

Engineered Graphene Materials: Synthesis and Applications for Polymer Electrolyte Membrane Fuel Cells

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Engineered graphene materials (EGMs) with unique structures and properties have been incorporated into various components of polymer electrolyte membrane fuel cells (PEMFCs) such as electrode, membrane, and bipolar plates to achieve enhanced performances in terms of electrical conductivity, mechanical durability, corrosion resistance, and electrochemical surface area. This research news article provides an overview of the recent development in EGMs and EGM-based PEMFCs with a focus on the effects of EGMs on PEMFC performance when they are incorporated into different components of PEMFCs. The challenges of EGMs for practical PEMFC applications in terms of production scale, stability, conductivity, and coupling capability with other materials are also discussed and the corresponding measures and future research trends to overcome such challenges are proposed.

1. Introduction

As a type of electrochemical energy storage and conversion technology, fuel cells, in particular polymer electrolyte membrane fuel cells (PEMFCs, **Figure 1a**), can convert chemical energy into electrical energy through a reaction between an anodic oxidation of sustainable H₂ or low-carbon fuels and a cathodic oxygen reduction. As recognized, several advantages such as high energy/power densities and low/zero emissions^[1–3] can be seen when PEMFCs served as the power source in automobiles, portable electronics, and stationary/backup power stations.

As shown in **Figure 1a**, a PEMFC consists of an electrolyte membrane with a gas-diffusion anode and cathode, both of which have their individual catalyst layers (the most practical catalysts being platinum (Pt)-based materials) and

bipolar plates. It has been identified; however, that component degradation during PEMFC operation can cause lowered durability of the device, mainly by the instability of electrode/membrane materials.^[4,5] In this regard, high-cost and insufficient durability are both major challenges for PEMFC technology. To overcome these challenges, many advanced materials, such as carbon-based nano-materials (bucky nano-balls, nanotubes, nanofibers, graphite particles and graphene nano-sheets, etc.) have been explored as new catalyst/composite membrane/bipolar materials for PEMFCs.^[6–9] Among these carbon materials, graphene has become the most distinguished new material for PEMFC applications.

However, if graphene sheets are not specifically engineered, they are insoluble and infusible, hindering their practical applications. Therefore, engineering processes by surface or inter-layering functionalization to obtain solutions with processable graphene particles of desired surface and bulk properties are vital. In regards to this, the most effective engineering process appears to be the tailoring of graphene properties by covalent or noncovalent functionalization. Following this, the functionalized graphene materials, serving as the catalyst/membrane/bipolar plate material, can be integrated into PEMFCs to achieve improved performance as reported in many articles.^[5,7,10–13] In this research news article, we will focus on recent advancements in improving PEMFC performance through the use of engineered graphene materials (EGMs) in catalyst layers, polymer electrolyte membranes, and bipolar plates.

2. Engineered Graphene Materials (EGMs)

In general, well-defined graphene sheets possess fascinating properties such as outstanding specific surface area ($\approx 2600 \text{ m}^2 \text{ g}^{-1}$), high thermal conductivity (5000 W mK^{-1}), high electron mobility ($2.5 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), and strong chemical stability.^[14,15] However, graphene sheets without engineering/functionalization are insoluble and infusible, rendering them unsuitable for practical applications. A variety of methods employing several engineering strategies have already been developed for the synthesis of EGMs. Current methods for graphene engineering can be categorized into oxygen-doped

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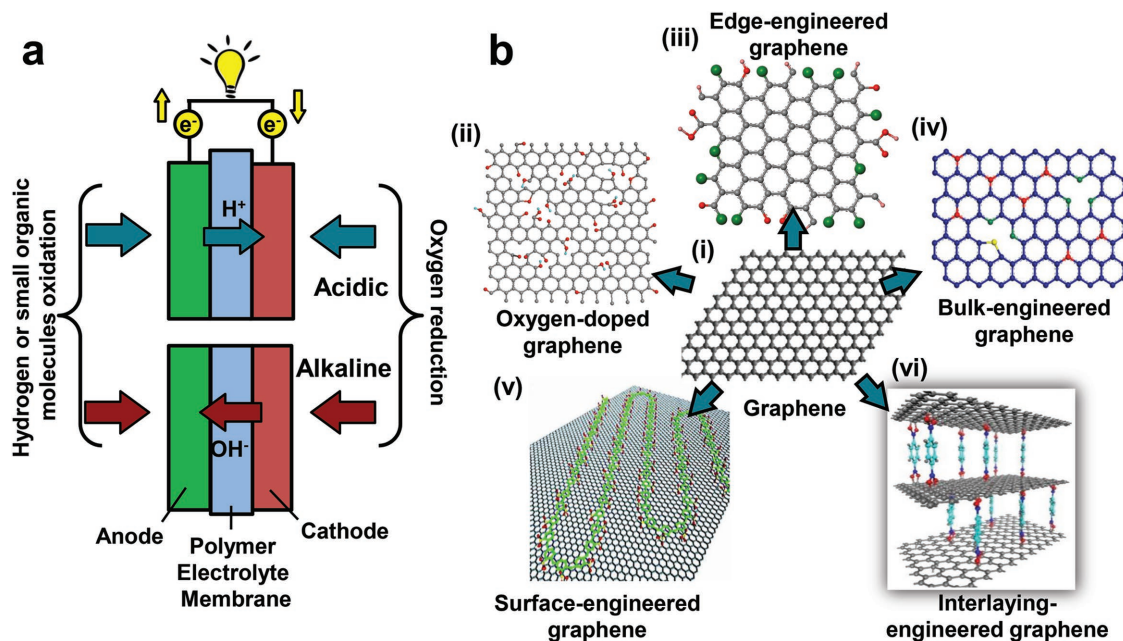


Figure 1. a) Schematic illustration of PEMFCs (the upper portion is the acidic PEMFC, and the lower is the alkaline PEMFC). b) Schematic representation of (i) graphene, (ii) oxide-doped graphene,^[16] (iii) edge-engineered graphene,^[17] (iv) bulk-engineered graphene,^[20] (v) surface-engineered graphene,^[26] and (vi) interlayering-engineered graphene.^[27] (ii) Reproduced with permission.^[16] Copyright 2010, Nature publishing group. (iii) Reproduced with permission.^[17] Copyright 2012, National Academy of Sciences. (iv) Reproduced with permission.^[20] Copyright 2009, American Chemical Society. (v) Reproduced with permission.^[26] Copyright 2010, Royal Society Chemistry. (vi) Reproduced with permission.^[27]

graphene, edge engineered, bulk-engineered, surface engineered, and interlayering-engineered (Figure 1b):

2.1. Oxygen-Doped Graphene

Pristine graphene sheets (Figure 1b (i)) are very difficult to blend with other functional composites. To overcome this difficulty, a solution of processable oxygen-doped graphene (GO) (Figure 1b (ii)) has been used as a starting material for engineered graphene. The GO, prepared by a liquid phase exfoliation, usually contains some structural defects and residual oxygen-containing functional groups. With further reduction of the oxygen-containing groups, the graphene structure can be partially restored (rGO) with a thin structural framework similar to graphene, but bearing oxygen-containing functional groups.^[16]

2.2. Edge-Engineered Graphene

Edge-engineered graphene (Figure 1b (iii)) has active edge sites with dangling bonds serving as covalent attachment of various chemical moieties to enhance solubility, film-forming capability, and/or reactivity for further chemical functionalization. They can be fabricated using ball-milling methods.^[17] More engineering strategies, such as creating pores^[18] on graphene and making graphene quantum dots,^[19] are also applied to increase active edges of the graphene and produce large-area graphene films.

2.3. Bulk-Engineered Graphene

Heteroatom (N, B, P or S)-doping into the graphene bulk basal plane to change both the electronic characteristic of π - π conjugation and to create specific defect structures has been used to engineer graphene materials (Figure 1b (iv)).^[20–24] For example, N-doped graphene was tested to have an n-type behavior, indicating that N-doping can effectively change the electrical properties of graphene.^[20]

2.4. Surface-Engineered Graphene

Functionalization of graphene, noncovalent surface engineering through van der Waals forces, or π - π interactions of aromatic molecules have also shown some success.^[25,26] This engineering method can produce special properties such as water solubility, which has been widely explored for the synthesis of graphene-based composite materials (Figure 1b (v)).

2.5. Interlayering-Engineered Graphene

To prevent the aggregation of graphene sheets, engineering graphene by introducing interlayering spacers between 2D graphene nanosheets to produce a 3D nanostructure has been demonstrated to be an effective approach (Figure 1b (vi)).^[27–29] In this method, the unique engineered graphene 3D nanoarchitecture cannot only exhibit a larger surface area but also greater

hydrophilicity and faster mass transfer properties when compared to pristine graphene.

3. Engineered Graphene Materials for PEMFC Catalyst Layers

To speed up both the rates of cathode oxygen reduction reaction (ORR) and the rates of anode hydrogen oxidation reaction (HOR) or small organic molecules oxidation reaction (SOMOR) in PEMFCs, the most commonly used and practical electrocatalysts for both cathode ORR and anode HOR or SOMOR of PEMFCs currently are Pt-based catalysts (carbon black-sup-

ported Pt or Pt alloys). To reduce the cost of these Pt-based catalysts as well as improve Pt utilization efficiency and stability of carbon supports, EGMs have been explored as a carbon support material or even as a non-Pt catalyst material.^[30,31]

3.1. Engineered Graphene Materials for Anode Catalyst Layers

To improve the catalytic activity of Pt-based catalysts for PEMFC anode reactions such as the methanol oxidation reaction (MOR) in direct methanol fuel cells (DMFCs), chemically reduced graphene oxide-supported Pt hybrid catalysts (Pt/GNS) were prepared, and exhibited significantly higher current densities for MOR when compared to Pt/C, as shown in Figure 2a left.^[32]

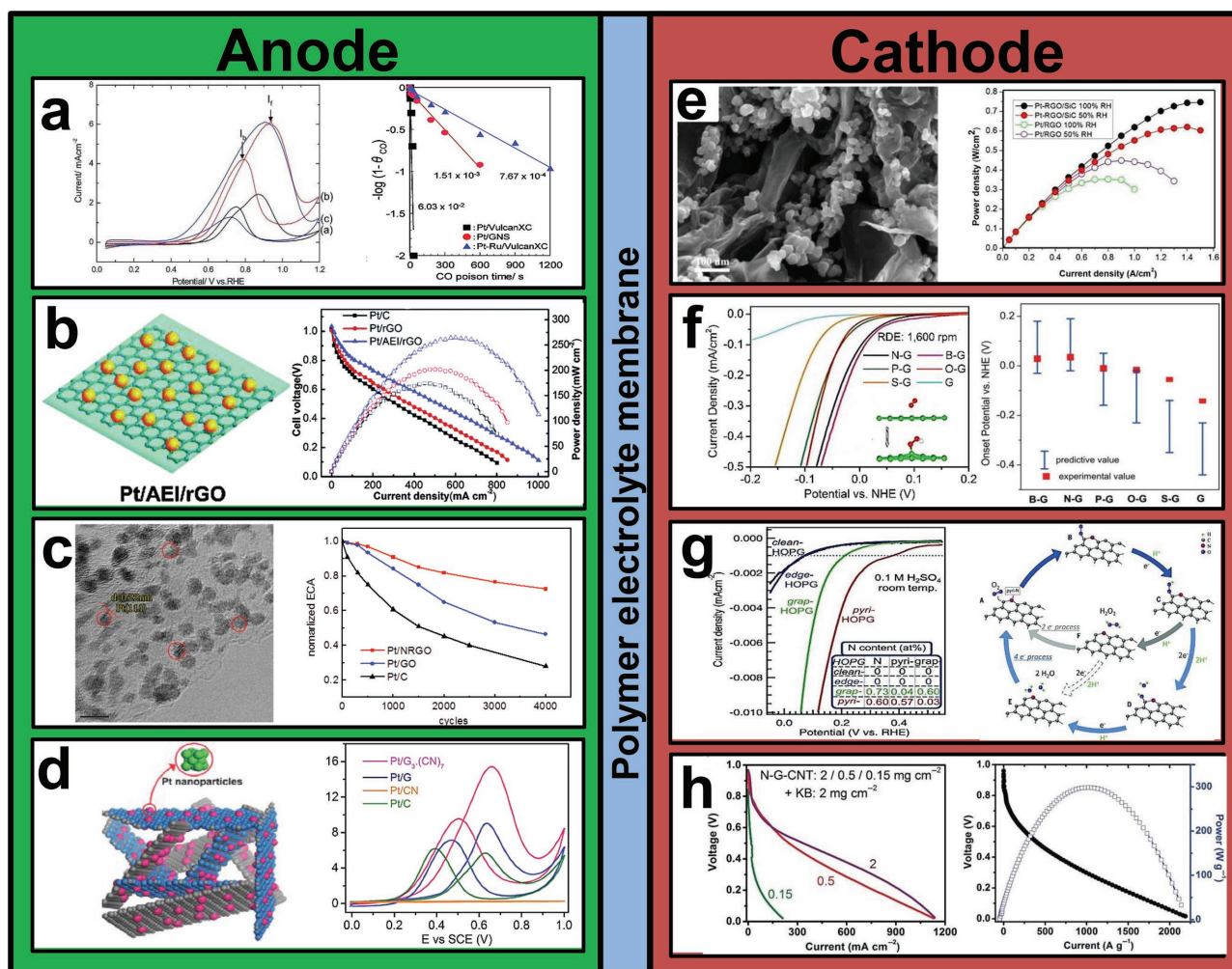


Figure 2. a) Methanol oxidation reaction catalyzed by Pt/Carbon Black, Pt/rGO, and Pt-10 wt% Ru/Carbon Black, respectively (left), and rates of CO adsorption at various catalysts (right). Reproduced with permission.^[32] Copyright 2009, American Chemical Society. b) Schematic of Pt/AEI/rGO catalyst (left), power densities and polarization curves for a H₂/O₂ fuel cell with a total of 20 wt% ionomer (right). Reproduced with permission.^[37] Copyright 2015, Elsevier. c) TEM image of Pt/N-doped graphene (left), changes in ECA of different catalysts as a function of the number of potential cycles (right). Reproduced with permission.^[39] Copyright 2013, Elsevier. d) Schematic of Pt/G₃-(CN)₇ catalyst (left), methanol oxidation reaction catalyzed by Pt/G₃-(CN)₇, Pt/G, Pt/CN and Pt/C catalysts, respectively (right). Reproduced with permission.^[41] e) SEM images of the Pt-RGO/SiC catalyst (left), single fuel cell power densities for Pt-RGO/SiC and Pt/RGO electrodes (right). Reproduced with permission.^[44] Copyright 2015, Nature Publishing Group. f) ORR performance catalyzed by different catalysts (left), experimentally (red squares) and theoretically predicted (blue bars) on-set potentials catalyzed by doped graphene materials (right). Reproduced with permission.^[51] Copyright 2014, American Chemical Society. g) ORR results for model catalysts (left), schematic illustration for oxygen reduction reaction on nitrogen-doped carbon materials (right). Reproduced with permission.^[52] Copyright 2016, Science Publishing Group. h) Polarization curves of N-G-CNT with different carbon loadings at cathode (left), cell performance using N-G-CNT/KB (0.5/2 mg cm⁻²) as cathode catalyst (right). Reproduced with permission.^[13] Copyright 2015, Science Publishing Group.

The improved performance can be attributed to reduced carbonaceous intermediates production on the catalyst surface.^[33] Moreover, the adsorption rate of CO on Pt/GNS was 40 times slower than that on Pt/C, as shown in Figure 2a (right). To increase Pt utilization and thus reduce Pt loading, EMGs with both high specific surface areas and sufficient conductivities have been explored as the support material for Pt catalysts.^[34] However, the inert basal plane surface of graphene has weak interactions with metal species. To increase this interaction, polymers were used to form noncovalent bonds with the graphene sheet surface.^[35–37] Zeng et al.^[37] synthesized an anion exchange AEI ionomer to engineer graphene-supported Pt catalyst for PEMFCs (Figure 2b, left). Their fuel cell performance with the Pt/AEI/rGO catalyst achieved higher performance (Figure 2b, right).

Heteroatom (N, B or S)-doped graphene materials have also been used as catalyst supports for PEMFCs.^[20–22,38] The doped atoms also serve as nucleation sites for graphene-metal binding, which is very beneficial for the deposition of uniform-sized metal nanoparticles (Figure 2c, left). With this catalyst, both the high activity and stability of the PEMFC anode catalysts can be enhanced (Figure 2c, right).^[39] Huang et al. reported an N-S-doped graphene (NS-G) as a high-quality support for Pt nanoparticles. When the prepared Pt/NS-G hybrid was applied into DMFCs as an anode electrocatalyst, it displayed a very impressive improvement in electrocatalytic activity, durability, and poison tolerance.^[40]

To prevent the irreversible restacking effect of graphene sheets, pillars can be introduced into the spaces between sheets to achieve a 3D architecture of interlayer-engineered graphene.^[41] This Pt-decorated 3D architecture (Pt/G-CN) can improve catalytic performance for MOR (Figure 2d). The significantly increased performance of Pt/G-CN can be attributed to the 3D architecture of G-CN, which not only provides a fast transportation channel for reactants and resultants but also increases the electrical conductivity of catalysts.

3.2. Engineered Graphene Materials for Cathode Catalyst Layers

3.2.1. Engineered Graphene as Pt Supports for PEMFC Cathode Catalysts

Similar to the anode catalysts discussed above, EGMs have also been intensively explored as Pt or Pt-alloy catalyst supports for cathode ORR catalysts. Guo et al.^[42] reported that when uniformed FePt nanoparticles (around 7 nm) were supported on reduced graphene oxides, significantly increased stability was observed by a potential scan test for 10 000 cycles in 0.1 M HClO₄. Jitendra et al.^[43] deposited ≈1.4 nm Pt clusters on genomic double-stranded DNA–graphene oxide composites (gDNA–GO) to form an ORR catalyst (Pt/gDNA–GO), which showed both higher ORR activity and stability after 10 000 cycles of accelerated degradation tests. The high ORR performance and stability can be attributed to the strong interaction between nanosized Pt clusters and DNA–graphene oxide composite supports though a modulation of electronic structures. In our previous work,^[44,45] tailored graphene nanosheets

(GNS) were used to form a 3D platinized graphene/nano-ceramic sandwiched architecture for PEMFC cathode catalysts to achieve enhanced high power density (Figure 2e).

3.2.2. Engineered Graphene Materials as Pt-Free PEMFC Electrocatalysts

EGMs have also been explored in an effort to replace expensive Pt catalysts. There are functional agents that can be covalently attached onto the edge of graphene to form non-noble and non-metal catalyst materials for ORR. For this purpose, a dry ball-milling method was used to modify graphite samples.^[46] In the study, edge-selectively functionalized graphene nanoplatelets (EFGnPs) with different functional groups were successfully synthesized. A semimetal, antimony (Sb), was also doped onto the edge of the graphene with the resultant material, exhibiting a profoundly electrocatalytic ORR activity along with a high tolerance against CO poisoning and methanol crossover.^[47] Li et al.^[48] developed Pt-free ORR electrocatalysts based on N-doped CNTs and graphene complexes (NT–G). These showed a comparable ORR activity to that of commercial Pt/C in 0.1 M KOH. Palaniselvam et al.^[49] generated nanopores in N-doped graphene, which gave distinct ORR activity in an alkaline electrolyte. Yang et al.^[50] synthesized a S-doped graphene by direct annealing of graphene oxide and benzyl disulfide in argon with the resultant material showing both high ORR catalytic activity and durability in alkaline media. Jiao et al.^[51] had drawn a roadmap for heteroatoms engineered graphene-based metal-free ORR catalysts to make an effort to understand the catalytic ORR mechanism (Figure 2f, left). Figure 2f (right) shows the experimental observations, which are in agreement with theoretical DFT calculation predictions. Guo et al.^[52] demonstrated that the ORR active sites of N-doped carbon materials can be induced by pyridinic N (Figure 2g). Most recently, a high-performance and durable acidic PEMFC was reported by Shui et al.^[13] (Figure 2h), using nitrogen-doped carbon nanotubes and graphene composites as cathode catalyst layers. This work represents a good example for application in acid PEMFCs. Yang et al. also found that the graphene/carbon nanotube hybrid structure with N and P co-doping presented high ORR activity and stability in both alkaline and acid solution.^[53] In addition, the ORR performance of heteroatom engineered graphene can be further enhanced by hybridizing it with other non-noble materials such as Co₃O₄ or Fe₃O₄.^[54,55] By using Fe/Co-N-doped nanoporous graphene as the cathode electrocatalysts, Palaniselvam et al.^[56] assembled a single cell of alkaline PEMFC, which shows a comparable power density (≈35 mW cm⁻²) to the Pt-based system (60 mW cm⁻²).

4. Engineered Graphene Materials for PEMFC Membranes and Bipolar Plates

4.1. Engineered Graphene Materials for Membranes

Currently, the most commonly used solid polymer electrolyte for acidic PEMFCs is the Nafion membrane,^[57] which appears to be inadequate in terms of production costs, ion conductivity,

mechanical stability, as well as methanol permeability.^[4,58,59] To improve the performance, EGMs with unique structures can be introduced into Nafion to form a composite membrane. Choi et al.^[60] reported a Nafion/GO nanocomposite (Nafion/GO) for a PEMFC membrane that demonstrated 40% less methanol crossover than the Nafion membrane while maintaining a similar ionic conductivity, resulting in a marked enhancement in

PEMFC performance. In **Figure 3a**,^[61] the enhanced proton conductivity and reduced methanol permeability can be observed by forming a hybrid membrane material (SGON). Zhang et al. fabricated phosphonic acid-functionalized GO (PGO)-doped Nafion nanohybrid membranes. The nanohybrid membrane with 2wt% PGO (Nafion/PGO-2.0) manifests 1.2 and 6.6 times higher proton conductivity than that of the pristine

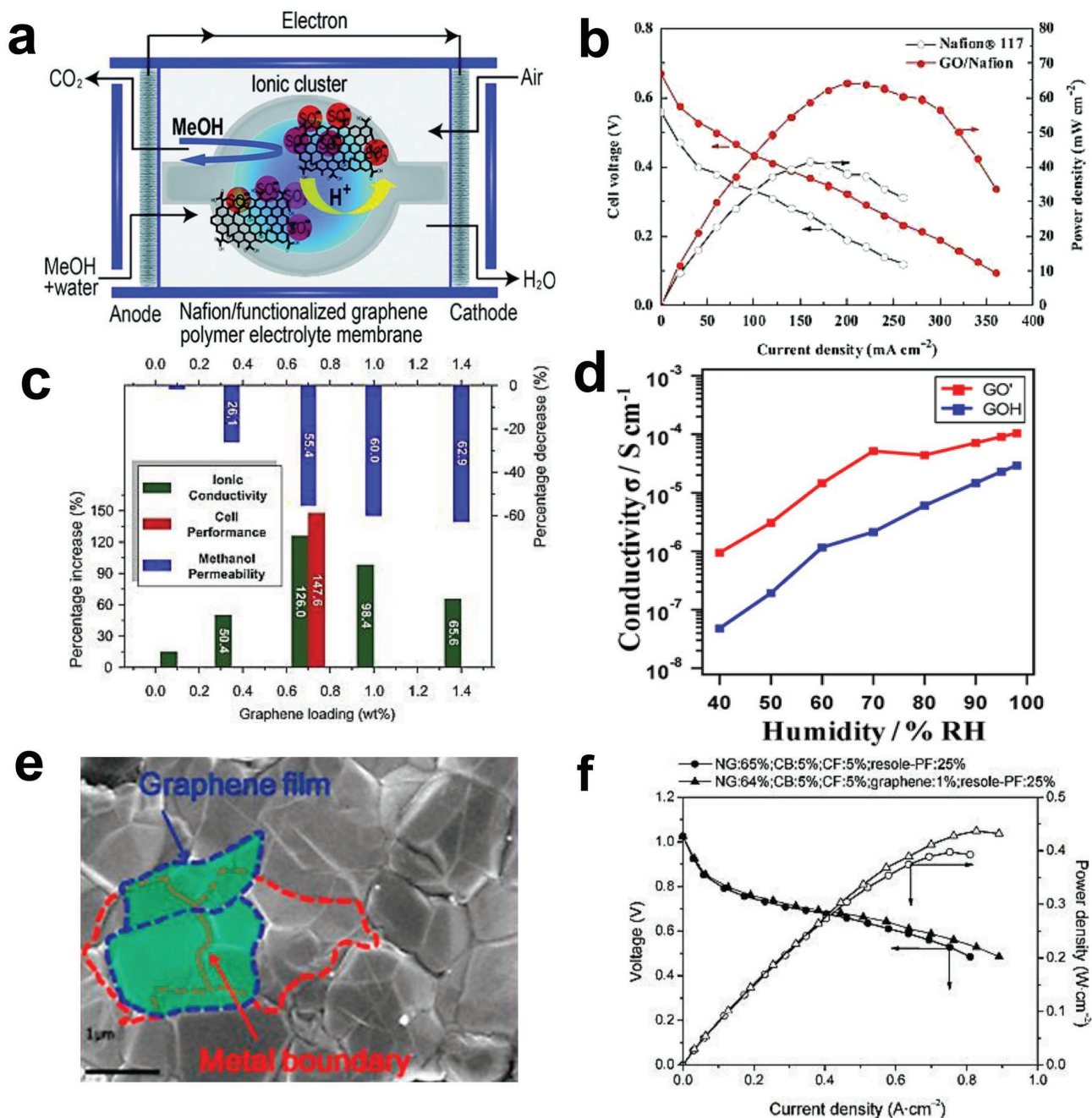


Figure 3. a) Schematic illustration of tunable transport properties of Nafion/functionalized graphene polymer electrolyte membranes. Reproduced with permission.^[61] Copyright 2011, American Chemical Society. b) Polarization curves and power density of a single cell using graphene-based membrane and Nafion 117 membrane. Reproduced with permission.^[64] Copyright 2015, Elsevier. c) Percentage changes of PVA/graphene composite membranes versus various weight ratios of graphene. Reproduced with permission.^[66] Copyright 2013, Elsevier. d) Proton conductivities of graphene-based materials in respect to humidity.^[67] e) SEM image of graphene-coated stainless steel bipolar plate surface. Reproduced with permission.^[68] Copyright 2015, Elsevier. (f) PEMFC performance using composite bipolar plates with and without graphene. Reproduced with permission.^[71] Copyright 2013, Elsevier.

Nafion membrane at 100 °C with 100% relative humidity, and 80 °C with 40% relative humidity, respectively. Meanwhile, the Nafion/PGO-2.0 membrane-based PEMFC displays a higher fuel cell performance compared to that of pristine Nafion membrane.^[62] A more in-depth study was conducted by Paneri et al.^[63] to understand the parameters affecting the transport characteristics of graphene-based membranes. Recently, an orderly sandwich-shaped GO/Nafion composite membrane-based PEMFC displayed a high methanol tolerance at 60 °C (Figure 3b).^[64]

Regarding alkaline PEMFCs, EGMs were also used to form hydroxide conductive composite membranes.^[65] GO (QAFGO) composited by a DMAOP precursor was incorporated into a polybenzimidazole PBI membrane (pPBI) to form a QAFGO/pPBI membrane for an alkaline PEMFC. This exhibited a 2-fold higher power density than the baseline. Ye et al.^[66] reported a polyvinyl alcohol/graphene composite (PVA/graphene) membrane for a direct methanol alkaline fuel cell that presented improved ionic transport with low methanol crossover (Figure 3c). Karim et al.^[67] tested the proton conductivity of GO on a comb electrode and found that GO could exhibit superionic conductivity for protons (Figure 3d).

4.2. Engineered Graphene Materials for Bipolar Plates

The bipolar plate with flow field structures allowing good gas distribution and water removal capabilities is one of the key components in PEMFCs. EGMs with unique structures/properties have been explored as bipolar plate components in an attempt to increase the stability and to reduce the weight and cost of commonly used metallic and graphite bipolar plates. Pu et al.^[68] grew a thin and multilayered graphene film with full surface coverage on a stainless steel plate surface. The resulting coated plate showed a significant enhancement in corrosion resistance (Figure 3e). The graphene coated stainless steel plate also maintained both good conductivity and increased hydrophobicity. Lv et al.^[69] prepared rGO in amorphous nickel–phosphorus as bipolar plate coating and investigated their effects on corrosion resistance in a PEMFC environment, while the rGO modified coating achieved a higher corrosion resistance. Jiang et al.^[70] reported a new graphene–polymer composite prepared by using exfoliated graphene nanoplatelets (GNPs) and polymer matrix polyphenylene sulphide (PPS) (PPS/GNP) through a solid-state ball-milling/compression-molding technique. The resulting nanocomposite plates showed both excellent mechanical stability and gas permeability resistance when used as a plate material. A new carbon–polymer composite bipolar plate composited with graphene was synthesized using a compression-molding technique,^[71] which showed both super electrical conductivity and excellent corrosion resistance in the PEMFC (Figure 3f).

5. Conclusions

Engineered graphene materials (EGMs) with unique structures/properties can be introduced into major components of

PEMFCs, such as electrodes, membranes and bipolar plates. The incorporation of EGMs with desirable properties into these components can significantly improve their performance. A variety of strategies such as edge-function, heteroatom-doping, surface modification, and interlayering, etc. have been developed to achieve different types of EGMs. Although these engineering processes have demonstrated their feasibility in preparing effective PEMFC components (catalysts, membranes, and bipolar plates), there are still technical and commercial challenges to overcome before they are feasible for practical applications. Several challenges can be identified as follows. (1) Insufficient capability for large-scale production: Most of the engineered processes discussed throughout this review are limited to small lab-scaled productions. Mass production of EGMs remains a challenge. (2) Insufficient fundamental understanding: Although EGMs provide cheap alternatives for Pt catalysts and can produce comparable performances in PEMFCs, both the role and mechanism of EGM catalysts are still unclear. (3) Insufficient activity and stability: The catalytic activity and stability of EGM-based ORR catalysts are still insufficient for practical applications. (4) Low membrane conductivity: Although EGMs-based membranes show distinct properties for reducing fuel permeation and facilitating high temperature operation, ultra-thin membranes and increased ion (H^+ or OH^-) conductivity are difficult to achieve. Lastly, (5) Low coupling capability with other materials to form bipolar plates: Challenges still exist in coupling EGMs with metallic materials for bipolar plates and achieving special interfaces with different properties.

To overcome the challenges discussed above, continued efforts are required for EGMs to become practically viable. Research directions may be suggested as follows: (1) developing more efficient engineering technologies for the large-scale production of EGMs; (2) further combining theoretical calculations and experimental results to investigate the role/mechanism of EGM-based PEMFCs catalysts; (3) focusing further efforts on carefully tuning the electronic configuration and nanostructure of graphene in order to achieve better performance of EGM-based non-Pt catalysts in acid electrolytes; (4) addressing the size effect and ion transform problem regarding EGMs-based electrolyte membranes by turning the engineered graphene sheets to quantum dots, the graphene quantum dots with more activity edges are a favorite for coupling with ion polymer to form supermolecules in the membrane; and (5) pursuing a promising route to integrate graphene on metallic bipolar plate surfaces to obtain hydrophobic or hydrophilic surfaces for different types of PEMFC applications through epitaxial growth.

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- [1] N. G. Sahoo, Y. Z. Pan, L. Li, S. H. Chan, *Adv. Mater.* **2012**, *24*, 4203.
- [2] Y. Jiao, Y. Zheng, M. Jaroniec, S. Z. Qiao, *J. Am. Chem. Soc.* **2014**, *136*, 4394.
- [3] D. Higgins, P. Zamani, A. Yu, Z. W. Chen, *Energy Environ. Sci.* **2016**, *9*, 357.
- [4] U.S. Drive, Fuel Cell Technical Team Roadmap, http://energy.gov/sites/prod/files/2014/02/f8/fctt_roadmap_june2013.pdf (Accessed: February, **2016**).
- [5] N. G. Sahoo, Y. Z. Pan, L. Li, S. H. Chan, *Adv. Mater.* **2012**, *24*, 4203.
- [6] X. Huang, X. Qi, F. Boeya, H. Zhang, *Chem. Soc. Rev.* **2012**, *41*, 666.
- [7] F. Bonaccorso, L. Colombo, G. H. Yu, M. Stoller, V. Tozzini, A. C. Ferrari, R. S. Ruoff, V. Pellegrini, *Science* **2015**, *347*, 1246501.
- [8] Z. W. Chen, D. Higgins, A. P. Yu, L. Zhang, J. J. Zhang, *Energy Environ. Sci.* **2011**, *4*, 3167.
- [9] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* **2004**, *306*, 666.
- [10] L. M. Dai, *Acc. Chem. Res.* **2013**, *46*, 31.
- [11] D. Higgins, M. A. Hoque, M. H. Seo, R. Wang, F. Hassan, J.-Y. Choi, M. Pritzker, A. P. Yu, J. J. Zhang, Z. W. Chen, *Adv. Funct. Mater.* **2014**, *24*, 4325.
- [12] V. Chabot, D. Higgins, A. P. Yu, X. C. Xiao, Z. W. Chen, J. J. Zhang, *Energy Environ. Sci.* **2014**, *7*, 1564.
- [13] J. L. Shui, M. Wang, F. Du, L. M. Dai, *Sci. Adv.* **2015**, *1*, 1.
- [14] A. K. Geim, K. S. Novoselov, *Nat. Mater.* **2007**, *6*, 183.
- [15] M. J. Allen, V. C. Tung, R. B. Kaner, *Chem. Rev.* **2010**, *110*, 132.
- [16] A. Bagri, C. Mattevi, M. Acik, Y. J. Chabal, M. Chhowalla, V. B. Shenoy, *Nat. Chem.* **2010**, *2*, 581.
- [17] I. Y. Jeon, Y. R. Shin, G. J. Sohn, H. J. Choi, S. Y. Bae, J. Mahmood, S. M. Jung, J. M. Seo, M. J. Kim, D. W. Chang, L. M. Dai, J. B. Baek, *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 5588.
- [18] Y. W. Zhu, S. Murali, M. D. Stoller, K. J. Ganesh, W. W. Cai, P. J. Ferreira, A. Pirkle, R. M. Wallace, K. A. Cychosz, M. Thommes, D. Su, E. A. Stach, R. S. Ruoff, *Science* **2011**, *332*, 1537.
- [19] D. Y. Pan, J. C. Zhang, Z. Li, M. H. Wu, *Adv. Mater.* **2010**, *22*, 734.
- [20] D. C. Wei, Y. Q. Liu, Y. Wang, H. L. Zhang, L. P. Huang, G. Yu, *Nano Lett.* **2009**, *9*, 1752.
- [21] K. Chang, D. S. Geng, X. F. Li, J. L. Yang, Y. J. Tang, M. Cai, R. Y. Li, X. L. Sun, *Adv. Energy Mater.* **2013**, *3*, 839.
- [22] Y. Zheng, Y. Jiao, S. Z. Qiao, *Adv. Mater.* **2015**, *27*, 5372.
- [23] Z. Yang, Z. Yao, G. Li, G. Fang, H. Nie, Z. Liu, X. Zhou, X. Chen, S. Huang, *ACS Nano* **2011**, *6*, 205.
- [24] J. Zhang, Z. Zhao, Z. Xia, L. M. Dai, *Nat. Nanotechnol.* **2015**, *10*, 444.
- [25] Q. Su, S. P. Pang, V. Aljani, C. Li, X. L. Feng, K. Müllen, *Adv. Mater.* **2009**, *21*, 3191.
- [26] K. P. Loh, Q. L. Bao, P. K. Ang, J. X. Yang, *J. Mater. Chem.* **2010**, *20*, 2277.
- [27] J. W. Burrell, S. Gadipelli, J. Ford, J. M. Simmons, W. Zhou, T. Yildirim, *Angew. Chem. Int. Ed.* **2010**, *49*, 8902.
- [28] D. P. He, K. Cheng, T. Peng, M. Pan, S. C. Mu, *J. Mater. Chem. A* **2013**, *1*, 2126.
- [29] P. Wu, H. F. Lv, T. Peng, D. P. He, S. C. Mu, *Sci. Rep.* **2014**, *4*, 3968.
- [30] N. C. Cheng, M. N. Bani, J. Liu, A. Riese, X. Li, R. Y. Li, S. Y. Ye, S. Knights, X. L. Sun, *Adv. Mater.* **2015**, *27*, 277.
- [31] D. P. He, Y. Y. Rong, Z. K. Kou, S. C. Mu, T. Peng, R. Malpass-Evans, M. Carta, N. B. McKeown, F. Marken, *Electrochem. Commun.* **2015**, *59*, 72.
- [32] E. Yoo, T. Okata, T. Akita, M. Kohyama, J. Nakamura, I. Honma, *Nano Lett.* **2009**, *9*, 2255.
- [33] R. Mancharan, J. B. Goodenough, *J. Mater. Chem.* **1992**, *2*, 875.
- [34] L. T. Soo, K. S. Loh, A. B. Mohamad, W. R. W. Daud, W. Y. Wong, *Appl. Catal., A* **2015**, *497*, 198.
- [35] Y. Shao, S. Zhang, C. Wang, Z. Nie, J. Liu, Y. Wang, Y. Lin, J. Power Sources **2010**, *195*, 4600.
- [36] D. He, K. Cheng, H. Li, T. Peng, F. Xu, S. Mu, M. Pan, *Langmuir* **2012**, *28*, 3979.
- [37] L. Zeng, T. S. Zhao, L. An, G. Zhao, X. H. Yan, C. Y. Jung, *J. Power Sources* **2015**, *275*, 506.
- [38] H. Wang, Y. Zhou, D. Wu, L. Liao, S. Zhao, H. Peng, Z. Liu, *Small* **2013**, *9*, 1316.
- [39] D. P. He, Y. L. Jiang, H. F. Lv, M. Pan, S. C. Mu, *Appl. Catal. B* **2013**, *132*, 379.
- [40] H. J. Huang, J. X. Zhu, W. Y. Zhang, C. S. Tiwary, J. F. Zhang, X. Zhang, Q. G. Jiang, H. Y. He, Y. P. Wu, W. Huang, P. M. Ajayan, Q. Y. Yan, *Chem. Mater.* **2016**, *28*, 1737.
- [41] H. J. Huang, S. B. Yang, R. Vajtai, X. Wang, P. M. Ajayan, *Adv. Mater.* **2014**, *26*, 5160.
- [42] S. J. Guo, S. H. Sun, *J. Am. Chem. Soc.* **2012**, *134*, 2492.
- [43] J. N. Tiwari, K. Nath, S. Kumar, R. N. Tiwari, K. C. Kemp, N. H. Le, D. H. Youn, J. S. Lee, K. S. Kim, *Nat. Commun.* **2013**, *4*, 2221.
- [44] X. Chen, D. P. He, H. Wu, X. F. Zhao, J. Zhang, K. Cheng, P. Wu, S. C. M., *Sci. Rep.* **2015**, *5*, 16246.
- [45] S. C. Mu, X. Chen, R. H. Sun, X. B. Liu, H. Wu, D. P. He, K. Cheng, *Carbon* **2016**, *130*, 449.
- [46] I. Y. Jeon, H. J. Choi, S. M. Jung, J. M. Seo, M. J. Kim, L. Dai, J. B. Baek, *J. Am. Chem. Soc.* **2013**, *135*, 1386.
- [47] I. Y. Jeon, M. Choi, H. J. Choi, S. M. Jung, M. J. Kim, J. M. Seo, S. Y. Bae, S. Yoo, G. Kim, H. Y. Jeong, N. Park, J. B. Baek, *Nat. Commun.* **2015**, *6*, 7123.
- [48] Y. G. Li, W. Zhou, H. L. Wang, L. M. Xie, Y. Y. Liang, F. Wei, J. C. Idrobo, S. J. Pennycook, H. J. Dai, *Nat. Nanotechnol.* **2012**, *7*, 394.
- [49] T. Palaniselvam, M. O. Valappil, R. Illathvalappila, S. Kurungot, *Energy Environ. Sci.* **2014**, *7*, 1059.
- [50] Z. Yang, Z. Yao, G. Li, G. Fang, H. Nie, Z. Liu, X. Zhou, X. Chen, S. Huang, *ACS Nano* **2012**, *6*, 205.
- [51] Y. Jiao, Y. Zheng, M. Jaroniec, S. Z. Qiao, *J. Am. Chem. Soc.* **2014**, *136*, 4394.
- [52] D. H. Guo, R. Shibuya, C. Akiba, S. Saji, T. Kondo, J. Nakamura, *Science* **2016**, *351*, 361.
- [53] J. Yang, H. Y. Sun, H. Y. Liang, H. X. Ji, L. Song, C. Gao, H. X. Xu, *Adv. Mater.* **2016**, *28*, 4606.
- [54] Y. Y. Liang, Y. G. Li, H. L. Wang, J. G. Zhou, J. Wang, T. Regier, H. J. Dai, *Nat. Mater.* **2011**, *10*, 780.
- [55] Z. S. Wu, S. Yang, Y. Sun, K. Parvez, X. Feng, K. Mullen, *J. Am. Chem. Soc.* **2012**, *134*, 9082.
- [56] T. Palaniselvam, V. Kashyap, S. N. Bhanage, J. B. Baek, S. Kurungot, *Adv. Funct. Mater.* **2016**, *26*, 2150.
- [57] K. A. Mauritz, R. B. Moore, *Chem. Rev.* **2004**, *104*, 4535.
- [58] H. L. Tang, Z. H. Wan, M. Pan, S. P. Jiang, *Electrochem. Commun.* **2007**, *9*, 2003.
- [59] X. C. He, H. L. Tang, M. Pan, *J. Appl. Polymer. Sci.* **2008**, *108*, 529.
- [60] B. G. Choi, Y. S. Huh, Y. C. Park, D. H. Jung, W. H. Hong, H. S. Park, *Carbon* **2012**, *50*, 5395.
- [61] B. G. Choi, J. Hong, Y. C. Park, D. H. Jung, W. H. Hong, P. T. Hammond, H. Park, *ACS Nano* **2011**, *5*, 5167.
- [62] B. Zhang, Y. Cao, S. T. Jiang, Z. Li, G. W. He, H. Wu, *J. Membr. Sci.* **2016**, *518*, 243.
- [63] A. Paneri, Y. Heo, G. Ehlert, A. Cottrill, H. Sodano, P. Pintauro, S. Moghaddam, *J. Membr. Sci.* **2014**, *467*, 217.
- [64] L. S. Wang, A. N. Lai, C. X. Lin, Q. G. Zhang, A. M. Zhu, Q. L. Liu, *J. Membr. Sci.* **2015**, *492*, 58.
- [65] H. Zarrin, J. Fu, G. Jiang, S. Yoo, J. Lenos, M. Fowler, Z. Chen, *ACS Nano* **2015**, *9*, 2028.

- [66] Y. S. Ye, M. Y. Cheng, X. L. Xie, J. Rick, Y. J. Huang, F. C. Chang, B. J. Hwang, *J. Power Sources* **2013**, 239, 424.
- [67] M. R. Karim, K. Hatakeyama, T. Matsui, H. Takehira, T. Taniguchi, M. Koinuma, Y. Matsumoto, T. Akutagawa, T. Nakamura, S. Noro, T. Yamada, H. Kitagawa, S. Hayami, *J. Am. Chem. Soc.* **2013**, 135, 8097.
- [68] N. W. Pu, G. N. Shi, Y. M. Liu, X. L. Sun, J. K. Chang, C. L. Sun, M. D. Ger, C. Y. Chen, P. C. Wang, Y. Y. Peng, C. H. Wu, S. Lawes, *J. Power Sources* **2015**, 282, 248.
- [69] J. L. Lv, L. Tongxiang, W. Chen, *Int. J. Hydrogen Energy* **2016**, 41, 9738.
- [70] X. Jiang, L. T. Drzal, *J. Power Sources* **2012**, 218, 297.
- [71] B. K. Kakati, A. Ghosh, A. Verma, *Int. J. Hydrogen Energy* **2013**, 38, 9362.
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