# Electrochemical Synthesis with Ceramic Electrolytes

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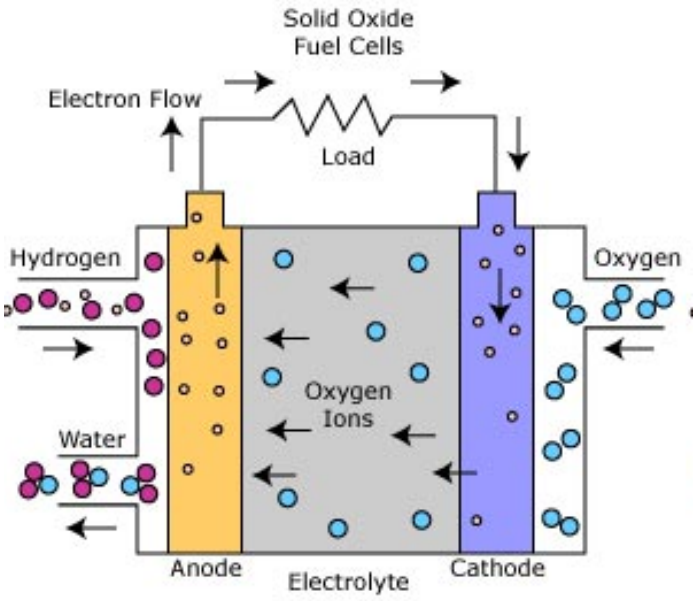
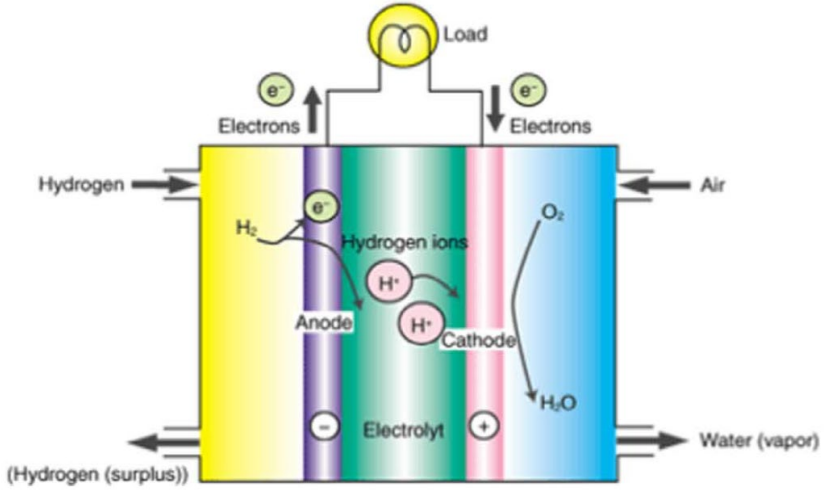
**Oxygen Ion Conductors (Y-doped $ZrO_2$)** **Proton Conductors ($BaCeO_3$/$BaZrO_3$)**

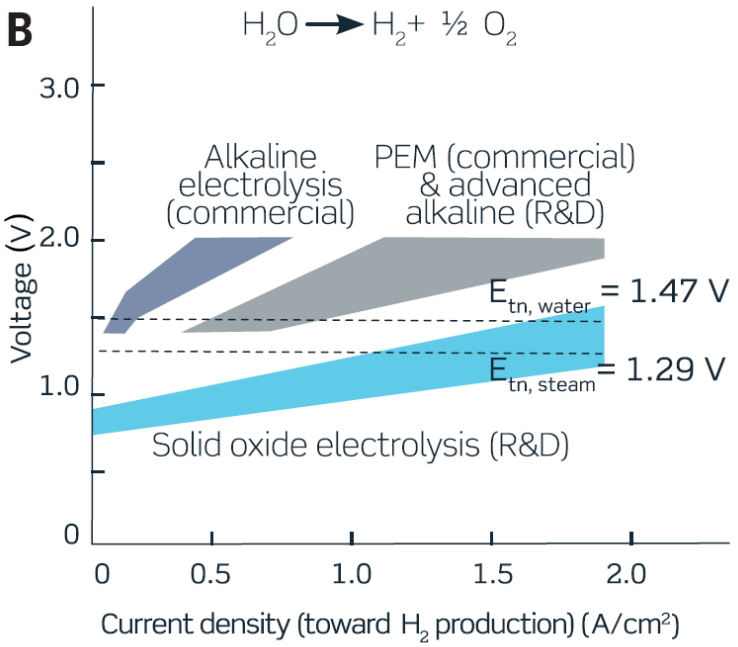


## Water Electrolysis ($H_2$ production)

1. **100% Faradaic efficiency.**
2. **Lower operating voltage.**
3. **Heat recovery easier at high T.**

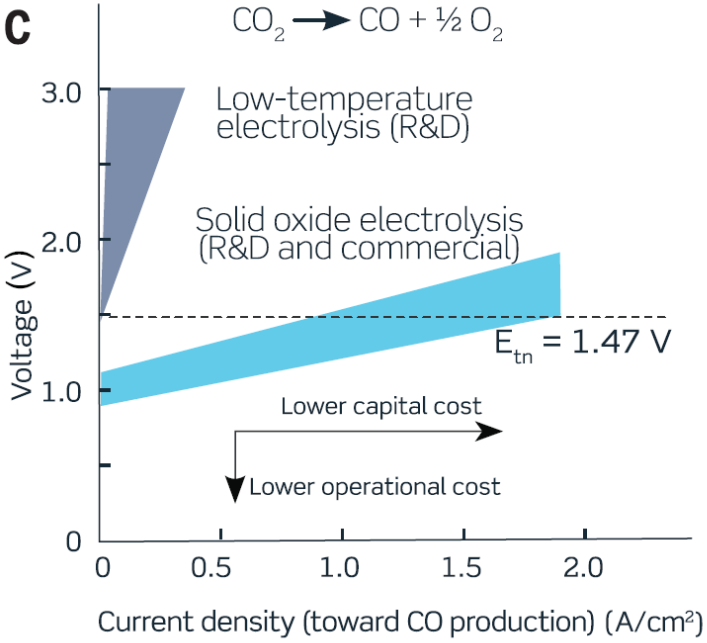
Hauch et al., *Science* **370**, 186 (2020)




## $CO_2$ Electrolysis (CO, $O_2$ production)

1. **Recent Mars Rover experiments**
2. **Already being commercialized for on-site CO production**

Rainer Küngas, 2020 *J. Electrochem. Soc.* **167,** 044508



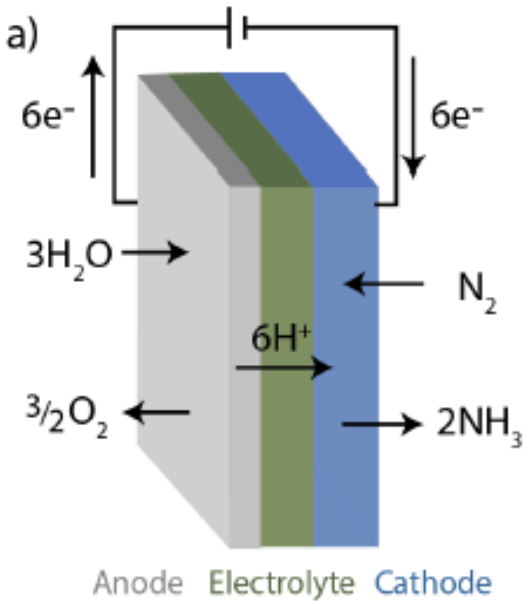
# $NH_3$ Synthesis

**Many high-profile publications… *No* results!**

1. **Most publications used proton-conducting ceramics.**
2. **Proton-conductors have conductivity ~ 400 °C.**

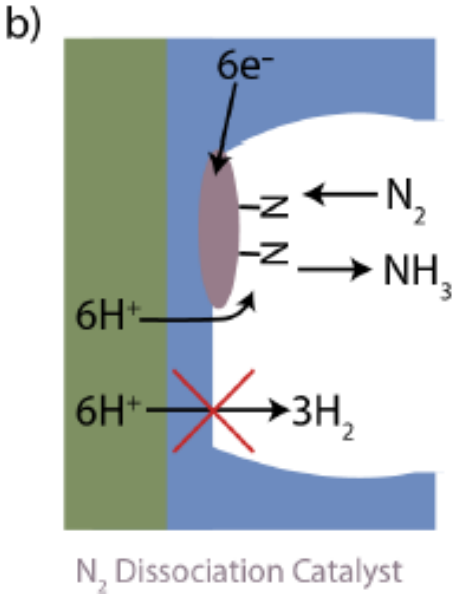
**But….**

1. **Amounts of $NH_3$ produced were so low that some question whether they are detectable.**
2. **$H_2$-$NH_3$ selectivity; equilibrium yields at low pressures are poor.**
3. **No advantage to performing electrolysis and Haber-Bosch in the same system.**



**Our concept:**

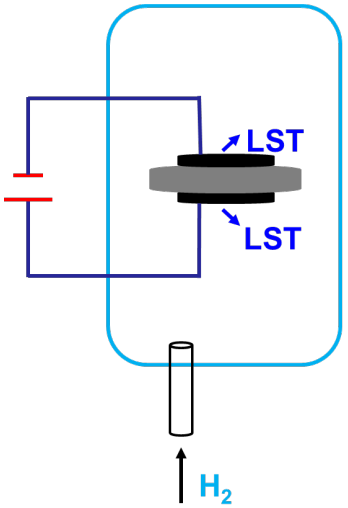
- **Use composite electrode**
- **With $e^-$ conducting ceramic (e.g. $La_{0.3}Sr_{0.7}TiO_3$)**
- **$N_2$ dissociation metal (W, Mo, Re)**

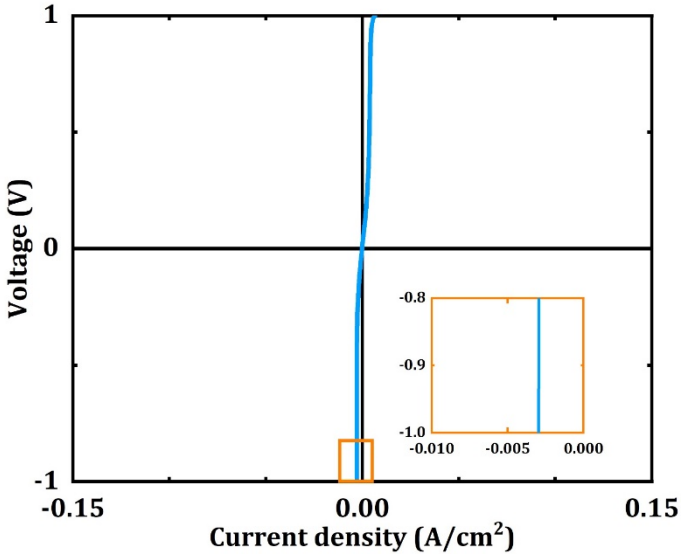


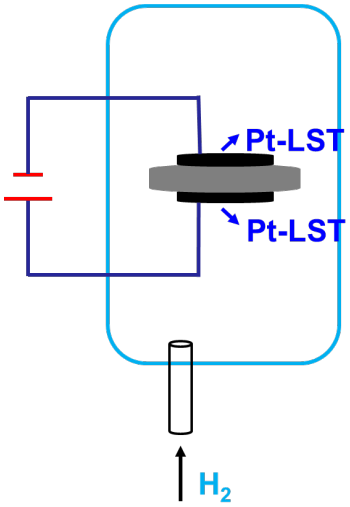

1. **Avoid H recombination catalysts (Pt, Ni, Ru, etc)**
2. **Plan for high electrode overpotential**
   **$P_{H_2}$ increases with ln{η}; 0.1 V ~ 1000x increase**

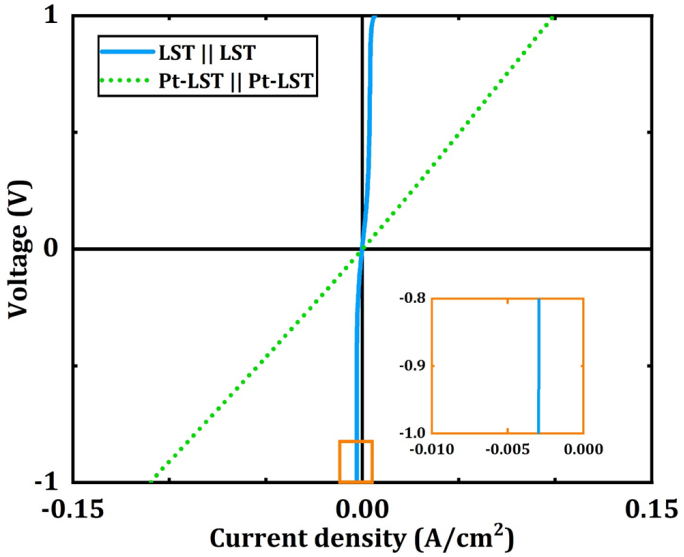
# Symmetric Cell, 500 °C, BZCYYb electrolyte

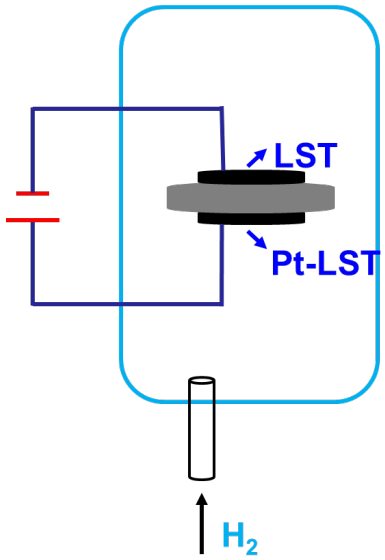
Jian Chang *et al* 2021 *J. Electrochem. Soc.* **168** 044522

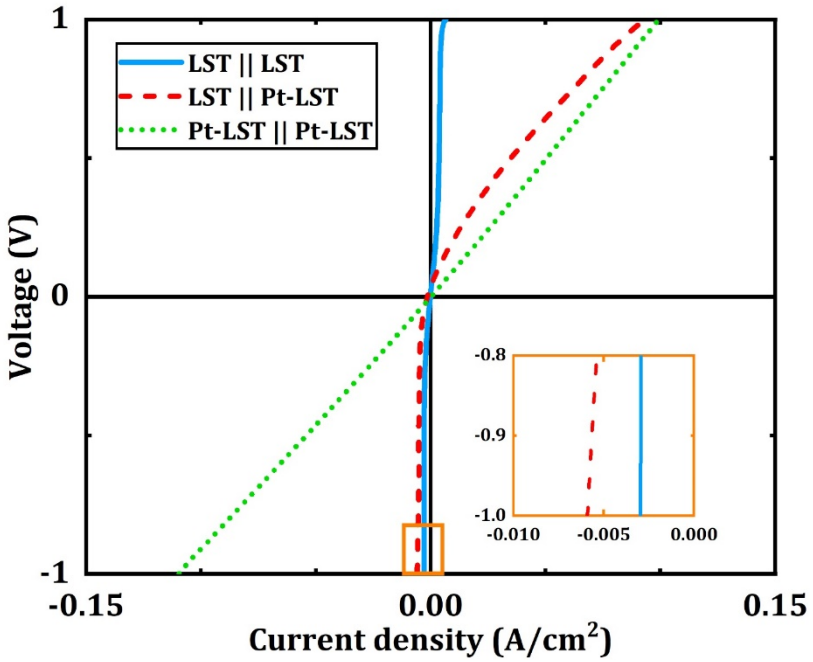





- Catalyst is required to dissociate $H_2$.
- But H recombination can occur on the electrolyte without catalyst.
- DFT also indicates H recombination is barrierless on $BaZrO_3$.

# What is the path forward?

1. Alternative electrolytes? Coating on electrolyte?
2. Completely different approach (e.g. Energy Environ. Sci., 2017, 10,1621)