

# *“Electrochemical Syntheses in Ionic Liquids”*

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# Outline

- ❑ Motivation: Why electrochemistry in ionic liquids  
*Water can be a poison!*
- ❑ Basics of ionic liquids Electroplating
- ❑ Reactive metals: analogy between Aluminum and Silicon
- ❑ New method Si electroplating in ionic liquids
- ❑ Fuel Cells and Hydrogen Storage
- ❑ Conclusions and questions

# Making Metals that react with Water

*requires Water-Free Processing to avoid Metal-oxide*

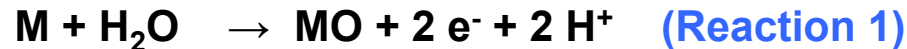
- **Driving Force to make Metal-oxide** in the presence of water is ...

Heat of formation of metal oxides

	<u>Metal Oxide</u>	<u><math>\Delta H_{\text{formation}}</math> (calories/gram)</u>
<b>reactive metals</b>	aluminum oxide ( $\text{Al}_2\text{O}_3$ )	- 4000 (= -1675.7 kJ/mole)
	silicon dioxide ( $\text{SiO}_2$ )	- 3418
<b>coinage metals</b>	copper oxide ( $\text{Cu}_2\text{O}$ )	- 278
	gold oxide ( $\text{Au}_2\text{O}$ )	> 0 (Au oxide unstable)

- **Rapid surface oxide formation** prevents Al smelting in air

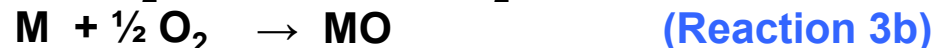
- Water ( $\text{H}_2\text{O}$ ) reacts with a reactive metal (M), like aluminum or silicon, forming undesirable metal oxide (MO) as is schematically shown below.



-The liberated electrons are consumed by proton to form hydrogen (reaction 2a) or by oxygen reduction 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) .



*Electron is more stable on  $\text{H}^+$  or  $\text{O}_2$  than on a reactive metal so undesirable reactions 3a and 3b are spontaneous in the presence of water.*

# General characteristics of an Ionic liquid (IL)

- ❑ **“Ionic liquid”** is the name for salts whose melting point is below 100°C.
- ❑ An **ionic liquid** contains only ions – can exclude water.
- ❑ ILs have low vapor pressure because of coulombic attraction (no VOCs)
- ❑ **Room temperature ionic liquid (RTIL)**: Salt that is liquid at room temperature
- ❑ One of the earliest **RTILs** is  $[\text{EtNH}_3]^+ [\text{NO}_3]^-$  which melts at 12°C.  
  - *P. Walden, Bull. Acad. Sci. St. Petersburg 1914, 405-422*
- ❑ RTILs were developed as electrolytes for aluminum plating.  
  - mixtures of alky-nitrogen-heterocyclic halides and halogeno-aluminates
  - *H. L. Chum, V. R. Koch, L. L. Miller, R. A. Osteryoung (1975). [J. Am. Chem.Soc.](#) 97: 3264.*

# Simple preparation

Amine + Acid

Stirring in acetone/dry-ice bath

Solution

Heated at 120°C in Silicon bath

H<sub>2</sub>O Removal

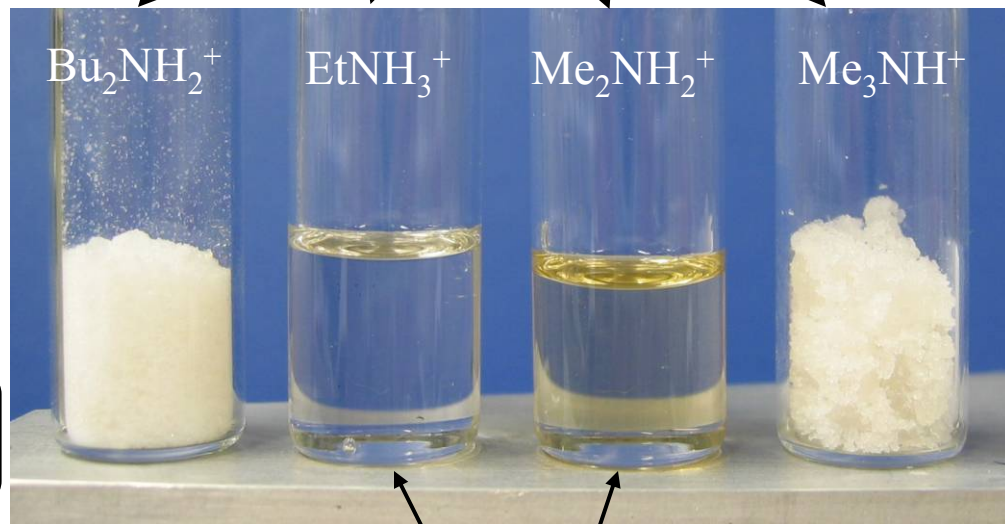
Dried in Vacuum Oven at 90°C

Mass analysis, Karl-Fischer titration

Samples : H<sub>2</sub>O = 100 : <1 (mol%)

Example: hydrogen sulfates

HSO<sub>4</sub><sup>-</sup>



2 RTILs

# Typical room temperature ionic liquids (RTILs)

- Room temperature ionic liquids (RTILs) consist of:
  - ❖ Bulky and asymmetric organic positive ions (cations), such as:
    - 1-alkyl-3-methylimidazolium,
    - 1-alkylpyridinium,
    - N-methyl-N-alkylpyrrolidinium
    - ammonium ions.
  - ❖ Negative ions (anions) include:
    - halides (Cl<sup>-</sup>, F<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>) which generally give high melting salts,
    - Inorganic anions such
    - tetrafluoroborate
    - hexafluorophosphate
    - large organic anions
    - bistriflimide
    - triflate
    - tosylate
    - formate
    - alkylsulfate
    - alkylphosphate
    - glycolate

# Ionic Liquids “Designer Solvents”

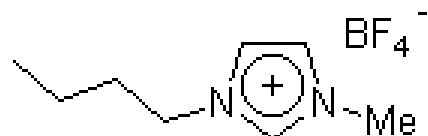
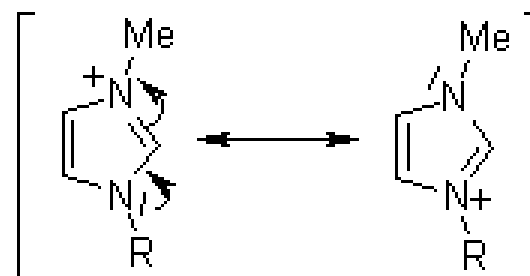
Substituents on the organic cation and the anion determine properties, such as *melting point, viscosity, and solubility*



[emim][BF<sub>4</sub>]

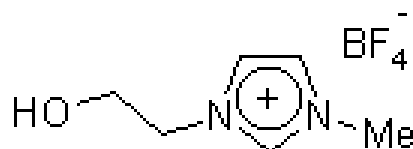
e: ethyl  
m: methyl  
im: imidazolium

others: [emim][PF<sub>6</sub>], [emim][NO<sub>3</sub>]  
[emim][ClO<sub>4</sub>], [emim][CF<sub>3</sub>SO<sub>3</sub>]

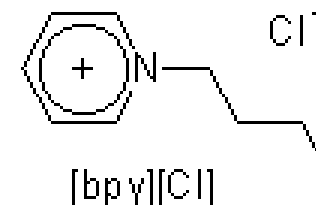


[bmim][BF<sub>4</sub>]

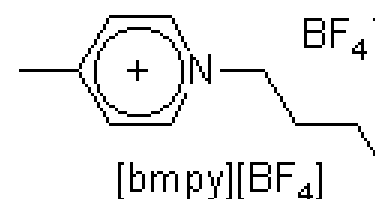
others: [bmim][Br], [bmim][Cl], [bmim][PF<sub>6</sub>]



[hydemin][BF<sub>4</sub>]



[bpy][Cl]



[bmpy][BF<sub>4</sub>]

1-butyl-3-methylimidazolium tetrafluoroborate **[bmim][BF<sub>4</sub>]** melts at -80°C and is a colorless liquid with high viscosity at room temperature.

# Requirements of Electrolytes For Plating Active Metals

## ❑ CONDUCTIVITY

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

## ❑ COMPATIBILITY WITH ELECTROPLATING OF ACTIVE METALS

- No water

## ❑ STABILITY

- Stable to electric field; no reaction with products, reactants

❖ All electrolyte properties accessible by tailoring the ionic liquid

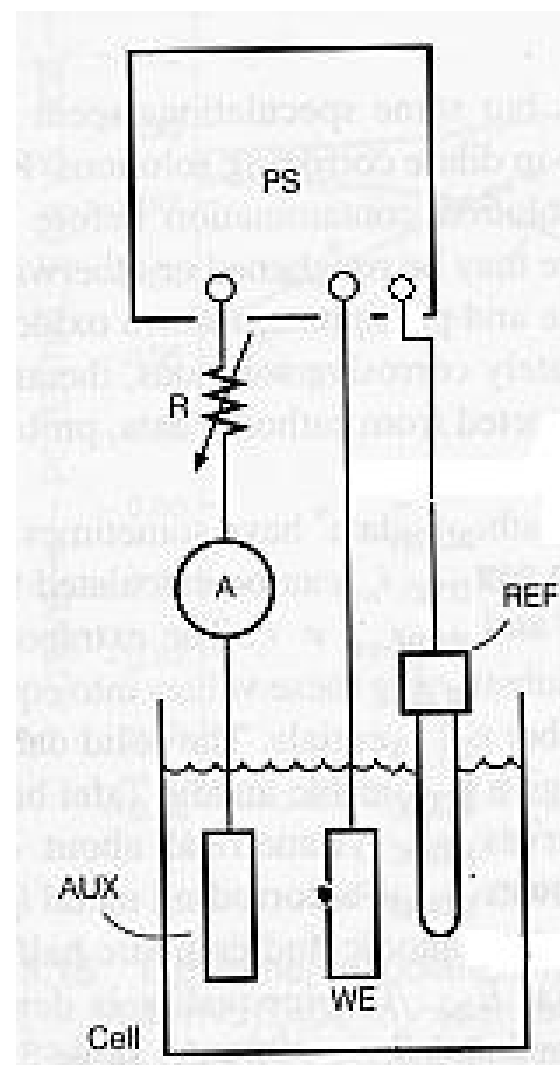
Abedin, S. Z. et al. *“Electrodeposition of Metals and Semiconductors in Air- and Water-Stable Ionic Liquids”* Chemphyschem [2006] 7 pg:58 -61

# Basics of Electrochemistry: 3- Electrode Cell

## Cell composed of:

- Cathode (WE)
- Anode (AUX)
- Reference (REF)
- Electrolyte (Ions, reactants)

Electrolyte	Potential Window
Water/aqueous	1.23 V
Ionic Liquids	5 V <sup>1</sup>

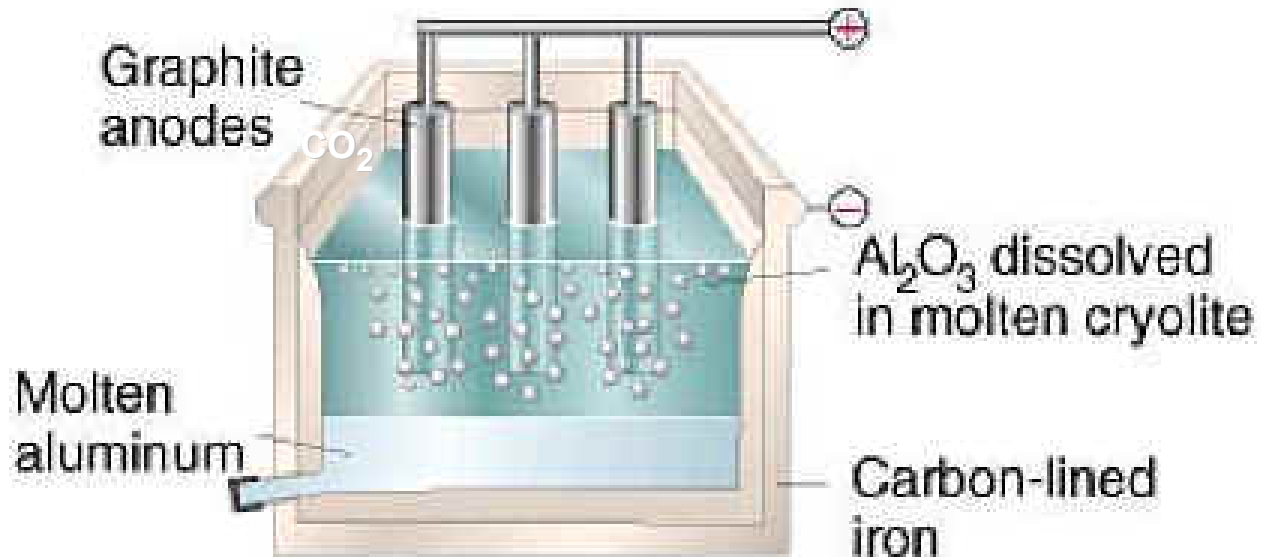


<sup>1</sup> Abedin, S. Z. et al. "Electrodeposition of Metals and Semiconductors in Air- and Water-Stable Ionic Liquids" Chemphyschem [2006] vol:7 issue:1 pp. 58-61

# Electroplating of a Metal that is Reactive with Water

## □ Hall Process: water-free Aluminum electroplating

- Al metal electroplated from Al-oxide in molten salt
  - Molten salt composition: Cryolite ( $\text{Na}_3 \text{AlF}_6$ ),  $\text{AlF}_3$ ,  $\text{Al}_2\text{O}_7$
  - Large voltage window achievable in cryolite salt electrolyte
    - Al electroplates on a cathode at  $900^\circ\text{C}$  and a potential of  $-1.662$  volt vs. S.H.E.



# Low Temperature Al Electroplating

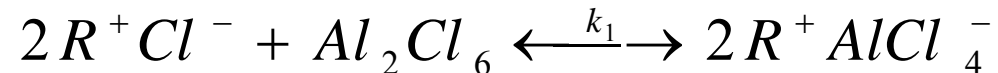
Electrodeposition of Al from Low Temperature Ionic Liquids pioneered by **Robert Osteryoung** (SUNY Buffalo)

*Osteryoung, R.A., Welch, B.J., "Electrochemical Studies in Low Temperature Molten Salt Systems Containing Aluminum Chloride". Journal of the Electrochemical Society, 118 (1981), pp. 455-466.*

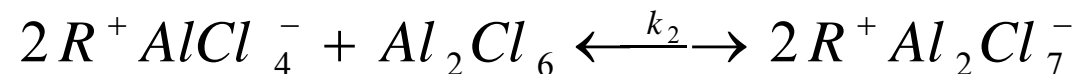
## □ Conditions

- for an  $\text{AlCl}_3$  and n-butylpyridinium chloride (RCl) salt electrolyte the melting temperature is  $30^\circ\text{C}$  and the plating potential is  $-2.1\text{V}$  vs. Ag/AgCl
- for an  $\text{AlCl}_3$  and NaCl (RCl) salt electrolyte the melting temperature is  $175^\circ\text{C}$  and the plating potential is  $-1.9\text{V}$  vs. Ag/AgCl
- Electrolyte forming reactions:

- **At low Al concentrations, the Al species in the melt forms as:**



- **At high Al concentrations, the Al species forms as:**



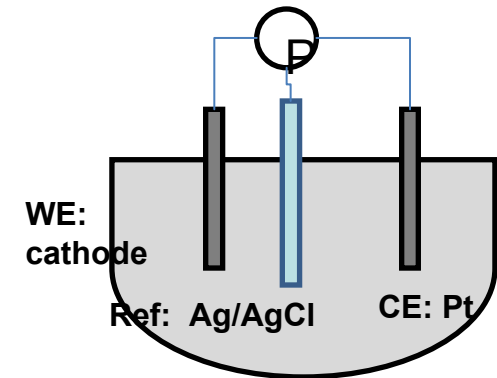
# What Did We Learn From Aluminum?

- Electrolyte is key to plating an active metal, like Al
  - o Cannot plate an active metal from an aqueous electrolyte
    - Aluminum metal quickly reacts with water forming aluminum oxide
    - Resistive surface oxide form preventing plating
  - o Molten salt has no water; allows Al electroplating
  
- Room Temperature Ionic Liquids (RTILs) give a convenient alternative to high temperature molten salts for electroplating desirable active metals and metal compounds, such as,
  - Complex conducting Al and semiconducting Si structures, sodium borohydride (hydrogen storage solution).

## Electroplating versus conventional Si processing

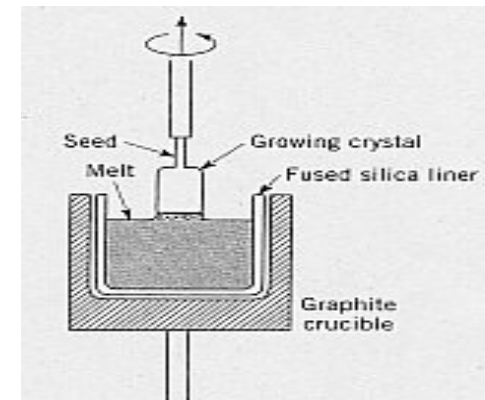
### □ Electroplating Active Metal from Ionic Liquid:

- 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 and 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 prepn Wafer sliced, lapped, polished, masked, etched, etc.
  - High temp process, Doping, annealing, oxide growth, etc.
- Hazardous waste and process fluids (HF, SiH<sub>4</sub>)
- High cost



# Prior Methods in Electroplating Si

- Two methods previously explored by other research groups
  - 1) Low temp (25°C) plating of Si from organic solvent and  $\text{SiCl}_4$ <sup>1</sup>
  - 2) High temp (750°C) Molten Salt plating of Si (similar to Hall process)<sup>2</sup>

1. Gobet, J., Tannenberger, H., “Electrodeposition of Silicon from a Nonaqueous Solvent”. Journal of the Electrochemical Society, vol. 135, Issue 1, January 1988, pp. 109-112
2. Cohen, Uri. “Epitaxial Growth of Silicon or Germanium by Electrodeposition from Molten Salts”. (1975) U.S. Patent No. 3983012. Washington, D.C. U.S. Patent and Trade Office.

# New Method:

## Room Temperature Ionic Liquid (RTIL)

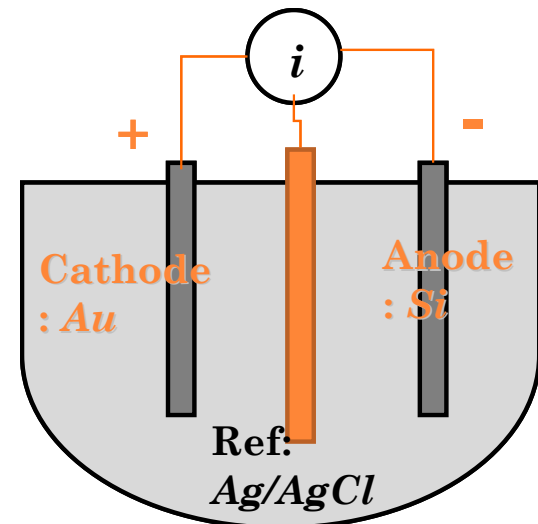
- Ionic liquid electrolyte: RCl (n-butylpyridinium chloride) and silicon ( $\text{SiCl}_4$ ,  $\text{NaSiF}_6$ ,  $\text{SiHCl}_3$ , or  $\text{Si}_2\text{Cl}_6$ ).

- Reactions



- 3 electrode cell

- Cathode, reference (Ag/AgCl), anode
  - 120°C operating temp
  - CV & Chronoamperometry
  - 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

# Characterization of Si Electroplate

- Characterization methods
  - Topography and Structure
    - SEM,
    - STEM
    - XRD
  - Composition characterization
    - EDX
    - Auger
    - Reflectance FTIR

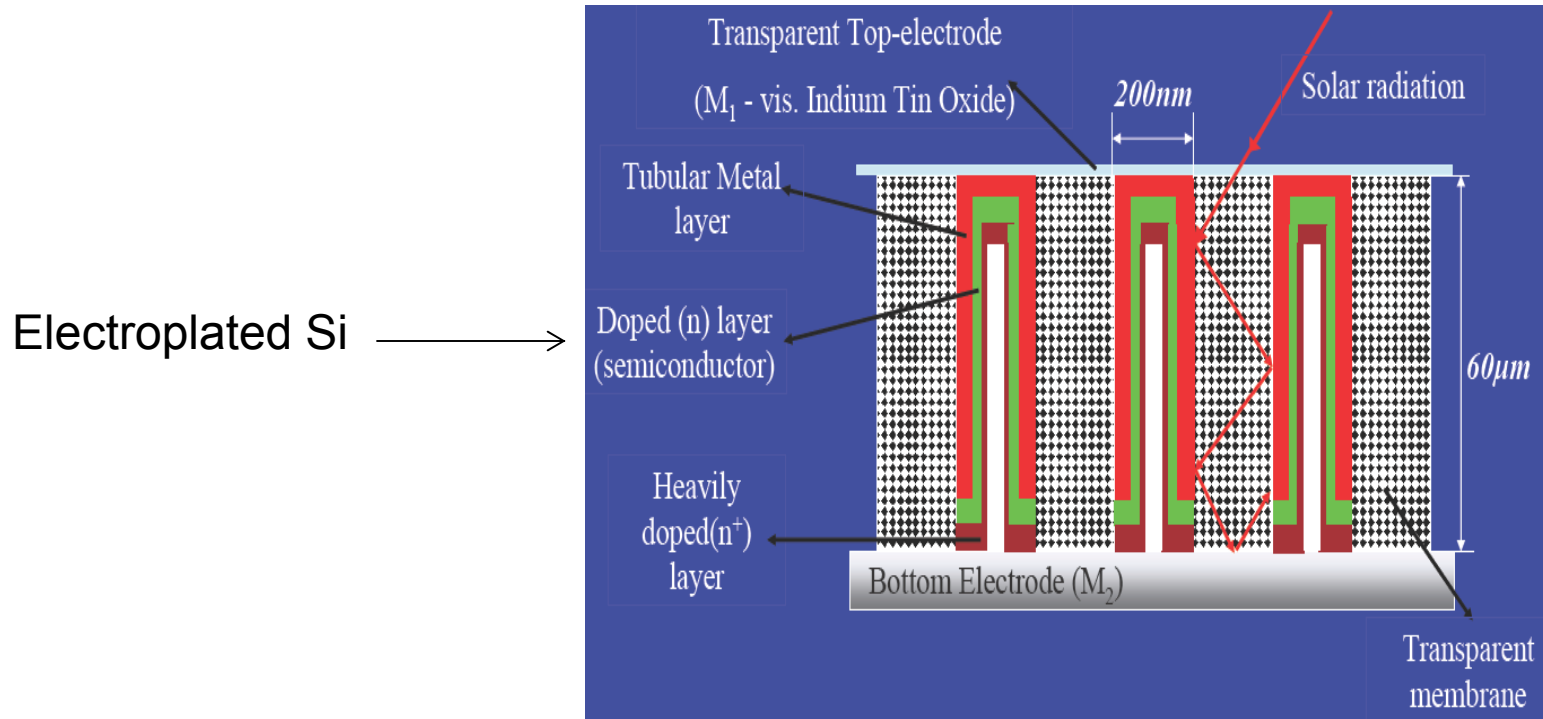
**- Electronic Device performance!**

# Conclusion

- Electrochemistry in ionic liquids gives a convenient, energy efficient and clean route to many valuable materials that are difficult to make otherwise, such as:
  - Electrical energy (fuel cells in ionic liquid electrolytes)
  - Semiconducting silicon,
  - Aluminum lines on fragile supports
  - Hydrogen
    - Hydrogen pump membrane
    - Regeneration of hydrogen storing sodium borohydride
  
- Electroplating of silicon is especially attractive as an inexpensive yet more versatile way to produce thin and complex semiconducting silicon structures to make:
  - thin film electronics: including backplanes for flexible displays,
  - thin films transistor and
  - photovoltaics.

# EXTRA SLIDES

## Novel solar cell with vertically oriented nano-structured Schottky diodes



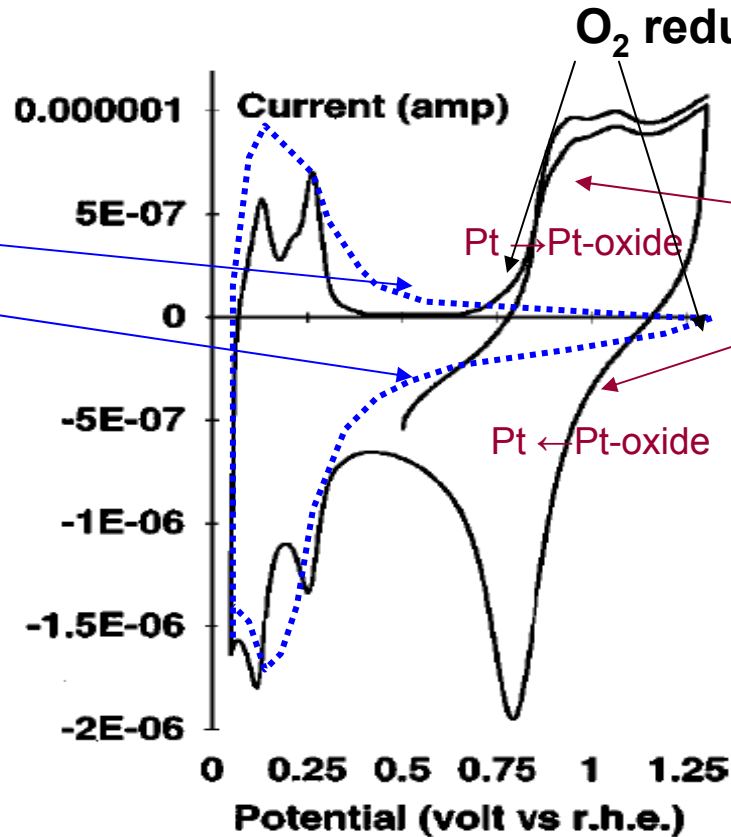
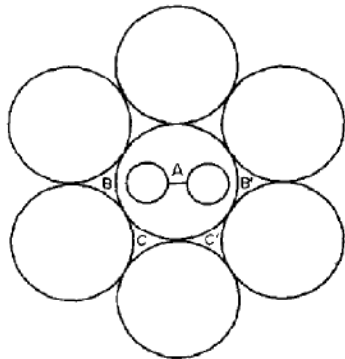
# Effects of Ionic Liquid & Aqueous Electrolytes on Pt catalyst

With protic salt electrolyte

There is

- no Pt-oxide formation
- nor reduction

to impede O<sub>2</sub> reduction.



With aqueous electrolyte

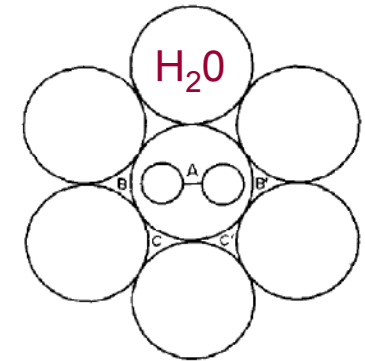
Pt-oxide formation



Pt-oxide reduction



Pt-oxide impedes O<sub>2</sub> reduction.



## Cyclic voltammogram of Pt surface...

- in aqueous sulfuric acid electrolyte (solid black line)
- versus ionic liquid (dotted blue line).

# Basics of Electrochemistry



## □ Thermodynamics of plating

- Nernst Eqn.

$$E = E^\circ + \frac{RT}{nF} \ln \left( \frac{[Ox]^a}{[Red]^b} \right)$$

## □ Kinetics of plating: current $\propto$ exp (potential)

- Butler-Volmer Eqn. (reversible)

$$i = i_o \left( \frac{(C_{red})_i}{(C_{red})_o} \exp \left( \frac{\alpha_a F \eta}{RT} \right) - \frac{(C_{ox})_i}{(C_{ox})_o} \exp \left( - \frac{\alpha_c F \eta}{RT} \right) \right)$$

- Tafel Eqn. (irreversible)

$$i = i_o \exp \left( - \frac{\alpha n F \eta}{RT} \right) \quad \text{in which } \eta = | E - E^\circ |$$