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# CSIRO Hydrogen to Ammonia R&D Project

## Mid-term Knowledge Sharing Report

Sarb Giddey, Chris Munnings, Ani Kulkarni, HyungKuk Ju,  
Gary Paul, Louis Wibberley, Renata Lippi, David Alexander,  
Woo Jin Lee, Thuy Huynh, Scott Barnes, Ben Muir, Geoff  
Brent, Greg Conroy, Mark Rayson

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# Abbreviations

GRDC: Grains Research and Development Corporation

MMR: Metal membrane reactor

NG: Natural Gas

PEM: Polymer electrolyte membrane

PV: Photovoltaic

PSA: Pressure Swing Adsorption

SME: Small to Medium Enterprises

TRL: Technology Readiness Level

# 1 Project summary and scope

## 1.1 Rationale:

Currently most of the ammonia is globally produced by sourcing hydrogen from Natural Gas (NG) and making this hydrogen react with nitrogen in the presence of a catalyst in a Haber-Bosch reactor at around 450°C and pressures in excess of 150 bar. The major aim of the proposed work is to develop an alternative technology that can produce ammonia at much lower pressures (~30 bar) by sourcing hydrogen directly from a PEM electrolyser and scale-up the technology to build a prototype capable of producing ammonia with the only inputs being water, air and solar PV. In the conventional ammonia synthesis Haber-Bosch reactor hydrogen to ammonia conversion rates of around 15% are achieved in a single pass and with multiple passes, over 90% hydrogen utilisation is achieved. In the previous project in collaboration with Orica, a metal membrane-based process was developed to convert hydrogen to ammonia. Hydrogen is driven across a hydrogen permeating membrane (i.e. Pd) by a partial pressure difference, and the permeated hydrogen species react in the presence of a catalyst with nitrogen supplied to the other side of the membrane. The technology was developed to TRL 3, with ammonia synthesis rates of up to  $10^{-6}$  mol cm<sup>-2</sup> s<sup>-1</sup> and hydrogen conversion rates of up to 4% at pressures much lower than used in the conventional H-B reactor. The technology was demonstrated in the lab at a small scale by sourcing hydrogen directly from a PEM electrolysis cell. [Figure 1](#) shows the basic concept of the current technology for renewable ammonia synthesis.

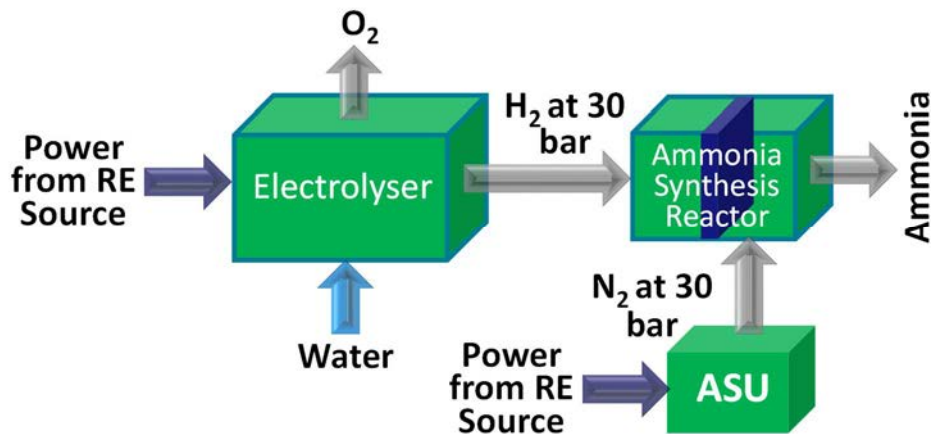


Figure 1: The basic concept of current technology for producing renewable ammonia

## 1.2 Objectives:

The major aim of the proposed work is to enhance hydrogen conversion rates to 15% at pressures below 35 bar (current capability of PEM electrolysers to produce hydrogen) and scale-up the technology to build a prototype unit capable of producing ammonia with the only inputs being water, air and solar PV. This work involves the development of catalyst, modifications to catalyst/membrane interfacial structures, reactor design optimisation for the process conditions and scale-up of the reactor to showcase the commercial viability of the technology by building a prototype that produces ammonia from renewable hydrogen produced by a PEM electrolyser.

## 2 Progress update

The current milestone relates to the establishment of ammonia synthesis test facilities, development of catalyst, investigations of catalyst/membrane interfacial structures and reactor design to achieve the required hydrogen to ammonia conversion rates and the ammonia content in the product stream.

As part of the test facilities, two test stations were constructed to carry out the ammonia synthesis at temperatures up to 500°C and pressures up to 30 bar. These stations allow testing of different reactor designs, catalysts, interfacial modifications, and can be operated for long periods of time, while the ammonia synthesis rates are continuously monitored. Further, these test stations are connected to each other to feed in the ammonia product stream from one station to the other to investigate separation / recycling of unreacted gases.

In the catalyst development program of the project, a library of 300 catalysts has been designed, and a total of 60 samples of catalysts were synthesised: 48 synthesised using robotics and 12 using bench chemistry techniques. Catalyst material for the remaining 240 samples of catalysts has been synthesised and these catalysts with promoters will be synthesised using robotics in 5 sets of 48 samples (i.e. 5 designs).

In the metal/catalyst interface modification studies, several strategies were explored to increase the reactive sites to enhance the ammonia synthesis activity. This activity also involved the characterisation of the interface before and after the testing to clearly understand the synthesis reaction and the active sites, and how the operating process conditions effect the interfacial structure for a long-term performance. These investigations show that metal membrane/catalyst interface composition and structure play an important role in enhancing the ammonia synthesis rates. The catalyst compositions as investigated by the catalyst development team and the optimised interfacial conditions learned from the metal/catalyst interfacial studies were further employed to improve the ammonia synthesis rates in the metal membrane reactor. The effect of the reactor design and the operating process parameters such as pressure, temperature and flow rate of gases on the nitrogen utilisation was also studied. The peak ammonia content in the product stream achieved at 450°C / 30 bar pressure is 4.8 vol% in a single pass. However, it was demonstrated that 76- 90% of the unused hydrogen can be recovered by passing the product stream through another reactor (or section of the same reactor) and reused in the synthesis process. This results in increasing the ammonia content in the product stream to 11.3%.

Additional work (not part of this milestone, but is crucial for the final project milestone and the successful outcome of this work) has been carried out in the areas: Flow sheeting and energy requirement calculations for ammonia separation from the ammonia product stream containing 5-15 vol% ammonia; flow sheeting for energy and capital requirement for the metal membrane ammonia production process under various scenarios of hydrogen and ammonia separation; estimation of hydrogen costs for different scenarios of hydrogen production for ammonia synthesis; energy and capital requirements for nitrogen production for the distributed scale of ammonia production. Two more activities (not part of the project) that were initiated by GRDC to support this project were (1) the techno-economic review of distributed renewable ammonia production (ITP report organised and funded by GRDC); and (2) the approval of funding (applied by GRDC in

consultation with CSIRO and Orica) from the Business Research and Innovation Initiative (BRII) (Department of Industry, Innovation & Services) to seek innovative solutions for obtaining hydrogen from farm waste (biomass) in order to feed the ammonia production technology that we are working on. Further details of these two initiatives are in the report.

In terms of IP generation and registration, a patent on the technology has been granted in several jurisdictions, a PCT has been filed on the developed catalyst composition, and an invention disclosure report on a new concept that encompasses the current technology for ammonia synthesis has been submitted to CSIRO IP management team for consideration.

The project area has been presented / discussed at three international conferences as part of the knowledge sharing activity.

### 3 Key highlights and difficulties

The project team consists of scientists / engineers from CSIRO and Orica, and the staff from GRDC attending regular project meetings and providing their input. There have been regular fortnightly meetings with staff from all three organisations, where the project progress, results, new ideas and concepts are discussed, and new strategies put in place for the successful delivery of the project. These meetings have been very useful especially considering Orica's experience in the ammonia production industry and GRDC's vision for the distributed ammonia / fertiliser production for the farming community.

The current membrane technology relies on the use of expensive metal membranes and catalysts based on noble metal materials. The performance achieved from the current technology and employing these materials has been remarkable considering the process conditions of only 30 bar pressure. The ammonia synthesis using the current MMR design and the developed catalyst can achieve in a single pass hydrogen to ammonia conversion rates of up to 11.5% and ammonia content of up to 4.8 vol%. The later has been further increased to 11.3 vol% with hydrogen separation and with nitrogen supplied close to stoichiometric values.

CSIRO and Orica have held several discussions on the commercial viability of the technology, and this has led to some changes to the project strategy, and future experimental work. The major focus in the future work would be to employ low cost and non-noble materials for this technology for the ammonia synthesis. Most of the recent work after the change in project strategy has been carried out with iron-based catalyst, and the performance has been half compared to with noble metal catalyst. This is very encouraging considering substantially lower cost of the iron-based catalyst. The experimental work using cheaper metal membrane has been also found to be very encouraging, with hydrogen to ammonia conversions achieved as high as 10% at significantly lower temperatures. There have been some concerns on the energy required for the ammonia separation and recycling of the unreacted hydrogen/nitrogen gases at low pressures as used in the current technology. This concern is also being dealt with by performing flow sheeting and energy calculations and devising strategies to mitigate these concerns. One strategy that has been trialled is to use a hybrid reactor approach that does not require a separate feed of the reactant gases to the reactor, and the separation of unreacted gases for recycling to the reactor. This strategy has shown great promise.



## 4 Commercialisation prospects

Additional work, though not part of this milestone, however, is crucial for the successful commercialisation of the technology has been carried out and is described below.

### **Energy requirements for ammonia separation**

A process was devised to recover high purity ammonia product from hot reactor gases. In practice this process enables the reactor to operate at optimum conversion conditions and continuous removal of product ammonia will also improve reactor equilibrium and kinetics.

The process chosen is a highly recuperative absorber-stripper combination. The main steps involve:

1. Cooling the feed gas from the reactor
2. Absorbing  $\text{NH}_3$  from the cooled feed gas using water at  $25^\circ\text{C}$  and returning the  $\text{NH}_3$  lean gas to the reactor
3. Distilling off a high purity  $\text{NH}_3$  product stream using a stripper and recycling the  $\text{NH}_3$  lean water solution back to the absorber

The process was modelled using DWSIM, with CAPE-OPEN models being used for the absorber and stripper unit operations. The process model was used to determine at what concentration of  $\text{NH}_3$  in the synthesis gas would allow recovery to be thermally autogenous. The outcome of this study was that ammonia can be separated from the product gas from the reactor using the thermal heat from the synthesis process when ammonia content in the product stream from the current reactor is between 5 and 15 vol%.

### **Energy and capital requirements for ammonia production under various scenarios of hydrogen and ammonia separation**

Whether considering conventional or membrane production, equilibrium conditions will dictate that recycle must be utilised in order to achieve economic production. When compared to Haber-Bosch, the membrane process has the distinction that hydrogen and nitrogen enter the reactor at different points in the process, and so recycle of feed will entail downstream separation, a potentially capital and energy intensive process.

Flow sheeting and energy calculations for un-reacted gasses and ammonia separation, and the recycling of un-reacted gases to the metal membrane reactor have been performed under various scenarios by staff from Orica. Some challenges have been identified in terms of requirement of pure gases supplied to the reactor and low-pressure operation. Strategies and solutions for these challenges have been proposed and put in place for further investigations. The new strategies allow the presence of mixed gases on both sides of the membrane, and ammonia separation at low pressures as mentioned in the previous section, using an absorber-stripper combination. Further solutions are being investigated that allow a hybrid reactor approach and reduce the requirement of separation of gases for recycling.

## Hydrogen costs for different scenarios of production

Analysis by ITP Thermal, CSIRO and Orica have shown that the main driver of the cost of ammonia production is the cost of the hydrogen. This is irrespective of the process, with the cost of the hydrogen in either fossil or renewable ammonia processes typically making up around 70-80% of the levelized cost of ammonia. This cost is driven by the cost of the primary energy used to produce the hydrogen. In the case of renewable hydrogen there are 2 main potential sources of hydrogen for distributed ammonia production:

- Biomass derived hydrogen
- Hydrogen from electrolysis powered by renewables

The main driver for the levelized cost of renewable ammonia is the cost of the hydrogen in the process. Where available, biomass is considered a cost-effective hydrogen source for distributed ammonia production. The cost of ammonia may approach \$600/t in some regions using this approach. This, however, is unlikely to be competitive with large scale conventional ammonia production plants which can typically produce ammonia at around \$200-300/t or in regions that have easy access to low cost natural gas or coal. The economics change somewhat if carbon capture and storage costs are included with biomass derived ammonia likely to be cost competitive in some instances with these plants.

Scenario's involving hydrogen produced via electrolysis are more complex in nature. This is largely due to the wide variation in cost of electricity and the capacity factor / utilisation of the hydrogen production plant (electrolysers) in different scenarios. In the case of dedicated renewables or in the case of very high solar scenarios the capacity factor / utilisation of the hydrogen production plant is low leading to higher levelized costs of ammonia in all instances. Even relatively extreme scenarios where a zero cost of electricity is used, the resulting costs are between \$470-800/t of ammonia. Ammonia produced in this manner may be cost competitive in regions where transport of ammonia is cost prohibitive or if carbon capture is required due to legislation. Clear cost reductions are possible in scenarios where the capacity factor can be increased whilst maintaining relatively modest electricity prices. These scenarios would lead to a reduction in the overall cost of the hydrogen, but it is unlikely that, even at large scale, that renewable ammonia will be lower cost than large scale conventional unabated ammonia production from coal or natural gas in the short to medium term. Further R&D efforts in the fields of hydrogen production from electrolysis could lead to the reduction of the cost of hydrogen to around \$2/kg. This would represent a significant reduction in the costs that were obtained in this study and could lead to a future where hydrogen derived from renewable sources could produce ammonia at a slight premium of around \$50-150/t.

## Energy and capital requirements of nitrogen for distributed scale ammonia production

Currently established industrial scale nitrogen production technologies are:

1. Cryogenic separation
2. Pressure swing adsorption
3. Membrane separation

In general, only cryogenic separation and pressure swing adsorption are considered as practical for large scale production of high purity nitrogen with membrane systems generally producing comparatively lower purity nitrogen. Analysis by ITP Thermal has found that for plants requiring 5,000-50,000 Nm<sup>3</sup> nitrogen per day PSA systems are generally considered optimal. This would correspond to approximately 7.5 - 75 t/day ammonia output [[ITP Thermal](#)]. Plants that require significantly more nitrogen are typically more suited to cryogenic separation. In terms of the cost impact of nitrogen production, it was found that the total cost of nitrogen made up less than 4% of the levelized cost of ammonia in the case of electrolysis and less than 6% of the levelized cost of ammonia in the case of biomass gasification. In general, the energy requirement for nitrogen is significantly lower for nitrogen separation from air compared to hydrogen production from water. Overall, the range of energy required for cryogenic separation of nitrogen from the air is typically in the range 0.1-0.3 kWh/Nm<sup>3</sup> and 0.25-0.36 kWh/Nm<sup>3</sup> when pressure swing absorption is used [[Nitrogen, Ullmann's encyclopedia of industrial chemistry](#)]. This is compared to hydrogen production which is typically between 3.8 – 4.4 kWh/Nm<sup>3</sup> in commercial electrolysis units [[NEL product specification page](#)]. This variation in power consumption is particularly stark considering for every nitrogen molecule, three hydrogen molecules are required. This leads to greater than 50 times the energy requirement for hydrogen production when compared to nitrogen production.

## 5 Knowledge sharing activities

### **Patents granted, PCT, Invention disclosures:**

1. Processes utilising selectively permeable membranes; US patent 9895652, now also granted in Europe, Australia, Japan, South Korea, China.
2. PCT on “Ruthenium promoter catalyst compositions” filed in March 2020.
3. Prepared an invention disclosure report on “ammonia synthesis to produce ammonia contents above equilibrium contents”; Submitted CSIRO IP management staff, May 2020.

### **Conferences / Forums where the project was discussed:**

1. Invited Talk at AFORE (Asia-Pacific Forum on Renewable Energy), 2019, Nov.13-16, JeJu, Korea: Australian initiatives to develop renewable energy export systems, Sarb Giddey and David Harris.
2. World Hydrogen Technologies Convention (WHTC) 2019, June 2-7, 2019, Tokyo, Japan: Technological barriers for using ammonia as a renewable energy vector, Sarbjit Giddey, Aniruddha Kulkarni, Christopher Munnings, David Viano and Louis Wibberley.
3. Invited talk at AIChE Annual Meeting October 28 – November 2, 2018, Pittsburgh, PA: A low pressure membrane based renewable ammonia synthesis, Sarb Giddey, Danielle Kennedy, Ani Kulkarni, Gary Paul, David Alexander.
4. Invited talk at Positioning Hydrogen 2020: Opportunities and Challenges, Webinar organised by Prism Scientific Australia, June 19, 2020: Sustainable technologies for renewable fuels production and power generation.

### **Knowledge sharing surveys:**

Completed all on-line knowledge sharing surveys as time to time requested by ARENA.

### **Other initiatives that led to knowledge sharing of the project activities:**

1. *Techno-economic review of distributed renewable ammonia production:*

GRDC had engaged ITP Thermal to prepare a report on this, and this work was funded by GRDC. ITP produced this report in August 2019 [[ITP Thermal](#)]. The aim of this study was to analyse the techno-economic feasibility of distributed renewable ammonia production. It provides technology and cost overviews and resulting levelised costs of renewable ammonia for conditions pertinent to grain growing regions in Australia. This report has been shared by GRDC with CSIRO and Orica on confidential terms.

2. *Hydrogen from farm waste (Biomass):*

GRDC is one of the partners in this project. GRDC had applied for funding via the Business Research and Innovation Initiative (BRII) (Department of Industry, Innovation & Services) to seek innovative solutions in the form of feasibility studies [[BRII Challenge](#)] from three to four SMEs.

The solutions would be addressing the challenge of obtaining hydrogen from farm waste (biomass) in order to feed the ammonia production technology that we are working on. This application of GRDC has been successful. GRDC will work now with BRIL to select SMEs to do the feasibility study. Each SME would receive approximately \$100,000 over 3 months to conduct the study. One of these SMEs can then apply for further funding (up to \$1M over 18 months) from BRIL to develop a Proof of Concept, which should result in a prototype. GRDC has requested CSIRO's support in terms of attending meetings / discussions in this activity.

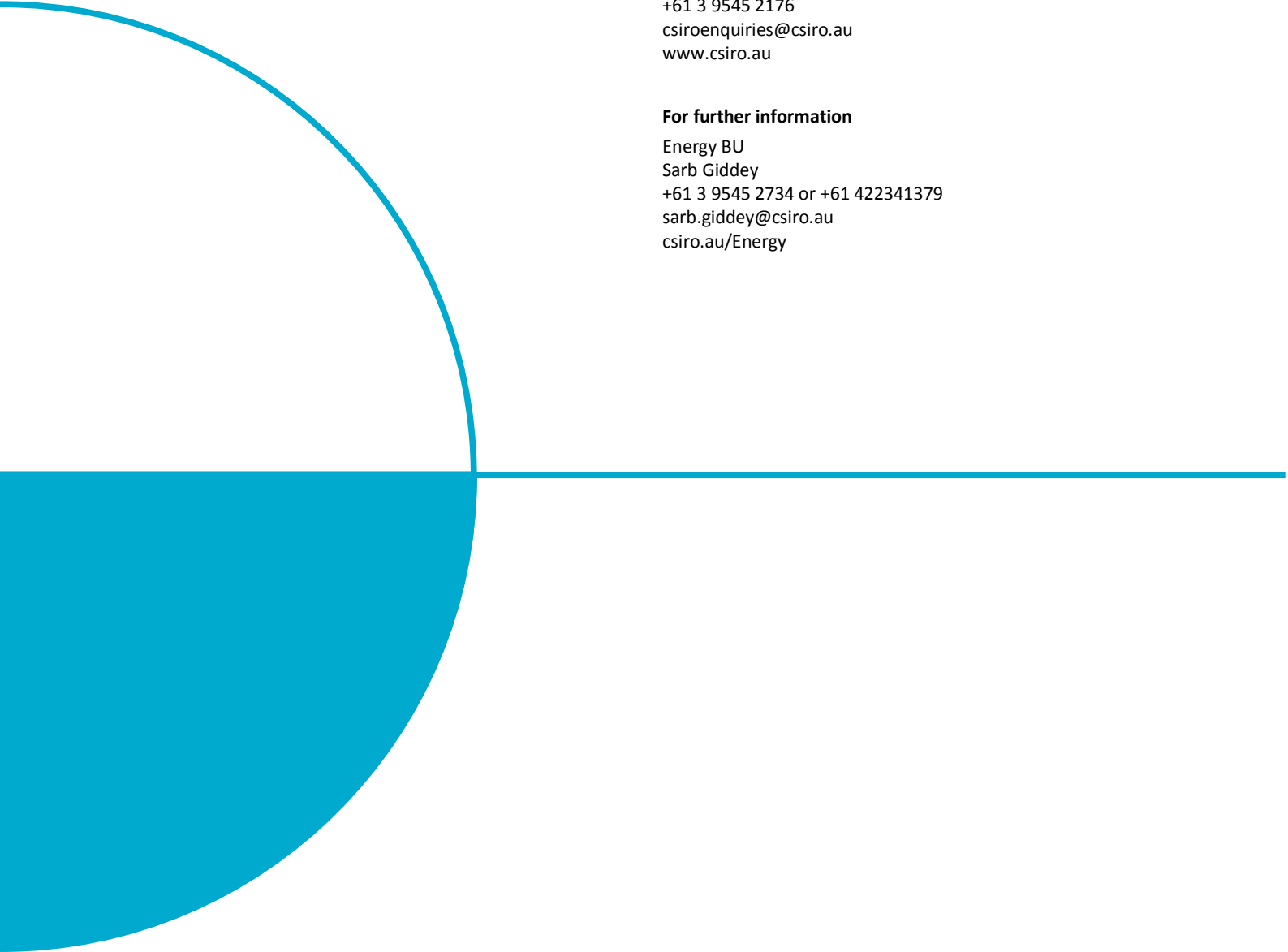
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**Contact us**

1300 363 400  
+61 3 9545 2176  
[csiroenquiries@csiro.au](mailto:csiroenquiries@csiro.au)  
[www.csiro.au](http://www.csiro.au)

**For further information**

Energy BU  
Sarb Giddey  
+61 3 9545 2734 or +61 422341379  
[sarb.giddey@csiro.au](mailto:sarb.giddey@csiro.au)  
[csiro.au/Energy](http://csiro.au/Energy)