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## Novel composite proton exchange membrane materials for intermediate temperature fuel cells

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Fuel cells are becoming an increasingly popular alternative to conventional energy sources and internal combustion due to climate change concerns and the depletion of natural resources of fossil fuels. Proton Exchange Membrane Fuel Cells (PEMFCs) are desirable because they operate in a convenient temperature range (70 – 200 °C), have a solid but light electrolyte and can be connected in series to increase power output. These properties make them ideally suited for portable and automotive applications. However, cost and long term durability of these systems continue to be barriers to the commercialisation of PEMFCs.

These barriers are strongly associated with the proton exchange membrane (PEM) in two ways. Firstly, common PEMs show optimum performance at 100 %RH necessitating expensive humidification systems. Secondly, degradation of the PEM leads to fatal degradation of the fuel cell due to short circuit of the cell.

Nafion, the current market leader for PEMFC membranes, is a perfluorinated sulfonic acid (PFSA) ionomer with outstanding qualities, including high proton conductivity. One drawback is the inability to operate at high temperature and low humidity and a propensity to chemical and thermal degradation during long operating periods. Composite PEM materials, which are doped with various inorganic fillers, are currently intensively researched for PEMFCs to operate at intermediate temperature (120-130 °C). These materials are considered to enhance the proton conductivity of traditional materials because the hydrophilic fillers increase the water uptake ability. Performance at high temperature and low humidity operation is enhanced by a higher level of water retention which also prevents degradation due to dehydration. The mechanical properties are also enhanced if chemical interaction between the filler and the host polymer matrix is promoted.
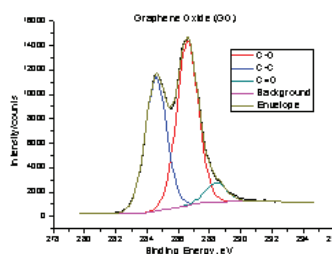


**Figure 1** C1s XPS spectra showing C-O peaks for GO prepared at the University of Birmingham

Composite PEMs can be prepared by dispersion of nano or micro size filler particles in an ionomer solution and then cast using traditional methods (solution casting, dip coating, spin coating etc). Another method is to grow filler particles in a pre-formed membrane or in an ionomer solution. To avoid a negative influence on the conduction mechanism within the PEM it is important to consider the effect of filler particles on the properties of the host polymer membrane. The shape, type, size, amount and orientation of the filler can have an effect and the most commonly used inorganic fillers are metal oxides, clays, zeolites, mineral acids, solid acids, heteropoly acids and more recently graphene oxide (GO) [1].

Various studies have found that the addition of GO to a proton conducting polymer can enhance the performance of the material. Zarrin et. al. [1], Tseng et. al. [2] and Wang et. al. [3] have reported such results for Nafion, sulfonated polyimide (SPI) and polybenzimidazole. The level of oxide groups on the GO (Figure 1) makes it electrically insulating and offers high solubility in water, good interaction with the host polymer and at the same time good scope for chemical functionalisation [4]. The very large surface area makes it attractive as a nanoscale filler for composite membrane materials as it can largely increase the number of acid groups and hence positively influence the water uptake and retention capabilities. This has been proven in recent results by Zarrin *et. al.* [1] (Figure 2) where GO was functionalised with sulfonic acid groups, increasing the water uptake, ion exchange coefficient and single cell performance.
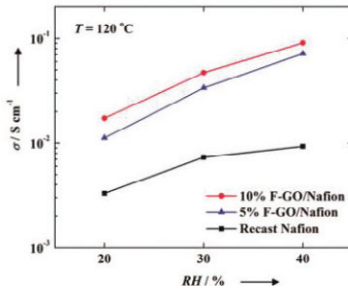


**Figure 2** Increased water uptake and IEC for functionalised GO doped Nafion membranes [1].

The current study investigates the effect of GO on the properties of commercial Nafion. This includes an investigation of ideal casting, purification and drying methods for GO composite membranes prepared with commercial Nafion® solution. The functionalisation and the effect of the size, concentration and orientation of filler particles in the polymer matrix will also be investigated.

Initial studies involved the preparation of a series of membranes using different solvents. Solvents with varying boiling points and dielectric constants were added to Nafion solution to evaluate the effect on the properties of the PEM. For each solvent, one membrane was prepared without GO filler as a reference and consecutive membranes were prepared with increasing loadings of GO. One control set was also prepared without any additional solvent. This series of PEMs were evaluated for water uptake (WU), ion exchange coefficient (IEC) and tensile properties. Thermal characteristics were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).
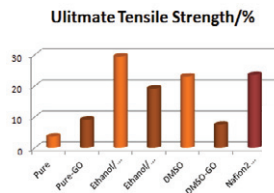


**Figure 3** Ultimate tensile strength measurements containing 5 wt% GO

The addition of GO lead to an increase in the ultimate tensile strength % of the pure-GO sample, but the samples with added ethanol/IPA and DMSO showed reduced strength. Further tests will be undertaken to confirm these data.
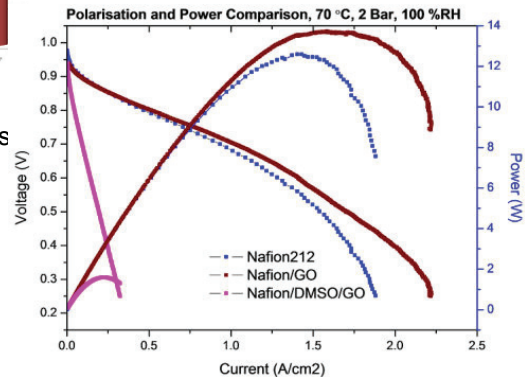


**Figure 4** Single cell performance of GO-doped pure Nafion (red), commercial Nafion 212 (blue) and GO-doped Nafion/DMSO (pink) membranes.

Single cell testing was undertaken using pure hydrogen and air (Figure 4). Membrane electrode assemblies (MEAs) were prepared using the recast membranes with commercial gas diffusion electrodes (GDEs) and were

compared to an MEA prepared with Nafion212.   The best single cell results to date were found for the pure-GO sample, this would however in some extent be due to the thinner thickness of the composite materials (~20 μm vs. ~50 μm) which would reduce the resistance.  The DMSO-GO sample (pink) showed poor performance, possibly due to a slightly lower water uptake than the pure-GO sample or uneven GO dispersal.

Further ex-situ and single cell testing is currently underway to confirm the reported findings and evaluate the remaining samples.

### References

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