IChemE Andrew Fellowship - Final Report

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Advancing Spatially-Resolved Magnetic Resonance Methods for Investigating Heterogeneous and Electrocatalytic Systems

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1. Introduction

The Andrew Fellowship, awarded by the IChemE in June 2021, supported a programme of research that combined magnetic resonance (MR) techniques with the challenges of heterogeneously catalysed and electrocatalytic systems. My work has spanned across both fundamental and applied studies, with the aim of developing new experimental methodologies and deriving insight into the properties of catalytic systems, particularly under conditions of confinement and electrical current.

The two major scientific directions pursued during the fellowship period were: (i) the application of spatially-resolved MR techniques to a working electrolysis cell, with a focus on imaging and quantifying transport properties of thin porous catalyst layers under applied current, and (ii) the use of MR diffusometry and relaxometry to study phase behaviour, droplet coalescence and wetting characteristics of emulsions of Fischer-Tropsch products confined within mesoporous catalyst supports.

These research directions share a common framework: both address how structure and confinement govern transport and phase behaviour in catalytic materials, and both apply non-invasive MR methods to probe dynamic, in-situ environments. Across both projects, a consistent focus has been on understanding spatial, compositional or structural heterogeneity, and the role it plays in defining system performance.

Through the development of experimental hardware, MR pulse sequences, and analytical frameworks, this work has established a set of methods that can now be applied to other multiphase, electrochemical or confined catalytic systems. The purpose of this final report is to summarise the technical achievements of the fellowship, the experimental results obtained, and the broader impact of the findings on catalysis and MR methodology.

2. Achievements

2.1 Magnetic Resonance Toolkit for Electrolysis Cells

Electrochemical devices such as electrolysers are composed of layered, multifunctional materials that operate under simultaneous ionic, electronic and fluid transport. Characterising transport across the thin catalyst and membrane layers, particularly when the device is operating, is difficult due to small signal volumes, interference from current and magnetic components, and geometric complexity; however this has recently become a vibrant area of research due to the clear impact electrolysers and batteries have towards achieving net-zero sustainable fuel production[1-3]. The goal of this project was to develop a test platform for applying MR techniques to operating electrolysers and to determine whether spatially-resolved MR parameters such as diffusivity, relaxation times, and signal intensity can be measured *in-operando*.

An electrolysis cell (the “E-cell”) was designed and constructed, in collaboration with redox.me and the electrochemical research department at Shell Energy Transition Campus Amsterdam (ETCA), to allow MR compatibility. The design was informed by practical considerations including minimising conductive surface area, achieving leak-tight sealing with thin catalyst and membrane layers, and permitting MR visibility in all three spatial dimensions. The final design consisted of a polyether ether ketone (PEEK) cell body with serpentine flow channels, tantalum electrical connections, FKM washers for compression, and removable graphite flow plates acting as current collectors.

CAD schematics and detailed layer descriptions are shown in Figure 1. The cell had external dimensions of 50 mm × 50 mm × 14 mm and a central catalyst region of <2 mm thickness. The primary challenge was to achieve sufficient SNR for thin layers (membrane, catalyst) within a system that also contains metals and conducts current.

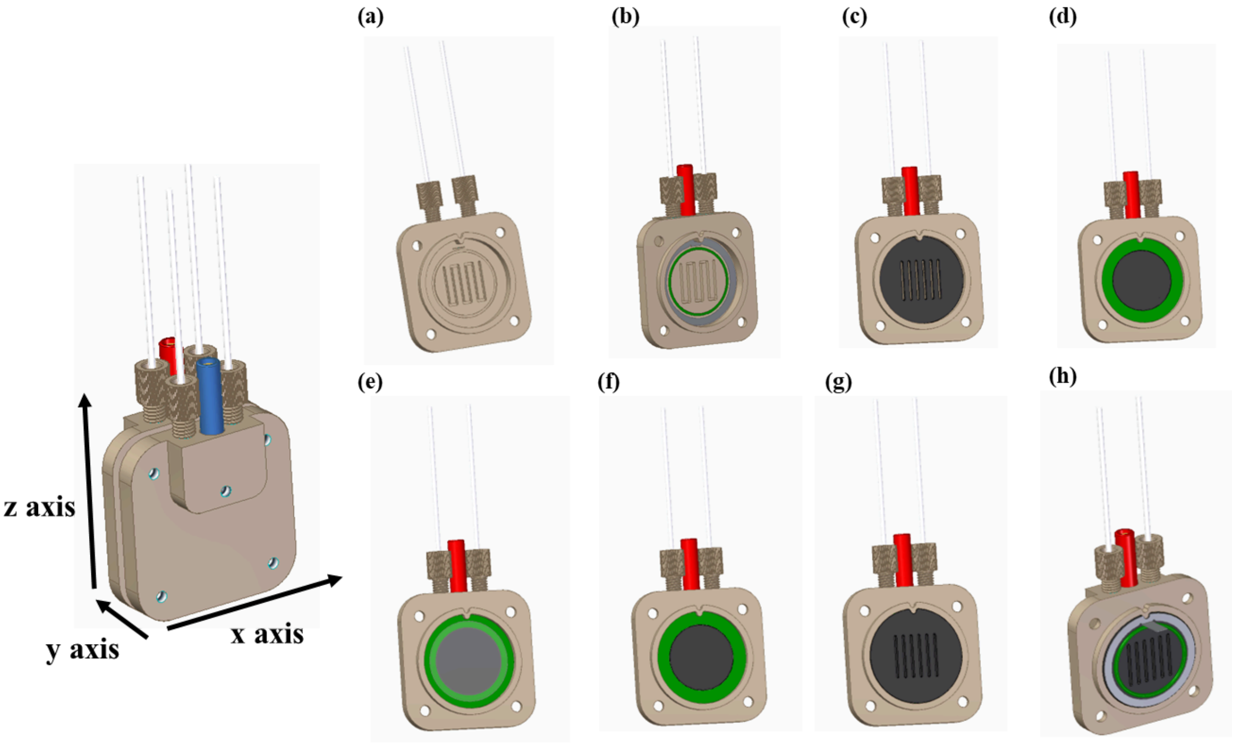

Figure 1: Computer-aided design schematics for the E-cell. (a). The cell body is made of polyether ether ketone (PEEK), and serpentine flow fields are machined into the cell body to allow imaging. (b). The electrical contact to the banana plug on the cathode side is made of tantalum. An O-ring is inserted to provide a leak seal. (c). The cathode side flow graphite flow plate is machined with cuts to match the flow fields in the PEEK body. This acts a current collector/distributor. (d). FKM washers allow compression control; the porous cathode electrocatalyst layer. (e). The polymer electrolyte membrane layer. (f). The porous anode electrocatalyst layer. (g). The graphite flow plate on the anode side. (h). The anode-side O-ring and tantalum contact.

To probe the system, the following pulse sequences were developed and optimised:

- **RARE imaging** for visualising flow channels and bubble formation,
- **2D CSI** for detecting chemical species and reaction products,
- **1D slice-selective diffusion (1D-D)** to extract spatially-resolved diffusion coefficients in the catalyst layer,
- **1D slice-selective T1 relaxometry (1D-T1)** to probe adsorption behaviour and heterogeneity,
- **2D velocity mapping** for flow profile quantification.

Pulse sequence selection was based on a balance between spatial resolution, time constraints, and expected SNR. Table 1 summarises the rationale for each sequence. All experiments were performed in a 300 MHz MR magnet using custom HPLC pump systems for fluid flow and standard DC power electronics to deliver stable electrical current.

E-cell characteristic	pulse sequence	reasoning
complex 3D geometry; different in all 3 dimensions	slice selective	all sequences to have spatial resolution capability in all 3 dimensions; all sequences to have slice selection
low SNR system due to thin (µm) catalyst and membrane layers and presence of conductive materials/metals	-	2D imaging only viable in flow field imaging; 1D profile imaging sequences for catalyst and membrane layers
electrolysis forms bubbles that are carried out in flow fields; bubble size is a key parameter in flow and mass transfer limitations	RARE (RApid imaging with Refocused Echoes)	high-resolution RARE imaging of flow fields should allow statistical determination of bubble sizes
Reaction progresses along length of flow field	2D CSI	2D CSI of flow fields will allow conversion calculation and identification of species present
mass transfer in electrocatalyst and membrane layer is rate limiting to the overall reaction	1D-D, 1D-T_1	1D-D sequence (diffusion imaging in 1 spatial dimension with slice selection in another) will provide diffusion coefficients and indicate any spatial heterogeneity in mass transfer, whilst 1D-T_1 (T_1 imaging in 1 spatial dimension with slice selection in another) probes surface interaction and will indicate any spatial heterogeneity in adsorption in the electrocatalyst and membrane layers

Table 1: Justification for the choice of selected pulse sequence based on the E-cell characteristic that the sequence is intended to probe

Half-Cell Experiments: Diffusion and T1 Imaging Under Current

A half-cell configuration was chosen to simplify interpretation, consisting of graphite plate/ Ag/C cathode/ graphite plate only, with no membrane or anode catalyst. Deionised water flowed through the system at 3 mL/min using two pumps in counter-flow. Current was applied at 200 mA cm^{-2}. Slice-selective profiles were obtained in both zero-current and current-on conditions.

The key findings were:

- Signal was clearly observed from the electrocatalyst layer in 1D slice-selective experiments, despite being undetectable in 2D imaging (Figure 2).
- A ~6 mm region of lower signal intensity in the centre of the catalyst was associated with lower diffusion coefficients and lower T_1 values (Figure 3).
- Electrical current increased the diffusion coefficient by approximately 10–15%, most likely due to local heating.

These data represent the first direct MR measurement of transport heterogeneity within a porous electrocatalyst layer under current. The spatial variations in T_1 and D suggest heterogeneous adsorption and restricted diffusion, potentially linked to microstructural features such as catalyst distribution or pore alignment. Importantly, the application of 200 mA cm^{-2} current did not prohibit signal acquisition, validating the methodology for future full-cell experiments.

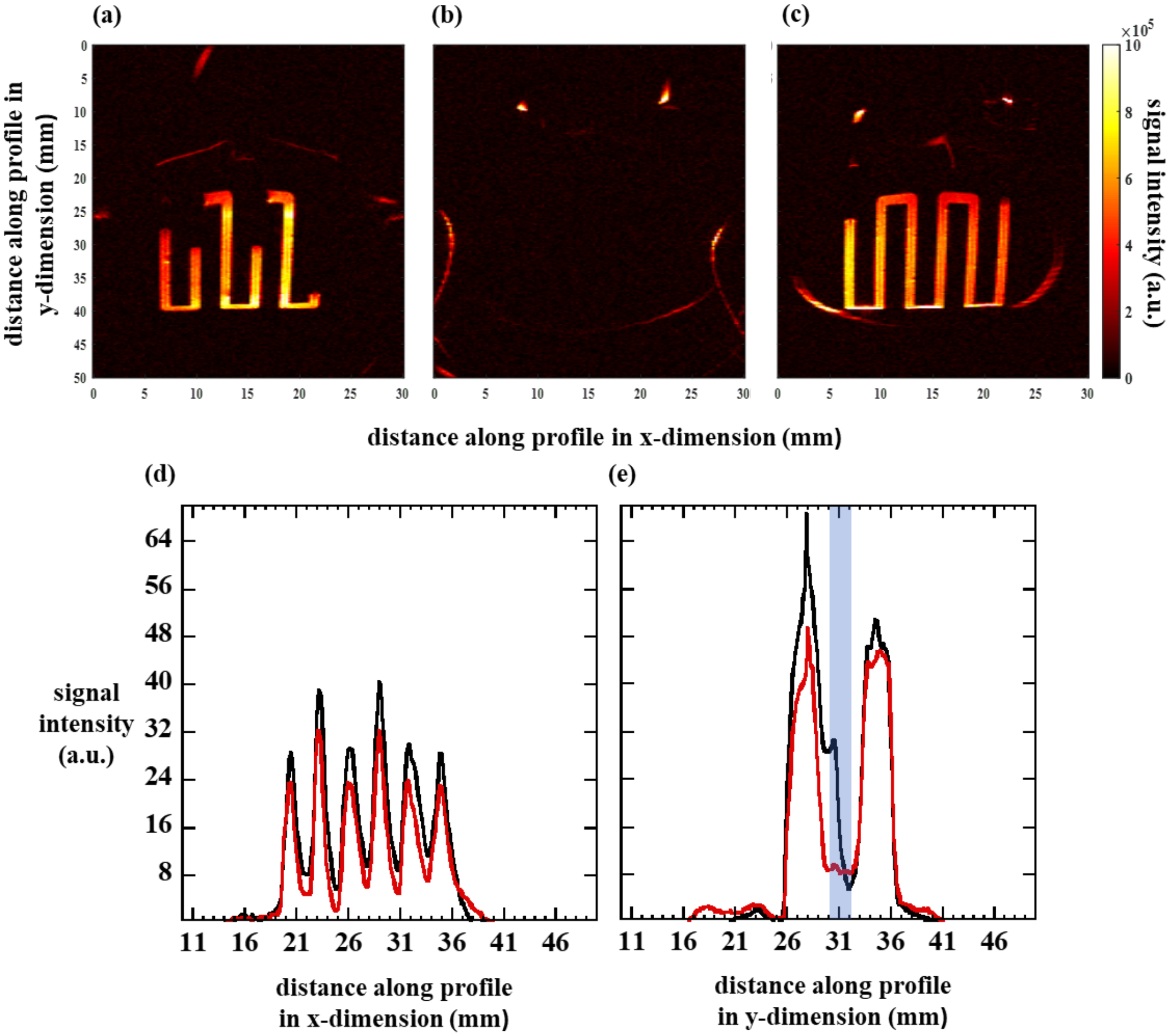

Figure 2: 2D xz signal intensity image of water flowing through the E-cell: (a). The anode side flow fields; (b). the catalyst layer and (c). The cathode side flow fields. Flow enters via the top left at the cathode side and the top right at the anode side. (d,e) are 1D image profiles of the E-cell under water flow in (c) the x-dimension and (b) the y-dimension. The thin blue shaded area indicates the 2 mm slice in the y-dimension taken to isolate signal from the electrocatalyst layer. The black lines are data from zero electrical current, and the red data are from 200 mA cm^{-2} current density.

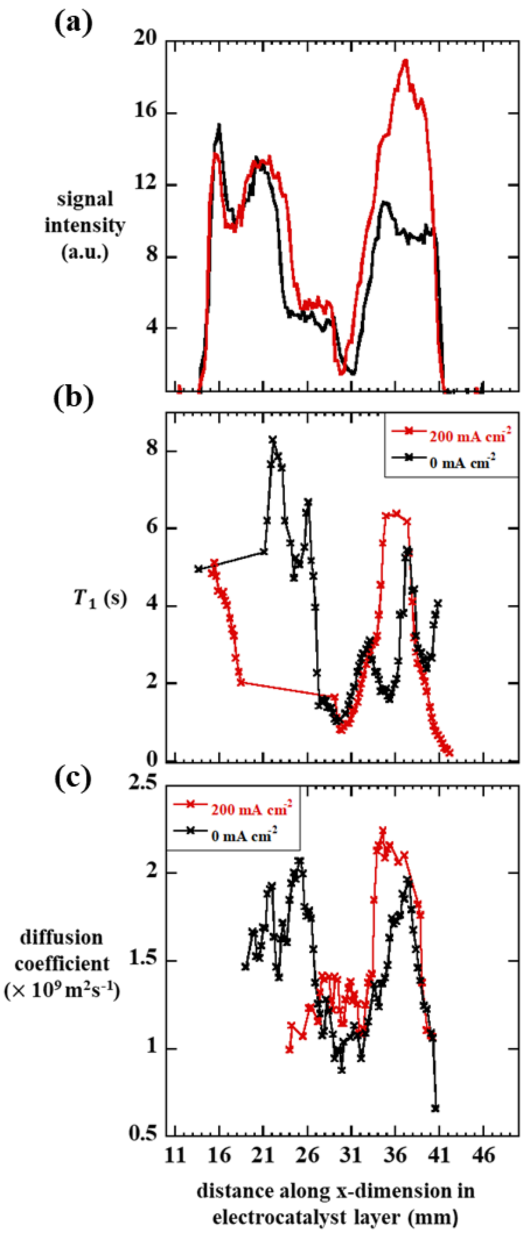

Figure 3: 1-D image profiles along the x-dimension of the (a) 1H signal intensity, (b) T1 relaxation time of water and (c) the diffusion coefficient of water measured in the electrocatalyst layer of the half cell. Black data is acquired under no electrical current and red data is acquired under a current density of 200 mA cm^{-2}. Both are acquired under water flow of 3 ml min^{-1}. Since the SNR of the acquired data was very low, presented in figs. 3b and 3c are running averages of the direct data, chosen to clearly represent the trend without obfuscation by the influence of noise. Where data is not present in a region that signal is expected, it has been removed as the SNR was too low to extract reliable parameters.

2.2 Emulsions of Fischer-Tropsch Products in Confined Mesopores

In Fischer-Tropsch (FT) catalysis, hydrocarbon-in-water emulsions may form within the mesopores of catalyst particles, particularly at high time-on-stream when water and long-chain hydrocarbons coexist. The phase behaviour[4,5] and dynamics of such emulsions under confinement had not previously been studied. This project aimed to understand how confinement in pores (14-39 nm) affects droplet size and surface wetting behaviour, and what implications these have for FT catalysis.

Binary (n-octacosane-in-water) and ternary (n-octacosane + stearic acid-in-water) emulsions were prepared and confined within silica spherules. MR measurements were carried out at 80°C using a 300 MHz magnet. Droplet size distributions were determined using the Alternating Pulsed-Gradient STimulated Echo (APGSTE) diffusion sequence and analysed via Tikhonov inversion coupled with the Murday-Cotts decay kernel for restricted diffusion in a sphere. Relaxometry was performed using inversion recovery sequences to obtain T_1 values, from which surface wetting behaviour was deduced[6,7]. APGSTE has been successfully used in prior work to disentangle the complex diffusion behaviour in highly-confining pore spaces[8,9].

Droplet Coalescence Induced by Confinement

Across the binary systems, droplet coalescence increased as pore size decreased. In 14 nm pores, only large droplets (modal radius > 2 μm) were present; in 39 nm pores, both small and large droplet populations were observed. This trend was amplified in the ternary systems containing stearic acid. The data indicate that the droplet sizes exceeded the pore diameters by over an order of magnitude and were not spherical, instead forming ganglia spanning multiple pores (Figure 4).

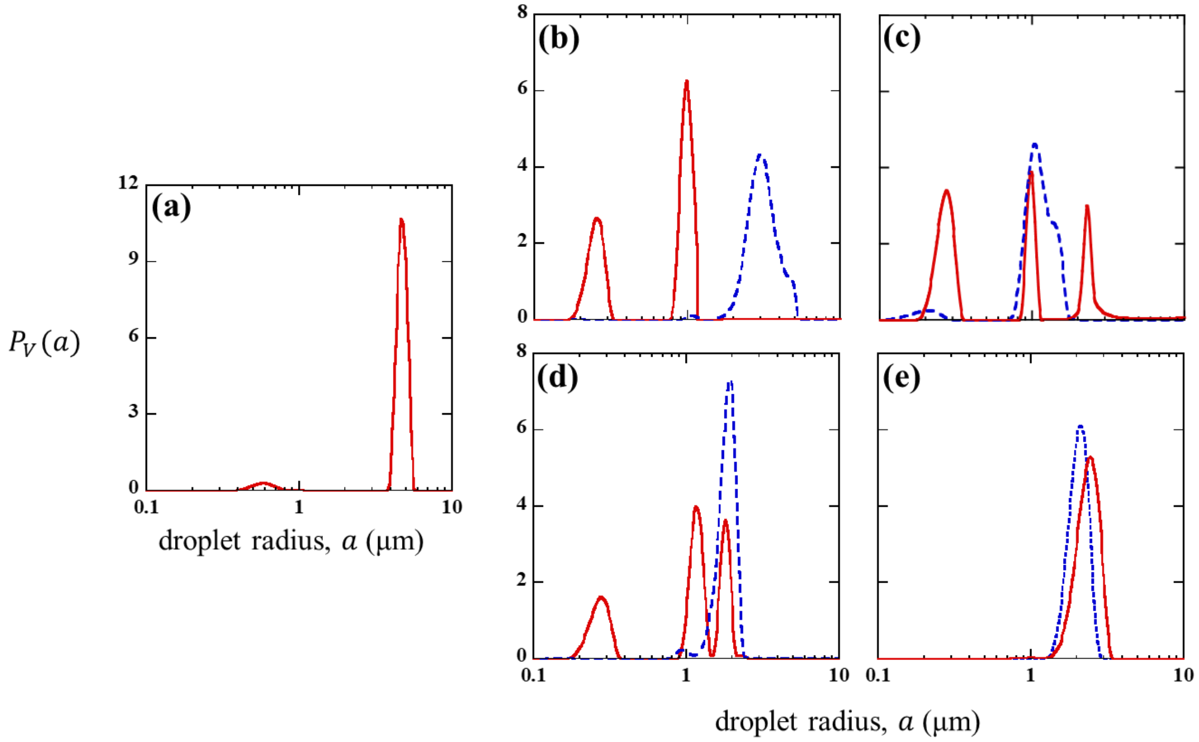

Figure 4: The volume-weighted droplet radius distributions for the discrete phase (*n*-octacosane) in the binary system (solid red line) and the discrete hydrocarbon phase (*n*-octacosane + stearic acid) in the ternary system (dashed blue line). (a). The bulk binary system. (b – e). The binary and ternary system confined in silica with pore diameters of: (b) – 39 nm; (c) – 27 nm; (d) – 20 nm and (e) – 14 nm. The distributions are an average taken from 3 APGSTE data sets on the same sample using an observation time Δ of 250 ms, 600 ms and 1000 ms, which were all sufficient to fully characterise the droplet size. Distributions are normalised such that the area is 1 using the base-10 logarithm of droplet radii.

Wetting Reversal in the Ternary System

Relaxometry results showed that in the binary system, water was always the wetting phase. However, in the ternary system, the wetting phase switched from hydrocarbon to water as the pore size decreased from 27 nm to 20 nm (Figure 5). This wetting reversal was not associated with chemical grafting of the stearic acid, as confirmed by ^{29}Si MAS NMR, but rather arose from a physical confinement effect. This is the first experimental demonstration of confinement-driven wetting reversal in mesoporous systems.

These findings imply that catalyst pore size strongly influences the internal phase behaviour of products in FT catalyst pores. In particular:

- Decreasing catalyst pore size and the presence of *n*-alkanoic acids significantly promote the coalescence of hydrocarbon droplets into larger entities within Fischer-Tropsch (FT) catalysts. This is consistent with a reduced selectivity to longer-chain hydrocarbons (C5+).
- In the presence of n-alkanoic acids, a novel wetting reversal occurring as pore size decreases implies increased catalyst deactivation in smaller FT catalyst pores due to the higher water content at the surface.
- The study demonstrates that variations in pore size are the direct cause of both observed droplet coalescence and wetting reversal, rather than changes in surface chemistry. This establishes pore size as a critical parameter for designing FT catalysts to control activity and selectivity.

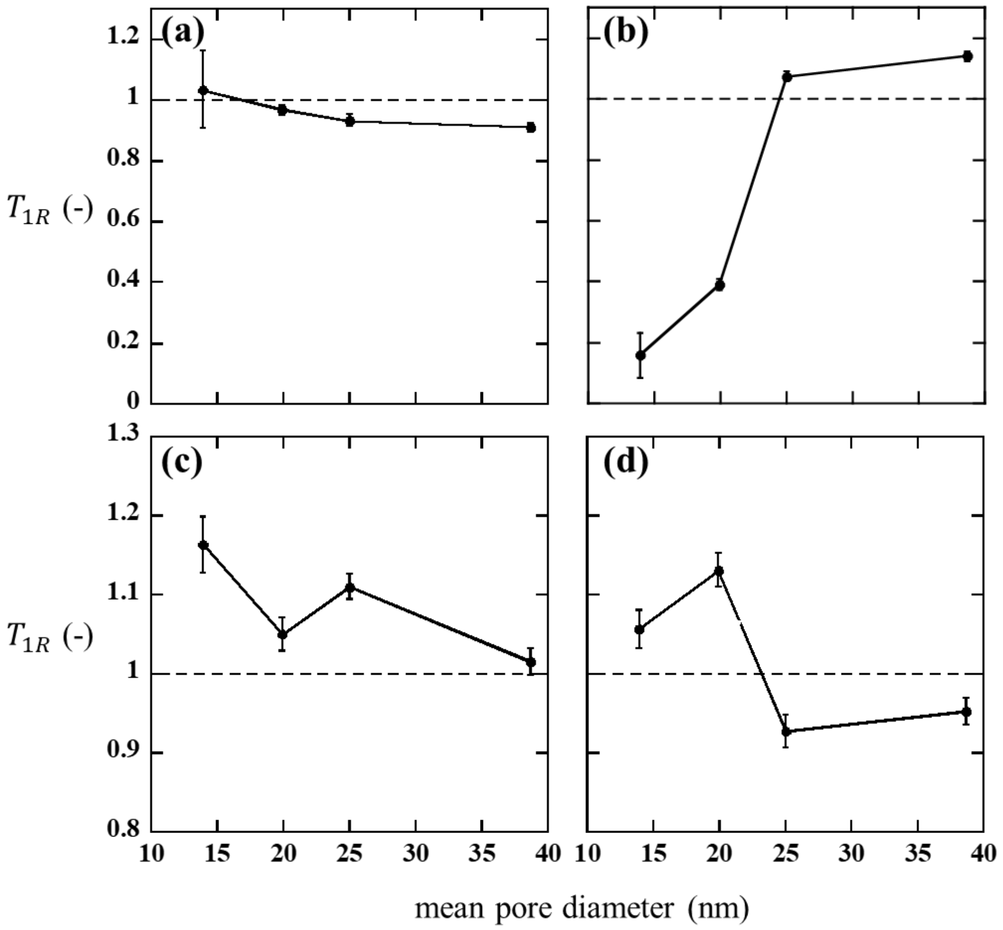

Figure 5: The variation of the spin-lattice relaxation time ratio T_{1R} of different phases of the confined emulsions. This ratio is equal to the value of T_1 of the liquid composing a phase when in an emulsion divided by the value of T_1 of the liquid composing the phase when it is present as a pure liquid in the same pore space. (a). The T_{1R} ratio of water (continuous phase) in the binary system (b). The T_{1R} ratio of water (continuous phase) in the ternary system (c). The T_{1R} ratio of *n*-octacosane (discrete phase) in the binary system. (d). The T_{1R} ratio of the discrete hydrocarbon phase (i.e. ^{1}H-weighted mixture of *n*-octacosane and stearic acid) in the ternary system. The error bars in the y-direction are the standard errors calculated from 3 repeat measurements on the same sample. A T_{1R} greater than 1 indicates the phase is located away from the pore surface; if this is less than 1, the phase is located adjacent to the pore surface.

3. Conclusion and Future Plans

The Andrew Fellowship has enabled the development and application of a novel suite of MR methodologies targeted at probing electrocatalysis and FT catalysis under realistic operational and confinement conditions. Through the design of a bespoke E-cell and the implementation of advanced MR sequences, it has been shown that transport parameters can be spatially resolved in electrocatalytic systems even during current flow. Work on emulsion systems aimed at simulating products inside FT pores has established the role of confinement in governing droplet dynamics and surface interactions, leading to the first direct observation of confinement-driven wetting reversal. It is hoped the methodologies developed during this work are used to further investigate FT with the aim of optimising synthetic fuel production, and for application to various electrolysis systems to improve design and drive towards sustainable hydrogen and carbon dioxide production.

Since January 2025, I have taken on the role of Head Engineer at Syntholene Energy, a US-based synthetic fuel startup focused on electrochemical hydrogen production and thermochemical conversion into sustainable liquid fuels. My work involves leading the design and build of a demonstration system, integrating heat and mass transfer infrastructure, and coordinating campaigns in Iceland. The insights and methodologies developed during the Andrew Fellowship have directly informed this work, particularly in guiding engineering design decisions with an emphasis on transport, reaction environments, and operando diagnostics.

References

1. Zhu, Z., Luo, R. & Zhao, E. W. Operando NMR methods for studying electrocatalysis. *Magn. Reson. Lett.* 4, 100096 (2024).
2. Jovanovic, S. *et al.* In operando NMR investigations of the aqueous electrolyte chemistry during electrolytic CO2 reduction. *Commun. Chem.* 6, 268 (2023).
3. Cao, S. H. *et al.* Operando magnetic resonance imaging for visualizing electrochemical triple-phase boundary. *Angew. Chem.* e202506183 (2025).
4. Zheng, Q. *et al.* Water-Wax Behaviour in Porous Silica at Low Temperature Fischer-Tropsch Conditions. *Appl. Catal. A, Gen.* 572, 142–150 (2019).
5. Papavasileiou, K. D. *et al.* Molecular Dynamics Simulation of the n-Octacosane-Water Mixture Confined in Graphene Mesopores: Comparison of Atomistic and Coarse-Grained Calculations and the Effect of Catalyst Nanoparticle. *Energy Fuels* 35, 4313–4332 (2021).
6. Bernewitz, R., Guthausen, G. & Schuchmann, H. P. NMR on Emulsions: Characterisation of Liquid Dispersed Systems. *Magn. Reson. Chem.* 49, S93–S104 (2011).
7. Johns, M. L. & Hollingsworth, K. G. Characterisation of Emulsion Systems using NMR and MRI. *Prog. Nucl. Magn. Reson. Spectrosc.* 50, 51–70 (2007).
8. Williams, J. *et al.* In Situ Determination of Carbon Number Distributions of Mixtures of Linear Hydrocarbons Confined within Porous Media Using Pulsed Field Gradient NMR. *Anal. Chem.* 92, 5125–5133 (2020).
9. Williams, J. H. *et al.* Probing the Diffusion Mechanism of n-Alkanes in Mesoporous Confinement Using Pulsed Field Gradient NMR. *J. Phys. Chem. C* 127, 15326–15335 (2023).