Ammonia Synthesis in a Modified IT SOFC System

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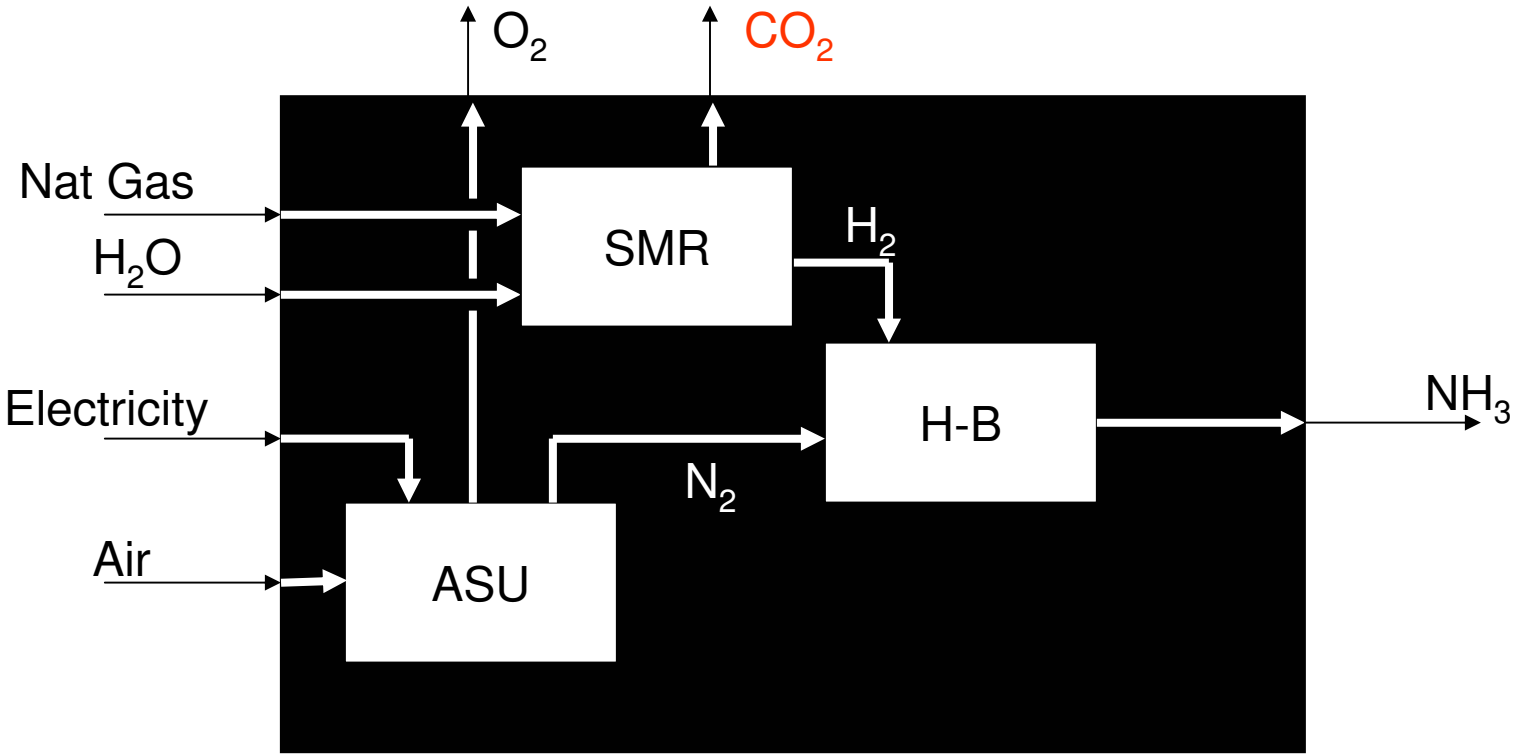
Presentation Overview

- Introduction: electrolytic ammonia synthesis
- Concept of micro-tubular system
- Fabrication of micro tubular IT-SOEC system
- Conclusions

Inside the Black Box: Steam Reforming + Haber-Bosch

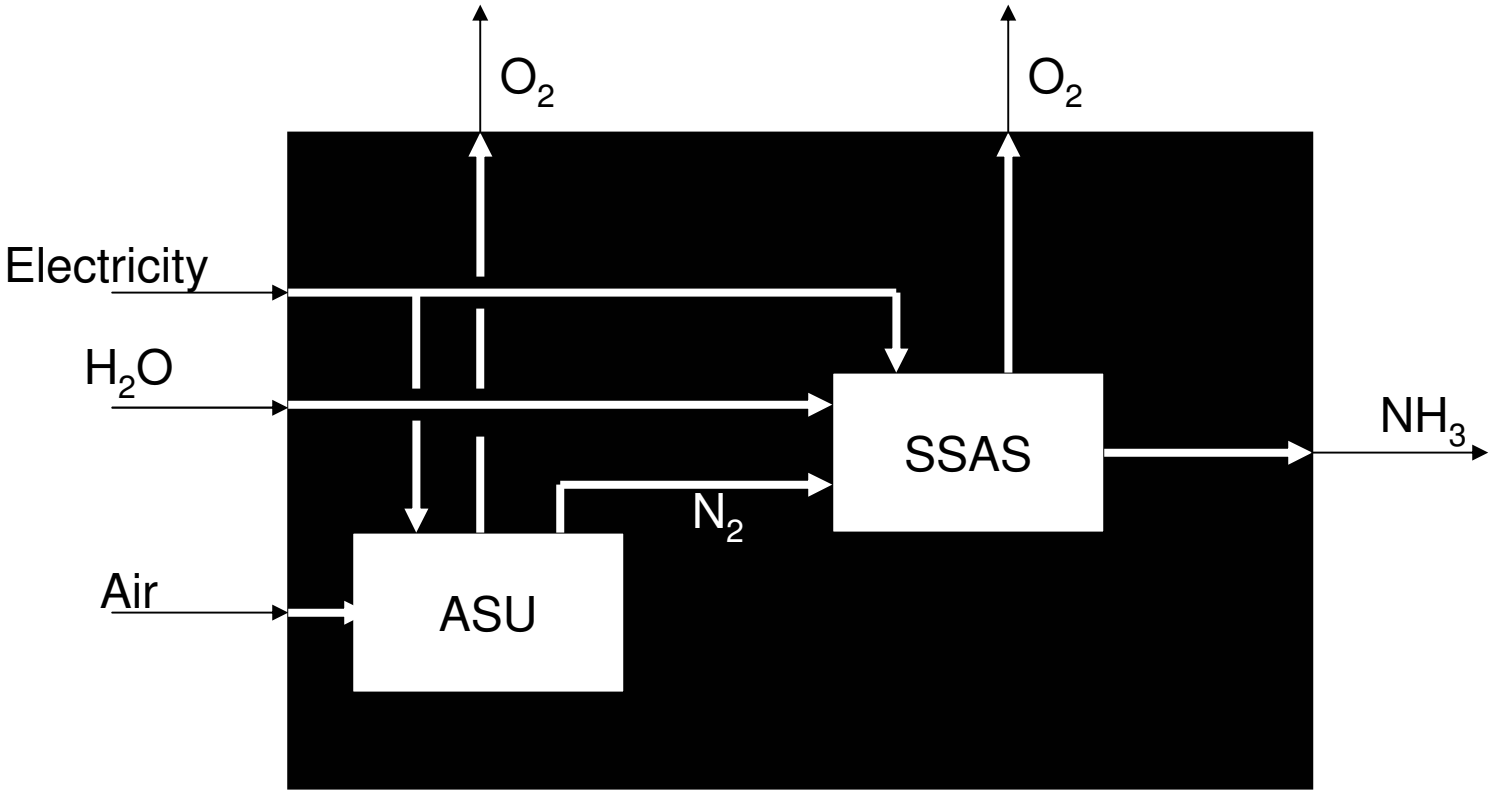
$$3\ CH_4 + 6\ H_2O + 4\ N_2 \rightarrow 3\ CO_2 + 8\ NH_3$$



Energy consumption ~33 MBtu (9500 kWh) per ton NH_3

Inside the Black Box: Electrolytic Ammonia Synthesis

$$6\ H_2O + 2\ N_2 \rightarrow 3\ O_2 + 4\ NH_3$$

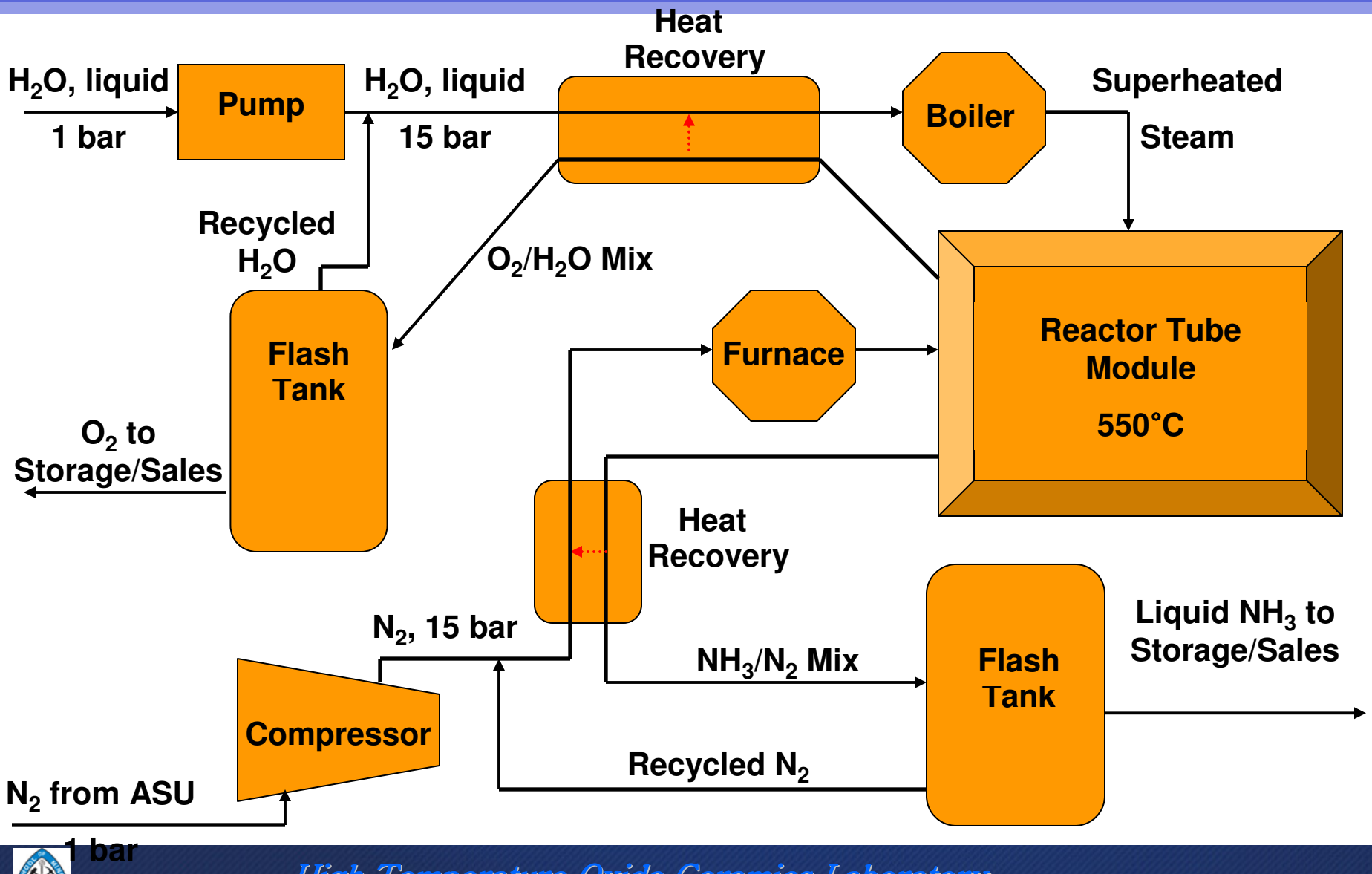


Energy consumption 7000 - 8000 kWh per ton NH_3

General Process Features

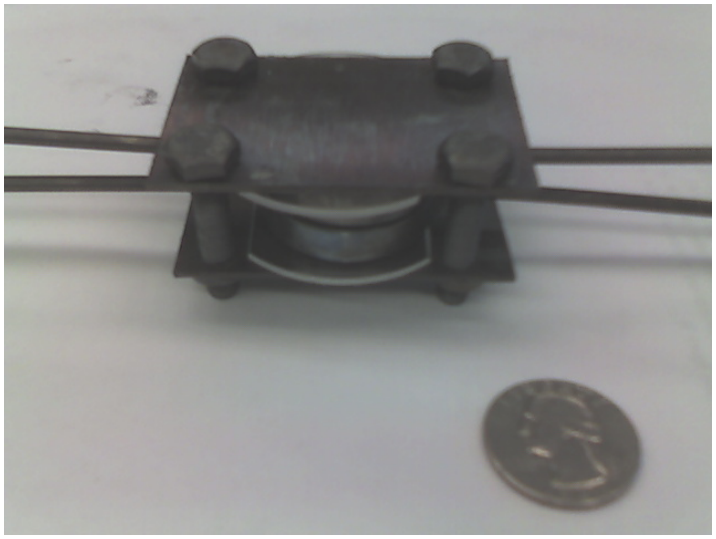
- **Solid-state electrochemical process**
- **Water (steam) decomposed at anode**
- **Hydrogen atoms adsorb, stripped of electrons**
- **Hydrogen conducts (as proton) through proton-conducting ceramic electrolyte**
- **Protons emerge at cathode, regain electrons, and react with adsorbed, dissociated nitrogen atoms to form NH_3**
- **Patent application – February 2007, published August 2008**

Production Scale Concept



Early Work: Button Cells

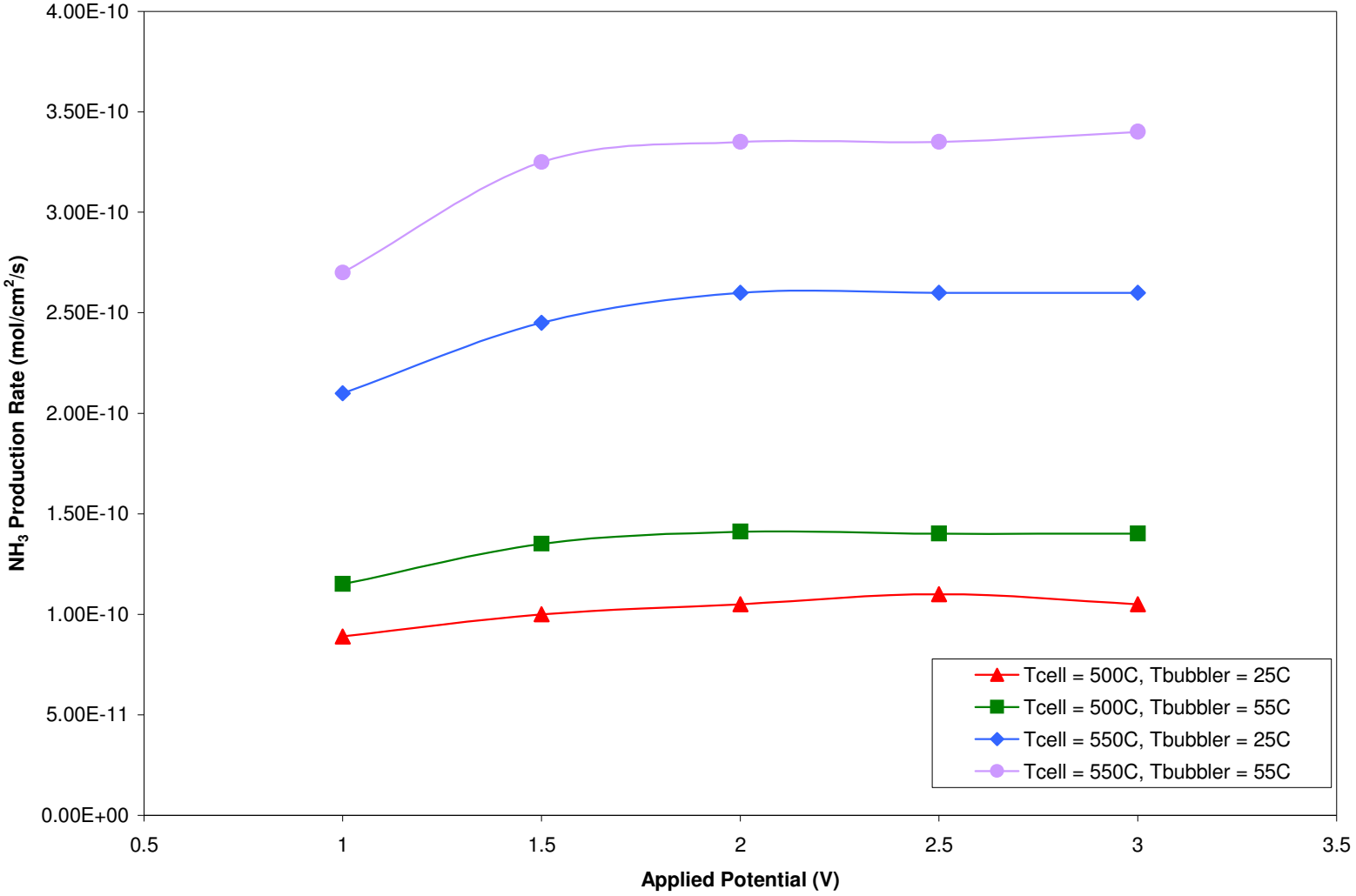
- Electrolyte supported, ~1 mm thick
- Pressed powder, sintered at high temperature to densify
- Simple to prepare, Pt metal catalysts for anode and cathode
- Tested for leaks using "fuel cell mode"
- Supply gases switched to N_2 and humidified argon
- DC voltage (1.0 – 3 VDC) applied to cell
- NH_3 collection quantified by bubbling through weak hydrochloric acid solution



Ammonia Production Experiments

- Button cells: approx. size of US quarter dollar
- 10 mA total current, exposed electrode area of 2 cm^2
- Higher temp: easier proton conduction, but more ammonia cracking is possible
- Rates increase with partial pressure of steam (bubbler temperature)
- Limitation: Higher applied voltage does not increase production beyond maximum rate
- Overall: cells are most limited by proton conductivity of electrolyte

Ammonia Production Tests



Process Improvement Areas

- Primary goal: higher rate of proton transport at a lower cell temperature
  - Less ohmic loss in electrolyte, less power wasted as heat
  - Lower temperature reduces ammonia cracking
- May be achieved by a higher conductivity electrolyte material, OR:
  - Thinner electrolyte layer
  - Increasing steam partial pressure (eventually, 1 atm or more)
- Cylindrical geometry: greater thermal expansion/shock resistance than large planar cells
- Expanded total surface areas improves measurement accuracy for ammonia formation

Fabrication of Micro-tubular Electrolyte on Anode Support

Cell Preparation

0.8-1.8 mmΦ NiO-GDC support tube

↓

In situ electrolyte formation

↓

Co-fired at 1450° C for 6h

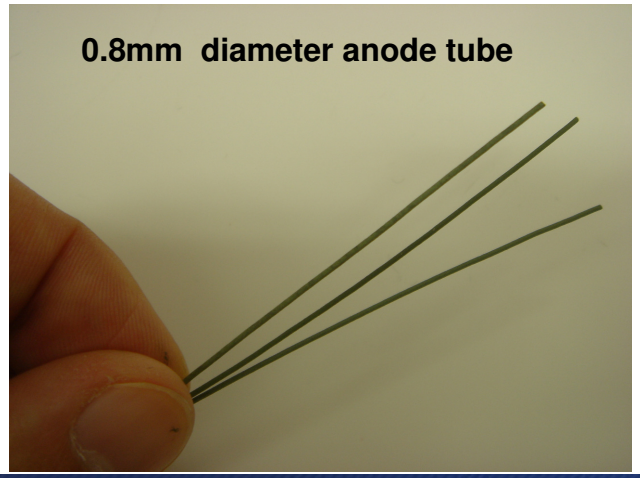
↓

Dip-coating of electrode

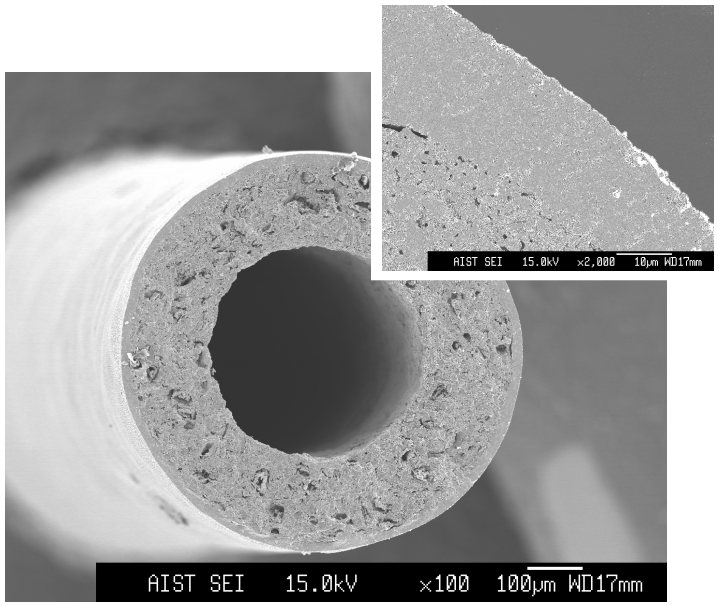
↓

Sintered at 1000° C for 1 h.

Support : Nickel oxide-ceramic composite (200μm in thickness)
Electrolyte : Perovskite protonic ceramic (10-20μm in thickness)
Electrode : LSCF-ceramic composite (40μm in thickness)

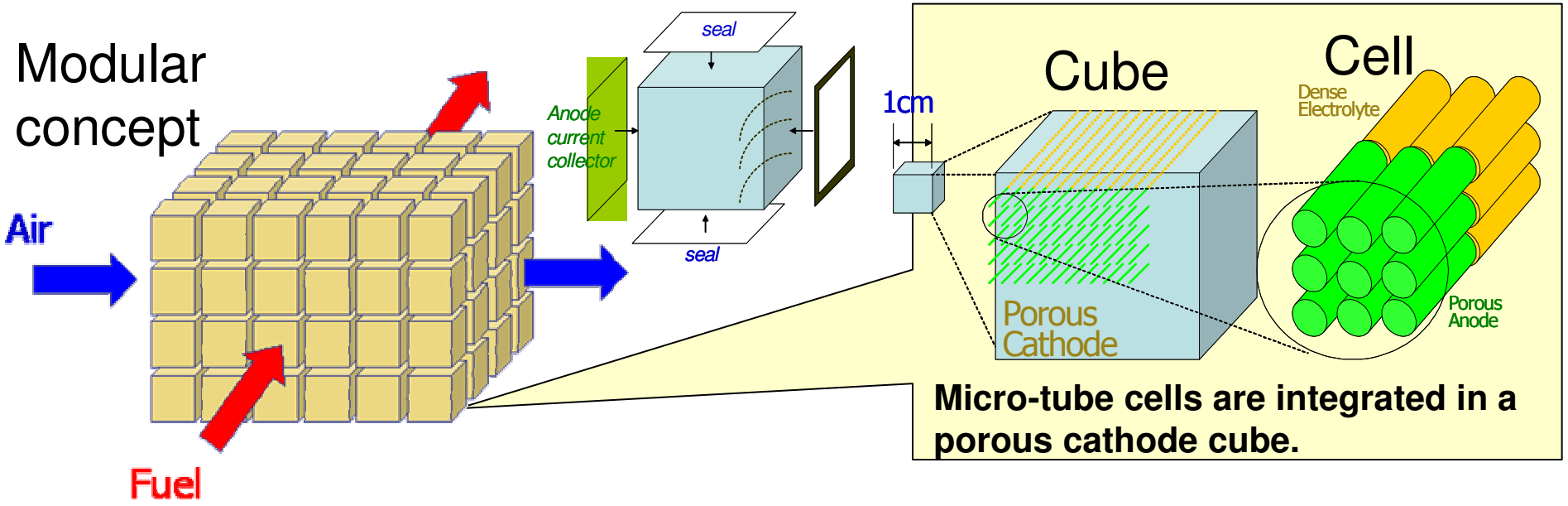


0.8mm diameter support tube with electrolyte



Reactor Tube Bundle Concept

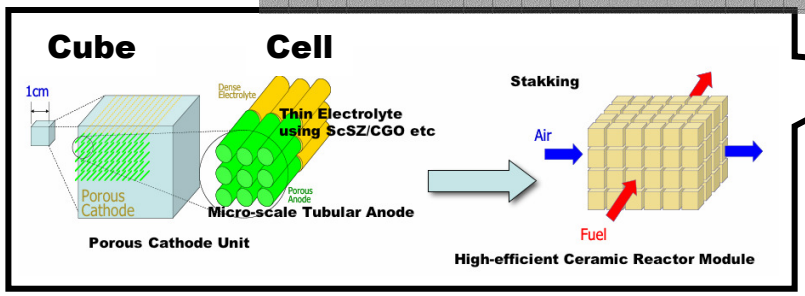
- **micro-tubular designed cell**
  - → **high thermal shock proof**
  - → **high production rate per volume**
- **intermediate temperature operation (500 - 600°C)**
  - → **quick start-up (in a few minutes)**
- **modularized design**
  - → **reduced unit footprint**

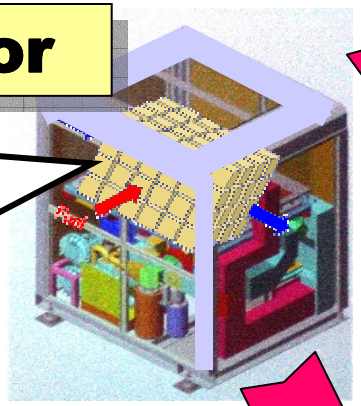


Ceramic Reactor Applications

high efficiency on energy conversion and Selective reactions

Ceramic reactor

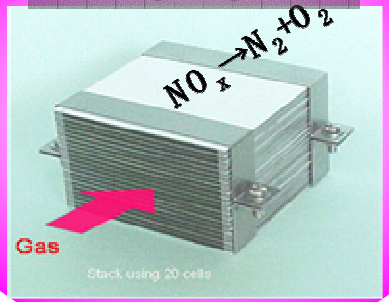




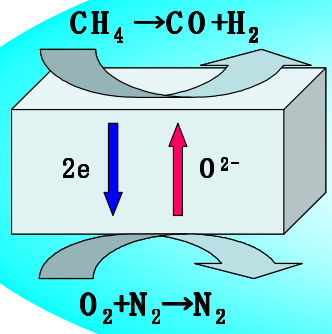
Fuel Cells

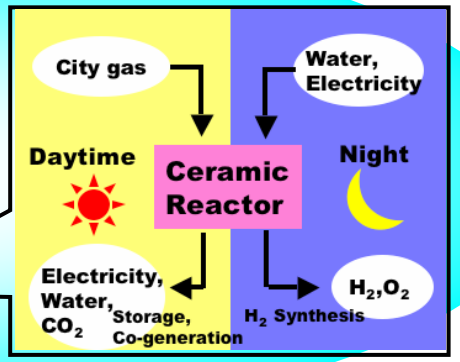
APU for Vehicles

Environment Purifying



Chemical Syntheses





Fabrication of Anode Support Tube

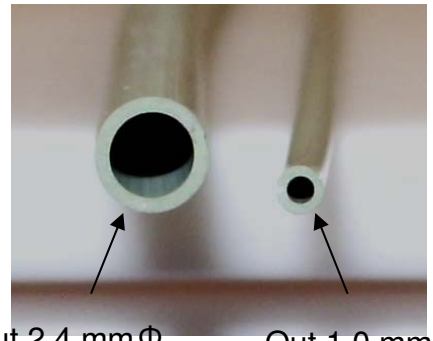
Extrusion Molding of Anode Tube

Die size

Outer diameter : 1.0 - 2.4mmΦ
Inner diameter : 0.5 - 1.0 mmΦ

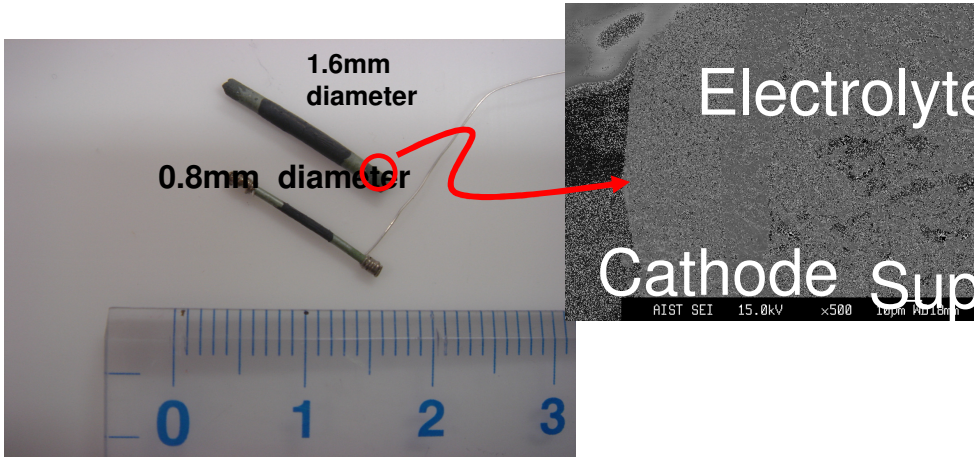
0.8 - 2.0mmΦ GDC/NiO Anode Tubes prepared using Extrusion Method.

Extruded NiO/GDC Green Tube



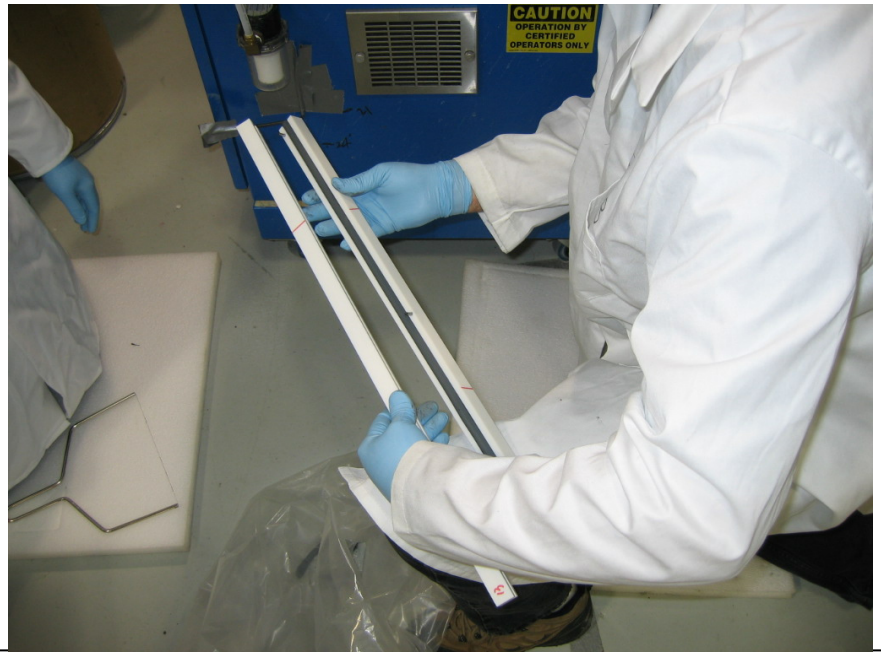
Out 2.4 mmΦ
In 1.8 mmΦ

Out 1.0 mmΦ
In 0.6 mmΦ



Tube Fabrication Equipment

- Hydraulic Extruder
- Tube Holders

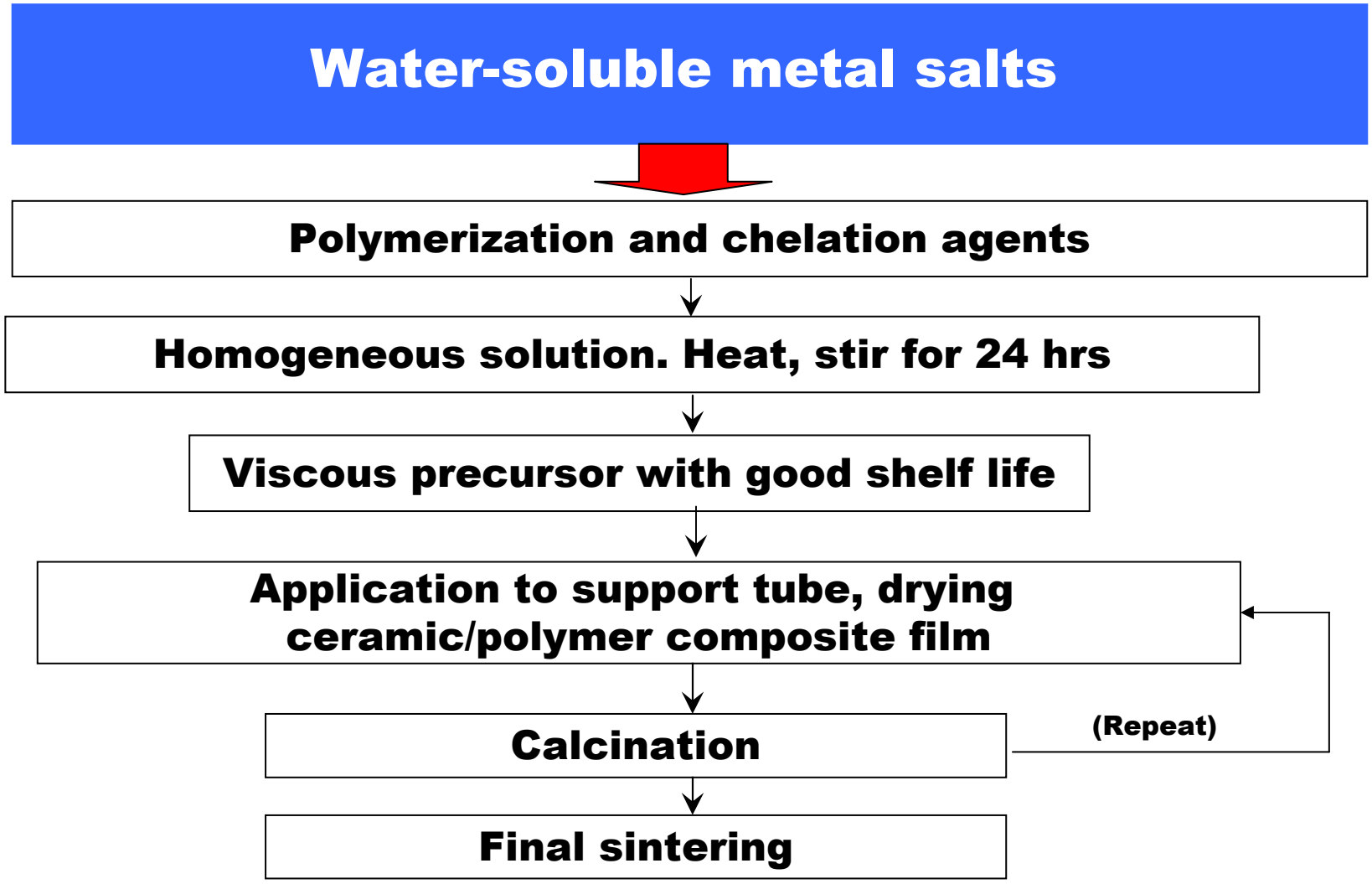


Fabrication Goals

Low Temperature Sintering of perovskite ceramic on support tube

- Deposition of thin layer of 10~20 μm
- Low temperature sintering below 900 °C

Low Temperature Sintering Procedure

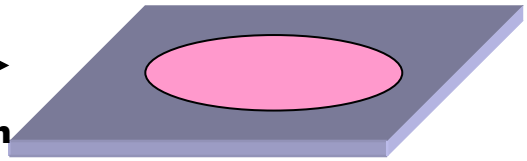


Coating Methodology

Preparation of polymer precursor

Viscosity ranges between 90 and 190 cp at 25 °C
Ex) Spin coating: 1500 ~ 3000 rpm (thin film) or
Brush painting to get a thick film

Thick thickness may cause the cracking of the dense film due to the bubble evaporation



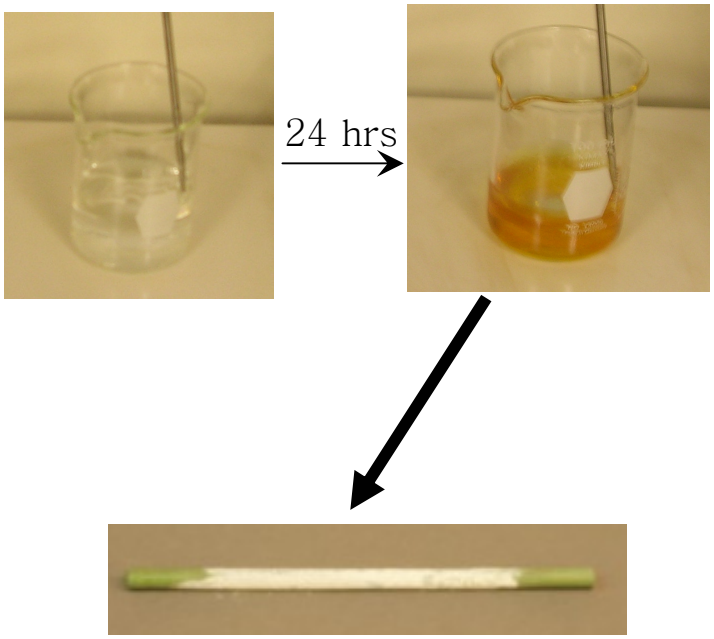
Drying
(solvent evaporation)

1. Anneal above 200°C to burn out the organic compounds and convert the coating on the substrate into a substantially solid, amorphous oxide
2. Sintering to create a continuous, dense ceramic film

Fabrication and Synthesis

Preparation of Liquid Precursor

- Metal salts in water solution with polymerization agent and thermocatalyst
- Polymerization for 24 hrs under stirring conditions



Coating on the anode support

- Coating by spin coating (planar) or dip coating (tubular)
- May be repeated a number of times to tailor thickness of polymer composite film

Calcination at low temperature

- Organic burnout
- Repeat several times to tailor overall oxide thickness

Sintering

- Dense layer formation

Conclusions

- Anode Supported Electrolyte was fabricated using the low temperature sintering technique
- Calcination process for low temperature sintering was the most important parameter to make thick electrolyte layer
- This study can be used to make very thin layer such as reactive layer between cathode and anode, or coating layer to filling the pores in the unit cell
- Various approaches are now being investigated to make a electrolyte layers with a range of thicknesses


Thank You !!!