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Development of Direct Ammonia Fuel Cells for Efficient Stationary CHP Applications

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CLEAN ENERGY TECHNOLOGIES

“Ammonia, a Sustainable, Emission-Free Fuel”

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Canada

Rationale for Direct Ammonia Fuel Cells

Current alternatives for hydrogen supply

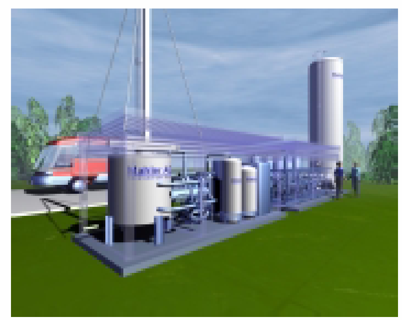
Large scale hydrogen production

To fuelling stations with tube truck as either CH2 or LH2

To fuelling stations with pipelines from central production unit

Local hydrogen production

On-site water electrolysis on fuelling station based on electricity and water



On-site natural gas reforming on fuelling station

Other alternatives:

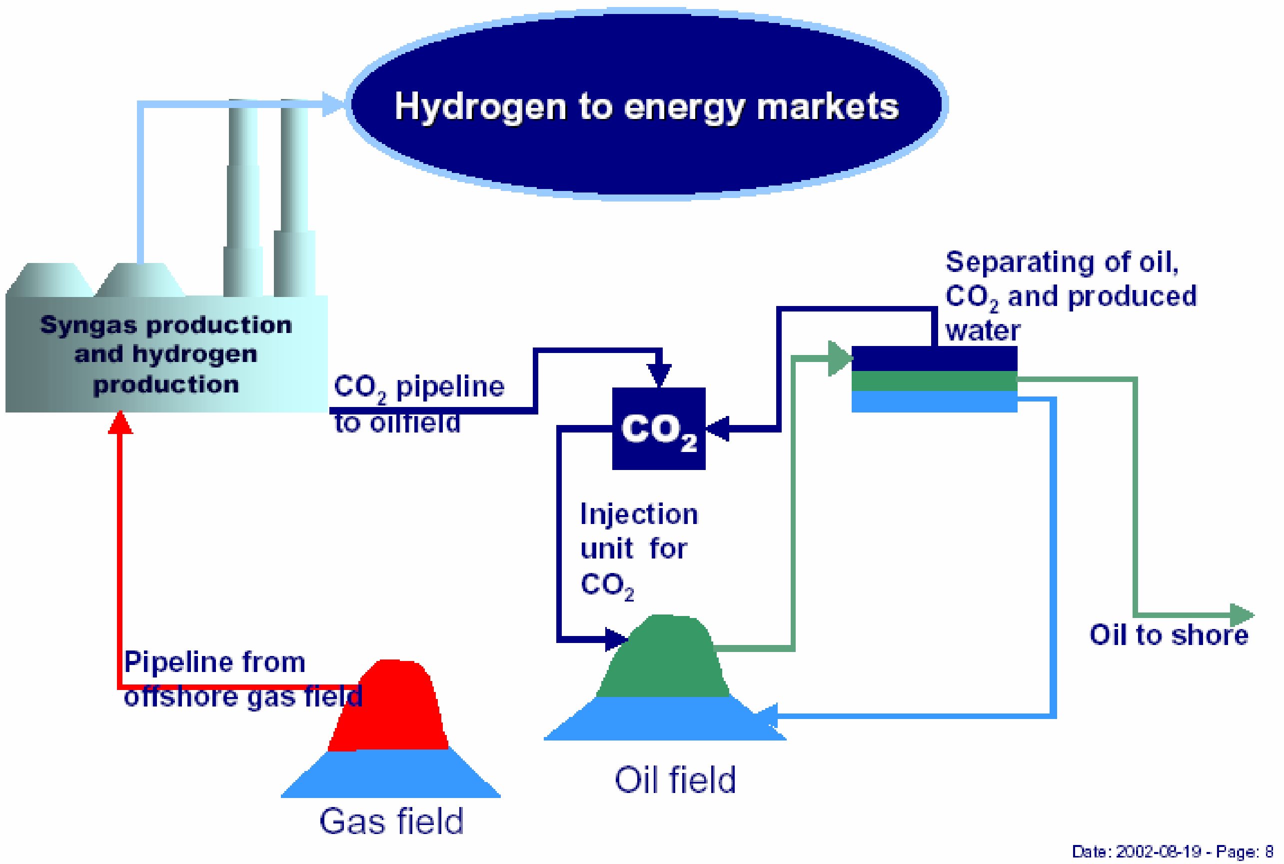
- H_2 from ammonia
- H_2 from methanol

Energy

Date: 2002-08-19 - Page: 9

Source: Norsk Hydro

Large scale CO_2 free hydrogen production



Source: Norsk Hydro

Overall Efficiency and CO_2 Emissions During Production and Distribution of Hydrogen Energy Carriers

(H. Anderson, World Hydrogen Energy Conference, Montreal, 2002)

Conclusions drawn from studies done by Norsk Hydro:

- CO_2 capture and sequestration contributes only slightly to the losses in the full hydrogen value chain
- **Central hydrogen and ammonia production seem to be the most efficient way to produce CO2-free energy carriers**
- **Ammonia infrastructure development is easier because truck transport is possible** – supply and demand will be in balance through time
- On site natural gas reforming and methanol steam reforming have highest CO_2 emissions

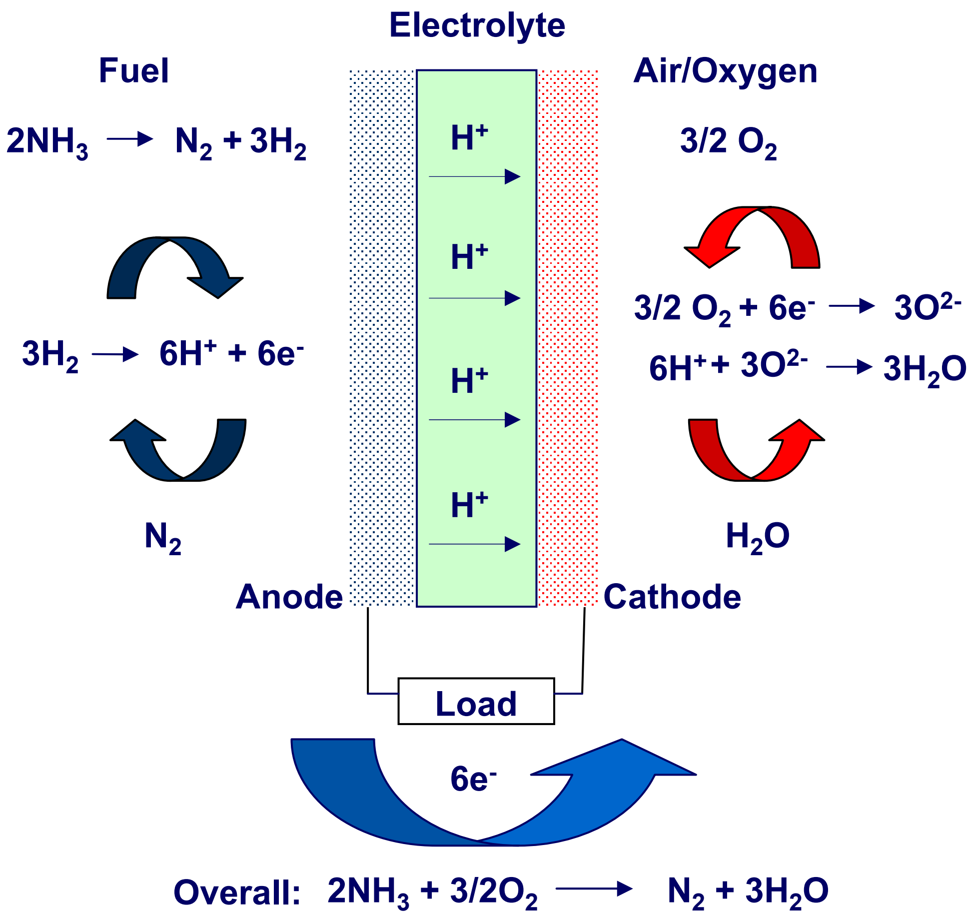
How does ammonia measure up as a fuel for fuel cells?

Fuel property	Ammonia	Methanol
Energy consumed to make, GJ/m.t.	27-28	28-31
Energy density, MJ/Kg (HHV)	22.5	22.7
Hydrogen content, % by weight	17.8	12.6
CO_2 emissions, Kg/Kg	0	1.38
Hazards	nonflammable toxic corrosive	flammable toxic noncorrosive
Transport/Storage	liquified gas 126 psia@20°C	liquid
Volume equiv. to 50L gasoline	137	101

Solid Electrolyte Ammonia Fuel Cell

What is the concept?

- Ammonia is catalytically decomposed to $N_2 + H_2$ at anode
- high temperature, low pressure favors equilibrium limited decomposition
- Protons transport across a solid proton conducting electrolyte.
- Removal of hydrogen at the anode drives decomposition reaction to completion.
- H_2/air oxidation at the cathode provides chemical driving force for the fuel cell AND provides the heat of reaction for ammonia decomposition.
- Products of the fuel cell are nitrogen, water, electric power and heat.



Electrochemical Reactions in a Direct Ammonia Fuel Cell Using Proton Conducting Electrolyte

ANODE
(fuel side)

$$2\,NH_3 + \text{heat} \rightarrow 3\,H_2 + N_2$$

$$3\,H_2 \rightarrow 6\,H^+ + 6\,e^-$$

CATHODE
(air side)

$$3/2\,O_2 + 6\,e^- \rightarrow 3\,O^{2-}$$

$$6\,H^+ + 3\,O^{2-} \rightarrow 3\,H_2O + \text{heat}$$

OVERALL

$$2\,NH_3 + 3/2\,O_2 \rightarrow N_2 + 3\,H_2O$$

What is the ammonia fuel cell energy balance?

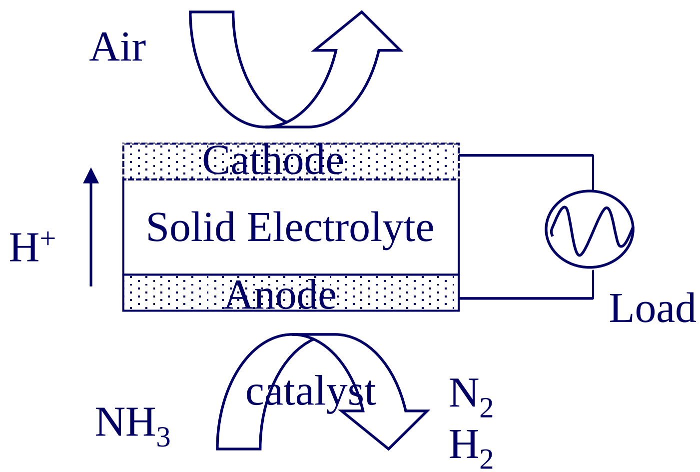
Ammonia Cracking

$$2\,NH_3 \rightleftharpoons N_2 + 3\,H_2$$

$\Delta H = 92.4$ kJ/mol

$= 2.7$ MJ/kg NH_3

Solid Oxide Fuel Cell



9.0 MJ/kg-h
2.5 kW thermal

10.8 MJ/kg-h
3.0 kWe
~55% eff.

-22.5MJ/kg-h

Relative Cost of Ammonia as Fuel for "Green" Electricity

The historical market price of anhydrous ammonia in the past decade has been about $150/ton:

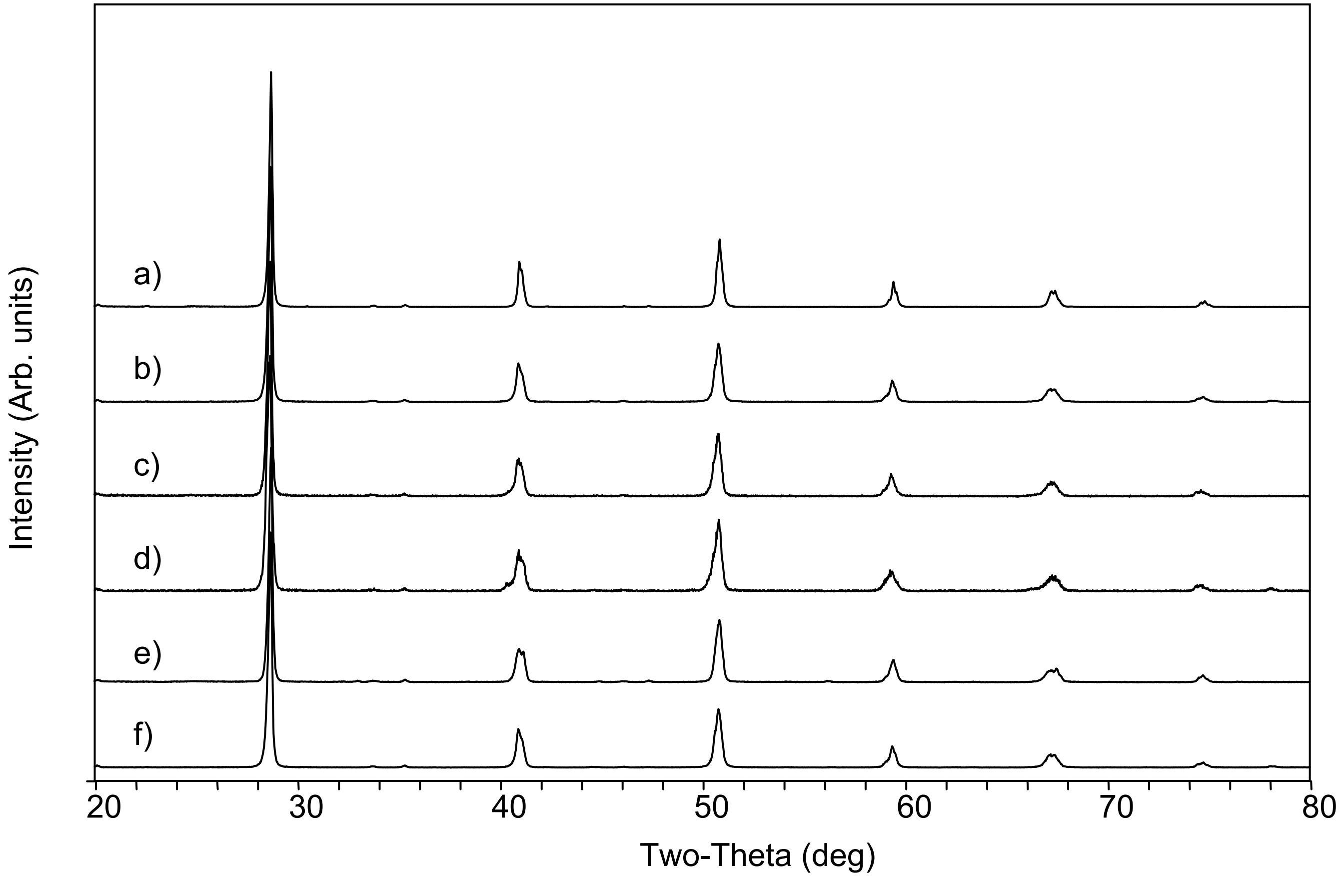
At $150/ton, the fuel cost of electricity is:	$0.05/KWH
At $300/ton…	$0.10/KWH

In Q4 2003, Ontario wholesale spot market for electricity (NGCC power at $7MMBtu/MWH) was around $0.05/KWH. Renewable "Green" power traded at around $0.09-$0.10/KWH.

A CO_2 emissions penalty of $150/ton for electricity generation is equivalent to about $0.05/KWH (NGCC).

Fuel Cell Materials R&D Activities

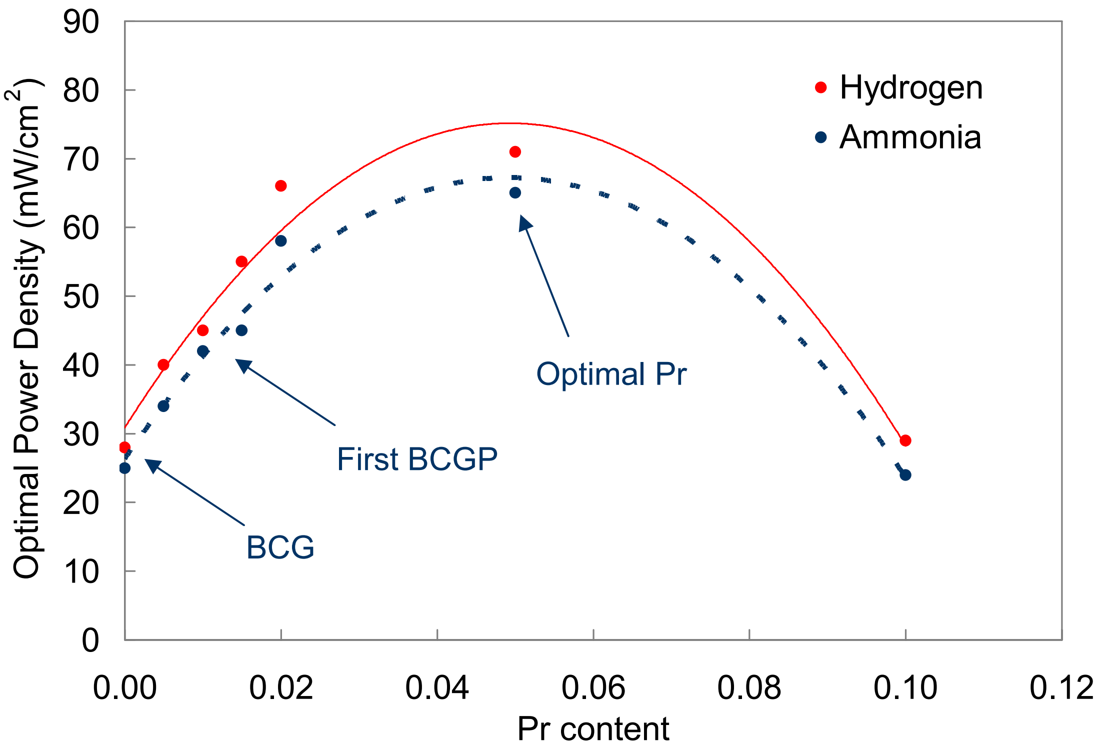
Doubly-doped BCGP electrolyte



Powder XRD patterns of $BaCe_{0.8}Gd_{0.2\text{-}X}Pr_X$ where X=0.1(a), X=0.05 (b), X=0.02 (c), X=0.015 (d), X=0.01 (e), X=0.005 (f).

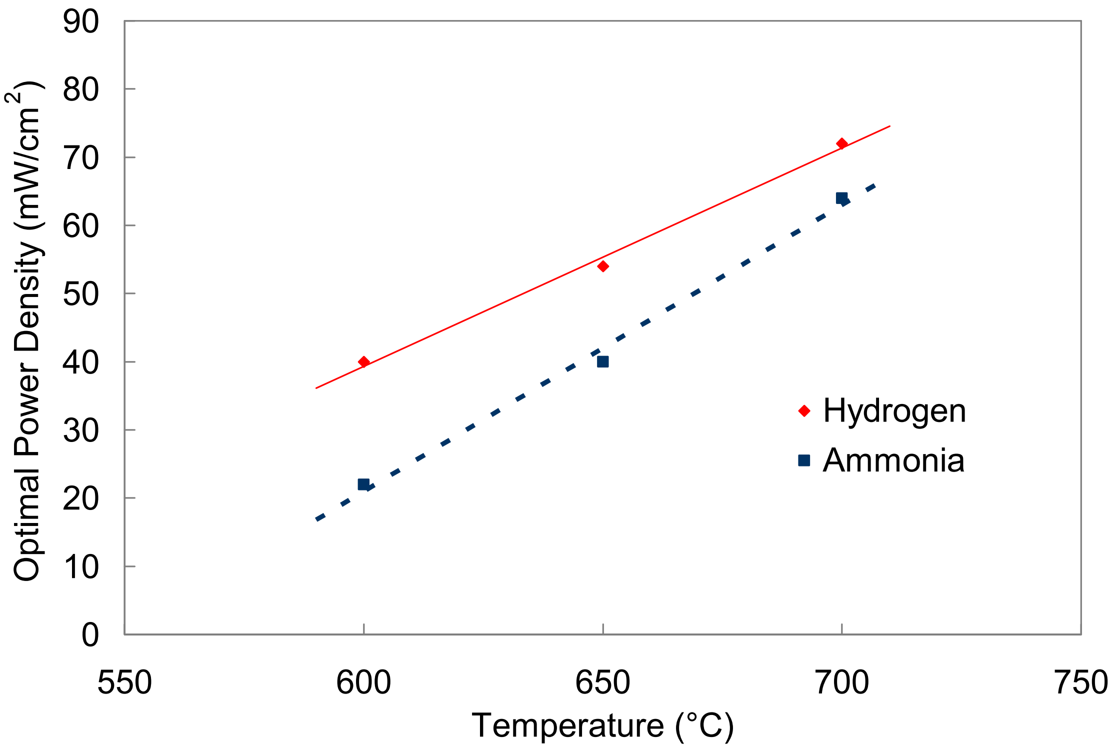
Pt/BCGP/Pt Ammonia Single Cell Fuel Cell

- Cell performance as a function of Pr concentration (700°C).
- Optimization at approximately Pr – 0.05 ($BaCe_{0.8}Gd_{0.15}Pr_{0.05}$).
- Related to increased material density and decrease of cell unit volume.



Fuel Cells, volume 7, issue 4 (2007) 323.

Pt/BCGP/Pt Ammonia Single Cell Fuel Cell

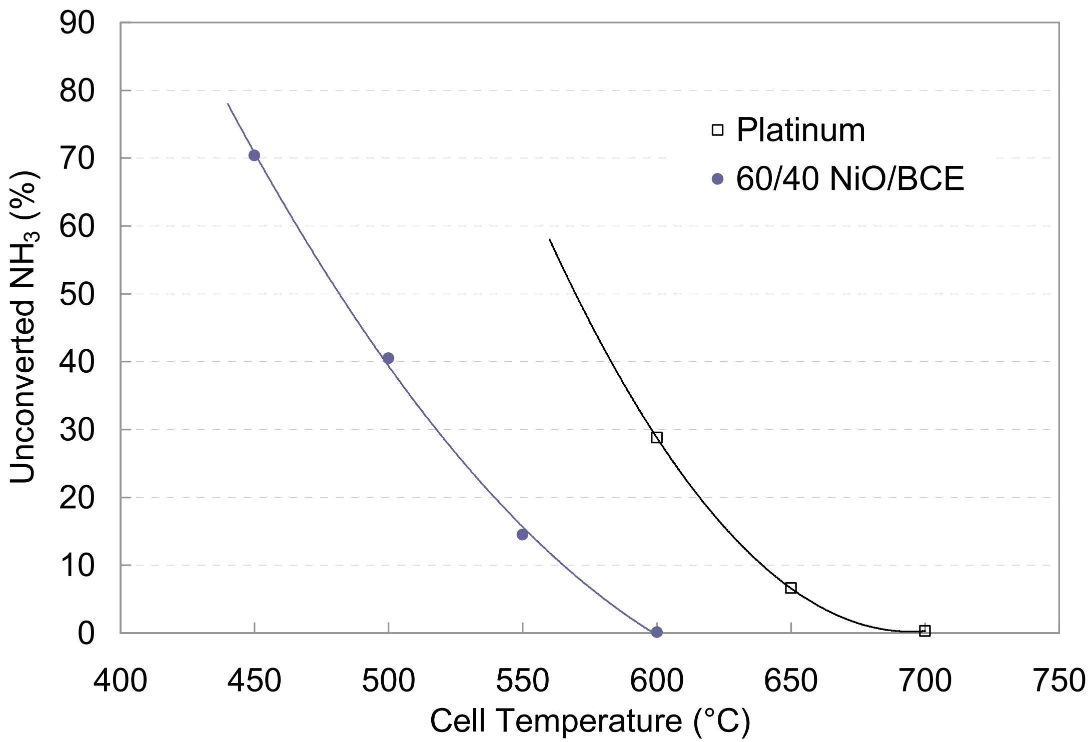


Fuel Cells, volume 7, issue 4 (2007) 323.

- Cell performance as a function of temperature with $BaCe_{0.8}Gd_{0.15}Pr_{0.05}$ electrolyte.
- Difference between hydrogen and ammonia is greater at lower temperatures.
- As the temperature is lowered, the amount of unconverted ammonia in the anode gas stream increases.
- Ammonia FC will require an efficient ammonia cracking catalyst to replace the costly Pt.

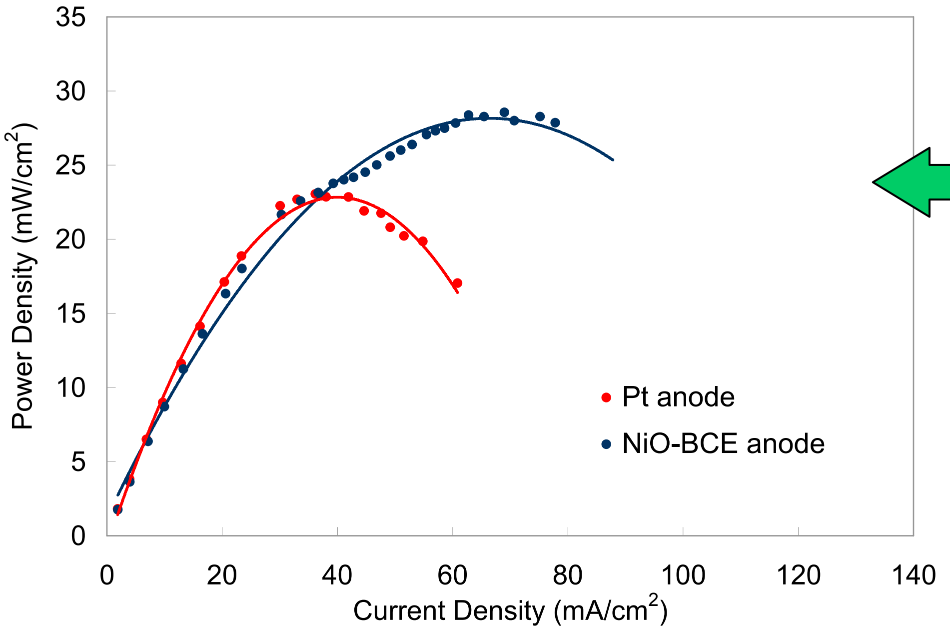
Mixed ionic and electronic conducting anode

- Europium-doped barium cerate material (BCE) proved to be a mixed conducting electrolyte (high ionic and electronic conduction).
- NiO/BCE cermet is a better ammonia cracking catalyst than Pt. Even compositions with NiO concentrations as low as 1%.
- In a monolithic electrolyte supported FC, ammonia cracks at a lower temperature with the NiO/BCE anode than with a Pt anode.
- NiO/BCE is an ideal candidate for an anode supported material.



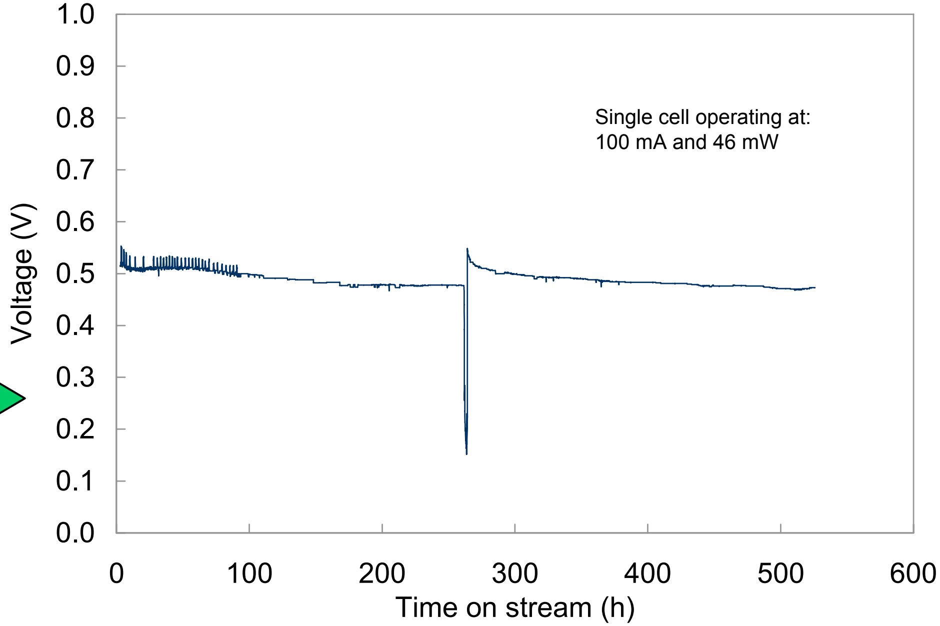
J. Power Sources 2007, *(in press)*

Mixed ionic and electronic conducting anode

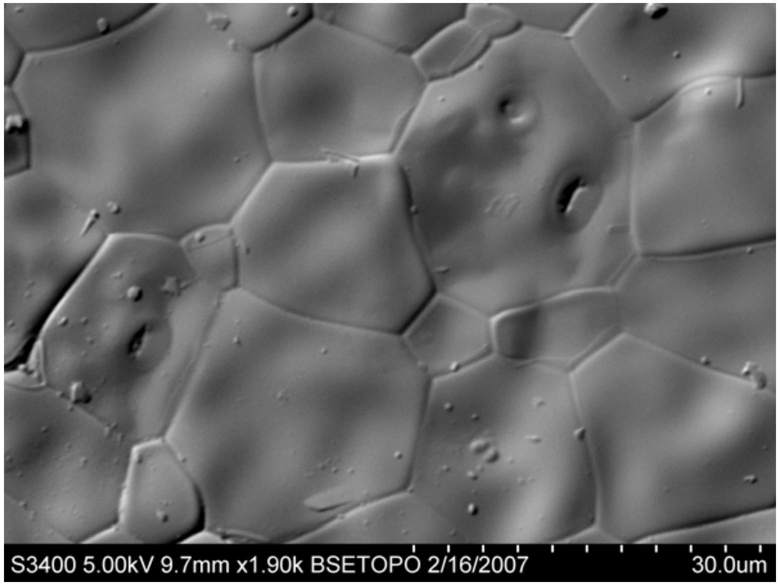


NiO-BCE anode outperformed Pt anode in a BCGP electrolyte supported fuel cell at 600°C in NH_3

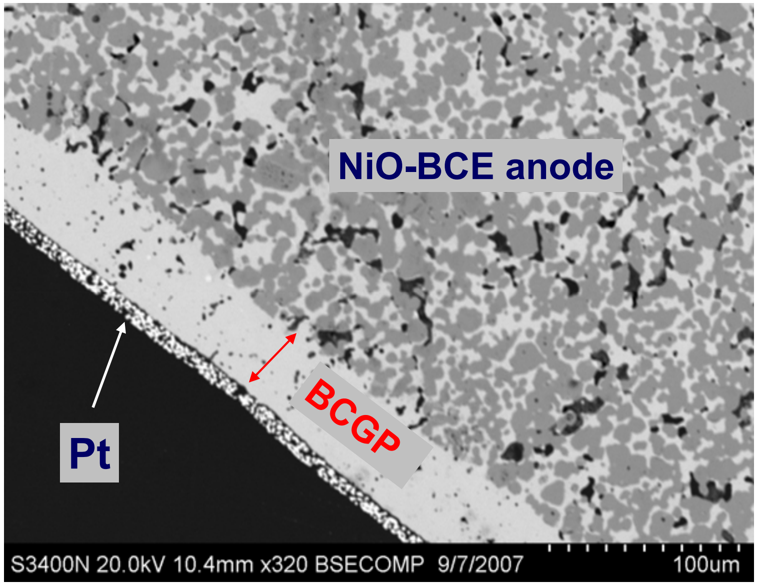
Cell was stable for over 500 h on ammonia fuel with very little degradation in performance.



Anode supported cell development



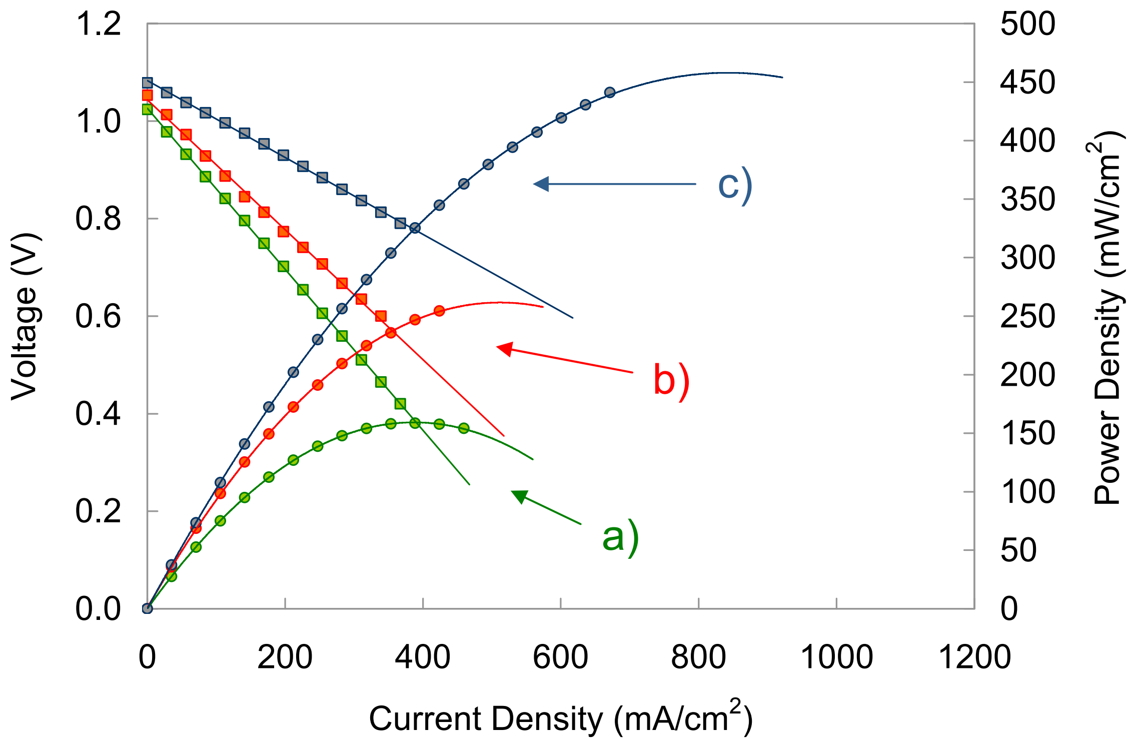
SEM micrograph (back-scatter mode) of sintered BCGP electrolyte surface coated on NiO-BCE anode.



Cross-section SEM of NiO-BCE anode supported BCGP with Pt cathode.

Anode supported cell development

- Co-pressed application of yttria-doped barium cerate (BCY) on anode support, yielded a 50 µm thick electrolyte (a).
- Thinner layers (10-15 µm) of BCY were deposited by wet colloidal spray combined with a cold isostatic pressing (CIP) treatment (b).
- Composite cathodes (BSCF and BCZY) demonstrated high performance providing alternatives for the costly Pt (c).



I-V characteristics of anode supported cells at 600°C under fuel mixture of 75% H_2 and 25% N_2.

R&D Activities Using Commercially Available Conventional SOFC

Commercial Opportunities for Direct Ammonia Fuel Cells

Agreement from industry partners (fuel cell manufacturer, ammonia producer) to modify a natural gas fueled 5KW SOFC system to run on anhydrous ammonia, and to conduct a field trial at a suitable site.

Commercial Opportunities for Direct Ammonia Fuel Cells

- In late 2006 Acumentrics Ltd. acquired assets and key personnel from Fuel Cell Technologies Inc. and established a Canadian subsidiary in Kingston Ont.
- FCT's core expert team, as Acumentrics Canada, will continue to develop and commercialize SOFC systems using the US-based parent company's proprietary SOFC technology.
- A contract is being finalized which will allow Acumentrics Canada to begin work on testing ammonia in their proprietary SOFC stack.

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