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* (800°C)

- 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.”
<table>
<thead>
<tr>
<th>Property</th>
<th>Target</th>
<th>Stretch Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Stability (liquid)</td>
<td>≥ 800 °C</td>
<td>= 1300 °C</td>
</tr>
<tr>
<td>Melting Point</td>
<td>≤ 250 °C</td>
<td>≤ 0 °C</td>
</tr>
<tr>
<td>Heat Capacity</td>
<td>≥ 1.5 J/g/K</td>
<td>≥ 3.75 J/g/K</td>
</tr>
<tr>
<td>Vapor Pressure</td>
<td>≤ 1 atm</td>
<td></td>
</tr>
<tr>
<td>Viscosity</td>
<td>≤ 0.012 Pa-s @ 300 °C;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>≤ 0.004 Pa-s @ 600 °C</td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>≤ 6,000 kg/m³ @ 300 °C;</td>
<td>≤ 5,400 kg/m³ @ 600 °C</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>≥ 0.51 W/m/K @ 300 °C;</td>
<td>≥ 0.58 W/m/K @ 600 °C</td>
</tr>
<tr>
<td>Pipes and container</td>
<td>Corrosion rate &lt;100 µm/year</td>
<td></td>
</tr>
<tr>
<td>materials compatibility</td>
<td>Metals carbon steel (&lt;425 °C), Stainless Steel (&lt;650 °C) and Nickel alloys (850 °C).</td>
<td></td>
</tr>
<tr>
<td>Materials Cost</td>
<td>≤ $1 / kg</td>
<td></td>
</tr>
</tbody>
</table>

*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°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. AlCl3 (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.**

   \[
   \text{ZnCl}_2 \text{ or AlCl}_3 \ + \ NaCl \ 	ext{and/or KCl} \ \rightarrow \ 2 \ Na^+ (\text{and/or } 2 \ K^+) \ ZnCl_4^{-2} \ 	ext{and/or Na}^+ (\text{and/or } K^+) \ AlCl_4^{-} \\
   \text{Lewis acid} \ + \ \text{Lewis Base} \ \rightarrow \ \text{Lewis salt}
   \]
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

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Vapor pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>825°C</td>
<td>0.9 atm (13.2 psi)</td>
</tr>
</tbody>
</table>

Meets DoE requirement for vapor pressure < 1 atmosphere at working temperatures > 800°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.

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

Less Noble $\quad \longrightarrow \quad$ 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.

**TABLE 19.1 Standard Reduction Potentials at 25°C**

<table>
<thead>
<tr>
<th>Half-Reaction</th>
<th>$E^\circ$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Fe}^3+(aq) + 3e^- \rightarrow \text{Fe}^{2+}(aq)$</td>
<td>0.77</td>
</tr>
<tr>
<td>$\text{H}_2(g) + 2e^- \rightarrow 2\text{H}^+(aq)$</td>
<td>0.00</td>
</tr>
<tr>
<td>$\text{Mn}^{2+}(aq) + 2e^- \rightarrow \text{Mn}(s)$</td>
<td>1.51</td>
</tr>
<tr>
<td>$\text{Cl}_2(g) + 2e^- \rightarrow 2\text{Cl}^-(aq)$</td>
<td>1.36</td>
</tr>
<tr>
<td>$\text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s)$</td>
<td>0.80</td>
</tr>
<tr>
<td>$\text{Cu}^2+(aq) + 2e^- \rightarrow \text{Cu}(s)$</td>
<td>0.34</td>
</tr>
<tr>
<td>$\text{H}_2^+(aq) + 2e^- \rightarrow \text{H}_2(g)$</td>
<td>0.85</td>
</tr>
<tr>
<td>$\text{Fe}^{2+}(aq) + e^- \rightarrow \text{Fe}^{3+}(aq)$</td>
<td>0.77</td>
</tr>
<tr>
<td>$\text{SO}_4^{2-}(aq) + 2\text{H}_2O(l) + 2e^- \rightarrow \text{SO}_4^{2-}(aq) + 4\text{OH}^-(aq)$</td>
<td>0.40</td>
</tr>
<tr>
<td>$\text{Cu}^+(aq) + e^- \rightarrow \text{Cu}^{2+}(aq)$</td>
<td>0.15</td>
</tr>
<tr>
<td>$\text{Na}^+(aq) + e^- \rightarrow \text{Na}(s)$</td>
<td>0.41</td>
</tr>
<tr>
<td>$\text{Cr}^{2+}(aq) + 2e^- \rightarrow \text{Cr}(s)$</td>
<td>0.29</td>
</tr>
<tr>
<td>$\text{Zn}^{2+}(aq) + 2e^- \rightarrow \text{Zn}(s)$</td>
<td>0.76</td>
</tr>
<tr>
<td>$\text{H}_2O(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq)$</td>
<td>0.83</td>
</tr>
<tr>
<td>$\text{Fe}^{2+}(aq) + 2e^- \rightarrow \text{Fe}(s)$</td>
<td>0.44</td>
</tr>
<tr>
<td>$\text{Cr}_2O_3(s) + 3\text{H}_2O(l) + 6e^- \rightarrow 2\text{Cr}^{3+}(aq) + 7\text{H}_2O(l)$</td>
<td>1.33</td>
</tr>
<tr>
<td>$\text{MnO}_2(s) + 4\text{H}^+(aq) + 2e^- \rightarrow \text{Mn}^{2+}(aq) + 2\text{H}_2O(l)$</td>
<td>1.32</td>
</tr>
<tr>
<td>$\text{NiO}(s) + 4\text{H}^+(aq) + 2e^- \rightarrow \text{Ni}^{2+}(aq) + 2\text{H}_2O(l)$</td>
<td>1.23</td>
</tr>
<tr>
<td>$\text{CuO}(s) + 4\text{H}^+(aq) + 2e^- \rightarrow \text{Cu}^{2+}(aq) + 2\text{H}_2O(l)$</td>
<td>1.23</td>
</tr>
<tr>
<td>$\text{Fe}_2O_3(s) + 3\text{H}_2O(l) + 6e^- \rightarrow 2\text{Fe}^{3+}(aq) + 7\text{H}_2O(l)$</td>
<td>1.33</td>
</tr>
<tr>
<td>$\text{Cr}_2O_3(s) + 3\text{H}_2O(l) + 6e^- \rightarrow 2\text{Cr}^{3+}(aq) + 7\text{H}_2O(l)$</td>
<td>1.33</td>
</tr>
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</tr>
<tr>
<td>$\text{Fe}_2O_3(s) + 3\text{H}_2O(l) + 6e^- \rightarrow 2\text{Fe}^{3+}(aq) + 7\text{H}_2O(l)$</td>
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</tr>
<tr>
<td>$\text{Cr}_2O_3(s) + 3\text{H}_2O(l) + 6e^- \rightarrow 2\text{Cr}^{3+}(aq) + 7\text{H}_2O(l)$</td>
<td>1.33</td>
</tr>
</tbody>
</table>
Where do all 3 of these “design rules” lead ??
Materials for collecting solar-thermal power at high temperatures

Useful molten chloride salts

<table>
<thead>
<tr>
<th>Salt formula</th>
<th>NaCl</th>
<th>KCl</th>
<th>ZnCl$_2$</th>
<th>Melting point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mole percent</td>
<td>13.4%</td>
<td>33.7%</td>
<td>52.9%</td>
<td>204 °C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Salt formula</th>
<th>KCl</th>
<th>MgCl$_2$</th>
<th>Melting point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mole percent</td>
<td>68.0%</td>
<td>32%</td>
<td>430</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Salt formula</th>
<th>NaCl</th>
<th>KCl</th>
<th>MgCl$_2$</th>
<th>Melting point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mole percent</td>
<td>27.5%</td>
<td>32.5%</td>
<td>40</td>
<td>383</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Chemical composition (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>alloy</td>
</tr>
<tr>
<td>------</td>
</tr>
<tr>
<td>C-276</td>
</tr>
<tr>
<td>H 230</td>
</tr>
</tbody>
</table>
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 cm$^2$ 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

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

$\Delta Wt$ is the weight loss in grams
$\rho$ is density (g/cm$^3$) of the Hastelloy
$A$ is the total immersed area in cm$^2$
$T$ is the immersion duration in days
Quartz cell (with two caps) for controlling atmosphere during Gravimetric Corrosion Test

Cell cap with *long gas inlet* to send gas into (sparge) the salt during the initial degassing of salt.

Side tube to send gas above the salt.

Cell cap with *short gas inlet* to send gas above the salt.
Quartz cell in the furnace

- Side inlet for sending argon gas above the salt
- Cell cap with short gas inlet and outlet
- Tube containing the salt with the metal sample at 800°C
Quartz cell in the furnace

- Salt fill level inside quartz cell
- Metal coupon
- Alumina spill tray
Results of 3 immersion tests

1. Aerobic (cell open to atmospheric air)

Corrosion rate = 1700 µm/year

- high corrosion rate due to high flux of O₂ and water (oxidants) from air into salt at high temperature.

2. Anaerobic without initial degassing

Corrosion rate = 113 µm/year

- corrosion rate decreased.
- lower corrosion rate because Argon blanket cut off air supply (oxidant flux) into salt
- CR still greater than 80 µm/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 µm/y**

- Corrosion rate of metal significantly decreased even more with sparging.
- CR now lower than the DoE target value (≤ 80 µm/y).
- Salt was effectively isolated from the atmosphere air.
- Air (O₂ 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 H₂O and O₂ (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

- **3-electrode cell**
- **Furnace**
- **Argon Gas Cylinder**
- **Thermocouple**
- **Potentiostat with Computer Control and Data logging**

- **CRUCIBLE**
- **FURNACE**
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

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

- \( k_1 = 3.27 \text{ in } \mu m \text{ g } \mu A^{-1} \text{ cm}^{-1} \text{ yr}^{-1} \)
- \( i_{corr} = \text{corrosion current density in } \mu A \text{ cm}^{-2} \)
- \( EW = \text{equivalent weight (27.01 g/eq)} \)
- \( \rho = \text{density (8.89 g cm}^{-3}) \)
Graphical estimation of parameter, $i_{\text{corr}}$ at $E_{\text{corr}}$ (OCP), needed to find CR

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

where:

- $k_1 = 3.27$ in $\mu m$ g $\mu A^{-1}$ cm$^{-1}$ yr$^{-1}$
- $i_{\text{corr}} =$ corrosion current density in $\mu A$ cm$^{-2}$
- $EW =$ equivalent weight (27.01 g/eq)
- $\rho =$ density (8.89 g cm$^{-3}$)
According to JJ Lingane, you need 2 reference electrode to have a reference electrode, … we made 4
Typical data for finding corrosion rate of metal in salt by Electrochemical method

C-276 Hastelloy in NaCl-KCl-ZnCl₂ at different temperatures in air

Current density, log I (A/cm²)

Potential (V vs. Ag/AgCl)
**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**

<table>
<thead>
<tr>
<th>Temperature (°C) / Atmosphere</th>
<th>Surface area for WE and CE</th>
<th>Corrosion potential, $E_{corr}$ (V)</th>
<th>Corrosion current density, $I_{corr}$ (µA/cm²)</th>
<th>Corrosion rate, (µm/y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 …… Air</td>
<td>WE=17.5 cm², CE=27.3 cm²</td>
<td>-0.115</td>
<td>5</td>
<td>49.7</td>
</tr>
<tr>
<td>500 …… Air</td>
<td>WE=17.5 cm², CE=27.3 cm²</td>
<td>0.08</td>
<td>43.6</td>
<td>433</td>
</tr>
<tr>
<td>800 …… Air</td>
<td>WE=17.5 cm², CE=27.3 cm²</td>
<td>0.291</td>
<td>240</td>
<td>2380</td>
</tr>
<tr>
<td>300 … Argon</td>
<td>WE=14 cm², CE=24.5 cm²</td>
<td>-0.08</td>
<td>0.795</td>
<td>7.89</td>
</tr>
<tr>
<td>500 … Argon</td>
<td>WE=14 cm², CE=24.5 cm²</td>
<td>-0.057</td>
<td>1.86</td>
<td>18.5</td>
</tr>
<tr>
<td>800 … Argon</td>
<td>WE=14 cm², CE=24.5 cm²</td>
<td>0.166</td>
<td>3.16</td>
<td>31.4</td>
</tr>
</tbody>
</table>

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

*Ecehm and gravimetric methods agree CR = 1700 grav = 2380 echem micron per year in air*
“Local cell corrosion mechanism” of metal in molten salt
O₂ or H₂O (or both) from air sustain corrosion by accepting electrons from the metal

Anodic reactions in “local cell” corrosion

\[ \text{M (Cr, Ni, and Fe)} \rightarrow \text{M}^{n+} + n\text{e}^- \]

Cathodic reactions in “local cell”

\[ \text{O}_2 + 4\text{e}^- \rightarrow 2\text{O}^{2-} \]

and/or

\[ \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + \text{O}^{2-} \]

Charge balance reactions in molten chloride salt Na-K-Zn-Cl₄

\[ \text{M}^{n+} + n\text{NaCl} \rightarrow \text{M}^{n+}\text{Cl}^- + n\text{Na}^+ \]

\[ 2n\text{Na}^+ + n\text{O}^{2-} \rightarrow n\text{Na}_2\text{O}_2 \]

Schematic diagram of “local cell” mechanism

Local anode site

Local cathode sites

Chemical and Environmental Engineering, University of Arizona
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

Connecting salt tank and pump.

Port for pressure gauge

Thermal expansion to be absorbed by bellows.
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\textsubscript{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°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°) of the metal oxide

<table>
<thead>
<tr>
<th>Metal Oxide</th>
<th>ΔHformation (calories/gram)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>reactive metals</strong></td>
<td></td>
</tr>
<tr>
<td>aluminum oxide (Al₂O₃)</td>
<td>- 4000 (= -1676 kJ/mole)</td>
</tr>
<tr>
<td>silicon dioxide (SiO₂)</td>
<td>- 3418</td>
</tr>
<tr>
<td><strong>unreactive metals</strong></td>
<td></td>
</tr>
<tr>
<td>copper oxide (Cu₂O)</td>
<td>- 278</td>
</tr>
<tr>
<td>platinum oxide (PtO₂)</td>
<td>- 84 (= -80 kJ/mole)</td>
</tr>
<tr>
<td>gold oxide (Au₂O)</td>
<td>&gt; 0 (Au-oxide unstable)</td>
</tr>
</tbody>
</table>

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 \( (\text{H}_2\text{O}) \) reacts with a reactive metal \( (M) \), like aluminum or silicon, forming undesirable metal oxide \( (\text{MO}) \) as :

\[
M + \text{H}_2\text{O} \rightarrow \text{MO} + 2\text{e}^- + 2\text{H}^+ \quad \text{(RXN 1)}
\]

- The liberated electrons are consumed by proton to form hydrogen (reaction 2a). \( \text{e}^- \) can be consumed by oxygen to form water (reaction 2b).

\[
\begin{align*}
2\text{e}^- + 2\text{H}^+ & \rightarrow \text{H}_2 \quad \text{(RXN 2a)} \\
2\text{e}^- + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} & \rightarrow 2\text{OH}^- \quad \text{(RXN 2b)}
\end{align*}
\]

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

\[
\begin{align*}
M + \text{H}_2\text{O} & \rightarrow \text{MO} + \text{H}_2 + \text{heat} \quad \text{(RXN 3a)} \\
M + \frac{1}{2}\text{O}_2 & \rightarrow \text{MO} + \text{heat} \quad \text{(RXN 3b)}
\end{align*}
\]

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

Similarly, in the presence of oxygen from air, RXN 3b occurs because \( \text{e}^- \) is more stable on \( \text{O}_2 \) 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

Silicon Plating from Ionic Liquid Electrolyte

- Ionic liquid electrolyte: RCl (n-butylpyridinium chloride) and silicon (SiCl$_4$, NaSiF$_6$, SiHCl$_3$, or Si$_2$Cl$_6$).

- Reactions
  - IL Rxn with Si: \(2 R^+ \text{Cl}^- + \text{Si}_2\text{Cl}_6 \rightarrow 2 R^+ \text{SiCl}_4^-\)
  - Cathode Rxn: \(R^+ \text{SiCl}_4^- + 3 \text{e}^- \rightarrow \text{Si} + R^+ \text{Cl}^- + 3 \text{Cl}^-\)
  - Anode Rxn: \(\text{Si} + R^+ \text{Cl}^- + 3 \text{Cl}^- \rightarrow R^+ \text{SiCl}_4^- + 3 \text{e}^-\)
  - Net Rxn: \(\text{Transfer of Si from anode to cathode}\)

- 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

Silicon plating on Metal

Electrodeposition of silicon on titanium in a room temperature ionic liquid: butyl, 3-methylimidazolium chloride, [Bmim] BF$_4$

Cyclic voltammogram of titanium in [Bmim]BF$_4$ with ferrocencene but no SiCl$_4$ under N$_2$ atmosphere. Scan rate: 10mV/s. Temperature: 25°C.

Cyclic voltammogram of titanium in [Bmim]BF$_4$ saturated with SiCl$_4$ under N$_2$ 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

<table>
<thead>
<tr>
<th>Element</th>
<th>W%</th>
<th>At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>NK</td>
<td>0.31</td>
<td>0.07</td>
</tr>
<tr>
<td>TiK</td>
<td>99.69</td>
<td>98.93</td>
</tr>
<tr>
<td>Matrix</td>
<td>Correction</td>
<td>ZAF</td>
</tr>
</tbody>
</table>

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

Scanning Electron Microscopy (SEM) of Ti and Si on Ti
Cost versus Efficiency Tradeoff

Efficiency per length $\propto \tau^{1/2}$

(where $\tau$ is hole-electron pair recombination time)

Long $d$
Requires High $\tau$
High Cost

Short $d$
Allows Lower $\tau$
Low Cost

Thin electrodeposited Si films allow high efficiency with low $\tau$
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

Chemical and Environmental Engineering, University of Arizona
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

Brews and Palusinski

Chemical and Environmental Engineering, University of Arizona
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 hydrogen

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 cm². Frequency range: 50 kHz to 10 Hz. AC amplitude: 50mV. Thickness of sputtered Pt el= 20nm. ETEK electrodes (0.5 mg of Pt per cm²) used as gas diffusion layer. Pt screen current collectors. J4 ITP membrane.

H2 / O2 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 cm²) 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 was out of PA loaded benzyltrimethylammonium (BTMA) groups on a polyphenlene 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.
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!
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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