Experiment Proposal

Experiment number GP2023086

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Co-investigator	Dr Tom Miller, University College London, UNITED_KINGDOM
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Co-investigator	
Co-investigator	
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Experiment title	Characterization of recycled perfluorosulfonic acid membrane for a circular hydrogen economy		
MRF Instrument	**Dynamic Mechanical Analyzer**	**Days requested:** 4	
Access Route	Direct Access	**Previous GP Number:** No	
Science Areas	Energy	**DOI:** -	
Sponsored Grant	None	**Sponsor:** -	
Grant Title	-	**Grant Number:** -	
Start Date	-	**Finish Date:** -	
Similar Submission?	ILL; for Figaro and Spin Echo		
Industrial Links	-		

Non-Technical 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) and 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 using the DMA instrument of the IM@IT Unit University of Rome Tor Vergata and the particle size analyser (international MRF) at UCL.

Publications

Nafion matrix and ionic domain tuning for high performance composite proton exchange membranes. Advanced Functional Materials, 2304061; 2023

Disentangling water, ion and polymer dynamics in an anion exchange membrane. Nature Materials 21 (5) 555; 2022

Foglia F, et al. Aquaporin-like water transport and nanoconfinement in nanoporous crystalline layered carbon nitride. Science Advances 6 (39), eabb6011; 2020

Internationa MRFs	**Particle Size Analyser**	**Days requested:** 2
ISIS neutron and muon source		**IM@IT E-platform:** No

Instruments	**Days Requested:**
Access Route	**Previous RB Number:**
Science Areas	**DOI:**
Sponsored Grant	**Sponsor:**
Grant Title	**Grant Number:**
Start Date	**Finish Date:**
Similar Submission?	
Industrial Links	

ISIS@MACH ITALIA

ISIS Neutron and Muon Source

Science and Technology Facilities Council

Sample record sheet

Principal contact	Mr Keenan Smith, University College London, UNITED_KINGDOM		
MRF Instrument	**Dynamic Mechanical Analyzer**	**Days Requested:** 4	
Special requirements:			

SAMPLE

Material	$C_7HF_{13}O_5S{\cdot}C_2F_4$	-	-
Formula	$C_7HF_{13}O_5S{\cdot}C_2F_4$	-	-
Forms	Solid		
Volume	cc		
Weight	100 mg		
Container or substrate	sample is thin-film	-	-
Storage Requirements	-	-	-

SAMPLE ENVIROMENT

Temperature Range	83 - 473 K	-	-
Pressure Range	- mbar	-	-
Magnetic field range	- T	-	-
Standard equipment	None	-	-
Special equipment	no	-	-

SAFETY

Prep lab needed	No	-	-
Sample Prep Hazards	no	-	-
Special equip. reqs	no	-	-
Sensitivity to air	No	-	-
Sensitivity to vapour	Yes	-	-
Experiment Hazards	no	-	-
Equipment Hazards	-	-	-
Biological hazards	no	-	-
Radioactive Hazards	no	-	-
Additional Hazards	-	-	-
Additional Details	-	-	-
Sample will be	Removed By User	-	-

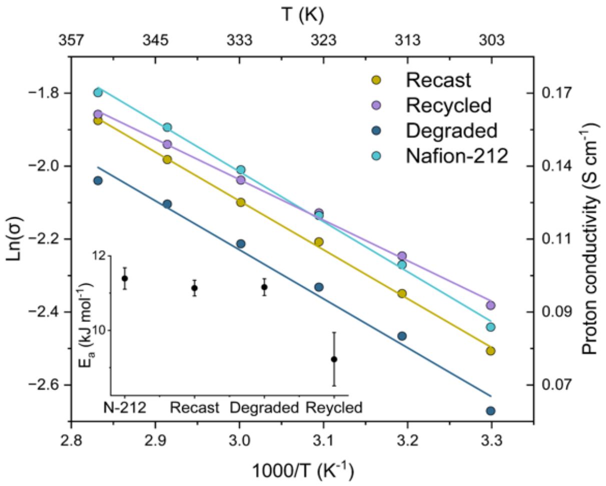
Characterization of recycled perfluorosulfonic acid membrane for a circular hydrogen economy

1. Background and Context

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 form PFSA waste pructs[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. Thin film confinement of Nafion on a substrate has been shown to induce anisotropic phase separation in plane, which has been used to understand morphological arrangement due to ionomer side chain length and EW[6]. 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.

We have already been performed time on FIGARO (ILL reflectometer; experiments were scheduled in April 2023) to study structural changes and got allocated time on WASP (ILL Spin Echo spectrometer; experiments are scheduled in November 2023) to investigate water dynamics within these membranes and, therefore, best understand the structure dynamics interplay. We now intend to extend our study using DMA 1 Star Systems – Mettler Toledo – to measure the mechanical and viscoelastic properties of our sample as a function of temperature, and relative humidity levels. This project is related to our work carried out within the EPSRC fellowship (EP/V057863/1).

2. Proposed experiment

We plan to perform experiments using the DMA 1 Star Systems – Mettler Toledo – available via ISIS@MACH to measure the mechanical and viscoelastic properties on recycled Nafion and compared these with untreated as well as degraded Nafion. Additionally, we wish to perform light scattering experiments using the Mastersizer Particle Size Analyser at UCL through the international MRF route. This will give insights into potential degradation processes of the Nafion materials.

3. Justification of experimental proposals request

Experiments will be performed on: i) pure recast Nafion; ii) FC degraded recycled Nafion (Nafion-FC); and iii) Fenton's reagent degraded Nafion (Nafion-FT) at low-hydration (λ~7; where λ represents the water uptake per sulphonic group). Based on the number of membranes (three) and conditions (6 Temperatures from 83 to 473 K at both λ~7 and ~18) to be investigated we plan for a Total: 36 samples; we therefore request a total of **4 days**. All samples will also be analysed using the Mastersizer at UCL. We request **2 days**, one day to establish this new technique and to determine the optimal experimental conditions for measuring our samples, and a second day for measuring the actual samples.

References:

[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);
[6] UN Shrivastava, H Fritzsche & K Karan, Macromolecules **51**, 9839 (2018).