

University of Leicester PhD studentship

Funding Source: CENTA DTP

Proposed start date: 23rd September 2024

Closing date for applications: See our web page

Eligibility: UK/International

Department/School: Chemistry

Supervisors: **PI: Dr Sandy Kilpatrick**, School of Chemistry, University of Leicester, afrk1@le.ac.uk

Co-I: Dr Phil Bird, Argo Natural Resources (trading as Descycle)

Co-I: Prof. Karl Ryder, Centre for Sustainable Materials Processing, University of Leicester, k.s.ryder@le.ac.uk

Project Title: Carbon capture and utilisation (CCU), Sustainable resources, Renewable energy.

Project Description:

Project Highlights:

- Utilisation of compounds derived from metal waste recycling directly in catalysis, to progress towards a circular economy.
- Development of greener electrolyte systems using Deep Eutectic Solvents (DES), to reduce waste and pollution.
- Testing catalyst systems for CO₂ capture and conversion to high-value products, powered by renewable electrical energy.

Overview:

Carbon dioxide (CO₂) levels on Earth have reached an all-time high, and mitigating anthropogenic (man-made) climate change is a defining challenge of our era. However, the global economy and our society are critically dependent on fossil fuels, which meet 80% of the world's energy demands and feed the production of 95% of all chemical commodities, we rely on in our everyday lives. Nature uses CO₂ as its primary one-carbon building-block for biomass and now the chemical industry is beginning to realise its potential as a cheap, renewable feedstock for the production of vital chemicals.

Conversion of CO₂ is challenging as the molecule is chemically very stable, and a vast energy input is required to make it react. Catalysts are needed to lower this energy barrier and transition metals (such as copper and nickel) present the best sites for CO₂ activation. However, mining of these metals has significant environmental impacts which need to be addressed for a truly sustainable process to be developed at scale. Furthermore, although an overwhelming number of catalysts have been developed to generate one-carbon products from CO₂, there are very few examples in which multi-carbon (C₂₊) products are formed. This presents an opportunity with massive potential impact for the sustainable chemicals industry, since 2-carbon compounds like ethylene present the best trade-off between high economic value and a reduction in global warming potential, if they could be produced from CO₂ using renewable electrical energy.

Altering the composition of the solvent-electrolyte media is one of the main approaches for improving overall catalyst efficiency in the electrochemical CO₂ conversion. Ionic liquids (ILs) are

promising in this regard, but there are issues with their ecotoxicity and non-biodegradability. Natural deep eutectic solvents (DES) present a more sustainable alternative to ILs in that they are non-toxic, and highly bio-compatible. DES have been successfully applied in metal-catalysed and biocatalysed reactions, however, their potential in the catalytic conversion of CO₂ to high-value chemicals has yet to be realised.

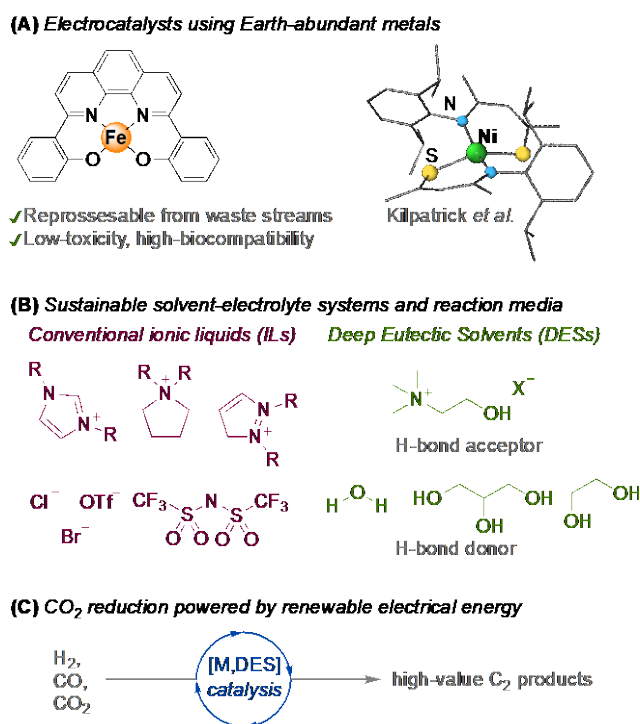


Figure 1. Harnessing renewable energy with captured CO₂ for the chemical value chain.

Methodology:

The student will carry out synthesis and characterisation of catalysts based on Earth-abundant metals in the Kilpatrick group laboratories (Figure 1A). The potential for recovering the active metals (e.g. nickel, iron) from primary mining waste streams will be investigated.

Deep Eutectic Solvents (DES) will be investigated as a more “green” solvent-electrolyte media, while maintaining high catalyst efficiency and stability (Figure 1B). The performance of DES in catalytic CO₂ conversion will be probed via analytical and bulk electrochemical experiments. Initial studies will employ known molecular catalysts, in combination with DES, both neat and as an additive in various solvents (water, acetonitrile, propylene carbonate, 2-(2-ethoxyethoxy)ethanol).

This CENTA project aims to validate a hypothesis that by creating an increased local CO₂ concentration and stabilising key intermediates, carbon-carbon bond forming reactions will be promoted. Accordingly, a new class of sustainable catalysts for the conversion of CO₂ into economically valuable C₂⁺ products will be developed (Figure 1C).

References:

Chen, Y. and Mu, T. (2019) ‘Conversion of CO₂ to value-added products mediated by ionic liquids’, *Green Chemistry*, 21(10), pp. 2544–2574. doi: 10.1039/c9gc00827f.

Grim, R. G. et al. (2020) ‘Transforming the carbon economy: Challenges and opportunities in the convergence of low-cost electricity and reductive CO₂ utilization’, *Energy and Environmental*

Science, 13(2), pp. 472–494. doi: 10.1039/c9ee02410g.

Smith, E. L., Abbott, A. P. and Ryder, K. S. (2014) 'Deep Eutectic Solvents (DESs) and Their Applications', *Chemical Reviews*, 114(21), pp. 11060–11082. doi: 10.1021/cr300162p.

Vasilyev, D. V *et al.* (2019) 'A General and Facile Approach for the Electrochemical Reduction of Carbon Dioxide Inspired by Deep Eutectic Solvents', *ChemSusChem*, 12(8), pp. 1635–1639. doi: 10.1002/cssc.201900579.

Zhang, J. *et al.* (2023) 'Molecular tuning for electrochemical CO₂ reduction', *Joule*, 7(8), pp. 1700–1744. doi: 10.1016/j.joule.2023.07.010.

Funding details:

NERC CENTA studentships are for 3.5 years and are funded by NERC. In addition to the full payment of your tuition fees, you will receive the following financial support:

- Annual stipend, currently set at £18,622 (2023/4 – new figures to be confirmed spring 2024)
- Research training support grant £8,000 (RTSG)

If you are not eligible for UK Fees the University of Leicester will fund the difference between UK and International fees for the duration of your studies

For more details of the CENTA consortium please see the CENTA website: www.centa.org.uk.

Entry requirements:

Applicants are required to hold/or expect to obtain a UK Bachelor Degree 2:1 or better in a relevant subject.

The University of Leicester English language requirements apply where applicable.

Application advice:

To apply please refer to our web page for further information and read carefully the How to Apply section before submitting your application

<https://le.ac.uk/study/research-degrees/funded-opportunities/centa-phd-studentships>

In the funding section please specify that you wish to be considered for **Ref CENTA2-CHEM2-KILP**

In the proposal section please provide the name of the supervisors and project title (a proposal is not required)

Project / Funding Enquiries to: CENTA@le.ac.uk or afrk1@le.ac.uk

Application enquiries to pgradmissions@le.ac.uk