A High Performance Direct Methanol Fuel Cell Technology Enabled by Mediating High Concentration Methanol through Graphene Aerogel

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Abstract:

We demonstrate a facile methodology to fabricate graphene aerogel (GA), and its application in direct methanol fuel cell (DMFC) for the first time. A new GADMFC design was proposed by using GA to replace two main components within the DMFC - gas diffusion layer (GDL) and flow field plate (FFP). Results indicate a 24.95 mW / cm² maximum power density of air polarisation was obtained at 25 °C. The membrane electrolyte assembly (MEA) has a 63.8% mass reduction compared to ordinary one, which induced 3 times higher mass power density. Benefiting from its excellent organic solvent absorbency, the methanol cross over effect has been dramatically suppressed while using 12 M methanol, therefore, higher concentration or even pure methanol can be refilled into the fuel cell. Due to the excellent fuel storage function of GA, the methanol cartridge and complicated fuel circulation system in DMFC can be eliminated, which can reduce manufacturing cost for DMFC. We expect this research will promote the application of GA in fuel cell applications, as well as shed a light on the novel fuel cell technology to address future energy challenges.
Main Text:

Direct methanol fuel cell (DMFC) have been considered as one of the most predominating power sources in future electronics and automotive engineering, for its high energy density and quick refuelling properties [1]. Constrained by the current technologies on materials and design, the energy performance for conventional DMFCs was significantly underdeveloped due to the mandatory usage of diluted methanol solutions as media, yielding a limit methanol transportation efficiency and the detrimental consequences [2, 3].

Graphene aerogels (GAs), a group of carbon metamaterials, have attracted considerable interests for its potential applications, such as supercapacitors [4], electrodes [5, 6], catalysis [7, 8], sensors [9] and environmental remediation [5, 10, 11]. Their unique properties - high porosity, high surface area, ultralight weight (<10 mg cm$^{-3}$) [12, 13], excellent elasticity (>90% in compression) [14, 15], high electrical conductivity (~10 S cm$^{-1}$) [8, 16, 17] has enabled wide applications as electrodes and current collectors in polymer electrolyte fuel cells (PEFCs) [17, 18, 19, 20]. By far, most of the reported fabrications of GAs are in lab scale, i.e. chemical vapour deposition (CVD) [21], template-mediated assembly [22], 3D printing based rapid manufacturing [14, 23] and self-assembly [12, 24]. A fabrication strategy with potential to be scaled-up to being integrated to current industrial process, would be highly desired. Taking the advantages of high porosity and high surface area, GAs can kinetically improve the electro-chemical performance by offering diffusion based mass transport, high absorption capacities and ultrafast absorption rate for organic solvents and oils, as being explored previously by other researchers. The interesting results reported by Sun et. al. showed that their GA can absorb 344 times of its own weight toluene completely within 5 seconds [13]. Li and co-workers prepared GA with absorption capacity of 229 times ethanol and 465 times chloroform of its own weight, respectively [24].
Traditional DMFCs require multiple components to fulfil the functions, e.g. methanol cartridge as reservoir, gas diffusion layer (GDL) and flow field plate (FFP) for mass and heat transfer, current collection, fuel and oxygen diffusion and kinetic control. Comparing to the remarkable progresses on materials innovations for high energy performance, optimization of DMFC design for high energy output has been less exploited, therefore, challenges remains such as ohmic losses induced by the poor electrical conductivity of GDL and FFP; bulky and heavy weigh of FFP, because it was made from graphite block, carbon/polymer composite or stainless steel etc. Using GA to replace GDL and FFP can also alleviate the conventional fuel cells’ rib and channel architecture issues which cause liquid accumulation. Ahn and co-workers reported a homogenization of the methanol and oxygen transportations which led to a higher power performance of their DMFCs with using foam like porous electrodes \cite{25}. From the perspective of structural optimization, GA, with its intrinsic properties such as light weight, high porous, high absorption capability, etc. holds another key potential towards an efficient DMFC design by providing higher compatibility.

In this work, we demonstrate a facile strategy to fabricate GA, and propose a highly integrated DMFC design by using GA to replace the components in conventional DMFCs. The favoured DMFC design was assembled based on carefully controlling the hierarchical structure of GA and associating the functions to the structures correspondingly, i.e. porosity configurations, surface conditions, etc. With the new GADMFC, we achieved a higher power density under air polarisation at 25 °C, and successfully fuel the device with methanol of 12 M, a highest concentration with minimum methanol crossover ever reported in DMFC.

The GA with co-contineous graphene-melamine hierarchical structure was achieved through a solution based multiple stage process (see experimental section), the fabrication procedure of GA and GA electrode is shown in Figure 1a. This facile fabrication method is highly integrable to the existing manufacturing technology without any re-investments on the
infrastructure. To prepare the electrodes, commercially available Pt/C and PtRu/C were employed as cathode and anode catalysts for the GA electrodes. Nafion solution and ethanol were used to make the catalyst ink. The ink was spray coated onto the GAs (thickness = 1 cm) with a metal loading of 2 mg / cm². SEM images of the side and top view of the electrodes with different magnifications are shown Figure 1b and c.

The electrical conductivity testing result of GA (without catalyst) indicates a competitive conductivity for the samples (Figure S1 and Table S1), compared to other common used electrodes and current collector materials, TGPH-060 carbon paper and graphite block. Since the GAs are highly elastic, with a youngs module of 0.256 MPa, we also assess the conductivity under mechanical compression. Interestingly, the conductivity of GA remains unchange when we apply the compression strain (Figure S2 and Table S2), which could lead to a stable performance by uniformly transferring the generated electrons. The porous 3D network, as being observed under SEM (Figure 1b), offers an ultra low bulk density for GA of ~ 0.03 g / cm³, which is only ~ 6.6% of that of carbon paper (0.44 g / cm³, Toray TGPH-060) and ~ 0.16% of that of graphite block (~1.82 g / cm³). This large difference on density can bring a significant mass reduction (up to 63.8%, Table S3) compared to ordinary DMFC, therefore, yield an possible 3 times increase in mass power density and 9.2 times increase if the methanol fuel is not included.

The surface physical property is critical when it comes to use GAs as electrodes for DMFCs, because DMFCs requires GA to absorb certain amount of water to provide –OH that is essential for methanol oxidation reaction on the catalysts’ surface. Researchers have discovered pure graphene based GAs with high hydrophobicity and oleophilicity [25], which can be used to absorb organic compounds in the aqueous/oil mixtures [11, 13, 19, 20, 23]. Our GA is found hydrophobic to pure DI water, with an apparent contact angle of 116.1°. When we used the methanol/aqueous solution with varied methanol concentrations (1, 3, 6, 9 and 12 M),
the surface become more friendly to the mixture droplet with a decreased contact angle value (Figure 2). The droplet with 12 M methanol was absorbed instantly into the GA with a absorbing rate of 0.158 L per second, the rest methanol solution adsorption results are shown in Table S4 with the top view observations of GA surface after absorbing the methanol/aqueous solutions (Figure S3). We also demonstrated a robust fuel storage function for our GAs by achieving a 25 absorption (immerse in 12 M methanol for 15 minutes) and desorption (squeeze and dry in open air oven for 2 hours) cycles for 12 M methanol, where reference considered 20 cycles as robust enough for practical usage [20].

The half-cell cyclic voltagrammes (CVs) results, measured in N₂ saturated 0.5 M H₂SO₄ aqueous electrolyte at 25 °C, for Pt/C and PtRu/C spray coated GA electrodes (Figure 3a and b) reveal clear Pt and PtRu alloy catalysis properties at hydrogen under potential region, double layer region, oxidation and reduction region, without any differences from traditional electrodes – glassy carbon electrode and carbon paper electrode.

We next characterise the anode polarisation, anode performance, cathode air polarisation and methanol crossover in a customerised miniature DMFC (Figure S4). Round button shape aerogel cathode and anode with diameter of 4 cm were sandwiched between Nafion 117® membrane as the MEA. A reference testing fabricated with Toray TGPH-60 carbon paper electrodes MEA in graphite block FFP is used to compare the performance of GADMFC design. The fuel was 11 mL of 12 M methanol, detailed procedure can be found in experimental section. The anode polarisation curves of GADMFC in Figure 4a suggests that a long oxidation was completed after 47 scans. However, in Figure 4b, the results shows DMFC made from Toray TGPH-60 carbon paper in a traditional graphite fuel cell body last only 5 scans, which means the methanol exhausted much sooner in traditional DMFC. This reflects that the GADMFC holds much better storage function, offering a long lasting reaction cycle with one single charging of methanol into the cell unit. This offers an opportunity of
elimination of the methanol cartridge in traditional DMFCs. Unlike the carbon paper electrode, clear methanol oxidation peaks are found with no hysteresis between the onward and backward scans, probably due to that the surface of PtRu catalyst did not form oxide layer, and the existence of plenty of methanol surrounds the nanoparticles. GA can offer a completed methanol oxidation and there is a fast diffusion of generated CO$_2$ due to the high porous structure of GA. After analysing the data using Autolab gpes software, it is found that 416,743 Colum generated through the whole testing which is 71.8% of the calculated value when using 11 mL of 12 M methanol as a fuel. The output from GADMFC is over eight folds of that from traditional MEA with using carbon paper, where only 50,507 Colum was generated. The anode performance was further evaluated by using the same experimental set-up of anode polarisation and aimed to monitor the kinetic activity of the anode. In Figure 4c, the results show a reasonable low overpotential for our GA electrodes with a typical output in the range of 0.025 V to 0.6 V vs. RHE using a step potential of 0.025 V and holding the potential for 10 s per reading, when using 11 mL of 12 M methanol as a fuel.

We also assessed the cathode performance using air polarisation. The experiment was performed at room temperature (≈ 25 °C), interestingly, we noted a gradual temperature increase of 8 °C for the cathode at the 41th scan, then slowly returned to 26 °C when testing was finished. This can be attributed to the good thermal conductivity of GA (Figure S5), which can essentially improve the sustainability of electrode under the reaction cycle. The polarisation curve shows a 24.95 mW/cm$^2$ maximum power density was obtained (Figure 4d), which is slightly higher than the MEA made from Toray carbon paper (23.01 mW/cm$^2$). However, the mass power density of GADMFC reached 5.02 W/kg, which is 3 times higher than ordinary DMFC and 9.2 times higher if the methanol fuel is not included. (mass of fuel cell chamers and fuel circulation system etc. are not included, see detailed mass calculation in Table S3).
The durability and fuel storage function of the GADMFC were measured under air polarisation and maximum power output vs. cycle number relation was plotted in Figure 4e. The results suggest a stable power density for GADMFC till the 31st scan, then followed by a gradual decrease, which agrees well with the anode polarisation curves for the fuel storage function (Figure 4a). There are two reasons for this high power density in our GADMFC, i.e. the improved fuel and air distribution within the porous GA electrode provide better efficiency for mass transfer; removal of the rib channel structure result in a higher ‘contact area’ between catalysts and electrodes, and homogenous pressure distribution, therefore, no liquid fuel accumulates within anode and no product water blocks the cathode and resulting in power being generated uniformly.

When a potential is applied to the cathode, the methanol crossing over to the cathode is oxidised into protons, electrons and CO₂. The protons diffuse back through the membrane where they are reduced to H₂ creating a reference electrode and the electrons create a current from anode to cathode. From our methanol crossover measurement (Figure 4f), we also found that a dramatically suppressed methanol cross over effect at high methanol concentration (12 M) for our GADMFC, which agrees with both anode and cathode polarisation curves. This suppressing of methanol crossover is very unique, compare to the carbon paper based MEA [2, 26]. Our hypothesis is that the aerogel created a buffering effect as it retains the residual methanol for those haven’t engaged in the reaction yet. Once those methanol absorbed on the catalyst oxided to CO₂, the retained methanol will be released to fuel the reaction so to keep it going in a sustainable manner. This would renew the current DMFC kinetic control knowledge by utilising the structural materials to bring the in-situ kinetic control, thus, it would be likely to use methanol/aqueous mixture with higher methanol concentration (even pure methanol) to achieve higher performance in GADMFC.
In conclusion, GA was prepared through a solution processing based conventional template method. We fabricated GA with a low bulk density of $\sim 0.03 \text{ g/cm}^3$ and demonstrate a robust fuel storage function by achieving a 25 absorption and desorption cycles for methanol aqueous solution with 12 M methanol. Our GADMFC design was proposed based on using GA to replace GDL and FFP in traditional DMFCs. Results indicate that an improved maximum power density of 24.95 mW/cm$^2$ was achieved and the mass power density of GADMFC reached 5.02 W/kg, which is 3 times higher than ordinary DMFC. Benefiting from the intrinsic feature of GA, methanol cross over effect was dramatically suppressed while using 12 M methanol as the fuel. These gave the possibility of using high concentration or even pure methanol to fuel the cell. The GADMFC design with removing the rib channel structure FFPs will also reduce manufacturing cost for DMFC, hence, will lead to higher economic & societal impacts.
Experimental Section

Aerogel Preparation

Commercial melamine foams were immersed into the GO aqueous solutions (4 mg ml\(^{-1}\), Gaoxi Tech.) at room temperature. Then, the GO-melamine foam was taken out, rinsed and degassed at 80 °C until the water totally evaporated. After that, the GO-melamine foam was chemically reduced under the hydrazine vapor environment at 90 °C for 12 hours to get the rGO-melamine GA.

Morphology and Contact Angle Testings

To characterise the surface morphology, scanning electron microscopy (SEM) was performed using a FEG Tescan MIRA3. The surface contact angle measurement was performed using a Krüss DSA30, we measured the methanol aqueous solution droplets with different methanol concentrations on the GA surfaces.

GA Electrodes Preparation and Electrochemical Chaterisations

Commercially available Pt/XC72R (HiSPEC4000 40%w. Pt) and PtRu/XC72R (HiSPEC10000 40%w. Pt and 20%w. Ru) were used as cathode and anode catalysts for the GA electrodes. The catalysts were uniformly sprayed onto the GAs (thickness = 1 cm) with a metallic loading of 2 mg / cm\(^2\). Small samples in square shape (~ 1 cm × 1 cm) were prepared for half-cell testing, each sample was mounted on a gold wire then immersed in the electrolyte, Pt wire and Ag/AgCl were used as counter and reference electrodes. For miniature fuel cell testing, samples in circular shape (diameter = 4 cm) were cut from each electrodes, then sandwiched between Nafion 117\(^{®}\) membrane. The acrylic based cell unit was used for this experiment as shown in Figure S4. Gold wire was attached to the electrodes and connected with the Autolab PGSTAT302N potentiostat / galvanostat. Anode polarisation measurement uses 11 mL of 12 M methanol injected into the anode, the cathode is flushed.
with pure hydrogen acting as reference electrode and the fuel cell is operated at driven cell mode. At 25 °C, anode polarisation curves were recorded constantly at 2 mV s⁻¹. Anode performance analysis was carried out using the same experimental set-up with potential range from 0.025 V to 0.6 V vs. RHE using a step potential of 0.025 V and holding the potential for 10 s per reading. For cathode air polarisation, instead of hydrogen, air was flushed through the cathode at flow rate of 100 cm³/min. The scan rate was 2 mV s⁻¹, the starting operation temperature was 25 °C, an infra-red temperature metre was used to monitor the temperature.

For methanol crossover effect analysis, 12 M methanol applied to the anode and N₂ is purged through the cathode. No potential is applied to the anode so no methanol is consumed there. Potential from 0.2 – 1.1 V vs. RHE with a step of 0.05 V (held for 10 s for each step) was applied to the cathode.
Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Reference


Figure 1 (a) Preparation process of GA and GADMFC electrode; SEM image of GA electrode’s (a) catalyst layer with thickness of 2.2 mm, and (b) catalyst supported graphene layer
Figure 2 Contact angles of droplets of (a) DI water, and methanol solution with concentrations of (b) 1 M, (c) 3 M, (d) 6 M, (e) 9 M and (f) 12 M
Figure 3 Cyclic voltammetry of (a) Pt/C and (b) PtRu/C catalysts supported on GA electrodes, the scan rate is 50 mV / s
Figure 4 Anode polarisation curves of (a) GADMFC and (b) traditional carbon paper DMFC, (c) anode performance curve for GADMFC, the cells were operated at driven cell mode; (d) cathode air polarisation curves of GADMFC; (e) graph of maximum power output for each cycle, and (f) methanol crossover measurement for GADMFC
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**Graphene aerogel** is used to replace gas diffusion layer and flow field plate (current collector) of direct methanol fuel cell (DMFC). Compare to traditional carbon paper DMFCs, the mass power density was 3 times improved with dramatically suppressed methanol cross over effect while using 12 M methanol as the fuel. It also shows fuel storage function, therefore methanol cartridge and fuel circulation system can be eliminated.

**Keyword**
Graphene aerogel, direct methanol fuel cell, fuel storage, mass power density, high methanol concentration

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Methanol

300% Higher Mass Power Density

Fuel Storage Function