Optimising milling of anion exchange ionomers for alkaline anion exchange membrane fuel cells

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Introduction

The persistent and unrestricted processing and consumption of fossil fuels over the previous century has resulted in an unforeseen, rapid rise in carbon dioxide levels within earth's atmosphere which has resulted in a rising average global temperature. Fossil fuels are also posing energy security dilemmas as their supply line is non-renewable. [1]

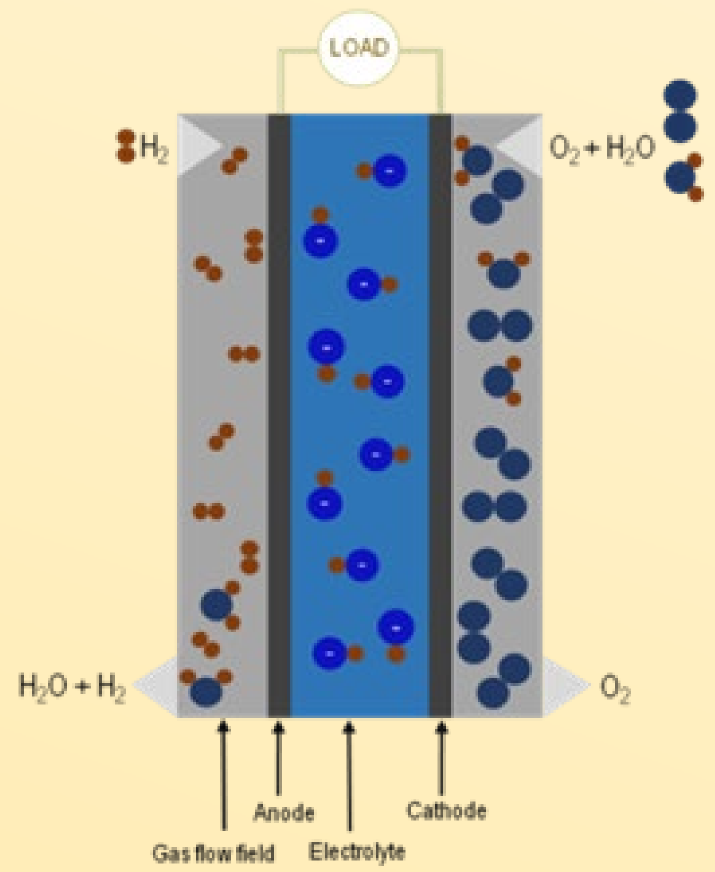
This predicament naturally lends itself to the growth and development of the renewable energy sector. Meanwhile, the majority of fossil fuel based machinery, systems, infrastructure, vehicles will be phased out by non-fossil fuel based alternatives such as battery powered and fuel cell systems.

How fuel cells operate

In the simplest of terms, fuel cells convert chemical energy, via redox reactions, into electrical energy using a chemical fuel such as hydrogen and oxygen in air. Their basic set up consists of an anode, a cathode, and an electrolyte junction, which form the membrane electrode assembly (MEA).

In the case of alkaline anion exchange membrane fuel cells (AAEMFCs) which are involved in this project, the ion being conducted is the hydroxide ion (figure 1). [2]

And the set-up consists of a polymer anion exchange membrane (AEM) film which conducts hydroxide ions in the electrolyte region and also polymer anion exchange ionomers (AEIs) powder which conduct hydroxide ions in the catalyst layer of the electrodes. [3]



$$2H_{2(g)} + 4OH^- \rightarrow 4e^- + 4H_2O_{(l)}$$

$$4e^- + 2H_2O_{(l)} + O_{2(g)} \rightarrow 4OH^-$$

Figure 1. Representation of an alkaline fuel cell in conjunction with redox equations

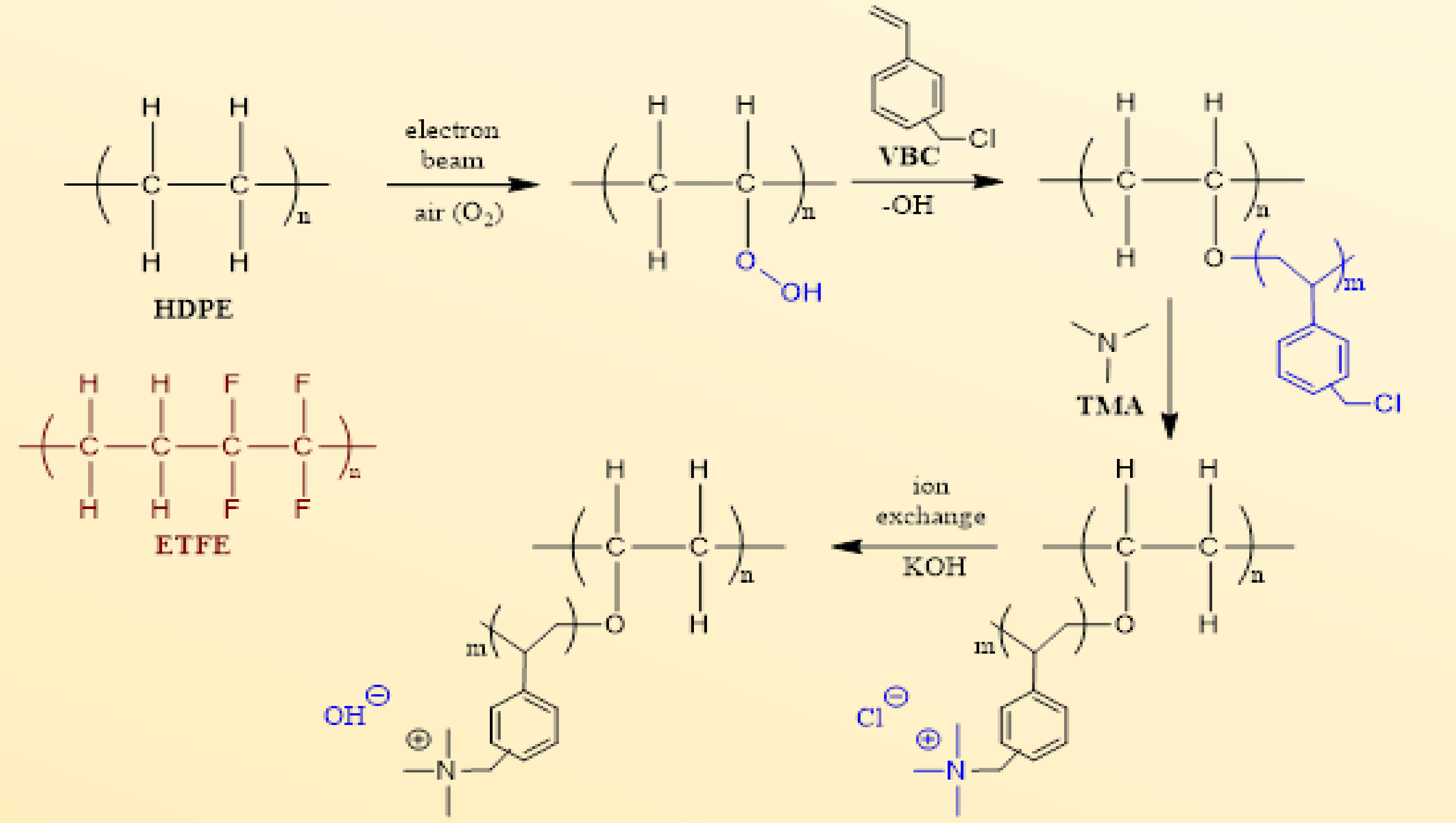
Project Aims

The aim of the project involves optimisation of new AEMFC electrodes containing radiation grafted AEI powders to achieve new benchmark performances. This aim will be met by:

- Establishing benchmark fuel cell performances with the use of the current state-of-the-art materials and electrode configurations;
- Analysing the differences in the performances of fuel cell electrodes containing anion-exchange ionomer powders of differing particle sizes and shapes (ground/milled using different methods);
- Investigating the differences in the performances of fuel cell electrodes containing the down-selected power/milling combination and different electrocatalysts

Radiation grafting and synthesis

The preparation of the AEI (as well as the AEM) begins with exposing the polymers to electron beam radiation which causes lesion of the C-H bonds to form radicals which react with air for form peroxides. These then undergo a grafting step with vinyl benzyl chloride (VBC) which displaces the –OH groups and subsequently polymerizes to form chains of poly VBC. Finally it is aminated with trimethyl ammonium (TMA) which replaces the chloride groups allowing the polymer to efficiently conduct anions. These polymers are stored with a chloride counter ion until used. [4]



Scheme 1. Outline of the synthesis of the HDPE-AEM sheets and ETFE-AEI (HDPE films replaced with ETFE powder)

Ongoing progress

The main aim of this project was to investigate different milling methods such as hand milling, ball milling and cryo-milling at different stages of the synthetic route to down-select the best method and stage to mill. So far it seems cryo-milling gives the best particle size distribution compared to the rest. This is likely due to the very low cryogenic temperatures which cause the polymers to become brittle and rigid allowing more efficient milling.

And grinding at the final step (after aminating) is also ideal as the particles agglomerate after each synthetic stage and therefore milling once at the final stage saves time. Milling at the initial stage before electron beaming was the worst in terms of reducing particle size effectively. In the subsequent final months of this project, these AEIs will be tested in fuel cells to establish their effects on fuel cell performance.

Finally, various analytical techniques were used including Raman spectroscopy, IR spectroscopy, SEM, DSC, and TGA to ensure the milling techniques were not degrading or altering the chemistry such as the crystallinity of the polymers.

References: [1] G. L. Foster, D. L. Royer and D. J. Lunt, Nature Communications, 2017, 8, 14845. [2] F. T. Bacon, Electrochimica Acta, 1969, 14, 569-585.. [3] S. D. Poynton, R. C. Slade, T. J. Omasta, W. E. Mustain, R. Escudero-Cid, P. Ocón and J. R. Varcoe, Journal of Materials Chemistry A, 2014, 2, 5124-5130. [4] L. Wang, J. J. Brink, Y. Liu, A. M. Herring, J. Ponce-González, D. K. Whelligan and J. R. Varcoe, Energy & Environmental Science, 2017, 10, 2154-2167.