DIRECT CARBON (COAL) CONVERSION BATTERIES AND FUEL CELLS

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by

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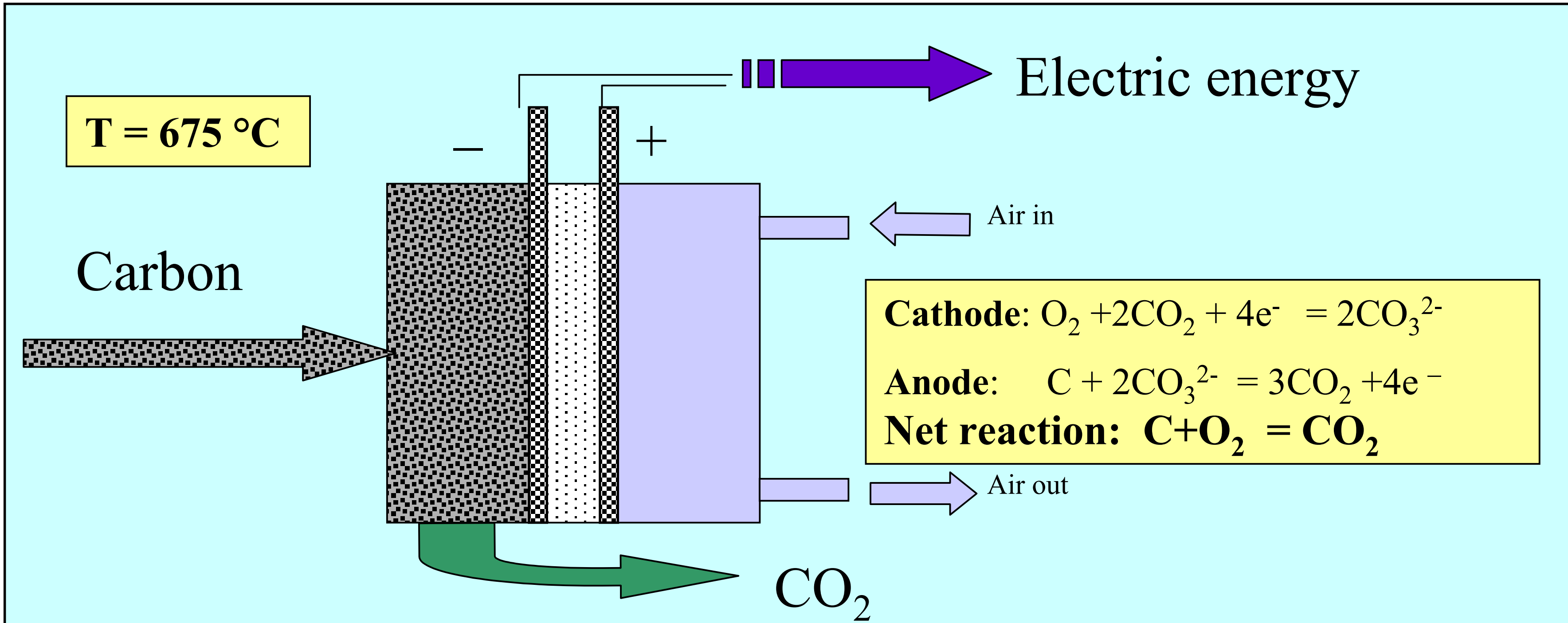
Topics

- Concept
- Thermodynamic and Chemical Basis
- Technical Approach and Results
- The Synthesis of Carbon Electrochemical Fuels
- Conclusions

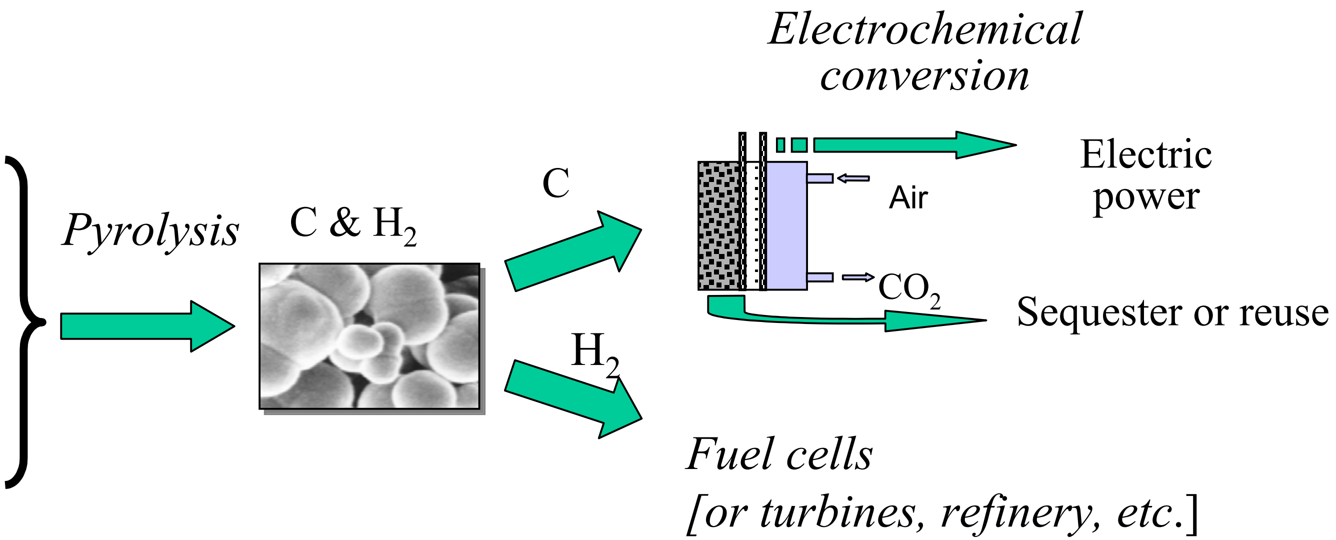
Direct Carbon Conversion Fuel Cell and Battery: Electricity From C/O2 Electrochemical Reaction



- **High fuel cell efficiency: 80% of $\Delta H°_{298}$ (HHV),**
  $\Delta H°_{298}$ = 32.8 MJ/kg-C [9.1 kWh/kg-C], $\Delta S \sim 0$, fixed C and CO_2 activities
- **High specific energy battery: 3-4 kWh/kg (~3.5 kWh/liter) at 100-133 W/kg**
- **Fixed C, CO_2 activities make possible invariant EMF and full fuel utilization**
- **Boudouard corrosion is expected only at low polarization: $C + CO_2 = 2CO$**

Routes to Power Production at Efficiencies > 70%

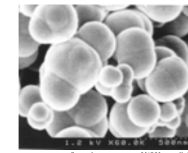
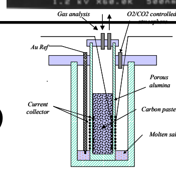
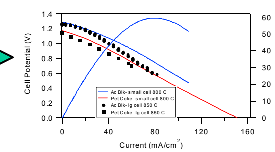
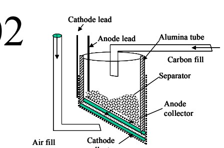
- Petro-coke
- Natural gas
- Petroleum
- Coal, lignite



70 – 80 % efficiency, HHV

- The pyrolysis of CH_x => C + (x/2)H_2 consumes 3-8% of fuel value; no ash
- H_2 co-product has multiple uses: fuel cells, chemical value, combustion

The Carbon Air Technology Evolved from LLNL Internal Research

Area	*Contribution*	*Sponsor/Year*
Nano-structures	Defined approach relating structure to rate; first full-cell experiments ever	CEES 1999 
Particle anodes	Particles + melt mimic rigid electrode Experimental slurries in full cells	CEES 1999 LDRD, IL-10479 
Anode R&D: rates and structure	Structure, conductivity effects studied; Carbon anode mechanism proposed; Data base of diverse fuels from slurry cells in full-cell configuration	LDRD, FY00-02  
Angled cell	Developed cell enabling scale up, refueling, controlled wetting of carbon	LDRD FY01-02 IL-10848 
Rigid anode JFC:Jun-03	Allows stacking and refueling of small assemblies; discovery of low-T materials; DOE NA22, ARL, ARO	FY2002-3 IL-11101 

Comparison of Fuels for Fuel Cells

Fuel	Theoretical limit = $\Delta G^o(T)/\Delta H^o_{std}$	Utilization efficiency, μ	V(i)/V(i=0) = ε_v	Actual efficiency = $(\Delta G/\Delta H^o_{std})(\mu)(\varepsilon_v)$
C	**1.003**	**1.0**	**0.80**	**0.80**
CH_4 [a]	0.895	0.80	0.80	0.57
H_2	0.70	0.80	0.80	0.45

Efficiency of a fuel cell

(electrical energy out) / (HHV thermal value of fuels in)

$[\Delta G(T)/\Delta H^o][\mu][V/V^o]$ = [theoretical eff][utilization][voltage efficiency]

--where $\Delta G(T) \equiv - nFV^\circ \equiv \Delta H - T\Delta S$

Fundamental advantages derive from thermodynamics of the C/O_2 reaction and fixed activities of the reactants

Technical background

Past efforts limited by ash entrainment, electrode fabrication and logistics

History

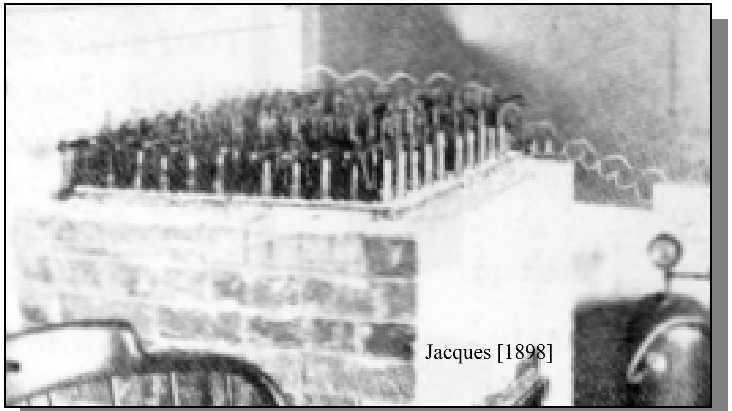
- Jacques [1898]: 15 kW coal batteries
  - $C + 2KOH + O_2 = K_2CO_3 + H_2O$
- ~10^2 papers in 20^{th} century
  - Efficiency not driver, CO_2 not pollution
- Weaver [1980]: found reactive cokes
  - >98% utilization at 750 C
  - Power levels => 0.8 kW/m^2 @ 1 kA/m2
- Vutetakis [1985]
  - Fundamental studies of ground C slurries
  - Suggested nano-scale disorder might enhance rate

Barriers to "electricity direct from coal"

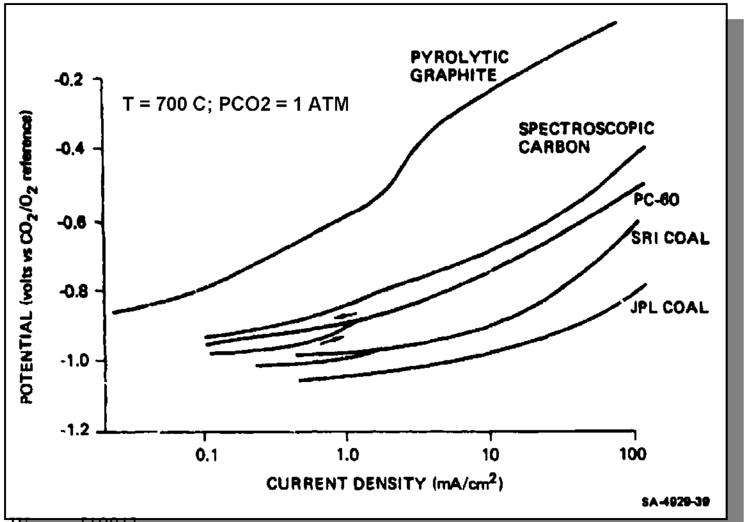
- Ash entrained into melt
- Electrode fabrication, distribution costs
- Resistance of rigid electrode,high polarization

Relation to Molten Carbonate Fuel Cell

- Similar cathode, melt
- No H_2 or steam corrosion
- More tolerant of S (no anode catalyst)



Jacques [1898]



Weaver [1981]

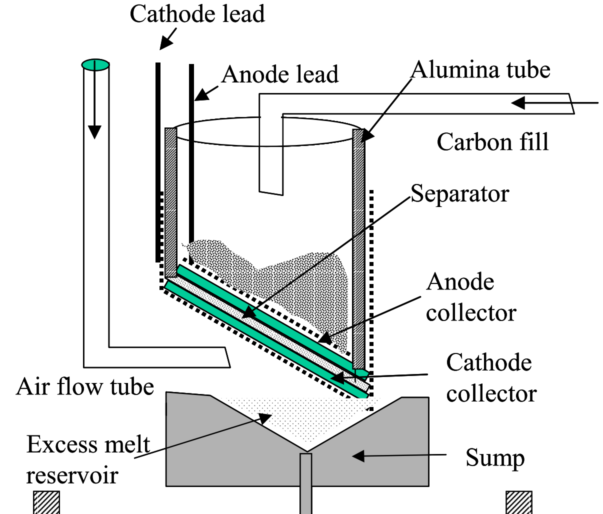
At Temperatures of 400-1100 °C, the Only Reaction is $C + O_2 \rightarrow CO_2$

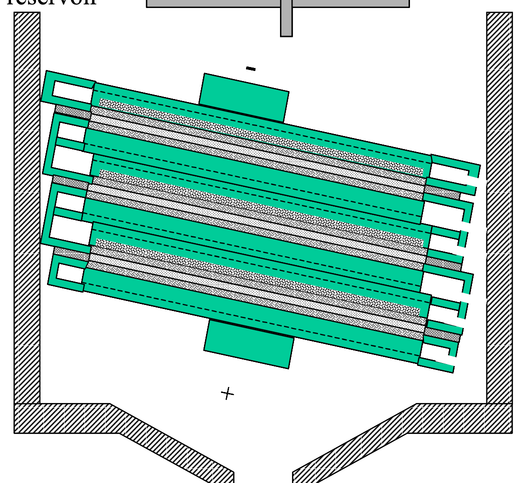
Conditions	Method used	Results	Reference
T = 700 C, graphite, carbonate	ΔW, dV/dt ~ I/nF	n = 4 u not reported	Tamaru & Kamada [1937]
T = 400-900 C, graphite, CO_3^{2-}	dV/dt; [CO]/[CO_2]	n = 4 u ~ 1.0	Hauser [1964]
T = 700-800 C, rigid reactive carbons and coke	dV/dt; ΔW	n = 4 u ~ 1.0	Weaver [1977-9]
T = 700 C, CO_3^{2-} Large volume, free slurry	d[CO_2]/dt = I/nF	n = 4 u poor	Vutetakis [1984]
T = 900-1100 C, $NaAlF_4 + Al_2O_3$, turbo & graphite	d[CO_2]/dt = I/nF anode CO ~ 0: no Boudouard rxn	n = 4 u ~ 1.0	Thonstad [1970]

Studies with 60 cm^2 Angled Cell Anticipate Fuel Cell

Cell in heater

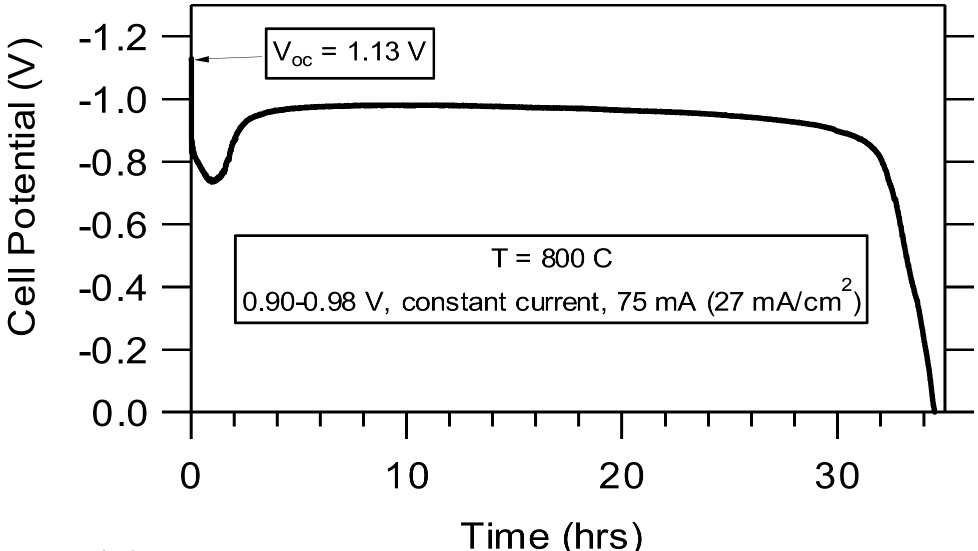
60 cm^2 angled cell



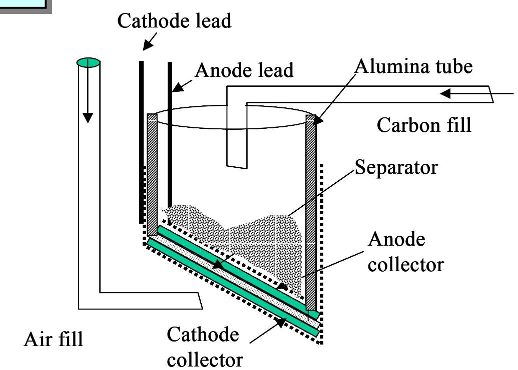


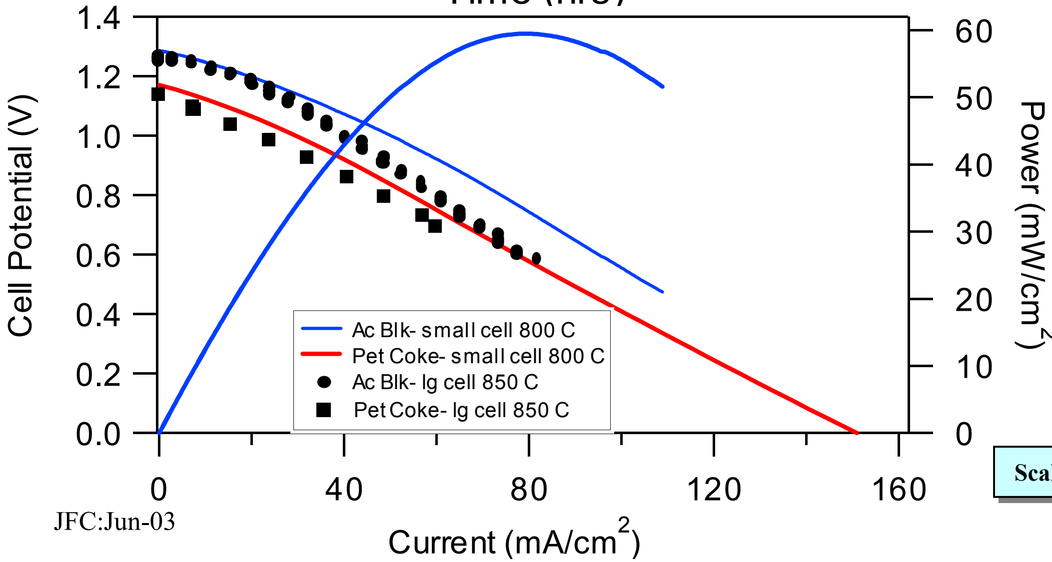
- Tilted orientation allows control of wetting
- Fuel cell option for exchange of electrolyte
- Basis of patent-pending

Voltage Stability, 80% Efficiency and Successful Scale-up of Powder-fed Fuel Cell



Stable voltage during 30 h test at constant load

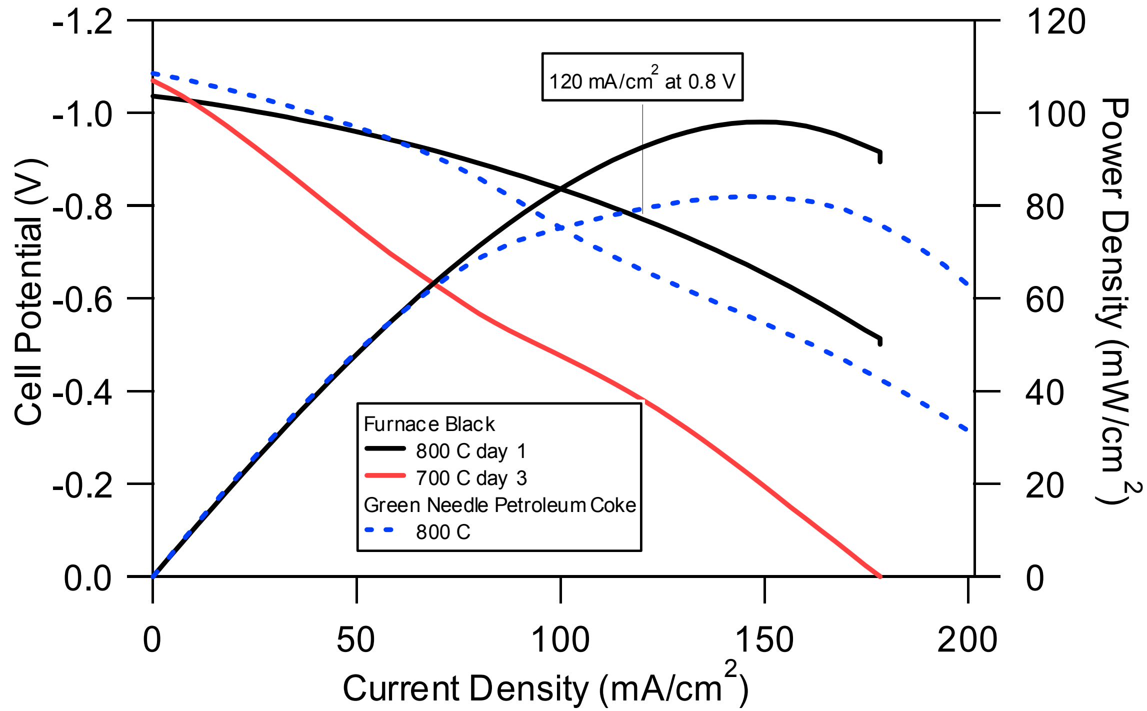




Scale up 2.8 to 60 cm²

JFC:Jun-03

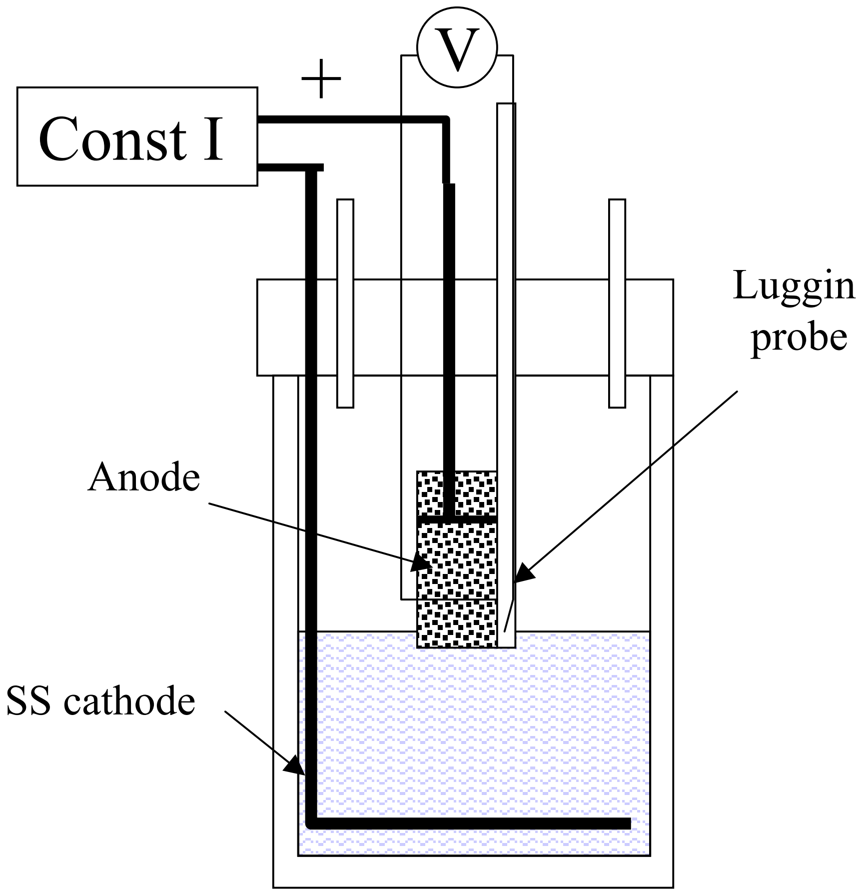
Demonstrated >100 mA/cm^2 at 80% Efficiency With Carbon Black Fuels



• **Performance sustained until fuel consumed (> 3 days)**

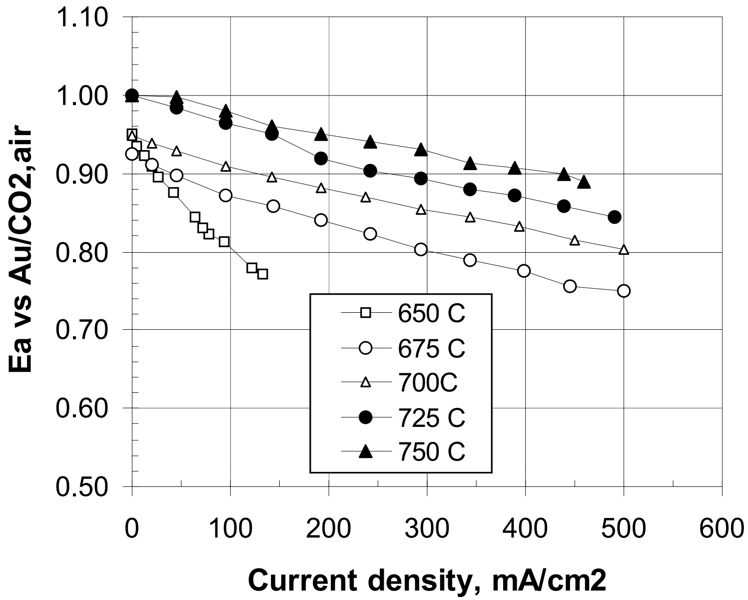
Data: N.Cherepy

New Rigid Block Materials: Half-Cell Research



Measures anode polarization against Au/0.28CO_2, 0.14O_2

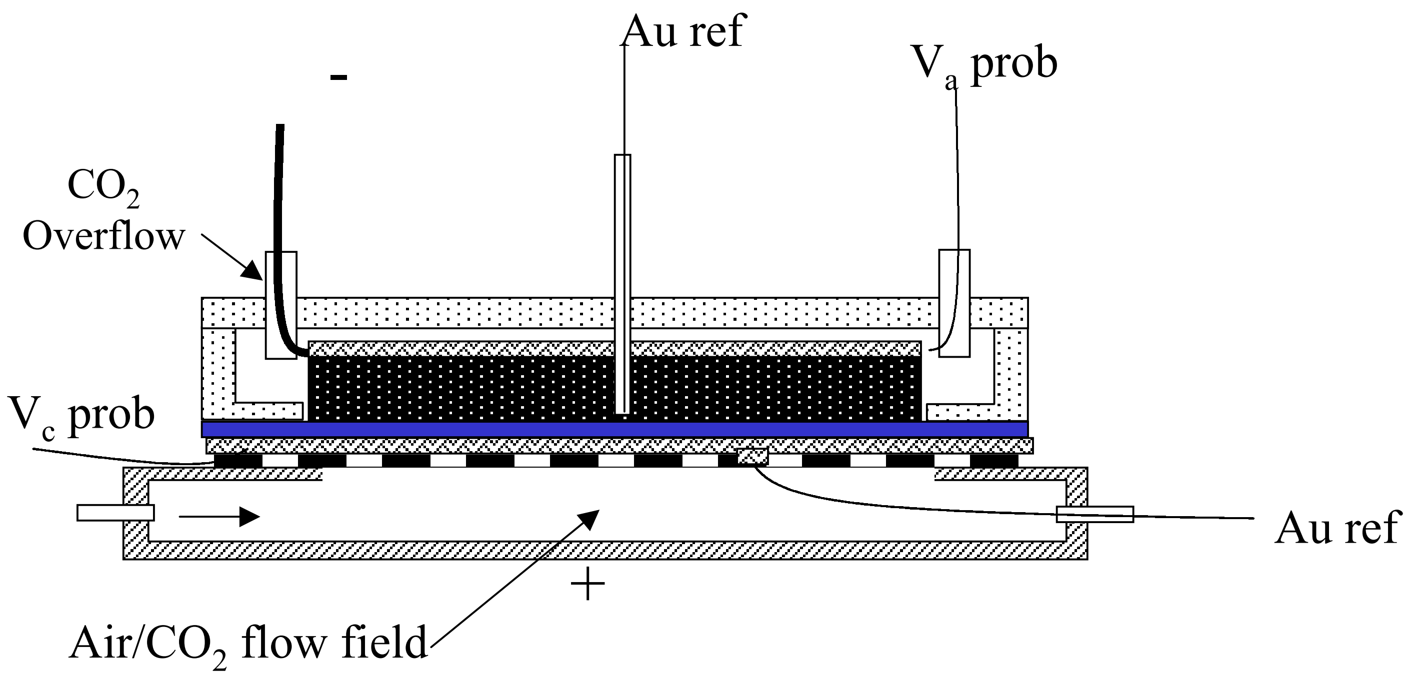
Enhanced Performance with Composite Plates at 650-700 °C



- Properties of composites
  Density: >25 % theoretical
  Conductivity > 25 $\Omega^{-1}cm^{-1}$
- With separator, cathode at 700 °C:
  - 1 kW/m^2 @ 80% efficiency
  - 4.5 kW/m^2 peak power
- Ongoing tests on 50 cm^2

Recently studied class of high-density C composite plates yielded twice previously achieved power at 100 °C lower T. Expected 80% efficiency at 50-500 mA/cm^2

Experimental Approach: Rigid Plate Anode with Flow Field and Improved Diagnostics



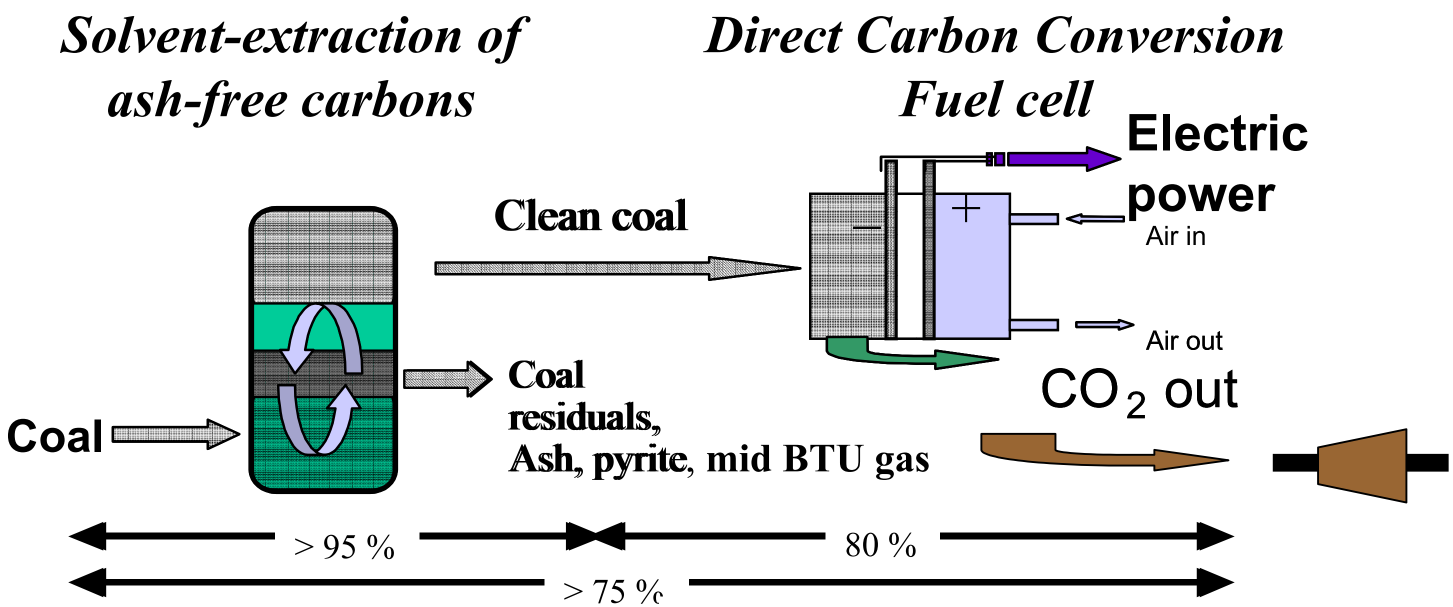
- Independent reference electrodes and voltage probes
- Precise control over gas composition and flow
- Isolation of reaction zone in rigid carbon block

DOE/NETL Project, FY 2003

JFC:Jun-03

The synthesis of carbon electrochemical fuels

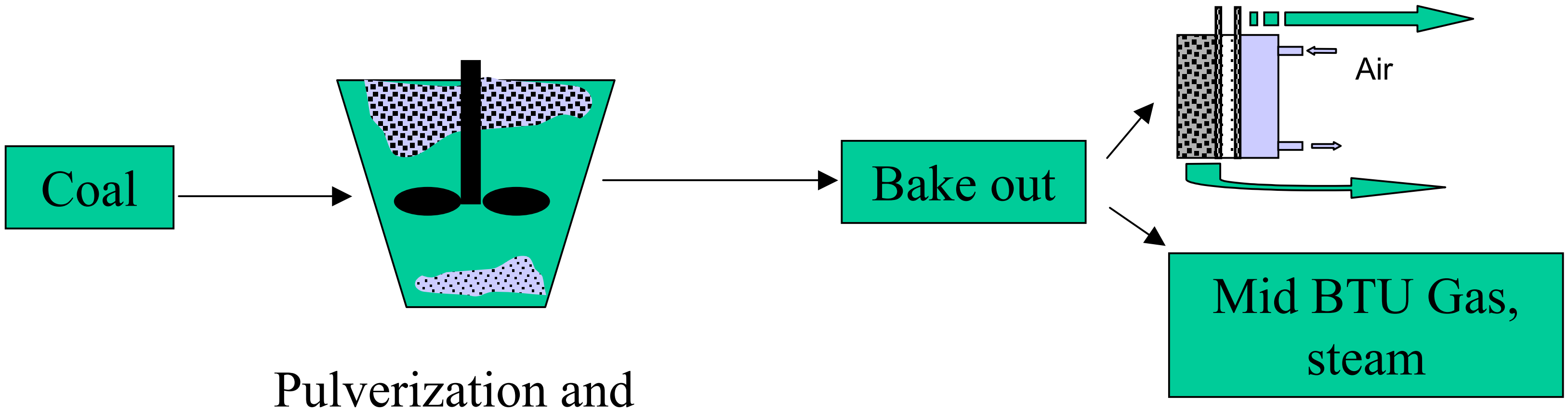
Extraction and Use of Carbon from Coal



- Solvent extraction yields coal with 0.01% ash
  - Recycles benign solvents, negligible loss (0.7 %) per cycle
  - Unconverted coal retains thermal value

A. Stiller, J. Zondlo, WVU; B. K. Parekh, U. Kentucky

Hydraulic Cleaning of Coal

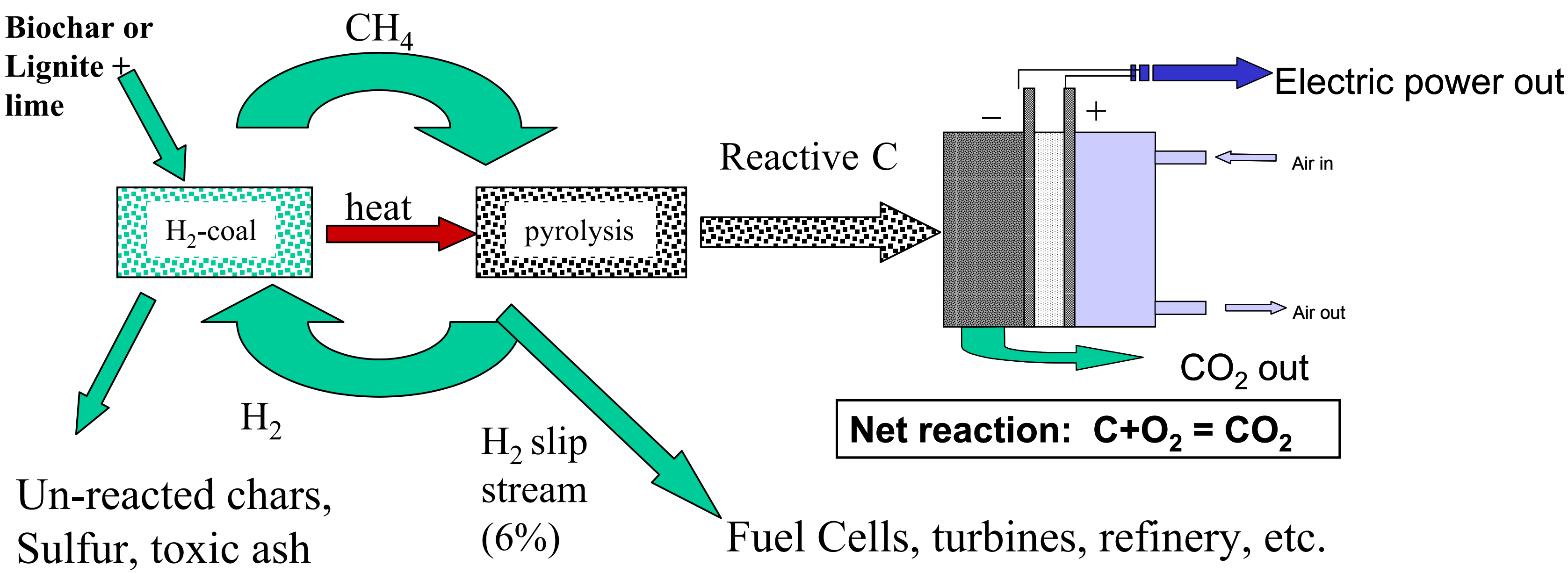


Pulverization and
Hydraulic Separation
from Ash & Pyrite

- Hydraulic separation of C (<1 % S, ash) from pyrite, ash
  - 65 kWh/ton (98 % retention of heating value)
  - Net coal-to-electricity efficiency 78 %
- Total cost \$60/ton => 0.8 ¢/kWh for fuel
- But: high ash requires further cleaning or periodic electrolyte exchange

Ref.: B. K. Parekh, U. Kentucky

Clean Carbon Fuels from Hydropyrolysis



Extraction of Carbon from Coal Seam by *in situ* methanation ?

How Often Must Electrolyte Be Replaced?

Interval between electrolyte replacement/recycle

– ***0.5% ash— hydraulic cleaned coal***	***200 days (twice yearly)***
– ***0.05% ash—solvent extracted coal***	***5.5 years (life of cell)***
– ***0.01% ash—pyrolyzed oil***	***N/A***

For 0.5% ash cleaned coal

- For common fuels under consideration, cost of electrolyte exchange is insignificant
- Lowest recycle cost if Na/K eutectic is used:
  $2.5/kW per exchange, assuming 20 ¢/lb salt
  200 days between exchange => 0.05 ¢/kWh

Summary: Efficient Processes for Cleaning Coal

- UK: hydraulic separation
  - grind to 30 μm; baking to remove mid-BTU gas; low-ash product
- UK-process: extraction of pitch with anthracene oil
  - 425 ºC, 200 atm; no hydrogenation; 40-70% yield; 0.05-0.1 % ash
- WVU-process: extraction of pitch with n-methyl pyrrolidone
  - Ambient pressure, 200 º C; 40-50% yield; 0.05-0.1 % ash

Process	***Efficiency***	***Yield***	***%Ash***	***%S***	***Cost***
UK-hydro	98%	100%	0.5-1	1-2	$60/ton, $3/GJ 0.8 ¢-fuel/kWh
UK-solvent	> 90%	40-70%	0.05	0.5	$200/ton, 2.4 ¢-fuel/kWh
WVU-solvent	> 90%	40-50%	0.05	0.5-1	$78-140/ton, 1-2 ¢-fuel/kWh

Initial Hardware Cost Estimates

Stack cost ~ \$250/m^2 at 2 kW/m^2

Component or factor	**Basis**	**Cost \$/kW**
Zirconia fabric	Zircar, Inc. retail price \$200/m^2	100
Nickel felt	Eltech, Inc. \$20/m^2 retail price	10
Stainless steel lid	Ni plated SS frame, \$5/lb	38
Graphite base, collector	\$1.00/lb design	10
Assembly	20% parts	32
G&A, profit	20% parts and labor	48
Total		\$237

Acknowledgments

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  - Nerine Cherepy, Chemistry
  - Larry Hrubesh, Physics
  - Ton Tillotson (advanced composite materials)
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  - Prof. Rob Selman IIT (Molten Carbonate Fuel Cell)
  - Dr. Kim Kinoshita (LBL, ret.; Carbon properties)
  - Meyer Steinberg (BNL) fossil fuel to carbon processing
  - MesoSystems Technology (Kennewick WA). Thermal engineering
- LDRD and CEES; DOE NA-22; ARL; ARO; DOE/NETL