Version June 2020

Sustainable Energy Authority of Ireland

National Energy Research, Development & Demonstration Funding Programme

FINAL REPORT TEMPLATE

SECTION 1: PROJECT DETAILS – FOR PUBLICATION

Project Title	LOHcell – Simplified on-demand utilisation of renewable energy stored by a virtual hydrogen carrier
Lead Grantee (Organisation)	Dublin City University (DCU)
Lead Grantee (Name)	Dr Michael Brandon
Final Report Prepared By	Dr Michael Brandon
Report Submission Date	28/02/2023

	Name	**Organisation**
Project Partner(s)	Dr Mary Pryce	DCU
Collaborators		

Project Summary (max 500 words)

A smooth transition from fossil fuels to renewables is complicated by frequent mismatch between the times and locations of maximum renewable energy generation, and end-user demand. Accordingly, long-term targets set by policy makers for decarbonising the energy and transport sectors are dependent on advances in energy storage technology. The conversion of electricity to ‘green’ hydrogen via water electrolysis is commonly presented as part of the solution, since the energy can be readily recovered when required. However, implementation is frustrated by difficulties related to the storage, handling and transport of gaseous hydrogen.

This project sought to circumvent this by exploring a variation on the emerging concept of hydrogen storage using organic liquid media. Electrolytically generated hydrogen can be reacted with unsaturated forms of certain organic liquids to form hydrogen rich, *Liquid Organic Hydrides (LOHs)*. LOHs can be stored and transported with the infrastructure currently used for gasoline, and reconverted to hydrogen (thermal dehydrogenation of the LOH) for subsequent conversion to electricity. However, the efficiency and practicality of this scheme would be improved if LOHs could be directly converted to electricity, without the need for first reverting to hydrogen (i.e. electrochemical dehydrogenation).

Our project sought to accomplish this through a *Direct LOH Fuel Cell*, which produces electricity while simultaneously regenerating the unsaturated liquid. Previous attempts to realise this vision have been hampered by the inadequacy of traditional, metal nanoparticle-based fuel cell catalysts. For this reason, we investigated the possibility of utilising molecular catalysts based on N4-metallomacrocycles to achieve the electrochemical oxidative dehydrogenation of LOHs. The main objectives of the project were therefore to; 1) identify a catalyst or catalysts capable of the electrochemical dehydrogenation of an LOH or LOHs, and; 2) to demonstrate the performance of such a catalyst under membrane fuel cell conditions.

During the course of the project a variety of N4-macrocycle molecules with a range of metal centres were synthesised. These were successfully immobilised onto carbon powder support materials to form candidate *N4-M/C* electrocatalyst materials. Initial laboratory testing with liquid electrolytes revealed that several of the candidate catalysts were capable of affecting oxidative dehydrogenation of alcohol based LOHs under alkaline conditions. This is a significant result since a very limited number of N4-macrocycle catalysts have previously been shown to be active for electrochemical oxidation reactions. It was observed that one particular (and previously unreported) *N4-M/C* catalyst offered impressive catalytic current and stability at application-relevant temperatures of ≥ 60°C. Practical fuel cells are based upon membrane electrode assemblies (MEAs) consisting of electrically contacted catalyst layers pressed onto ionic conducting membranes. The final phase of our project involved the preparation and testing of MEAs based upon our top- performing *N4-M/C* catalyst. Within the project timescale, observed performance was limited but this may be attributable to not-yet optimal membrane fabrication, and/or fuel cell operating conditions rather than catalyst issues. In summary, the headline outcome is that potential of metallomacrocycles to function as electrocatalysts for the oxidative dehydrogenation of some LOHs has been demonstrated, but further work is required to achieve device integration.

Keywords (min 3 and max 10)	energy storage, hydrogen, fuel cell, liquid organic hydride, electrochemical energy conversion

SECTION 2: FINAL TECHNICAL REPORT – FOR PUBLICATION (max 10 pages)

2.1 Executive Summary

Liquid Organic Hydrides (LOHs) are hydrocarbon (or hydrocarbon-derived) molecules into which hydrogen can be reversibly inserted or removed on-demand. Accordingly, they form the basis of an emerging approach to hydrogen energy storage. In its usual implementation, the concept involves the catalytic hydrogenation of the lean-LOH (exothermic) at the site of hydrogen production, and the thermal catalytic dehydrogenation (endothermic) of the resulting rich-LOH to release hydrogen gas at the location of utilisation. The LOHcell project involved an investigation of the possibility of direct extraction of the stored energy (as electricity) from rich-LOHs by electrochemical oxidative dehydrogenation – in other words the development of an anode for a direct LOH fuel cell. Previous reports indicated that conventional dispersed metallic fuel cell catalysis were inadequate for this purpose, so here it was elected to study the use of molecular catalysts (specifically N4-metallomacrocycle complexes) in their stead. The project commenced with the preparation of a range of complexes with metal centres of both first row transition metal or platinum group metal (PGM) elements. These were absorbed onto graphite electrodes for preliminary screening in a 3-electrode laboratory cell with LOHs introduced to aqueous electrolytes. This indicated that some of the PGM based complexes were active oxidative electrocatalysts under alkaline conditions. Unfortunately, complexes of less expensive first row metals did not display catalytic behaviour. Further development involved the immobilisation of the most promising complexes onto carbon black powder, and the dispersal of these supported catalysts in anion exchange ionomer based inks for spray coating onto gas diffusion electrodes. One complex, previously unreported as an oxidation catalyst, exhibited impressive catalytic performance and stability under application relevant conditions (60 – 80 °C, pH 14). In the final phase of the project this lead catalyst was tested in an anion exchange membrane test fuel cell. The performance was limited, but it is hoped that future optimisation can transfer the promising activity observed in aqueous electrolyte to a membrane electrolyte assembly environment.

2.2 Introduction to Project

By now, there exists widespread awareness across Irish society regarding the ongoing energy transition from fossil fuels to renewable sources, as the country seeks to make the necessary adjustments to meet its legal obligations on reducing greenhouse gas emissions. While SEAI data indicates that 39.1 % of electricity generation in 2020 came from renewable sources, significant technical challenges lie ahead in the pursuit of deeper decarbonisation. Renewable energy sources such as wind and solar PV are unpredictable and non-synchronous – i.e. there is often a disparity between the optimum times and locations for energy harvesting, and those of consumer demand. As the renewable share of the energy mix grows this poses problems for the stable operation of electricity grids. Smart grid management and interconnection can alleviate the issue, but cannot entirely guarantee smooth, uninterrupted operation. Furthermore, there are a number of areas, notably the wider transport sector (beyond plug-in battery vehicles), where continuous grid connection to renewable electricity is not possible. All of this strongly suggests an urgent need to develop storage solutions for renewable energy across different capacity- and time- scales.

The storage of large quantities of electricity over long time periods (hours to weeks) is challenging. Indeed, probably the most developed approach is that of 'pumped hydro' as implemented, for example, at Turlough Hill in Co. Wicklow. However geological constraints limit the large-scale deployment of this route, meaning that other energy storage methodologies must be developed. To this end, the use of hydrogen has been extensively proposed as the basis of a renewable energy storage option – the so-called 'hydrogen economy'. At its most basic, this involves the conversion of (excess) renewable electricity to 'green' hydrogen gas via water electrolysis, followed by storage of the hydrogen, prior to either on-demand reverse conversion to electricity in a fuel cell, or utilisation in a hydrogen combustion engine. This energy cycle is in principal carbon free. Hydrogen has a very high energy storage density per unit mass (39.72 kWh/kg, over three times that of petrol), however, as a gas at atmospheric pressure, it offers a low volumetric energy capacity (0.00297 kWh/L, over 3000 times lower than petrol). Therefore, while renewably produced hydrogen is a promising green energy vector, its low density and explosive nature present challenges with respect to its storage and transport at volume.

There are a number of approaches towards hydrogen storage, but in general they can be categorised as either physical or chemical storage. Physical methods involve the storage of molecular hydrogen (H_2) either as a compressed gas, in liquid form at temperatures below -253°C, or within highly porous solid materials. By contrast, chemical storage involves the reaction of hydrogen gas with 'host' species which may be metals (to form metal hydrides), gases including carbon dioxide (to form methanol or formic acid) and nitrogen (to form ammonia), or hydrocarbon based liquids. The reaction product is then stored and/or transported, and the hydrogen can be recovered when required. The various forms of storage are at different stages of technical maturity, and the method of choice will depend on the exact storage requirements, including factors such as scale, duration, and transport method and distance.

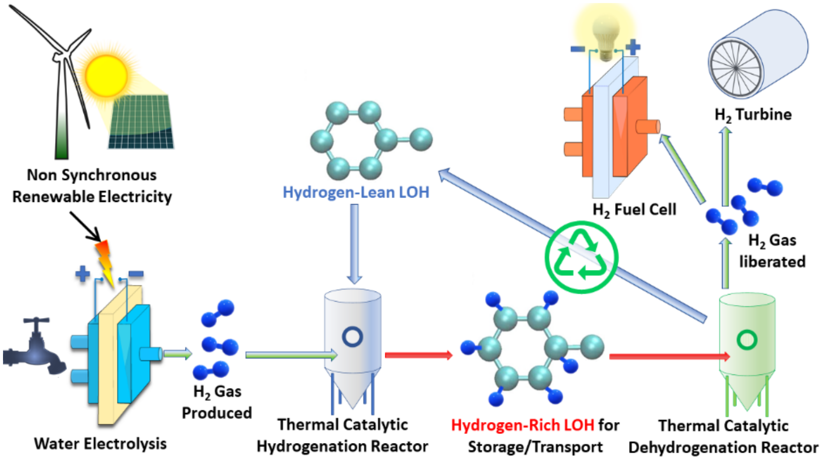

Figure 1: Hydrogen storage via a liquid organic hydride (LOH) host

This project centred on a chemical storage approach utilising Liquid Organic Hydrides (LOHs). These are hydrocarbons or hydrocarbon derivatives, usually liquids under ambient conditions, that can be reversibly transitioned between hydrogen-lean (or unsaturated) and hydrogen-rich (saturated) forms. A schematic diagram of an LOH based hydrogen storage system is presented in Figure 1.

The LOH system depicted in Figure 1 is toluene (lean) / methylcyclohexane (rich), however the principal is similar regardless of the exact LOH utilised. The commercialisation of hydrogen storage and transport via toluene/methylcyclohexane is being pursued by Chiyoda Corp of Japan. An alternative system based on dibenzyltoluene (lean) /perhydrodibenzyltoluene (rich) is under commercial development by a Germany company, Hydrogenious Technologies. In addition to these homocyclic hydrocarbons, heterocyclic species, or alcohols may serve as organic hydrogen carriers. A great advantage of LOH hydrogen storage lies in fact that many LOHs possess similar physiochemical properties to current liquid hydrocarbon fuels. This means that existing infrastructure and regulations for the storage and transport of hydrocarbons can readily be adapted to LOHs, reducing the capital investment required for some other hydrogen storage approaches.

The catalytic dehydrogenation of LOHs to recover the stored hydrogen is an endothermic process requiring temperatures up to 400°C, and as such, lowers the efficiency and increases the cost of the storage cycle. In light of this, it has been proposed that it would be beneficial to explore the possibility of direct electrochemical dehydrogenation of LOHs in a fuel cell device operating below 100°C as depicted in Figure 2.

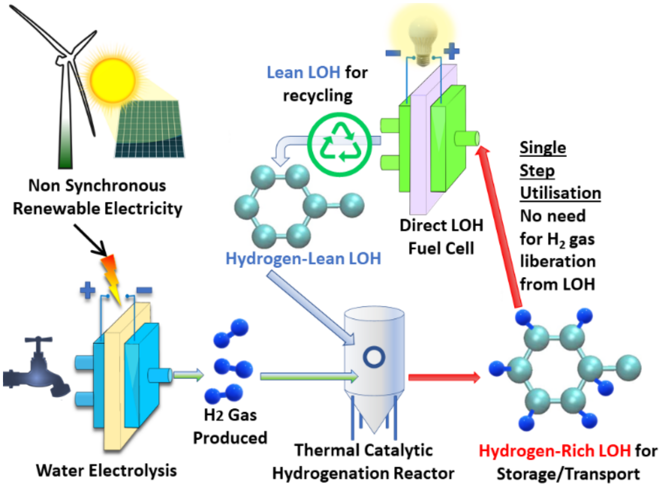

Figure 2: Alternative LOH scheme based on electrocatalytic dehydrogenation in a fuel cell

In addition to the lower heat requirement, other advantages of the electrochemical approach include the fact that electricity can be directly extracted from the rich-form LOH without the need for reconversion to hydrogen gas, while two conversion devices from Figure 1 (the thermal dehydrogenation reactor and the hydrogen fuel cell or turbine) are replaced with a single device (the direct LOH fuel cell) in Figure 2. The practical realisation of the scheme depicted in Figure 2 depends on the development of electrocatalyst materials for the anode of the direct LOH fuel cell. Such catalysts must be capable of promoting the efficient electrochemical oxidative dehydrogenation of rich-form LOH species to regenerate the lean-form for recycling. This RD&D project focussed on the synthesis and testing of molecular catalysts to accomplish this task.

Conventional fuel cell catalysts are typically metallic nanoparticles (often platinum or platinum alloys) dispersed onto carbon powder support materials. While these are suitable for the oxidation of hydrogen at the anode of a conventional fuel cell, studies have shown them to be inadequate for the effective oxidative dehydrogenation of various LOH species – in short a different type of catalyst is required. A possible alternative involves the use of molecular catalysts. Molecular catalysts (specifically in this project, organometallic complex catalysts) are molecular species centred on a single metal atom or ion, surrounded by an array of bound molecules or ions known as the coordinating ligand. Such catalysts can, in principle, offer a number of advantages relative to dispersed metals – for example they can deliver higher specificity for a target product, are often less prone to poisoning and make more efficient use of scare precious metal resources. For these reasons there has been a growth in research interest in the utilisation of molecular catalysts for energy-related photo- and electro-chemical reactions, including those pertaining to fuel cells and the reduction of CO_2.

In view of this, **the central concept of this project was to explore the possible use of molecular catalysts for the oxidative dehydrogenation of LOHs**. It was decided to focus on a particular group of metal complex molecules known as N4-metallomacrocycles which are based on ligands such as porphyrins, phthalocyanines, or chlorins. A number of these species are well known to be potent catalysts for electrochemical reduction reactions, such as the oxygen reduction reaction that occurs at the cathode of a fuel cell. Some, though far fewer, reports exist of their ability to function as anode catalysts (i.e. for oxidation reactions), although solution phase N4-metallomacrocycles have been documented to promote the dehydrogenation of some LOHs in homogeneous electrochemical reactions.

The project commenced with the synthesis of a range of N4-metallomacrocycles using both cheaper first row transition metals and precious metals. Fuel cells operate under either acidic or alkaline conditions, although in practical devices ion-conducting membranes (acidic proton exchange membrane (PEM) or alkaline anion exchange membrane (AEM)) are used rather than liquid electrolyte solutions. However, the construction of membrane electrode assemblies (MEAs) is a time and material intensive task, so standard practice in fuel cell catalyst development is to perform initial screening and fundamental studies with liquid electrolytes, before evaluating promising catalysts in test membrane fuel cells. Accordingly, for initial characterisation, the macrocycle catalysts were adsorbed onto graphite electrodes, and their catalytic performance was evaluated in aqueous acidic or alkaline electrolyte solution also containing an LOH. It was determined at this stage that none of the catalysts were active under acidic conditions. Furthermore, none of the metallomacrocycles based on first row metals exhibited catalytic behaviour, probably due to stability issues under the required harsh electrolyte conditions. Encouragingly, catalytic activity was noted in an alkaline environment for several of the molecular catalysts containing precious metal centres.

These species were brought forward for further development by immobilising them onto high surface area carbon black powders to yield the type of supported architecture required for practical application. Inks of the carbon supported molecular electrocatalysts dispersed in an anion exchange ionomer was sprayed onto porous carbon diffusion electrodes (closer to the device configuration) and further testing and optimisation was performed in alkaline test solutions at application relevant temperatures (60 - 80° C). Finally, MEAs containing the most promising catalyst were tested in a fuel cell fixture. During the timeframe of the project it proved difficult to replicate the catalytic performance observed in the liquid electrolyte laboratory cell when the catalyst was transferred to the membrane cell. However, these were the first trials we conducted with this fuel cell setup and this type of membrane, so we remain hopeful that, with further refinement, the encouraging fundamental results can be translated to a device relevant configuration beyond the end of this RD&D project.

2.3 Project Objectives

- Synthesis and characterisation of N4-metallomacrocycles as potential molecular anode catalysts for the electro-dehydrogenation of Liquid Organic Hydrides (LOHs)
- Initial screening of the catalysts for LOH electro-dehydrogenation in aqueous acidic and alkaline electrolytes to identify the most promising catalysts and operational pH
- Further development of the catalytic anode, by immobilisation of the lead catalyst onto a carbon powder support to permit spray coating onto gas diffusion electrodes
- Fuel cell assembly, demonstration and testing

2.4 Summary of Key Findings/Outcomes

- *Innovation 1: Demonstration of the ability of N4-macrocycle complexes to affect the oxidative dehydrogenation of hydrogen storage relevant alcohols under alkaline conditions.*

  While it was previously known that some rhodium macrocycles could catalyse the oxidation of isopropanol, this project has demonstrated for the first time that macrocycles of other platinum group metals can do likewise, and are also active for the oxidation of other relevant species such as cyclohexanol. Furthermore, one of the molecular catalysts that we have studied offers greater catalytic activity and significantly improved stability relative to the previously reported rhodium macrocycle at application relevant temperatures (≥ 60 °C)

- *Innovation 2: Broadening of the known range of N4-metallomacrocycles capable of the catalysis of energy relevant electrochemical oxidation reactions.*

  While a considerable amount of electrode immobilised molecular catalysts are known to be active for cathode (reduction) reactions including the oxygen reduction reaction, the hydrogen evolution reaction and carbon dioxide reduction, the amount of molecular catalysts reported for anode (oxidation) reactions is much lower. The project has added to the known number of N4-metallomacrocycles with oxidative catalytic properties. This may have relevance to other important electro-oxidation processes beyond our immediate targets. Indeed, we found that some of our catalysts were effective for other energy relevant oxidation reactions such as glycerol and ethylene glycol electro-oxidation.

- *Innovation 3: Demonstration of the compatibility of N4-metallomacrocycle catalysts with anion exchange ionomers.*

  Acidic, proton exchange based fuel cells are the more developed technology because superior proton exchange ionomers and membranes (principally Nafion®) have been commercially *available compared to their alkaline, anion exchange, counterparts. In previous studies Nafion was used to prepare catalytic films of N4-metallomacrocycles, even for studies in alkaline solution (in which it merely acts as a binder). In recent years, anion exchange ionomers have become commercially available. We have shown that, with some optimisation, catalytic inks (for electrode spray coating) can be prepared using a commercial anion exchange ionomer and N4-metallomacrocycles. This is an important requirement for the integration of this type of molecular catalyst into a practical anion exchange membrane fuel cell.*

2.5 Project Impact

This project was concerned with the preliminary stages of development of an electrochemical implementation of hydrogen storage via the Liquid Organic Hydride (LOH) concept, as presented schematically in section 2.2, Figure 2. During the course of the project we verified the fundamental proposition that molecular species based on certain N4-metallomacrocycles can catalyse the electrochemical oxidative dehydrogenation of some types of LOH. An initial attempt to transfer this observation towards practical application in a test anion exchange membrane (AEM) fuel cell in order to generate electricity while recovering the lean-form of the LOH, was less successful within the time-frame of the project. Nonetheless, as mentioned in section 2.7, the foundations for future R&D on electrochemical LOH dehydrogenation have been laid. At the conclusion of the project it is appropriate to reflect on the impact of its laboratory research and dissemination activities.

The impact of early stage research on a complex renewable energy concept will, by definition, take time to be realised in a deployment-ready technology. Nonetheless, during the course of this RD&D Fellowship project, and as we seek to take this research forward, the project team remains mindful of the impact of our work on the Irish, and indeed EU, energy sectors. Fundamentally, our project and the broader idea of LOH storage are about enabling the roll-out of hydrogen as a key-pillar of the future low carbon energy landscape.

The vital role of energy storage in enabling a renewables based energy system was emphasised in section 2.2. According to the Irish Government's *Climate Action Plan 2023* the share of renewably generated electricity is targeted to increase from 40% in 2020 to 50% in 2025, and to 80% by 2030. A headline quotation from the summary of that plan is that the government "will facilitate a large-scale deployment of renewables that will be critical to decarbonising the power sector as well as enabling the electrification of other technologies". The targets are justifiably ambitious – the attainment of "up to 9 GW onshore wind, 8 GW solar, and at least 7 GW of offshore wind by 2030." For the integration of this level of renewable energy harvesting capacity into the energy system, the plan also acknowledges the requirement for long term storage (4 hour plus). In the past renewable energy plans were often agnostic as to the nature of 'storage', however the 2023 plan clearly identifies a strong role for hydrogen in this regard. The climate plan (chapter 12) envisages that during the period of the second carbon budget (2026 – 2030), "green hydrogen can play a significant role in sector coupling (the increased integration of energy supply and end-use sectors), and in minimising the overall cost of decarbonisation across all sectors." This is formally stated as a 2030 KPI (Climate Action Plan, table 12.5) – "Green Hydrogen in production from surplus renewable electricity.” Moving beyond 2030, green hydrogen production is formally targeted from 2 GW of dedicated offshore wind capacity during 2031-2035, where this is seen as a key demand management measure.

Moving from an Irish to a European context, a 2020 communication from the European Commission entitled ‘A hydrogen strategy for a climate-neutral Europe’ (COM(2020) 301 final) lays out the expected role for hydrogen in the EU’s energy transition. According to this strategy, the share of hydrogen in Europe’s energy mix will grow from less than 2% in 2018 to 14% (or even 23% in some modelled scenarios) by 2050. The strategy is clear that between 2025 and 2030, “hydrogen needs to become an intrinsic part of an integrated energy system with a strategic objective to install at least 40 GW of renewable hydrogen electrolysers by 2030 and the production of up to 10 million tonnes of renewable hydrogen in the EU.” It is further outlined that during this period hydrogen “will start playing a role in balancing a renewables-based electricity system by transforming electricity into hydrogen when renewable electricity is abundant and cheap and by providing flexibility. Hydrogen will also be used for daily or seasonal storage, as a backup and provide buffering functions, enhancing security of supply in the medium term.”

It is therefore clear that policy-makers in Ireland and the EU believe that ‘hydrogen is going to happen’. At present the technological solutions exist to produce (PEM or alkaline electrolysers) and utilise (fuel cells, combustion) green hydrogen, albeit that further significant improvements are desirable. A strong argument can therefore be made that the weak-link in the hydrogen supply chain is storage and transport. In short, the grand vision of a hydrogen economy, now part of national and European policy, may not be realised if improved storage technologies are not researched, developed, and rolled-out during the next quarter century. This project is a part of that effort.

Considering the strategic importance now being placed on the role of hydrogen in decarbonising the economy and society, it is evident that this research project fits with SEAI’s remit to support solutions that will enable technical barriers to energy market uptake to be overcome. Furthermore, we believe that the project will enhance Ireland's capacity to access and develop international class energy RD&D. Our engagement on this project has brought us into contact with academic, commercial and industrial stakeholders within the field of hydrogen production and storage. Arising from this we have partaken in discussions and workshops (e.g. International Hydrogen/Hydrogen Safety Workshop, University College London, 13/02/23) with a view to further collaborative research. It is also our hope that the project has, and will, be able provide guidance and support to policy makers and public bodies. This was one of the motivations behind our hosting of a public roundtable meeting entitled ‘Large Scale Renewable Energy Storage for Ireland (DCU, 07/12/22) which heard from academic, industry and public sector experts on renewable energy, energy storage and policy. In this regard, the team has also been involved in several collaborations during the course of the project expected to yield publications in 2023, that will be of interest to policy and commercial decision makers. One of these, led by colleagues from the School of Mechanical Engineering at DCU, will constitute a critical review into the techno-economics of various hydrogen storage approaches. The other (with collaborators from the University of Strathclyde, Scotland, and UCC) focuses on a risk analysis tool for investors in pilot stage deployments of emerging green energy technologies.

The key impacts of the LOHcell project arise in several categories

Scientific & Technological

The main project outcomes as summarised in section 2.4 (listed innovations) have obvious wider scientific and technological impacts. Innovation 1 proves that immobilised N4-metallomacrocycle electrocatalysts are capable of facilitating the oxidative dehydrogenation of organic hydrogen carrier molecules. This result is significant in that it demonstrates that there are alternatives to conventional metal or metal oxide nanoparticles as anode catalysts for challenging energy related electro-oxidation reactions. Even if the exact catalysts developed and tested during this project cannot ultimately be transferred to device usage, our results indicate to the scientific community that further investigation into molecular (and other single atom) anode catalysts is a fruitful avenue for future innovation in electrochemical energy conversion devices. Innovation 2 constitutes a broadening of existing scientific knowledge. We have shown that chemistry previously principally associated with rhodium macrocycles is possible for similar complexes of another metal a result that may also have an impact in other areas of catalysis beyond electrocatalysis (e.g. photocatalysis and homogeneous catalysis). Innovation 3 is of more technical than fundamental scientific interest. By demonstrating the compatibility of our molecular electrocatalysts with anion exchange ionomers, we have shown that molecular species are potentially feasible electrode materials in alkaline fuel cells. This is significant because ongoing developments in anion exchange membranes (AEMs) are closing the performance gap with the more established proton exchange membrane (PEM), thereby opening the possibility of a new generation of electrochemical energy devices. It is our intention to disseminate innovations 1 – 3 in an open access journal article in 2023, thereby sharing the knowledge obtained during this project with the wider scientific community.

Societal

Warnings about the possibility of interruption to electricity supplies, and fuel rationing, reached the news headlines in the run-up to the winter of 2022 – 2023, as the war in Ukraine caused a tightening of supply, and price hikes on international wholesale oil and gas markets. This served as timely reminder of the extent to which our society and economy is dependent on a reliable, secure, and affordable energy supply. As Ireland and Europe progressively replace fossil fuels with intermittent renewables, new challenges arise to ensure resilience and security of supply. Since we are all energy users, everyone is deeply invested in this. By necessity, energy storage will be an indispensable component of a fit-for-purpose renewable based energy system. The commitments made by the Irish government and the EU on increasing green hydrogen production capacity can be seen as a vote of confidence in hydrogen as a key renewable energy storage medium. Yet it must be admitted that the success of large scale energy storage through hydrogen is dependent on the safe and cost effective storage of hydrogen itself. It is the belief of the project team that the LOH approach has the potential to play a major role in hydrogen storage, but continued research and development is essential to advance the maturity of the technology. In particular, research (as in our project) on improving the efficiency and flexibility of the 'bottleneck' dehydrogenation step is essential. Ultimately the main societal impact of our project, and others like it, will be public confidence in a secure renewable energy system, where stored hydrogen can support stable grid operation, and assist in the decarbonisation of transport and industry.

Economic

The *Irish Independent* (15-2-23) reported that the Minister for Environment, Climate and Communications, Eamon Ryan, addressing the annual conference of *Wind Energy Ireland*, predicted that Ireland would be a net exporter of renewable energy by the end of the present decade, with the possibility of becoming a much larger exporter into the 2030s. This is predicted to arise since the total installed renewable generation capacity (driven by a massive upscaling of offshore wind) will exceed peak domestic demand. The realisation of this scenario clearly offers a significant economic opportunity for the state. Export of the surplus capacity as electricity through interconnectors is one option but this requires the usual supply- and demand- end matching to avoid curtailment. In practice some of the excess electricity will be converted to green hydrogen – the Climate Action Plan 2023 envisages so much (2 GW offshore wind dedicated to electrolysis by 2035). A number of techno-economic studies (surveyed by us in a review article under preparation) suggest that chemical transport of hydrogen by either LOHs or ammonia can be cost competitive options for the international delivery of hydrogen. Therefore, current research into the further development of LOH storage may be viewed as an investment into a future route-to-market for a valuable national export resource in the coming decades.

Environmental

Any research into a technology that assists or facilitates the transition from fossil fuels to renewables may be said to have a positive environmental impact. However, from the viewpoint of life cycle assessment, the sustainability of the utilised materials is also an important consideration. Platinum group metals (PGMs) are listed as critical raw materials by the European Commission, and the most efficient possible use of this scarce resource must be pursued. To this end, we trialled N4-metallomacrocycles based on more abundant first row transition metals (manganese, iron, cobalt), but unfortunately they failed to display catalytic activity. Although the active catalysts identified in this project are complexes of PGM elements, this represents more efficient utilisation compared to conventional PGM nanoparticle fuel cell catalysts. For molecular catalysts all metal atoms/ions are in principal available to promote the target reaction, whereas for nanoparticles, only the fraction on the surface can be partake. The replacement of particle based catalysts with single atom catalysts (such as our N4-metallomacrocycles) offers a route to the more efficient exploitation of mineral resources.

2.6 Recommendations

While conducting this research project, the team have become increasingly familiar with the various approaches towards hydrogen storage, their current levels of technical development, their relative strengths and weakness, and the relevant techno-economic considerations. We are encouraged to see the commitment of policy makers in Ireland and Europe to green hydrogen as part of the energy transition. As outlined in section 2.5, this would appear to involve an initial increase in electrolyser capacity in the period 2025 – 2030, with significant scale-up envisaged in the 2030s. While this is to be welcomed, there seems to be little detail at present on how this hydrogen will be stored and transported. Existing gas pipelines will probably play a role, as will geological storage of compressed gas if suitable locations can be identified. Many of the published analyses that we have encountered suggest that chemical storage, be it through organic carriers or ammonia, can be competitive solutions especially where transport is required (e.g. export of green hydrogen) or for off-grid applications (mobility etc.). In any case, if the production of significant volumes of green hydrogen is expected to commence towards the end of the present decade, **we strongly recommend, as a priority, that policy makers in Ireland engage with the relevant stakeholders regarding storage**, if such a consultation is not already underway. It is worth noting that chemical hydrogen storage facilities (LOHs or ammonia) may beneficially be integrated with existing industrial sites. For example, waste heat from a facility such as a cement plant, could be used for thermal catalytic LOH dehydrogenation (see section 2.2, Figure 1), thereby improving the efficiency of the storage cycle. Additionally, the LOH hydrogenation step actually releases heat, which might be utilised for an industrial process currently relying on gas or electrical heating. A strategic analysis of sites where hydrogen storage might be integrated with industrial activity would be a worthwhile exercise.

2.7 Conclusions and Next Steps

The LOHcell project investigated the use of N4-metallomacrocycles as molecular electrocatalysts for the recovery of energy, stored as hydrogen, in liquid organic hydrides (LOHs). The approach was to start with the synthesis of the macrocycles, progress to electrocatalytic screening and evaluation with an aqueous electrolyte, and finally to try to implement the lead catalyst in a membrane electrode assembly test fuel cell. Following the successful synthesis of the complexes and their immobilisation onto test electrodes it was found that some of the macrocycles were active for the oxidative dehydrogenation of LOH-relevant species under alkaline conditions. These included macrocycles for which oxidative catalysis had not previously been reported. Initial attempts to transfer the catalytic performance observed with aqueous electrolyte to a device relevant anion exchange membrane based configuration yielded limited success within the timeframe of the project. The envisaged scientific, societal and environmental impacts of the project were outlined in section 2.5. A half-day public roundtable meeting was hosted by the project team to discuss the requirements and challenges for large scale renewable energy storage in Ireland. A recommendation arising from this event is that policy makers should engage in a consultation with stakeholders to map-out a hydrogen storage and transport strategy to match the planned deployment of electrolyser capacity from 2025 onwards.

The following next steps have been identified:

- the refinement of our LOH membrane test fuel cell setup to ensure that apparatus deficiencies are not limiting performance
- further optimisation of the membrane electrode assembly to achieve verifiable LOH dehydrogenation in the test fuel cell
- testing of the electrocatalytic activity of pyrolysed forms of the carbon supported N4-metallomacrocycles.
- Publication of the scientific results obtained to-date
- Engagement with academic and industrial collaborators on further development and funding opportunities based on the results obtained during the project