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# **SUPPLEMENTARY**

# Impact of fuel cells on hydrogen energy pathways in a Sustainable Energy

# Economy

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# **Supplementary Figures**

## Supplementary Figure S1



**Supplementary Figure S1.** A detailed version of Figure 1. The clean energy pathways assessed in this work for the emerging HEI related to the production of clean electricity for stationary applications. Blue and green hydrogen energy variants are identified via the colour scheme. This work focusses on the zone highlighted in red for the electrochemical conversion of fuel to electricity to determine impacts on HEPs. Only HEP's with FCs as the Use process is included in this Figure. FF transport to a second location and converted to hydrogen that is then used in a FC is not included.

# Supplement Figure S2

Sankey Energy Diagrams showing the efficiency of (A) PEMFC<sup>1,2</sup> and (B) SOFC<sup>3</sup> and schematics for (C) PEMFC and (D) SOFC.





<u>Supplement Figure S3</u> Schematic representation of the SOFC process with NG. The water gas shift reaction and presence of CO is not included for clarity. Refer Supplementary Note 2 for description.



# Supplementary Tables

# Supplementary Table S1

Three metrics were analysed for the Net Zero Emissions scenario for the same final hydrogen demand (102MT/year) at the end of each hydrogen energy pathway.

Metric	Equation	Purpose
Primary Energy E <sub>ES,j</sub> The amount of primary energy required at the start	$E_{ES,j} = \frac{E_u}{\Pi(\varepsilon_j)} \qquad (2)$	Each hydrogen energy pathway needs different amounts of primary energy source due to the aggregate efficiencies of the unit processes in the pathway $\Pi(\varepsilon_j)$ to deliver the same final hydrogen
of the Energy Source pathway for j <sup>th</sup> Hydrogen Energy Pathway.		demand. This metric determines the actual amount of energy needed from the primary energy source to deliver the same hydrogen demand at the end of each
		hydrogen energy pathway. The capacity factor (the ratio of actual energy produced compared to the assets maximum possible energy output over one year) for the primary energy source is not included.
		This metric reflects the amount of over design required in primary energy infrastructure due to the aggregate efficiencies of the different individual processes in each hydrogen energy pathway.
Fossil Fuel Mass M(FF) <sub>ES,j</sub> The mass of fossil fuel required at the start of the Energy Source pathway for j <sup>th</sup> Hydrogen Energy Pathway.	$M(FF)_{ES,j} = \frac{E_{ES,j}}{HHV_{FF}}$ (3)	This metric converts the primary energy metric to a mass of fossil fuel required to deliver the hydrogen demand at the end of each hydrogen energy pathway.
Mass of CO <sub>2</sub> emitted M(CO <sub>2</sub> ) <sub>HEP,j</sub>	$M(CO_2)_j = 3.67 * M(FF)_{ES,j} * f_{C,FF} $ (4)	Each hydrogen energy pathway has different amounts of direct CO <sub>2</sub> emissions that needs to be abated to deliver the same final hydrogen demand.
emitted that must be fully abated with each Hydrogen Energy Pathway.		This metric determines the mass of direct CO <sub>2</sub> emissions from the primary energy source to deliver the same hydrogen demand at the end of each hydrogen energy pathway.

# Supplementary Table S2

# Summary of calculations

			Hydrogen Vector (From Figure 1)									
	Efficiency		C1	C2	C3 (PEMEC)	C3 (SOEC)	N1b	N2	N3 (PEMEC)	N3 (SOEC)	R1 (PEMEC)	R1 (SOEC)
Parameter or Metric	Value, % (HHV)	References or Equations	Direct to SOFC	Coal Gasification to Blue H2	Coal to Ma to Blu	iins power Je H2	Direct to SOFC	SR to Blue H2	NG to Mains power to Blue H2		Via Green H2	
ε <sub>sr</sub>	0.76	Reference 4						0.76				
ε <sub>cg</sub>	0.62	Reference 5		0.62								
ε <sub>PP-COAL,SOFC</sub>	0.55	Reference 6	0.55									
ε <sub>pp-NG</sub>	0.443	Reference 7							0.443	0.443		
ε <sub>pp-coal</sub>	0.355	Reference 7			0.355	0.355						
ε <sub>PDL</sub>	0.95	Reference 8			0.95	0.95			0.95	0.95		
ε <sub>EC</sub>	0.83	Reference 9									0.83	0.83
ε <sub>PEMEC</sub>	0.65	Reference 10			0.65				0.65		0.65	
ε <sub>soec</sub>	0.82	Reference 10				0.82				0.82		0.82
ε <sub>pemfc</sub> ε <sub>h2-sofc</sub>	0.49	Reference 11		0.49	0.49	0.49		0.49	0.49	0.49	0.49	0.49
ε <sub>NG-SOFC</sub>	0.58	Reference 3					0.58					
ε <sub>s&amp;t,H2</sub>	0.744	Supplementary Note 2		0.744	0.744	0.744		0.744	0.744	0.744	0.744	0.744
ε <sub>s&amp;t,ng</sub>	0.873	Supplementary Note 2					0.873					
ES&T,COAL	0.99	Estimate	0.99									
FF Energy, TWh IEA,NZE Scenario		eqn 2	3617	8712	24641	19532	3889	7107	19746	15652	10012	7937
FF Energy Content HHV (MWh/T)		Coal Reference 12 NG Reference 13	7.04				14.50			-	-	
Mass of FF, MT IEA,NZE Scenario		eqn 3	514	1,237	3,499	2,775	268	490	1,363	1,079	0	0
Mass of C per Mass of FFref		Reference 14	0.65			0.75				-	-	
Mass of CO <sub>2</sub> ,MT to be captured IEA,NZE Scenario		eqn 4	1,227	2,950	8,347	6,619	736	1,349	3,751	2,970	0	0

## Supplement Table S3

FUEL (Note 1)	<i>n</i> (moles electrons per mole of fuel)	Gross Calorific Value or Heat of Formation (kJ/mol) (Note 2)	EPFE (moles electrons per MJ of fuel)
Hydrogen	2	286.64	8.279
Methane	8	892.92	8.959
NG, Domestic	8.07	907.109	8.893
NG, Exported	8.24	926.503	8.893

Values of Electrons Per Fuel Energy (EPFE) factor  $\left(\frac{n}{GCV}\right)$  for different fuels

Note 1: NG values are based on composition and information for Australian average domestic and average exported natural gas<sup>4</sup>.

Note 2: These values were extracted from Table 4 of SI Standards Publication BS EN ISO 6976:2016 and methods therein, at STP<sup>5</sup>.

## Supplementary Table S4

Pathway follows the legends in Figure 1 and Supplementary Figure 1. Carbon intensity used here is the mass (MT) of  $CO_2$  that needs to be abated for zero emissions (equation 4) to produce 1969TWh<sub>e</sub> at the end use as described in Methods. Relative Carbon Intensity is the mass ratio relative to the  $CO_2$  emitted from an incumbent coal fired power plant calculated to be 1,686 MT to produce 1969TWh<sub>e</sub> of electricity. Carbon intensity does not include energy consumed in manufacture or installation of energy assets.

Pathway	Carbon Intensity	Relative Carbon Intensity	Colour Scheme		
C1	1,227	73%	Blue		
C2	2,950	175%	Blue		
C3 PEMEC	8,347	495%	Blue		
C3 SOEC	6,619	393%	Blue		
N1b	780	46%	Blue		
N2	1,349	80%	Blue		
N3 PEMEC	3,751	223%	Blue		
N3 SOEC	2,970	186%	Blue		
R1	0	0%	Green		

#### **Supplementary Notes**

#### Supplementary Note S1

Note for Supplementary Figure S2

The NG-SOFC products are not usually considered part of hydrogen energy vectors, but hydrogen is an integral part of the SOFC process. Electricity is generated from the electrochemical oxidation of hydrogen that reacts with oxygen ions formed by the reduction of oxygen coming from the input air. Hydrogen is generated in steam reforming of C1+ (ethane, propane, butane) in a pre-reformer at around 400 °C where methane is passed through unreacted. Methane is steam reformed inside the SOFC stack at the anode side of the cells producing hydrogen and CO. A water gas shift reaction generates additional hydrogen and CO<sub>2</sub>.

Hydrogen is a transient intermediate in the SOFC reaction sequence, generated at the anode side cell layers exposed to the gas, and diffuses 10-100's microns through the micro porous structure from the steam reforming site to the electrochemical reaction site at the anode-electrolyte interface with a time constant in the millisecond time frame where it reacts with the oxygen ions to generate electrons. An SOFC can directly steam reform methane to CO and hydrogen inside the stack itself while electrochemical sites that oxidise the hydrogen are only 10's - 100's microns away from the fuel side flow channels of the stack. The lifetime of intermediate hydrogen in this reaction process is of the order of seconds with the electrochemical time constant for the diffusion process dominated by the diffusion rate of hydrogen inside the porous anode structure. A well-developed SOFC anode will have a very low concentration resistance resulting from the hydrogen diffusion process.

The chemical and electrochemical reactions in a SOFC system are described here in equations (S1) to (S6) below. A steam to carbon ratio of two is typically used with high quality water provided to a steam generator, using heat generated in the stack, to provide the required steam flow that is mixed with the incoming NG. Inside a pre-reformer catalyst bed at ~400°C located before the stack, and heated by the heat generated in the stack, the C1+ hydrocarbons are steam reformed (equation S1) with CO undergoing a water gas shift (WGS) (equation S2). The minor C1+ components in NG must not be exposed to the SOFC stack due to their propensity to undergo carbon cracking rather than steam reforming. Carbon cracking causes significant performance degradation due to blockage of pore structures that then constrains gas diffusion and increases the anode concentration overpotential. The resulting gas mix of methane,  $H_2$ , CO, steam and  $CO_2$  is preheated by the hot exhaust gas to the required gas inlet temperatures and flows into the inlet sections of the stack.

$$C_nH_{2n+2} + nH_2O \rightleftharpoons nCO + (3n+1)H_2$$
 (SR, n≠1, ~400°C) (S1)

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$
 (WGS, ~400°C) (S2)

Inside the stack at the inlet of each layer (>650 °C) the methane is steam reformed (MSR) (equation S3) and there is a further water gas shift reaction (equation S4). The resulting gas mixture of  $H_2$ , CO and CO<sub>2</sub> with any excess steam flows across the fuel electrode (anode).

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad (MSR, n=1, ~650^{\circ}C) \quad (S3)$$
$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (WGS, ~650^{\circ}C) \quad (S4)$$

The rate of the MSR reaction (equation S3) over the full 3D temperature window of the SOFC stack depends on the catalytic capability of the anode side materials. The amount of steam added to the SOFC is critical to ensure there is no carbon deposition in the prereformer and stack and typical steam to carbon ratios used is close to 2:1. The outcome is that methane is 100% steam reformed internally in the SOFC stack with no slippage of unreacted methane in the exhaust of the stack. This result is important as it impacts the efficiency of the system. High efficiency systems require complete conversion of methane to hydrogen and CO across the stack from fuel inlet to the exit across the anode to ensure there is sufficient hydrogen to react with oxygen ions generated at the cathode.

Meanwhile, on the opposite side of the cells in the stack, oxygen in air, preheated by the hot exhaust gases, flows across the cathode and diffuses to the electrochemical reaction sites at the cathode-electrolyte interface where oxygen is reduced to oxygen ions (equation S5).

$$2O_2 + 8e \rightarrow 4O^{2-}$$
 (S5)

Oxygen ions conduct across the solid oxide electrolyte to the anode - electrolyte interface and oxidises hydrogen and CO that has diffused through the anode to electrochemical reaction sites (equation S6)

$$4O^{2-} + 4H_2 \rightarrow 4H_2O + 8e$$
 (S6)

The MSR reaction (equation S3) is endothermic which results in an efficiency gain due to close proximity of the cooler MSR zone with the exothermic reaction zone due to hydrogen oxidation and due to the internal resistance of the process causing I<sup>2</sup>R heating in the cell structures. This proximate thermal transfer allows for a lower air flow rate used for cooling purposes and smaller air blowers with fewer electrical losses in the balance of plant. The combination of engineering design factors for an SOFC system leads to high efficiency outcomes.

### Supplementary Note S2

#### Storage and transport losses for natural gas

The losses of NG in storage and shipping was estimated based on LNG shipping<sup>6</sup>. Losses of 9% are used from the energy consumption required for liquefaction. A shipping distance of 4057 nautical miles between Gladstone, Australia to Tokyo, Japan is used and an average 0.175% per 480 nautical miles to give an estimate of losses during shipping of 1.4%. Losses of 2.3% is used for regasification. This totals 12.7% energy loss used in the analysis.

### Storage and transport losses for hydrogen

Liquefaction losses are based on 6kWh/kg energy consumption that is 15% of the higher heating value of hydrogen (39.4kWh/kg). Losses in shipping liquified hydrogen are estimated to be 8% based on Boil Off Gas (BOG) during transportation relative to the quantity delivered shown in Table 5 of a recent analysis<sup>7</sup> for transport from Qatar to Japan and adjusted for the shorter distance between Gladstone and Japan. Regasification losses of 0.7% is used for hydrogen that is a third that for LNG based on the heat of evaporation values for liquid hydrogen (0.899kJ/mol or 0.125kWh/kg)<sup>8</sup> and LNG (508.82kJ/kg or 0.142kWh/kg)<sup>9</sup> relative to their higher heating values of 39.4kWh/kg for hydrogen and 14.5 kWh/kg for NG. An additional 1.9% loss is assumed for venting purposes due to hydrogen safety protocols. Loss of hydrogen via permeation through materials is assumed to be relatively negligible compared to the above losses and is ignored in the analysis. This totals 25.6% energy loss used in the analysis.

## Supplementary Note S3

The corresponding analysis for the HEP that uses coal (pathway C2) is based on an efficiency for hydrogen production from coal gasification (CG). In this case, the parameter ( $\varepsilon_{CG}$ ) is used in [eqn. (2)] instead of a value for NG SR. The production of hydrogen from coal gasification is known to have an efficiency  $\varepsilon_{CG} = 60-64\%$  (HHV)<sup>10</sup> for bituminous (black) coal and a much lower level for lignite (brown) coal. For this study, we use values for black coal. In this case, coal is the transportable and stored energy form and an efficiency  $\varepsilon_{S\&T,Coal} = 99\%$  is assumed in this study. The mass of black coal required is calculated from a higher heating value (HHV) of 7.04MWh/T for bituminous coal<sup>11</sup> in an as received form that includes moisture and ash.

The outcomes for the three metrics based on this HEP (C2 in Figure 1) that starts with black coal at the ES pathway, producing blue hydrogen from CG and ending with the same 1,969TWh<sub>e</sub> electricity delivered to the user using H2-PEMFC as for the above NG HEP N2 is:

- $E_{ES,C2}$  = 8,712TWh<sub>coal</sub>/year [eqn. (2)]
- $M(FF)_{ES,C2}$  = 1,237MT/year of black coal [eqn. (3)]
- $M(CO_2)_{C2}$  =2,950MT/year [eqn. (4)], *i.e.*, the total abatement of CO<sub>2</sub> required at the CG plant per year, using CCUS to achieve zero emissions.

This imposes twice the techno-economic and environmental risk for a CCUS pathway compared to using NG for the same electrification outcome.

## Supplementary Note S4

## **Emissions Case Study**

The values for the key factors used here are not considered definitive and are an *example* only to display the workings described in the manuscript. A time frame of 100 years is used for GWP values and captured  $CO_2$  retention rate.

Table	S4 Case	Studv	factors	and	ranae	of	values	assessed	
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Factors	Case study range – example only
GWP Methane	34
GWP Hydrogen	5.8
Methane Leakage Rate from NG well to reactor	0.5% - 3.5%
Methane leakage rate from coal mining TCH4 per Tcoal	0.001 - 0.0064
produced	
Hydrogen Leakage Rate from production to FC	0.5% - 5%
Additional energy consumption required for CC	0.05 - 0.2
CO <sub>2</sub> Capture efficiency (E <sub>cc</sub> )	0.9-0.98
Captured $CO_2$ year-on-year retention ( $R_{cc}$ )	0.995 – 0.998

There are various methods to determine the effectiveness of CCUS and one method may be to use the average value of the fraction of  $CO_2$  captured initially and the fraction of  $CO_2$  retained captured after y<sup>th</sup> year, for example,

Effectiveness of CCUS =  $0.5 * Fraction of CO2 Captured * \{1 + (Annualised Retention Rate)^y\}$ 

Where the Fraction of  $CO_2$  Captured is that achieved by the CC process at the start of year 1 and the Annualised Retention Rate is the fraction of  $CO_2$  that remains captured year-on-year and y is the number of years used for the GWP value (either 20 years or 100 years).

In the example ranges above;

Effectiveness of CCUS =  $0.5 \times E_{cc} (1 + R_{cc} \cdot 100) = 0.72 - 0.89$ 

Example values used for three scenarios are provided in the Table below.

Table S5 Factors and range of values assessed in three emissions scenarios over 100 year time frame including methane and hydrogen: "No CC" scenario is where there is no CC process and all CO2 is emitted, "Best Case" includes a CC effectiveness where 98% of CO2 is captured and has an annualized retention rate of 99.8%, "Worst Case" includes a CC effectiveness where 90% of CO2 is captured and has an annualized retention rate of 99.5%.

Factors	No CC	Best Case	Worst Case
Time Frame, years	100	100	100
GWP Methane	34	34	34
GWP Hydrogen	58	5.8	5.8
Methane Leakage Rate from NG well to reactor	2%	0.5%	3.5%
Methane leakage rate from coal mining TCH4 per Tcoal produced	0.0037	0.001	0.0064
Hydrogen Leakage Rate from production to FC	2.8%	0.5%	5%
Additional energy consumption required for CC	0	5%	2%
CO2 Capture efficiency E <sub>cc</sub>	0	0.98	0.9
Captured CO2 year-on-year retention $R_{cc}$	0	0.998	0.995
Effectiveness of CCUS	0	0.89	0.72

Plots S4-S6 below show the equivalent CO2 emission rates for each HEP in each scenario analysed. Further plots below in S7 and S8 show that each scenario has the same trend across all HEP's analysed in Figure 2. However, this example uses the same values for each factor across all HEP's whereas in practice they will differ that may change the relative impacts between HEP's. A more exhaustive analysis is beyond the scope of this work.

## Figure S4: Scenario with no CC.



Figure S5: Best Case Scenario that includes a CC effectiveness where 98% of CO2 is captured and has an annualized retention rate of 99.8%





Figure S6: Worst Case Scenario that includes a CC effectiveness where 90% of CO2 is captured and has an annualized retention rate of 99.5%

Figure S7: Scenario outcomes with corresponding values used in Figure 2.



Figure S8: Trend of values from scenario's with each HEP with corresponding values used in Figure 2. This example uses the same values for each factor across all HEP's whereas in practice they will differ that may change the relative impacts between HEP's and actual trend is not likely to be as linear as this plot suggests.



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