Solid Oxide Fuel Cells

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MIT-Stanford-Berkeley Nanotech Forum

July 12, 2005

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http://www.kainosenergy.com

a

NanoGram corporation

Company

Outline

Solid Oxide Fuel Cells

Applications

Status

Nano Aspects

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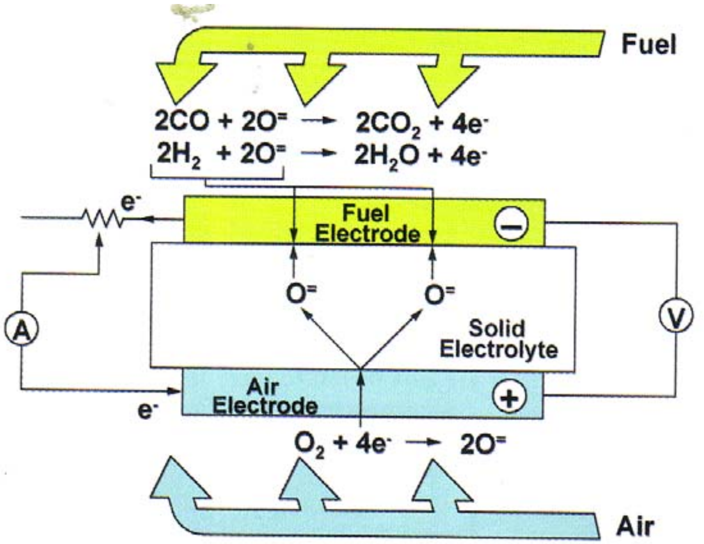
Solid Oxide Fuel Cells

Solid Oxide Fuel Cells



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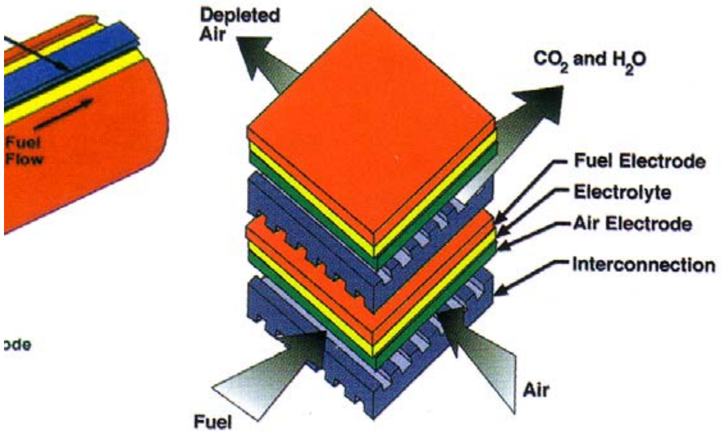

from: Ramanarayanan et al., *Electrochem Soc. Interface*, **10**(2001)22

- Direct conversion of chemical energy to electrical energy
- Nernst (1899)
  - solid oxide electrolytes
- Bauer and Preis (1937)
  - tubular SOFC
- Peters and Mobius (1958)
  - planar SOFC
- Operating temperatures from 550^{o}C to 1000^{o}C
  - fuel flexibility
  - high efficiency
  - cogeneration
- Each cell produces ~ 0.7V
- Cells are extended in footprint and stacked in series to build power

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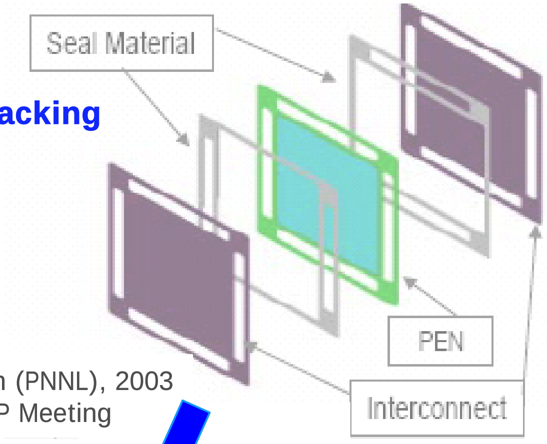
SOFC Stacks and Systems

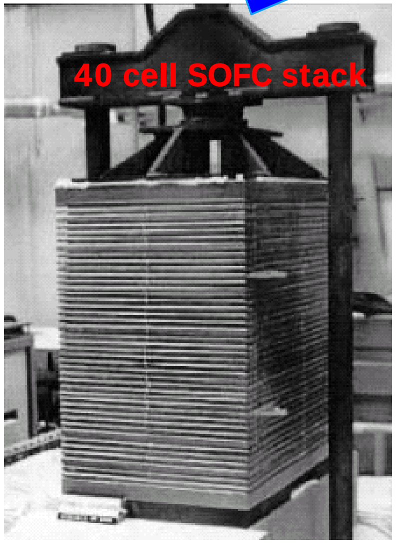
SOFC stacking



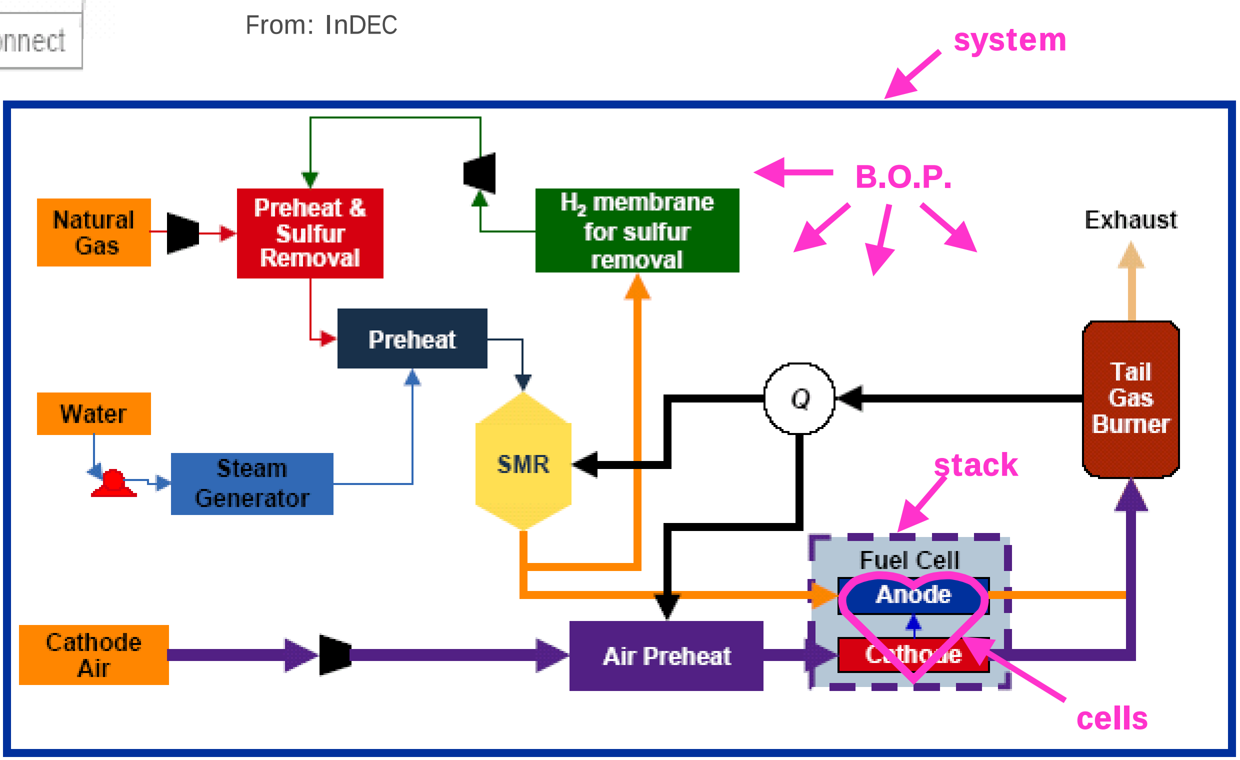
From: P. Singh (PNNL), 2003
SECA CTP Meeting

From: InDEC

- Hierarchy
  - system
  - balance of plant
  - stack
  - cells



From: Research Center, Juelich



Source: TIAX Report to DOE NETL, June 2002

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Applications

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Fuel Cell Markets

Application	*Current Sources*	*Power (kW)*	*Markets*	*FC Types*
Stationary/ Distributed Generation	Utility Grid (Fossil, Hydro, Nuclear)	1 - 10,000	Utility, Industrial, Commercial, Residential	SOFC MCFC PEMFC
Transportation (Auxiliary Power Unit – APU)	IC Engine	5-10	Trucks, Airplanes, Luxury cars, RV's, Buses	SOFC PEMFC
Transportation (Drive)	IC Engine	50 - 200	Automotive, Marine, Aerospace	PEMFC SOFC
Portable	Battery	<1 - 5	Electronics, Military, Portable Generators	PEMFC DMFC SOFC

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SOFC Applications

- Stationary
  - SOFCs offer highest overall efficiency combined with fuel flexibility/system simplicity
  - see Dan Rastler's talk
- Transportation – drive unit
  - SOFCs not ideally suited for major drive unit
    - Start-up time (high operating temperature)
    - Cost (<$50/kW for system)
- Portable
  - Several companies developing small portable SOFC power systems (10 – 100W)
    - Mesoscopic Devices, Adaptive Materials, Nanodynamics
  - Several laboratories and small companies pursing small SOFC systems for mobile applications (~ 10-20W)
    - See Alan Jankowski's talk
- Transportation – APU
  - Essentially an on-board genset

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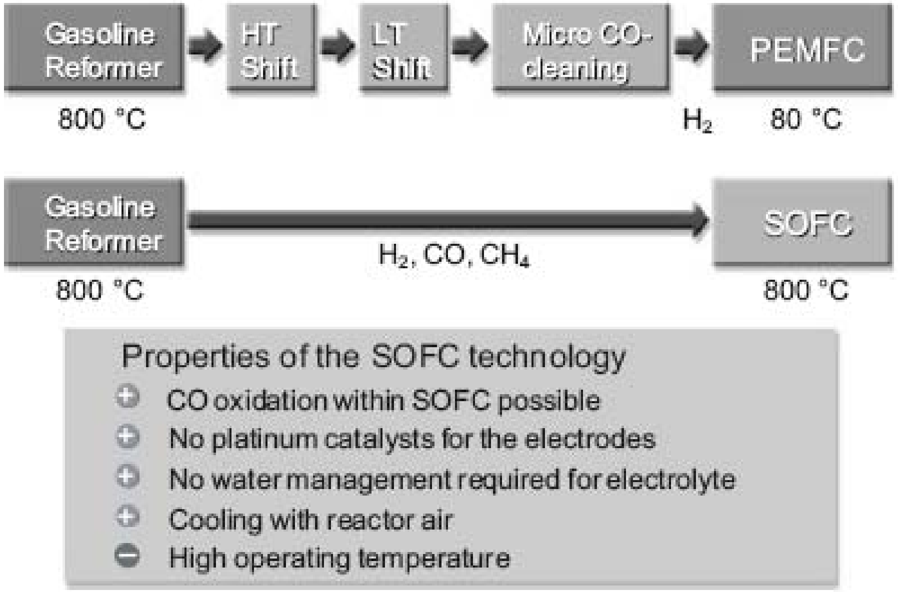
SOFC APUs

- SOFC based APUs
  - Simpler system than PEMFC
  - Provides onboard electricity at higher efficiency vs. alternator
    - Fuel → IC engine → 12V alternator: 10 – 17%
    - Fuel → IC engine → 42V alternator: 14 – 22%
    - Fuel → SOFC APU: 35 – 50%
  - Enables new features in light duty
    - e.g. drive by wire, electrical AC, mobile office
  - Substantial economic and environmental incentives for heavy duty
    - e.g. hotel power, refrigeration
    - Reduces "idling" fuel consumption and emissions up to 85%



Properties of the SOFC technology

⊕ CO oxidation within SOFC possible
⊕ No platinum catalysts for the electrodes
⊕ No water management required for electrolyte
⊕ Cooling with reactor air
⊖ High operating temperature

Fig. 4 Comparison of SOFC and PEM systems for use with gasoline as fuel.

source: Lamp et al., *Fuel Cells* **3**(2003)146

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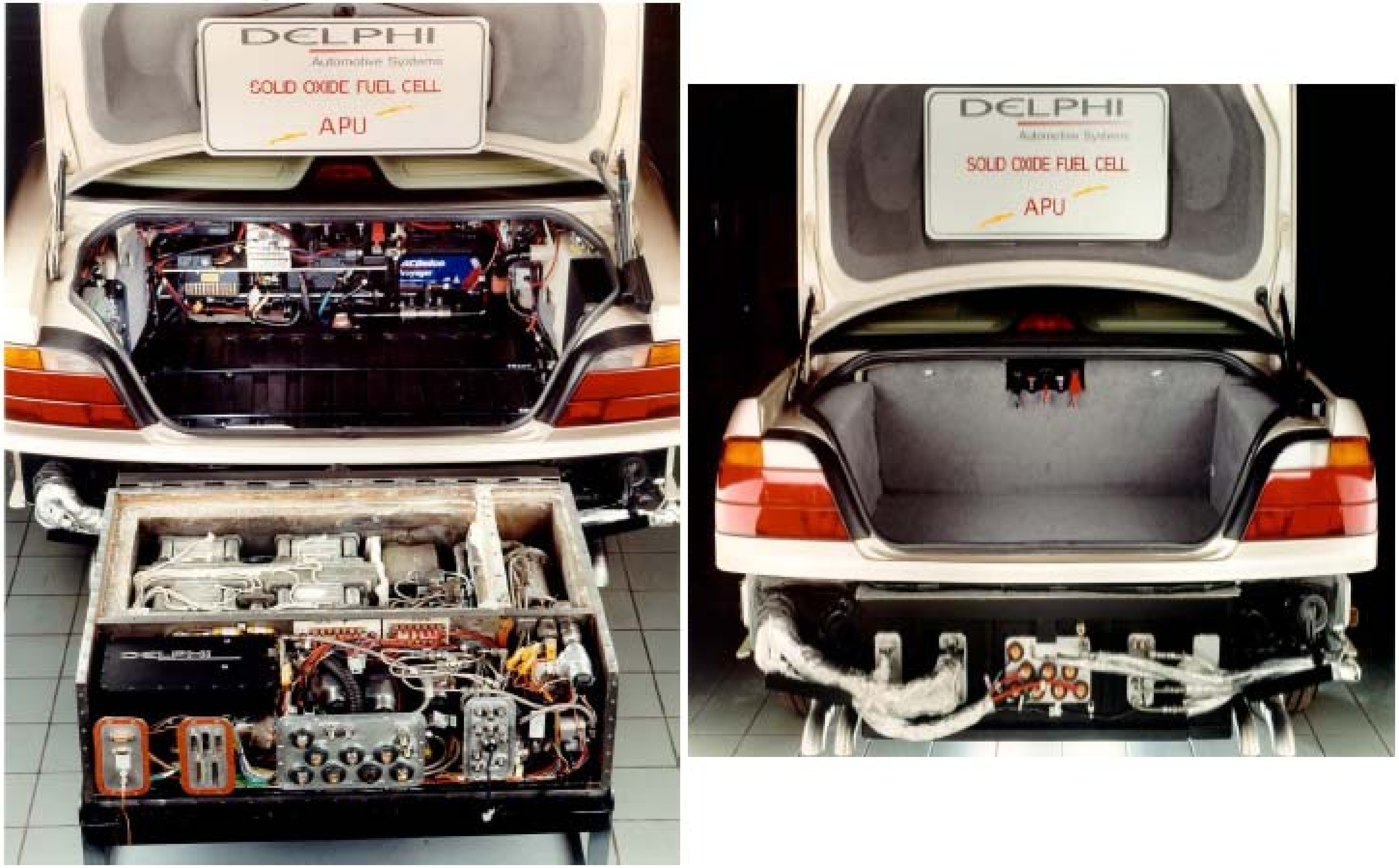
SOFC APUs

- Delphi demonstration of a SOFC APU for BMW 7-series



source: Lamp et al., *Fuel Cells* **3**(2003)146

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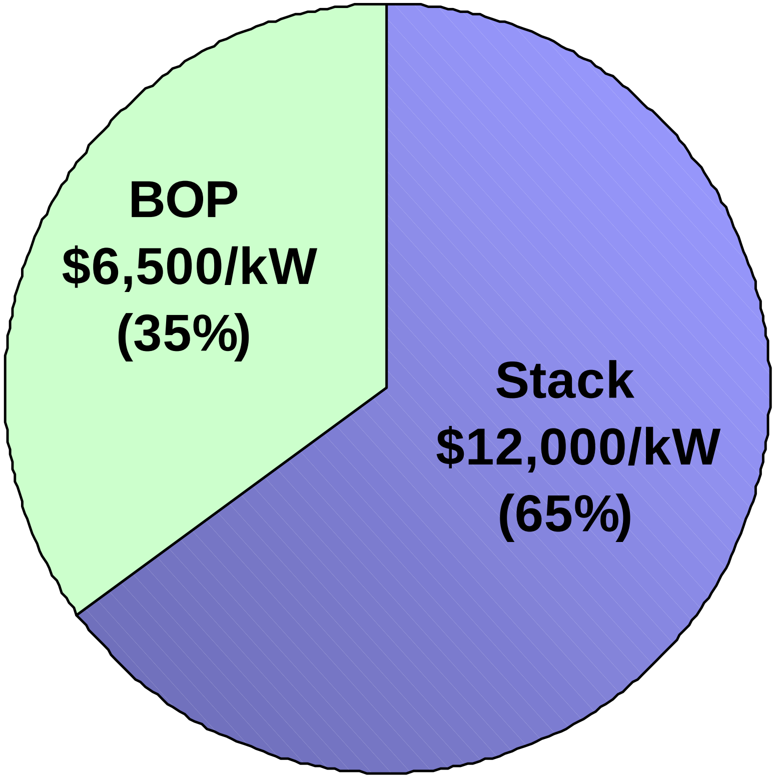
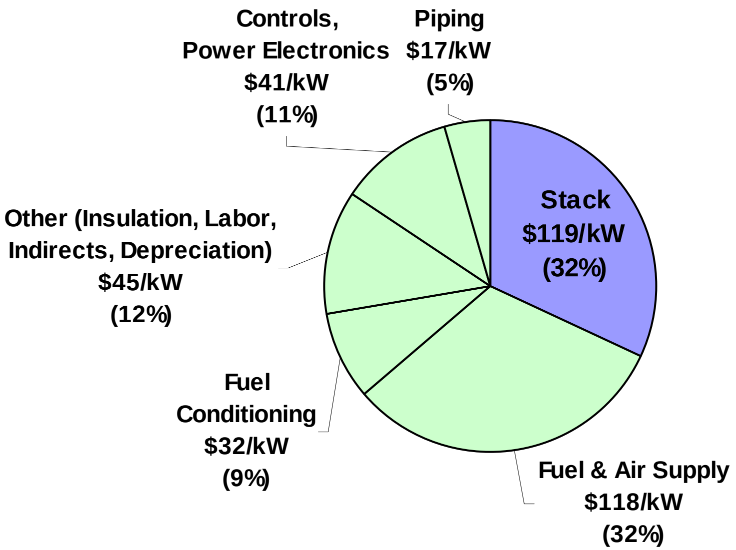
Status

SOFC Stack Cost Inhibiting Multi $Billion Market



Current system price is
~ $18,500/kW

Source: Frost & Sullivan - Dec 2003



Mass commercialization target is
$800 to $1,000/kW installed price

Source:State Energy Conversion Alliance (SECA) < $400/kW system cost target

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SOFC: Key Issues for Commercialization

- Cost
  - Present mfg. methods are expensive and require development of supply chain
    - tape casting, tape calendering, vacuum spraying, etc
  - Costs (> 10,000 $/kW) are at least an order of magnitude higher than targets:
    - ➢ $400/kWe for SOFC system
    - ➢ $100/kWe for SOFC stack
- Operating Temperature
  - High operating temperature is problematic
    1. requires expensive metal interconnects & BOP components
    2. increases thermal stresses
    3. promotes material interaction
    4. accelerates aging
  - Barriers to lower operating temperature include
    1. high cell resistance
    2. poor electrode performance
- Reliability
  - Degradation mechanisms affecting reliability include
    1. material interaction
    2. electrode sintering/aging
    3. cell thermal fracture (operation, cycling) &/or seal failure
    4. reformer stability
    5. hotbox component aging

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The Nano

Nanoscale Material Benefits to SOFC

- Nanomaterials can have two major effects on SOFCs
  - lower processing temperatures
  - higher performance (W/cm^2, fuel utilization)
- Lower processing temperature
  - Source: Nano-effect on sinterability
  - Impact(s):
    - Lower manufacturing cost
    - Higher reliability
    - Lower operating cost
    - Faster start-up
- Higher performance
  - Source: Increased reaction area
  - Impact(s):
    - Lower system cost
    - Higher reliability
    - Lower operating cost
- Nanomaterials and their benefits are very challenging to realize, in both fabrication and cost, via conventional methods.

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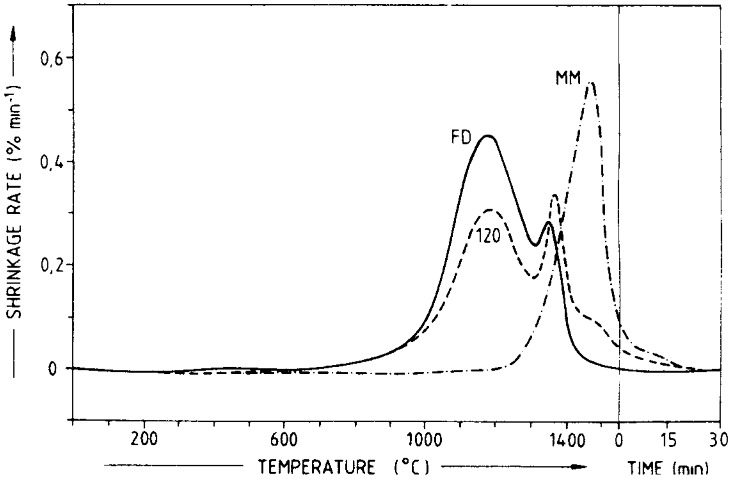
Nanoscale YSZ Processing

- Studies have demonstrated increased sinterability with reduced particle size in YSZ

Effects of Powder Characteristics on Sintering Activity of CSZ

Powder Characteristics			**Compact Char.**	**Sintering Properties**	
Powder Type	agglomerate size, nm	crystallite size, nm	green density, % theo.	sintering activity @ 1250C	temp of max shrinkage, deg C
MM	1700	423	56.0	0.19	1470
120	1900	16	40.8	1.56	1195, 1370
FD	700	16	39.7	9.96	1185
definition:	d_{50}	d_x		$\frac{(SD-GD)}{(100-SD)}$	



from Roosen et al in "Advanes in Zirconia II" 1984

- Reduces material interactions, manufacturing costs

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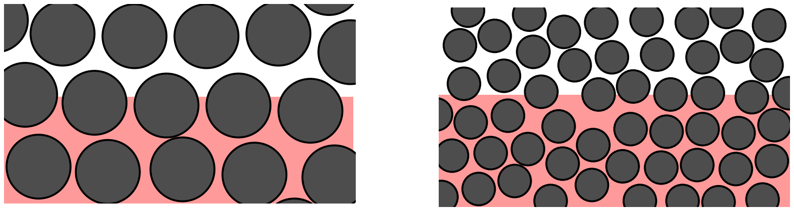
Binder Systems

- Binder & other organics are processing aides to get powders in the right form.
- Higher surface area powders require greater amounts of binder.
- Binder removal is long, sensitive to particle size & composition, and produces hazardous vapors.

Particle Size Effects

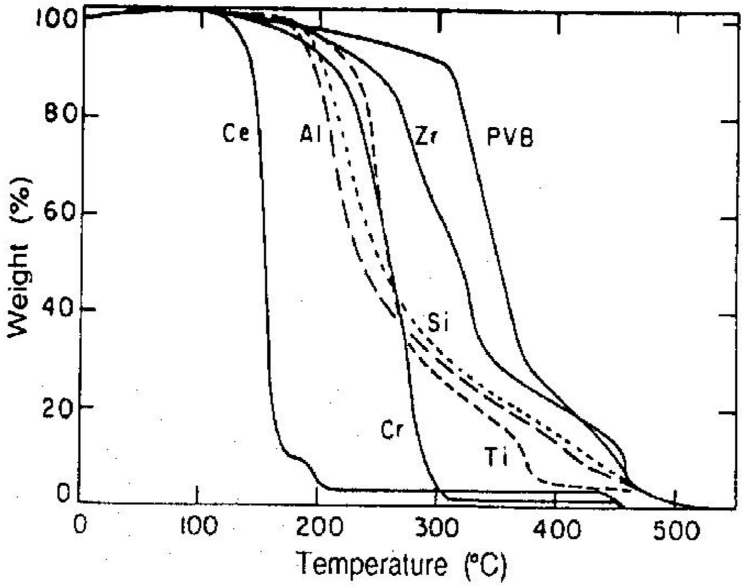
during binder burnout



bulk

submicron or nano

Composition Effects



from: S. Masia et. al, J Mater Sci **24**(1989)1907

slows development cycle, adversely impact yield, increases costs and regulatory risk

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Nano Enhanced Performance

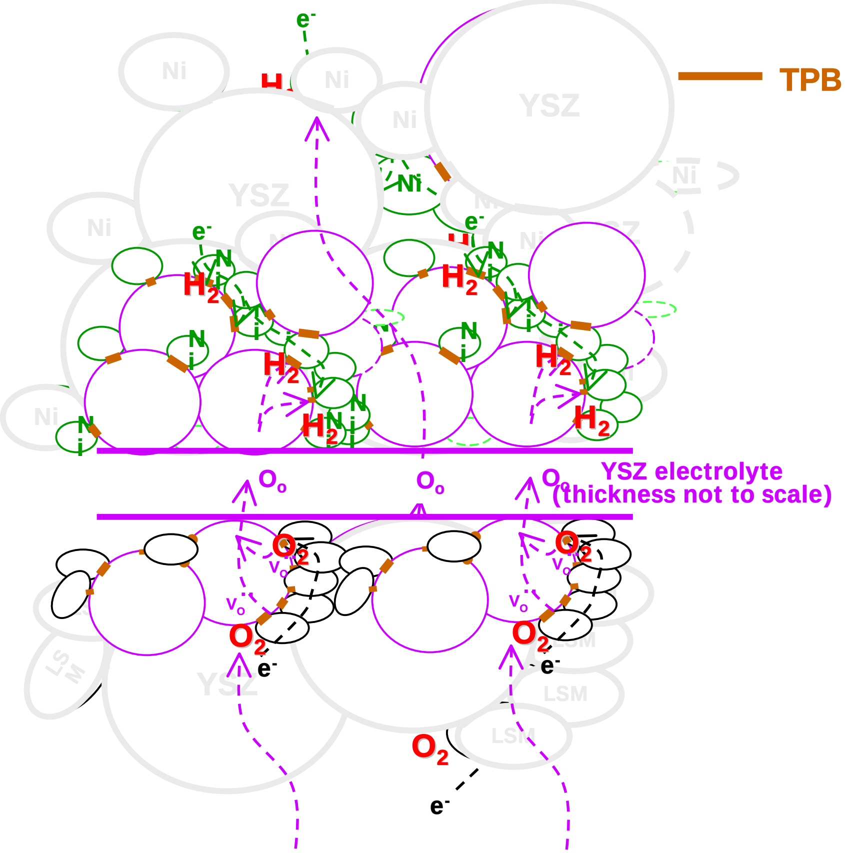
- SOFC Reactions take place at electrode’s triple-phase boundary (TPB)
  - Reaction at SOFC anode:
    - $H_{2(g)}+O_{O,YSZ} \Leftrightarrow H_2O_{(g)}+V^{\cdot\cdot}_{O,YSZ}+2e^{-}_{Ni}$
    - TPB is intersection of pore, YSZ particle, & Ni particle
  - Reaction at SOFC cathode:
    - $O_{2(g)}+4e^{-}_{LSM}+2V^{\cdot\cdot}_{O,YSZ} \Leftrightarrow 2O_{O,YSZ}$
    - TPB is intersection of pore, YSZ particle, & LSM particle
- Greater TPB area translates to higher electrode performance
- Nano enables higher performance electrodes

  ⇓ particle size ⇒ ⇑ surface area

  ⇑ surface area ⇒ ⇑ interfacial area

  ⇑ interfacial area ⇒ ⇑ TPB

  ⇑ TPB ⇒ ⇑ voltage efficiency
- Current barriers to nanoscale SOFC materials
  - stability at high operating temperatures (650 to 800ºC)
  - difficult to incorporate into tape-based processes
  - high added cost of powder and cell processing



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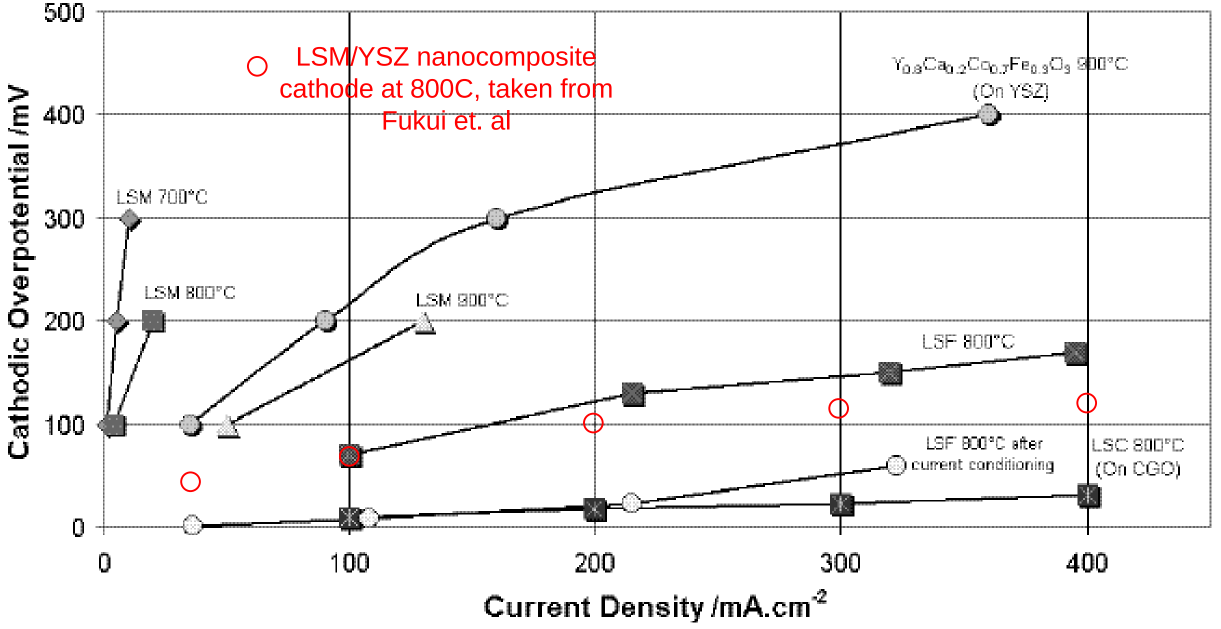
Nano Enhanced Performance

- Dramatically improved performance achieved with nanocomposite of conventional, robust LSM/YSZ cathode
- High power density & efficiency at low $T_{operation}$



LSM/YSZ nanocomposite cathode at 800C, taken from Fukui et. al

Fig. 5. Cathodic Overpotentials for Different Cathode Materials on CGO and YSZ.

from:

M. Krumpelt et. al, "Materials for Low-Temperature SOFCs"
5th Euro SOFC Forum, July 2002

T. Fukui et. al, "Morphology Control of the Electrode for SOFCs By Using Nanoparticles" J Nanoparticle Research 3(2001)171

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Electrolyte Effects

- Lower operating temperature requires lower electrolyte resistance
  - ➢ increase electrolyte conductivity via new materials (interactions?, stability?)
  - ➢ reduce layer thickness (durability?)
- Some groups pursuing nanofilms for very low temperature operation

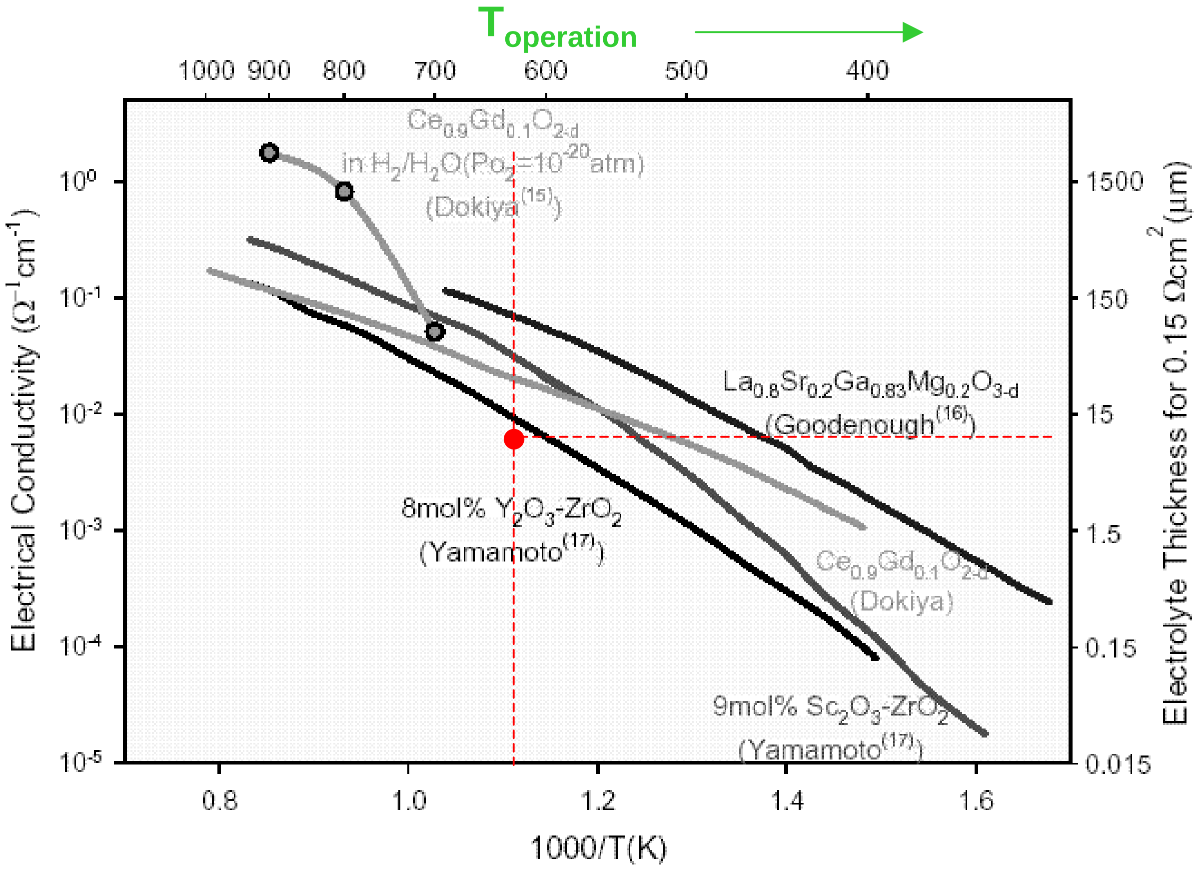

Figure 1. Comparison of Ionic Conductivities for Various Electrolytes.

thinner electrolyte

from M. Krumpelt et. al,
"Materials for Low-Temperature SOFCs"
5th Euro SOFC Forum, July 2002

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At A Glance

The Company:

- Kainos Energy uses a proven efficient manufacturing process to build high performance SOFC stacks to achieve:
  - order of magnitude cost reduction vs. current costs
  - 50% of SECA commercialization cost target, at 10% of SECA's target manufacturing volume
- Kainos Energy is an early stage start-up
- Kainos Energy is a subsidiary of NanoGram

Ownership:

- Private
- Investors: ATA, Nth Power, Bay Partners, Rockport, IVP, SBV

Technology & Business Model:

- Core process technology proven by NanoGram
- Kainos Energy awarded NSF Phase I SBIR in 2004
- Business model proven by NanoGram Devices

IP & License:

- Full license to NanoGram's patent portfolio for SOFC applications

  >100 patents and applications

NanoGram Affiliates:

- NeoPhotonics (Planar Lightwave Circuits) – raised $42M in March 2004
- NanoGram Devices (medical batteries) – spun out Jan 2003, acquired by WGB Tech in March 2004 for $48M

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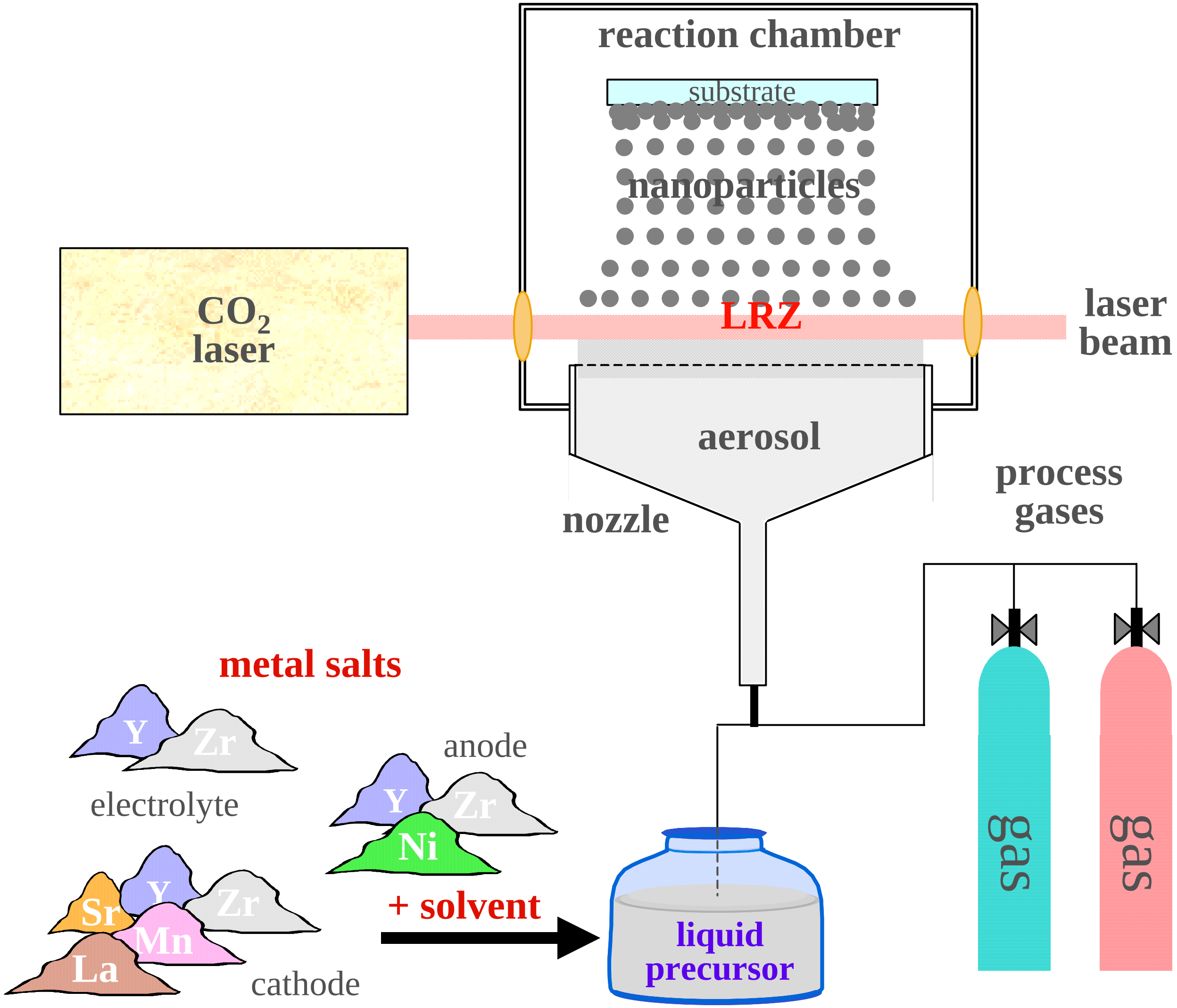
Overview of LRD™ Process for SOFC cell

- Sequential deposition of SOFC (cell) layers in LRD™ reactor.



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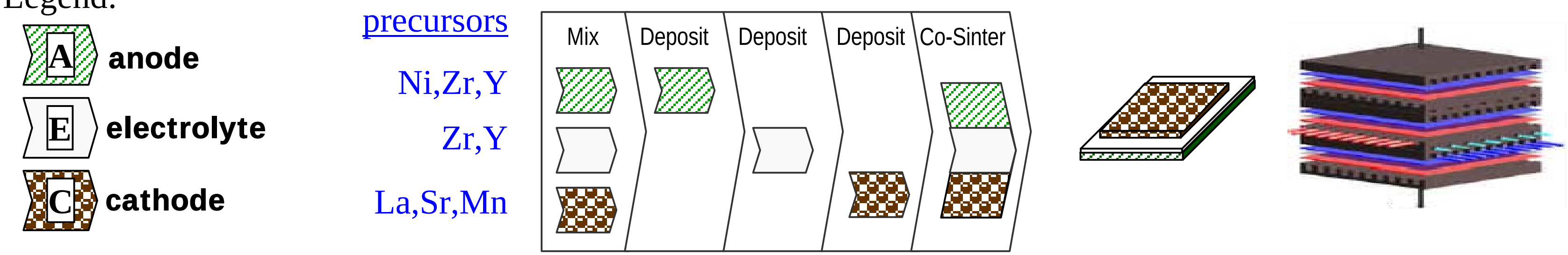
LRD™-based SOFC Manufacturing

- **Direct Conversion™ technology simplifies cell development and manufacturing**
  - Eliminates 66% of the steps and 50% of the equipment
  - Dramatically reduces cycle time; accelerates development, improves scalability
    - 10s of hours versus 100s of hrs at best for conventional methods

Kainos Energy Process



Legend:

A anode

E electrolyte

C cathode

precursors

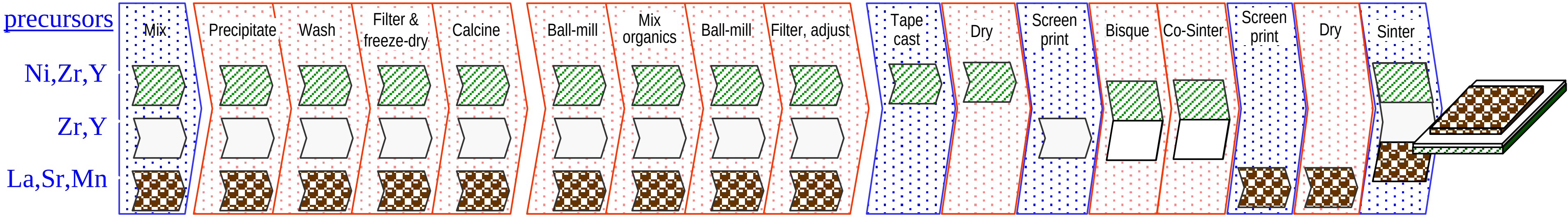
Ni,Zr,Y

Zr,Y

La,Sr,Mn

Mix | Deposit | Deposit | Deposit | Co-Sinter

Conventional cell manufacturing



precursors

Ni,Zr,Y

Zr,Y

La,Sr,Mn

Mix | Precipitate | Wash | Filter & freeze-dry | Calcine | Ball-mill | Mix organics | Ball-mill | Filter, adjust | Tape cast | Dry | Screen print | Bisque | Co-Sinter | Screen print | Dry | Sinter

Powder preparation

Slurry preparation

Cell manufacturing

Eliminated steps | Replaced steps

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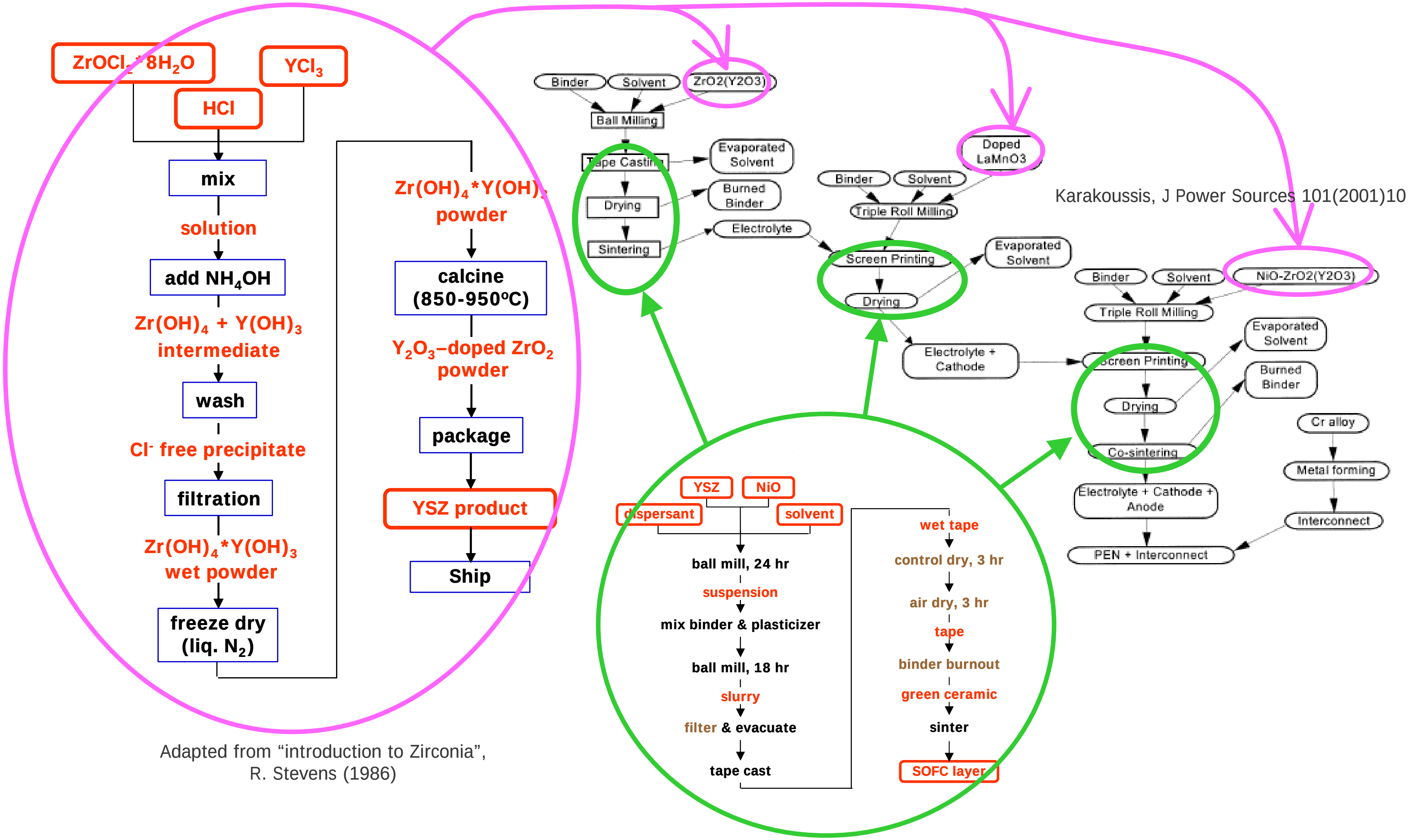
Conventional SOFC Manufacturing

- The sequence of steps in conventional processing of SOFC cells



$ZrOCl_2*8H_2O$

YCl_3

HCl

mix

solution

add NH_4OH

$Zr(OH)_4 + Y(OH)_3$ intermediate

wash

Cl^- free precipitate

filtration

$Zr(OH)_4*Y(OH)_3$ wet powder

freeze dry (liq. N_2)

$Zr(OH)_4*Y(OH)_3$ powder

calcine (850-950ºC)

Y_2O_3–doped ZrO_2 powder

package

YSZ product

Ship

Adapted from “introduction to Zirconia”,
R. Stevens (1986)

YSZ

NiO

dispersant

solvent

ball mill, 24 hr

suspension

mix binder & plasticizer

ball mill, 18 hr

slurry

filter & evacuate

tape cast

wet tape

control dry, 3 hr

air dry, 3 hr

tape

binder burnout

green ceramic

sinter

SOFC layer

Karakoussis, J Power Sources 101(2001)10

MIT-Stanford-Berkeley Nanotech Forum, 050712

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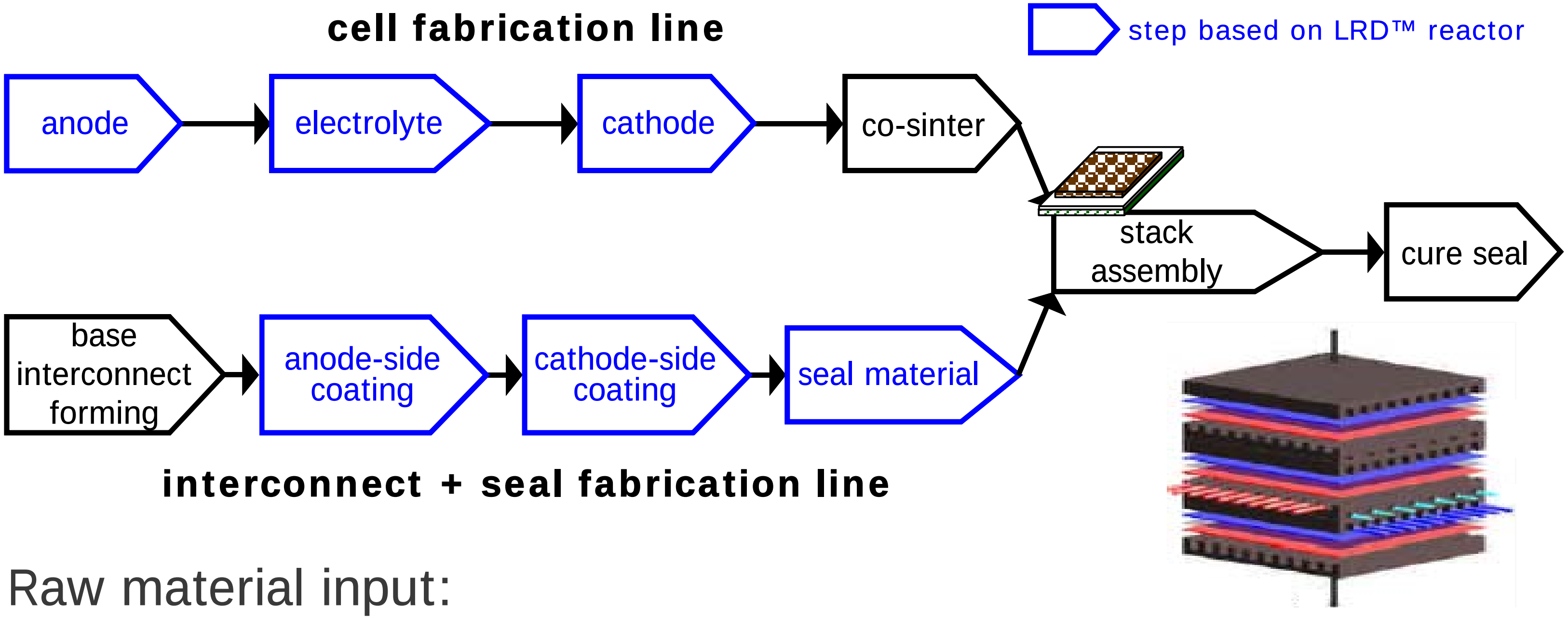
LRD™-based SOFC Manufacturing

- Kainos Energy technology is extendable to interconnects, seals to create a complete solution for stack manufacturing that is simpler and more efficient than conventional methods.



cell fabrication line

step based on LRD™ reactor

anode → electrolyte → cathode → co-sinter

base interconnect forming → anode-side coating → cathode-side coating → seal material

stack assembly → cure seal

interconnect + seal fabrication line

Raw material input:

- process gases
- electricity
- precursor chemicals
- interconnect form

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SOFC Information Sources

- International SOFC Symposium Proceedings
  - Electrochemical Society, Pennington NJ   www.electrochem.org
  - SOFC-IX in May 2005
- Solid-State Energy Conversion Alliance (SECA) Workshop Proceedings
  - www.seca.doe.gov
- Fuel Cell Handbook (DOE)
  - 7th Edition released in 2004
  - www.netl.gov
- High Temperature Solid Oxide Fuel Cells,
  S.C. Singhal and K. Kendall, Eds. Elsevier.
  Oxford, UK. 2003
- Science and Technology of Ceramic Fuel Cells,
  N.Q. Minh and T. Takahashi. Elsevier Science.
  Amsterdam. 1995
- Journals
  - Journal of the Electrochemical Society,   Electrochemical and Solid State Letters
  - Journal of the American Ceramic Society
  - Nature Materials,   Chemistry of Materials
  - Journal of Power Sources, Solid State Ionics

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questions?

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