Alkaline Anion Exchange Membranes based on KOH-treated Multilayer Graphene Oxide

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Abstract

A novel class of alkaline anion exchange membrane (AAEM) is presented, in the form of KOH-modified multilayer graphene oxide paper (GO_{KOH}). Such membranes can be easily fabricated at large scale with varying thickness using conventional filtration techniques, and have high tensile strength (24.5 MPa). However, a large degree of swelling is observed. SEM investigations show that the morphology of GO changes after KOH-treatment, whilst XPS measurements and XRD analysis confirm successful chemical modification. The hydrogen gas permeability is several orders of magnitude lower than conventional polymer-based ionomer membranes. The maximum anion conductivity is 6.1 mS/cm at 70°C, and the dominant charge carrier is confirmed to be OH^- by utilization of anion and proton-conducting blocking layers. The ion exchange capacity is 6.1 mmol/g, measured by titration. A water-mediated reverse Grotthuss-like mechanism is proposed as the main diffusion mode of OH^- ions. Finally, a prototype AAEM fuel cell is fabricated using a GO_{KOH} membrane, confirming the applicability to real systems.

Keywords

Alkaline fuel cell, anion exchange membrane, fuel cells, graphene oxide, ionic conductivity

1. Introduction

Ion exchange membranes are selectively permeable to specific ions whilst generally being insulating to electrons. The charge carriers can be cations (e.g. H^+ , or Li^+), or anions (such as OH^-). Ion exchange membranes have important industrial applications in electrodialysis (e.g. seawater desalination, demineralization, food processing, and glycerin purification), and electrolysis (e.g. water splitting, and the chloralkali process for Cl_2 and NaOH production) [1,2]. In particular, they are a fundamental component in polymer electrolyte membrane fuel cells (PEFCs), providing mechanical support, an electron barrier, and high through-plane ionic conductivity [1,3]. The most commonly utilized ion exchange membranes are proton exchange membranes (PEMs) such as Nafion[®] (E.I. DuPont de Nemours & Co., Inc.), Flemion[™] (Asahi Glass, Japan), Neosepta-F[™] (Tokuyama, Japan), and Aciplex[™] (Asahi Kasei Chemicals Corporation, Japan) [4,5]. Nafion[®] is by far the most-used membrane in PEFCs [3] due to high proton conductivity ($> 0.1 \text{ S/cm}$), good mechanical properties (e.g. 29.4 MPa tensile strength) and excellent chemical stability [6]. Automobile manufacturers focus on Nafion-based PEFCs for fuel cell vehicles (e.g. Toyota MIRAI, Japan), and stationary combined heat

and power fuel cell systems (e.g. Enefarm, Japan) also mainly utilize Nafion. However, the proton conductivity of Nafion depends strongly on hydration, and at $>100^{\circ}\text{C}$ the mechanical stability decreases significantly. Another disadvantage is fuel crossover, which increases with operation temperature and has a big influence on performance and efficiency in both direct methanol fuel cells (DMFCs) [7], and hydrogen fuelled PEFCs [8]. Finally, the cost of Nafion is still far higher than U.S. Department of Energy targets ($\sim 40 \text{ \$/m}^2$) [3]. For PEFCs in general, the high cost, poor stability, and the susceptibility of platinum to CO poisoning are major barriers to wide-spread commercialization [5,9–11].

In alkali anion exchange membranes (AAEMs), the charge carrier is a negatively charged ion, such as OH^- [1,2,12,13]. The first practical alkaline fuel cells (AFCs) utilized aqueous alkali electrolytes, which presented various challenges in terms of sealing and separation. Later, solid polymer AAEMs were developed. Alkaline anion exchange membrane fuel cells (AAEMFCs) have several advantages over PEFCs [12,14–18]; non-noble metal catalysts can be used due to faster cathode reaction kinetics [19]; the alkaline environment is less corrosive than acid allowing the use of cheaper materials; and fuel crossover is reduced because electroosmotic drag is in the opposite direction compared with PEFCs. Additionally CO poisoning is diminished due to faster oxidation of CO in AAEMFCs. These factors can drastically reduce the cost compared with PEFC systems. There are currently several commercially available AAEMs in production: Tokuyama A 201 (Tokuyama Co. Ltd.); Aciplex (Asahi Chemical Industry Co.); Selemion (Asahi Glass Co. Ltd.); and FuMA-Tech FAD (FuMA-Tech GmbH) [12]. However, none of these dominate in the same way that Nafion does in PEFCs, since no membrane satisfies all the necessary conductivity, durability, gas-permeability and cost requirements.

AAEMs can be distinguished into different classes, namely: homogenous membranes; heterogeneous membranes; hybrid membranes; and interpenetrating polymer network membranes [12,20]. Most commercially available AAEMs are fabricated from a single polymer phase, and are therefore homogeneous membranes. They are generally composed of a fluorocarbon (or hydrocarbon) polymer backbone with cationic functional side groups, which act as anion transport sites. These can be quaternary ammonium ($-\text{NR}_3^+$), phosphonium, sulfonium, or metal-based functional groups [1,2,12,13,20]. In heterogeneous AAEMs a polymer without intrinsic anion conduction, such as polyvinyl alcohol (PVA) or polybenzimidazole (PBI), is doped with KOH to induce anionic conductivity. Conductivities range from e.g. 1 mS/cm at RT [12] to e.g. 100 mS/cm at 90°C for high KOH concentrations. However, a lack of mechanical stability and leaching of KOH are problems that need to be solved in such membranes [12,20]. Hybrid membranes consist of an anion-conducting polymer combined with an inorganic component to provide mechanical strength. The conductivity is generally lower than in heterogeneous AAEMs. One example is polyethylene oxide (PEO) hybridized with siloxane ($[\text{Si}(\text{OCH}_3)_3]_2$), with a conductivity of 3 mS/cm at RT [12]. Another is PVA-KOH hybridized with zirconia (ZrO_2), with a particularly high conductivity of 267 mS/cm at 20°C [12,21]. In interpenetrating-polymer-network (IPN) AAEMs, two different polymers are at least partially interlaced at a molecular scale but are not covalent bonded to each other. For example, PVA can be interlaced with cationic polyelectrolytes such as polyethyleneimine (PEI), poly(diallyldimethylammonium chloride), or polyacrylamide. IPN-AAEMs usually have high chemical and mechanical stability, however conductivity is low (e. g. 3.5 mS/cm), and decreases significantly during aging [12,20]. The preparation of anion exchange membranes is generally quite complicated and expensive, and the carcinogen chloromethyl methyl ether is often used [12]. Therefore the field is wide open for new mechanically strong membranes with high gas barrier properties, and good ionic conductivity.

Graphene oxide (GO) is formed by chemical oxidization and exfoliation of graphite into individual two-dimensional sheets, using e.g. Hummer's or Brodie's methods [22,23]. It is readily dispersible in water, and forms strong free-standing membranes when dried. Large, thin GO membranes can be fabricated by e.g. filtration [24], bar-coating, or printing [25,26]. GO is essentially a graphene sheet, but with hydroxyl, epoxy and carboxyl functional groups attached to the edges and basal planes. These

oxygen-containing groups promote water uptake and can also be used as starting points for further chemical modification. GO has already been found to be beneficial in PEFC or DMFC membranes as a composite material. Blending with Nafion or sulfonated polyimides (SPI) enhances proton conductivity while decreasing methanol cross-over by an order of magnitude [27]. Nafion incorporating GO functionalized with sulfonic acid displayed high proton conductivity and fuel cell performance at 120°C and low relative humidity (RH), compared to recast Nafion [28]. In DMFCs, Nafion laminated with GO showed improved performance at high methanol concentration, due to suppressed cross-over [29]. Pure GO also has proton conductivity [30]. Tateishi et al. fabricated a fuel cell utilizing a 20 µm multilayer GO membrane. The conductivity was 0.1 mS/cm at room temperature and 20% RH, and the fuel cell power density was 13 mW/cm² [31]. We have reported the proton conductivity of GO membranes (0.6 mS/cm), and achieved power densities of 34 mW/cm² in GO membrane fuel cells (GOMFCs) with 16 µm thick membranes [32]. We have also explored the impedance and permittivity of such membranes in detail [33]. Functionalization of GO with sulfonated acid groups leads to even higher conductivity (12 mS/cm) and higher power densities (113 mW/cm²) [34]. Karim et al. reported the through-plane conductivity of GO pellets with 10 mS/cm [35]. Recently Hatakeyama et al. investigated proton conductivity in single layer and multilayer GO and reported increasing proton conductivity with increasing film thickness (from 0.04 mS/cm for a monolayer, to 0.4 mS/cm for a 200 nm thick membrane [36]).

GO has been investigated in AAEMFC membranes, but to a much lesser extent. For example, Yang and Wang recently incorporated graphene and sulfonated graphene (obtained by thermal reduction of GO) into a PVA/chitosan composite, obtaining a conductivity of 93 mS/cm at 80 °C and doubling the tensile strength of pure PVA [37]. They did not incorporate their membrane into an AAEMFC. Movil et al. incorporated PDDA-functionalized GO into PVA-based composite membranes and observed conductivity of 21 mS/cm at 80 °C, improved thermo-mechanical stability, and AAEMFC power density of 17 mW/cm² [38]. Liu et al prepared composite membranes by incorporating quaternized graphene into aryl polymers, resulting in high Young's modulus (5240 MPa) and tensile strength (205 MPa), and *bicarbonate* conductivity of 18.7 mS/cm at 80°C [39]. Zarrin et al. prepared functionalized GO with quaternary ammonium groups and made a composite with PBI. The conductivity was 85 mS/cm at 65°C, and an AAEMFC incorporating this membrane achieved a power density of 86.7 mW/cm² at 50°C and 100% RH [40]. Finally, Chen et al. functionalized GO with imidazolium, and composited this with chitosan. The conductivity was 10 mS/cm at 90 °C and 100% RH, whilst the open circuit voltage (OCV) was 0.71 V and the maximum AAEMFC power density was 75.8 mW cm⁻² [41]. All of the above work has been on GO composited with well-known anion conducting materials. To date, the conductivity and fuel cell performance of pure-GO-based AAEMs has not been reported.

Here we report the preparation and characterization of a novel heterogeneous anion exchange membrane based on multilayer graphene oxide paper. Reacting carboxyl or hydroxyl groups with KOH results in the following neutralization reaction, forming a carboxylate salt, or an alkoxide:

In the case of GO, the OH and COOH functional groups are attached to the surface of the graphene sheet. Similar surface neutralization reactions have been performed on acid-oxidized multiwall carbon nanotubes [42]. Following this neutralization with excess KOH, the GO dispersion is filtered and dried to form membranes. The conductivity of these is investigated and the performance in GO-based AAEM fuel cells is presented.

2.# Experimental

2.1. Preparation of multilayer graphene oxide alkali anion exchange membranes

To make an alkaline GO dispersion, 210.8 mg of potassium hydroxide (*Wako Pure Chemical Industry*, assay value $\geq 85.0\%$) was dissolved in 43.01 ml graphene oxide dispersion (*Graphene Supermarket*, flake size 0.5. to 5 μm , 5 mg/ml) and stirred at room temperature for 24 hours. The amount of KOH added to the GO dispersion was calculated to be approximately stoichiometric with the oxygen functional groups on the GO, as calculated from elemental analysis. The pH of the as-purchased GO dispersion was 2.3 before addition of KOH, changing to 12.5 after the cation exchange reaction. Herein, KOH-treated graphene oxide is labelled GO_{KOH} . Membranes were prepared by vacuum-filtration from dispersion onto Millipore filters (pore size 0.025 μm , 35 mm diameter). These were then dried at room temperature for 48 hours and peeled off the filter, yielding freestanding and flexible GO_{KOH} membranes.

2.2. Morphological and Chemical Analysis

The morphologies of the membrane surface and cross-section were investigated by scanning electron microscopy (SEM, *Hitachi S-5200*, 15 kV). Transmission electron microscopy (TEM) was performed on a JEOL ARM 200CF, with an acceleration voltage of 120 kV. Chemical composition of the membrane sample was determined using X-ray photoelectron spectroscopy (XPS, *KRATOS Analytical ESCA-3400* with Mg K α radiation, 12 kV, 10 mA). X-ray diffraction (XRD) was measured using a *Smartlab* X-ray Diffractometer with Cu K α radiation ($\gamma = 1.5418 \text{ \AA}$, $0.01^\circ/\text{step}$).

2.3. Tensile Strength Testing

The tensile strength of GO and GO_{KOH} membranes was measured at room temperature and around 63% relative humidity (ambient lab conditions). The samples were cut into strips 10 mm in length and 2 mm wide. Tensile load was applied using a hydraulic testing machine force gauge (*SHIMPO FGO-C-TV*), until rupture. Applied force and elongation were recorded. The tensile stress (S) was calculated using $S = F/A$, where F is the applied force and A is the initial cross-sectional area of the sample. Strain (ϵ) was calculated using $\epsilon = L/L_0 \times 100\%$, where L is the length of the sample during elongation and L_0 is the initial sample length. Elastic modulus E is defined as the slope of the stress-strain curve in the elastic region, and was calculated using $E = S/\epsilon$.

2.4. Ion Exchange Capacity (IEC)

The H^+ IEC of GO membranes was immersing and sonicating the dry GO membrane in 1M NaCl solution to exchange the acidic protons of GO with Na^+ . The released protons were titrated to neutral pH with 0.01 M NaOH solution. The OH^- IEC was obtained by redispersing a dry GO_{KOH} membrane in 15 mL of milli-Q H_2O with the assistance of sonication. The dispersion was titrated back to the original pH of GO solution (≈ 3.5) using 0.01 M HCl solution. The IECs (in mmol/g) were determined from the following equation, where V_x and C_x are the volume and concentration, respectively, of NaOH or HCl:

$$E = \frac{V_x \times C_x}{\text{Membrane Weight}} \quad (3)$$

2.5. Water Uptake

Water uptake and swelling were measured on GO_{KOH} and GO samples with a size of 5 x 5 mm², and thicknesses of 21 and 19 μm, respectively. Five different samples were measured for reproducibility. The dry mass was determined using an analytical balance (*Mettler Toledo* XP2UV, ± 0.1 μg). The alkaline membranes displayed strong swelling in water, affecting the mechanical properties to the extent that handling freestanding samples was impossible. Therefore the membranes were supported on silicon wafers and a water droplet was placed over the membrane covering it completely. After saturation, excess water was carefully removed using an absorbent wipe and the mass was measured. Water uptake (WU) was calculated using Equation (2), where m_{wet} and m_{dry} are the wet and dry masses, respectively;

$$WU(\text{wt}\%) = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \cdot 100\% \quad (4)$$

2.6. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) of GO_{KOH} and GO was performed under air flow (50 ml/min) using a *Rigaku* Thermo plus EVO2 TG8121. The samples were heated from room temperature to 1400°C at a rate of 5 K/min, and the change in mass was recorded as a function of temperature. The initial masses of GO and GO_{KOH} were 9.72 and 10.77 mg respectively.

2.7. Hydrogen Permeation Rate

For gas permeance measurements the membrane area was masked with kapton and alumina tapes to form a circle of desired diameter and area ($d = 1 \text{ cm}$, $S = 0.785 \text{ cm}^2$). Additionally, to prevent bending under vacuum the membrane is placed on a porous polycarbonate support filter (1.2 μm pore size). Dry hydrogen permeation through the GO and GO_{KOH} membranes was measured at 30 °C using a GTR-11A/31A gas barrier testing system with a GTR-31AKU attachment (*GTR Tec Corp., Japan*). A differential-pressure method is used in which gas permeation is induced by a vacuum on the permeate side and extra pressure at the feed side, as shown in the supplementary information (Figure 1a). The total pressure difference was 200 kPa, and the sample collection time at the sweep side of the membrane was 30 minutes. The collected gas was transferred to a gas chromatograph (GC) with a thermal conductivity detector (TCD) (*Yanaco G3700T, Japan*) and the volume measured, as shown in the supplementary information (Supplementary Figure 1b). The operation parameters of the GC are listed in the Supplementary Table 1 of supplementary information. The permeance in gas permeation units (GPU) and permeability in barrers were estimated for membranes of different thickness [43] and compared to the reference Nafion membrane.

2.8. Ionic Conductivity

Ionic conductivity was investigated at different temperatures and humidity using a membrane testing device (*MTS-740, Scribner*) coupled with an impedance analyzer (*Solatron SI1260*) [44]. A membrane with 37 μm thickness was measured with an AC amplitude of 10 mV in the frequency of 30 MHz to 10 Hz. The impedance was measured with increasing temperature from 30 to 70°C, with isothermal changes in relative humidity (RH) from 100 to 0% RH. Before measurements, the sample was pretreated at 100% RH for 4 hours, followed by 1 hour pretreatment at each humidity step. Impedance plots are fitted to an equivalent circuit using ZPlot (*Scribner*), from which the membrane resistance, R (Ω), was determined from the membrane thickness, L (cm), and cross-sectional area, A (cm²), (0.5 cm²). Conductivity, σ (S/cm), was calculated using $\sigma = L/(R \cdot A)$.

In order to separate the anionic and protonic contributions from the total conductivity of the membranes, i.e. to confirm the anion conducting nature of the membranes, blocking layer measurements were performed. Commercially available anion conducting membranes were used as proton blocking layers (Tokuyama A201, 28 μm), and commercially available proton conducting

membranes (Nafion[®] 212, 50 μm) was used as anion blocking layers. The GO_{KOH} membranes (27 and 28 μm , respectively) were sandwiched between the respective blocking layers, as shown in **Error! Reference source not found.**e. The impedance was measured as described above. The resistance of the blocking layers was determined in previous measurements, and was subtracted from the total resistance of the multilayer system. The protonic and anionic conductivity of GO_{KOH} was finally calculated using the same equation mentioned above.

2.9. Fuel cell performance test

A membrane electrode assembly (MEA) was prepared using a GO_{KOH} membrane with a thickness of 16 μm . Catalyst ink was prepared by mixing Pt/C electrocatalyst (*Tanaka Kikinzoku Kogyo K.K.*, 46.2 wt % Pt) with 5 wt% anion conducting polymer solution (*Tokuyama*, Japan), ethanol (*Chameleon*, Japan), and deionized water. The catalyst ink was stirred overnight, then sonicated before use for 30 min (SMT Ultra Sonic Homogenizer UH-600). The catalyst ink was sprayed onto the GO_{KOH} membrane (*Nordson K.K.* Spraying Device, C-3J) using a mask to create an electrode size of 0.5 cm^2 with a catalyst loading of 0.3 mgPt/cm^2 for both electrodes. Hydrophobic carbon paper (EC-TP1-060T) gas diffusion layers (GDLs), were precisely positioned over the electrocatalyst layers. The prepared MEA was placed into a single cell test holder (1 cm^2) and installed in a home-made fuel cell testing system. The cell was preconditioned for 30 minutes at 30°C and a nitrogen gas flux of 100 ml/min (95% RH). The gas flux was changed to hydrogen and air (100 ml/min, 95% RH) and after ten minutes a performance test was conducted. Polarization curves and power density were investigated using a VersaSTAT-4 (*Amtek*).

3.# Results and Discussion

3.1 Microscopy

Error! Reference source not found. (a-d) shows surface and cross-sectional SEM images of GO and GO_{KOH} membranes. Both GO and GO_{KOH} membranes have a layered structure, characteristic of multilayer GO paper. However, the GO_{KOH} membrane surface is more strongly corrugated, with more prominent surface features than the GO membrane. Such corrugation has been observed in, for example, reduced GO [45]. Alternatively, the change in morphology may be induced by the introduction of significantly altered surface charge as a result of the neutralization reaction.

Figure 1 (e-h) shows high-resolution TEM images comparing few-layer GO and GO_{KOH} sheets. In the lower magnification images, GO appears much lighter compared to GO_{KOH} . This may simply be due to a difference in thickness of the samples. At the edges of both samples, slightly brighter areas indicate even thinner regions, a few monolayers thick. Some crumpling and folding is also observed. At high magnification, the hexagonal arrangement of the underlying carbon in GO can be resolved in some regions. However in GO_{KOH} , such detail could not be resolved.

3.2 X-ray Photoelectron Spectroscopy

XPS was performed on GO and GO_{KOH} for chemical and elemental analysis. **Error! Reference source not found.**a shows the wide scan spectrum with three major peaks corresponding to O 1s (532 eV), K 2p (292 eV), and C 1s (284 eV). The elemental composition is: 77.5% carbon and 22.5% oxygen for GO; and 78.5% carbon, 15.9% oxygen, and 5.7% potassium for GO_{KOH} . The oxygen content is slightly lower in GO_{KOH} . **Error! Reference source not found.**b shows the C1s spectra deconvoluted into six peaks ascribed to different bonds. GO_{KOH} shows a clear decrease in the proportion of epoxy groups. The proportion of hydroxyl groups decreases slightly and an energy shift is observed, as a result of the cation exchange reaction. The deconvoluted O 1s spectra are shown in **Error! Reference source not found.**c. The decreased intensity reflects the decreased oxygen content in GO_{KOH} . Epoxy groups are highly reactive due to the highly strained bonds, and open up to generate hydroxyls in basic environment [46]. The peak at ~530.6 eV indicates oxygen-alkali bonds, providing evidence of successful cation exchange [47]. **Error! Reference source not found.**d shows two potassium peaks at 292.8 eV and 295.6 eV attributed to the K 2p_{3/2} and K 2p_{1/2} spin-orbit-split doublet of potassium oxides and cations. The K 2p_{3/2} peak is deconvoluted into two contributions reflecting the different chemical environments of potassium ions. The major assignment is at 292.7 eV for the potassium associated with the carboxylic acid groups of GO, located in a position similar to that of the analogous small molecule potassium acetate [48], whilst a minor contribution is attributed to unbound KOH. The

presence of K-O bonds and the decreased proportion of epoxy and hydroxyl functional groups confirm the successful chemical modification of GO. The decrease in oxygen content, especially of certain functional groups indicates partial reduction of GO in the strongly alkaline environment (pH 12.5), as previously reported [49,50].

3.3 X-ray Diffraction (XRD)

Error! Reference source not found.a shows XRD spectra of GO and GO_{KOH} measured at ambient temperature and relative humidity. GO has a major peak at $2\theta = 11.53^\circ$ corresponding to an interlayer distance of 0.77 nm, similar to reported values under similar conditions [32]. GO_{KOH} has a major peak at $2\theta = 10.32^\circ$ corresponding to a much larger interlayer spacing of 0.86 nm. In general, the interlayer spacing in GO decreases with decreasing oxygen content [51]. The larger interlayer spacing in GO_{KOH} despite the lower oxygen content reflects the much larger ionic radius of K⁺ ions (~ 0.13 nm) [52], compared with H⁺ ($\sim 8.4 \times 10^{-7}$ nm) [53]. The appearance of a second peak in the GO_{KOH} spectrum at $2\theta = 21.2^\circ$ corresponds to an interlayer spacing of 0.42 nm. This has been associated with potassium-graphite intercalation compounds [54], and may be a further indicator of partial reduction of the GO to a graphite-like state. The lack of characteristic Bragg reflections for bulk KOH indicates that little or no excess KOH is present [55].

3.4 Gas Barrier Properties

Crossover of hydrogen from the anode to cathode is an important issue in fuel cells and should be avoided. One of the main advantages of using GO as an ionomer membrane is that it is highly impermeable, and therefore crossover should be minimal. As a result of this, much thinner membranes could be utilized, reducing cell resistance. Here we measure the hydrogen gas barrier properties of membranes with different thickness (GO: 17 and 37 μm ; GO_{KOH}: 15 and 37 μm) at 30°C. **Error! Reference source not found.**b shows the permeance and permeability. The values are extremely low for both membranes; and several orders of magnitude lower than Nafion (~ 25 barrer). The hydrogen permeance decreases with increasing thickness for both GO and GO_{KOH}. This is as expected since the permeance is the pressure-normalized gas flux through the membrane and is dependent on the diffusion coefficient (constant), the concentration of permeate (constant), and the thickness of the membrane. The permeability is approximately constant with thickness, as expected for this thickness-normalized value. These results are contrary to a previous high-profile study which claims that GO is completely impermeable to liquids and gases except water [56]. This disparity is attributed to the much larger pressure differential used in our work, resulting in higher, more measurable hydrogen permeation rates. The permeance and permeability of GO_{KOH} are around 5 times lower than in GO, indicating that KOH treatment can improve the hydrogen gas barrier properties, despite the larger interlayer spacing. This may be due to the added effect of potassium ions, which completely change the electronic structure within the membrane. As such, both GO and GO_{KOH} membranes are ideally suited to minimize crossover in fuel cells.

3.5 Mechanical Strength and Water Uptake

The tensile strength (24.5 ± 2.0 MPa) and Young's modulus (290.3 ± 66 MPa) of GO_{KOH} are smaller compared to our previously reported values for GO (54.5 ± 3.3 MPa and 680 ± 9.7 MPa, respectively) [32]. This may be due to reduced van der Waals forces between the individual GO_{KOH} sheets because of the intercalated potassium ions. However, the values are comparable to conventional ionomer materials. The elongation before rupture is $11 \pm 1.6\%$, significantly lower than previously observed for GO ($22 \pm 1\%$).

The water uptake of GO is 1434 wt%, compared with 1099 wt% for GO_{KOH}. The lower water uptake in GO_{KOH} is attributed to lower oxygen content and therefore reduced hydrophilicity. Both membranes show an extremely high degree of swelling, much greater than we previously reported (i.e. 31 % at 80°C), and resembling a hydrogel [57]. The high degree of swelling is attributed to the smaller area of the membrane samples allowing water absorption throughout the entire membrane on much faster timescales.

3.6 Thermal Stability

The thermal stabilities of GO and GO_{KOH} were investigated by thermogravimetric analysis (TGA) in air. GO displays four main mass loss peaks (**Error! Reference source not found.**). The endothermic peak centered at ~80°C is associated with evaporation of physisorbed water intercalated in the GO. There is a small exothermic mass loss peak at around 160°C which we attribute to early onset reduction of the GO, i.e. the decomposition of one of the weakly-bonded functional groups (e.g. -OH), or loss of chemically bound water molecules. The exothermic mass loss peak at ~220°C is attributed to decomposition of all other oxygen-containing functional groups. The final exothermic mass loss peak at ~520°C is attributed to combustion of the remaining carbon to form CO₂.

GO_{KOH} also exhibits four mass-loss peaks. The first is related to water evaporation, at ~80°C. A small exothermic mass loss occurs at 140°C, again attributed to loss of weakly bound oxygen-containing functional groups or chemically bound water. The third, exothermic mass loss peak occurs at ~380°C attributed to the formation of potassium carbonate. This is more thermally stable than carbon and accounts for the stability of this phase up to >800°C. Finally, two strong endothermic signals corresponding to the glass transition and melting points of K₂CO₃ are observed [58], followed by complete mass loss at around 1100°C, corresponding to decomposition of K₂CO₃ to CO₂ and gaseous potassium. These results show that GO_{KOH} is slightly less thermally stable than GO.

3.7 Ion Exchange Capacity, Ionic Conductivity, and Activation Energy

The ion exchange capacity (IEC) of the membranes, i.e. the number of moles of charge carrier per unit mass, was determined by titration. The GO and GO_{KOH} membranes have IECs of approximately 2.6 and 6.1 mmol/g for H⁺ and OH⁻ respectively. As there is a slight excess of OH⁻ in the alkaline membrane compared to the H⁺ present in the untreated membrane, we conclude that there is a small excess of free KOH in the GO_{KOH} membrane, as confirmed by the K 2p XPS data. This excess of KOH also explains why the IEC is higher than in commercially available membranes, e.g. 1.8 mmol/g for Tokuyama A201.

Impedance spectroscopy was used to determine the through-plane ionic conductivity of the membranes. **Error! Reference source not found.**a shows the dependence of conductivity on humidity and temperature for GO_{KOH}. The proton conductivity of GO at 100% RH is included for comparison. In general, the conductivity increases with increasing humidity and increasing temperature. This is as expected for ionic charge carriers, in which higher temperature overcomes the activation barrier for ion mobility and high humidity provides enhanced ion mobility via water-mediated transport mechanisms. The highest anionic conductivity of GO_{KOH} is 6.1 mS/cm at 70°C and 100% RH. This is around 20 times higher than the value of proton conductivity of GO, suggesting that the alkaline ion exchange reaction was successful in fundamentally changing the nature of ion transport in the material. It compares reasonably well with commercially available AAEMs, e.g. Tokuyama A201, which has a through-plane conductivity of 7.1 mS/cm at 30°C [59].

However, at low humidity and high temperature (70°C) the conductivity of the GO_{KOH} membranes increases with decreasing humidity, as also observed for GO membranes [33]. This is indicative of electronic conduction under these conditions. At high humidity electronic conductivity is negligible due to the presence of intercalated water and the large interlayer spacing, blocking electron-conducting pathways between sp² regions of the carbon. At low relative humidity the interlayer spacing decreases as water is removed from the membrane [60]. This provides the opportunity for electron percolation from layer to layer, along a pathway of local sp² regions [61]. Although electronic conduction is not desirable in fuel cell membranes, this effect is not observed under fuel cell conditions (i.e. high humidity), and additionally there are potential applications of GO membranes as mixed ionic conductors.

Arrhenius plots of the conductivity data are presented for different humidities in **Error! Reference source not found.b**. The slopes correspond to activation energies, which are plotted against humidity in **Error! Reference source not found.c**. Due to the unusual behavior observed at 70°C and attributed to mixed conduction, fitting was limited to the 30 to 60°C range. The activation energies are quite high at high humidity (~0.4 eV, or 38.6 kJ mol⁻¹). Generally values of between ~0.1 - 0.2 eV (~10 - 25 kJ/mol) [62,63], are reported for anion conducting membranes. The activation energy gradually decreases with decreasing humidity, possibly related to the gradual change in interlayer spacing with RH. At low RH, the activation energy is just 0.01 eV (1.0 kJ/mol), most likely indicating electron transfer, and confirming that the membranes are mixed ionic conductors when dry. The larger activation energy compared with conventional anion membranes accounts for the low conductivity despite the large IEC.

3.8 Determination of Dominating Ionic Species

Blocking layer measurements were performed on the membranes in order to confirm the dominance of OH⁻ anion conduction, and to discount H⁺ or K⁺ ion conduction (**Error! Reference source not found.d**). Accordingly, GO_{KOH} membranes were sandwiched between anion-blocking (Nafion) or cation-blocking (Tokuyama) layers, as shown schematically in **Error! Reference source not found.e**. The negatively charged SO³⁻ groups in Nafion block OH⁻ ions by electrostatic repulsion, just as the positively charged cations in Tokuyama membranes repel protons. When proton-blocking layers are utilized, the conductivity closely follows that of GO_{KOH} with no blocking layers. When anion-blocking layers are used, the conductivity drops significantly across the whole temperature range. These results confirm that the dominant charge carriers are OH⁻ anions. These results also discount majority K⁺ conduction, since neither blocking layer is a known K⁺ conductor. However, a small proportion of H⁺ conduction appears to occur (~6 %). A small discrepancy is observed between the reference sample and the sum of the anion- and proton-blocked samples, especially at higher temperature. This may be due to a small amount of K⁺ conduction, or potassium carbonate formation and associated CO₃²⁻ ion conduction [2]. However due to the barrier properties of GO and nanoconfinement between the individual GO sheets, movement of such ions through the membrane by the vehicular mechanism is expected to be highly restricted [56]. The discrepancy may also be attributed to a small proportion of electronic conduction.

The above results confirm that the dominant charge carriers in GO_{KOH} membranes at high humidity are OH⁻ ions. The specific mechanism for OH⁻ conduction in GO_{KOH} is hypothesized to be either vehicular, or reverse Grotthuss. In the vehicular mechanism, an OH⁻ ion physically travels through the membrane. However, this is problematic in the case of GO, since it is widely accepted that due to the highly impermeable nature of this material, only protons and water can pass between GO sheets. The reverse-Grotthuss mechanism is related to the conventional Grotthuss mechanism, in which acidic protons hop from e.g. a hydronium ion (H₃O⁺) to a water molecule, forming a new hydronium ion and leaving

behind a water molecule. The reverse-Grotthuss mechanism dominates in alkaline conditions, where there is a large excess of OH^- ions. Here, protons hop from a water molecule onto an adjacent OH^- ion, forming a new water molecule and leaving behind a new OH^- ion [64–66]. In this way the diffusion of positively charged protons effectively results in a net backwards diffusion of OH^- ions (schematically represented in **Error! Reference source not found.**). This is analogous to the transport of vacancies in p-type semiconductors, or the transport of O^{2-} ions in solid oxide fuel cell (SOFC) electrolytes. The activation energy for Grotthuss-type proton hopping is expected to be much lower (~ 0.13 eV) than the measured 0.4 eV [65]. This hints that nanoconfinement between the layers of GO fundamentally affects the activation energy required for ionic transport, due to steric effects [67].

3.9 Fuel Cell Performance

Due to the interesting anion conductivity measured in these novel AAEMs, a proof-of-concept AAEMFC was fabricated. A single-cell MEA was prepared using an 18 μm thick GO_{KOH} electrolyte membrane, and installed in a fuel cell test system. **Error! Reference source not found.**a shows the resulting polarization curves and power density of the cell. The open circuit voltage (OCV) is 0.94 V. This is reasonable, but still lower than for commercially available AAEMs (1.02 V), or for proton-conducting GOMFCs (1.01 V) [32]. The low OCV cannot be attributed to fuel crossover, because of the excellent hydrogen barrier properties of the membrane. Therefore, it is attributed to mixed ionic conductivity, as observed in the blocking layer measurements. There is a small initial voltage drop of ~ 0.05 V attributed to activation losses. This is much smaller than observed in GOMFCs (~ 0.2 V), reflecting the faster reaction kinetics in alkaline environment. The ohmic region is linear but steep, indicating relatively high ohmic losses. From this slope, the total cell resistance is calculated to be $204 \Omega\text{cm}^2$, around 1000 times higher than in AAEMFCs made with commercially available anion conducting membranes [69]. The resistance of the membrane is calculated to be $0.48 \Omega\text{cm}^2$ from the conductivity measurements at 30°C , so this is clearly not the main contributor to the cell resistance. Therefore it is attributed to the electrocatalyst layer, or the interface between the electrocatalyst layer and the membrane. Hot pressing is usually utilized during fabrication of MEAs in order to improve contact between ionomer and the electrocatalyst. In GO_{KOH} AAEMFCs the hot-pressing step was omitted, since high temperature reduces GO and destroys the ion-conducting properties. Therefore the interaction between the polymer anion-conducting ionomer and the electrocatalyst is not optimized, increasing the resistance of the layer. Additionally, the presence of KOH in the membrane could lead to the formation of potassium carbonate upon exposure to CO_2 in the air. Many studies utilize pure oxygen rather than air at the cathode to prevent this, but such conditions are not realistic for practical fuel cells. Carbonate formation leads to neutralization of the membrane, quickly decreasing the conductivity (i.e. increasing the resistance) [2]. The carbonate could also potentially result in an inert layer at the interface with the electrocatalyst, acting as a barrier to ion conduction and increasing the cell resistance. No mass transport limited region is observed, due to the relatively low power density. The maximum power density is 0.97 mW/cm^2 at 2.09 mA/cm^2 . This is much lower than in commercial AAEMFCs operated under similar condition (e.g. 8 to 100 mW/cm^2) [12]. Improvements in the performance of GO_{KOH} AAEMFCs are expected by optimization of the ionomer-catalyst ratio in the electrocatalyst layer; utilizing pure oxygen rather than air; decreasing the membrane thickness; and laminating the GO_{KOH} with thin polymeric anion conducting layers [70]. However, despite the relatively low power density at present, this is an important proof-of-concept device.

The durability of the GO_{KOH} AAEMFC was investigated at 30°C at a constant load current of 1 mA (**Error! Reference source not found.**b). The cell voltage drops significantly in the first 5 minutes of operation. After the initial drop in cell voltage, a slower degradation in performance is observed. Similar behavior was reported in acid-based GOMFCs, and related to reduction of GO in the strongly reducing hydrogen atmosphere increasing the proportion of electronic conduction through the membrane [32]. In less than an hour the cell voltage dropped by 0.5 V, to 0.2 V. After the durability measurement, the cell performance was again investigated. The OCV was just 0.65 V, confirming that

increased electronic conductivity is a factor in the degradation process. The maximum power density was just 0.44 mW/cm² at 1.60 mA/cm².

4.# Conclusions

Novel alkali anion exchange membranes were prepared via cation exchange of pure graphene oxide dispersions, followed by simple vacuum filtration. Hydrogen gas permeation through the membranes was several orders of magnitude below that of conventional polymers. The maximum conductivity was 6.1 mS/cm at 70°C, approaching that of commercially available anion conducting membranes, and the dominant charge carrier was confirmed to be OH⁻, by careful use of blocking layer measurements. A demonstration alkaline fuel cell utilizing a GO_{KOH} membrane was fabricated. The initial OCV was 0.94 V, and the maximum power density was ~ 1 mW/cm². The relatively low performance is attributed to carbonate formation upon exposure to CO₂, and the fact that hot pressing cannot be used without reducing the graphene oxide, and we are now working on these engineering challenges. However, this is an original and important proof-of-concept for the application of pure graphene oxide-based alkaline exchange membranes in electrochemical devices.

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Graphical abstract