Experimental report

06/03/2024

Proposal: **9-11-2088** **Council:** 10/2022

Title: Characterization of recycled perfluorosulfonic acid membrane for a circular hydrogen economy

Research area: Materials

This proposal is a new proposal

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Samples: NAFION

Instrument	Requested days	Allocated days	From	To
FIGARO	3	2	13/04/2023	15/04/2023
IN5	2	0		

Abstract:

Proton exchange membranes (PEM) are essential components of devices, where is required to transport H+ while blocking the flow of other ions and molecules used as reactants. They are typically ionomeric materials with the most common being perfluorosulfonic acid (PFSA) polymers known by the trade name Nafion®. Fuel cell lifetime is, however, curtailed by chemical and physical degradation; furthermore, with increased adoption of sustainable energy technologies, increased demand for PFSAs is forecast. All that translates into the necessity to recycle membrane components. Here we intend to study the structure of recycled Nafion and tested against the pure recast and degrade Nafion.

1 **PRINCIPAL INVESTIGATOR**
Name and institution of the Principal Investigator
Fabrizia Foglia - UCL

2 **EXPERIMENT DETAILS**	
Experiment No: 9-11-2088	
Title: *Characterization of recycled perfluorosulfonic acid membrane for a circular hydrogen economy*	
Instrument: FIGARO	
Dates scheduled:13/04/23-15/04/23	No. Days allocated: 3
Date of experimental report: 06/03/24	

3 **EXPERIMENT OBJECTIVES**

Ion transport is a critical element of energy conversion devices such as fuel cells (FC), water electrolysers and flow batteries. Perfluorinated sulfonic-acid (PFSA) ionomers, such as Nafion introduced by DuPont >50 years ago[1], are a class of ion-conducting polymers known for their remarkable ion conductivity and chemical and mechanical stability. PFSA ionomers are typically formed from a hydrophobic Teflon-like backbone with pendent hydrophilic sulfonic acid bearing side chains which phase separate to form a morphology with superior ion and water transport[2]. PFSAs are essential in both the proton exchange membrane (PEM), transporting H^+ ions between electrodes while blocking the flow of reactant gases and ions (H_2, O_2 and VO^-), and as thin, 2-50 nm films, coating catalyst particles in the electrodes for efficient electrocatalysis[3]. FC lifetime is, however, curtailed by chemical degradation from peroxides/radicals and physical degradation of pinholes and microcracks due to high temperature and low humidity operation[4].

With increased adoption of sustainable energy technologies, an increased demand for PFSAs is forecast as well as generation of increased quantity of used PFSA material. PFSA synthesis relies on precursors from non-renewable fossil fuel industries and requires reaction steps exceeding 500 °C. Current end-of-life technologies are based on hydrometallurgical and pyro-hydrometallurgical methods for the recovery of noble metal catalysts whilst generating corrosive and hazardous fluorine and HF gas from PFSA waste products[5]. Therefore, an approach to separate, regenerate and re-use the various material components of spent devices will establish a sustainable life cycle for hydrogen technologies, with environmental and economic benefits.

At UCL we have developed a low-cost solvent-based approach to extract PFSA from the carbon and platinum in degraded FC membrane electrode assemblies (MEAs) allowing both components to separately be regenerated. Through subsequent processing and assembly, the PFSA component can be incorporated into 2nd life FCs as the PEM or electrode ionomer with no deterioration in FC performance. Producing a recycled ionomer also has the potential to realise composite membranes as well as advanced fabrication methods, such as direct membrane deposition, due to the solution cast nature.

Whilst recast membranes achieved equivalent conductivities to pristine Nafion, reduced mechanical strength, despite similar crystallinity and chemical signatures, raise questions of atomic structure and molecular morphology. PFSA's chemical and mechanical properties are interrelated through their phase-separated morphology, where the transport properties are primarily due to the hydrated ionic domains, while the hydrophobic backbone provides the mechanical support. These features arrange at multiple length scales and thus a complete understanding of chemical changes requires approaches investigating different length scales. Degradation induced main chain or side chain scission or sulphonic anhydride crosslinking will affect the domain and crystallite morphology and result in modified transport processes. Structural and dynamical investigation are critical to reveal these changes.

[1] KA Mauritz & RB Moore, Chem. Rev. **104**, 4535 (2004); [2] A Kusoglu & AZ Weber, Chem. Rev. **117**, 987 (2017); [3] TAM Suter, et al, Nanomaterials **11**(10), 2530 (2021); [4] R Borup, et al, Chem. Rev. **107**, 3904 (2007); [5] L Duclos, et al, Green Chem. **22**, 1919 (2020).

4 EXPERIMENT REPORT

Sample membranes were prepared by spin coating ~20 nm films of Nafion, recycled Nafion and Fentons degraded Nafion on Silicon blocks. Reflectivity profiles were obtained at fixed RH between 0 – 100% in vapour generated from null match water (NMW) and D_2O. To investigate the internal morphology requires the NR profiles to be modelled. Initial multilayer attempts for Nafion are shown in Figure 1, but show complications when simultaneously fitting several isotopic contrasts of wet and dry films. Further investigation of the structure of thin film Nafion (GISAXS) are underway to help construct an accurate NR model that can be fit to the samples investigated here.

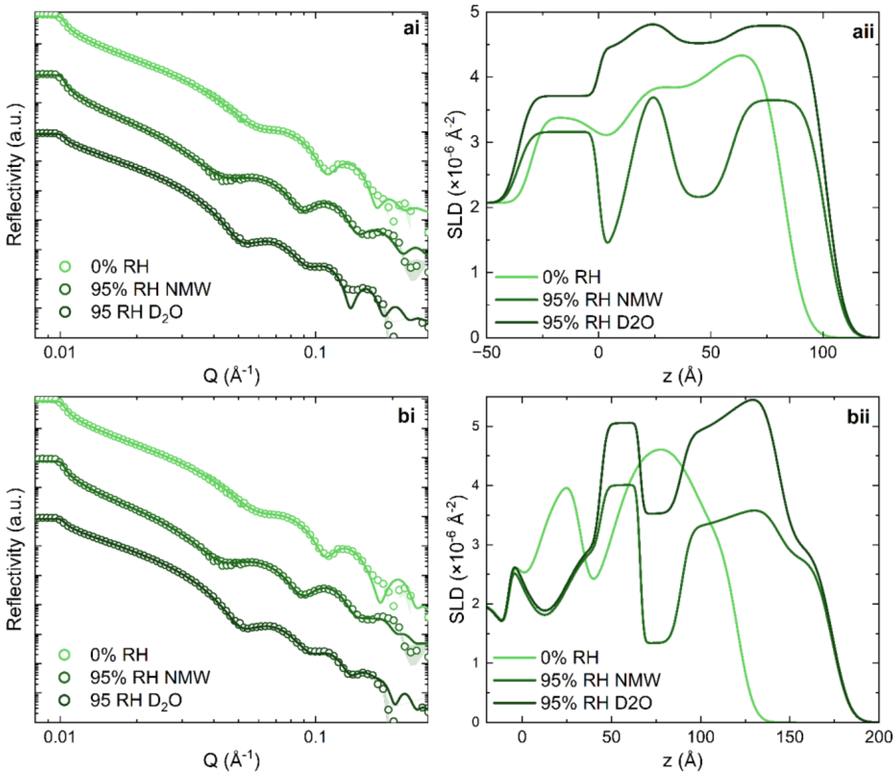

Figure 1. i) NR scattering experimental data of Nafion (circles) and ii) corresponding SLD profile using a) four-layer model fit and b) seven-layer model fit.

Corresponding dynamics investigation (WASP- ILL) will be used to improve our understanding of the structure-dynamics interplay. At the culmination of our investigation, we will be able to correlate fully analysed neutron scattering results with actual membrane performance data; this will offer us an opportunity to establish the link between molecular packing, dynamics and transport properties, for this important class of energy conversion materials.

5 LIKELY OUTCOMES FROM EXPERIMENT	
Journal publication	X
Follow-up experiment at ILL	X