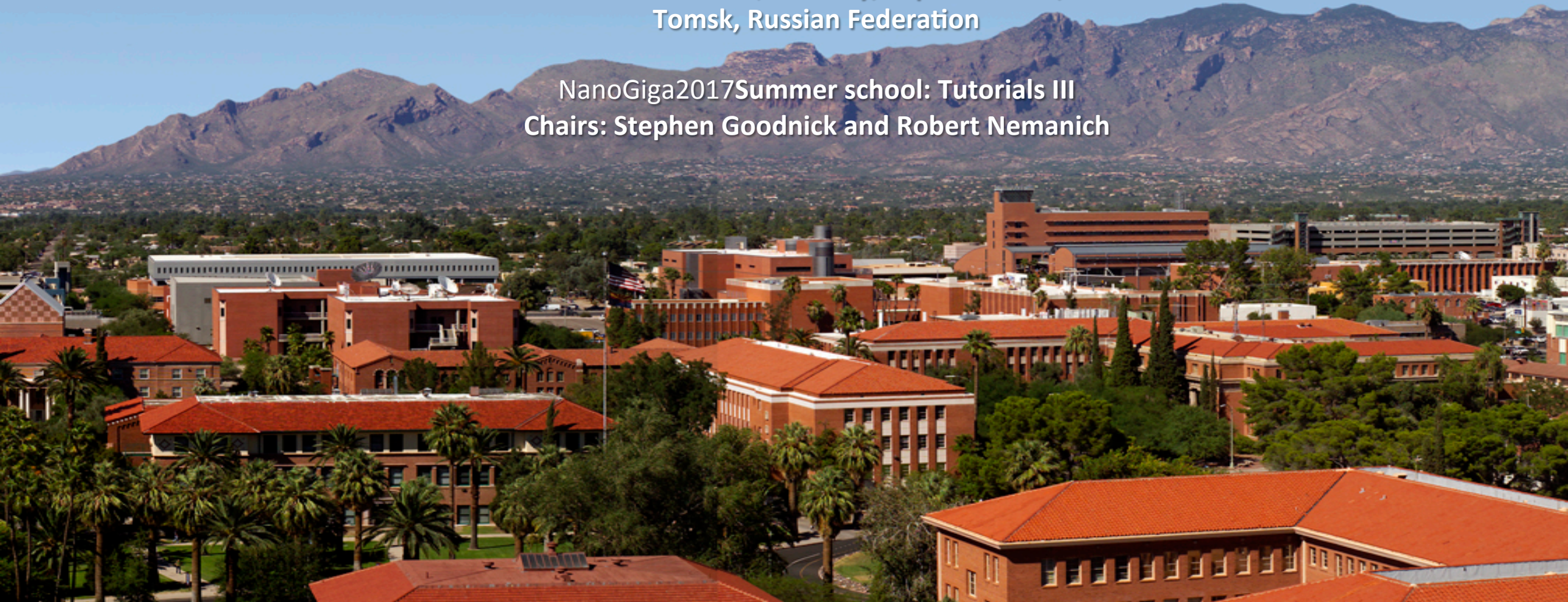


Challenges in Solar Energy Generation and Energy Storage

Dominic Gervasio, Department of Chemical and Environmental Engineering,
University of Arizona, Tucson Arizona USA

10:00 am – 10:45 am, Tuesday, September 19, 2017
Tomsk, Russian Federation

NanoGiga2017Summer school: Tutorials III
Chairs: Stephen Goodnick and Robert Nemanich



Outline

- Solar thermal electrical conversion at high temperatures
- Storage of solar energy by sensible heating of salt (in video)

Other applications of molten salt to chemical processing (Thursday)

- Metallurgy
- Low cost photovoltaics by Si electroplating
- Storage of photovoltaic solar energy as hydrogen
- Fuel cell for power generation of stored hydrogen

Solar thermal electrical conversion at *high temperatures* (800C)

- Molten Chloride Salts are new high temperature Heat-Transfer Fluids (HTFs) enabling:
 - Concentrating Solar Power - solar thermal electrical-power generation and storage
 - Cooling next-generation nuclear reactors for electrical-power generation

Outline of CSP discussion

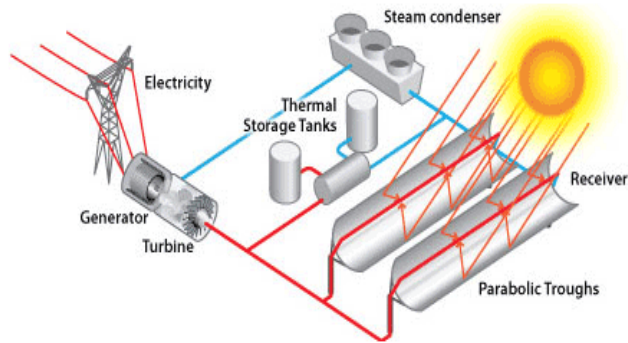
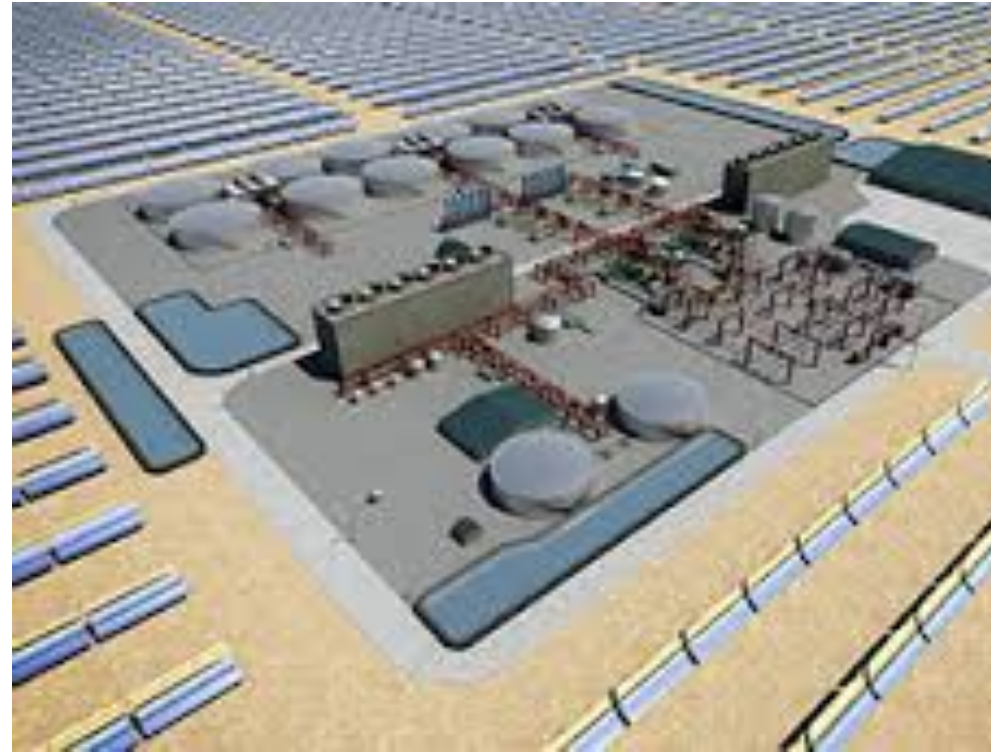
- Introduction to Concentrating solar power technology
- New Materials for collecting solar-thermal power at high temperatures
 - Molten salts
 - Hastelloys
- Corrosion of Hastelloy in Molten salts at 800 to 900°C
- Conclusions

Solar Concentrating solar power (CSP) to thermal to electrical power

Current best Heat Transfer Fluid (HTF), nitrate salts
500°F (260°C)
1000°F (538°C)

Need HTF to operate up to 800°C to use supercritical CO₂ instead of water to spin generator turbine

Generation 3
CSP will use molten chloride salt HTF operating between 500°F and 800°C



- ❑ University of Arizona developed and demonstrated molten chloride salts as advanced heat transfer fluids for CSP.
- ❑ Chloride HTF raise operating temperature for higher efficiency, lower cost and store energy storage without using water.
- ❑ The Secretary of the U.S. Department of Energy said, *“Advanced concentrating solar power systems represent a promising pathway for utilities to provide reliable, affordable solar electricity to American families and businesses.”*

DoE Targets for Advanced Gen 3 Heat-Transfer Fluids

	Target	Stretch Target
Thermal Stability (liquid)	$\geq 800\text{ }^{\circ}\text{C}$	$= 1300\text{ }^{\circ}\text{C}$
Melting Point	$\leq 250\text{ }^{\circ}\text{C}$	$\leq 0\text{ }^{\circ}\text{C}$
Heat Capacity	$\geq 1.5\text{ J/g/K}$	$\geq 3.75\text{ J/g/K}$
Vapor Pressure	$\leq 1\text{ atm}$	
Viscosity	$\leq 0.012\text{ Pa-s @ } 300\text{ }^{\circ}\text{C}; \leq 0.004\text{ Pa-s @ } 600\text{ }^{\circ}\text{C}$	
Density	$\leq 6,000\text{ kg/m}^3\text{ @ } 300\text{ }^{\circ}\text{C}; \leq 5,400\text{ kg/m}^3\text{ @ } 600\text{ }^{\circ}\text{C}$	
Thermal Conductivity	$\geq 0.51\text{ W/m/K @ } 300\text{ }^{\circ}\text{C}; \geq 0.58\text{ W/m/K @ } 600\text{ }^{\circ}\text{C}$	
Pipes and container materials compatibility	Corrosion rate $<100\mu\text{m/year}$ Metals carbon steel ($<425^{\circ}\text{C}$), Stainless Steel ($<650^{\circ}\text{C}$) and Nickel alloys (850°C).	
Materials Cost	$\leq \$1 / \text{kg}$	

Virtually all met with molten chloride salt HTFs

**Design rules for molten chloride salt HTFs
allowing targets to be met**

Sodium chloride is a low-cost and stable molten salt but melts at $> 800^{\circ}\text{C}$ which is too high!

2 design rules for making a stable low melting molten halide salt formulation

1. low melting and high boiling

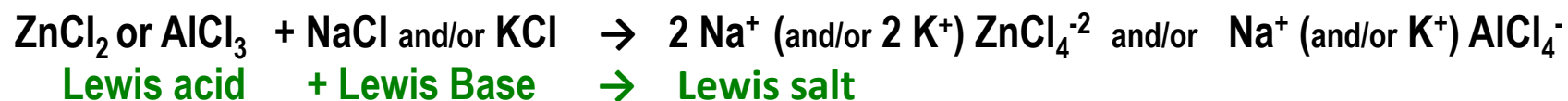
Question: How can you reduce melting point of molten NaCl to use as a heat-transfer fluid???

Answer: **MISMATCH: SIZE and SHAPE and BONDING of positive ion and negative ion to make disorder leading to liquid salt at low temperatures (low m.p.) e.g. AlCl_3 (large covalent tetrahedron) and NaCl (small ionic cube)**

2. Mixing at the molecular level

Question: What drives mixing of covalent and ionic chloride salts at molecular level ?

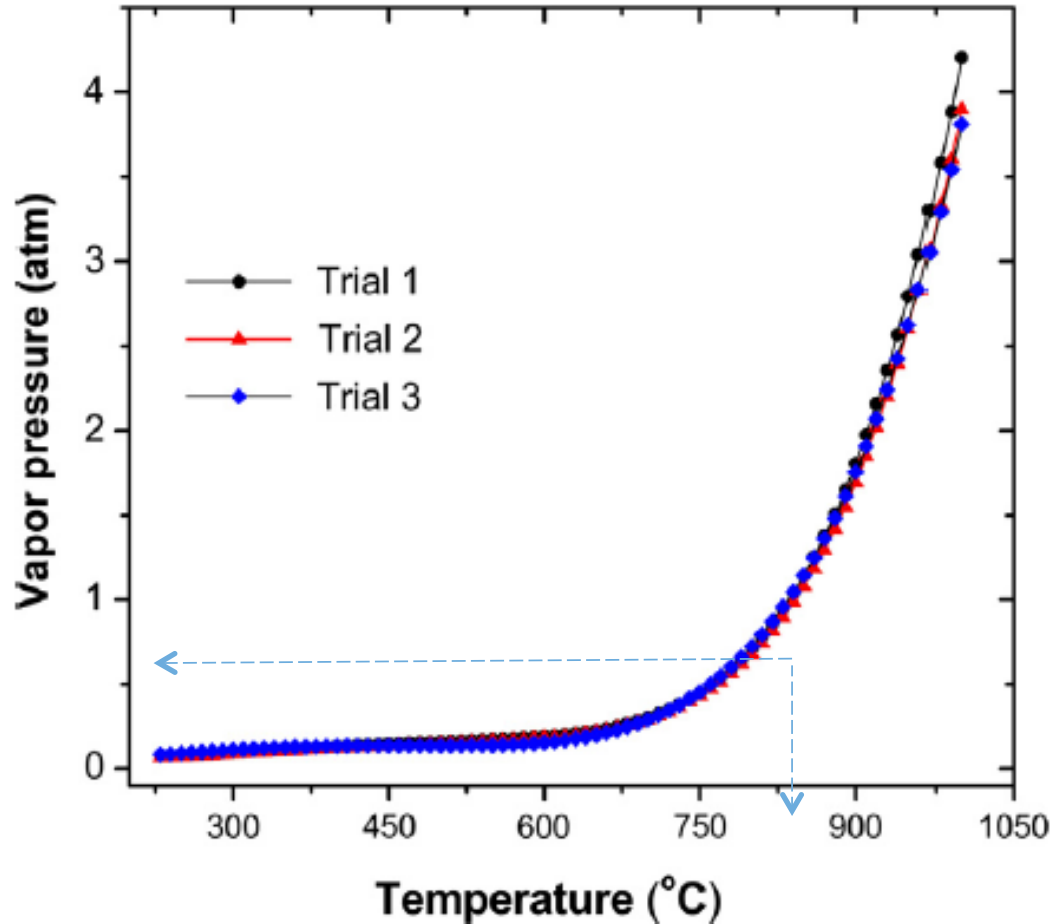
Answer: **Use Lewis acid base chemistry to attract one component to another.**



Physical stability of System

Vapor pressures as a function of temperature for molten NaCl–KCl–ZnCl₂

(13.4–33.7–52.9 mol%) eutectic molten-salt mixture (m.p. = 204°C).



Vapor pressures
for NaCl–KCl–ZnCl₂

Temperature

0.9 atm (13.2 psi)

825°C

**Meets DoE requirement for vapor
pressure < 1 atmosphere at working
temperatures $\geq 800^{\circ}\text{C}$**

What about chemical stability? *Next: stability design rules*

Chemical stability of System

Still another Design Rule, Design rule 3, for Stable Molten Salt HTFs *and* Stable Metal Pipes

3. Stability of *inside* of a metal pipe housing molten chloride salts

Question: How can one have a stable metal container for a molten metal salt ?
Won't the inside corrode??

Answer: Use tables of Standard Reduction Potentials in aqueous electrolytes to choose **metal ions in salt** that are less noble than pipe metal.

$E_{\text{Al, K, Na, Zn, Cr}}$ (**molten salts**) \ll E_{Fe} (stainless, carbon steel) $<$ E_{Ni} (**Hastelloys**)

Less Noble \longrightarrow More Noble

Standard Reduction Potentials, E , of metals *in aqueous electrolytes*

The reduction potentials for species at unit activity in water are useful for guiding selection of non-aqueous molten salt HTFs in metal containers

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TABLE 19.1 Standard Reduction Potentials at 25°C*

Half-Reaction	$E^\circ(\text{V})$
$\text{F}_2(\text{g}) + 2\text{e}^- \longrightarrow 2\text{F}^-(\text{aq})$	+2.87
$\text{O}_3(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{O}_2(\text{g}) + \text{H}_2\text{O}$	+2.07
$\text{Co}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Co}^{2+}(\text{aq})$	+1.82
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow 2\text{H}_2\text{O}$	+1.77
$\text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 2\text{e}^- \longrightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}$	+1.70
$\text{Ce}^{4+}(\text{aq}) + \text{e}^- \longrightarrow \text{Ce}^{3+}(\text{aq})$	+1.61
$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}$	+1.51
$\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \longrightarrow \text{Au}(\text{s})$	+1.50
$\text{Cl}_2(\text{g}) + 2\text{e}^- \longrightarrow 2\text{Cl}^-(\text{aq})$	+1.36
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}$	+1.33
$\text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}$	+1.23
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \longrightarrow 2\text{H}_2\text{O}$	+1.23
$\text{Br}_2(\text{l}) + 2\text{e}^- \longrightarrow 2\text{Br}^-(\text{aq})$	+1.07
$\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^- \longrightarrow \text{NO}(\text{g}) + 2\text{H}_2\text{O}$	+0.96
$2\text{Hg}_2^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Hg}_2^{2+}(\text{aq})$	+0.92
$\text{Hg}_2^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow 2\text{Hg}(\text{l})$	+0.85
$\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}(\text{s})$	+0.80
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{H}_2\text{O}_2(\text{aq})$	+0.68
$\text{MnO}_4^-(\text{aq}) + 2\text{H}_2\text{O} + 3\text{e}^- \longrightarrow \text{MnO}_2(\text{s}) + 4\text{OH}^-(\text{aq})$	+0.59
$\text{I}_2(\text{s}) + 2\text{e}^- \longrightarrow 2\text{I}^-(\text{aq})$	+0.53
$\text{O}_2(\text{g}) + 2\text{H}_2\text{O} + 4\text{e}^- \longrightarrow 4\text{OH}^-(\text{aq})$	+0.40
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cu}(\text{s})$	+0.34
$\text{AgCl}(\text{s}) + \text{e}^- \longrightarrow \text{Ag}(\text{s}) + \text{Cl}^-(\text{aq})$	+0.22
$\text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{SO}_2(\text{g}) + 2\text{H}_2\text{O}$	+0.20
$\text{Cu}^{2+}(\text{aq}) + \text{e}^- \longrightarrow \text{Cu}^+(\text{aq})$	+0.15
$\text{Sn}^{4+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Sn}^{2+}(\text{aq})$	+0.13
$2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{H}_2(\text{g})$	0.00
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Pb}(\text{s})$	-0.13
$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Sn}(\text{s})$	-0.14
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Ni}(\text{s})$	-0.25
$\text{Co}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Co}(\text{s})$	-0.28
$\text{PbSO}_4(\text{s}) + 2\text{e}^- \longrightarrow \text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq})$	-0.31
$\text{Cd}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cd}(\text{s})$	-0.40
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Fe}(\text{s})$	-0.44
$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \longrightarrow \text{Cr}(\text{s})$	-0.74
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Zn}(\text{s})$	-0.76
$2\text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83
$\text{Mn}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Mn}(\text{s})$	-1.18
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \longrightarrow \text{Al}(\text{s})$	-1.66
$\text{Be}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Be}(\text{s})$	-1.85
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Mg}(\text{s})$	-2.37
$\text{Na}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Na}(\text{s})$	-2.71
$\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Ca}(\text{s})$	-2.87
$\text{Sr}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Sr}(\text{s})$	-2.89
$\text{Ba}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Ba}(\text{s})$	-2.90
$\text{K}^+(\text{aq}) + \text{e}^- \longrightarrow \text{K}(\text{s})$	-2.93
$\text{Li}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Li}(\text{s})$	-3.05

Increasing oxidizing strength ↑

Increasing reducing strength ↓

*For all half-reactions the concentration is 1 M for dissolved species and the pressure is 1 atm for gases. These are the standard-state values.

Where do all 3 of these “design rules” lead ??

Materials for collecting solar-thermal power at high temperatures

Useful molten chloride salts

Salt formula	NaCl	KCl	ZnCl ₂	Melting point
Mole percent	13.4 %	33.7 %	52.9 %	204 °C
Salt formula		KCl	MgCl ₂	Melting point
Mole percent		68.0	32	430
Salt formula	NaCl	KCl	MgCl ₂	Melting point
Mole percent	27.5	32.5	40	383

Practical pipe metals: Hastelloy C-276 and Haynes alloy 230

Chemical composition (wt. %)												
alloy	Ni	Cr	Mo	W	Co	Fe	Mn	Si	Al	C	La	B
C-276	57	16	16	4	1	5	1	0.08	-	0.01	-	-
H 230	57	22	2	14	5	3	0.5	0.4	0.3	0.1	0.02	0.015

Determining metal corrosion rate in molten chloride salt

e.g., C-276 Hastelloy pipe metal in molten NaCl-KCl-ZnCl_2

Consider...

Atmospheres equilibrated with molten salt during metal corrosion to 800 C

- Aerobic - salt equilibrated with stagnant air or flowing dry or humidified air
- Anaerobic - salt equilibrated with dry or humidified Argon; stagnant or flowing

Methods for determining Corrosion Rate (CR)

1) Gravimetric - by weighing metal before and after immersion in molten salt

- Reliable standard method, but takes a long time (days to weeks) to do.

2) Electrochemical – by determining corrosion current of metal in salt in 3 electrode cell

- New method, takes a short time (minutes) to do;
- BONUS: gives a basis for a “state of health” (SOH) pipeline sensor.

Gravimetric determination of Corrosion rate (CR)

Procedure

- ~50 cm² of metal ground with SiC paper with 200 to 600 grit
- Degas salt using Ar sparging at 175 SCCM at 500°C for 1 hour
- Immerse metal in 300 gm of degassed salt
- Continue for 50 hours (2 days) at 800°C.

Data analysis

$$CR (\mu m/y) = 365 \times 10^4 \times \frac{\Delta Wt}{\rho \times A \times T}$$

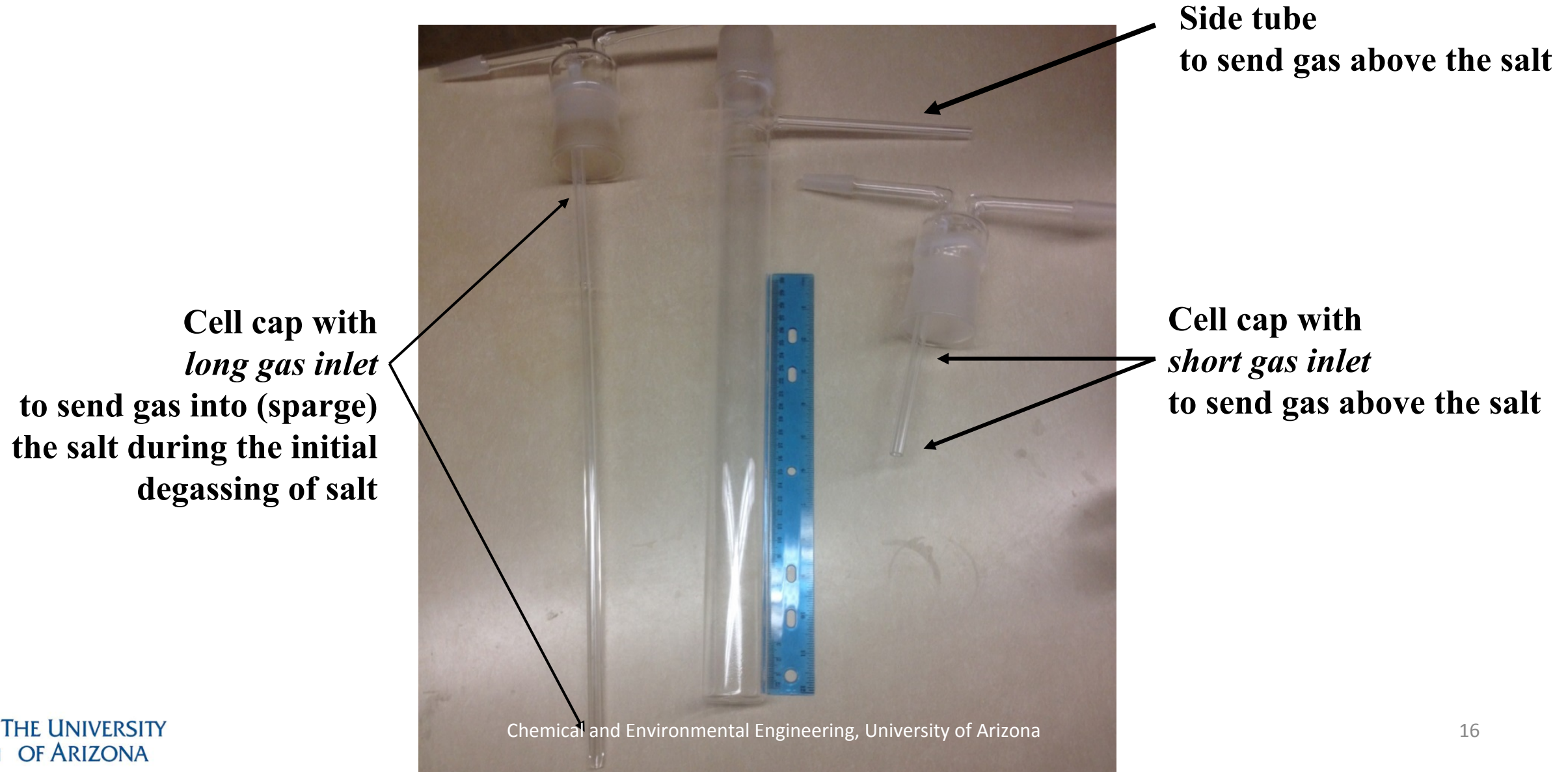
ΔWt is the weight loss in grams

ρ is density (g/cm³) of the Hastelloy

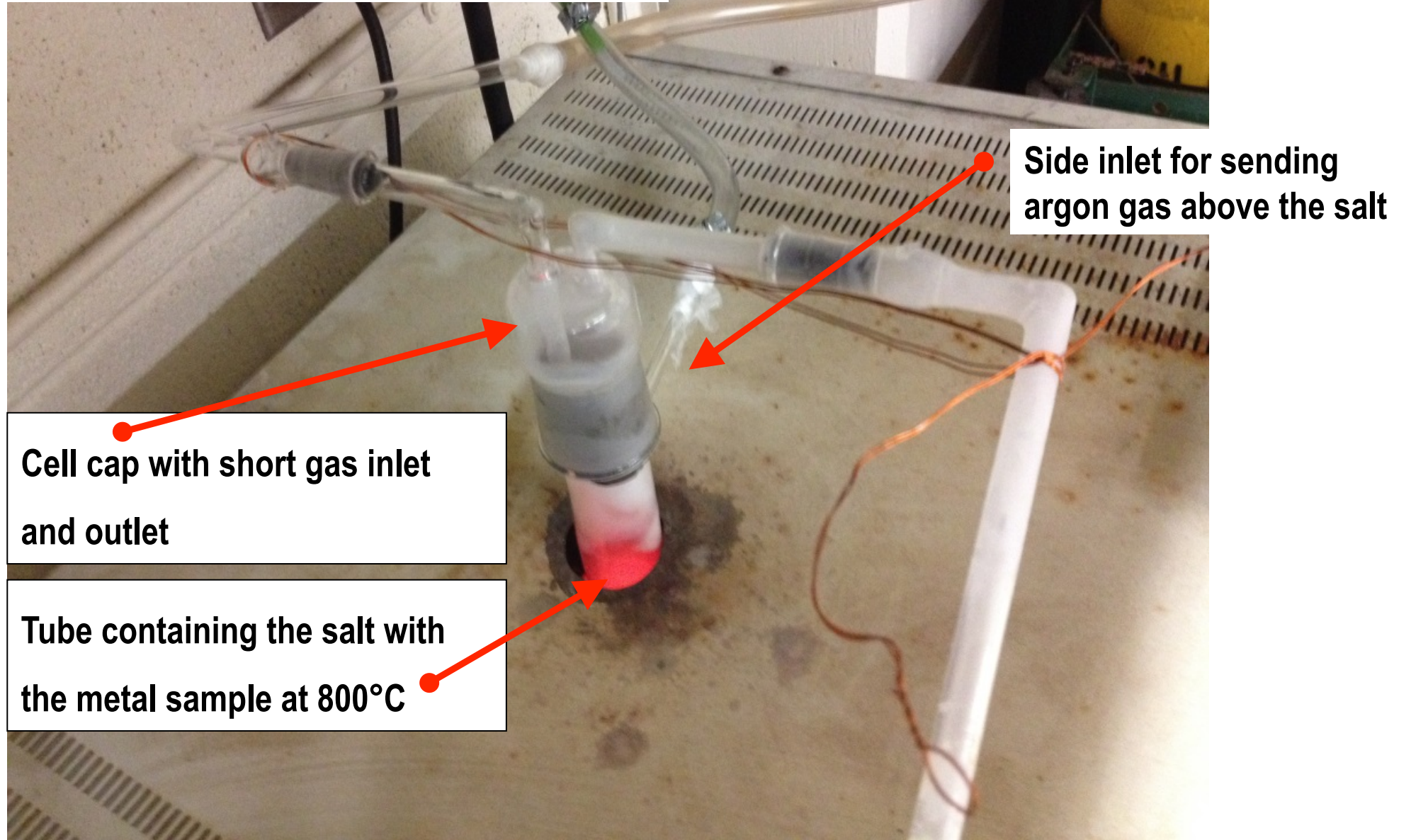
A is the total immersed area in cm²

T is the immersion duration in days

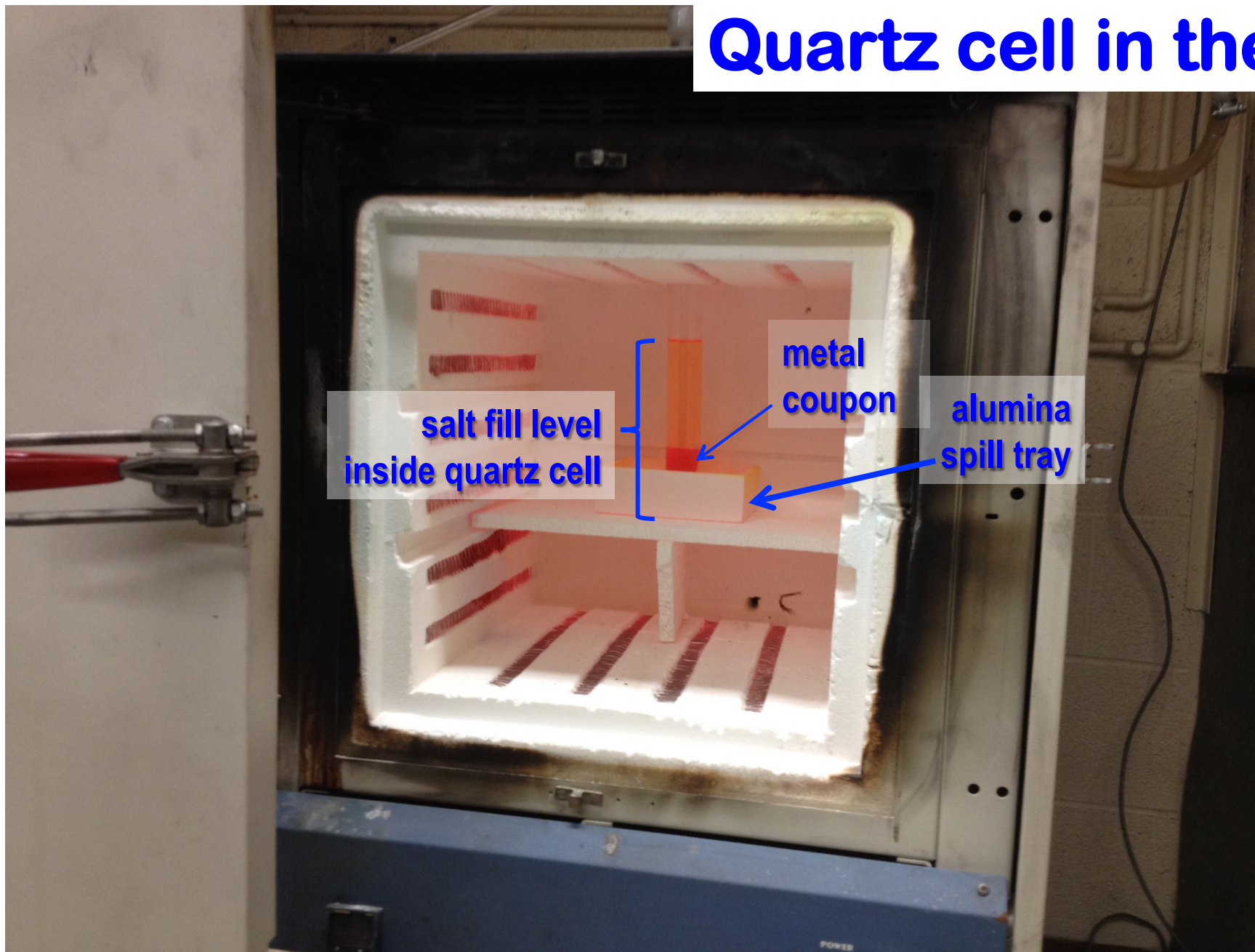
Quartz cell (with two caps) for controlling atmosphere during Gravimetric Corrosion Test



Quartz cell in the furnace



Quartz cell in the furnace

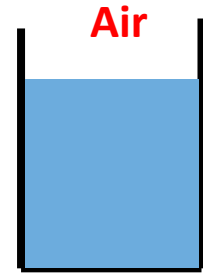


Results of 3 immersion tests

1. Aerobic (cell open to atmospheric air)

Corrosion rate = 1700 $\mu\text{m}/\text{year}$

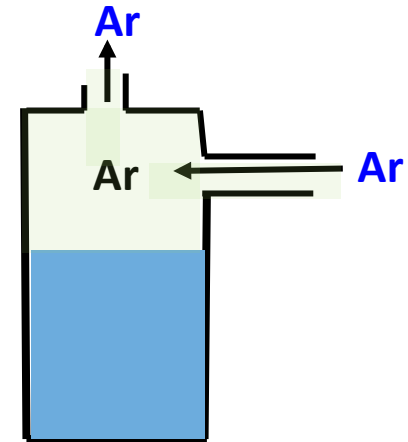
- *high corrosion rate due to high flux of O_2 and water (oxidants) from air into salt at high temperature.*



2. Anaerobic *without* initial degassing

Corrosion rate = 113 $\mu\text{m}/\text{year}$

- *corrosion rate decreased.*
- *lower corrosion rate because Argon blanket cut off air supply (oxidant flux) into salt*
- *CR still greater than 80 $\mu\text{m}/\text{y}$, the DoE target value for CR.*

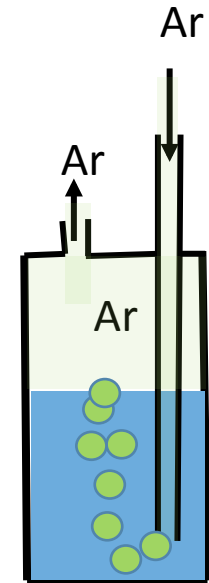


Why so high in anaerobic salt? Pretreatment of salt is a key processing step

3. Anaerobic *with* initial degassing (1h Ar gas sparging at 500°C)

Corrosion rate = 53 $\mu\text{m/y}$

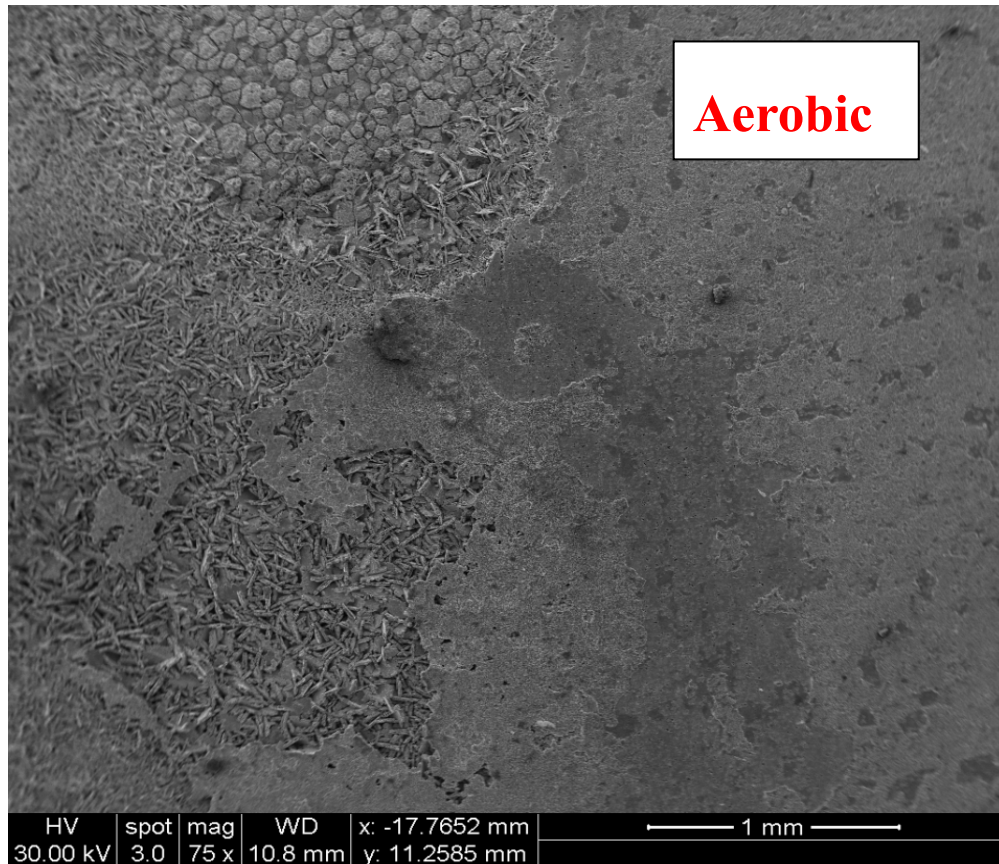
- *Corrosion rate of metal significantly decreased even more with sparging.*
- *CR now lower than the DoE target value ($\leq 80 \mu\text{m/y}$).*
- *Salt was effectively isolated from the atmosphere air.*
- *Air (O_2 and water vapor) in salt was displaced by Argon*
- *Attaining lower metal CR after sparging confirms the convection of the salt during the degassing process effectively removes H_2O and O_2 (the main oxidants from air) from the salt.*



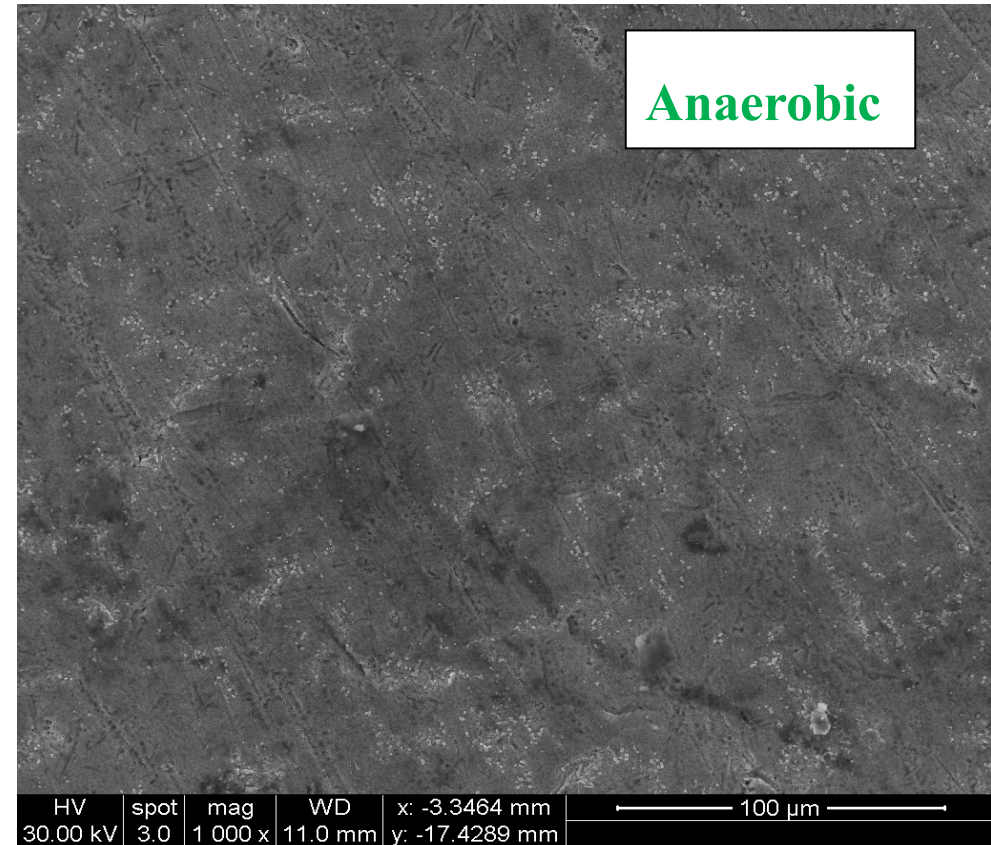
Residual low corrosion due to tightly bound water which is depleted in time with salt inside a sealed pipe

Appearance of metal after exposure

... to **aerobic** and **anaerobic** molten salt at 800°C

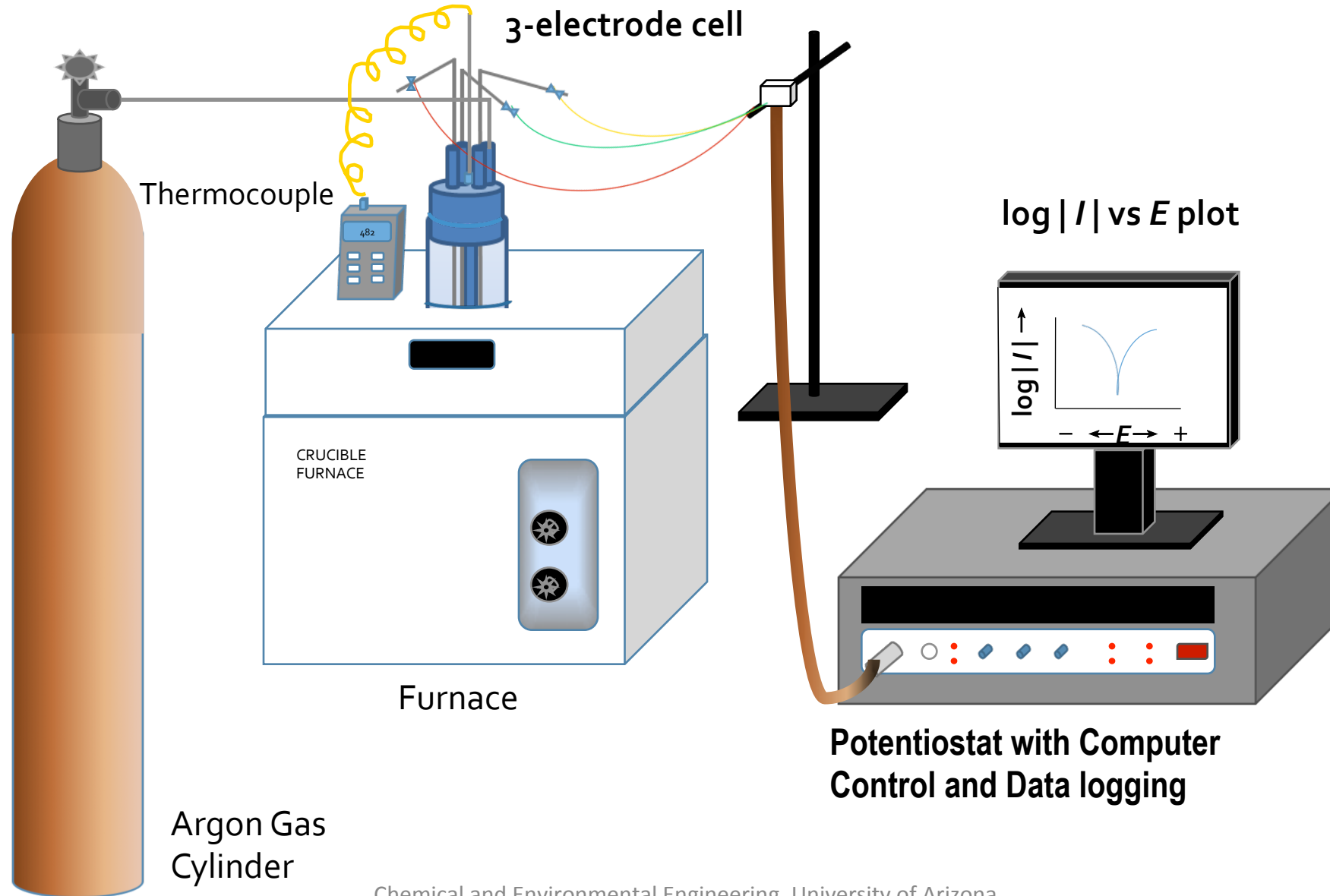


High corrosion rate in aerobic salt
Pitting roughening of the metal surface



Low corrosion rate in anaerobic salt gives uniform
Smooth metal surface

Electrochemical corrosion test setup



Electrochemical determination of corrosion rate (CR)

Non-destructive Stern-Geary polarization test procedure

- *unlike Tafel methods, S-G allows repeated testing of metal sample in salt*

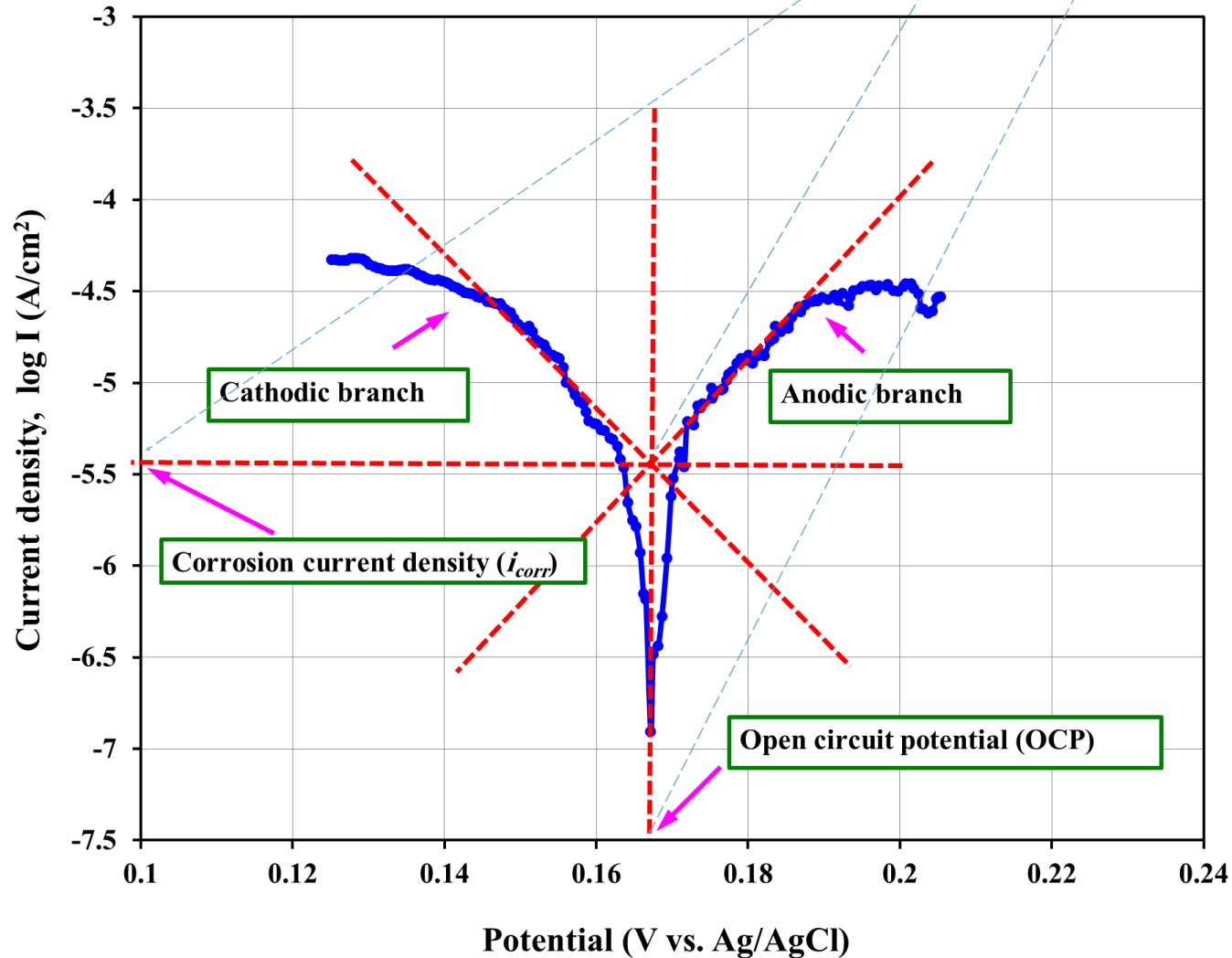
- Metal wet polished to 600 grit with SiC paper
- Salt degassed by Ar sparging at 175 SCCM at 500°C for 1 hour.
- Metal immersed in 150 gm of salt.
- Metal potential scanned from -30 mV vs OCP to +30 mV vs OCP at scan rate 0.2 mV/s
- Potentials were measured vs. Ag/AgCl *reference electrode*.

Analysis of data to find corrosion rate of the C-276 Hastelloy

$$CR (\mu\text{m/y}) = k_1 [i_{\text{corr}} EW / \rho]$$

$$k_1 = 3.27 \text{ in } \mu\text{m g } \mu\text{A}^{-1} \text{ cm}^{-1} \text{ yr}^{-1}$$
$$i_{\text{corr}} = \text{corrosion current density in } \mu\text{A cm}^{-2}$$
$$EW = \text{equivalent weight (27.01 g/eq)}$$
$$\rho = \text{density (8.89 g cm}^{-3}\text{)}$$

Graphical estimation of parameter, i_{corr} at E_{corr} (OCP), needed to find CR



$$CR (\mu m/y) = k_1 \left[\frac{i_{corr} EW}{\rho} \right]$$

where:

$$k_1 = 3.27 \text{ in } \mu m \text{ g } \mu A^{-1} \text{ cm}^{-1} \text{ yr}^{-1}$$

i_{corr} = corrosion current density in $\mu A \text{ cm}^{-2}$

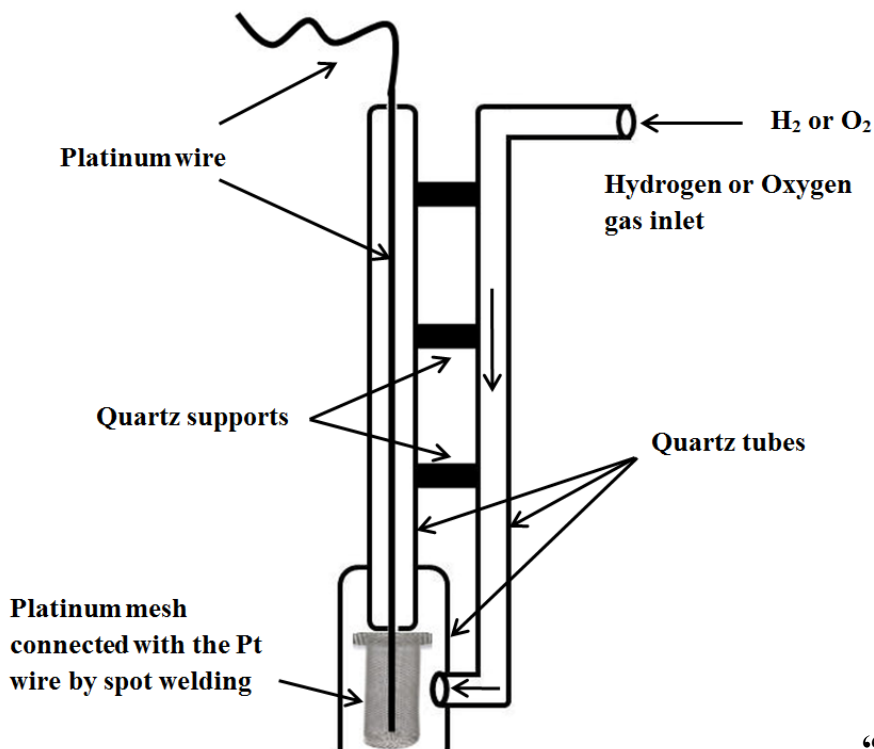
EW = equivalent weight (27.01 g/eq)

ρ = density (8.89 g cm^{-3})

Reference Electrode and Cell for Electrochemical determination of corrosion rates (CR)

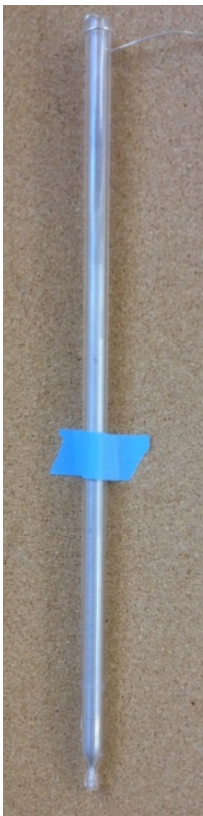
Reversible gas reference electrode

(H₂ or O₂)



According to JJ Lingane, you need 2 reference electrode to have a reference electrode,
... we made 4

Ag/AgCl (SSE)

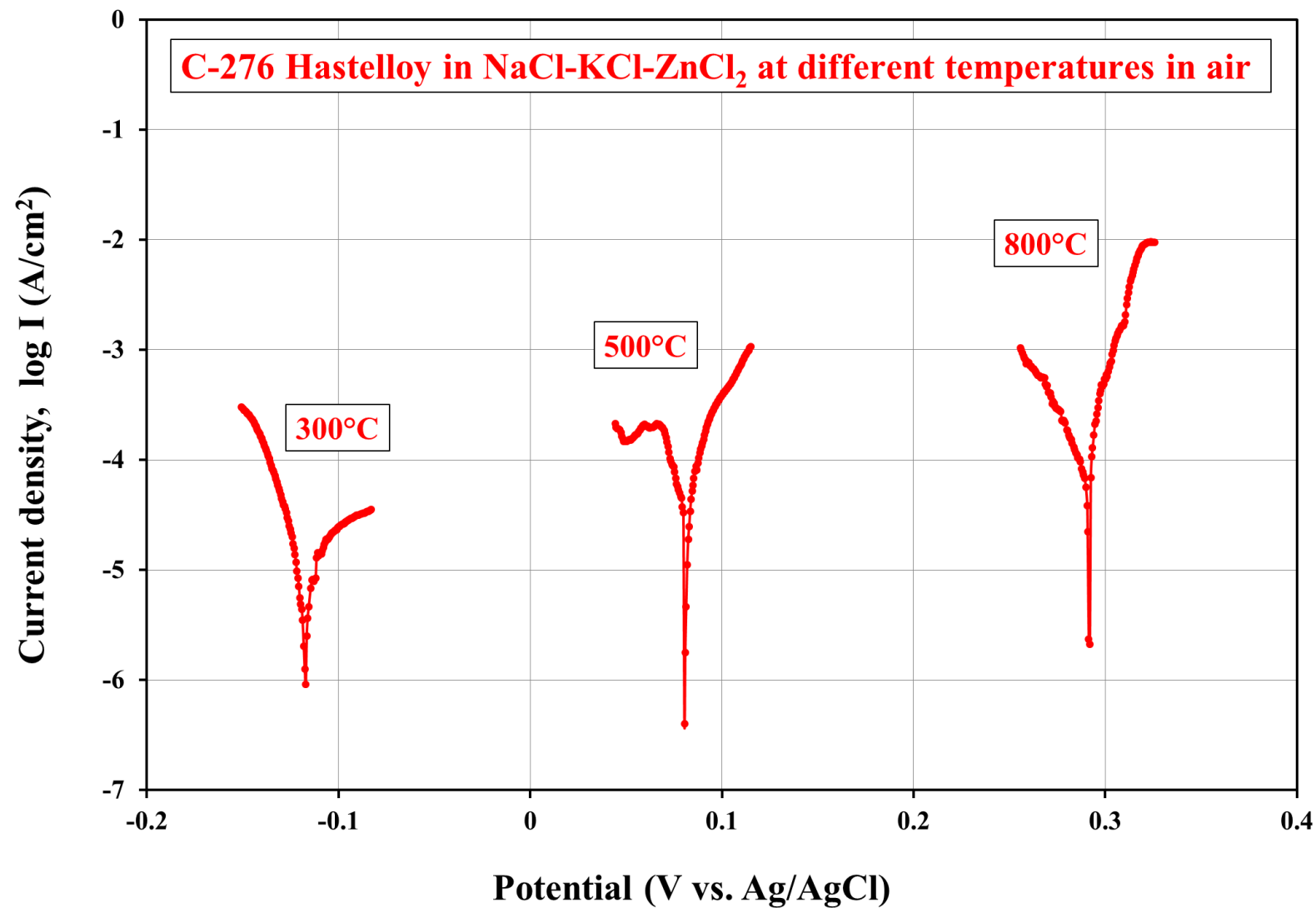


“High Temperature Reference Electrode” (UA 14-043) – Provisional application filed November 23, 2015; non-provisional patent application pending, 2017.

Electrochemical cell



Typical data for finding corrosion rate of metal in salt by Electrochemical method



Corrosion rates for Hastelloy C 276 in ternary Na K Zn chloride salt

equilibrated with aerobic and anaerobic atmospheres & found by the Electrochemical Stern-Geary Method

Temperature (°C) / Atmosphere	Surface area for WE and CE	Corrosion potential, E_{corr} (V)	Corrosion current density, I_{corr} ($\mu\text{A}/\text{cm}^2$)	Corrosion rate, ($\mu\text{m}/\text{y}$)
300 Air	WE=17.5 cm ² CE=27.3 cm ²	-0.115	5	49.7
500 Air	WE=17.5 cm ² CE=27.3 cm ²	0.08	43.6	433
800 Air	WE=17.5 cm ² CE=27.3 cm ²	0.291	240	2380
300 ... Argon	WE=14 cm ² CE=24.5 cm ²	-0.08	0.795	7.89
500 ... Argon	WE=14 cm ² CE=24.5 cm ²	-0.057	1.86	18.5
800 ... Argon	WE=14 cm ² CE=24.5 cm ²	0.166	3.16	31.4

As temperature increases, transport of oxidants, E_{corr} and CR increase.

Echem and gravimetric methods agree CR = 1700 grav = 2380 echem micron per year in air

“Local cell corrosion mechanism” of metal in molten salt

O_2 or H_2O (or both) from air sustain corrosion by accepting electrons from the metal

Anodic reactions in “local cell” corrosion



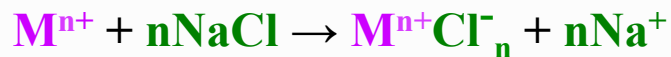
Cathodic reactions in “local cell”



and/or

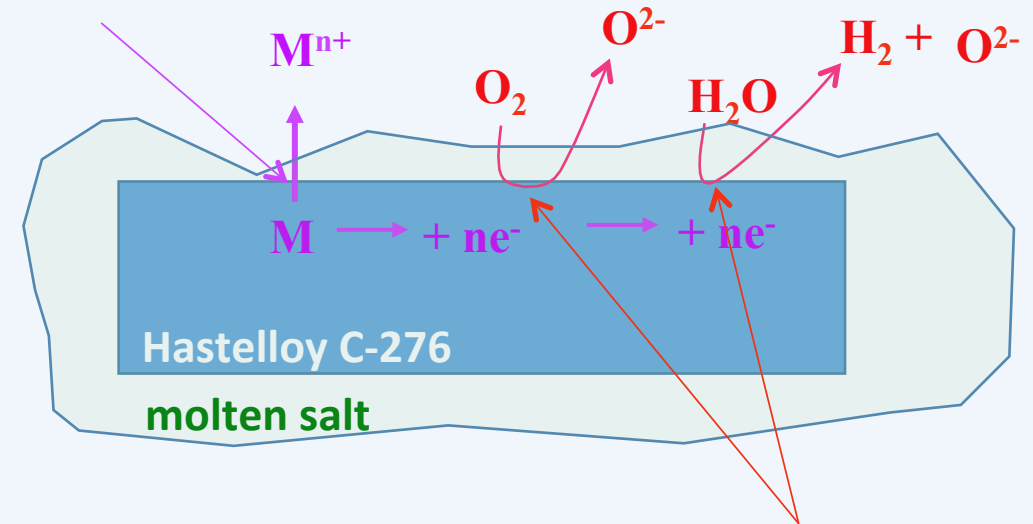


Charge balance reactions in molten chloride salt Na-K-Zn- Cl_4



Schematic diagram of “local cell” mechanism

Local anode site

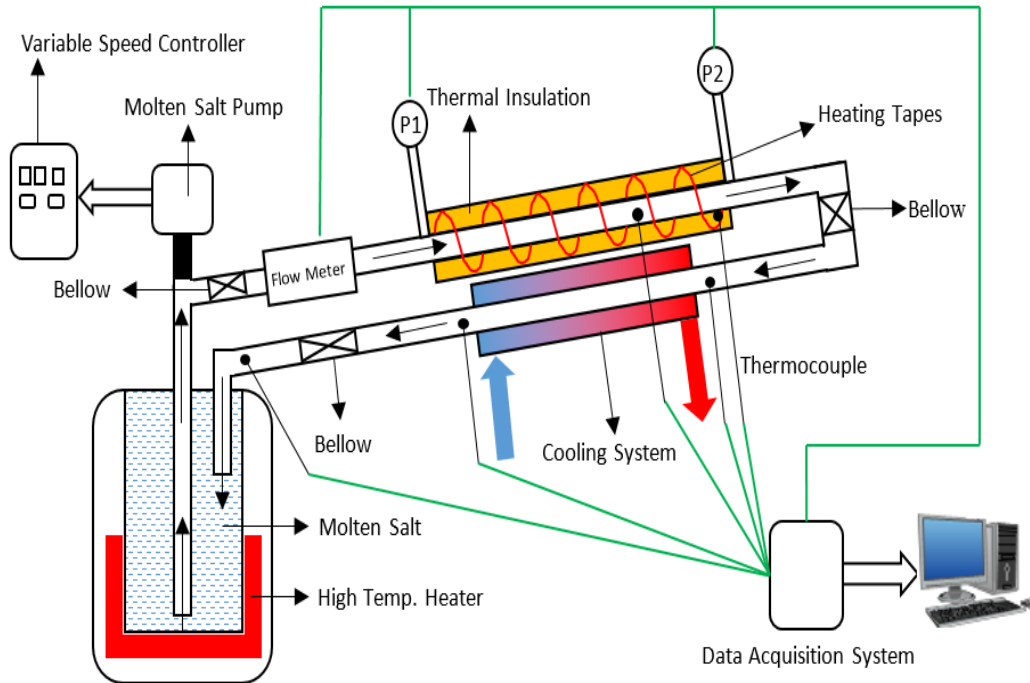


Local cathode sites

Molten chloride salt in Haynes alloy being built and tested

in lab of Prof. Perry Li of the Mechanical ENGINEERING Department at University of Arizona

Heat transfer fluid test loop ...



...under construction at the University of Arizona



Conclusions about molten chloride salt and CSP

- Mixed chloride salt are low melting, high boiling liquid heat transfer fluid HTFs for solar-thermal-electrical power
 - inexpensive (<\$1 per kilogram) and show
 - good thermal properties (heat capacity, heat transfer coefficient) and
 - good physical properties (melting point, vapor pressure, viscosity, density) as required by industry
- Corrosion of metals in molten salt is a key issue.
 - gravimetric and electrochemical methods similar corrosion rates under an inert atmosphere
 - Corrosion rates are < 60 micron per year for Haynes 230 and C-276, as required
 - Corrosion of metal in chloride molten salt is due to the presence of water and oxygen in the salt
 - Heating and bubbling dry inert (N_2 or Ar) gas into molten salt stops corrosion by dehumidifying and deoxygenating salt.

In conclusion, molten chloride salt give useful heat transfer fluids for two attractive applications:

- 1) CSP systems for electrical power generation and storage**
- 2) as coolant in next-generation nuclear (thorium) reactors for electrical power generation.**

Applications of Chloride molten salts

Abundant, inexpensive chloride salt materials were designed and have been validated as a route to low-cost, highly efficient, high temperature ($> 800^{\circ}\text{C}$) solar-thermal-driven electrical power generator that is clean, sustainable and with no need for *water*!

Other uses of chloride molten salts ... chemical processing

- Extraction and deposition of metals
- Fabricating low cost photovoltaics
- Advanced batteries and fuel cell
- Hydrogen generation and storage of renewable powers: solar, wind, etc.

To hear about other uses please come back Thursday...

“Chemical Processing in Molten Salts” by D. Gervasio

10:00 to 10:30, Thursday, September 23, 2017

In Energy Transformation and Storage Session

Chairs: Dominic Gervasio and Koichi Yamashita

Acknowledgements for CPR work

U.S. DoE Sunshot

Levi Irwin, Technical Monitor



Thank you for your attention

Low cost photovoltaics by Si electroplating

Different eutectic molten-salt materials

1.Salt #A1: 36 NaCl–14 KCl–50 AlCl₃ (mol%) : mp = 132 C

2.Salt #A2: 26.25 NaCl–15 KCl–58.75 AlCl₃ (mol%) : mp = 91 C

May also be useful heat transfer fluids but are at the same time potentially valuable electrolytes for electrodeposition of ultra high purity silico

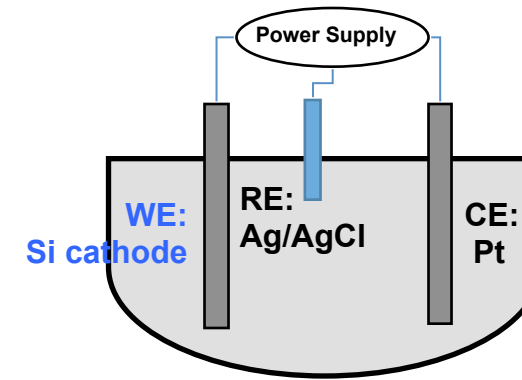
Si Electroplating vs. conventional Si processing

Motivation for electroplating Silicon

it's a cleaner, lower energy and more versatile alternative to conventional Si processing

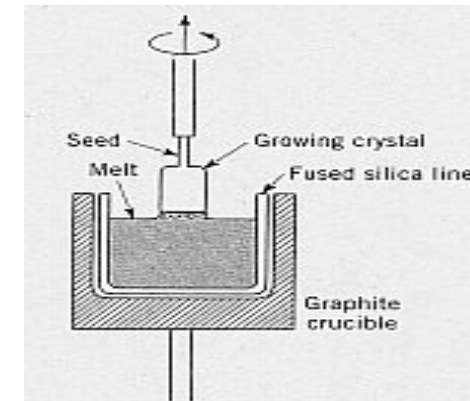
❑ Electroplating Si from Ionic Liquid

- Simple process to make complex structures
- Can plate doped Si
- Relatively low T process (< 120°C)
- Environmentally friendly (no VOCs)
- Relatively low cost



❑ Silicon production from Si-wafer processing

- **High temperature, Energy Intensive process**
 - React sand w/ Zn metal (950°C) OR
 - CVD on pure Si rod (1150°C)
 - Purified material melted down (1414°C), Czochralski process
- **Complex processes to make structures in wafer**
 - Si wafer prep.: Wafer sliced, lapped, polished, masked, etched, etc.
 - High temp process, Doping, annealing, oxide growth, etc.
- **Hazardous waste and process fluids (HF, SiH₄)**
- **High cost**



Rationale for electrodeposition from ionic liquids and molten salts

Why use non-aqueous salt electrolytes for Si electroplating?

It is really the only option because ...

Metals spontaneously react with molecular water in aqueous electrolytes.

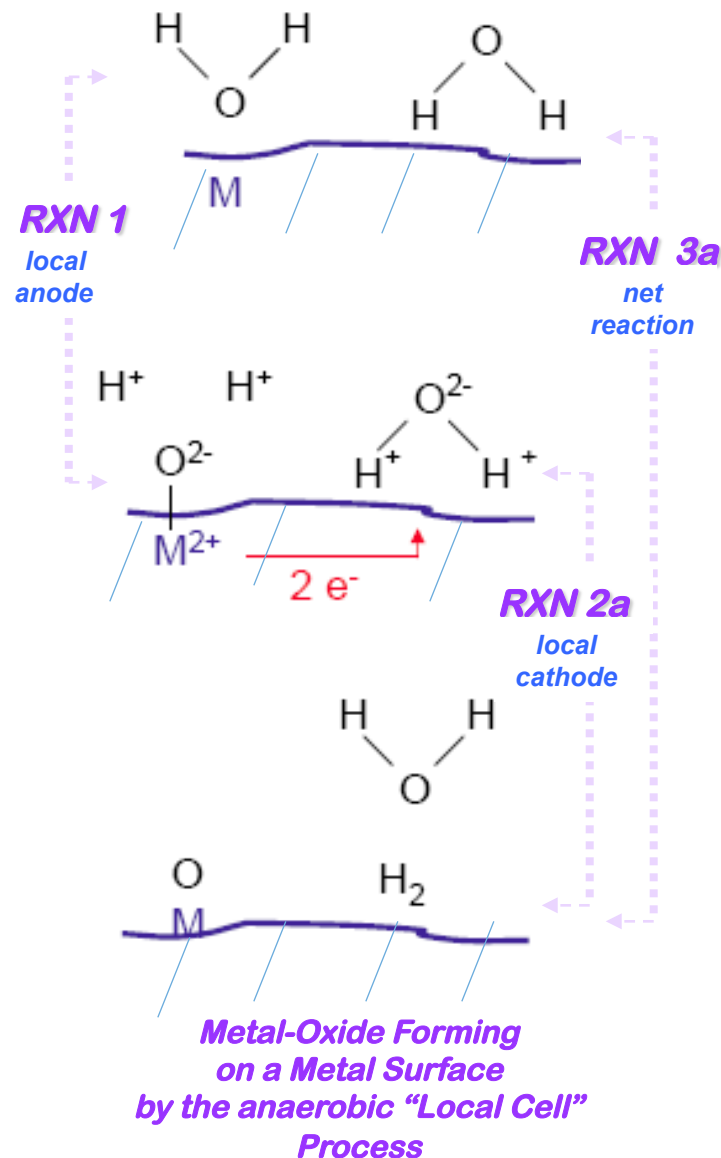
The driving force to form a metal-oxide from a metal in the presence of water is the heat of formation (ΔH^f) of the metal oxide

	<u>Metal Oxide</u>	<u>$\Delta H^{\text{formation}}$ (calories/gram)</u>
<i>reactive metals</i>	aluminum oxide (Al_2O_3)	- 4000 (= -1676 kJ/mole)
	silicon dioxide (SiO_2)	- 3418
<i>unreactive metals</i>	copper oxide (Cu_2O)	- 278
	platinum oxide (PtO_2)	- 84 (= -80 kJ/mole)
	gold oxide (Au_2O)	> 0 (Au-oxide unstable)

In aqueous electrolytes, metal forms metal-oxide by the “Local Cell” process, which

- prohibits the smelting of a “reactive” metal, e.g., aluminum, in air
- even interferes with catalysis by an “unreactive” noble metal, platinum

The “Local Cell” Process

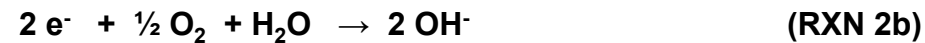
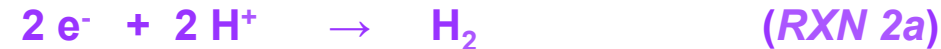


Shows how water is corrosive

- Water (H₂O) reacts with a reactive metal (M), like aluminum or silicon, forming undesirable metal oxide (MO) as .



- The liberated electrons are consumed by proton to form hydrogen (reaction 2a). e⁻ can be consumed by oxygen to form water (reaction 2b).



- Adding reaction 1 with reaction 2a (or reaction 2b) gives the net undesirable metal oxide formation reaction, reaction 3a (or reaction 3b) .



METAL-OXIDE (MO) FORMATION (RXN 3a) occurs in the presence of WATER even in anaerobic environments because the electron (e⁻) is more stable on H⁺ than on the reactive metal (M).

Similarly, in the presence of oxygen from air, RXN 3b occurs because e⁻ is more stable on O₂ than M.

Requirements of Electrolytes For Plating Active Metals

CONDUCTIVITY

- Conductor for ions, Ionic Conductivity $> 10^{-2}$ Siemen/cm
- Insulator for electrons, Electron Conductivity $< 10^{-9}$ Siemen/cm

COMPATIBILITY WITH ELECTROPLATING OF ACTIVE METALS

- No water, no passive layer (metal oxide, “tar”) formation

STABILITY

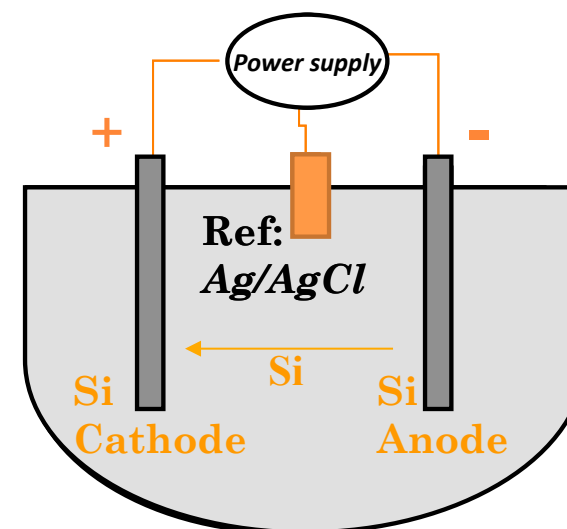
- Stable to electric field; no reaction with products

All electrolyte properties accessible by *tailoring* the ionic liquid

For example, Abedin, S. Z. et al., “**Electrodeposition of Metals and Semiconductors in Air- and Water-Stable Ionic Liquids**”, Chemphyschem [2006] **7**, 58-61

Silicon Plating from Ionic Liquid Electrolyte

- Ionic liquid electrolyte: RCl (n-butylpyridinium chloride) and silicon (SiCl_4 , NaSiF_6 , SiHCl_3 , or Si_2Cl_6).
- Reactions
 - IL Rxn with Si: $2 \text{R}^+ \text{Cl}^- + \text{Si}_2\text{Cl}_6 \rightarrow 2 \text{R}^+ \text{SiCl}_4^-$
 - Cathode Rxn: $\text{R}^+ \text{SiCl}_4^- + 3 \text{e}^- \rightarrow \text{Si} + \text{R}^+ \text{Cl}^- + 3 \text{Cl}^-$
 - Anode Rxn: $\text{Si} + \text{R}^+ \text{Cl}^- + 3 \text{Cl}^- \rightarrow \text{R}^+ \text{SiCl}_4^- + 3 \text{e}^-$
 - Net Rxn: *Transfer of Si from anode to cathode*
- 3 electrode cell
 - Cathode, reference (Ag/AgCl), anode
 - RT to 120°C operating temp (avoid water)
 - Inert gas purge

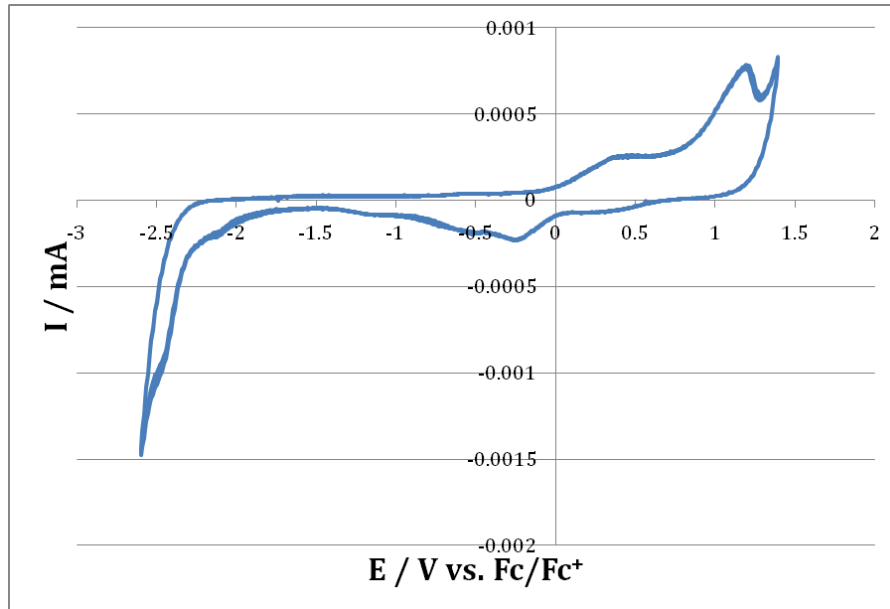


N. Borisenko et al., "In Situ STM Investigation of Gold Reconstruction and of Silicon Electrodeposition on Au(111) in the Room Temperature Ionic Liquid 1-Butyl-1-methylpyrrolidinium Bis(trifluoromethylsulfonyl)imide", J. Phys. Chem. B 2006, 110, 6250-6256

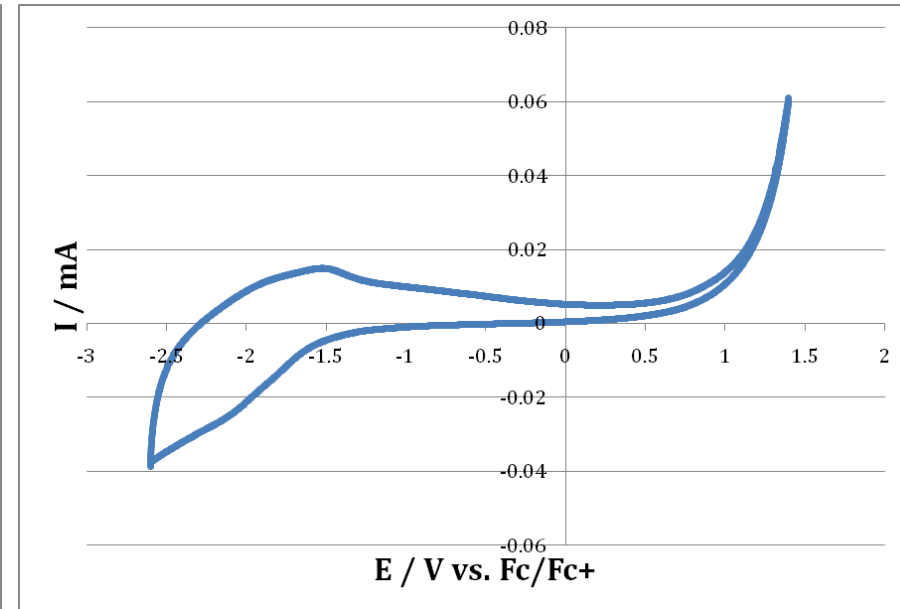
Abedin, S. Z. et al., "Electrodeposition of Metals and Semiconductors in Air- and Water-Stable Ionic Liquids", Chemphyschem [2006] 7, 58-61

Silicon plating on Metal

Electrodeposition of silicon on titanium in a room temperature ionic liquid: butyl, 3-methylimidazolium chloride, [Bmim] BF₄

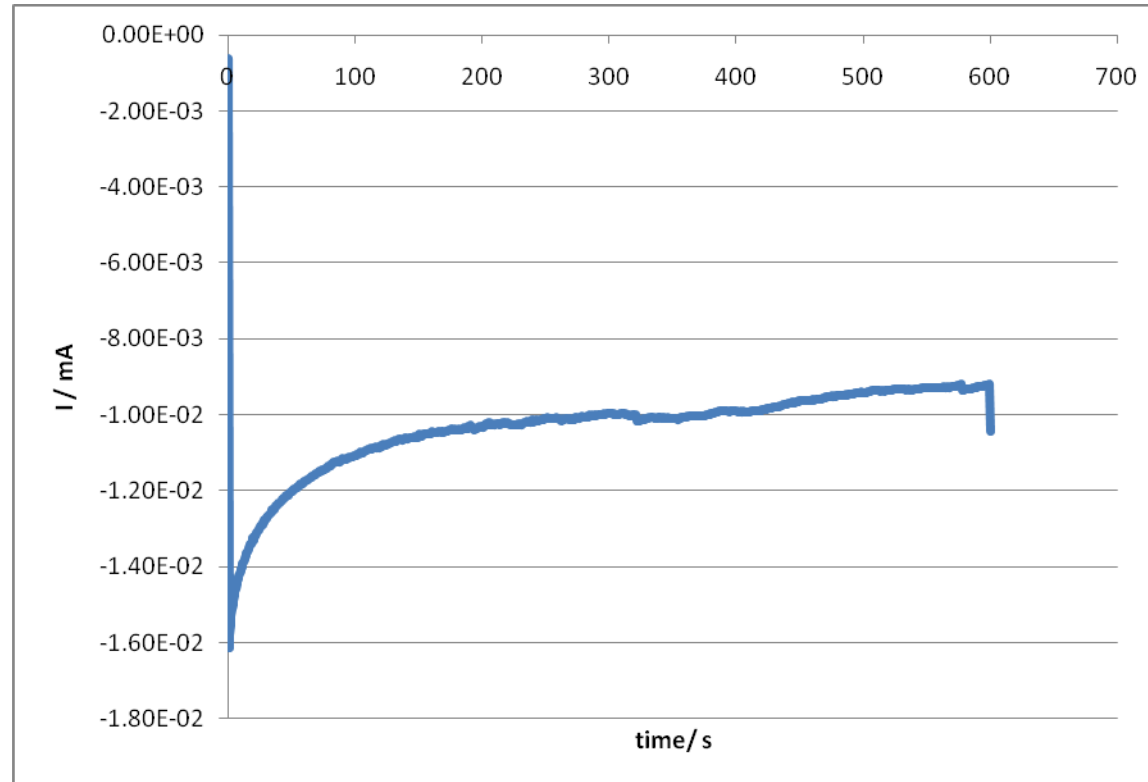


Cyclic voltammogram of titanium in [Bmim]BF₄ with ferrocene but no SiCl₄ under N₂ atmosphere. Scan rate: 10mV/s. Temperature: 25°C.



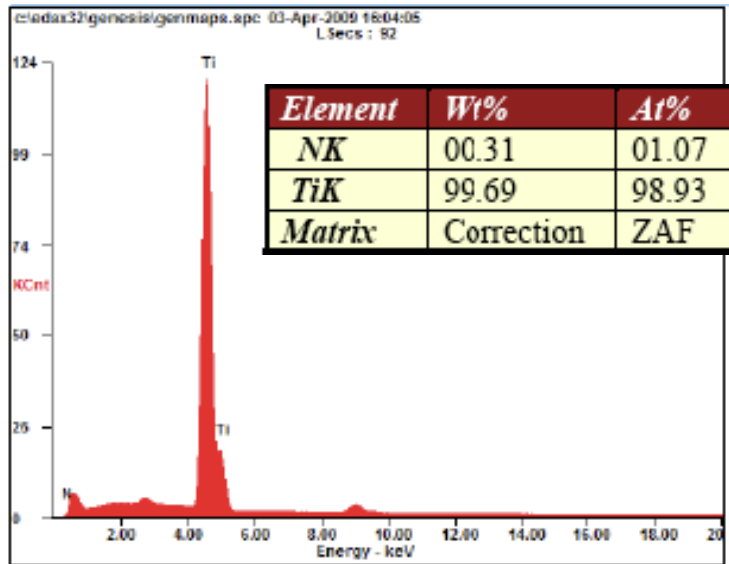
Cyclic voltammogram of titanium in [Bmim]BF₄ saturated with SiCl₄ under N₂ atmosphere. Scan rate: 10mV/s. Temperature: 25°C.

Electroplating of Si on titanium metal at constant potential

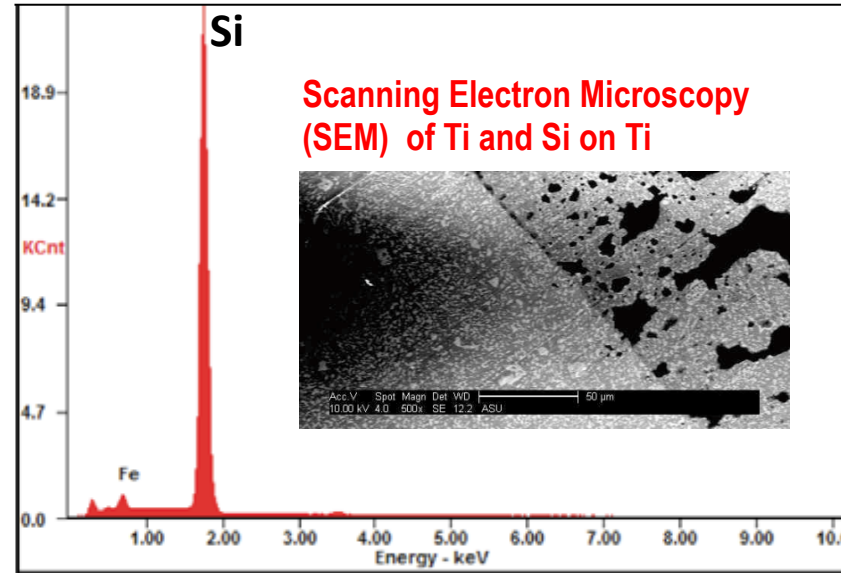


Chronoamperometry of titanium metal in [Bmim]BF₄ electrolyte saturated with SiCl₄ at constant potential of -2.0 V vs. Fc/Fc⁺ under a N₂ atmosphere at a temperature of 25°C.

Energy Dispersive Absorption of X-rays (EDAX) Analysis of Silicon on Titanium



**EDX for the Ti sample
before Si electrodeposition**



**EDX for the Ti sample with Si deposited
at -2.0V for 10 minutes**

Cost versus Efficiency Tradeoff

Thick Film
Large Grain

Single
Crystal Si

CVD Si



d

Long d
Requires High τ

High Cost

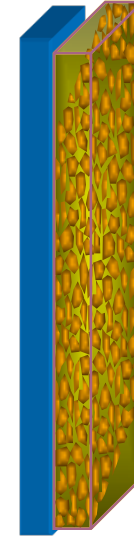
Efficiency per length $\propto \tau^{1/2}$
(where τ is hole-electron pair
recombination time)



Thin Film
Small Grain

Polycrystalline
Solids

Electroplated Si



d

Short d
Allows Lower τ

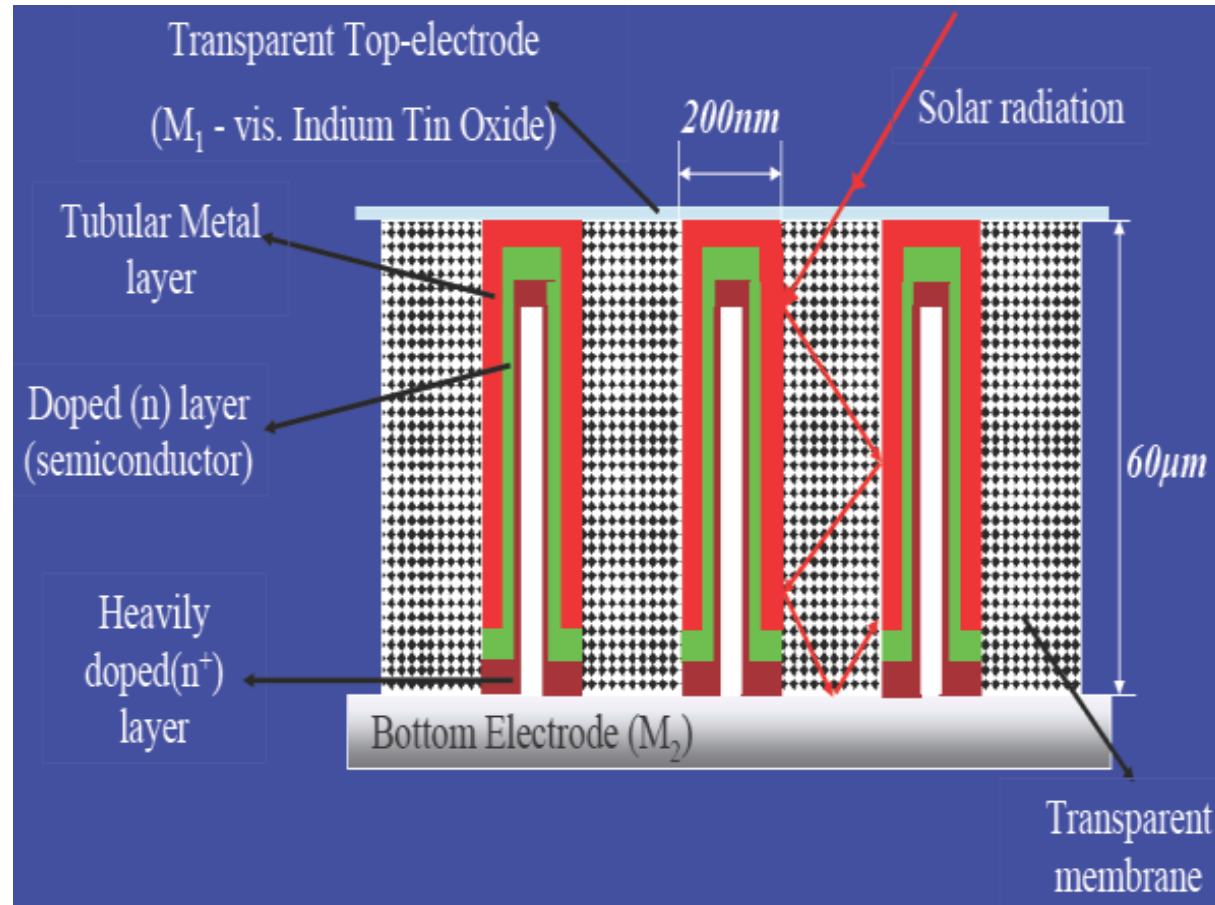
Low Cost

***Thin electrodeposited Si films allow high efficiency with low τ
lead to low cost !***

"RADIAL PN JUNCTION, WIRE ARRAY SOLAR CELLS", B. M. Kayes, M. A. Filler, M. D. Henry, J. R. Maiolo III, M. D. Kelzenberg, M. C. Putnam, J. M. Spurgeon, K. E. Plass, A. Scherer, N. S. Lewis, H. A. Atwater California Institute of Technology, Pasadena, CA 91125

Versatility of electroplating Si : *Photovoltaics*

ELECTROPLATING allows forming *complex Si structures* at low temperatures
This is almost **IMPOSSIBLE** to make using **CONVENTIONAL Si PROCESSING**



e.g., Vertically oriented nano-structured Schottky diodes

Conclusions about Si plating

- ❑ **Electrochemical conversion in salt electrolytes avoids water and gives a low cost and clean manufacturing process for making thin layers of semiconducting silicon**
 - photovoltaics on a small (<1 Watt) to large (1 Mega W) scale
 - TFTs for displays, power chips etc.
- ❑ **Electroplating in nanoporous substrates allows mass manufacture of practical and inexpensive semiconducting silicon devices**
 - TFTs
 - Photovoltaics (nano Schottky diode array)

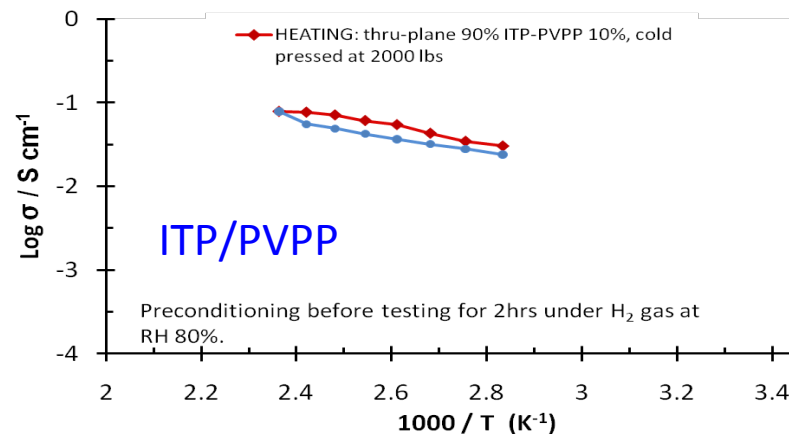
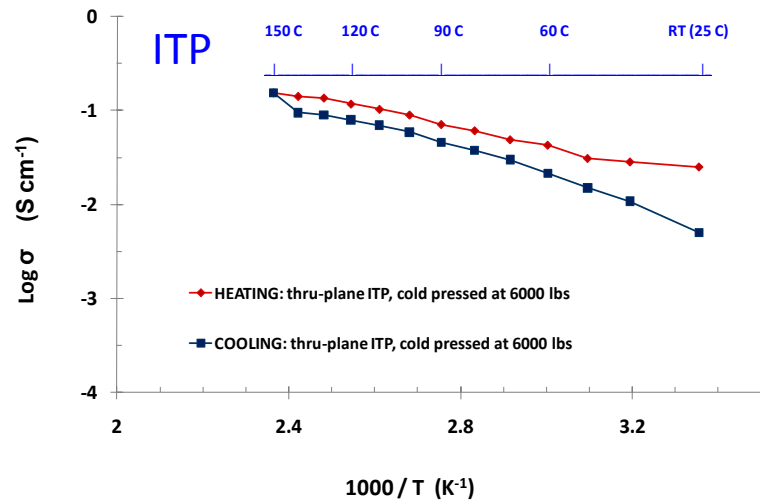
A hybrid photovoltaic-capacitor device electrodeposited within the same monolithic structure that is stable to chemical, thermal and radiation exposures

- overcomes stability problems in grid due to intermittencies (sub-second to minutes) intrinsic with solar derived power
- stores energy to give power when solar generator is not on for long times (hours...when sun is not out)
- provides a renewable power-source
- can provide grid power or autonomous power in remote locations.

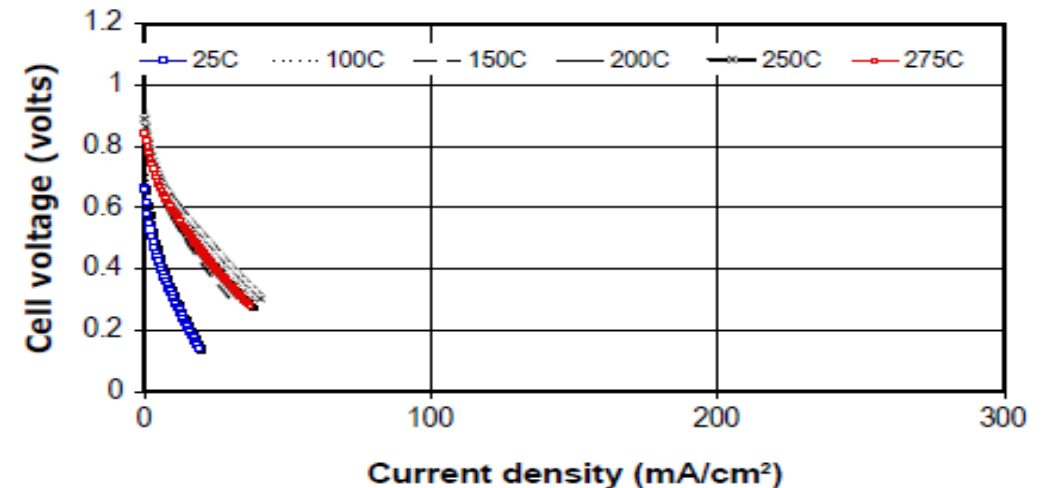
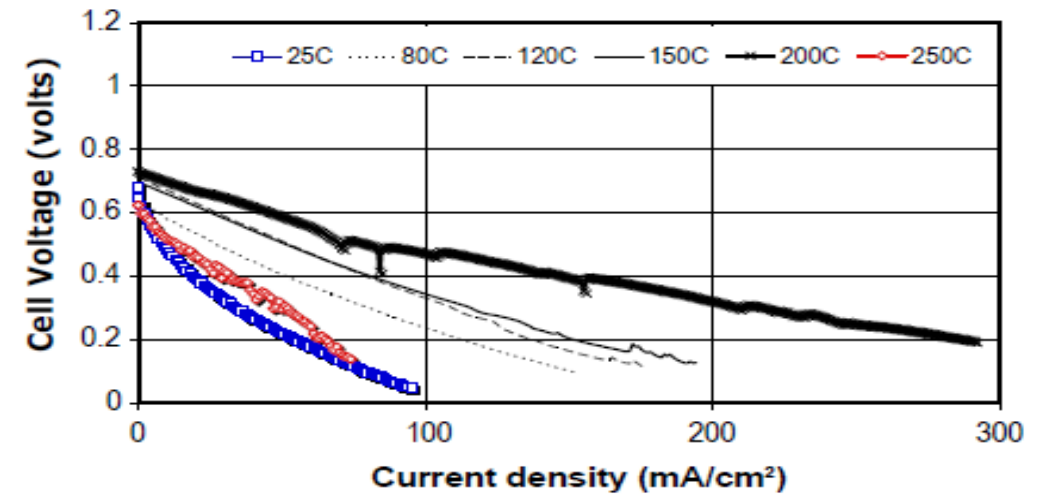
- Storage of electrical energy as hydrogen
- Fuel cell for power generation of stored hydroge

A suitable proton conducting membrane is the key

Inorganic and organic composition polymer electrolyte membrane (PEM)



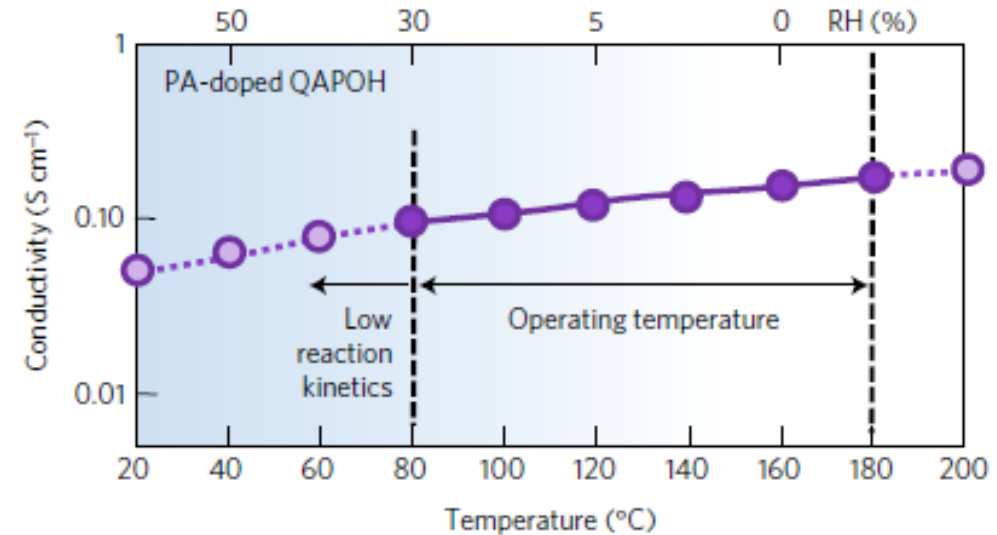
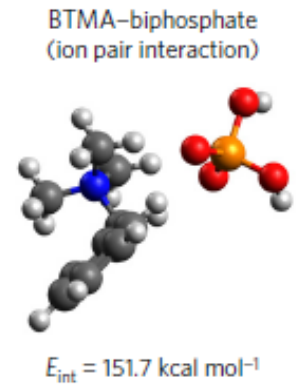
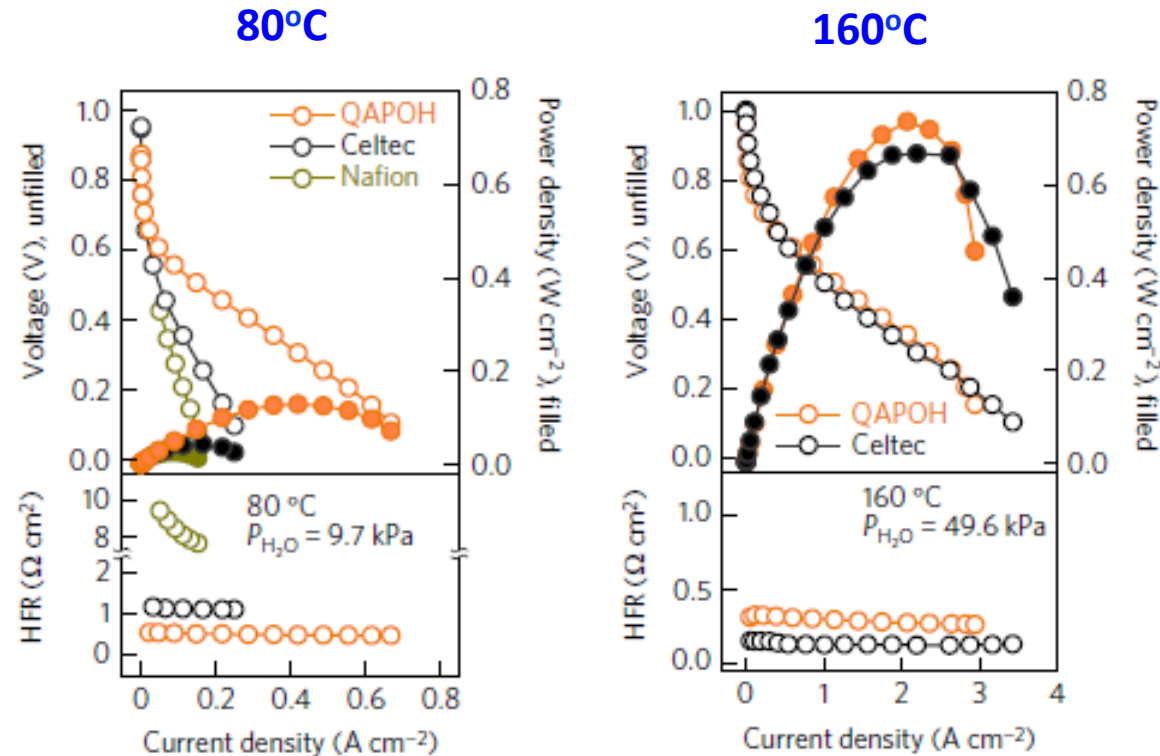
Through-plane conductivity of a pure ITP (top) and 90%ITP/10%PVPP (bottom) membrane with electrodes under dry hydrogen atmosphere. Membrane thickness = 1.65mm, and area = 0.484 cm^2 . Frequency range: 50 kHz to 10 Hz. AC amplitude: 50mV. Thickness of sputtered Pt el= 20nm. ETEK electrodes (0.5 mg of Pt per cm^2) used as gas diffusion layer. Pt screen current collectors. J4 ITP membrane.



H_2 / O_2 Fuel cells made with a pure ITP membrane (top) and a membrane with an 90% ITP/ 10% PVPP blend (bottom). ETEK electrodes (0.5 mg of Pt per cm^2) used as gas diffusion layer. Pt screen current collectors.

HT PEM Fuel cell based on quaternary ammonium-biphosphate ion pairs

Cy Fujimoto (Sandia National Lab) and Yu Seung Kim (LosAlamos National Lab)



Fuel cell performance

Unlike phosphoric acid (PA) loaded PBI the phosphoric acid does NOT wash out of PA loaded benzyltrimethylammonium (BTMA) groups on a polyphenylene backbone membrane. This quaternary ammonium (QA) group on polyphenylene backbone reacted with phosphoric acid gives a new class of stable PEM fuel cell that can operate at low temperatures and retain phosphate even when water wet and has high conductivity and fuel cell performance at high temperatures to 180°C.

Proton Conductivity of PA-doped QAPOH PEM fuel membrane

Some markets for HT-PEMFC technology:

1. micro-CHP (emergency and off-grid residential electricity and heat)
2. power production (distributed generation)
3. portable power (automotive)
4. hydrogen generation, separation (electrolysis of water)
5. Hydrogen storage (electrochemical hydrogen compression)
6. electrical power *inside* airplanes
7. remote communications stations and battery chargers
8. Storage of renewables, like solar during sundown, wind during calm, etc. by electrolysis of water

Too much for now...a topic for another time!

Acknowledgements



U.S. DoESunshot
Levi Irwin, Technical Monitor

Edson Foundation

Army Research Office,
ARO Project No. W911-NF-04-1-0060
Dr. Robert Mantz, Project Monitor



NASA-Glen
NASA Project No. NC04GB06G
Dr. James Kinder, Project Monitor



U. S. Department of Energy
DoE Project No. DE-FG36-06G016029
Drs. Kathi Epping, Gregory Kleen Project Managers

and

Boeing

Drs. Joanna Moore, James Kinder and Jean-Phillipe Belieres
Project Monitors



Thank you for your attention