## **Green Hydrogen and Ammonia** Production

## **Challenges and opportunities**

John T. S. Irvine

**University of St Andrews** 

**IET Online Workshop** 

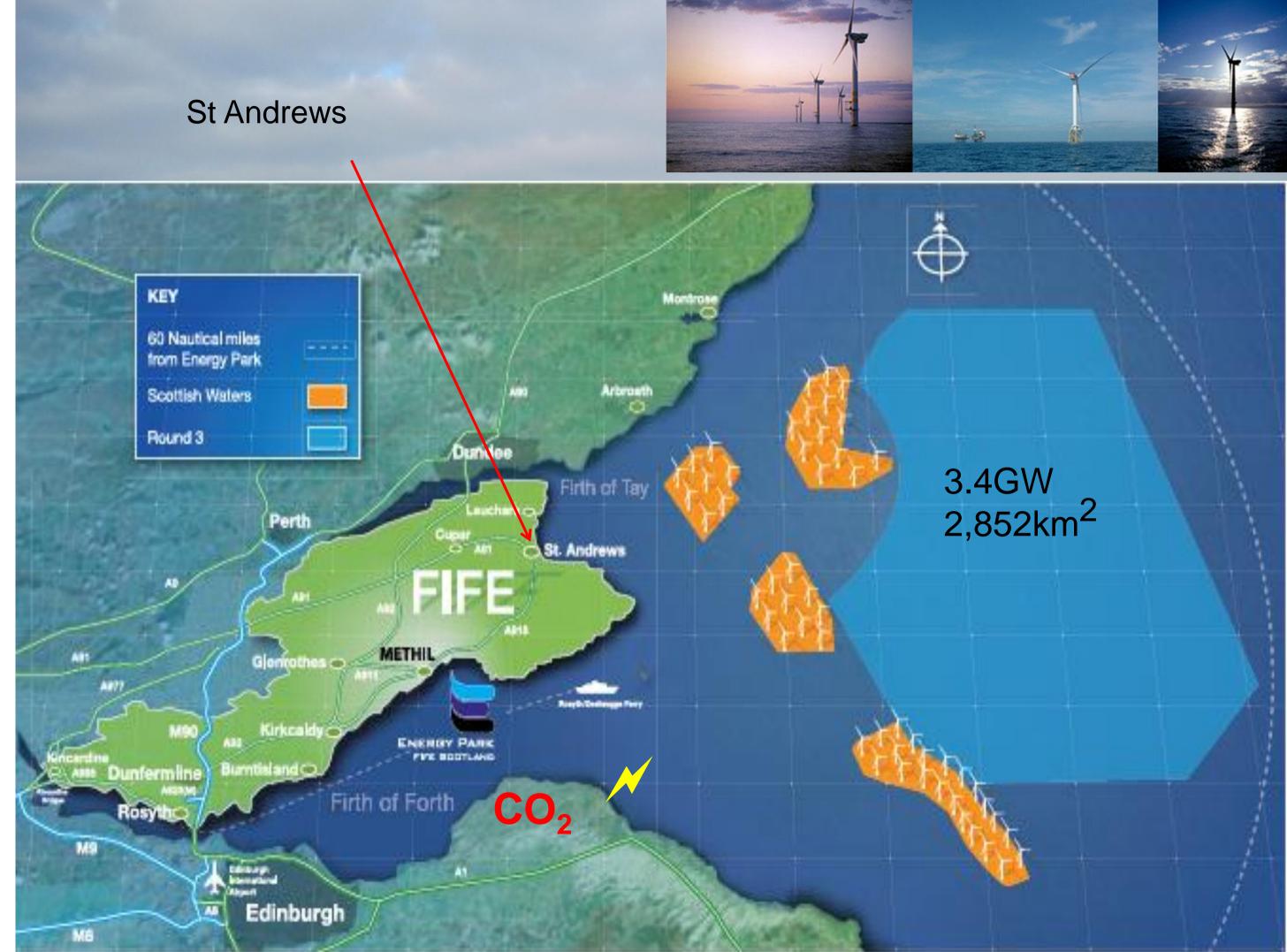




#### **28th July 2021**



- Renewables
- Green Hydrogen Production and Electrolysis
- Ammonia
- Solid Oxide Cells
- CO<sub>2</sub> and co-electrolysis



# Saipem 7000 marks the start of offshore work on the Neart na Gaoithe (NnG) wind farm, August 2020

- Owned by EDF Renewables and ESB
- 15 km off the Fife coast
- •54 turbines

#### 2023

- Power 375,000 homes
- •450 megawatts

https://ocean-energyresources.com/



## **Zero Emission Train Project**



https://www.scottish-enterprise-mediacentre.com/news/hydrogen-train-project-looks-back-to-thefuture





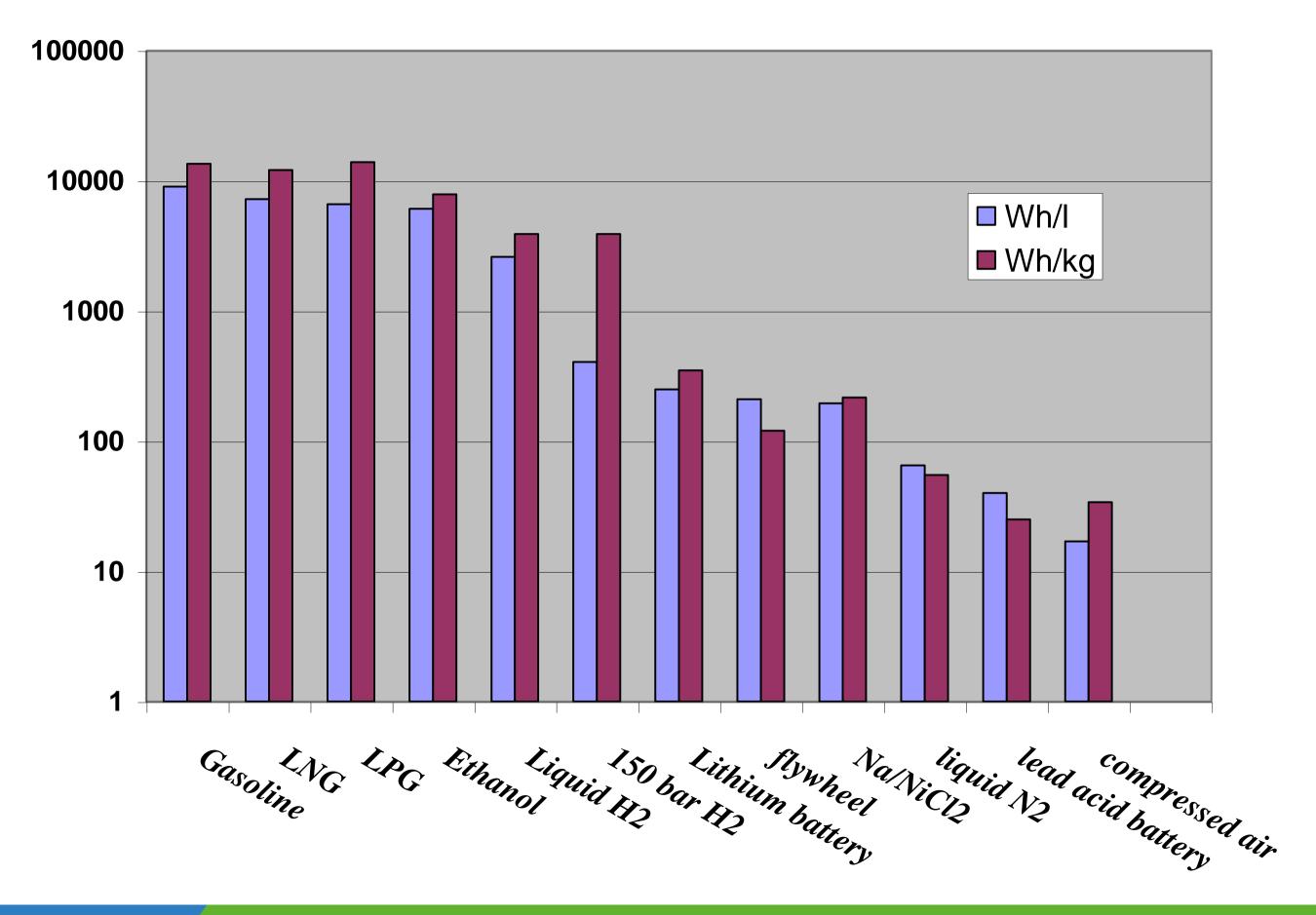
### Hydrogen Fuel Cell Electric Trains Our decarbonised rail network in Scotland, 2035

- Electrified network; some 1,622 of single track kilometres to be electrified. Sections of route may include discontinuous electrification and the use of battery/electric bi mode trains, e.g the Fife Circle.
- Alternative traction transition solution(i.e. the use of alternative technology prior to electrification).
- Alternative traction permanent solution (i.e. the use of battery and/or Hydrogen traction).

Rail Decarbonisation Plan launched at the end of *July 2020*. Decarbonisation of the rail network by 2035. First market engagement by **September 2020** 



### **Energy Storage Technologies**



## Alternative hydrogen carriers

- Ammonia
- Methanol
- Methane
- Hydrocarbons
- Diesel

## Ammonia

- Ammonia is one of the most important industrial chemicals
- Widely used in agriculture as a fertiliser for food production.
- Conventionally ammonia is produced at very large scale utilising fossil energy sources
- Cost via  $H_2$  SMR is very low, even lower than bulk hydrogen
- Historically produced utilising hydrogen produced from Hydro power.

## industrial chemicals for food production.

er than bulk hydrogen n produced from Hydro

#### HISTORICAL LARGE SCALE PLANTS





Rjukan, Norway; 1927 - 1970's

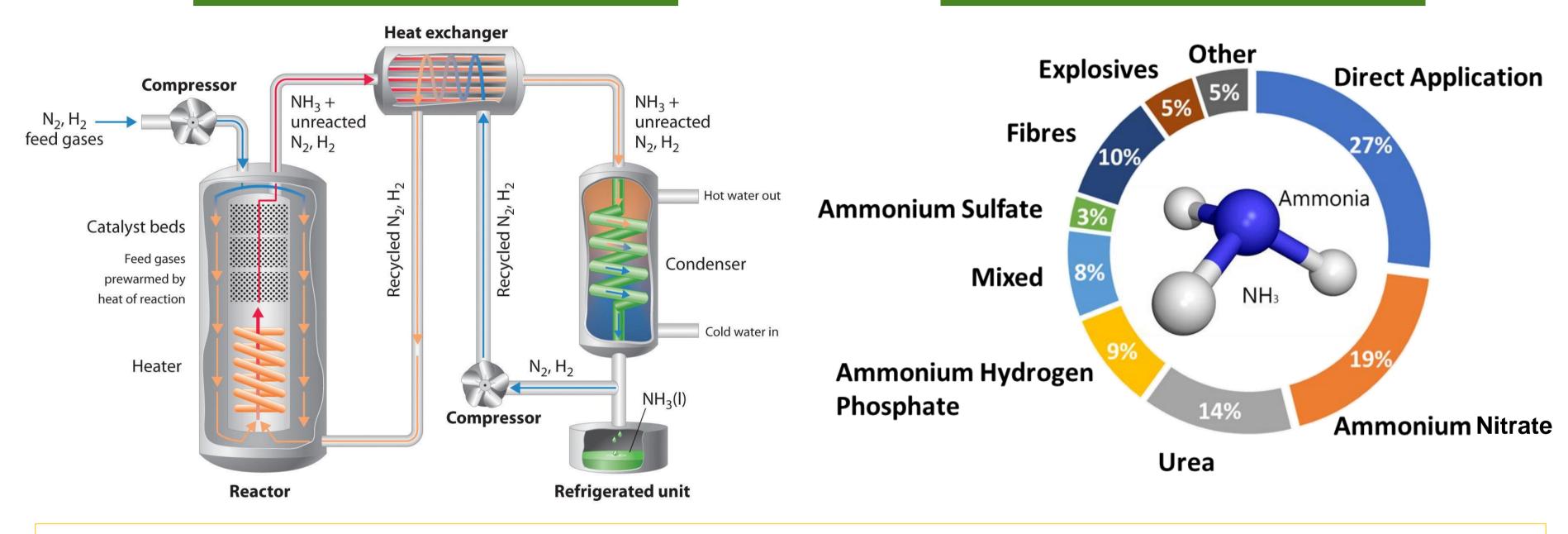
Glomfjord, Norway; 1953 - 1991

- Two largest electrolyser plants worldwide •
- Capacity: 30 000 Nm<sup>3</sup>/h each ٠
- Energy consumption: approximately 135 MW each
- Supplied by renewable hydro power .





#### Haber-Bosh Process



High temperatures (400–500 °C) High pressures (150–200 atm)

#### **Alternative energy-saving pathway?**

#### Main applications

#### $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \Delta H = -92 \text{ kJ mol}^{-1}$



### Wind and ammonia

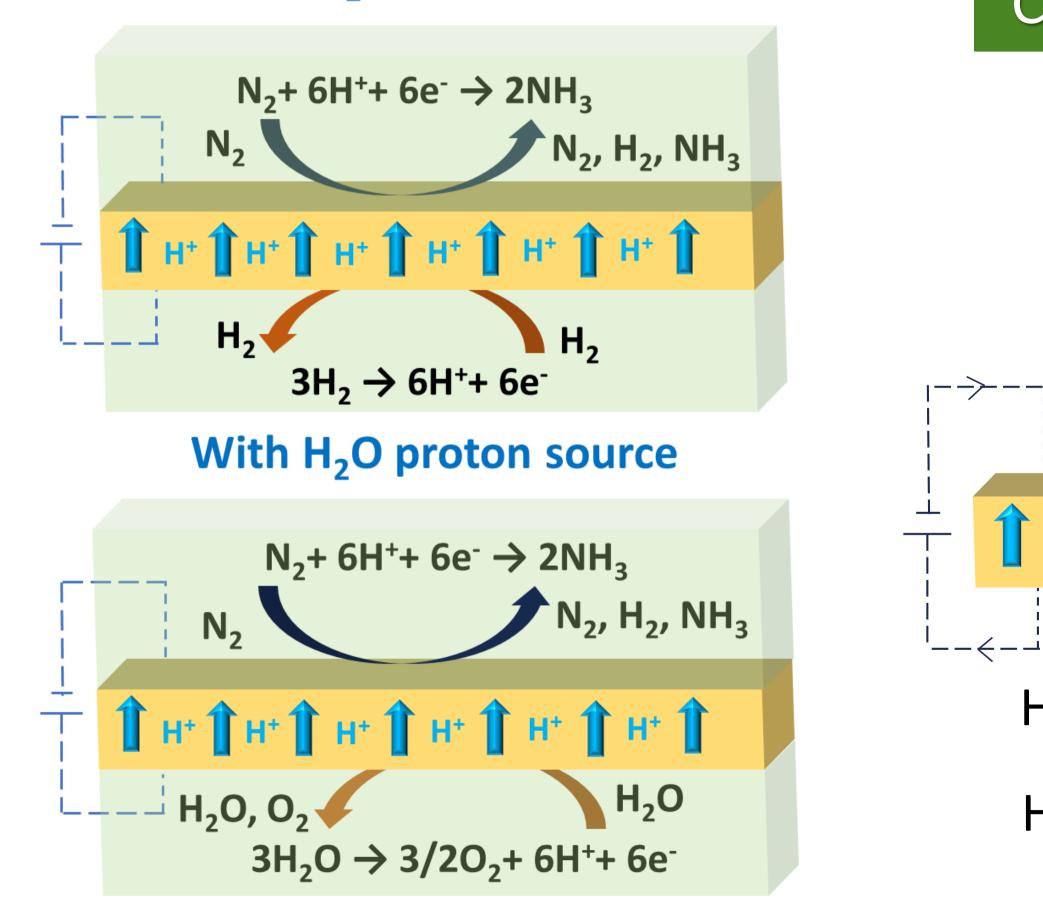


http://freedomfertilizer.com/



#### Protonic ceramic conductors

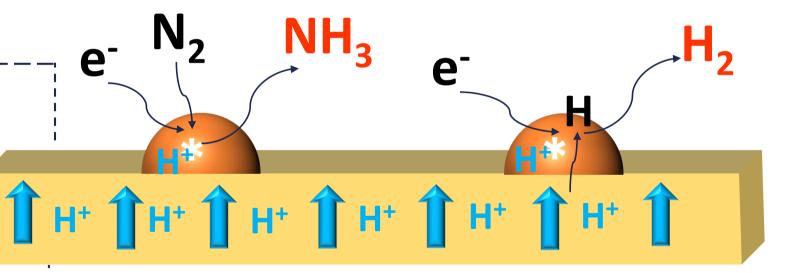
#### With H<sub>2</sub> proton source



#### Competing mechanisms

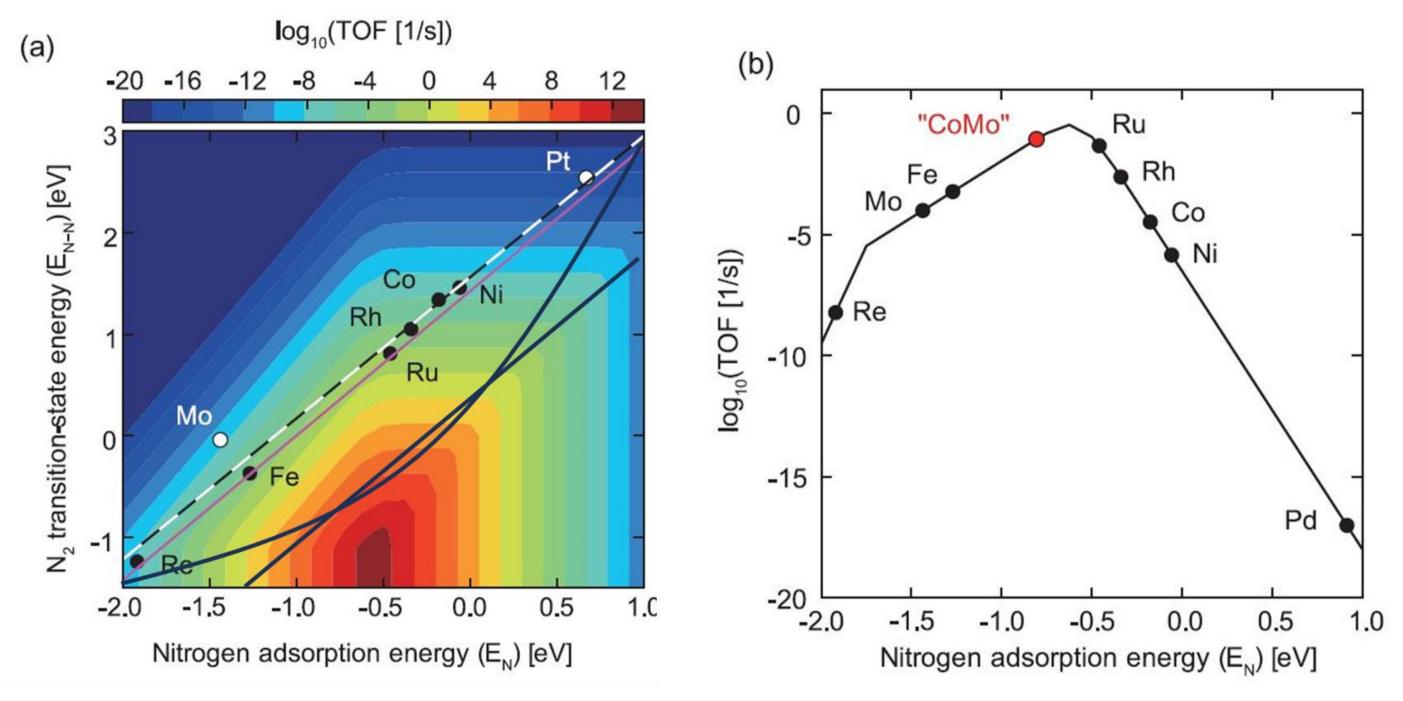
- $H^+ + e^- + * \rightleftharpoons *H$ (1)
- $N_2 + * \rightleftharpoons * N_2$ (2)

**e**<sup>-</sup>



 $H^+ + e^- + *N_2 \rightleftharpoons *N_2 H$ (3)  $H^+ + e^- + *H \rightleftharpoons H_2 + *$ (4)

#### Electrocatalysis

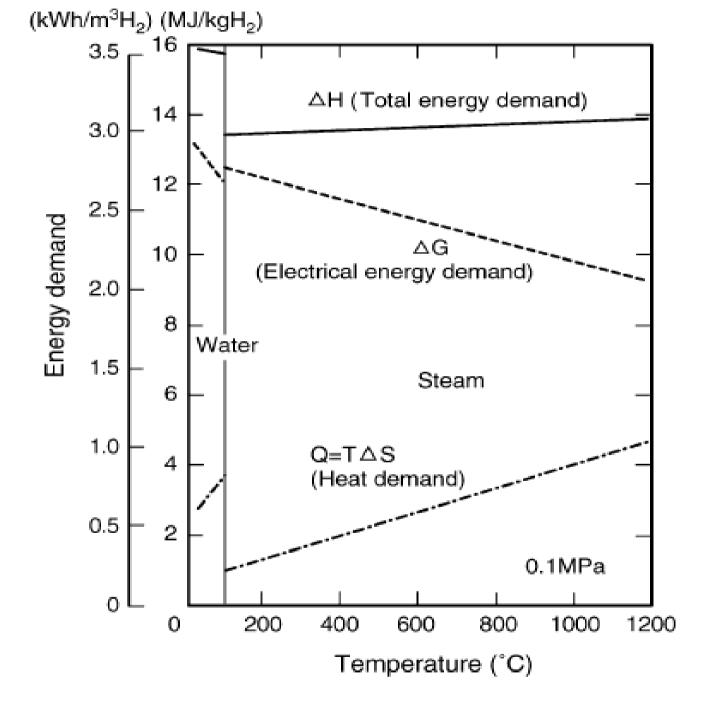


Vojvodic, A.; Nørskov, J. K. Natl. Sci. Rev. 2015, 2, 140–143.

### **Solid Oxide Electrolysis**

 $\Delta H = \Delta G + T\Delta S$  $H_2O \rightarrow H_2 + 1/2O_2$  $\Delta H = 285.8 \text{ kJ/mol at } 25^{\circ}C$ 

 $\Delta G = -zEF = -2EF$ .



### The 3 modes of HTSE

- Thermoneutral:
  - Joule heating = heat consumed by the endothermic reaction
  - Electrical-to-chemical efficiency = 100 %
- Exothermic:
  - Joule heating > heat consumed by the endothermic reaction
  - Electrical-to-chemical efficiency < 100 %
- Endothermic:
  - Joule heating < heat consumed by the endothermic reaction
  - External heat source required
  - Electrical-to-chemical efficiency > 100 %

## Switching on electrocatalytic activity in solid oxide cells

### **Electrochemical vs Chemical Reduction**

 $La_{0.43}Ca_{0.37}Ni_{0.06}Ti_{0.94}O_{3-\gamma}$ 

J-H. Myung, D. Neagu, DN. Miller & JTS. Irvine, Nature, 2016. 537, 528-531

### Electrode with in situ exsolved metal particles

2.381µm

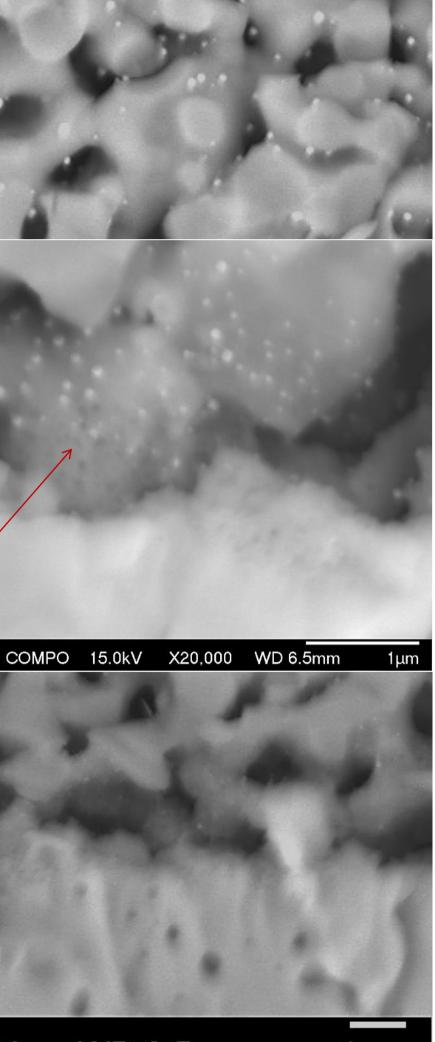
#### Electrolyte

St Andrews

COMPO 15.0kV X5,000

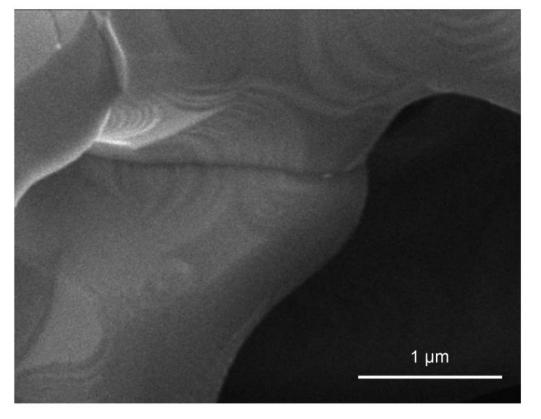
2.045µm

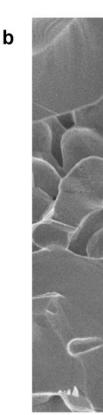
St Andrews



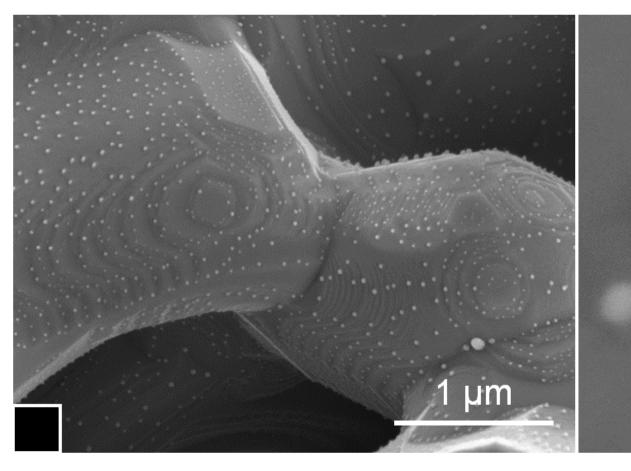
WD 6.5mm

1µm

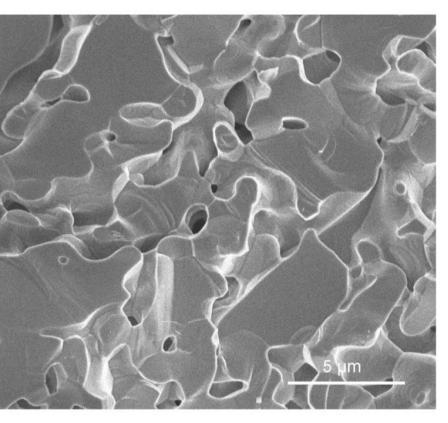


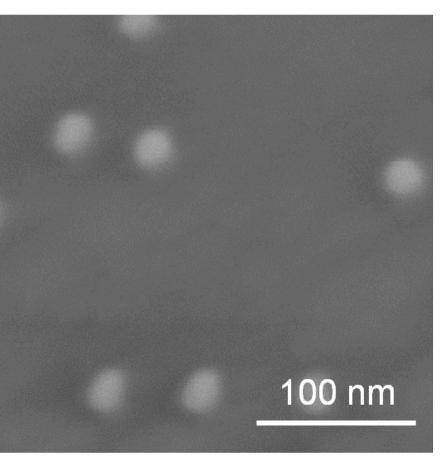


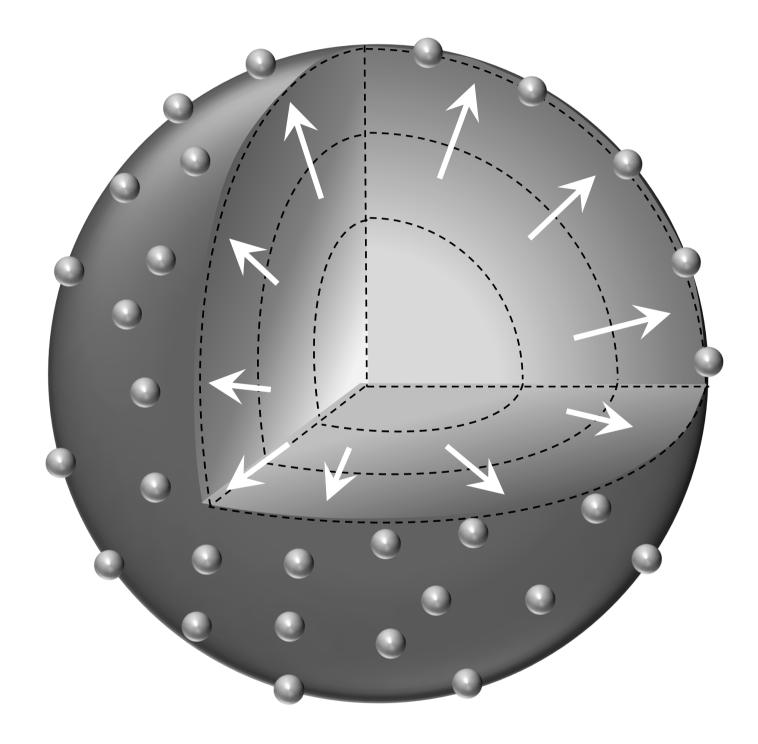
#### Microstructures of as-prepared electrode, before any reduction



#### After reduction in 5%H<sub>2</sub>



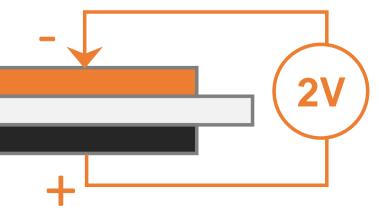


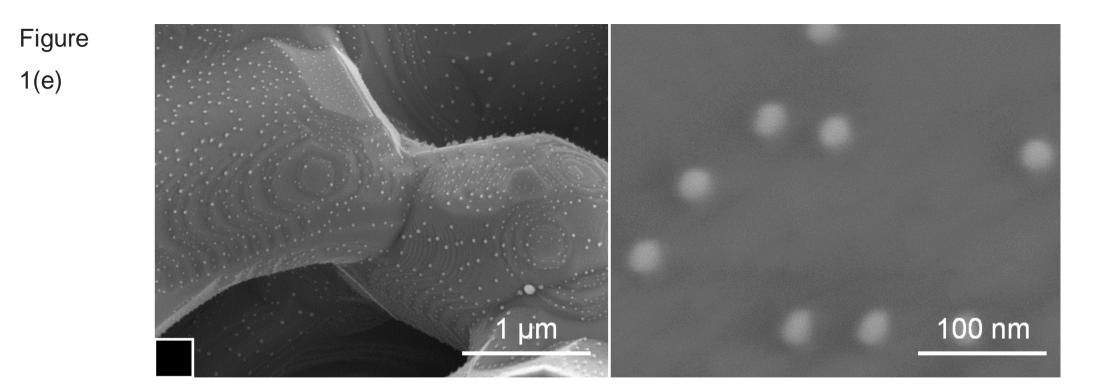


#### $5\% H_2/N_2$ (pO<sub>2</sub> ~ 10<sup>-19</sup> atm)

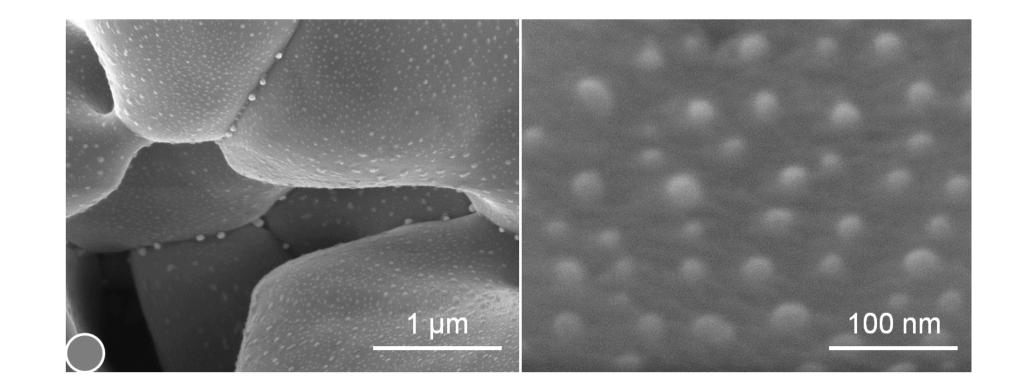


#### $50\% H_2O/N_2$ (pO<sub>2</sub> ~ 10<sup>-35</sup> atm)









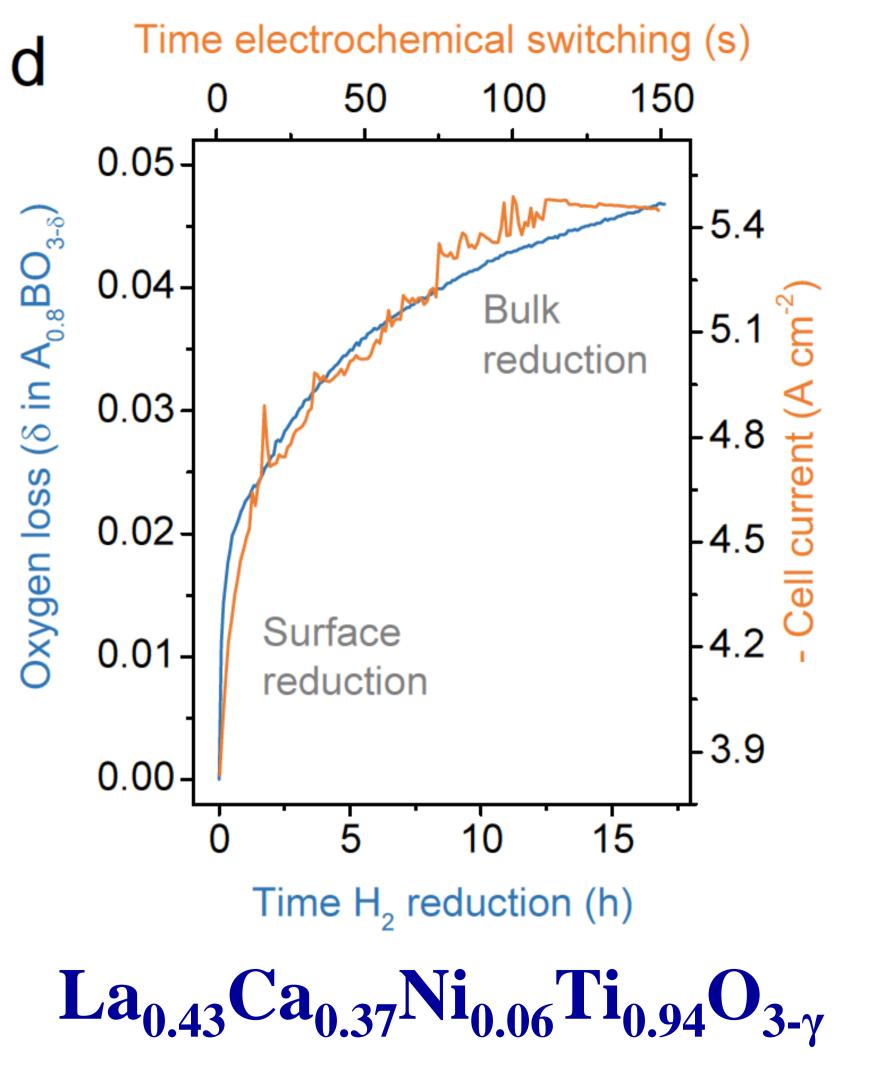
Reduction by  $H_2$  at 900 °C for 20 h

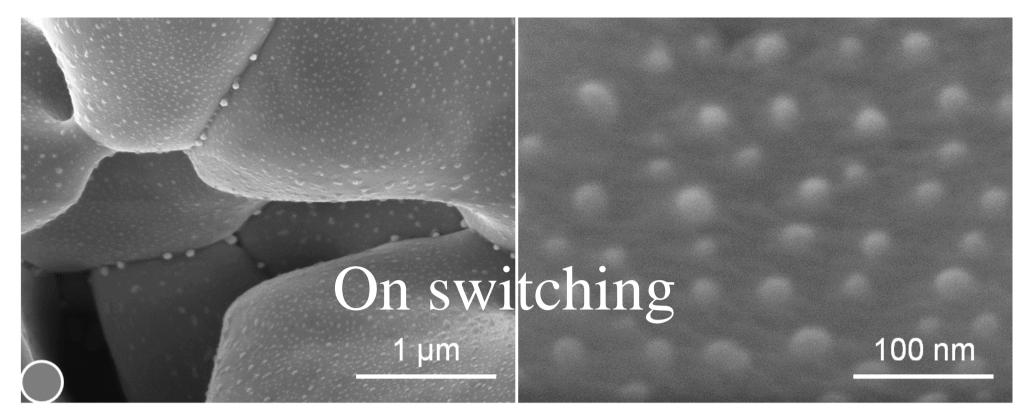
Chemical reduction

Compared to

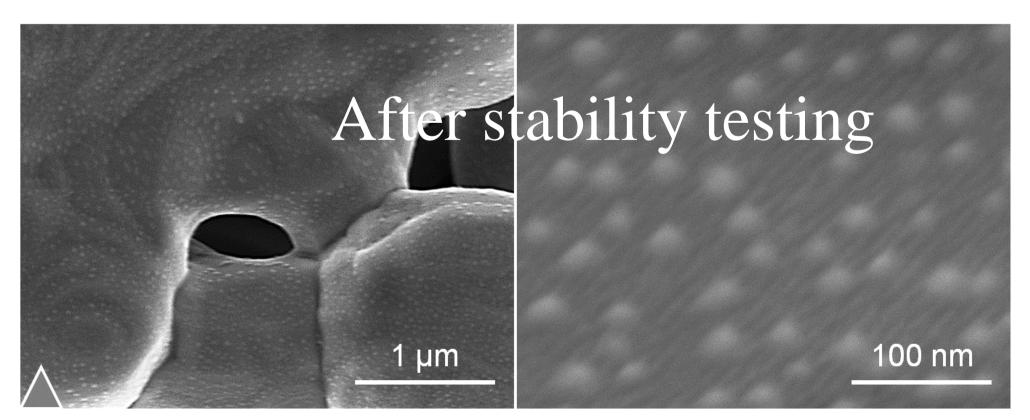
Electrochemical Switching

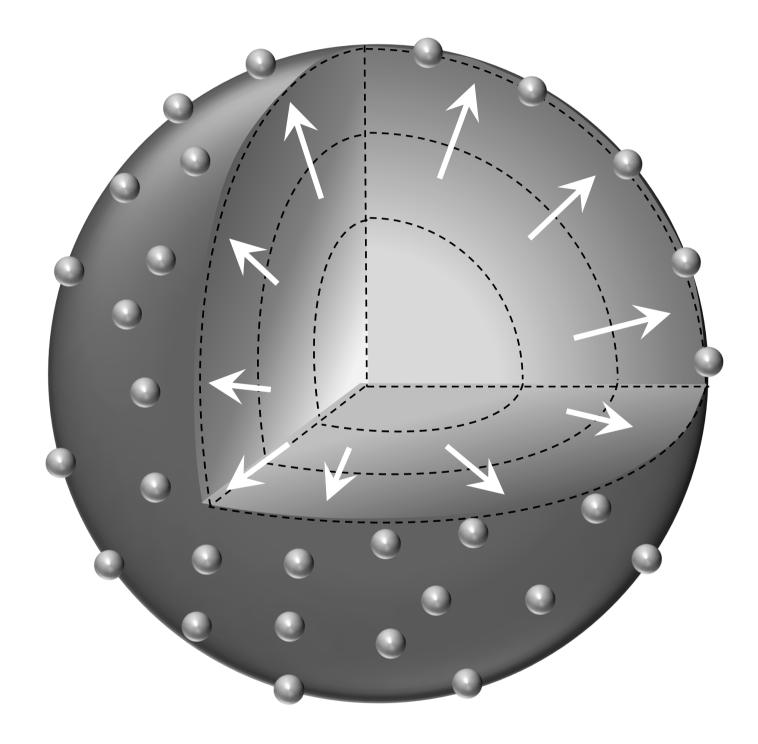
Under 50% H<sub>2</sub>O/N<sub>2</sub>, 900 °C, 150 s





## after 100 h of fuel cell testing at 750 $\,^\circ\!\!C$ in 3% $H_2O/H_2$ at 0.7 V

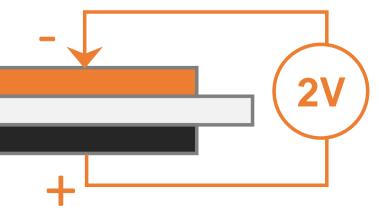


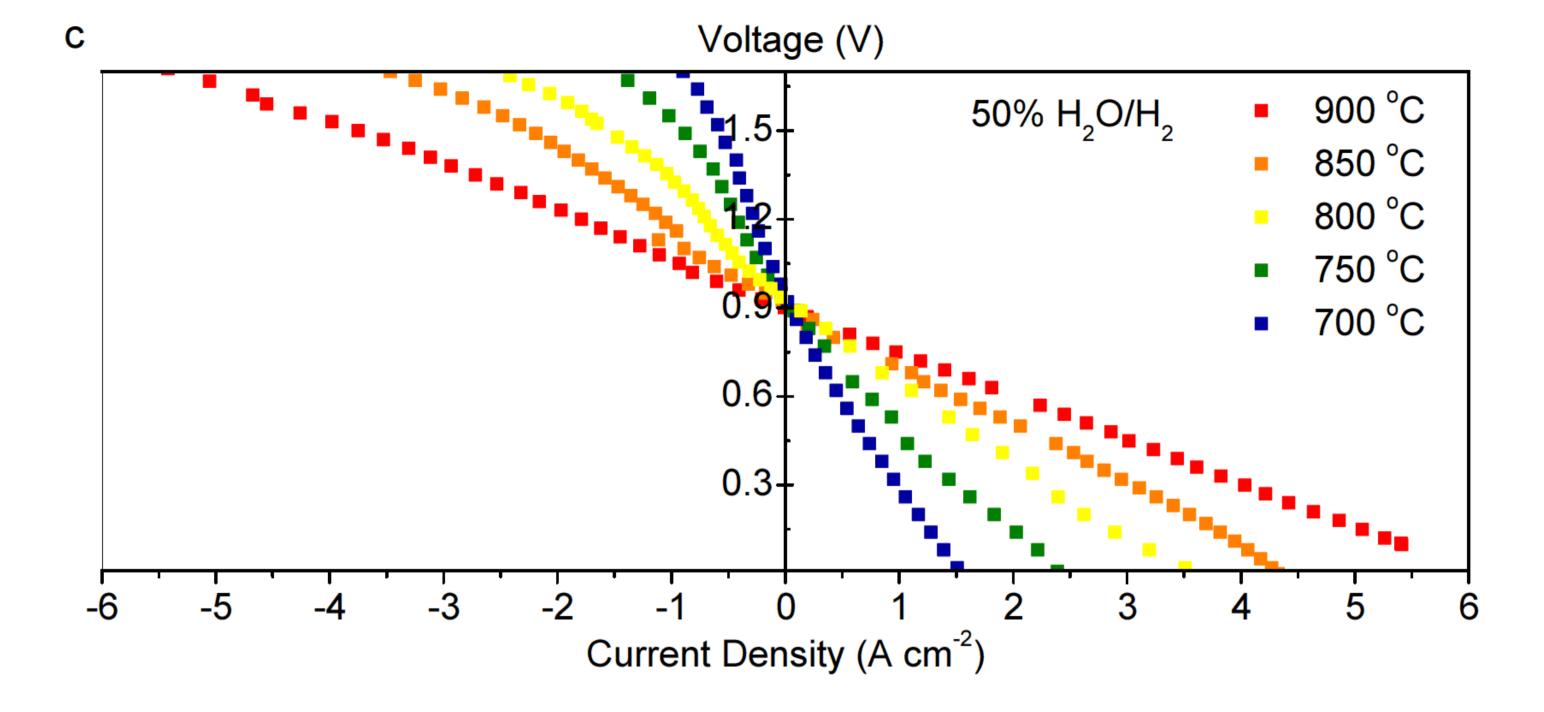


#### $5\% H_2/N_2$ (pO<sub>2</sub> ~ 10<sup>-19</sup> atm)

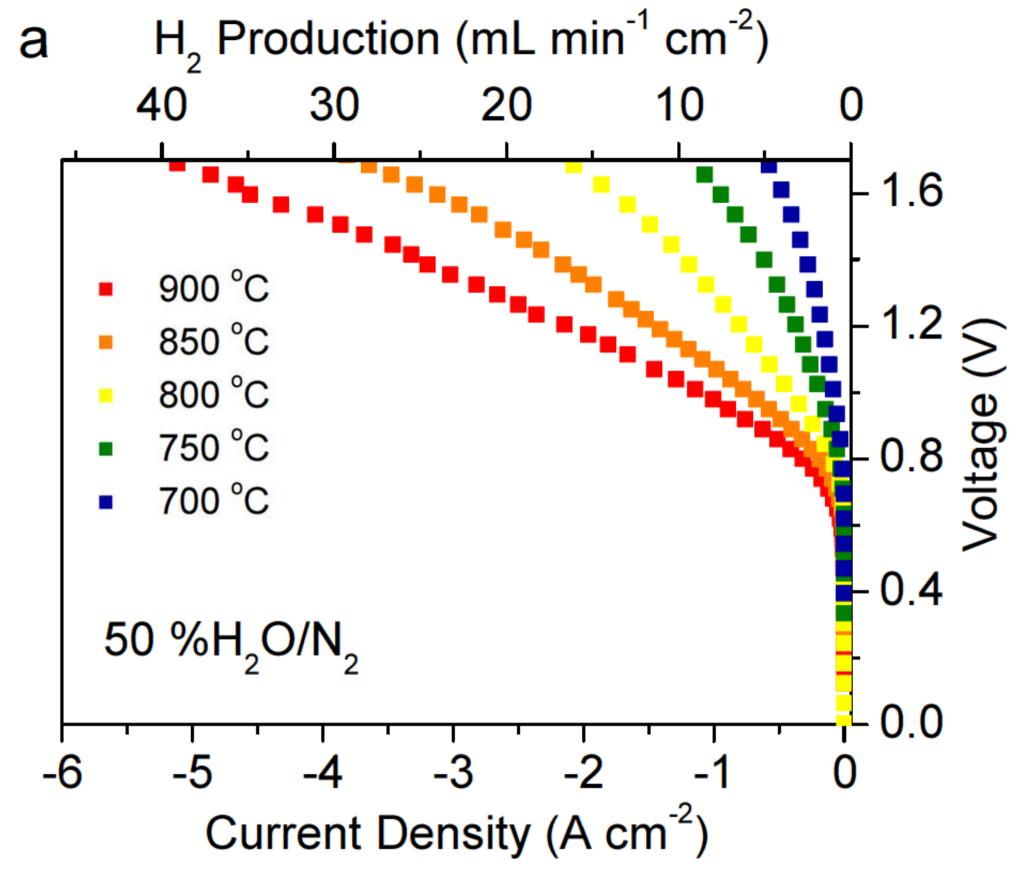


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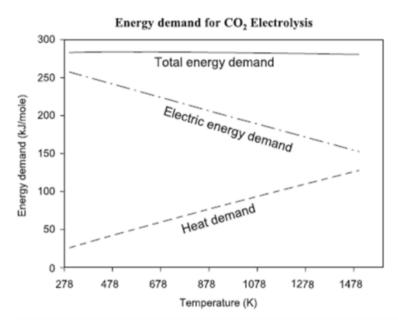
Solid oxide cell based on electrochemical switching. reversible cell mode in 50%  $H_2O/H_2$ . 80 µm thick electrolyte



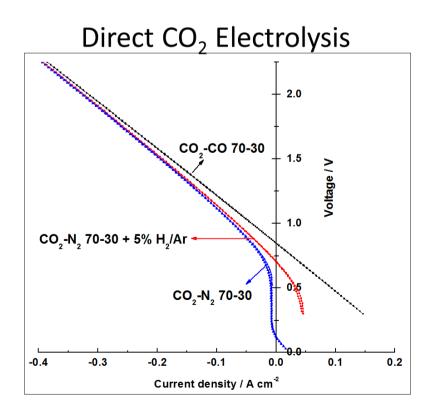
Solid oxide cell based on electrochemical switching. Current-voltage curves (square symbols) electrolysis mode under 50%  $H_2O/N_2$ , also showing equivalent  $H_2$  production assuming 100% Faradaic efficiency



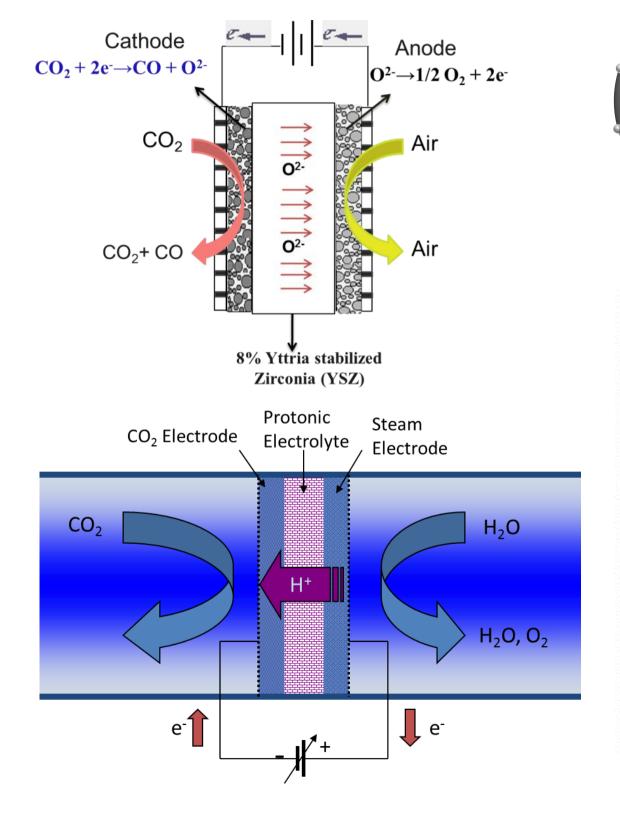
# Carbon Dioxide electrolysis to syngas via oxide or protonic conduction

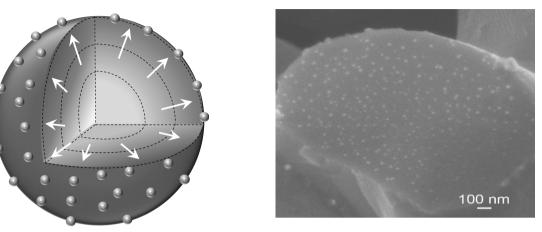


Advantage of high temperature CO<sub>2</sub> electrolysis

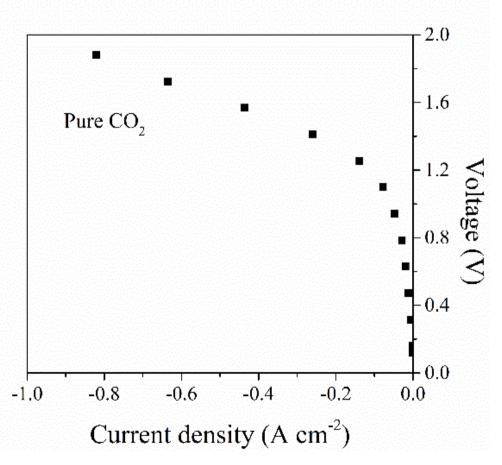


**GDC impregnated LSCM cell** 





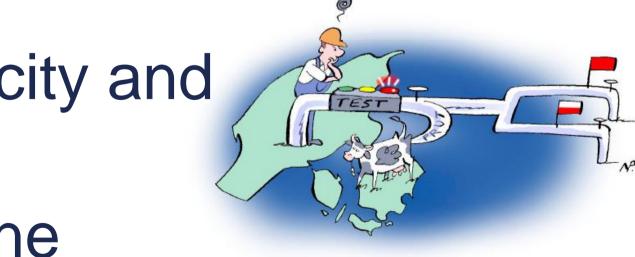
**CO<sub>2</sub> Electrolysis at La<sub>0.43</sub>Ca<sub>0.37</sub>Ni<sub>0.06</sub>Ti<sub>0.94</sub>O<sub>3</sub> Electrochim. Acta. <b>306**, 159



#### Danish 2050 model Green gas system linked to SOFCs and SOECs

- Increased use of methane and "green" gases
- SOEC can produce methane to the gas system when electricity prices are low
- Possibilities for storage of heat and gas help prevent overflow and deficiency in the electricity system
- High prices: SOFC production of electricity and heat
- Low prices: SOEC production of methane

gases s system



#### Acknowledgements

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