Notes on Completion: Please refer to the appropriate NIA Governance Document to assist in the completion of this form. The full completed submission should not exceed 6 pages in total.

NIA Project Registration and PEA Document

Date of Submission

Aug 2023

Project Reference Number

NIA_NGGT0190

Project Registration

Project Title

Composite membranes for H2 purification

Project Reference Number

NIA_NGGT0190

Project Licensee(s)

National Gas Transmission PLC

Project Start

August 2023

Project Duration

2 years and 8 months

Nominated Project Contact(s)

Helen Dugdale, box.GT.innovation@nationalgas.com

Project Budget

£72,666.00

Summary

Sustainable membrane-based technologies can cut the energy requirements, operational and capital costs by up to 50% for energy intensive processes such as H2 capture from methane.

Although polymer membranes dominate the gas separation market, controlling permeability/selectivity at high pressures is challenging. Recently mixed matrix membranes (MMMs), where an inorganic material embedded into a polymer matrix, have attracted attention as they can combine the functionality of the porous material with polymer processability.

Metal–organic frameworks (MOFs) that are comprised of metal ions connected by organic linkers, are the most promising ones due to their diverse and flexible structure.

This PhD application will explore the development of MOF/polymer MMMs, by increasing selectivity to enable membrane based H2 purification.

Third Party Collaborators

University of Nottingham

Nominated Contact Email Address(es)

Box.GT.Innovation@nationalgrid.com

Problem Being Solved

At present there is not enough research into new membrane materials that could disrupt the gas separation marketplace, traditional materials continue to be used which are expensive and can contain raw earth metals. This sponsored PhD application will address the following problem areas over the course of the 4 year application:

1. Determining the suitable Metal–organic frameworks (MOF) characteristics (pore size, volume and particle size)— synthesis, modification and drying procedures will be determined in order to increase the permeability and selectivity of the membranes while promoting particle-polymer interaction.

2. Poor interface properties of mixed matrix membranes (MMMS)— The major factor that defines the performance of MMMs is the compatibility of polymer and the particles. The interface between particles and polymer matrix directly affects the transport properties of MMM such as selectivity and permeability. There should be sufficient chemical interaction between phases to prevent void formation while avoiding any blockage of particle pores by polymer phase. Otherwise, selectivity drops as the permeating species bypass the particles.

3. Low polymer stability at high pressures— Usually rubbery polymers such as polydimethyl siloxane have been used as the continuous phase due to their high permeability. However, these polymers are not stable at high pressures as their polymer chains get loosen by the gas streams. Therefore, highly permeable more rigid glassy polymers will be explored as the polymer phase and their stability under high pressure gas streams containing, H_2 and CH_4 will be determined.

Method(s)

The PhD project will consist of a four (4) year study with the first year consisting of mostly lectures, literature review and early research, for the 2nd, 3rd and 4th years 90% of the student's time will be on project work with 10% on other activities. Following this the final report and PhD thesis will be created. The project will consist of 3 main stages:

Synthesis of Metal–organic frameworks (MOF)s

The goal is to synthesise crystals between 50-500 nm in size with various morphologies.

- Task 1.1 The development of synthesis, activation and drying protocols will be developed. This will include the use of mixed solvents, varying metal/linker ratio and synthesis time, giving exceptionally fine control over crystal size, porosity, morphology and stability.

- Task 1.2 We will explore the effect of pyrazine functionalisation, employing groups such as amines ($-NH_2$), which it is anticipated, will lead to enhanced CH_4 adsorption capacity and reduced pore size that may increase selectivity. By preparing MOFs doped with amino-pyrazine linkers, we will determine the limiting concentration of functional groups, where possible. We will also attach linker groups on external surface of MOF crystals to promote MOF-polymer binding during membrane fabrication.

- Task 1.3 Samples will be screened using a diverse range of characterisations. X-ray diffraction (XRD) is the first test of phase purity and crystal structure. Thermal gravimetric analysis (TGA) will allow us to measure the solvent residue in MOF crystals after activation and drying. Fourier Transform Infrared (FTIR) Spectroscopy of the samples will show the degree of functionalisation. Scanning electron microscopy (SEM) images will allow determination of crystal morphology and size. Adsorption isotherms of CO_2, CH_4, H_2 and water will be measured before and after activation and functionalisation of MOF crystals. Diffusion coefficients of gases will also be determined using a Hiden gravimetric sorption analyser.

Fabrication and Characterisation of MOF/Polymer mixed matrix membranes (MMMs)

· Task 2.1 Tuning the manufacture conditions of MOF-polymer MMMs. Flat sheet MMMs containing up to 50 wt% MOFs will be fabricated by solution-casting technique. We will use commercially available high flux glassy polymer Matrimid® 5218. Membranes will be dried in vacuum oven in order to remove the residual solvent. The thickness of dried membranes will be ~ 10-50 µm. We will tune the conditions via solvent/polymer ratio, solvent type and using Hildebrand solubility parameters to promote adhesion at the MOF-polymer interface, while exploring the solvent-particle, solvent-polymer and particle-polymer interactions for various MOF. Crystal agglomeration will be controlled using ultrasonic bath or low viscosity solvents such as acetone.

· Task 2.2 Interface characterisation and surface modifications. Task 2.1 will be tailored further for selected MOF structures. We will coat external surface of MOF crystals up to 20 nm thick Matrimid® layer in order to improve interaction at the interface. We will examine MOF-polymer compatibility and interfacial void spacing with spectroscopic (e.g., Atomic Force Microscopy) and computational methods. We will determine the effect of MOF type, crystal and pore size on defect formation. The information generated in this Task will be communicated with other tasks.

· Task 2.3 Characterisation of MMMs. Thickness of MMMs and MOF dispersion will be determined via SEM. Crystallinity of MOFs in films will be determined via XRD. TGA will allow evaluating the effectiveness of drying.

Single/Mixed Gas Separation Tests

Single/mixed gas separation tests of MMMs will be conducted using a gas flow system, where the gas compositions analysed using Gas Chromatography/Mass Spectroscopy. This system uses a membrane cell, which accommodates film sample up to 10 cm diameter. Inlet and exit gas streams and pressure are controlled by flow controllers, meters and pressure controller, respectively.

· Task 3.1 Development of analysis and calibration methods for GC/MS system. Initial tests using commercial membranes will start immediately. We will also modify the system by adding membrane cells running parallel to each other. This will allow us to test several membranes using the same control systems.

· Task 3.2 Mixed gas permeability and selectivity of MMMs. These will be evaluated at 20-40 oC and up to 40 bar pressure drop. Mixtures of CH4 and H2 in the ranges of 10-90% will be tested. We will compare permeability and selectivity of MMMs in order to determine the effect of manufacture and MOF/polymer types.

· Task 3.3 Revisiting separation performance in the presence of impurities e.g., water and H2S. These impurities will be included into mix gas streams to determine the stability and change in permeability/selectivity. Results will be evaluated to alter surface modifications.

· Task 3.4 Long-term performance of selected membranes. This will be determined at elevated temperatures (50 oC) to accelerate degradation in comparison to pure Matrimid® membrane.

Data Quality Statement (DQS): The project will be delivered under the NIA framework in line with the agreed Energy Networks Innovation Process document NGGT internal policies. Data produced as part of this project will be subject to quality assurance to ensure that the information produced with each deliverable is accurate to the best of our knowledge and sources of information are appropriately documented. All deliverables and project outputs will be stored on our internal SharePoint platform ensuring backup and version management. Relevant project documentation and reports will also be made available on the ENA Smarter Networks Portal and dissemination material will be shared with the relevant stakeholders.

Measurement Quality Statement (MQS): The project is rated low in the common assessment framework detailed in the ENIP document after assessing the total project value, the progression through the TRL levels, the number of project delivery partners and the medium level of data assumptions. No additional peer review is required for this project.

Scope

This project, for the first time, will explore the potential of Metal–organic frameworks (MOF) incorporated polymer membranes as a cheaper and more efficient alternative to metal membranes for H2 separation from CH4. We will demonstrate the methods for incorporation of nanosized MOFs e.g., SIFSIX and TIFSIX crystals, into polymers in order to utilise the excellent selectivity of MOFs. We will then determine the gas separation performance in terms of permeability and selectivity at the relevant industrial conditions e.g., pressure and mixture content. The influence of MOF structure and MOF-polymer interactions at the interface in determining the 'physicochemical properties' and 'gas separation performance' of MOF-polymer mixed matrix membranes (MMMs) will also be studied.

Whilst benefits to the consumer will be a long time to realise, it is recognised that research is needed in this area if the concept of gas separation on the gas networks is to become a reality. Gas separation or 'deblending' will have the potential to assist in the transition to cleaner fuels as it can be used to protect customers who aren't ready yet, whilst letting those are begin their transition.

Objective(s)

The objectives of the project stage of the PhD application are:

(i) synthesise and modify properties (e.g., particle and pore size) of ultramicropore MOF materials such as SIFSIX and TIFSIX series, to enhance their selectivity towards desired gas molecule(s).

(ii) determine the manufacturing conditions of MOF incorporated polymer flat sheet membranes by changing e.g., thickness, casting solvent and drying procedures.

(iii) understand and control interface interaction and defect formation in MMMs via MOF surface modification and characterisation techniques such as electron microscope.

(iv) test performance of MMMs for the separation of H2/CH4 and H2/CO2 mixtures in the presence of impurities where relevant up to 40 bar pressure drop, temperature range of 25-40 oC and using mixed gas streams.

(v) determine the long-term stability of the polymer phase under high pressure.

Consumer Vulnerability Impact Assessment (RIIO-2 Projects Only)

Not applicable to transmission projects as the effects of this PhD will not affect customers in vulnerable situations.

Success Criteria

We will evaluate the success of the project by the deliverables, outcomes and the objectives met alongside releasing a completed PhD thesis on the topic.

Project Partners and External Funding

Project split 50/50 between University of Nottingham and National Grid Gas Transmission.

University of Nottingham - £54,500 by EPSRC funding

National Grid Gas Transmission - £67,822.00

Potential for New Learning

The outcome of the project will create research papers, national/international conference presentations, stake holder events, CDT annual conference and mutual patents, where applicable. Besides contributing to the scientific knowledge on nanoparticles, mixed matrix membranes, separation performance of the membranes will be the outcomes.

Specific deliverables:

1. MOFs optimised for gas transport, with well-defined synthetic protocols and controlled particle size.

2. Manufacturing procedures for flat sheet MMMs with MOFs and detailed analysis and improvement techniques for interface properties.

3. Mixture gas permeability/selectivity and long-term stability data of flat sheet MMMs with an understanding the effect of impurities on performance.

The output from the project will also be discussed and presented at the annual dissemination conferences led by the energy networks and uploaded to the Smarter Networks Portal.

Scale of Project

As this is a PhD application the scale of the project is set based on the four year study program.

Technology Readiness at Start

TRL3 Proof of Concept

Technology Readiness at End

TRL5 Pilot Scale

Geographical Area

University of Nottingham, Engineering laboratories (University Park) and Research Acceleration & Demonstration Building (Jubilee Campuses), Nottingham

Revenue Allowed for the RIIO Settlement

N/A

Indicative Total NIA Project Expenditure

£72666

Project Eligibility Assessment Part 1

There are slightly differing requirements for RIIO-1 and RIIO-2 NIA projects. This is noted in each case, with the requirement numbers listed for both where they differ (shown as RIIO-2 / RIIO-1).

Requirement 1

Facilitate the energy system transition and/or benefit consumers in vulnerable situations (Please complete sections 3.1.1 and 3.1.2 for RIIO-2 projects only)

Please answer **at least one** of the following:

How the Project has the potential to facilitate the energy system transition:

It is viewed that the concept of gas separation and deblending will be very important in the energy system transition. This technology could allow customers to still receive the gas composition they need even if they are not able to accept higher concentrations of hydrogen in the short term. This will allow National Grid to introduce higher levels of hydrogen into the national transmission system (NTS) as we transition to green gases and still provide 100% natural gas to a customer if required. By driving down the cost of gas separation equipment by using new materials the technology will be more accessible and there would be a higher level of adoption, this could further assist during the energy transition.

How the Project has potential to benefit consumer in vulnerable situations:

N/A

Requirement 2 / 2b

Has the potential to deliver net benefits to consumers

Project must have the potential to deliver a Solution that delivers a net benefit to consumers of the Gas Transporter and/or Electricity Transmission or Electricity Distribution licensee, as the context requires. This could include delivering a Solution at a lower cost than the most efficient Method currently in use on the GB Gas Transportation System, the Gas Transporter's and/or Electricity Transmission or Electricity Distribution licensee's network, or wider benefits, such as social or environmental.

Please provide an estimate of the saving if the Problem is solved (RIIO-1 projects only)

N/A

Please provide a calculation of the expected benefits the Solution

At this early research stage, it is unknown what the expected savings will be although if these new materials can avoid the use of rare earth metals currently employed in some membrane technology then there is significant scope to reduce the cost of this technology which can be passed onto the consumer.

Please provide an estimate of how replicable the Method is across GB

Gas separation and deblending technology can be employed at every customer connection of the National Transmission System, including industrial and distribution offtakes.

Please provide an outline of the costs of rolling out the Method across GB.

Further work will be required with the OEMs of deblending technology to build up a cost of rolling out this technology across GB. This PhD will not focus on this aspect, instead focusing on the materials in the membranes themselves.

Requirement 3 / 1

Involve Research, Development or Demonstration

A RIIO-1 NIA Project must have the potential to have a Direct Impact on a Network Licensee's network or the operations of the System Operator and involve the Research, Development, or Demonstration of at least one of the following (please tick which applies):

☑ A specific piece of new (i.e. unproven in GB, or where a method has been trialled outside GB the Network Licensee must justify repeating it as part of a project) equipment (including control and communications system software).

☐ A specific novel arrangement or application of existing licensee equipment (including control and/or communications systems and/or software)

☐ A specific novel operational practice directly related to the operation of the Network Licensees system

☐ A specific novel commercial arrangement

RIIO-2 Projects

☑ A specific piece of new equipment (including monitoring, control and communications systems and software)

☑ A specific piece of new technology (including analysis and modelling systems or software), in relation to which the Method is unproven

☐ A new methodology (including the identification of specific new procedures or techniques used to identify, select, process, and analyse information)

☐ A specific novel arrangement or application of existing gas transportation, electricity transmission or electricity distribution equipment, technology or methodology

☐ A specific novel operational practice directly related to the operation of the GB Gas Transportation System, electricity transmission or electricity distribution

☐ A specific novel commercial arrangement

Specific Requirements 4 / 2a

Please explain how the learning that will be generated could be used by the relevant Network Licensees

Research and learning in this area can be used by all of the gas distribution networks as gas separation and deblending could be a technology employed on the distribution network as well to protect their larger customer offtakes. The technology will also be of interest to European and wider Transmission Operators.

Or, please describe what specific challenge identified in the Network Licensee's innovation strategy that is being addressed by the project (RIIO-1 only)

N/A

Is the default IPR position being applied?

☑ Yes

Project Eligibility Assessment Part 2

Not lead to unnecessary duplication

A Project must not lead to unnecessary duplication of any other Project, including but not limited to IFI, LCNF, NIA, NIC or SIF projects already registered, being carried out or completed.

Please demonstrate below that no unnecessary duplication will occur as a result of the Project.

In order for the PhD application to be successful a duplication check will be performed to ensure it has not been tried before. A literature review will also be completed in the first year to build on the knowledge gained to date. As gas separation is being looked at from a transmission perspective, no gas distribution companies have carried out research in this area.

If applicable, justify why you are undertaking a Project similar to those being carried out by any other Network Licensees.

N/A

Additional Governance And Document Upload

Please identify why the project is innovative and has not been tried before

In order for the PhD application to be successful a duplication check will be performed to ensure it has not been tried before. A literature review will also be completed in the first year to build on the knowledge gained to date. As gas separation is being looked at from a transmission perspective, no gas distribution companies have carried out research in this area.

Relevant Foreground IPR

N/A

Data Access Details

The data created as part of this project will be spreadsheets (results, ".xlsx", <50 MB), figures/images (samples/documents, “.PNG", <100MB) and third-party software outputs (results from sample characterisation, ".CSV", <50MB). The documentation/dissemination of the outputs will be presented in ".PDF".

In this project, University of Nottingham (UoN)-provided storage: Microsoft (MS) OneDrive will be used. This service provides up to 5TB free service. This is an ISO 27001 information security management compliant service that allows secure and controlled sharing of data. OneDrive encrypts data both in transit and at rest and is approved against the University’s Data Policy.

Research data created will be deposited in Zenodo repository that will store and maintain the data. The data will be made available at the end of October 2026. In the case of publications produced before this date, the relevant data will be made available at the time of publication. The data will be stored on the UoN supervisor’s OneDrive account.

Our dataset does not contain any personal information and thus will be shared via the Zenodo repository data archive. The original data will be publicised via a Data Access Statement in published outputs by including relevant dataset DOIs, via conference presentations and materials produced during the project.

Some commercially valuable data will be made publicly available after IP exploitation. In these cases, the commercially sensitive data will be stored in accordance with the above practices but will not be made publicly available immediately.

The UoN supervisor will be responsible for ensuring data is made publicly available, where applicable, using the Zenodo repository and appropriate DOIs are cited in all related publications and presentations of the project work.

Please identify why the Network Licensees will not fund the project as apart of it's business and usual activities

Business as usual activities for National Grid Gas Transmission currently focus on the transportation of natural gas only and do not include anything hydrogen or future of gas related and so this research cannot be funded by the business.

Please identify why the project can only be undertaken with the support of the NIA, including reference to the specific risks(e.g. commercial, technical, operational or regulatory) associated with the project

The support of NIA funding is required for this project as there is a risk that gas separation technology will either not be required on the transmission network or be too expensive and so prohibitive and not attract the required investment needed. Research such as this PhD thesis will help to reduce the cost of gas separation in the future and help to lower the risk of this technology not being used.

This project has been approved by a senior member of staff

☑ Yes