image of the synthesized single-layer Gr

anodes and cathodes paired with these membranes were fabricated according to the standard fabrication procedure described earlier. The preparation of modified PEM was similar to that described previously but with more options. This synthesis yields high-quality single-layer Gr samples with proton conductivity values described earlier [15]. This study analyzed three different types of Nafion[®]-based membranes modified with various forms of Gr, which were compared with a Nafion[®] 212 membrane as the baseline. In the preliminary studies, we found that swelling of Nafion, especially at high temperature and methanol concentration, compromises integrity of single-layer Gr and thus employed multiple layers of Gr, which were prepared by layer-by-layer sequential transferring procedure [22]. For example, MEA2 uses double-layer Gr on both sides, which were prepared via layer-by-layer sequential transferring procedure on each side. MEAs 3 and 4 use triple layer, which was separately produced first by transferring to layers onto graphene on copper and then hotpressed between two Nafion layers. All MEAs use identical anode and cathode GDEs. These MEAs and their respective components are detailed in Table 1.

All MEAs were activated according to the standard procedure detailed in previous sections using 0.25M methanol at 80 °C. Figure 5 details the performance comparisons between MEA1 and MEA2 at 80 °C.

Figure 5(a) shows that MEA1 (with pristine Nafion 212) has a much higher peak power density (71.4 mW/cm²) than MEA2 (with the Gr-coated Nafion 212) (49.6 mW/cm²) tested with 1M methanol. Both MEAs have very similar OCVs and ohmic

resistance (~20 mΩ). The peak power density of the Gr-coated Nafion is lower, probably due to the higher contact resistance between the catalyst layer and the membrane with the Gr coating and the low proton conductance of “as-synthesized” Gr [15]. When the methanol concentration is increased to 3M, the higher methanol crossover rate reduces the OCV and the peak power density of MEA1 but insignificantly changes for MEA2. The peak power density was dramatically reduced to only 21.7 mW/cm² with 3M methanol, which is a 70% reduction from the peak power density at 1M methanol. In comparison, the Gr-coated MEA2, with reduced methanol crossover, maintains a relatively high peak power density. The peak power density of the Gr-coated Nafion 212 tested with 3M methanol (46.8 mW/cm²) is similar to that of 1M methanol.

Unfortunately, when the methanol concentration was further increased to 7.5M, both MEAs showed limited power density (<10 mW/cm²). The Gr-coated membrane lost its capability to reduce the methanol crossover. Nafion membranes swell significantly when they are in contact with hot water or methanol solutions [8–10]. Since thin Gr layers are coated on the Nafion membrane, the high enough swelling produces large cracks and delamination of Gr. These cracks could be the source of methanol and water crossover and thus reduce the effectiveness of the modified PEM.

Scanning electron microscope (SEM) images of the PEM sample made from a CVD Gr layer sandwiched between two Nafion HP membranes before and after performance testing at 80 °C, shown in Fig. 6. It demonstrates the delamination of the layers in the

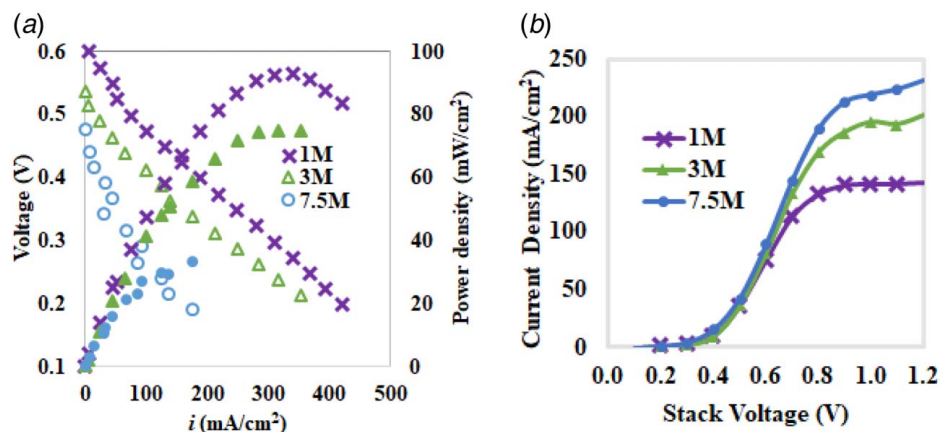


Fig. 4 A baseline test conducted at 80 °C using various concentrations of methanol solutions air (1 L/min and 50 kPa backpressure): (a) polarization curves and (b) crossover current density at different voltages

Table 1 MEAs utilized in the study of various graphene-enhanced Nafion® membranes

	Anode	PEM	Cathode
MEA1 (baseline)	TKK 50% approximately	Nafion® 212	JM Pt/C approximately
MEA2	4.5 mg/cm ² (TEC66E50)	2Gr N212 2Gr membrane	1.5 mg/cm ² (HiSPEC 9100)
MEA3		N211 3Gr N211	
MEA4		N_HP 3Gr N_HP	

membrane. The delamination of the membrane diminishes the effectiveness of reduced crossover. To minimize the membrane swelling and its negative impact on the fuel cell performance, we reduced the activation temperature to 30 °C for MEAs 3 and 4. The activation of MEAs at a lower temperature alleviates the delamination of the Gr layer from the Nafion membrane.

3.3 Performance at 30 °C. Performance tests of modified PEMs were conducted at a lower temperature (30 °C). Figure 7(a) shows the results of standard testing for MEA with commercial Nafion 212 (MEA1) and modified MEAs with Gr coating sandwiched between commercial Nafion 211 (MEA3), and Gr coating sandwiched between commercial Nafion HP (MEA4), at 1M and 30 °C. Since the Gr coating has a thickness of only a few nanometers, all three PEMs have similar thicknesses (~50 μm). A similar ohmic resistance (25–30 mΩ) indicates an insignificant drop of proton conductance of PEM from Gr coating. It is clear that the

peak power density at 30 °C (22.6 mW/cm² measured with Nafion 212) is much lower than the peak power density at 80 °C. This is expected due to the slower reaction rates, lower ionic conductivity, and more sluggish mass transfer.

The modified PEM with Gr coating sandwiched between two Nafion 211 membranes shows a similar peak power density (21.0 mW/cm²) to that of Nafion 212 (22.6 mW/cm²), while the modified PEM with Gr coating sandwiched between two Nafion HP membranes has a much lower power density (8.9 mW/cm²). The weaker performance of MEA4 is likely due to the delamination between the two membranes and the challenge of binding the PEM with the catalyst layers. Figure 7(a) indicates that both MEA1 and MEA3 have similar OCVs when tested with 1M. The slightly higher power density of MEA1 is partially due to its slightly lower ohmic resistance compared to MEA3 (25 mΩ versus 31 mΩ). When the methanol concentration is increased to 3M, the impact of methanol crossover becomes more significant (Fig. 7(b)). The higher methanol crossover in MEA1 in its lower

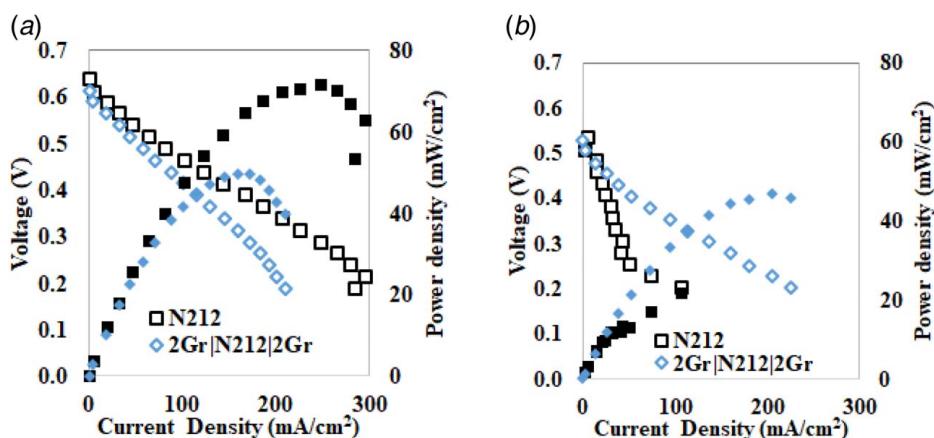


Fig. 5 Performance of MEAs tested with (a) 1M and (b) 3M at 80 °C: 1 mL/min fuel (1M), 0.1 L/min air, 50 kPa backpressure

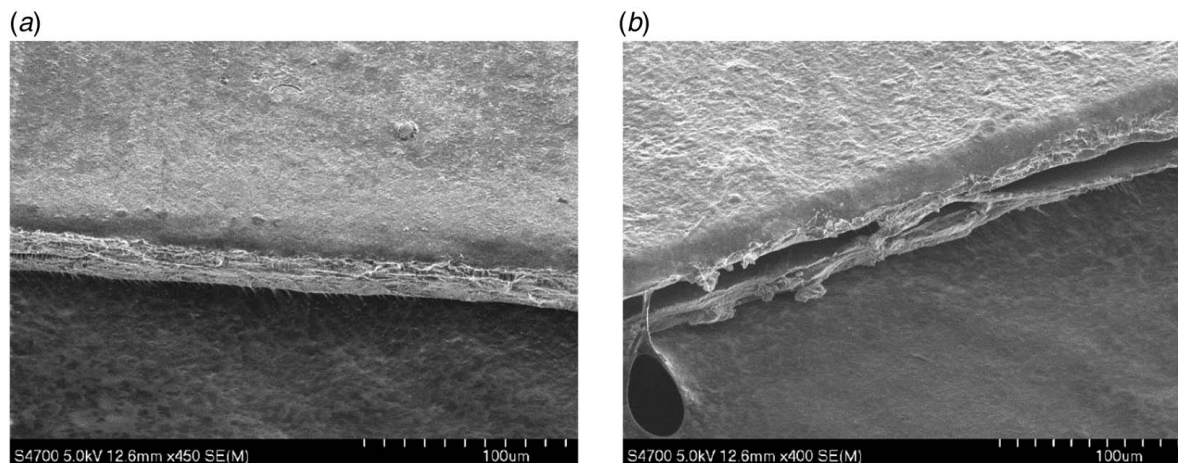


Fig. 6 SEM Images of MEA4 (a) before testing and (b) after testing, which shows delamination of Gr layers

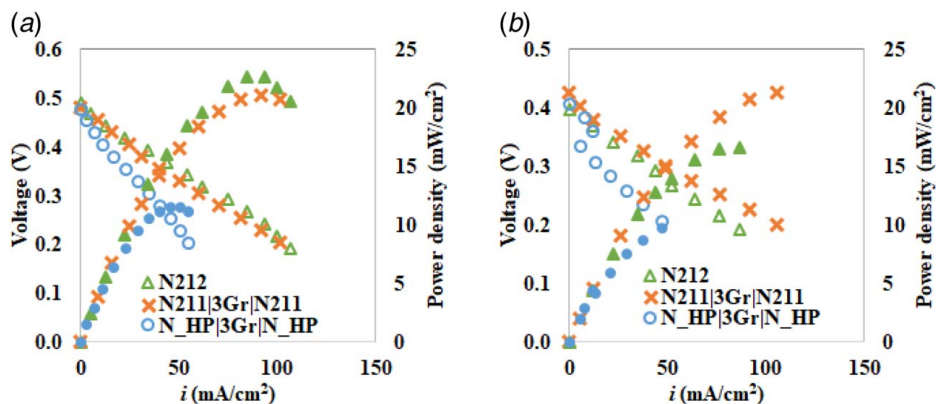


Fig. 7 Performance results of various MEAs tested with (a) 1M and (b) 3M methanol solutions. The operating conditions: 30 °C, 1 mL/min fuel (1M), 0.1 L/min air, 50 kPa backpressure

result OCV (0.39 V) compared to that for MEA3 (0.43 V). The reduction of the operating voltage leads to a lower peak power density in MEA1 (16.6 mW/cm²) than in MEA3 (21.2 mW/cm²).

Figure 8 highlights the benefits of using Gr coating with higher tolerance to increased methanol concentration. When the methanol concentration is increased to 7.5M, the effect of methanol crossover

is much more profound. The MEA3 demonstrates a significant peak power density of 9.5 mW/cm² even when tested using 14.1M (50 wt%) methanol, as seen in Fig. 8(a). In comparison, the peak power density of the pristine MEA1 is only 3.9 mW/cm² in 7.5M methanol and unmeasurable for 14.1M methanol, and both are not shown in the figure. To quantify the methanol crossover, we

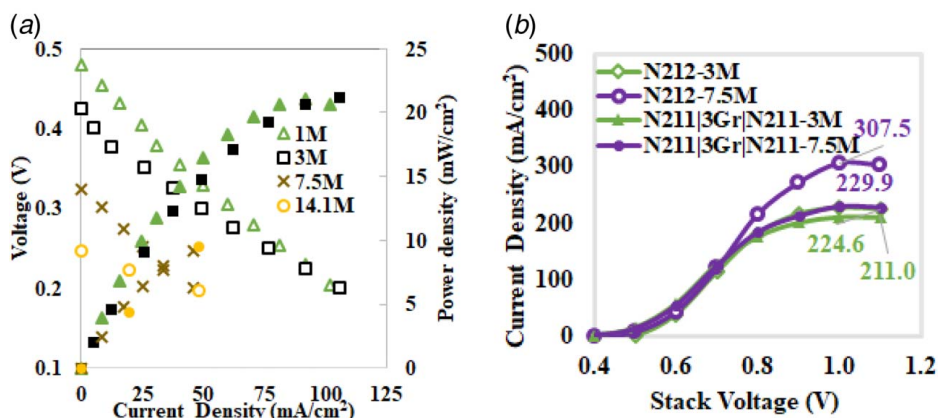


Fig. 8 (a) Performance of MEA with Nafion211|3Gr|Nafion211 (MEA3) tested with various concentrations of methanol solutions. (b) Crossover current density measured with 3M and 7.5M methanol solutions. The operating conditions: 30 °C, 1 mL/min fuel (1M), 0.1 L/min air at 50 kPa backpressure (performance) or 0.1 L/min N₂ with no backpressure (crossover).

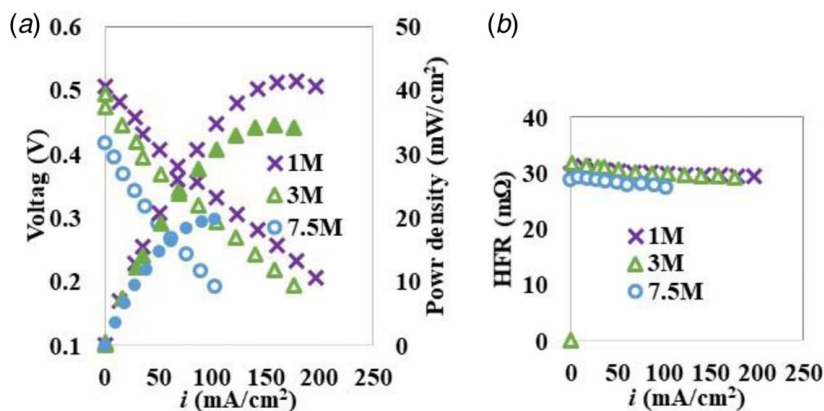


Fig. 9 Performance of MEA3 tested with 1–7.5M methanol solutions. The operating conditions: 65 °C, 1 mL/min fuel (1M), 0.1 L/min air, 50 kPa backpressure.

measured the crossover current densities at various voltages with 3M and 7.5 M methanol solutions. Figure 8(b) shows that the maximum crossover current density for MEA1 (224.6 mA/cm²) in 3M methanol is higher than that of the modified PEM in MEA3 (211.0 mA/cm²). When the methanol concentration was increased to 7.5M, the difference became more dramatic: the crossover current density in MEA1(307.5 mA/cm²) is 25% higher than in MEA3 (229.9 mA/cm²). The maximum crossover current density is proportional to the methanol crossover rate, and its drop with Gr coating correlates with the higher performance of MEA3, i.e., to prove the effectiveness of Gr coating. Intact Gr is impenetrable by methanol, and a nonzero crossover in MEA3 indicates that it does have holes in PEM due to the assembly procedure developed during operation. The main reason for that is the significant swelling of Nafion in water, especially in methanol solution, which cannot be sustained by Gr. Gr has maximum elongation before breaking on the order of 2–3%, while the Nafion swelling can be significantly larger [27–29]. Nevertheless, at methanol concentrations not exceeding 7.5 M and low temperatures, the overall positive effect of Gr coating is noticeable.

When highly concentrated methanol solutions are supplied as fuel, the lack of water may dehydrate the Nafion membrane and significantly increases the high-frequency resistance (HFR). The increase of HFR will not only reduce the power density but also cause performance instability. We measured the HFR of all MEAs and found that the modified PEM remained stable (around 30 mΩ) during all tests with various concentrations of methanol solutions. The fact that the MEA has stable HFR with up to 14.1M methanol is another indication of the positive outcome of applying Gr coatings on the PEM to improve fuel cell performance.

3.4 Performance at 65 °C. While the fuel cell performance at 30 °C illustrates the effectiveness of Gr coating to reduce the methanol crossover and improve the peak power at high methanol concentrations performance, the value of peak power densities at such a low temperature is still limited. At the same time, at 80 °C, the effectiveness of the coating in controlling methanol crossover significantly diminishes. To make the best use of Gr coating while providing decent peak power density, we tested the MEAs at an intermediate temperature of 65 °C, which is close to the boiling point of methanol at the atmospheric pressure and thus should have a less dramatic effect on Nafion swelling than at 80 °C. The results are shown in Fig. 9. It can be seen that the peak power density of the MEA3 at 65 °C tested with 1M (41.3 mW/cm²) is between the peak power densities at 30 °C and 80 °C. The difference in performance at 65 °C from that at 80 °C is that the modified PEM remains relatively high when the methanol concentration is increased to 3M (34.5 mW/cm²) and 7.5M (19.7 mW/cm²). The HFR of MEA3 also remains stable (~30 mΩ) with all concentrations of methanol at 65 °C. Thus, the effectiveness of Gr coating at this intermediate temperature is better. Combining the benefit of Gr coating with the relatively high reaction rates and mass transfer kinetics, the DMFC could obtain promising peak power density and efficiency.

4 Conclusions

In this study, we report the effect of Gr interlayers placed on commercial Nafion membranes in the methanol fuel cell performance. The modified PEMs show promising results in reducing the methanol crossover while not significantly decreasing the proton conductivity of PEM. Based on our experimental results, the following conclusions could be made:

- The modified PEMs with CVD Gr can be successfully employed in fuel cells with high methanol concentrations, at least not at elevated temperatures: 21 and 10 mW/cm² peak power densities were achieved at 30 °C for such PEMs with 7.5M and 14.1M methanol solutions,

respectively. All this is due to the reduced methanol crossover rate, which is by 25% lower in 7.5M methanol when compared to unmodified PEM.

- Operating at higher temperatures is still problematic due to the delamination of Gr from Nafion caused by a greater swelling of the latter at higher temperatures.
- Nevertheless, the same MEA at 65 °C demonstrates peak power density 34.5 mW/cm² and 19.7 mW/cm² with 3M and 7.5M methanol solutions, respectively.
- Among the different modifications studied, the best performance was observed for PEMs with Gr sandwiched between two Nafion 211 membranes because in this geometry Gr integrity is better protected during handling. While Gr itself has excellent mechanical strength of >100 GPa, due to its atomic thickness, it can still be easily damaged if not handled properly.

For future work, one should focus on finding the means to mitigate the negative effect of swelling. For example, it could be achieved by increasing the number of Gr layers. This would result in an undesired lowering of the proton conductance but, as was previously demonstrated, it could be mitigated by specially engineered proton-selective defects [15].

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Conflict of Interest

There are no conflicts of interest.

Data Availability Statement

The authors attest that all data for this study are included in the paper.

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