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Reactions of the Carbon Anode in Molten Carbonate Electrolyte

Direct Carbon Fuel Cell Workshop

NETL, Pittsburgh PA

by

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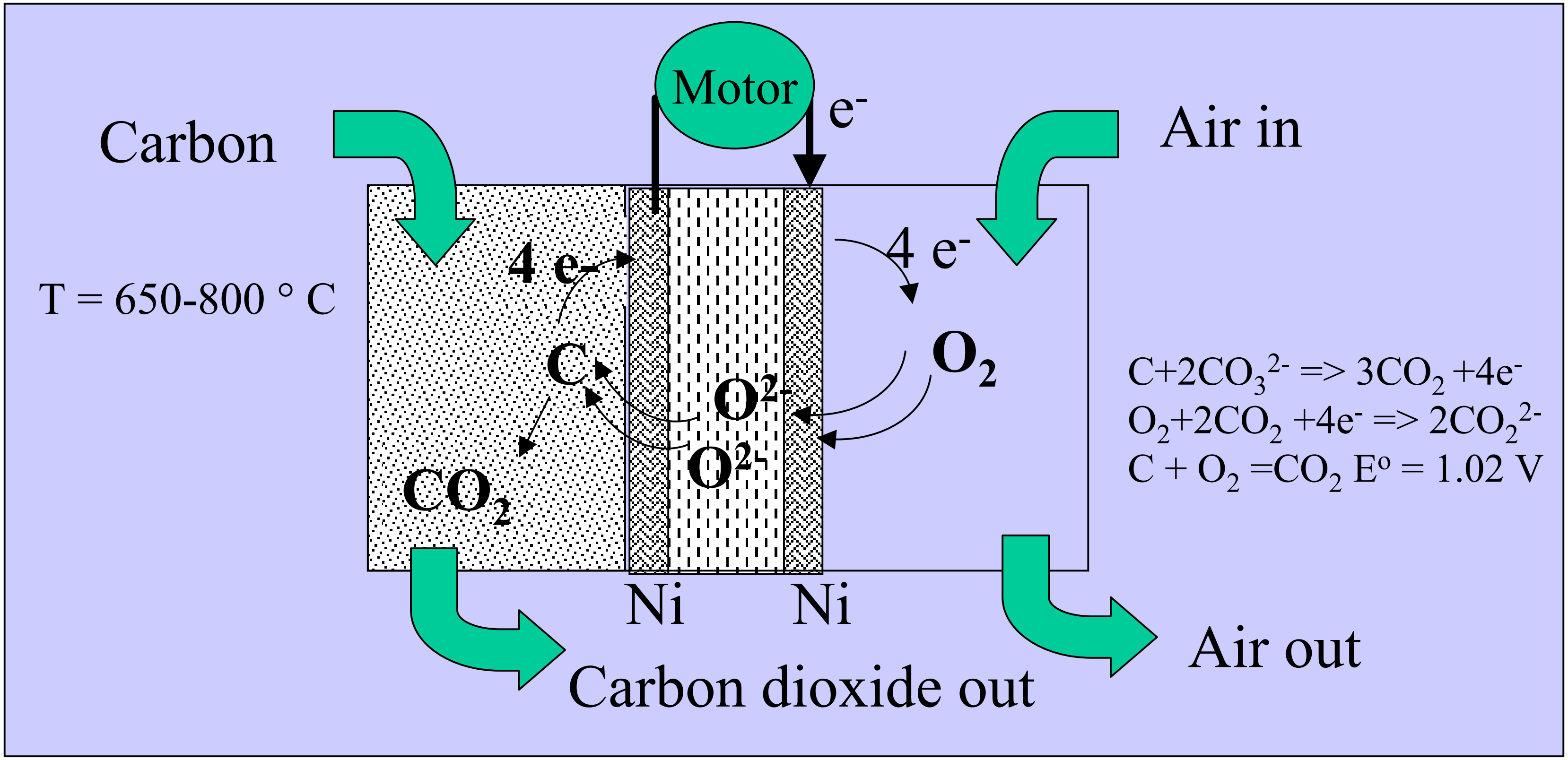
[1] Special Thanks to N. Cherepy and R. Krueger for data and equipment

Direct Carbon Fuel Cell (DCFC) Generates Power from Reaction of Carbon and Oxygen



- **High fuel cell efficiency: 80% of HHV based on $\Delta H°_{298}$ = 32.8 MJ/kg-C**
- **Electrolyte is unconsumed and invariant**
- **Fixed C, CO_2 activities ⇔ full conversion of C**
- **Actual anode and cathode reactions may involve CO_3^{2-} ion**

High C/air Efficiency is Derives from a Favorable Thermodynamics

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 or battery is defined:

≡ (electrical energy out) / (Heat of combustion (HHV) of fuels input)

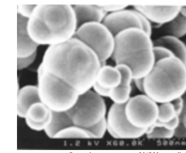
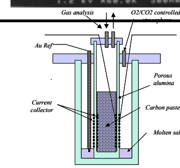
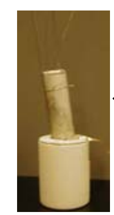
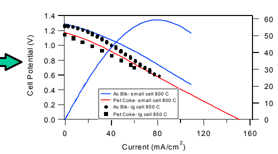
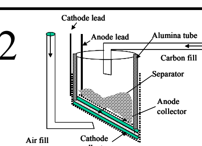
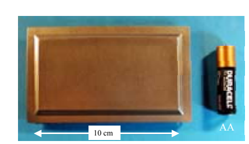
= [theoretical efficiency G/H][utilization fraction μ][voltage efficiency ε_v]

$= [\Delta G(T)/\Delta H^o][\mu][V/V^o] = [\mu][nFV]/\Delta H^o$

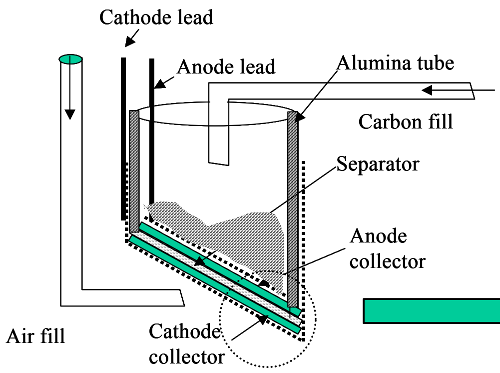
--where $\Delta G(T) \equiv - nFV^o \equiv \Delta H - T\Delta S$

Typical C/air efficiency is 80%
Must adjust for Energy Cost of Fuel Production

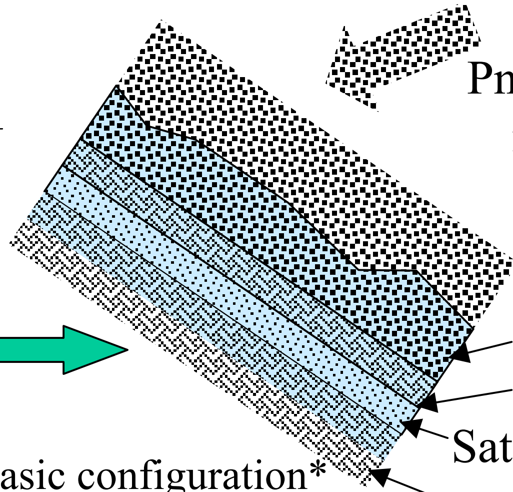
Current NAI and DOE/FE Efforts Evolved from Prior Research Activities

Area	*Contribution*	*Sponsor/Year*
Nano-structures	Defined approach relating structure to rate; first full-cell experiments <u>ever</u>	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 cell	Allows stacking and refueling of small assemblies; discover of low-T materials (IL-10847 addendum)	FY2002-3 

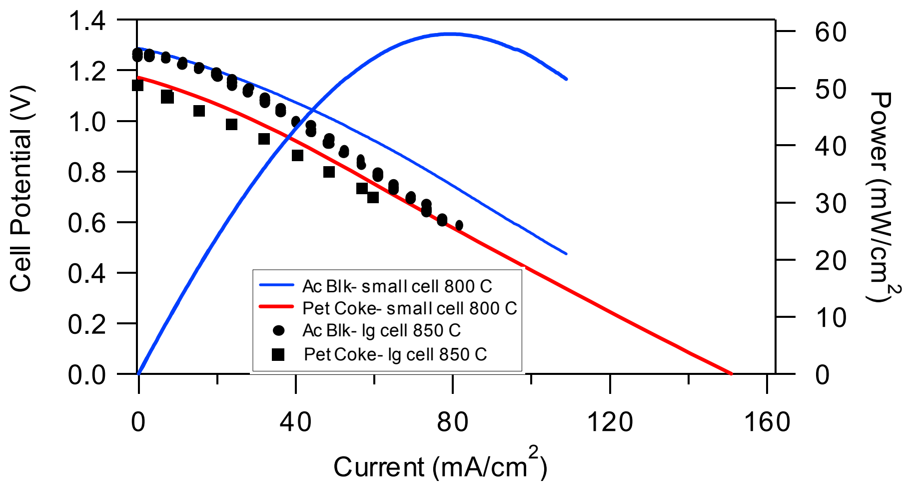
Successful Scale-up of Powder-fed Cells*



Tilted cell*



Basic configuration*

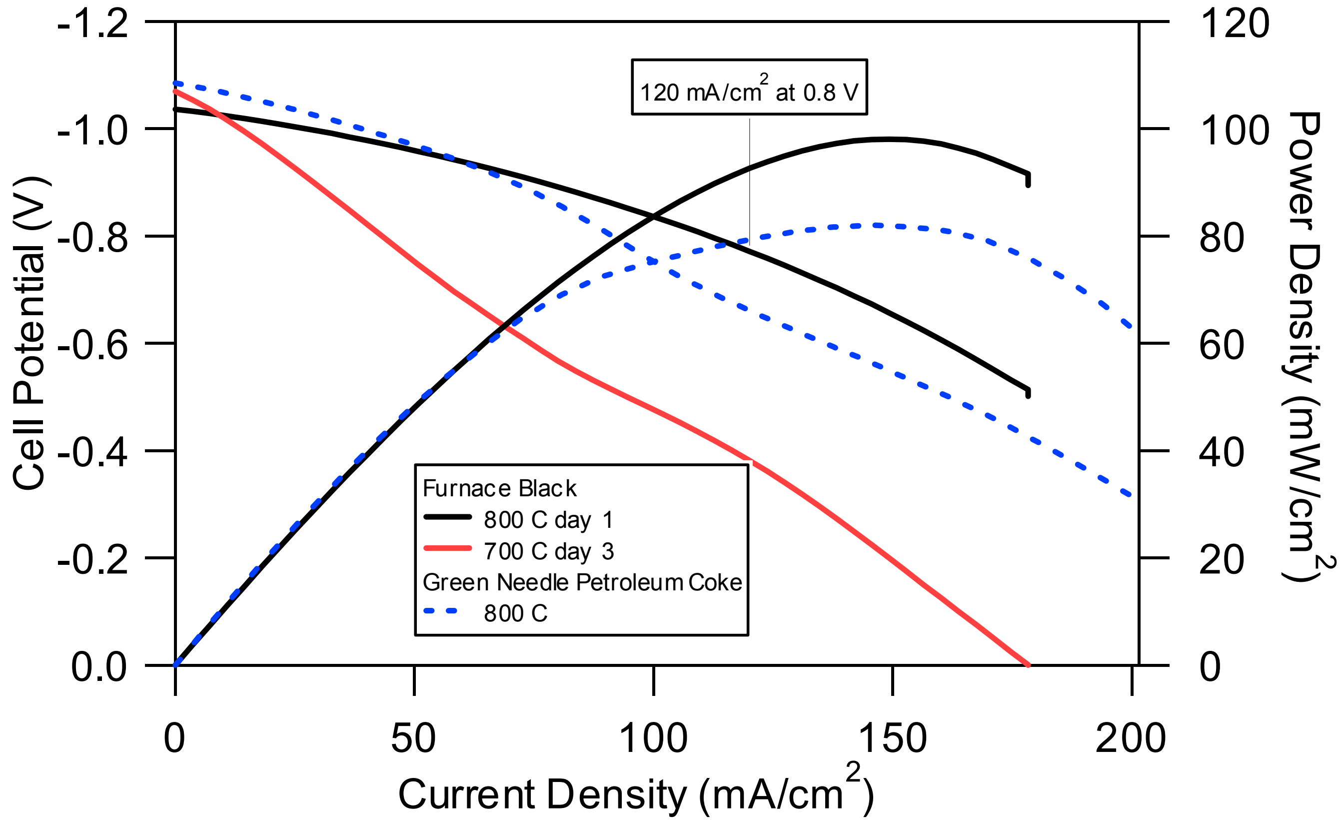


Cherepy 2001

- Angle controls wetting and prevents flooding
- Confines reaction zone to wetted carbon
- Discovered novel technique to promote wetting of C*

*Patent applications filed and pending

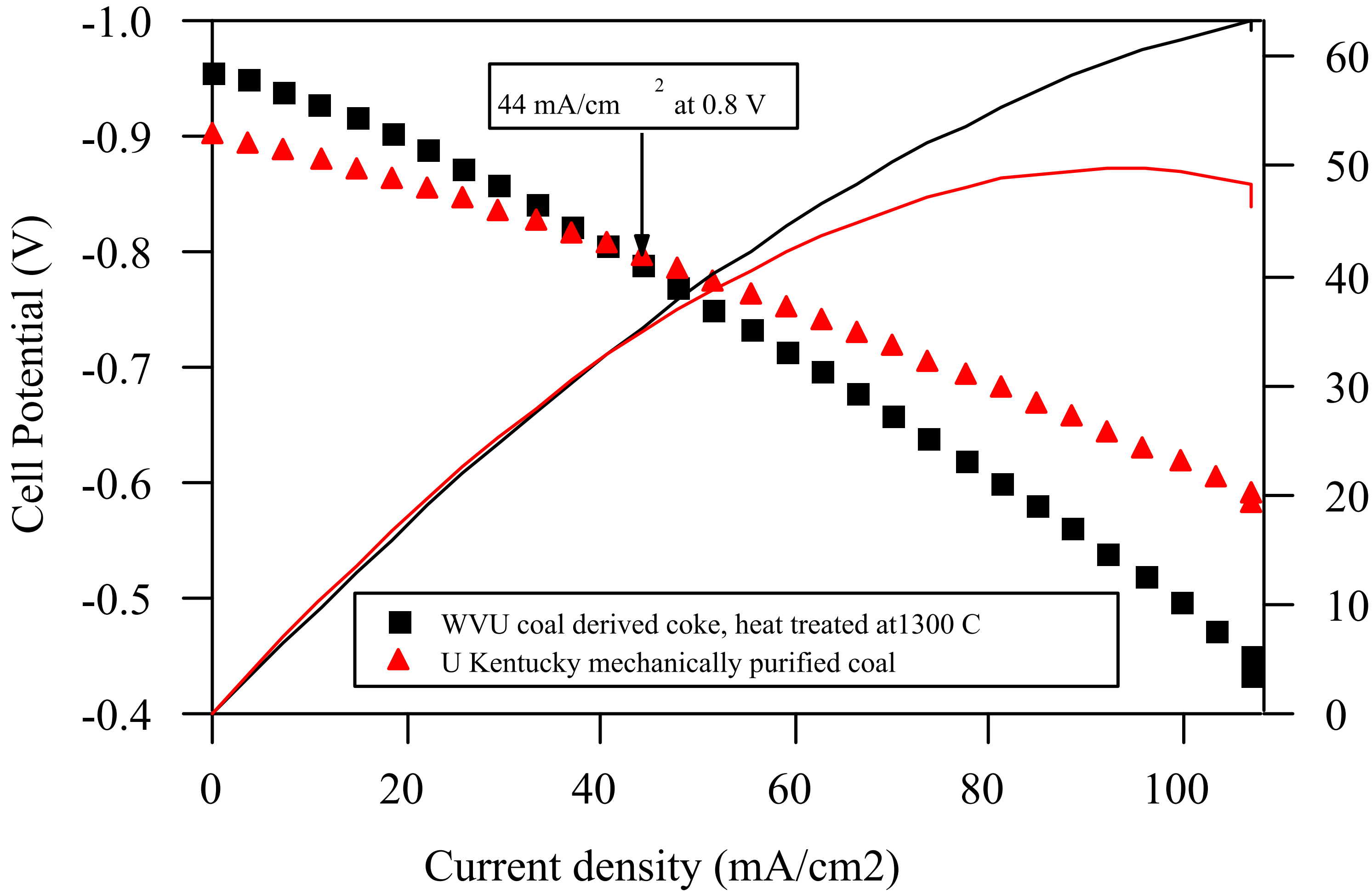
We have demonstrated >100 mA/cm² at 80% efficiency with carbon black fuels



- **State-of-the-art cathode**
- **Performance sustained until all fuel consumed (> 3 days)**

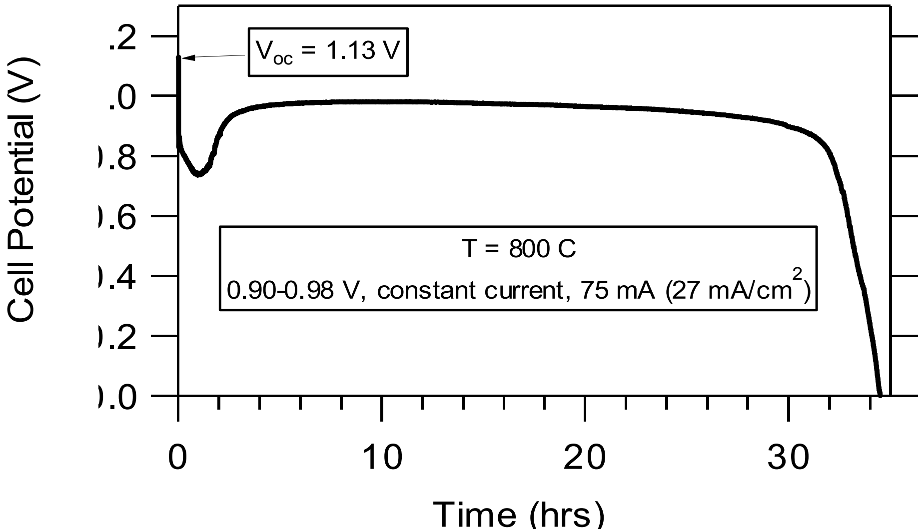
Source: Cherepy, Cooper & Ziagos UCRL-PRES-144849, June 2002

Coal-Derived Carbons Show Promise

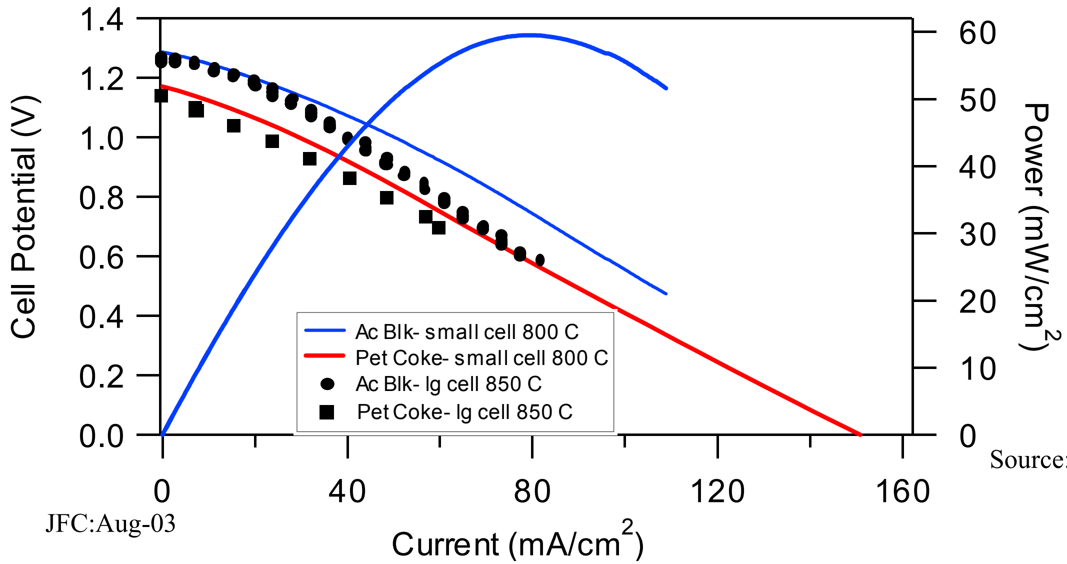


Source: Cherepy, Cooper & Ziagos UCRL-PRES-144849, June 2002

Voltage Stability and Successful Scale-up



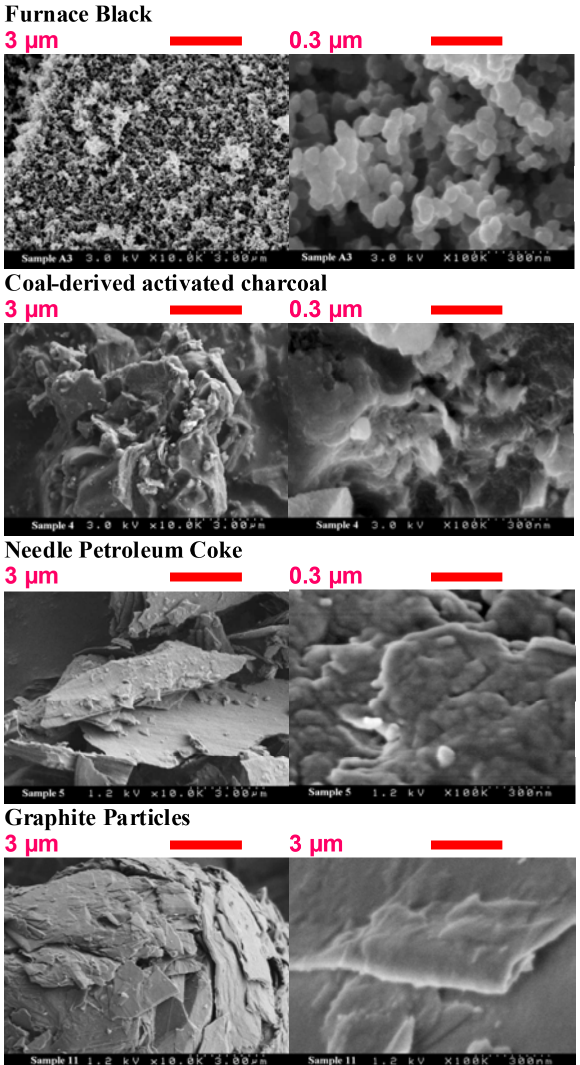
Stable voltage during 30 h test at constant load

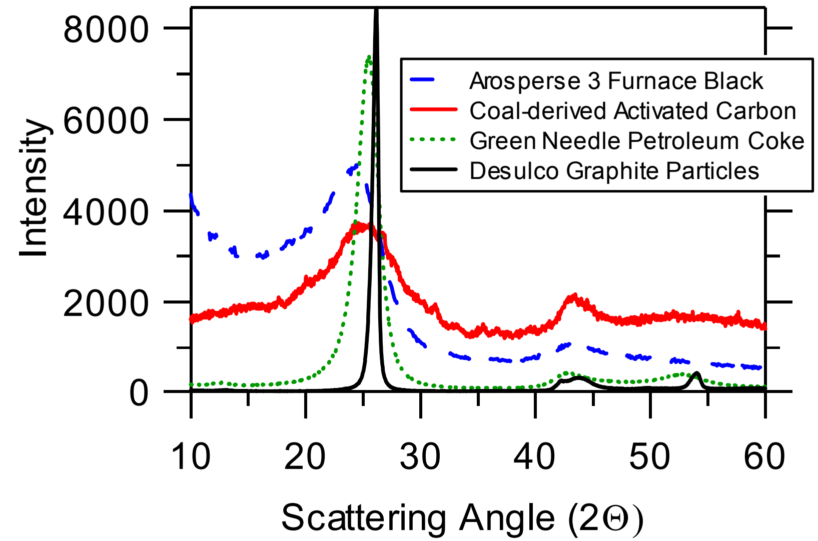


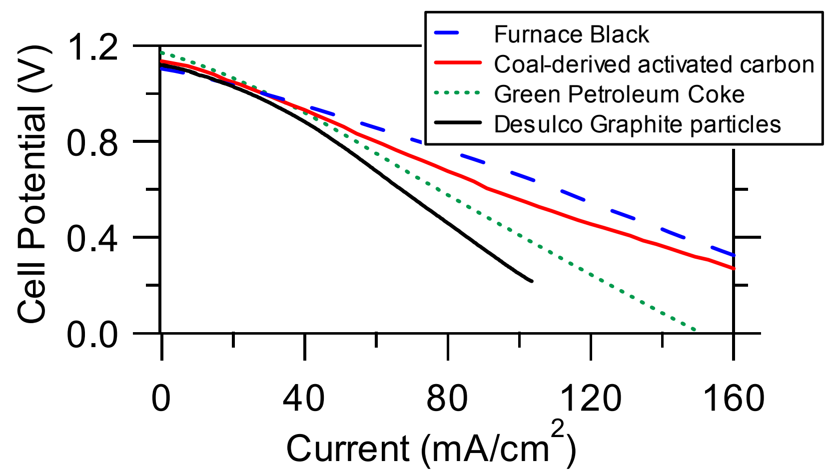
Scale up 2.8 to 60 cm^2

Source: Cherepy, Cooper & Ziagos UCRL-PRES-144849, June 2002

We have studied the relationship between carbon structure and current density







Source: Cherepy, Cooper & Ziagos UCRL-PRES-144849, June 2002

Disorder, Conductivity, Surface Area All Contribute to Carbon Discharge Rate

Sample	Surf. Area (m^2/g)	Primary Particle Size[a] (nm)	Crystallinity Parameter[b] (rank)	Peak Power (mW/cm^2)
Peach Pit AW activated carbon	>1000	30-3000	10	84
Carbon aerogel powder, pyrolyzed at 1050 °C (glassy sp2 carbon)	1225	fibers, <1000 d. spheres, 20000-100000 d.	9	61
Acetylene Black (from acetylene pyrolysis)	75	40 spheres	8	61
Coconut act carbon, AW, milled	1050	20 spheres	7	56
Coal-derived act carbon, AW, milled	950	60-10000	6	51
Arosperse 15, thermal black (from methane pyrolysis)	9	290 spheres	5	46
Low Q Green Needle Pet. Coke, milled	-------------	3000-100000 needles	4	48
SB 635 Graphite particles	9	5000-100000 stacked sheets	3	42
SO230-6 Pet Coke, heat treated, 1800 °C, milled	9	3000-10000 stacked sheets	2	36
Desulco Graphite particles	-------------	5000-30000 stacked sheets	1	46

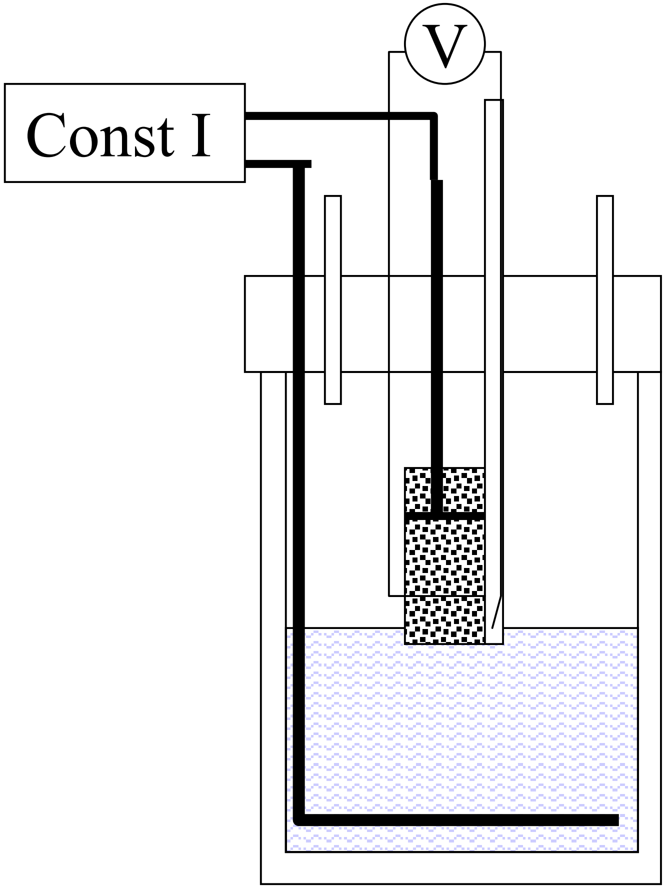
[a] from SEM

[b] from XRD- after H. Fujimoto, K. Tokumitsu, A. Mabuchi & T. Kasuh, *Carbon* **32**, 1249-1251 (1994).

Note, low peak powers here due to old-style cathode

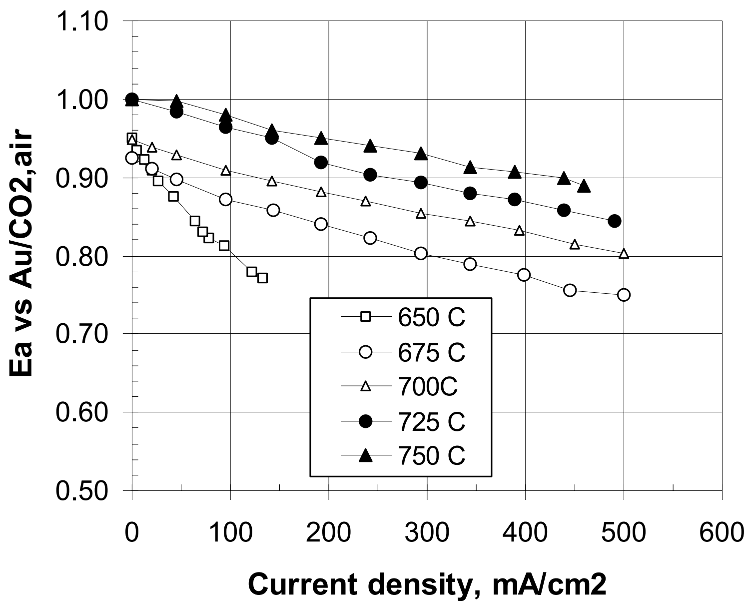
Source: Cherepy, Cooper & Ziagos UCRL-PRES-144849, June 2002

Initial Research in Half-cell Configuration



- Measures anode polarization against Au/0.28 CO_2, 0.14 O_2
- Separate reference and voltage probe circuit

Enhanced Performance at 650-700 °C



- Properties of composites
  - d = 0.56 g/cm^3
  - ρ = 0.04 Ω-cm
- With separator, cathode at 700 °C:
  - 1 kW/m^2 @ 80% eff.
  - 4.5 kW/m^2 peak power
- Ongoing tests on 50 cm^2

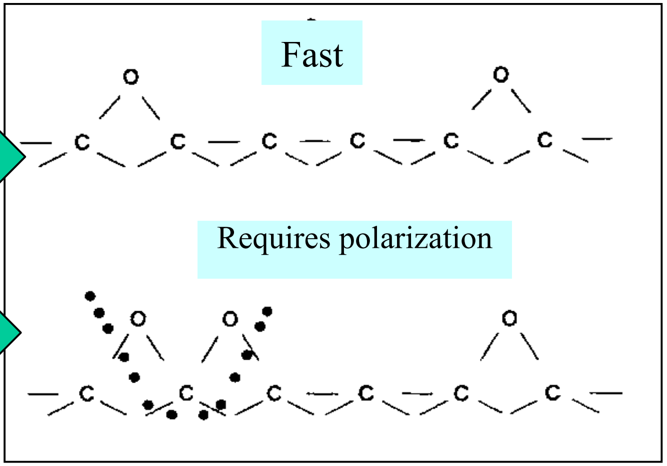
- New materials composites (@ 675 °C) yield 2x power of pastes at 800 °C
- Indicates 80% efficiency at 50-500 mA/cm^2

Two-Phase Anode Mechanism in Carbonate Proposed by Modification of Hall Anode Model

MECHANISM PROPOSED FOR HALL ELECTROLYTES AND MODIFIED FOR CARBONATES

$2Al_2O_2F_4^{2-} \leftrightarrow 2O_2^{2-} + 2Al_2OF_4$ Source of O_2^{2-} in Hall cryolite

$2CO_3^{2-} \leftrightarrow 2CO_2 + 2O^{2-}$	**Source of O_2^{2-} in carbonate melts**
$C_{rs} + O^{2-} \rightarrow C_{rs}\text{-}O^{2-}$	Adsorb O^{2-} at reactive site (rs)
$C_{rs}\text{-}O^{2-} \rightarrow C_{rs}O + 2e^-$	Fast 1e$^-$ discharges: CO on rs
$C_{rs}O + O^{2-} \rightarrow C_{rs}O\text{-}O^{2-}$	RDS: second O^{2-} adsorption
$C_{rs}O\text{-}O^{2-} \rightarrow CO_{2ad} + 2e^-$	Two 1e$^-$ discharges: CO_2 on rs
$CO_{2ad} \rightarrow CO_2$	Fast desorption
$C_{rs} + 2CO_3^{2-} \rightarrow 3CO_2 + 4e^-$	(overall anode reaction)



- Mechanism gives rise to observed cell voltage dependences on CO_2
  - -- $E = E° + RT/4F \ln [C][O_2][CO_{2,cath}]^2/[CO_{2,an}]^3$ [Vutetakis 1984]
- Mechanism accounts for high $C \rightarrow CO_2$ efficiency measurements
  - Our model of carbonate decomposition replaces Hall initiating step:

    $Al_2O_2F_4^{2-} \leftrightarrow O_2^{2-} + Al_2OF_4$ with carbonate dissociation, **$2CO_3^{2-} \leftrightarrow 2CO_2 + 2O^{2-}$**

    Hall Process mechanism after Haupin & Frank, Alcoa Tech Center [1981]
  - Thonstad [1970] measured Tafel slopes, found too great for e- transfer to be RDS

Summary of LLNL results

- Invention of particle/melt slurry anodes integrated into cells
  - Tested >20 materials; structure/reactivity theory
- Nano-structural disorder, not purity, controls rate and efficiency
  - Disorder, edge density, conductivity
  - Useful disorder with HC pyrolyzed below 1200 ºC
  - Mechanism proposed for full conversion, $C \rightarrow CO_2$
- Development of angled cell
  - Controls wetting and flooding
  - Provides for scaleup and removal/replacement of salt
- New materials for plate systems
  - Higher rates at lower T
- Similar polarization for carbon and cleaned coal
  - Trade cost against electrolyte stability
  - Role of H in coal not investigated

Needed R&D in Anode Electrochemistry

1. Mechanism for the anodic reaction of coal, coke
   --Reactions and mechanisms of H, N,S (bound and pyrite) under reducing conditions (E = -0.8 V vs Au/CO_2,O_2)
2. Determine catalytic effects of impurities found in coal and coal-derived carbon: minerals, water
3. Transport of CO_2, CO_3^{2-}, particulates and carbon in anode and matrix; gradients of oxide and carbonate; role of water
4. Surface chemistry: functional groups, wetting and site reactivity
5. Adaptation of cathode structures and catalysts for specific needs of C/Air cell