

Liquid Sunshine - Transforming Renewables into Fertilisers and Energy Carriers with Electromaterials

Douglas R. MacFarlane¹, Jaecheol Choi¹, Bryan H. R. Suryanto¹, Rouhollah Jalili², Manjunath Chatti¹, Luis Azofra^{3,4} and Alexandr N. Simonov¹

[1] Australian Centre for Electromaterials Science, School of Chemistry Monash University, Clayton Victoria 3800, Australia.

[2] School of Chemical Engineering, University of New South Wales (UNSW), Sydney, NSW 2052, Australia

[3] CIDIA-FEAM (Unidad Asociada al Consejo Superior de Investigaciones Científicas, CSIC, avalada por el Instituto de Ciencia de Materiales de Sevilla, Universidad de Sevilla), Instituto de Estudios Ambientales y Recursos Naturales (i-UNAT), Universidad de Las Palmas de Gran Canaria (ULPGC), Campus de Tafira, 35017, Las Palmas de Gran Canaria, Spain.

[4] Departamento de Química, Universidad de Las Palmas de Gran Canaria (ULPGC), Campus de Tafira, 35017, Las Palmas de Gran Canaria, Spain.

Abstract

It has become apparent that renewable energy sources are plentiful in many, often remote, parts of the world, such that storing and transporting that energy has become the key challenge. For long distance transportation by pipeline and bulk tanker a liquid form of energy carrier is ideal, focussing attention on liquid hydrogen and ammonia. Development of high activity and selectivity electrocatalyst materials to produce these energy carriers by reductive electrochemistry has therefore become an important area of research. In this Progress Report we discuss recent developments and challenges in the field of electrocatalytic materials for these processes, including the hydrogen evolution reaction (HER), the oxygen evolution reaction (OER) and the nitrogen reduction reaction (NRR). We highlight some of the mis-steps currently plaguing the nitrogen reduction to ammonia field. The rapidly growing roles that *in-situ/operando* and quantum chemical studies can play in new electro-materials discovery are also surveyed.

1. Introduction

Providing inexpensive and readily available food and energy to a growing global population is one of the grand sustainability challenges of this century. It is increasingly becoming clear that there is a plentiful supply of renewable energy available in many, sometimes remote, parts of the world and that the technology to harvest it is well developed at increasingly lower cost. The emerging challenge is therefore how to store and transport this energy at sufficient efficiency and low cost. At larger scale,

and for transportation over long distances, direct electrical supply and battery storage are not economic solutions. Attention has turned to chemical forms of energy carriers, including hydrogen, ammonia and reduced carbon compounds, as the carriers. These may be employed directly as fuels at point of use, or the carrier may be recovered and recycled; for this reason, the term “energy carrier” is often preferred as it covers a broad range of actual possibilities. Liquid state energy carriers are attractive because they offer the energy density of a condensed phase, along with the ease of generation and dispatch that solids and gases can lack.

Australia has an enormous potential to generate solar energy. Figure 1 shows a world map of Global Horizontal Solar Insolation that indicates the average solar energy per day and per year that is received per m^2 in various regions (horizontal in this context indicates that the receiver plane is parallel to the ground). It is apparent that the North West of Australia has an enormous land area of very high solar insolation. The same is true of several other regions of the world including the Atacama area of Chile, and areas of North and South Africa and the middle East. To put these land areas in perspective the small yellow square shown near Broome in Western Australia represents an area $250 \times 250 \text{ km}$, on which standard Si-PV cells could generate around 25,000 TWh of electrical energy per year. This is approximately the current electricity demand of the world. Combined, Australia’s four largest cattle stations occupy more than this land area. However, in almost all cases these potentially super-productive regions are remote from population centres. Hence, the need arises for the development of large-scale technologies to transform this solar energy into readily dispatchable forms such as liquid hydrogen, methanol and ammonia: in other words, Liquid Sunshine.

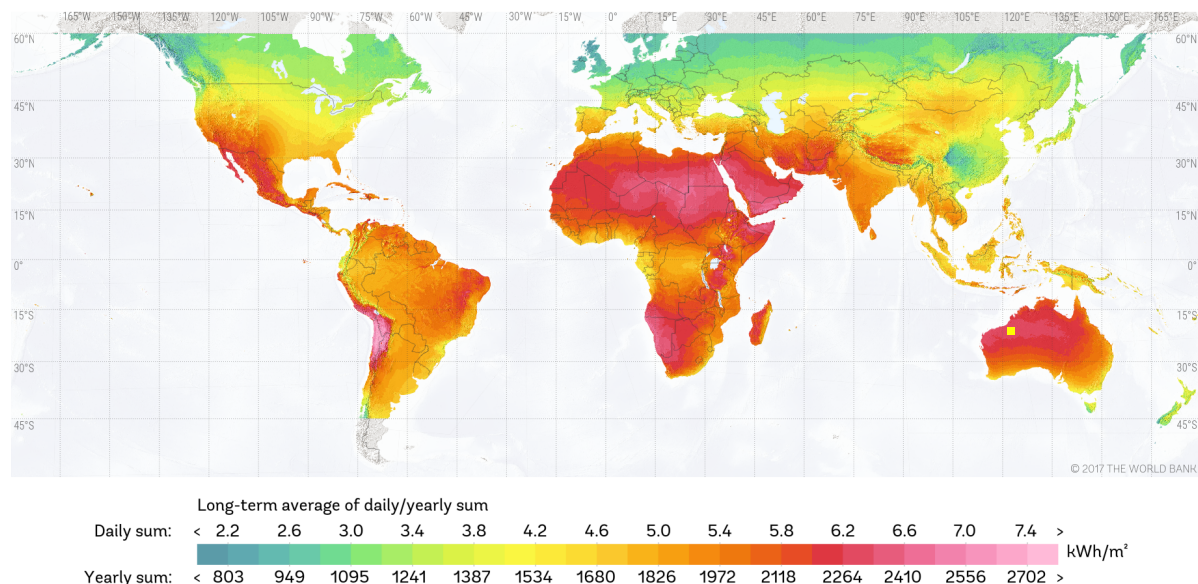


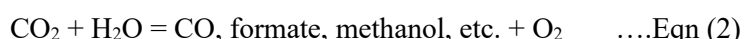
Figure 1. Map Global Horizontal Solar Insolation (Solar resource data obtained from the Global Solar Atlas, owned by the World Bank Group and provided by Solargis).^[1]

The process of transforming solar energy into an energetic chemical carrier can be achieved by either (i) direct solar-thermal routes or (ii) photovoltaic harvesting followed by electrochemical reduction of a substrate such as water, CO₂ or nitrogen gas. The relative merits of each of these is dependent on many factors, especially capital cost, and is a rapidly evolving scene as technologies develop. Here we focus on the direct electrochemical approach and the electro-materials challenges that it presents. Electrolysis of water to produce hydrogen (Eqn. 1) is a very well-known process that is commercially well-developed.



However, the cost of hydrogen produced by this means is currently prohibitive, compared to the cost of H₂ prepared via the steam reforming reaction of fossil fuels such as methane. In recent world-wide discussions, the former is increasingly referred to as “green hydrogen” and the latter as “black hydrogen”; these “colours” of course indicate the source rather than any colouration of the gas itself. There is also reference to “blue” H₂, being hydrogen from a fossil fuel source, but with associated carbon capture and sequestration or with some offset mechanism. Hydrogen as a gas is of relatively low volumetric energy density and must be either compressed, liquified or stored in a hydrogen storage material to become useful as an energy carrier. All of these options have cost implications. Hydrogen compression is expensive in capital and energy terms. For example, liquefaction consumes about 30% of the original energy content of the hydrogen and storage materials need to be recycled; hence both options are not ideal for long distance transportation. Nonetheless, small scale liquid-H₂ exports from Australia are already planned for 2020 to Japan and there is considerable commercial discussion about an increasing scale of liquid-H₂ exports in the future.

The cost and inefficiencies associated with hydrogen production has generated interest in similar reduction reactions involving either CO₂ (Eqn. 2) or N₂ (Eqn. 3) as the feedstock.



Both can produce liquid products directly. CO₂ has the disadvantage that it requires CO₂ capture to be part of the process at some stage and therefore is not immediately viable as a large-scale technology; we return to this difficulty in our discussion below. For this reason, ammonia has become of considerable interest as an energy carrier since at point of use the N₂ feedstock is regenerated and released to the atmosphere in an (in principle) closed-cycle process. CSIRO has recently demonstrated an ammonia cracker for this purpose.^[2] In fact, the need for a sustainable approach to ammonia generation had arisen before its role as an energy carrier was recognised; ammonia is currently produced by the Haber-Bosch process from coal or natural gas and is the source of a large fraction of the world's

fertilisers and therefore of world food supply. The process also contributes nearly 2% of global greenhouse gas emissions. Hence, for use both as an energy carrier and for fertilisers, interest in production of “green” ammonia has rapidly intensified in recent years.^[3, 4] Green ammonia can be made either via the nitrogen reduction reaction (NRR; Eqn 3) or by production of green H₂ (Eqn 1) and the use of this H₂ in the otherwise traditional Haber-Bosch plant. Although the former is likely to be ultimately more efficient and less capital intensive, the latter allows continued use of the considerable installed plant around the world and is likely to be the most immediate approach to green ammonia.

All of these reactions require highly efficient and inexpensive electrocatalytic materials to support high rates and it is in this area that an intense effort in electromaterials research has focussed in recent years. In this “Progress Report” we discuss recent developments in our own work as well as others, though we stress that it is not our intention to present a review as that would be a herculean task. We also highlight some of the challenging aspects of this field that are impeding progress and where further attention could support significant breakthroughs. We begin with a discussion of electromaterial structures in general including tethering as an approach to utilising the intrinsic activity of homogeneous reaction centres. All of the reduction reactions contemplated here must be combined with an efficient water oxidation reaction, as water to oxygen is the only ultimately sustainable anode process that could be acceptable in large scale; progress in this important area is discussed in section 3. We then focus on the electrocatalytic materials emerging for the hydrogen (section 3) and ammonia (section 4) reactions. Electromaterials research in general has been tremendously accelerated in recent years by the increasing availability of *operando* techniques that allow a “live” view of the process in action on the material, as discussed in section 5. The ability to model the processes at a high level of material and energetic detail is also emerging recently from quantum chemistry and we highlight examples and further challenges in this field in section 6.

2. Electrocatalytic Materials

Heterogeneous versus Homogeneous

Traditionally, electrocatalysts are thought of as heterogeneous catalysts in the sense that they are part of, or are formed on, the electrochemical surface as a different phase from the reaction solvent. The reactants and products may be present in that medium or may be supplied and removed via a gas stream. The latter of course is both very familiar, the hydrogen fuel cell, and is also very relevant to the likely situation that will arise for all of the reactions discussed here. Electrocatalysts in this morphology are strongly 2-D limited to interact with the other phases across an interface and much effort has been devoted in recent years in developing, high surface area nano-structures for the catalyst and the underlying electrode support that present high areal activity. These structures often in turn create mass transport constraints; this has stimulated interest in multiply-hierarchical structures that sacrifice some of the total possible surface area in favour of mass transport channels to feed the reaction centres.^[5]

On the other hand, dissolved metal complex molecules (e.g. those bearing porphyrin or phthalocyanine type ligands) have been shown to be some of the most promising electrocatalytic molecules for a wide range of multi-electron catalytic applications including carbon dioxide reduction,^[6-9] water splitting^[9, 10] and the alcohol oxidation reaction.^[8, 11] These homogeneous catalysts operate in solution and in broad terms are mimetic of enzymatic redox processes that are usually based on metal-ion catalytic centres. In contrast to the heterogeneous catalysts described in the previous paragraph, every metal atom in the complex is theoretically able to act as a single, catalytically active centre, leading to a high productivity and potentially to high selectivity in the catalytic reaction towards the desired products. Moreover, a variety of functional groups can be substituted on the ligands of metal complexes to tune the electrocatalytic mechanism at the molecular level.^[12]

However the use of homogeneous catalysts is often not preferable for practical energy conversion devices due to the following reasons.^[6, 13] Homogeneous catalysts have to be soluble in the electrolyte and diffuse into the diffusion layer adjacent to the electrode surface during the electrocatalytic reaction; in this case, the catalytic reaction can be limited by the intrinsic diffusion properties of the metal complex. Alternatively, a redox mediator or shuttle can be employed to shuttle between the electrode and the catalytic centre in solution, however this usually only works at the cost of additional energy losses in driving the extra electrochemical process. In addition, even if there is a significant concentration of metal complexes in the electrolyte solution, a limited number of metal complexes can be utilised in the electron diffusion layer for the catalytic reaction. Additionally, the homogeneous catalysts may not be easily separated from the products during the catalytic reactions. Finally, gaseous reactants and products generally must act as dissolved species in the reaction process, thereby being limited by their own mass diffusion and solubility factors.

Tethering homogeneous style catalysts onto surfaces

In order to overcome these drawbacks, major efforts have been devoted to tethering metal complex catalysts onto electrode surfaces, including conductive carbon-based supports such as reduced graphene oxide, carbon nanotubes and carbon black *via* covalent or non-covalent interactions.^[14, 15, 16] In particular, conductive carbon tethered metal-complex catalysts can produce enhanced electron transfer to the active centre, influence its electron density and thereby directly affect the binding energy to the reactants.^[17]

Even though tethering metal complexes to a surface is a promising approach for practical electrocatalytic applications, molecular aggregation on the surface can impede mass transport of reactants to the catalytically active centres, hindering the desired catalytic reactions.^[15, 18] Moreover, as discussed in our recent paper on a graphene tethered cobalt phthalocyanine catalyst,^[15] such molecular aggregation causes an overestimate of the number of catalytically active molecules participating in the electrocatalytic reaction, leading to a poor quantitative understanding of the intrinsic activity of the metal complexes in this context. In that work we defined and quantified the terms “effective Turn Over

Number” and “effective Turn Over Frequency” in order to accurately describe the activity of these materials.

Tethered materials immediately become constrained by the same issues as simple heterogeneous catalysts, hence means of creating a hierarchically structured support for the tethered structure becomes necessary. For example, as shown in Figure 2, we have recently described the preparation of an Fe-porphyrin catalysts tethered to a graphene framework which was then used to produce a 3D graphene hydrogel.^[16] The material produced high areal activity in reduction of CO₂ to CO.

Thus, in our view, the development of a highly efficient and robust tethered metal complex catalyst structures is an important strategy in achieving improved electrocatalytic materials performance. More detailed fundamental investigation of how metal complexes are most effectively tethered onto support materials could also play an important role in gaining an explicit mechanistic understanding of catalytic reactions on tethered metal complex catalysts.

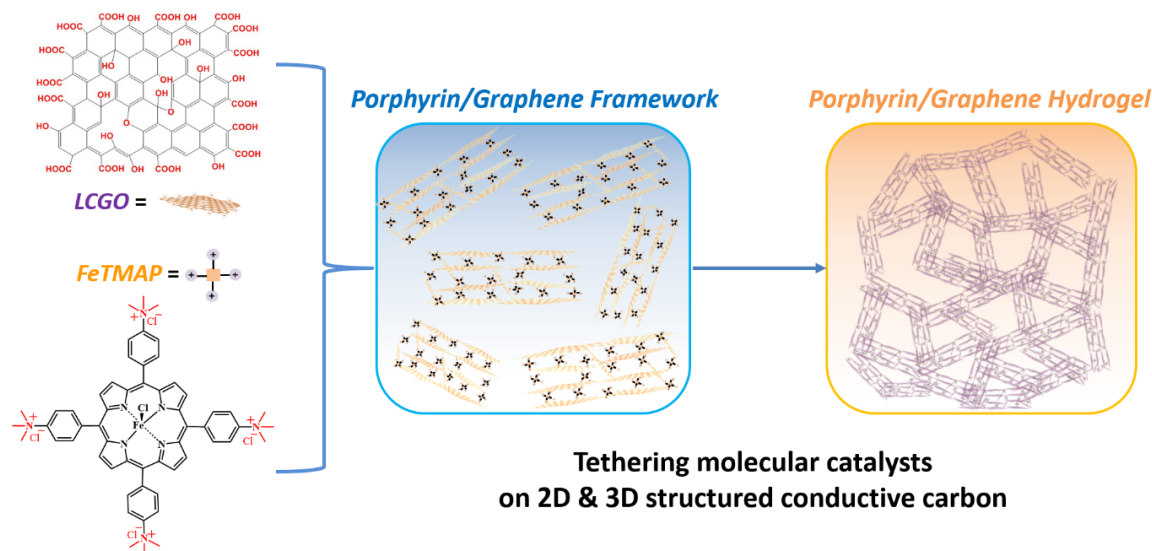


Figure 2. Tethering of a molecular porphyrin catalyst onto a Liquid Crystalline Graphene Oxide to form a graphene framework or graphene gel based electrocatalytic assembly. Redrawn from Ref ^[16]).

3. Progress and Challenges in HER and OER catalysts

Electrolytic splitting of water into hydrogen and oxygen gases was discovered more than two centuries ago, but has been largely ignored by industry due to the lack of sufficiently cheap electricity. The situation is changing now owing to the continuously decreasing price of renewable energy, which has reinvigorated interest in “green” hydrogen production. While the cost of the energy is no longer a significant economic barrier, the price of the electrolytic devices needs to be decreased to bring the capital expenditures to fossil fuel competitive levels. Among major components of the water electrolyser stacks, electrodes and catalysts contribute a very significant cost to the overall price of both alkaline and proton-exchange membrane (PEM) systems,^[19] instigating stirring research on the

development of cheap and robust electromaterials that would sustain high rates of the hydrogen evolution (HER; $2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{H}_2 + 2\text{OH}^-$) and oxygen evolution (OER; $4\text{OH}^- \rightleftharpoons \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$) reactions.

In terms of activity and stability during the HER in both acidic and alkaline media, platinum-based electrocatalysts are still unparalleled,^[20] and the research is now majorly focused on the development of alternative catalytic materials that might be not as active, but substantially lower cost and more abundant. An important milestone in the field was set by Nørskov and colleagues^[21] who rationalised the catalytic activity for H_2 evolution of molybdenum(IV) sulphide^[22] and introduced this material to the HER community as a realistic competitor to platinum. This work has engendered the whole new family of electrocatalysts, which now includes a variety of chalcogenides and their hybrid composites with other materials.^[23] MoS_2 still remains one of the most studied and best-performing HER catalyst of this class. Thus far, the most active molybdenum disulphide materials were reported by Hu *et al.*^[24] and our group^[25] following recent mechanistic and theoretical insights^[26] as a guide to the design of materials with maximised intrinsic catalytic activity. Interestingly, both studies employed microwave-assisted synthesis to produce the specific MoS_2 structures, which provides one of the many examples of the utility of this method in the fabrication of efficient electromaterials (see e.g.^[27, 28]).

The success of chalcogenides has inspired investigations of pnictides and carbides as electrocatalysts for the HER.^[23, 29] The catalytic activity of Ni_2P has been long known,^[30] but the recently revived research interest in this type of catalyst has generated new important advances.^[29, 31] One notable recent discovery was made by Dismukes and colleagues who have found that the HER catalytic activity of Ni_5P_4 is closely approaching that of Pt in both alkaline and acidic electrolyte solutions.^[32] Although this is a remarkable achievement, the current limitation of the P-deficient nickel phosphide catalysts is in their synthesis. Procedures to produce Ni_5P_4 in the form of highly dispersed particles with a sufficiently high surface area have not yet been developed, which prevents efficient integration of the material into electrolyzers. Moreover, the existing synthesis strategies are typically time and resource intensive, and often involve the use of sophisticated equipment, toxic gases, high vacuum processing, and/or high-temperature treatment.^[29, 32] Thus, the present core challenge of the phosphide-based HER catalyst field is in the development of economically feasible and easy to scale-up methods for the efficient production of these materials with the desired morphology and structure.

Similar to the HER, noble-metal based systems are the benchmark catalysts for the OER, the most active being oxides of iridium and ruthenium.^[33] However, for alkaline media, the initial activity of several recently developed earth-abundant water oxidation catalysts closely approaches, and sometimes even exceeds that of noble counterparts.^[34] Over the years, an immense variety of alkaline OER catalysts differing in composition, structure, and morphology has been reported (see *e.g.* a recent review^[35] and references therein). The most catalytically active are mixed oxides/(oxy)hydroxides of transition metals, among which the long-known nickel-iron combinations dominate the alkaline OER field as one of the most efficient and robust catalytic systems.^[35, 36] Beyond the nickel-iron domain, a

very limited number of prominent systems has been invented. One is the $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ material introduced by Suntivich *et al.* by following the insights from density functional theory (DFT) calculations.^[37] The authors have predicted and demonstrated that this mixed oxide exhibits an intrinsic OER catalytic activity higher than that of iridium and ruthenium oxides. Another noteworthy system is the iron-cobalt-tungsten mixed oxyhydroxide synthesised by Zhang *et al.* in the form of gelled, interwoven nanosheets.^[38] Again, DFT calculations were invoked to demonstrate that the adsorption energy of OH^* intermediate on cobalt sites can be tuned by introducing iron and tungsten to provide the lowest theoretical OER overpotential.

These and other studies were highly successful in improving the intrinsic catalytic activity of oxides/oxyhydroxides, but typically could not address another key limitation of these materials – poor electrical conductivity, which substantially limits their operation at high current densities. High current density is required to lower the capital cost of the electrolyser equipment per unit of hydrogen produced. A recent approach to overcome this limitation is the introduction of electrocatalysts derived *in situ* from metal chalcogenides and pnictides.^[23, 29] In both cases, the actual active species are still oxyhydroxides formed upon electrooxidation of the surface, while the much better conducting core of a phosphide, chalcogenide or other material sustains efficient charge-transfer between the electrode and catalyst.^[28, 39] Whether there are other promoting effects, *e.g.* changes in the electronic states provided by the core, is currently being investigated.

In contrast to the alkaline medium, there is a very limited number of noble-metal-free OER electrocatalysts designed for operation in acidic electrolytes, which is otherwise believed to provide several important technological advantages over the classical high pH systems.^[40, 41] Until recently, the only realistic competitor to the iridium-based catalysts were lead(IV) oxides with different dopants, that have been used in metal electrowinning and refining from acid baths for decades.^[42] While PbO_2 itself is not highly active towards the OER, it can accommodate other metals like cobalt, manganese and silver with substantially higher activity. In essence, the strategy of using a “matrix”, which is highly conductive and thermodynamically stable, to stabilise otherwise thermodynamically unstable, but more catalytically active, elements currently presents the most popular, and arguably the only feasible, approach for the development of robust and high-performance electrocatalysts for acidic water oxidation. It is also applied to the iridium-based systems,^[43] since even highly-active IrO_x monometallic catalysts do not provide sufficient stability.^[44] As an alternative to the classical PbO_2 matrix for non-noble-metal OER catalysts, which is highly advantageous in many technological aspects, but presents a significant toxicity problem, antimony oxides have been recently introduced by Lewis and co-workers.^[41] However, even this approach does not entirely solve the instability problem. After relatively short periods of operation, the active elements leach from the electrodes inducing significant losses in activity.

An efficient strategy to suppress the dissolution of metal oxides during the OER is to introduce corresponding dissolved cations into the electrolysed solutions, *i.e.* to enable a *self-healing* mechanism

of operation popularised by Kanan and Nocera for water oxidation in neutral solutions.^[45] Very recently, the self-healing strategy has been successfully coupled to the “matrix” approach in our laboratories to demonstrate unprecedented stability in operation of a noble-metal-free Co-Fe-Pb catalytic system for the OER in strongly acidic solutions (**Figure 3**).^[46] One of the key features of this work was the demonstration of robust operation of the catalyst at very high current densities of up to 0.5 A cm^{-2} (with a flat support) and at high temperatures, up to 80°C as required for the operation in a real electrolyser.

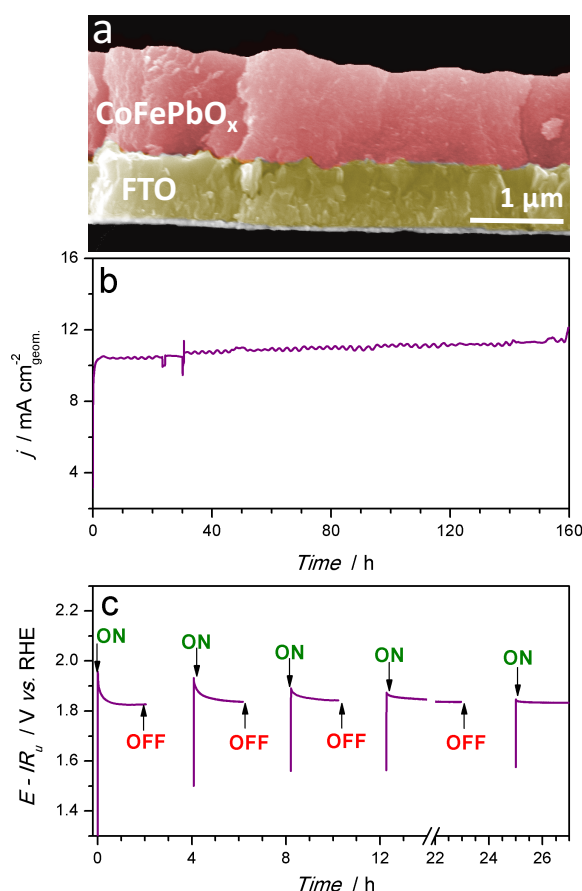


Figure 3. Microscopic and electrochemical analyses of a self-healing CoFePbO_x electrocatalyst. (a) Cross-sectional SEM image of electrode and (b) potentiostatic water (0.1 M H₂SO₄) oxidation at 23°C and at an applied potential of 2.03 V vs reversible hydrogen electrode (RHE). (c) Galvanostatic water oxidation in 1 M H₂SO₄ in an interrupted mode at 60°C . Redrawn from Ref ^[46].

This data contrasts with the approach of undertaking stability tests only under ambient conditions, as unfortunately is commonly the case in water splitting research on both anode and cathode catalysts. Unfortunately, results obtained in such a manner are un-informative in regard to the applicability of the developed materials for water splitting technology. This is especially problematic for the acidic OER catalysts, which slowly degrade even at ambient temperature (unless operating in a self-healing mode). Thus, it is clear that further breakthroughs in the design of practically efficient and robust water splitting catalysts requires reconsideration by reviewers and editors of what is considered meaningful in terms of materials testing. Similarly, in the applied context the initial activity, measured

in a voltammetric mode, does not present any value. Only performance on a sufficiently long timescale under conditions that are industrially relevant is meaningful.

4. Early steps and challenges in direct electrochemical NRR

Achieving the possibility of synthesizing ammonia under mild conditions using renewable electricity, to replace the Haber-Bosch process, has driven the recent surge of interest in the electrochemical nitrogen reduction reaction (NRR). The feasibility of a direct electrochemical process for the NRR was first demonstrated by Licht *et al.* in their seminal work.^[47] A catalytic system comprised of Fe₂O₃ nanoparticles suspended in molten hydroxides at 200 °C were optimized to deliver ammonia generation at 35% faradaic efficiency at a respectable current of 2 mA cm⁻² and a cell voltage of 1.23 V.

Subsequent research effort has focused on lowering the temperature towards ambient conditions by catalyst, electrolyte and cell design. However, as discussed in several recent commentaries^[3, 4], typically only very low faradaic efficiencies are achieved due to the competing hydrogen evolution reaction; this dominates due to both the inertness and the low solubility N₂ in aqueous media. The lower temperatures also result in lower production rates ($< 10^{-10}$ mol s⁻¹ cm⁻²) that are a long way from practical. Such generally low production rates give rise to a grand challenge in demonstrating genuine NRR *versus* background laboratory levels of ammonia. This issue arises from the presence of variable ambient levels of NH₃ and NO_x, emanating from anthropological activities, as possible contaminants that can result in detection of ammonia that is not due to the electrochemical NRR.^[3] For example, **Figure 4** shows a satellite NH₃ monitoring study by Van Damme *et al.*, mapping the atmospheric concentration of ammonia contamination around the world.^[48] These contamination levels are significant relative to the generally reported NH₃ yield rates from electrochemical processes (assuming rates between 10^{-12} to 10^{-10} mol s⁻¹ cm⁻² from 1 hour experiments). Gaseous NO_x and dissolved nitrite and nitrate species are also very common contaminants in the materials, gas supplies and the laboratory environment and these are very readily reducible to ammonia under the conditions typically used in NRR studies.

Beyond these many sources of contaminants, several studies have demonstrated that false-positives can be generated from reduction of structural/lattice nitrogen in the catalyst material rather than the supplied N₂. Despite the earlier plethora of positive results on the NRR activity of metal nitrides, recently groups including ours^[49] and Liu's^[50] have observed the generation of NH₃ from N-containing catalysts such as Mo₂N, VN and NbN, under Ar, with no increase when N₂ is supplied. As a result, efforts have been made from a number of research groups to design experimental protocols to ensure the validity of the observed NRR catalytic activity, if strictly followed.^[3, 4, 51]

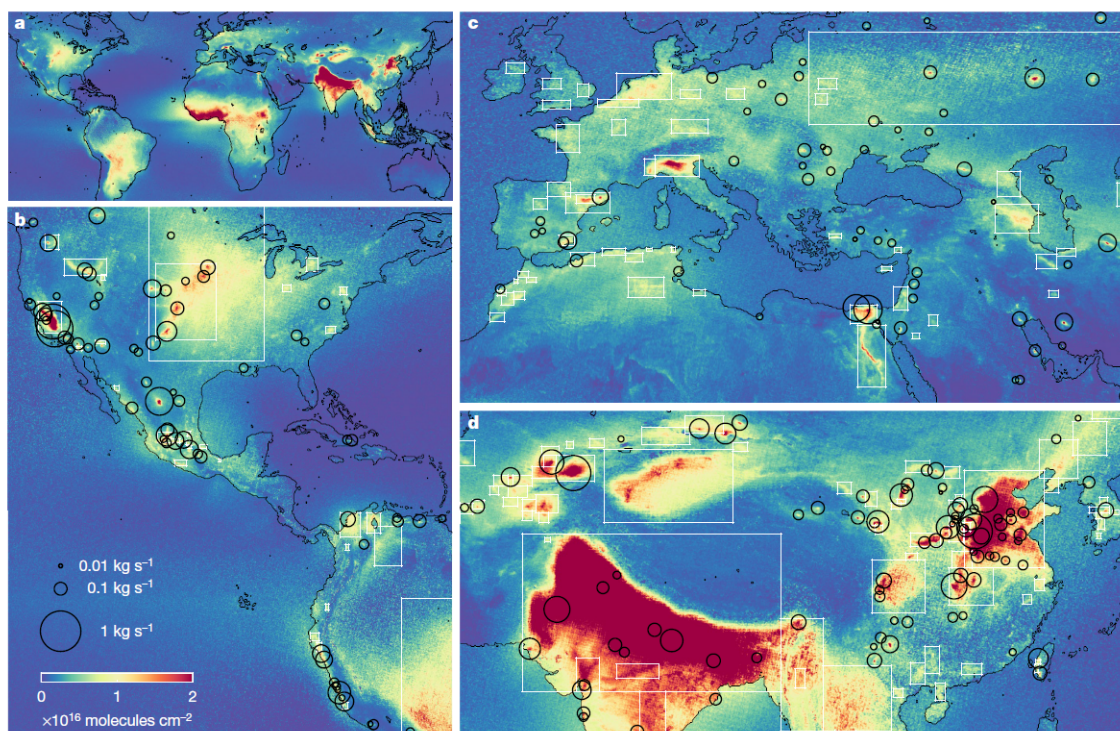


Figure 4. a, Nine-year global Infrared Atmospheric Sounding Interferometer (IASI) average NH_3 distribution (molecules cm^{-2}). b-d, High-resolution maps of average distribution of NH_3 in three major continents: (b) the North America and a part of Northern Latin America, (c) Europe with part of Northern Africa and the Middle East, and (d) Asia. Reproduced with permission from Ref ^[48].

The key to these protocols is ^{15}N -isotope labelling of the feed gas, to verify the production of $^{15}\text{NH}_3$ from electrochemical reduction of $^{15}\text{N}_2$ as a critical and compulsory step. To this end, several groups have proposed comprehensive guidelines for quantifying $^{15}\text{NH}_3$ using methods such as ^1H -NMR, mass spectrometry and gas phase FT-IR.^[51] The quantitative amount of $^{15}\text{NH}_3$ should be in reasonable agreement with the main experiments using $^{14}\text{N}_2$. Even at this point, only a proper $^{15}\text{N}_2$ handling practice can fully verify a genuine NRR. As evidenced by Dabundo *et al.*, there are significant amounts of $^{15}\text{NH}_3$, $^{15}\text{NH}_x$ and $^{15}\text{NO}_x$ contaminants in the commercially available $^{15}\text{N}_2$ gases that can result in a false-positive production of $^{15}\text{NH}_3$.^[52] The presence of $^{14/15}\text{NO}_x$ in the feed gas is particularly troublesome as no control experiment can discriminate between NO_x reduction and N_2 reduction and continuous experiments over long times with a continuous gas feed can be equally misleading. Hence the purity of the used $^{15}\text{N}_2$ needs to be assured before any quantitative $^{15}\text{NH}_3$ measurements can be meaningful. Unfortunately, in the present literature, the purification of $^{15}\text{N}_2$ gases and quantitative $^{15}\text{NH}_3$ measurement are often overlooked, allowing the oversight of contaminants that may give rise to false-positives. Consequently, it has become necessary to re-evaluate many of the reported electrocatalytic materials for NRR and the status of the field becomes very difficult to accurately assess. It is important

to note that a number of recent reviews do not attempt to address the quality of the results and are therefore of limited value.

Central to efficient NRR is the need to develop strategies to suppress the concurrent HER, which can be equally important to the screening of different well-known catalysts. A combination of sophisticated strategies can potentially suppress the HER towards a high rate and selectivity NRR. One effective strategy is to increase the solubility of N_2 to make it more competitive against proton reduction, for instance, through using an aprotic system of highly fluorinated ionic liquids as electrolytes.^[53] The high level of fluorination offers weaker van der Waals intermolecular interactions, allowing more N_2 to be dissolved.^[54] With the ability to control the concentration of proton sources (e.g. water) and dissolve higher amounts of N_2 (4.1 mmol L^{-1} versus 0.6 mmol L^{-1} in H_2O), we were able to demonstrate NRR faradaic efficiency of up to 66% with a NH_3 production rate of $4.7 \times 10^{-12} \text{ mol s}^{-1} \text{ cm}^{-2}$ at ambient pressure and temperature on an electrodeposited Fe catalyst. Further work has focused on mitigating the mass transport limitation of the generally viscous aprotic ionic liquids, by development of electrolyte systems based on a fluorinated solvent with higher fluidity and N_2 solubility, up to 12 mmol L^{-1} .^[55]

A recent study by Anderson et al, confirmed that HER is strongly predominant in aqueous media rather than NRR using many of the promising pure-metal catalysts.^[51] This demands a more sophisticated catalyst design strategy to effectively suppress HER on the surface of the catalysts. As an illustration, HER can be suppressed by selecting an appropriate support material that can retard the H-H bond formation from the surface activated H^+ that is required for ammonia formation. This has been demonstrated in our most recent work, utilizing the tuneable HER activity feature of MoS_2 polymorphs to support efficient aqueous NRR on the surface of Ru nanoparticles attached to the MoS_2 surface (**Figure 5**), achieving faradaic efficiency as high as 18 % and NH_3 yield rate of $1.1 \times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$ at ambient pressure.^[56]

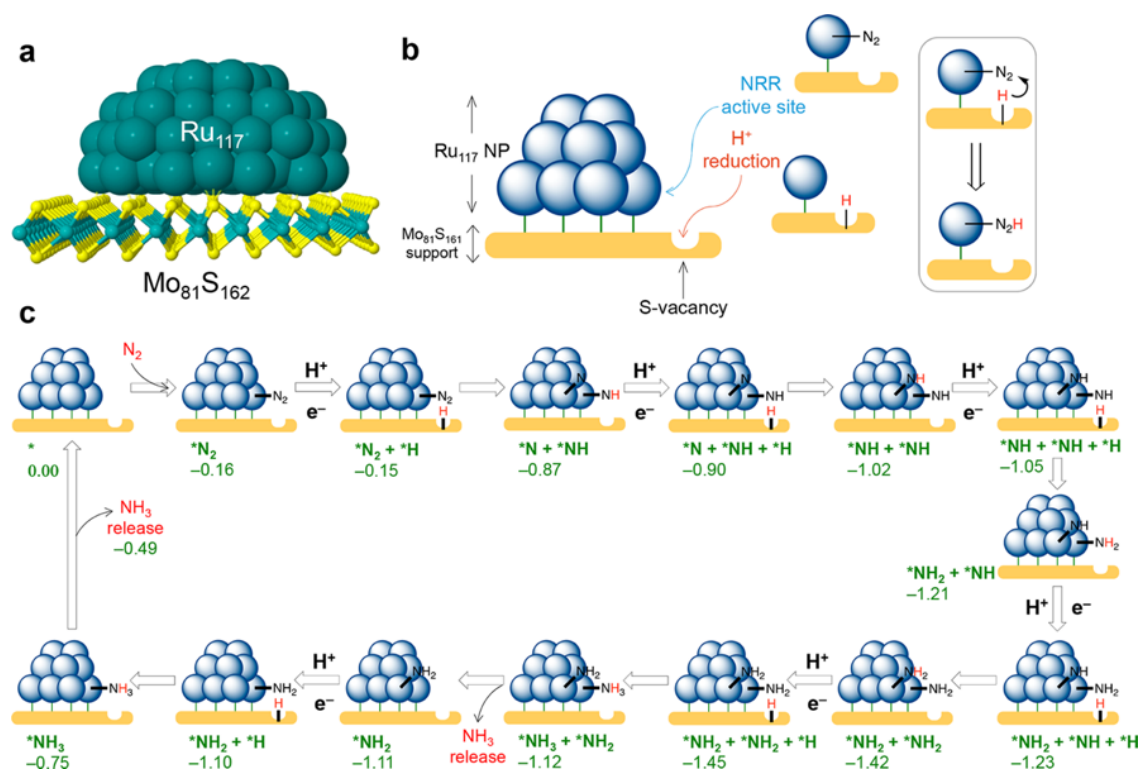


Figure 5. Mechanism of NRR on an Ru/2H-MoS₂ composite catalyst. DFT model consisting of a h.c.p. Ru₁₁₇ nanocluster on a 2H-MoS₂ supercell. (b) Schematic demonstrating how Ru/2H-MoS₂ supports NRR by absorption of N₂ on the Ru and H⁺ absorption on the 2H-MoS₂; (c) Minimum-energy pathway for NRR. Relative Gibbs free energies are shown in eV. Reproduced with permission from ref.^[56]

In summary, the NRR field has made significant conceptual progress in the past several years, but missteps in terms of false-positives are obscuring the true origins of catalytic activity and the viable pathways to highly selective electrocatalytic materials. Early identification of possible contaminations and pitfalls in experimental protocols are needed to underpin more effective and guided future development of electrocatalytic systems that can genuinely reduce N₂ to ammonia.

5. Mechanistic studies in electrocatalysis: electrokinetic modelling and *in situ* investigations

Understanding the mechanism of the process and the nature of key active sites is a prerequisite for the genuinely rational design of high-performance electrocatalysts. A significant advantage of the electrocatalytic systems as opposed to other modes of catalysis is direct access, via electrochemical measurements, to information not only on the reaction rate, but also on the key charge transfer events at the catalyst surface that drive the reaction. Identification and quantification of these processes is most efficient when using specialised techniques such as Fourier transformed alternating current voltammetry.^[57] This approach is particularly powerful when coupled to comprehensive modelling to extract the key thermodynamic and kinetic parameters of the faradaic and chemical processes in the

system as a function of reaction conditions or catalyst composition.^[58, 59] Electrochemical experiment vs. theory comparisons can then provide insights into the validity of the initial “guess” on the mechanism, and guide researchers in reconsidering the model if the theoretical predictions do not fit the experimental trends. However, the majority of the experiment-simulation comparisons are undertaken heuristically, *i.e.* relying on an unavoidably biased experimentalist’s decision on what “good” and “bad” levels of agreement are. A fundamental step forward in the field that is desperately needed is the broad implementation of automated fitting methods and extended statistic protocols, which have been used in other fields for many years, to provide a quantitative measure of the validity of a particular electrocatalytic model in relation to the system of interest.^[60]

No matter how sensitive the electroanalytical tools are, they can only measure the rate of electron transfer, while providing only indirect and often hard to interpret information on the chemical nature of the compounds involved. From this perspective, reliable assignment of the catalytic current can only be made by detecting the product by an independent analytical method and calculating the faradaic efficiency. Establishing the chemical nature of the associated redox transformations of the electrocatalyst underpinning the catalytic process is significantly more challenging. Although *ex situ* characterisation of an electrocatalyst before and after testing is always highly useful and desirable, it might only provide circumstantial evidence on the nature of the real, *operando*, active state of the material, and sometimes might be entirely non-informative from this perspective. Hence, *in situ* or *operando* spectroscopic analysis is required in most cases. Apart from the detection and identification of the active sites, *operando* analysis also enables identification of the degradation modes of the material, *i.e.* understanding the “weak” sites in the material as well. Taken together, the knowledge derived from *in situ* / *operando* experiments and *ex situ* before and after characterisation tests is critical to the efficient development of new electrocatalysts and upgrading the existing materials.

Most popular spectroscopic methods employed in electrocatalytic *in situ* work currently include the infrared and X-ray based spectroscopies.^[61, 62, 63] An obvious advantage of the former class of methods is the possibility of undertaking experiments in a conventional laboratory environment, while most informative *in situ* X-ray experiments like hard- and soft X-ray absorption spectroscopy (XAS) and near-ambient pressure X-ray photoelectron spectroscopy (XPS) require synchrotron radiation. Nevertheless, such specific instrumental requirements provide the possibility of highly sensitive, and element-selective, analysis of the structure and electronic states of the materials that is not available with alternative methods. Many examples of high-end *in situ* XAS and XPS studies on electrocatalysts have been reported over the last decade by us and others (see for example Refs.^[62, 64, 65]), revealing key mechanistic insights that shed light on the actual modes of operation of different systems. Important complementary direct information on both electrocatalytic mechanisms and also on the degradation modes of materials can be derived from online mass-spectroscopic (MS) analysis of the compounds released by electrocatalyst during operation.^[66] This technique becomes particularly powerful when using isotopically labelled reactants and/or catalysts in the differential electrochemical MS mode.^[63]

Another highly specialised and probably one of the most challenging emerging methods for probing electrocatalysts in action is *in situ* electrochemical transmission electron microscopy (TEM).^[62] However the wealth of information on the structural and morphological rearrangement of materials on the nanoscale available through *in situ* TEM completely justifies the instrumental effort and we look forward to this technique becoming more generally available.

Over the last decade, the rate of publications on *in situ* / *operando* characterisation in electrocatalysis has progressively grown, reflecting the broad recognition of the utility of the methods by the community. However, one aspect that often remains overlooked or under-interpreted in these studies is the direct correlation of the data derived from *in situ* measurements with the dynamics of key redox transformations of the probed electrocatalyst. Most commonly, researchers focus on conditions that provide reasonably high catalytic current, which however does not guarantee that the “starting” active state is present on the electrode surface in sufficient amount to be identified.^[59, 64] To ensure that the latter is the case and to make the *in situ* / *operando* analysis most meaningful, these experiments should be guided by comprehensive electrokinetic modelling as a function of current density based on a plausible hypothesis on the mechanism of the investigated reaction.^[64] Such a strategy would be highly efficient in terms of confirming or disproving the hypothesised mechanism and establishing the nature of the real active sites in the electrocatalyst.

6. DFT modelling – towards *in-silico* design of electromaterials

As described at various points in the discussion above, far from being a merely supportive technique capable of analysis of reaction mechanisms at the atomic level, DFT modelling has become a powerful tool for prior-to-synthesis prediction of reactive behaviours and energetics. Our own efforts in the employment of theoretical techniques are ultimately aimed at proactive identification of promising electrocatalytic materials, being therefore part of the concept commonly referred to as computer-aided molecular (or *in-silico*) design. The CO₂RR and NRR electrosynthesis mechanisms can be analysed *via* DFT modelling as a process of consecutive elementary steps of hydrogenation ($*A + H^+ + e^- \rightarrow *AH\bullet$). However, the CO₂ reduction into hydrocarbons and the electrochemical N₂-to-NH₃ conversion each present a series of unique features from the mechanistic point-of-view. Firstly, complete CO₂ reduction into methane is an 8e process, while nitrogen reduction reaction (NRR) only requires 6e to produce ammonia; together with the smaller number of types of centres to be potentially hydrogenated in the case of N₂, this entails a smaller number of reaction intermediates to be described in the latter case. Secondly, the obtaining of the less-reduced nitrogen compounds of diazene (N₂H₂) and hydrazine (N₂H₄) are thermodynamically unfavourable with respect to that of NH₃, whereas the CO₂RR has a number of intermediates or alternative products such as CO that need to be taken into account.

The proton-coupled electron transfer (PCET) approach ($*A + H^+ + e^- \rightarrow *AH\bullet$) is a key part of how these DFT studies are carried out. It assumes that the electron and proton reach the catalytic site in

a concerted way; this has been demonstrated to lead to lower energy intermediates, bypassing the high-energy intermediates of the alternative step-wise mechanisms. Our investigations of several materials (mostly metal surfaces and nanoparticles) have corroborated this fact, also estimating overpotential values very close to the experimental ones^[67] (the overpotential usually being indicated by the highest energy step of the mechanism). Undoubtedly, this PCET approach is a powerful and easy-to-handle methodology enabling a robust quantum mechanical description of electrocatalytic phenomena. However, in our view it should not be employed as an un-questioned mechanism for every system, and the validity of this assumption needs to be carefully evaluated in each case. As seen in enzyme catalysed reactions, there is certainly potential for the electron and proton delivery steps to be separated, with charge compensation provided by the surroundings or by electrolyte ions. The current materials-development literature is replete with examples of the unquestioning use of the PCET approach and the beginning researcher could be mistakenly convinced that this is a fundamental facet of every mechanism.

To make significant further progress the theoretical community working in DFT modelling of electrocatalysis faces a series of further challenges that need urgent resolution. Amongst them is the lack of a well-founded methodology for the searching of transition states (TS) in a system in which reactants and products differ in the number of electrons. This poor understanding of the details of kinetic phenomena in electrochemical reactions means that the estimation of overpotentials is usually based on the thermodynamic steps between intermediates, *i.e.*, the description of the largest endergonic step in the free energy profile of the reaction; this has a more direct relationship to the equilibrium potentials rather than the kinetic barriers. Recent studies in the estimation of NRR kinetics through the calculation of potential dependent electrochemical barriers^[68] show values greater than 1 eV in a series of late transition metal surfaces.^[69] However, some of these values are in considerable disagreement with observed experimental results (though it must be noted that many experimental results are questionable, as discussed above). Goddard and co-workers have recently performed quantum mechanical (QM) reactive metadynamics to evaluate the activation energies in CO₂RR.^[70] They estimated the barrier for the Cu-catalysed hydrogenation of adsorbed CO₂ into *COOH to be 0.37 eV, approximately as expected for this type of electrochemical process. This methodology, including multiple layers of explicit water as solvent, suffers from greater complexity and demands an extensive amount of computational resources, making it currently impractical for many researchers in the rapidly developing CO₂RR and NRR fields; yet it offers an ultimately more genuine insight into the process.

In many cases of interest, there are multiple, distinctly different, mechanistic pathways that the *in-silico* approach must be able to distinguish between. For example, in contrast to the high-pressure and temperature Haber–Bosch ammonia industrial process, in which a dissociative mechanism occurs by splitting of N₂ and H₂ reactants, one could expect that an associative mechanism for N₂ reduction, in which the N₂ molecule is progressively hydrogenated, would be preferred in NRR at ambient conditions. However, based on recent and independent investigations by Kitano^[71] and us (**Figure 5**),^[72]

it has shown that Ru exhibits an unprecedented behaviour as promoter of the spontaneous breaking of the $\text{N}\equiv\text{N}$ bond during the first electrochemical step. Currently, we are involved in a detailed DFT investigation of why ruthenium (and tentatively other metals) works in this way. Other, potentially linked, aspects under consideration focus on the deepening of our understanding of surface coverage effect. While this has been intensely investigated in related electrochemical transformations,^[73] we hypothesise that it is important to analyse how stabilised reduced species, such as $\ast\text{H}$ and $\ast\text{N}(\text{H})$, might affect the catalytic performance of the surface during reaction.

A further evolution of *in silico* design needs to be able to approach the question of *selectivity*, i.e. to understand how two or more parallel processes compete on a surface. This would support the design of second-generation catalysts (**Figure 6**) favouring NRR or CO_2RR over the competing hydrogen evolution reaction. Our recent work synthesising Ru nanoparticles embedded in pristine MoS_2 is a pioneering case in point since NRR was hypothesised as being promoted at the interface between the Ru nanoparticle and the S-vacancy of defective 2H-MoS_2 on a surface of low activity to HER.^[56]

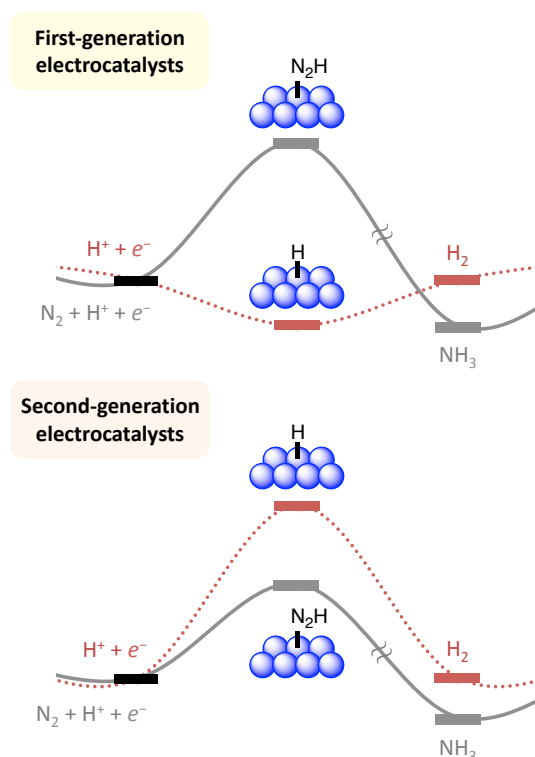


Figure 6. Schematic binding energy diagrams for classical (first-generation) and ideal (second-generation) NRR electrocatalysts where the first hydrogenated intermediate in NRR ($\ast\text{N}_2\text{H}$) demands a lower free energy of activation than the reduction of protons to produce the adsorbed $\ast\text{H}$ species, ie $\Delta G(\ast\text{N}_2\text{H}) < \Delta G(\ast\text{H})$.

The DFT modelling could also focus effort on the design of increasingly sophisticated and novel materials being capable of selectively stabilise the nitrogen intermediates compared to the adsorption of reduced protons, $\ast\text{H}$. This ideal behaviour, as has been explored recently by DFT studies of defected

bismuth,^[74] is the real challenge towards the design of efficient machineries for obtaining highly selective catalysts.

Last but not least, it is worth pointing out the need to establish a standard model for electrocatalytic modelling or at least for each type of reaction of interest (NRR, CO₂RR etc). It is common to observe the employment of a variety of different procedures in the literature, even within reported results from the same research group, without discussion of any conceptual development involved or comparison to other methods. A referential model would help in making the results reproducible in other laboratories as well as to discerning the value of using one method over others to address a specific mechanistic problem.

7. Conclusions and Perspectives

Liquid chemical energy carriers, without doubt, will form a very significant part of global society's energy future, and remote parts of Australia and other regions having vast resources of solar and wind energy will become the global power-houses.

We have focussed here on electromaterials for the energy- and atom- efficient catalysis of energy carriers including ammonia and hydrogen, along with the water oxidation reaction that is implicitly required to complete the electrochemistry. We have placed less emphasis on the CO₂RR, despite it being an intensely researched area, including from our own laboratories, because it is not ultimately clear that this family of reactions offers a sufficiently viable, large-scale solution to the "Liquid Sunshine" challenge. Used in any mode where captured fossil-CO₂ is the feedstock, the reduced energy-carrier form, for example methanol, is still a fossil carbon product and the carbon cannot ultimately be released to the atmosphere if this is to represent a direct contribution to fossil-carbon emissions reduction. We also note in passing that such processes also have the potential to represent a politically sensitive emissions-displacement mechanism between countries – the carbon load is transferred from the producer country to the user country. Used in an atmospheric carbon-capture mode where the feedstock is atmospheric carbon and the CO₂ is re-released to the atmosphere at point of use, the process becomes sustainable, but the challenge is to render such a combination of air-carbon capture + CO₂RR energetically competitive with any of the other processes discussed here. One could speculate that CO₂RR has potential in replacing high value hydrocarbons such as jet fuels, though it is interesting to note that already there is discussion amongst jet-engine designers about the use of ammonia as a short-haul jet fuel.

Clearly hydrogen and ammonia have significant potential as near-term and not-so-distant future energy carriers. The techno-economics of their competitive position versus traditional fossil fuels is altering rapidly in their favour as energy prices continue to tumble and research and development effort decreases the cost of the devices. Nonetheless, there remains much yet to be done in this regard and much of that is electromaterials research targeted at higher selectivity, higher activity and lower costs. The HER and OER fields are somewhat mature, however the renewed focus on acid electrolysis is

creating important new opportunities for imaginative materials discovery and development. It is interesting to note that the falling price of renewable energy is tending to shift the cost-emphasis more towards materials and production costs and less on energy efficiency. The NRR electrocatalysis field is at a relatively early stage and is making all of the early mistakes that important but challenging research typically produces; so, reader beware – in the view of the present authors if an article does not include quantified $^{15}\text{N}_2$ results, it is not worth reading. Nonetheless there are signs that this phase is passing and that a genuinely reliable literature is emerging. There is clearly huge potential for NRR electrocatalyst research at the fundamental and practical level and we commend the materials community to the important task of making Liquid Sunshine a reality

Acknowledgments

R.J. and DRM thank the ARC for financial support through their DECRA (DE180100215) and Laureate Fellowships respectively. L.M.A. is an ULPGC Postdoc Fellow, and thanks Universidad de Las Palmas de Gran Canaria (ULPGC)."

References

- [1] *Global Normal Solar Insolation*, <https://globalsolaratlas.info/downloads> accessed June 28 2019.
- [2] M. Dolan, <https://publications.csiro.au/rpr/pub?pid=csiro:EP172829> accessed Jul 29 2019, 2017.
- [3] B. H. R. Suryanto, H.-L. Du, D. Wang, J. Chen, A. N. Simonov, D. R. MacFarlane, *Nature Catalysis* 2019, 2, 290.
- [4] S. Z. Andersen, V. Čolić, S. Yang, J. A. Schwalbe, A. C. Nielander, J. M. McEnaney, K. Enemark-Rasmussen, J. G. Baker, A. R. Singh, B. A. Rohr, M. J. Statt, S. J. Blair, S. Mezzavilla, J. Kibsgaard, P. C. K. Vesborg, M. Cargnello, S. F. Bent, T. F. Jaramillo, I. E. L. Stephens, J. K. Nørskov, I. Chorkendorff, *Nature* 2019, 570, 504.
- [5] C. Xiao, X. Zhang, D. R. MacFarlane, *Electrochimica Acta* 2018, 280, 55.
- [6] N. Corbin, J. Zeng, K. Williams, K. Manthiram, *Nano Res.* 2019, 1.
- [7] C. Costentin, J.-M. Savéant, *Curr. Opin. Electrochem.* 2019, 15, 58.
- [8] J. H. Zagal, S. Griveau, J. F. Silva, T. Nyokong, F. Bedioui, *Coord. Chem. Rev.* 2010, 254, 2755.
- [9] J.-W. Wang, W.-J. Liu, D.-C. Zhong, T.-B. Lu, *Coord. Chem. Rev.* 2019, 378, 237.
- [10] R. Matheu, M. Z. Ertem, C. Gimbert-Suriñach, X. Sala, A. Llobet, *Chem. Rev.* 2019, 119, 3453; K. S. Joya, Y. F. Joya, K. Ocakoglu, R. van de Krol, *Angew. Chem., Int. Ed.* 2013, 52, 10426; M. L. Pegis, C. F. Wise, D. J. Martin, J. M. Mayer, *Chem. Rev.* 2018, 118, 2340.
- [11] A. Badalyan, S. S. Stahl, *Nature* 2016, 535, 406.
- [12] F. Franco, S. Fernandez, J. Lloret-Fillol, *Curr. Opin. Electrochem.* 2019, 15, 109; C. Costentin, S. Drouet, M. Robert, J.-M. Savéant, *Science* 2012, 338, 90; J. Choi, T. M. Benedetti, R. Jalili, A. Walker, G. G. Wallace, D. L. Officer, *Chem. - Eur. J.* 2016, 22, 14158.
- [13] C. Costentin, M. Robert, J.-M. Savéant, *Curr. Opin. Electrochem.* 2017, 2, 26; R. M. Bullock, A. K. Das, A. M. Appel, *Chem. - Eur. J.* 2017, 23, 7626.
- [14] D. Micheroni, G. Lan, W. Lin, *J. Am. Chem. Soc.* 2018, 140, 15591; J. Meng, H. Lei, X. Li, J. Qi, W. Zhang, R. Cao, *ACS Catal.* 2019, 9, 4551; J. Choi, P. Wagner, R. Jalili, J. Kim, D. R. MacFarlane, G. G. Wallace, D. L. Officer, *Adv. Energy Mater.* 2018, 8, 1801280; C. J. Kaminsky, J.

- Wright, Y. Surendranath, ACS Catal. 2019, 9, 3667; X. Zhang, Z. Wu, X. Zhang, L. Li, Y. Li, H. Xu, X. Li, X. Yu, Z. Zhang, Y. Liang, Nat. Commun. 2017, 8, 14675.
- [15] J. Choi, P. Wagner, S. Gambhir, R. Jalili, D. R. MacFarlane, G. G. Wallace, D. L. Officer, ACS Energy Lett. 2019, 4, 666.
- [16] J. Choi, J. Kim, P. Wagner, S. Gambhir, R. Jalili, S. Byun, S. Sayyar, Y. M. Lee, D. R. MacFarlane, G. G. Wallace, Energy Environ. Sci. 2019, 12, 747.
- [17] C. Costentin, H. Dridi, J.-M. Savéant, J. Am. Chem. Soc. 2015, 137, 13535.
- [18] M. Zhu, R. Ye, K. Jin, N. Lazouski, K. Manthiram, ACS Energy Lett. 2018, 3, 1381; J. Mizuguchi, J. Phys. Chem. A 2001, 105, 10719.
- [19] *Development-of-water-electrolysis-in-the-european-union*, <http://www.e4tech.com/reports/development-of-water-electrolysis-in-the-european-union/>.
- [20] C. C. L. McCrory, S. Jung, I. M. Ferrer, S. M. Chatman, J. C. Peters, T. F. Jaramillo, Journal of the American Chemical Society 2015, 137, 4347.
- [21] B. Hinnemann, P. G. Moses, J. Bonde, K. P. Jørgensen, J. H. Nielsen, S. Hørch, I. Chorkendorff, J. K. Nørskov, Journal of the American Chemical Society 2005, 127, 5308.
- [22] A. Sobczynski, Journal of Catalysis 1991, 131, 156.
- [23] S. Anantharaj, S. R. Ede, K. Sakthikumar, K. Karthick, S. Mishra, S. Kundu, ACS Catalysis 2016, 6, 8069.
- [24] J. Hu, B. Huang, C. Zhang, Z. Wang, Y. An, D. Zhou, H. Lin, M. K. H. Leung, S. Yang, Energy & Environmental Science 2017, 10, 593.
- [25] M. Chatti, T. Gengenbach, R. King, L. Spiccia, A. N. Simonov, Chemistry of Materials 2017, 29, 3092.
- [26] M.-R. Gao, M. K. Y. Chan, Y. Sun, Nature Communications 2015, 6, 7493.
- [27] Y. Han, M. Chatti, Y. Ge, C. Wang, Y. Chao, A. N. Simonov, G. G. Wallace, ChemElectroChem 2019, 6, 2338; R. B. N. Baig, R. S. Varma, Chemical Society Reviews 2012, 41, 1559.
- [28] M. Chatti, A. M. Glushenkov, T. Gengenbach, G. P. Knowles, T. C. Mendes, A. V. Ellis, L. Spiccia, R. K. Hocking, A. N. Simonov, Sustainable Energy & Fuels 2018, 2, 1561.
- [29] A.-M. Alexander, J. S. J. Hargreaves, Chemical Society Reviews 2010, 39, 4388.
- [30] N. P. Sweeny, C. S. Rohrer, O. W. Brown, Journal of the American Chemical Society 1958, 80, 799.
- [31] S. Carenco, D. Portehault, C. Boissière, N. Mézailles, C. Sanchez, Chemical Reviews 2013, 113, 7981.
- [32] A. B. Laursen, K. R. Patraju, M. J. Whitaker, M. Retuerto, T. Sarkar, N. Yao, K. V. Ramanujachary, M. Greenblatt, G. C. Dismukes, Energy & Environmental Science 2015, 8, 1027.
- [33] Y. Lee, J. Suntivich, K. J. May, E. E. Perry, Y. Shao-Horn, The Journal of Physical Chemistry Letters 2012, 3, 399.
- [34] J. H. Montoya, L. C. Seitz, P. Chakthranont, A. Vojvodic, T. F. Jaramillo, J. K. Nørskov, Nature Materials 2016, 16, 70.
- [35] M. S. Faber, S. Jin, Energy & Environmental Science 2014, 7, 3519.
- [36] I. Roger, M. A. Shipman, M. D. Symes, Nature Reviews Chemistry 2017, 1, 0003.
- [37] J. Suntivich, K. J. May, H. A. Gasteiger, J. B. Goodenough, Y. Shao-Horn, Science 2011, 334, 1383.
- [38] B. Zhang, X. Zheng, O. Voznyy, R. Comin, M. Bajdich, M. García-Melchor, L. Han, J. Xu, M. Liu, L. Zheng, F. P. García de Arquer, C. T. Dinh, F. Fan, M. Yuan, E. Yassitepe, N. Chen, T. Regier, P. Liu, Y. Li, P. De Luna, A. Janmohamed, H. L. Xin, H. Yang, A. Vojvodic, E. H. Sargent, Science 2016, 352, 333.
- [39] B. R. Wygant, K. Kawashima, C. B. Mullins, ACS Energy Letters 2018, 3, 2956.
- [40] M. Carmo, D. L. Fritz, J. Mergel, D. Stolten, International Journal of Hydrogen Energy 2013, 38, 4901.
- [41] I. A. Moreno-Hernandez, C. A. MacFarland, C. G. Read, K. M. Papadantonakis, B. S. Brunshwig, N. S. Lewis, Energy & Environmental Science 2017, 10, 2103.
- [42] X. Li, D. Pletcher, F. C. Walsh, Chemical Society Reviews 2011, 40, 3879.
- [43] L. C. Seitz, C. F. Dickens, K. Nishio, Y. Hikita, J. Montoya, A. Doyle, C. Kirk, A. Vojvodic, H. Y. Hwang, J. K. Nørskov, T. F. Jaramillo, Science 2016, 353, 1011.

- [44] S. Geiger, O. Kasian, M. Ledendecker, E. Pizzutilo, A. M. Mingers, W. T. Fu, O. Diaz-Morales, Z. Li, T. Oellers, L. Fruchter, A. Ludwig, K. J. J. Mayrhofer, M. T. M. Koper, S. Cherevko, *Nature Catalysis* 2018, 1, 508.
- [45] M. W. Kanan, D. G. Nocera, *Science* 2008, 321, 1072.
- [46] M. Chatti, J. L. Gardiner, M. Fournier, B. Johannessen, T. Williams, T. R. Gengenbach, N. Pai, C. Nguyen, D. R. MacFarlane, R. K. Hocking, A. N. Simonov, *Nature Catalysis* 2019, 2, 457.
- [47] S. Licht, B. Cui, B. Wang, F.-F. Li, J. Lau, S. Liu, *Science* 2014, 345, 637.
- [48] M. Van Damme, L. Clarisse, S. Whitburn, J. Hadji-Lazaro, D. Hurtmans, C. Clerbaux, P.-F. Coheur, *Nature* 2018, 564, 99.
- [49] H.-L. Du, T. R. Gengenbach, R. Hodgetts, D. R. MacFarlane, A. N. Simonov, *ACS Sustainable Chemistry & Engineering* 2019, 7, 6839.
- [50] B. Hu, M. Hu, L. Seefeldt, T. L. Liu, *ACS Energy Letters* 2019, 4, 1053.
- [51] A. C. Nielander, J. M. McEnaney, J. A. Schwalbe, J. G. Baker, S. J. Blair, L. Wang, J. G. Pelton, S. Z. Andersen, K. Enemark-Rasmussen, V. Čolić, S. Yang, S. F. Bent, M. Cargnello, J. Kibsgaard, P. C. K. Vesborg, I. Chorkendorff, T. F. Jaramillo, *ACS Catalysis* 2019, 5797.
- [52] R. Dabundo, M. F. Lehmann, L. Treibergs, C. R. Tobias, M. A. Altabet, P. H. Moisaner, J. Granger, *PLOS ONE* 2014, 9, e110335.
- [53] F. Zhou, L. M. Azofra, M. Ali, M. Kar, A. N. Simonov, C. McDonnell-Worth, C. Sun, X. Zhang, D. R. MacFarlane, *Energy & Environmental Science* 2017; C. S. M. Kang, X. Zhang, D. R. MacFarlane, *J. Phys. Chem. C* 2018, 122, 24550.
- [54] C. S. M. Kang, X. Zhang, D. R. MacFarlane, *J. Phys. Chem. C* 2018, 122, 24550.
- [55] C. S. M. Kang, D. R. MacFarlane, *Journal of Physical Chemistry C* 2019, in press.
- [56] B. H. R. Suryanto, D. Wang, L. M. Azofra, M. Harb, L. Cavallo, R. Jalili, D. R. G. Mitchell, M. Chatti, D. R. MacFarlane, *ACS Energy Letters* 2019, 4, 430.
- [57] Y. Zhang, A. N. Simonov, J. Zhang, A. M. Bond, *Current Opinion in Electrochemistry* 2018, 10, 72; A. M. Bond, D. Elton, S.-X. Guo, G. F. Kennedy, E. Mashkina, A. N. Simonov, J. Zhang, *Electrochemistry Communications* 2015, 57, 78.
- [58] A. N. Simonov, G. P. Morris, E. A. Mashkina, B. Bethwaite, K. Gillow, R. E. Baker, D. J. Gavaghan, A. M. Bond, *Analytical Chemistry* 2016; A. M. Bond, E. A. Mashkina, A. N. Simonov, in *Developments in Electrochemistry*, John Wiley & Sons, Ltd, 2014, 21.
- [59] S. A. Bonke, A. M. Bond, L. Spiccia, A. N. Simonov, *Journal of the American Chemical Society* 2016, 138, 16095.
- [60] M. Robinson, A. N. Simonov, J. Zhang, A. M. Bond, D. Gavaghan, *Analytical Chemistry* 2019, 91, 1944; D. J. Gavaghan, J. C. Cooper, A. C. Daly, C. Gill, K. Gillow, M. Robinson, A. N. Simonov, J. Zhang, A. M. Bond, *ChemElectroChem* 2017, 5, 917; G. P. Morris, A. N. Simonov, E. A. Mashkina, R. Bordas, K. Gillow, R. E. Baker, D. J. Gavaghan, A. M. Bond, *Analytical Chemistry* 2013, 85, 11780.
- [61] Z. Pavlovic, C. Ranjan, M. van Gastel, R. Schlögl, *Chemical Communications* 2017, 53, 12414; *In-situ Spectroscopic Studies of Adsorption at the Electrode and Electrocatalysis*, Elsevier Science B.V., Amsterdam 2007.
- [62] A. D. Handoko, F. Wei, Jenndy, B. S. Yeo, Z. W. Seh, *Nature Catalysis* 2018, 1, 922.
- [63] T. Reier, H. N. Nong, D. Teschner, R. Schlögl, P. Strasser, *Advanced Energy Materials* 2017, 7, 1601275.
- [64] M. Tesch, S. Bonke, T. Jones, M. Shaker, J. Xiao, K. Skorupska, R. Mom, J. Melder, P. Kurz, A. Knop-Gericke, R. Schlögl, R. Hocking, A. N. Simonov, *Angewandte Chemie* 2019, 58, 3426.
- [65] V. Pfeifer, T. E. Jones, J. J. Velasco Vélez, R. Arrigo, S. Piccinin, M. Hävecker, A. Knop-Gericke, R. Schlögl, *Chemical Science* 2017, 8, 2143.
- [66] I. Spanos, A. A. Auer, S. Neugebauer, X. Deng, H. Tüysüz, R. Schlögl, *ACS Catalysis* 2017, 7, 3768.
- [67] B. H. R. Suryanto, D. Wang, L. M. Azofra, M. Harb, L. Cavallo, R. Jalili, D. R. G. Mitchell, M. Chatti, D. R. MacFarlane, *ACS Energy Lett.* 2018, 4, 430.
- [68] G. Rostamikia, A. J. Mendoza, M. A. Hickner, M. J. Janik, *J. Power Sources* 2011, 196, 9228.
- [69] G. Rostamikia, S. Maheshwari, M. J. Janik, *Catal. Sci. Technol.* 2019, 9, 174.
- [70] T. Cheng, H. Xiao, W. A. Goddard, *J. Am. Chem. Soc.* 2016, 138, 13802.

- [71] M. Kitano, S. Kanbara, Y. Inoue, N. Kuganathan, P. V. Sushko, T. Yokoyama, M. Hara, H. Hosono, *Nat. Commun.* 2015, 6, 6731.
- [72] D. Wang, L. M. Azofra, M. Harb, L. Cavallo, X. Zhang, B. H. R. Suryanto, D. R. MacFarlane, *ChemSusChem* 2018, 11, 3416.
- [73] H. A. Aleksandrov, S. M. Kozlov, S. Schauermann, G. N. Vayssilov, K. M. Neyman, *Angew. Chem., Int. Ed.* 2014, 53, 13371; C. Shi, H. A. Hansen, A. C. Lausche, J. K. Nørskov, *Phys. Chem. Chem. Phys.* 2014, 16, 4720.
- [74] Y. Wang, M.-m. Shi, D. Bao, F.-l. Meng, Q. Zhang, Y.-t. Zhou, K.-h. Liu, Y. Zhang, J.-z. Wang, Z.-w. Chen, D.-p. Liu, Z. Jiang, M. Luo, L. Gu, Q.-h. Zhang, X.-z. Cao, Y. Yao, M.-h. Shao, Y. Zhang, X.-B. Zhang, J. G. Chen, J.-m. Yan, Q. Jiang, *Angew. Chem., Int. Ed.* 2019, 58, 9464.