



Graphene oxide based nanohybrid proton exchange membranes for fuel cell applications: An overview



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ABSTRACT

In the context of many applications, such as polymer composites, energy-related materials, sensors, 'paper'-like materials, field-effect transistors (FET), and biomedical applications, chemically modified graphene was broadly studied during the last decade, due to its excellent electrical, mechanical, and thermal properties. The presence of reactive oxygen functional groups in the grapheme oxide (GO) responsible for chemical functionalization makes it a good candidate for diversified applications. The main objectives for developing a GO based nanohybrid proton exchange membrane (PEM) include: improved self-humidification (water retention ability), reduced fuel cross-over (electro-osmotic drag), improved stabilities (mechanical, thermal, and chemical), enhanced proton conductivity, and processability for the preparation of membrane-electrode assembly. Research carried on this topic may be divided into protocols for covalent grafting of functional groups on GO matrix, preparation of free-standing PEM or choice of suitable polymer matrix, covalent or hydrogen bonding between GO and polymer matrix etc. Herein, we present a brief literature survey on GO based nano-hybrid PEM for fuel cell applications. Different protocols were adopted to produce functionalized GO based materials and prepare their free-standing film or disperse these materials in various polymer matrices with suitable interactions. This review article critically discussed the suitability of these PEMs for fuel cell applications in terms of the dependency of the intrinsic properties of nanohybrid PEMs. Potential applications of these nanohybrid PEMs, and current challenges are also provided along with future guidelines for developing GO based nanohybrid PEMs as promising materials for fuel cell applications.

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Abbreviations: APTES, 3-aminopropyl-triethoxysilane; CS, chitosan; DMF, dimethyl formamide; DMFC, direct methanol fuel cell; DGO, polydopamine modified graphene oxide; F-GO, functionalized graphene oxide; GO, graphene oxide; GtO, graphite oxide; iGtO, isocyanate modified GtO; IEMs, ion-exchange membranes; IEC, ion-exchange capacity; LbL, layer-by-layer; MEA, membrane electrode assembly; MGO, modified GO; MPS, 3-(methacryloxy) propyltrimethoxysilane; MPTMS, 3-mercaptopropyl trimethoxysilane; NMP, N-methyl-2-pyrrolidone; OCV, open circuit voltages; OGO, ozonated GO; PEM, proton exchange membrane; PDDA, poly(diallyldimethylammonium chloride); PDHC, 1,4-phenyl diamine hydrochloride; PEMFC, proton exchange membrane fuel cell; PW-mGO, phosphotungstic acid coupled graphene oxide; PEEKs, poly-(ether ether ketone)s; PAESs, poly(arylene ether sulfone)s; PPA, polyphosphoric acid; PBI, polybenzimidazoles; PGO, phosphorylated GO; PVA, poly(vinyl alcohol); PVC, poly(vinyl chloride); RGO, reduced graphene oxide; SGO, sulfonated GO; SGON, sulfonated GO/Nafion nanohybrid; SPI, sulfonated polyimide; S-GO-SiO₂, sulfonated graphene oxide-silica; SDBS, sodium dodecylbenzene sulfonate; SGtO, sulfonated GtO; SDBS, sodium dodecylbenzenesulfonate; SSi-GO, sulfonated organosilane functionalized graphene oxide; SCS, sulfonated chitosan; SDBS-HGO, sodium dodecylbenzenesulfonate adsorbed holey graphene oxide; SPB-FGO, SPES, sulfonated poly(ether sulfone) sulfonated polymer brush functionalized graphene oxide; THF, tetrahydrofuran; XRD, X-ray diffraction; ZC-GO, Zwitterion-coated GO.

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1. Introduction

Carbon allotropes have attracted significant attention for use in electrochemical applications, due to their enormous abundance, easy processability, excellent stability, and environmental adaptability [1]. Chemical (acid, base) and thermal stabilities of carbon allotropes are attractive features for their applications as electrode materials. Graphene is an exciting carbon allotrope with sp^2 -hybridized two-dimensional monolayer lattice [2]. A single-atom-thick carbon sheet with honeycomb arrangement showed improved stiffness and thermal and electrical conduction. Due to excellent thermal, mechanical, and electrical properties, graphene has been considered as a promising nanostructured carbon allotrope in the field of quantum mechanics and fundamental physics, materials science and condensed matter physics [3–7]. Further, the high mobility of charge carriers ($\sim 200,000 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$) [8–10], surface area ($\sim 2600 \text{ m}^2 \text{ g}^{-1}$) [1], Young's modulus ($\sim 1100 \text{ GPa}$) [11], thermal conductivity ($\sim 5000 \text{ Wm}^{-1} \text{ K}^{-1}$) [12], optical transmittance ($\sim 97.7\%$), and electrical conductivity make graphene an attractive material for electrochemical applications. In comparison with graphite and carbon nanotubes ($1300 \text{ m}^2 \text{ g}^{-1}$), graphene shows a high surface area ($\sim 10 \text{ m}^2 \text{ g}^{-1}$) [13], and is considered as a basic building block for graphitic materials [2].

A wide range of nanostructured materials based on modified graphene [10,14,15] were developed for diversified applications such as: polymer composites [13,16], energy-related processes [17], sensors and probes [18,19], 'paper'-like materials [14], field-effect transistors (FET) [20], photo-electronics [21,22], electro-mechanical systems [23],

hydrogen storage [24], and biomedical applications [25]. Further, inexpensive manufacturing sources (graphite) and the excellent properties of graphene encouraged considerable interest in developing cost-effective, high-performance polymer composites materials [26].

Graphene oxide (GO) exfoliated from graphite oxide (GtO), was prepared by strong oxidation using a strong mineral acid (conc. H_2SO_4) in the presence of an oxidizing agent (KMnO_4) (Hummers method), or by adding "potash of chlorate" (potassium chlorate; KClO_3) to a slurry of graphite in fuming nitric acid (HNO_3) as in the Staudenmaier or Brodie methods Fig. 1 [27–29]. GO contains closely located oxygenated functional groups ($-\text{O}-$, $-\text{OH}$, and $-\text{COOH}$) and a two-dimensional flat layer suitable for the formation of hydrogen-bonded proton conduction channels [30]. GO showed a large surface area and the presence of hydrophilic functional groups, providing a facile environment for proton conduction, by a "hopping" mechanism (improved water-retention, necessary for proton conduction in non-humid conditions). GO has been considered as an attractive organic filler for a polymer electrolyte membrane (PEM), and improved proton conductivity and water retention ability [31,32]. Further oxidation of GO ultimately disrupts the delocalized electronic structure of graphite and provides an electron-insulating environment [30]. The GO is well dispersed in several polar and nonpolar solvents, including water that make easy processing [33,34].

GO contains a high concentration of epoxide and hydroxyl functional groups on the basal plane, along with carboxylic acid groups around the periphery of the sheets (Fig. 2) [34,35]. GtO shows long-drawn-out interlayer distances (between the GO sheets) in comparison with graphite. Interlayer spacing depends on the humidity, and increases with hydrophilicity, due to the intercalation of water molecules between the sheets [14,36].

2. Different types of graphene oxide based PEMs

During recent years, nanostructured PEMs received great attention due to their unique structural features, improved stabilities, and versatile processing techniques. For developing nanostructured materials, generally elastomeric and flexible polymer matrices were considered, for achieving good elasticity, strength, flexibility, controlled surface and bulk properties. Among the structural polymeric matrices, the advanced nanohybrids, elastomers, thermoplastics, epoxy, block copolymers, and hydro/aerogels are widely used due to their unique physical and chemical properties.

For significant improvement in the performance of PEMs (water retention capacity, ionic conductivity, fuel cross-over and stability) at high operating temperature, various approaches were endeavoured. Extensive efforts were rendered to develop the GO based nanohybrid PEMs with a better understanding of molecular-level chemistry, morphology, transport behaviour, and polymer degradation. Incorporation of GO in the PEM matrix provides a more facile environment for proton conduction, by a "hopping" mechanism, and improved water-retention properties (necessary for proton conduction in non-humid conditions) due to the large surface area and the presence of hydrophilic functional groups [31,32]. These properties of GO could be further improved by chemical grafting of charged functional groups. Improved mechanical stability of modified GO has also been achieved by developing nanohybrid membranes.

Herein, we provide a broad literature survey on recent developments of modified GO based nanohybrid PEMs for fuel cell applications. Novel synthetic routes for nanohybrid membrane forming materials

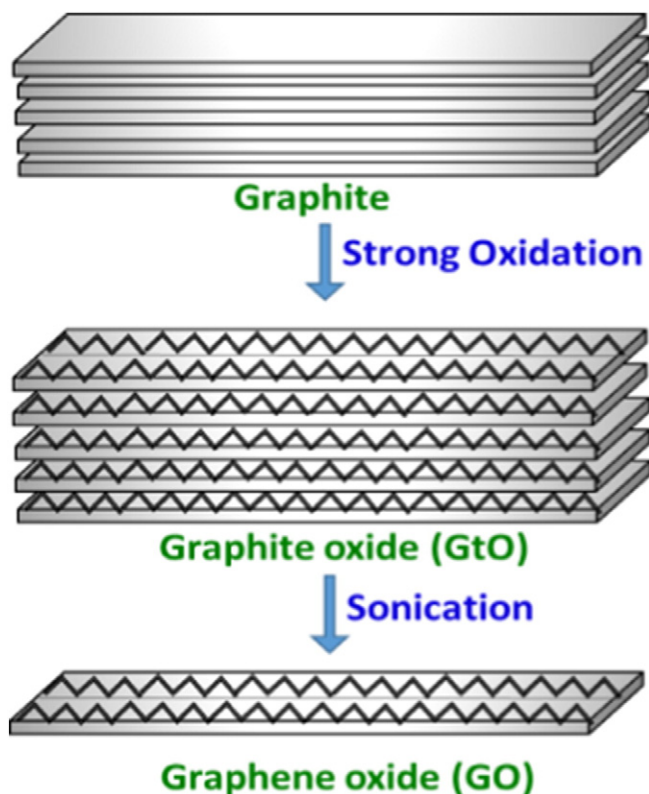


Fig. 1. Outlined oxidation/intercalation process for the preparation of GO.

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