# Experimental report

25/01/2024

**Proposal:** 9-11-2118 **Council:** 4/2023

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

**Research area:** Materials

**This proposal is a new proposal**


**Main proposer:** Fabrizia FOGLIA

**Experimental team:** Peter FOUQUET
Callum MARTIN
Andrew SEEL
Keenan SMITH
Fabrizia FOGLIA

**Local contacts:** Peter FOUQUET


**Samples:** NAFION

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| WASP | 5 | 3 | 07/11/2023 | 10/11/2023 |


## Abstract:

Perfluorinated sulfonic-acid (PFSA) ionomers, such as Nafion introduced by DuPont >50 years ago, are a superior class of ion-conducting polymers used in fuel cells and electrolysers due to their remarkable ion conductivity and chemical and mechanical stability. Fuel cell lifetime is, however, curtailed by chemical and physical degradation of the PFSA in the electrode and electrolyte membrane (amongst other mechanisms), which lead to unusable end of life cells. Furthermore, with increased adoption of sustainable energy technologies, increased demand for PFSAs is forecast. This translates into the necessity to recycle membrane components. Here we intend to study the water dynamics in degraded and recycled Nafion, as well as compare these to pure recast Nafion.

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

| 2 EXPERIMENT DETAILS | |
|---|---|
| Experiment No: 9-11-2118 | |
| Title: *Characterization of recycled perfluorosulfonic acid membrane for a circular hydrogen economy* | |
| Instrument: WASP | |
| Dates scheduled:7/11/23-10/11/23 | No. Days allocated: 3 |
| Date of experimental report: 25/01/23 | |

## 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 2$^{nd}$ 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 the previously described ultrasonic spray printing (USP). This procedure utilised ultrasonic waves to atomise, and deposit a continuous stream of Nafion and additive mix through a spraying nozzle. This fabrication technique provides a number of benefits over the standard solution casting method, including fine control over layer thickness to ensure all membranes had a uniform and reliable thickness of 50 µm. The water dynamics were assessed by WASP in fully $H_2O$-hydrated state (~18 water molecule per sulphonic group) at 5, 235, 250, 280, 300,330 and 353 K. These temperatures were chosen to probe dynamics of confined and bulk water, as well as temperatures relevant to those of an operating fuel cell, between 30 – 80 °C. This limited sample range was a result of only half of the requested beam time being allocated. In these conditions I(Q,t) follows a similar trend as predicted from the bulk conductivity measurements (degraded<recast~recycled). Quantitative analysis will be carried out using the most adapted models (jump diffusion, Fickian diffusion, confined diffusion), following the extensive work carried out on pure Nafion. Based on the bulk water nature within fully hydrated Nafion, further deviation could be probed using lower water contents that experience greater confinement.

Future measurements should thus be carried out on partially hydrated membranes (50% relative humidity; ~6 water molecule per sulphonic group). We have already performed some structural studies (on FIGARO - ILL) 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.

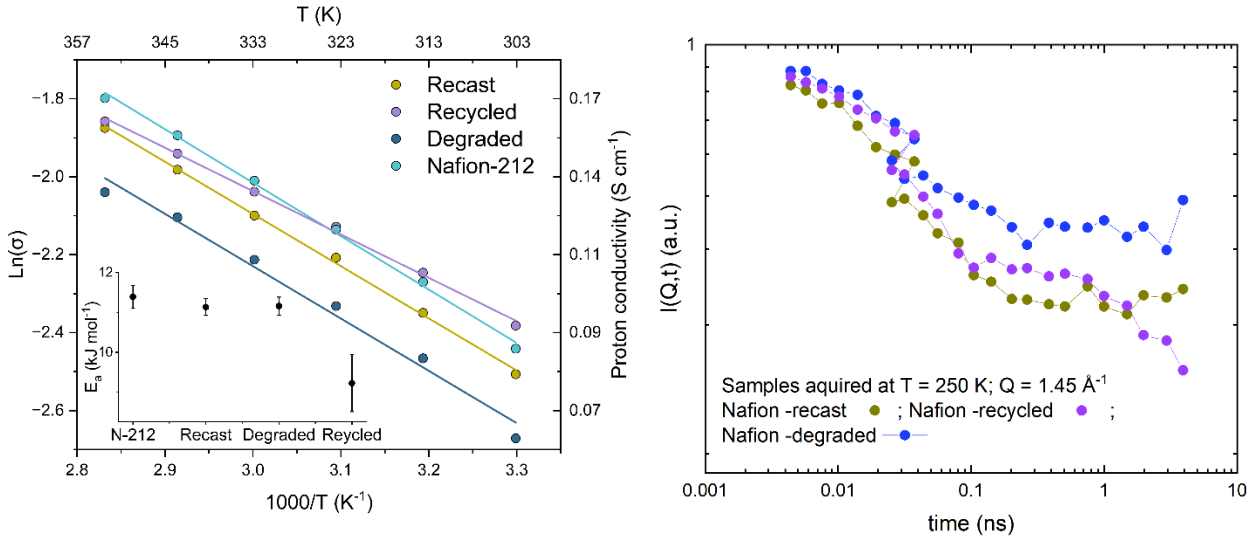


*Figure 1. Arrhenius-plots of proton conductivity of Nafion membranes and inset showing calculated activation energy of proton conduction. Intermediate scattering function obtained from WASP at Q=1.45 Å$^{-1}$ for fully hydrated membranes.*

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