A Study on Electrochemical Ammonia Synthesis with Proton-conducting Solid Oxide Electrolytic Cells Based on $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-d}$

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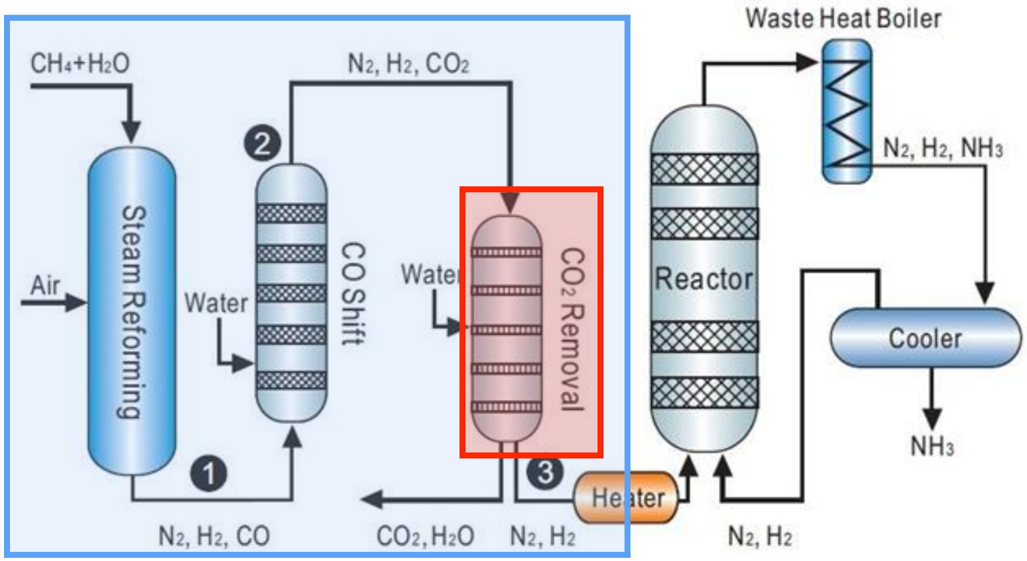
1. Introduction

- **Conventional NH_3 synthesis: Haber-Bosch process (invented in 1909)**

1. CO_2 emission with steam methane reforming (2.3 tons of CO_2/ton of NH_3)[1]

2. High pressure requirement



Overall process of the Haber-Bosch process[2]

- **Temperature: 400 ℃ ~ 500 ℃**
- **Pressure: 150 bar ~ 200 bar**
- **Fe-based catalysts**

[1] I. Rafiqul et al., Energy, 2005(30) 2787-2504
[2] Quantitech, Ammonia synthesis, http://www.quantitech.co.uk/entity-287-Ammonia-Synthesis.aspx

1. Introduction

- **Types of electrochemical NH_3 synthesis**

[3], [4]

Types	electrolyte	Features	Formation rate
Solid oxide electrolytic cell (SOEC)	• Doped metal oxide	• Solid electrolyte • 500 ~ 800 ℃ • Higher activity • Simple system	• $8.20 \times 10^{-9} \sim 5.00 \times 10^{-12}$ mol/cm²·s
Polymer exchange membrane electrolytic cell (PEMEC)	• Sulfonated tetrafluoroethylene (Nafion)	• Solid electrolyte • 60 ~ 80 ℃ • Water management • Incompatibility to ammonia	• $1.13 \times 10^{-8} \sim 1.10 \times 10^{-10}$ mol/cm²·s
Nitrogen ion conducting electrolytic cell	• Molten salt (LiCl, KCl)	• Liquid electrolyte • 200 ~ 500 ℃ • Low conductivity	• $2.00 \times 10^{-8} \sim 3.33 \times 10^{-9}$ mol/cm²·s
Li-mediated electrochemical synthesis	• $LiPF_6$ (Li-ion battery)	• Liquid electrolyte • 220 ℃ • Multi-step process	• 1.18×10^{-9} mol/cm²·s

※ No leading technology has been developed yet.

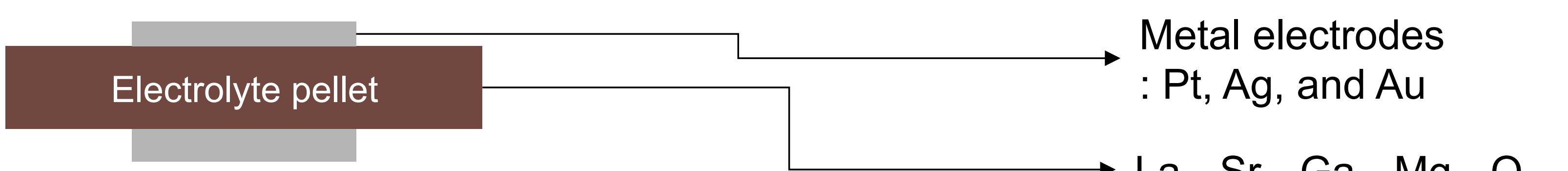
[3] V. Kyriakou et al., Catalysis Today 286 (207) 2–13
[4] Garagounis et al., frontier in ENERGY RESEARCH, 17(2014) 1-10

2. Experimental

- **Objectives**

  Feasibility test of LSGM based proton-conducting cell with metal electrodes

  1. **Catalyst selection with symmetric cells**
  2. **Modification of flow channels**
  3. **Improvement of formation rate**

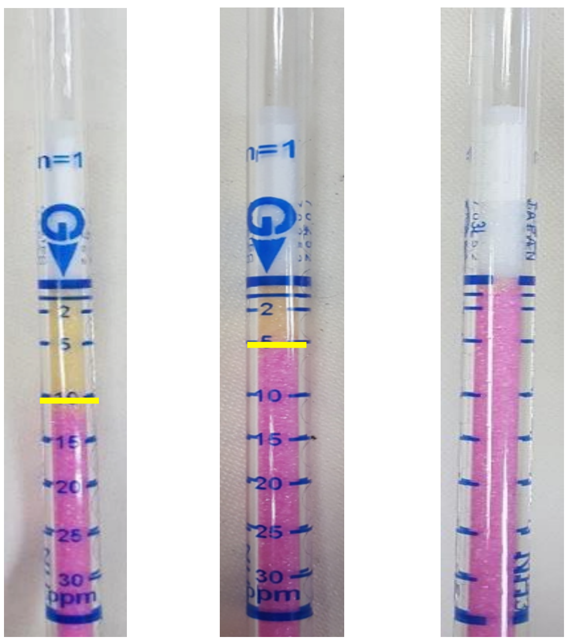


Simple schematic of a fabricated cell

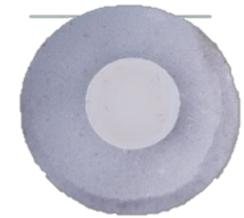
3. Results

- **NH_3 formation at symmetric cells**

At 600 ℃, 1.6 V



Ag paste 5ppm | **Pt paste 2.5ppm** | **Au paste ~0**



< SOEC with screen -printed Pt electrode >

➢ **Formation rate (ideal gas assumption)**

1) **Ag: 1.43×10^{-10} $mol/cm^2 \cdot s$**
2) **Pt: 0.71×10^{-10} $mol/cm^2 \cdot s$**

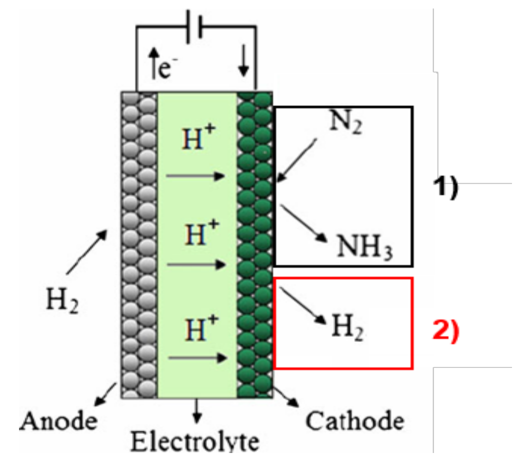
(Reported data: 8.20×10^{-9} ~ 5.00×10^{-12} $mol/cm^2 \cdot s$)

→Ag > Pt >> Au (∵ Higher selectivity of Ag)[5]

➢ **Cathodic reactions**

1) **$N_2 + 6H^+ + 6e^- \rightarrow 2NH_3$**
2) **$2H^+ + 2e^- \rightarrow H_2$**

(dominant on Pt electrode)



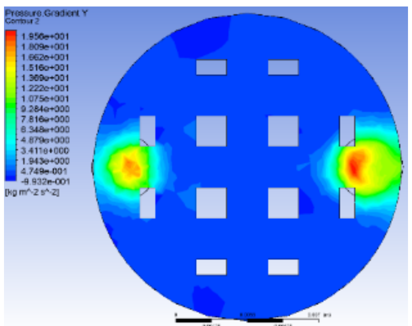
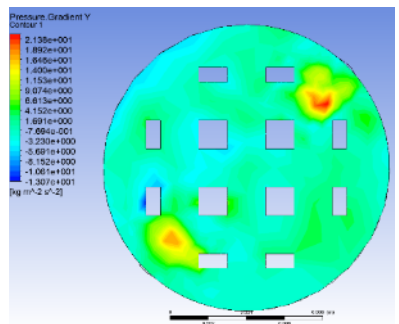
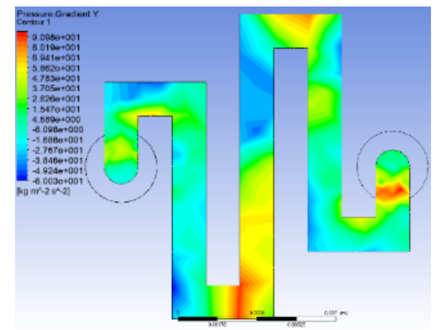
Possible cathodic reactions[6]

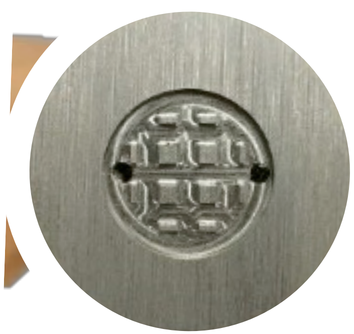
5] D.S. Yun et al., Journal of Power Sources 284(2015) 245 – 251
[6] Ibrahim A. Amar et al, J Solid State Electrochem (2011) 15:1845–1860

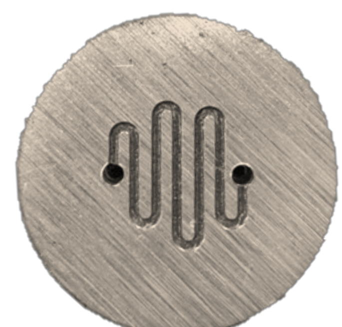
3. Results

- **Flow channel modification**

Pressure gradient to normal direction

<Previous>	<Input & output location modification>	<zigzag-type>
		
Range: -0.9932 ~ 19.56 kg/m^2s^2	-13.01 ~ 21.38 kg/m^2s^2	-60.03 ~ 90.98 kg/m^2s^2





NECS KAIST

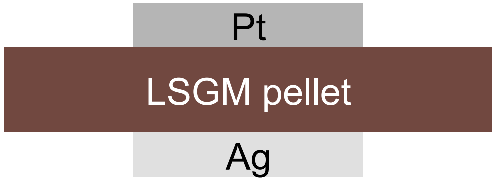
3. Results

- **Improvement of the formation rate with asymmetric cells**

Asymmetric cell

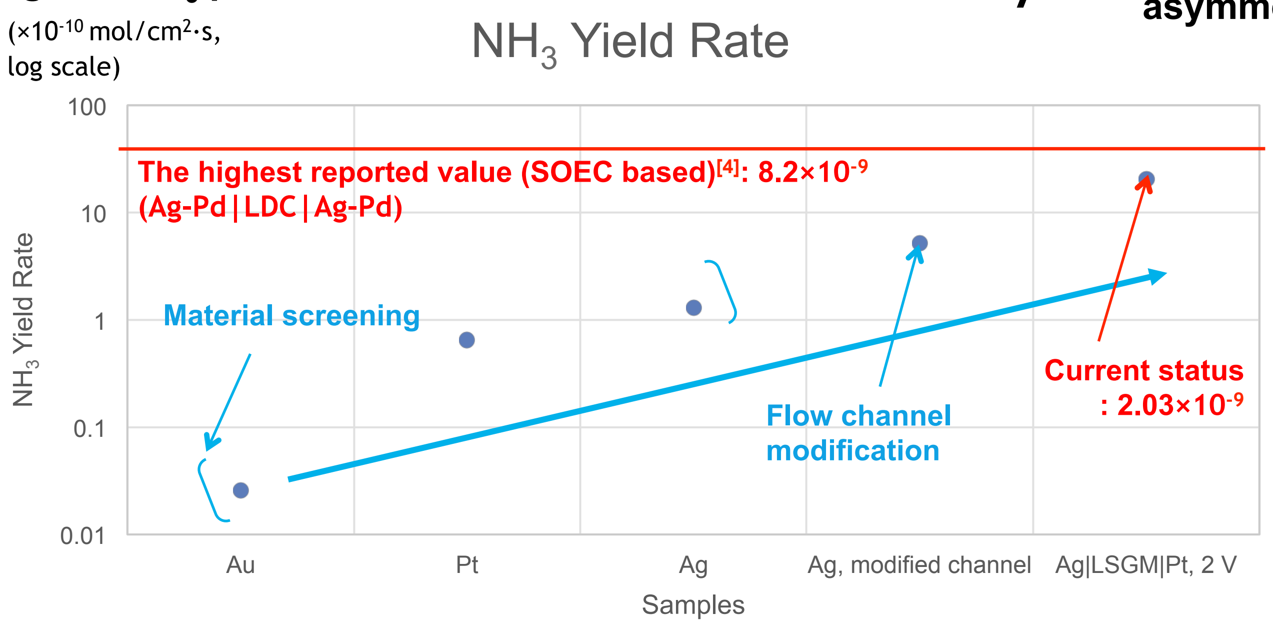
Anode: Pt (to promote hydrogen oxidation reaction)

Cathode: Ag (to selectively promote ammonia formation reaction)



Configuration of asymmetric cells

→ **The highest NH_3 production rate:** $2.03 \times 10^{-9}\ mol/cm^2 \cdot s$



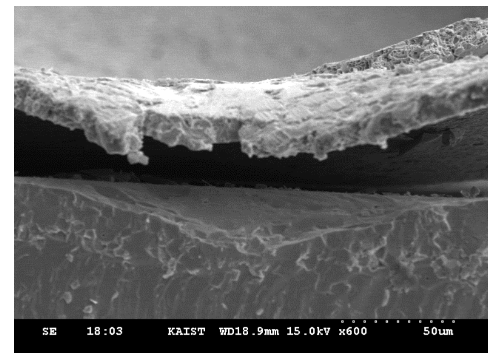
<Experimental data for electrochemical NH_3 synthesis>

3. Results

*CTE: Coefficient of thermal expansion

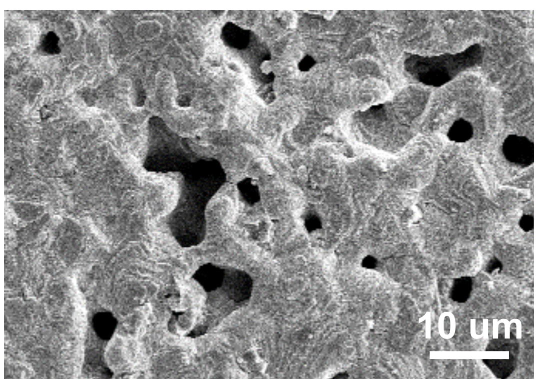
- **Discussion**
  - ✓ **Delamination of electrodes due to *CTE difference**

Delaminated electrode

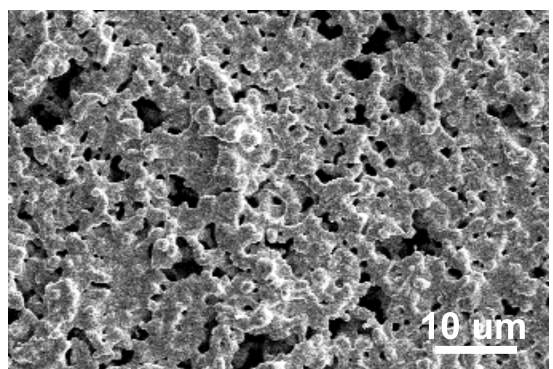


SEM image of delaminated electrode

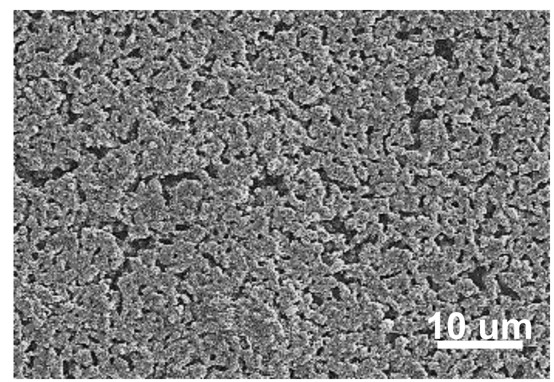
  - ✓ **Poor morphology**



Ag electrode



Pt electrode



Solid oxide electrode (LSGM)

3. Conclusion

1) LSGM electrolyte can work as a proton-conducting material.

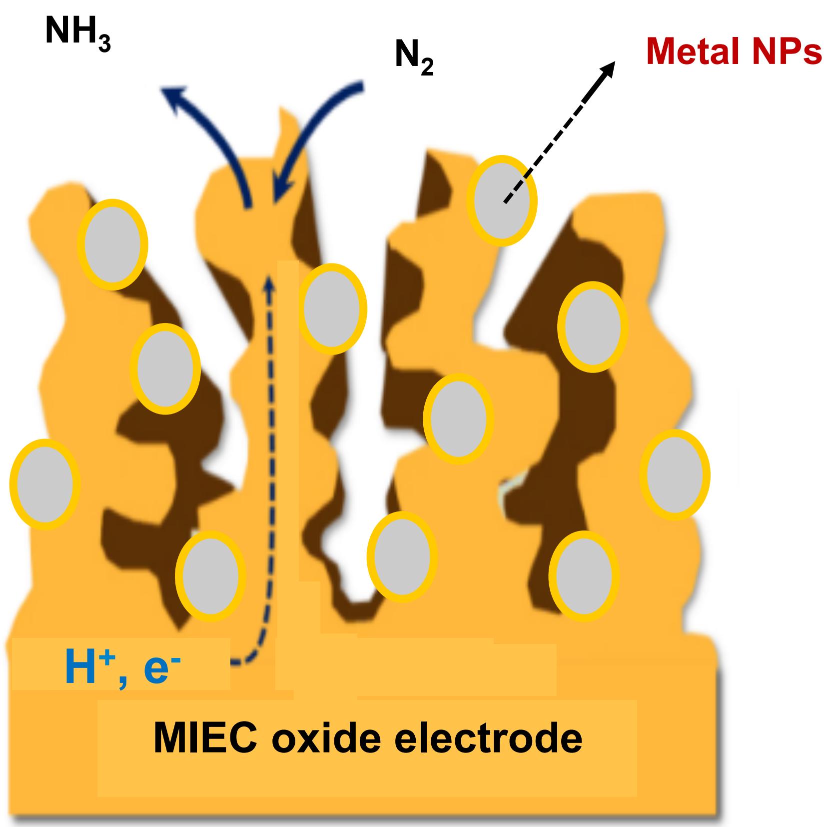
2) Electrochemical synthesis with the material is feasible and the formation rate is comparable to other solid oxides.

3) As a cathode material for ammonia synthesis, Ag shows a bett er performance than Pt.

4) Pure metal electrode shows typical challenges such as delamin ation or morphology.

4. Future work

- Introduction of scaffold-structured electrodes



1) Material selection for backbone

- With enough electric conductivity and ionic con ductivity

2) Morphological study

- Condition screening for optimal microstructure
- Particle size & sintering temperature

3) Methods for metal particle dispersion

- Conventional infiltration method
- Electroless plating

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