Insight into Mechanisms for Passivation of Copper in CMP Slurries Containing Peroxide and Glycine

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Small Feature Reproducibility

funded by the UC Discovery Grant

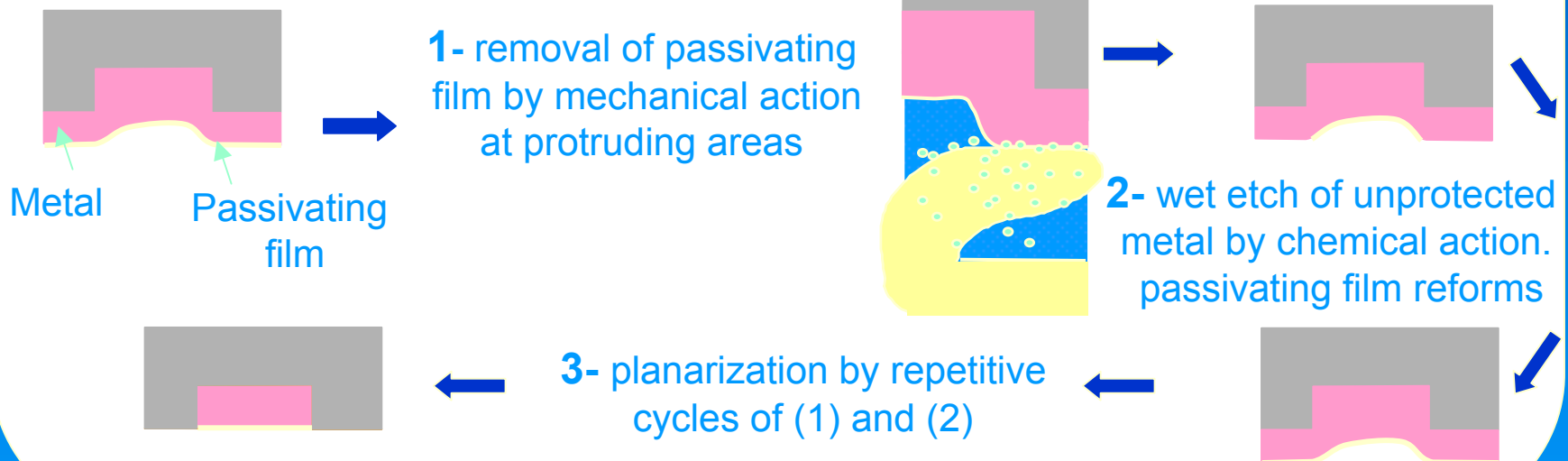*University of California at Berkeley*

Outline

- **Background and approach**
- Chemistry of copper-complexing agents
- Electrochemistry of copper in aqueous glycine
- Weight loss and polishing in presence of hydrogen peroxide
- Mechanisms for observed behavior
- Conclusions

Background and Approach

Kaufman's Model for Planarization of Tungsten
For effective planarization, must maintain higher removal at protruding regions and lower removal at recessed regions on the wafer

Metal

Passivating film

1- removal of passivating film by mechanical action at protruding areas

2- wet etch of unprotected metal by chemical action. passivating film reforms

3- planarization by repetitive cycles of (1) and (2)

Copper CMP

- **Several principles govern desirable attributes of a slurry**
  - ◆ If Kaufman's model is applicable, want passivation, not active etching of metallic surfaces
  - ◆ However, abraded debris should dissolve to prevent re-deposition, and the resulting ions should stay in solution
  - ◆ Also may want selectivity for metal over dielectric (not considered here)
- **Oxidizing agent needed**
- **Expect complexing agents to be beneficial, if there is also passivation**

Hypothesis

- **Since oxidizing agents change potentials in CMP systems, one can characterize and model their action through characterization and modeling of the electrochemical responses**
  - ◆ **Action of individual oxidizing agents can be correlated with their electrochemical effect**

  Anode: $M = M^{n+} + ne$ **Oxidation**

  Cathode: $O + me = R$ **Reduction**

  - ◆ **Should allow different oxidizing agents to be modeled using a generic approach**

Electrochemical Studies

- We have studied and previously reported the electrochemical behavior of copper in the presence of several different model complexing agents
  - The electrochemical behavior has been analyzed in terms of thermodynamic models of the system chemistry
  - Our aim is to develop predictive models based on the thermodynamics of different systems

Testing our Hypothesis

- **Here we report work done to test our hypothesis that electrochemical studies provide information applicable to models describing the effect of different oxidizing agents in CMP**

- **Hydrogen peroxide selected as model oxidizing agent**
  - ◆ **Broadly used, does not introduce extraneous ions**

- **Glycine selected as model complexing agent**

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Chemistry of Copper-Water System
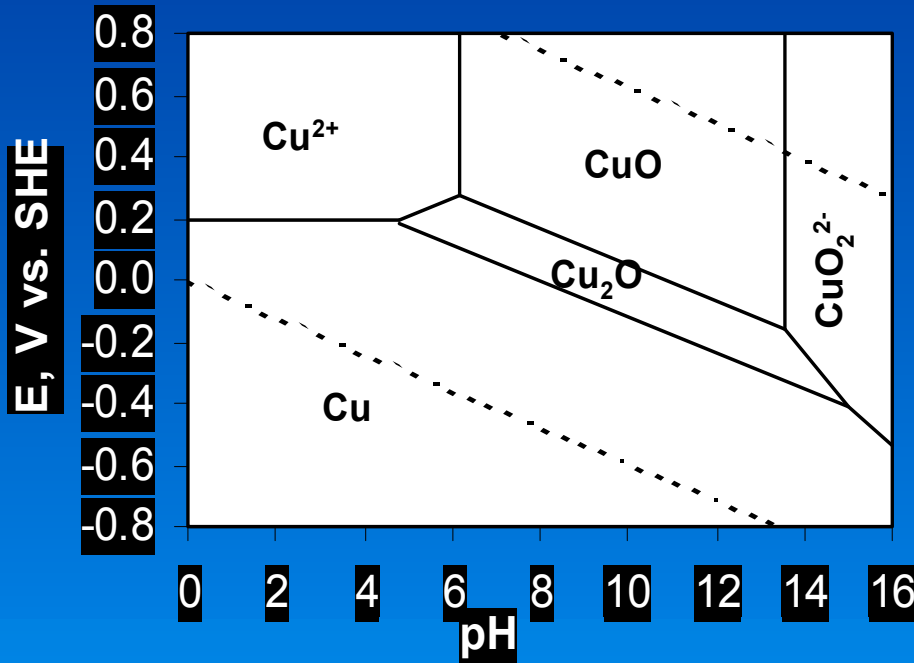
Potential-pH diagram, with {Cu$_T$} = 10^{-5}

Potential-pH diagram, with {Cu$_T$} = 10^{-4} or 10^{-6}, 4% H$_2$O$_2$ or 0.5M hydroxylamine
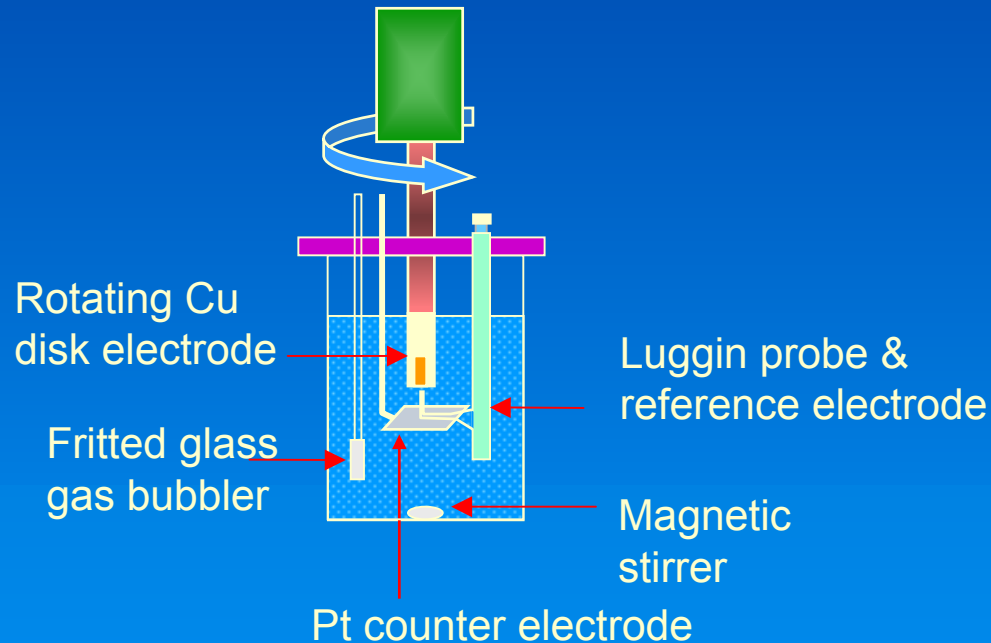*Tamilmani, Huang, Raghavan & Small, JECS, 2002*
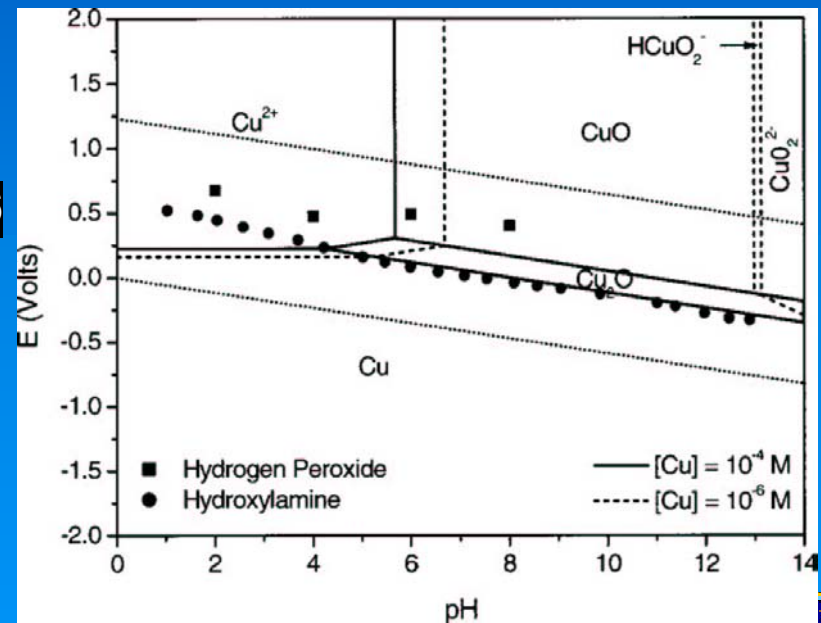
Chemistry of Glycine-Water System

$pK_{a1}=2.350$ $pK_{a2}=9.778$

$^+H_3NCH_2COOH$ $\leftrightarrow$ $^+H_3NCH_2COO^-$ $\leftrightarrow$ $H_2NCH_2COO^-$
Cation: H_2L^+ Zwitterion: HL Anion: L^-
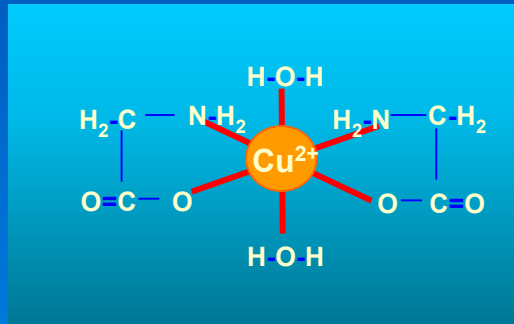
Cu(II) glycinate complexes
- $Cu(H_3NCH_2COO)^{2+}$: $CuHL^{2+}$
- $Cu(H_2NCH_2COO)^+$: CuL^+
- $Cu(H_2NCH_2COO)_2$: CuL_2

Cu (I) glycinate complexes
- $Cu(H_2NCH_2COO)^-_2$: CuL_2^-
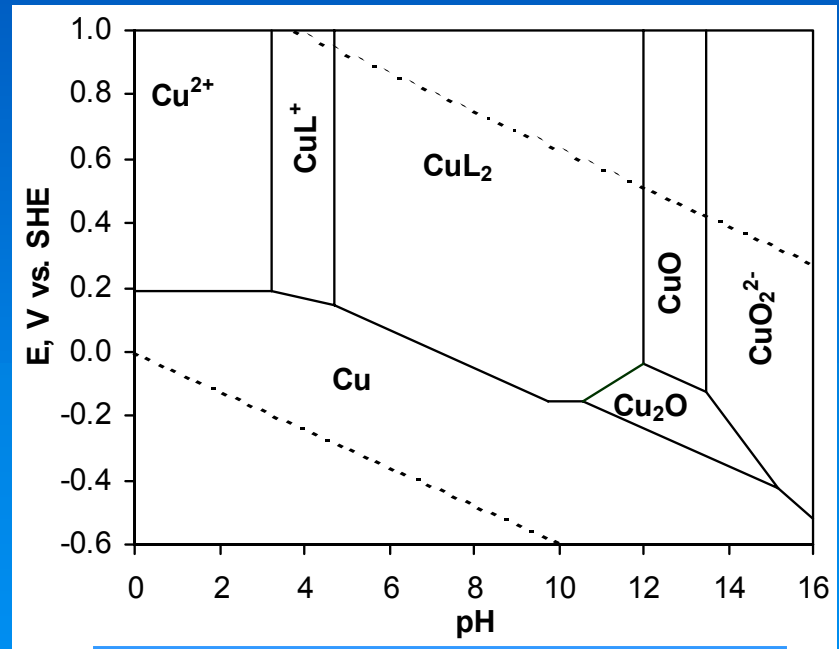
Potential-pH diagram, with $\{Cu_T\} = 10^{-5}$, $\{L_T\} = 10^{-2}$

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Polarization Measurements using Rotating Disk Electrode

Rotating Cu disk electrode

Fritted glass gas bubbler

Pt counter electrode

Luggin probe & reference electrode

Magnetic stirrer

Polarization Curves

- **At any potential, electrode passes both anodic and cathodic currents**
- **In aerated solutions used here, cathodic reaction principally reduction of oxygen:**

    $O_2 + 2H_2O + 4e = 4OH^-$

    current limited by transport of oxygen
- **Anodic reactions are oxidation of copper to Cu^{2+}, Cu_2O, $Cu(OH)_2$ or CuO – current may be limited by transport, blockage of sites or presence of passivating films**
- **Record the sum of these:**
    – **Anodic above E_{oc}**
    – **Cathodic below E_{oc}**
- **Behavior complex if there are multiple anodic or cathodic reactions**
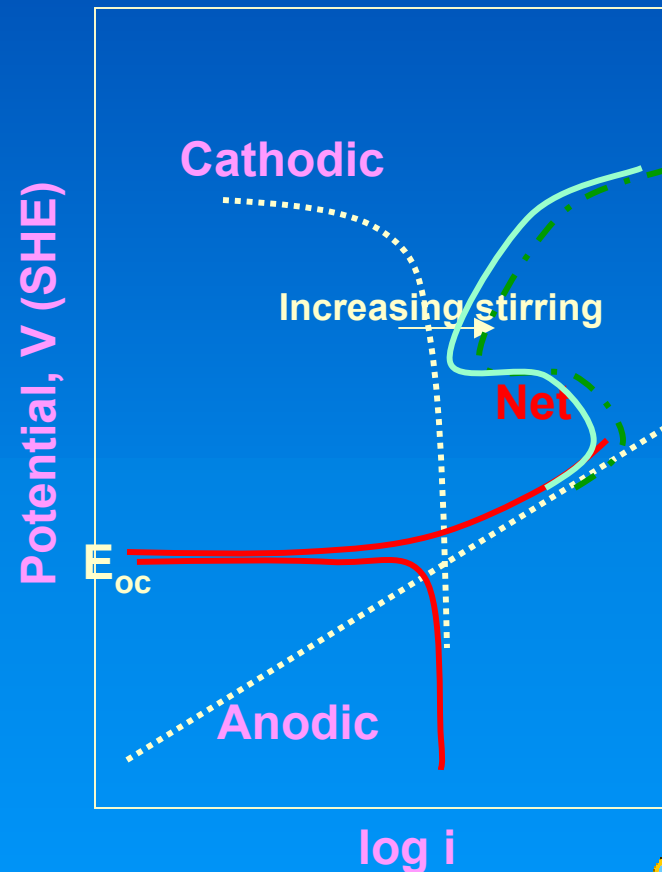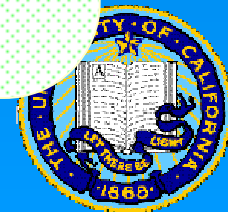
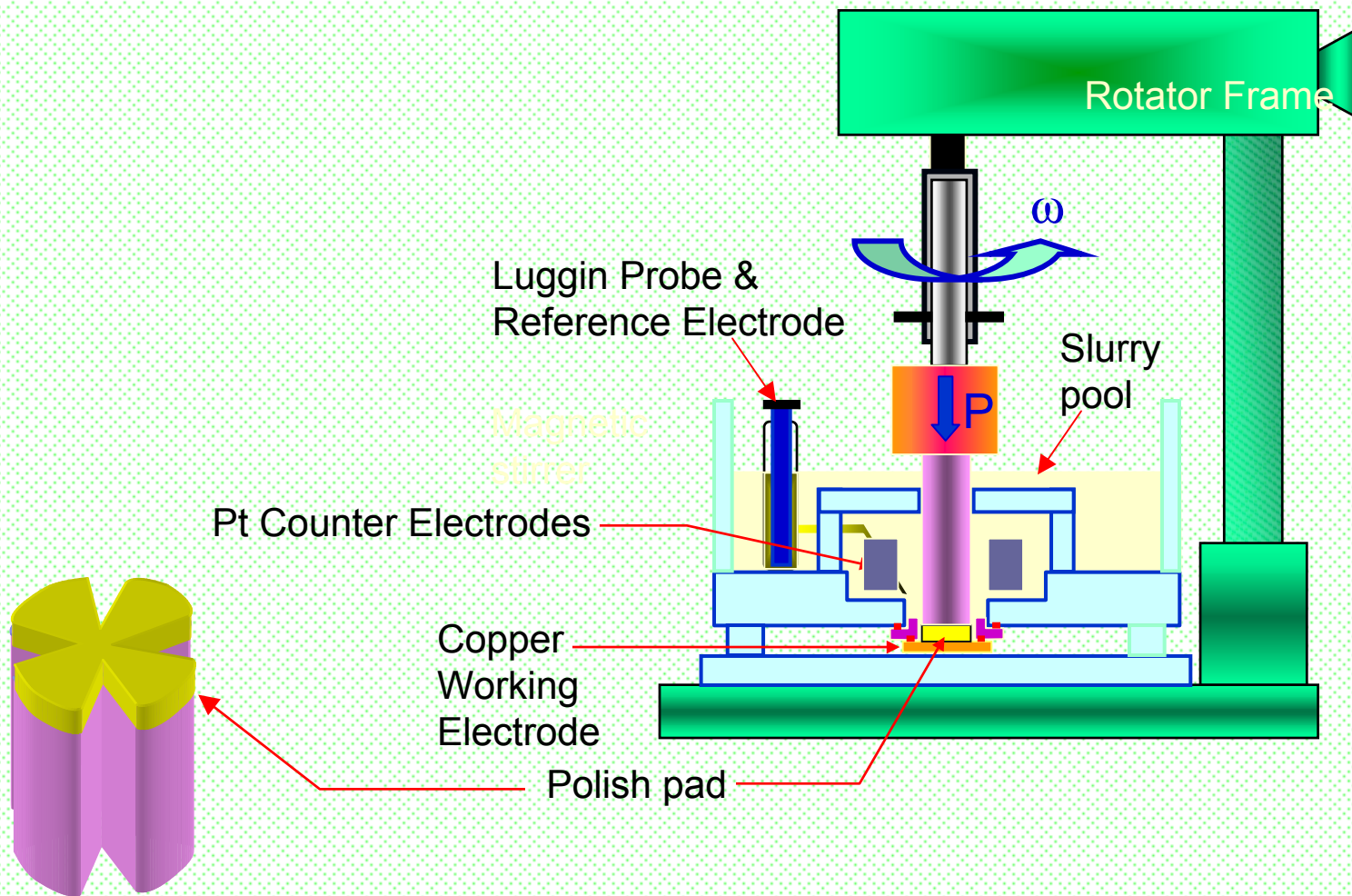# Polarization Curves in Cu-Glycine-H$_2$O
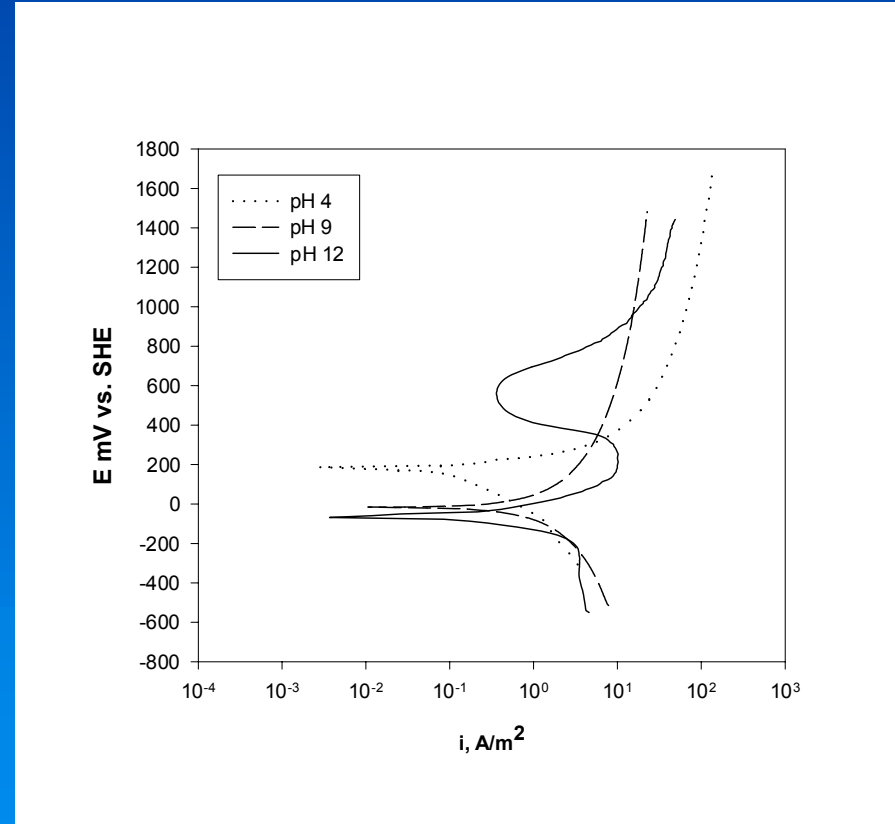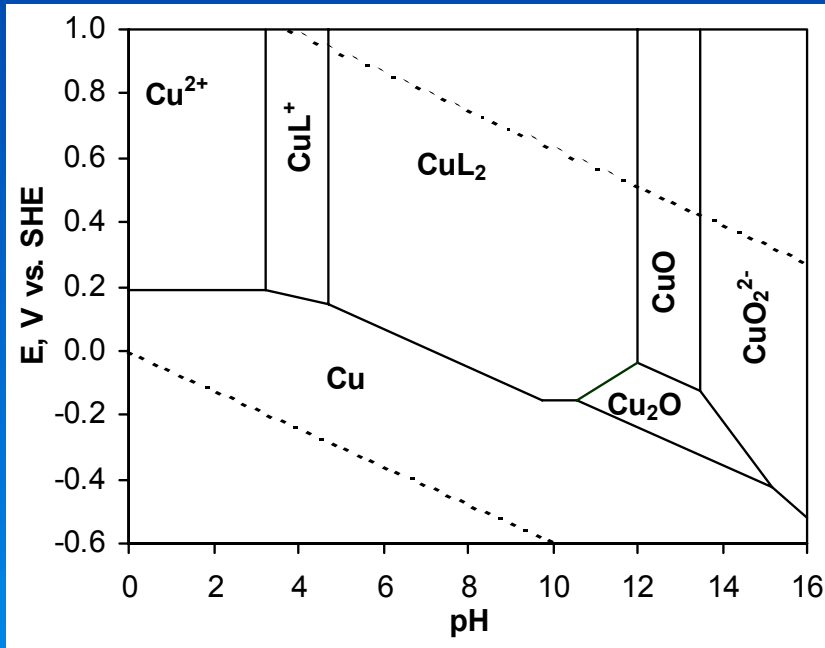
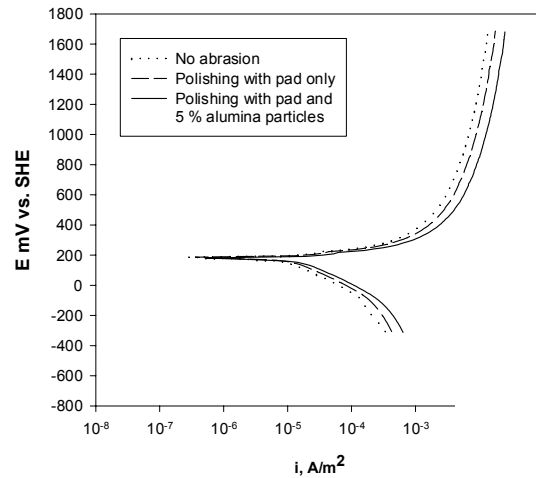$\{Cu_T\} = 10^{-5}$, $\{L_T\} = 10^{-2}$

$\{L_T\} = 10^{-2}$

In-situ Electrochemical Polarization

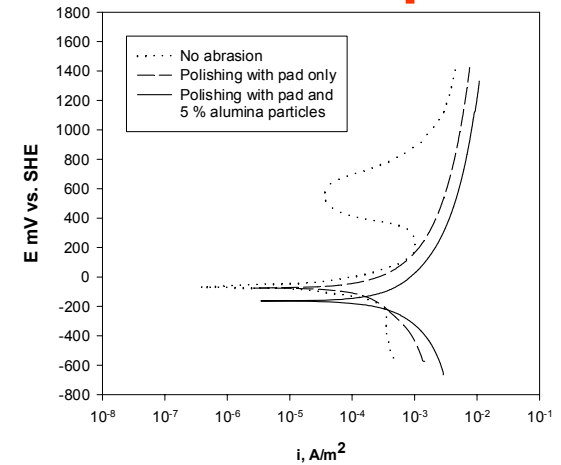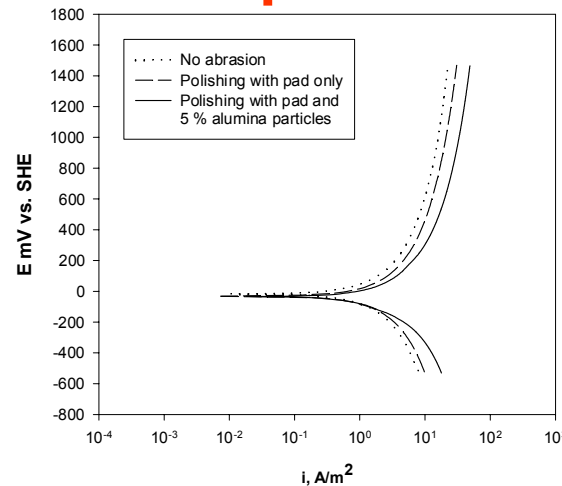# *In-situ* Polarization

pH 4
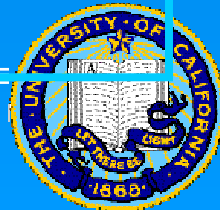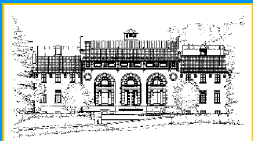
pH 12

pH 9

Aqueous 10^{-2} M glycine, 27.6 kPa, 200 rpm

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Kinetic Experiments Using H_2O_2

Dissolution

- Cleaned, weighed, copper coupons (50 x 25 x 1 mm, 99.999%) suspended in stirred solutions
- After tests, dried and weighed
- Copper removal rate determined by weight loss

Polishing

- Used same equipment used for *in-situ* polarization tests
- Electrochemical information unstable with peroxide
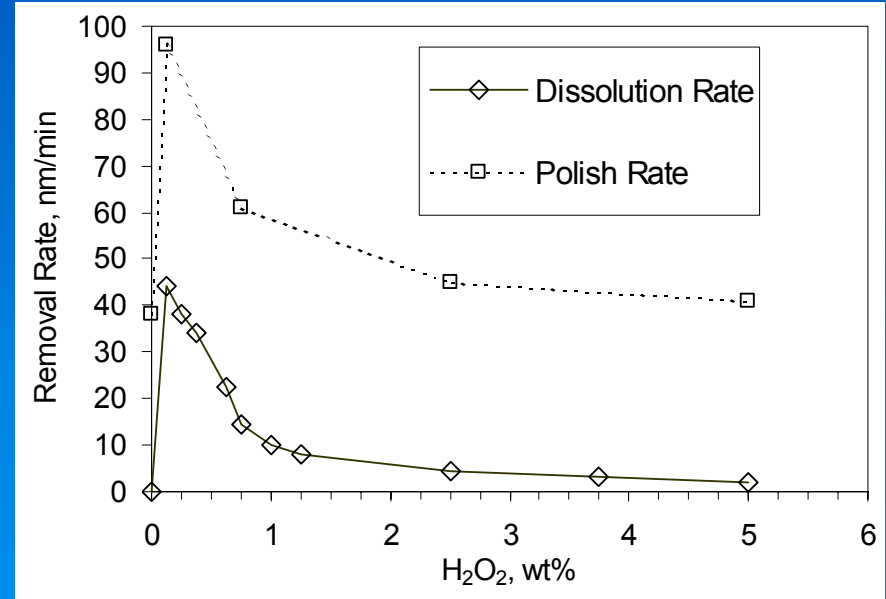- Polishing rates determined from weight loss measurements

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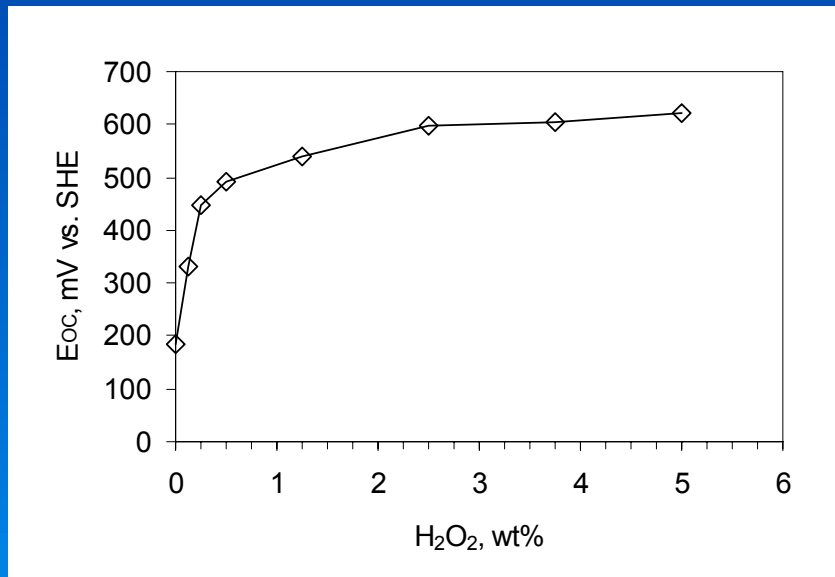# Effect of H$_2$O$_2$ on Dissolution and Polish Rates
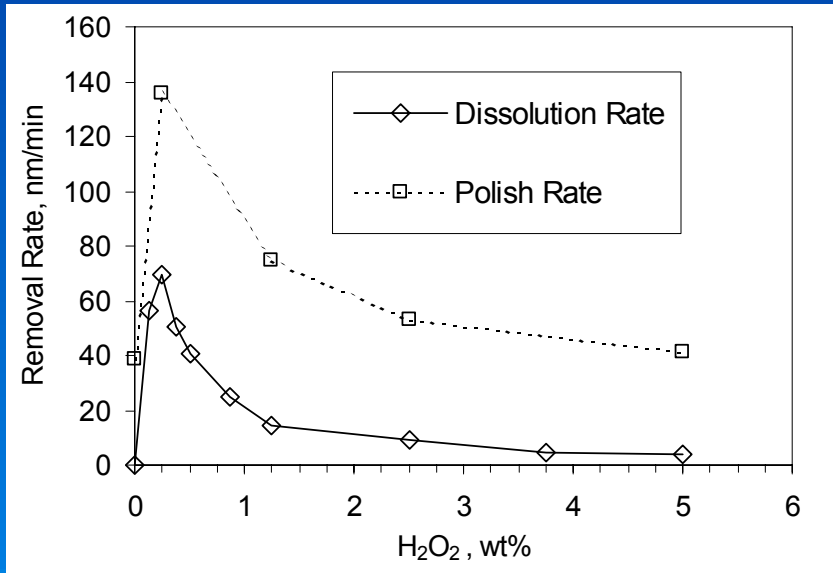
pH 4

pH 9

Aqueous 10^{-2} M glycine, 27.6 kPa, 200 rpm

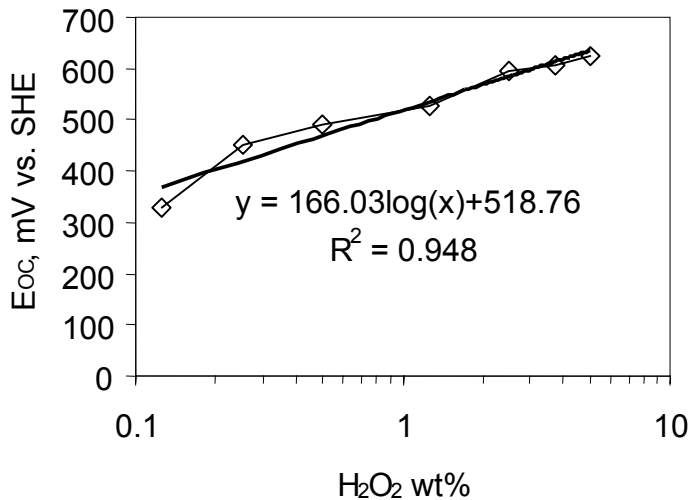# Effect of H$_2$O$_2$ on Open Circuit Potential in Aqueous, 10^{-2} M Glycine

pH 4
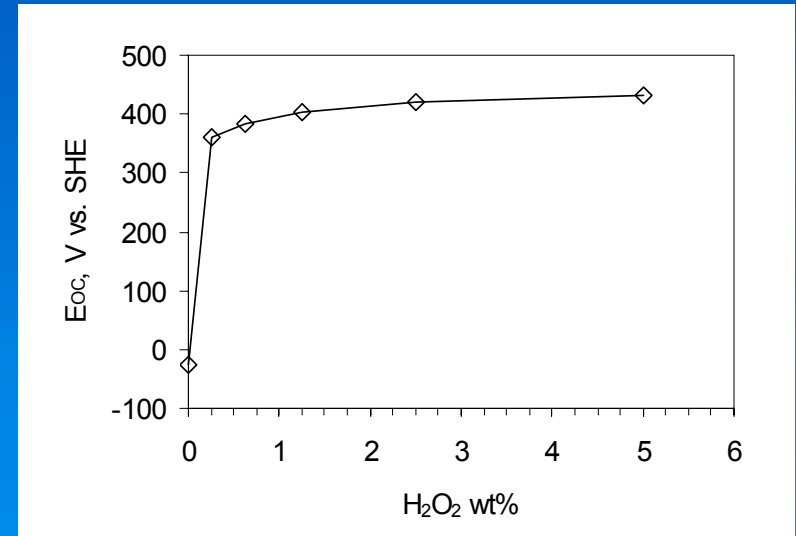
pH 9

Nernst Equation: E = E^o + 2.303RT/nF log Πa_{ox}/ Π a$_{red}$
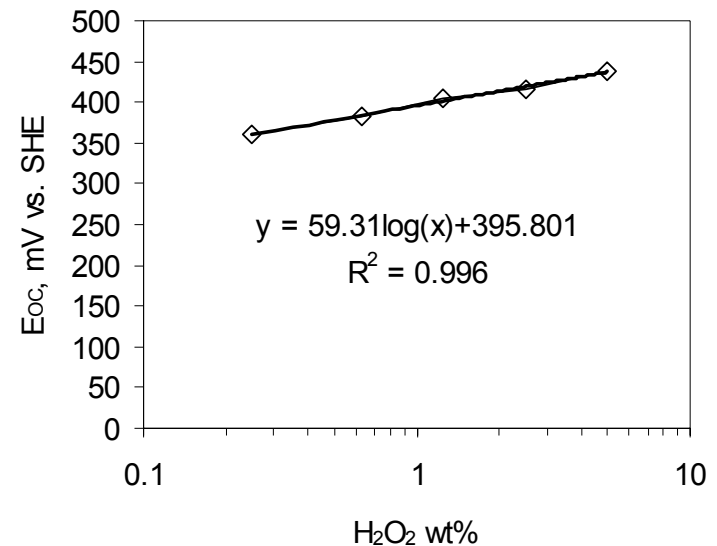
Effect of H$_2$O$_2$ on Open Circuit Potential in Aqueous, 10^{-2} M Glycine

pH 4

$y = 166.03\log(x) + 518.76$

$R^2 = 0.948$

pH 9

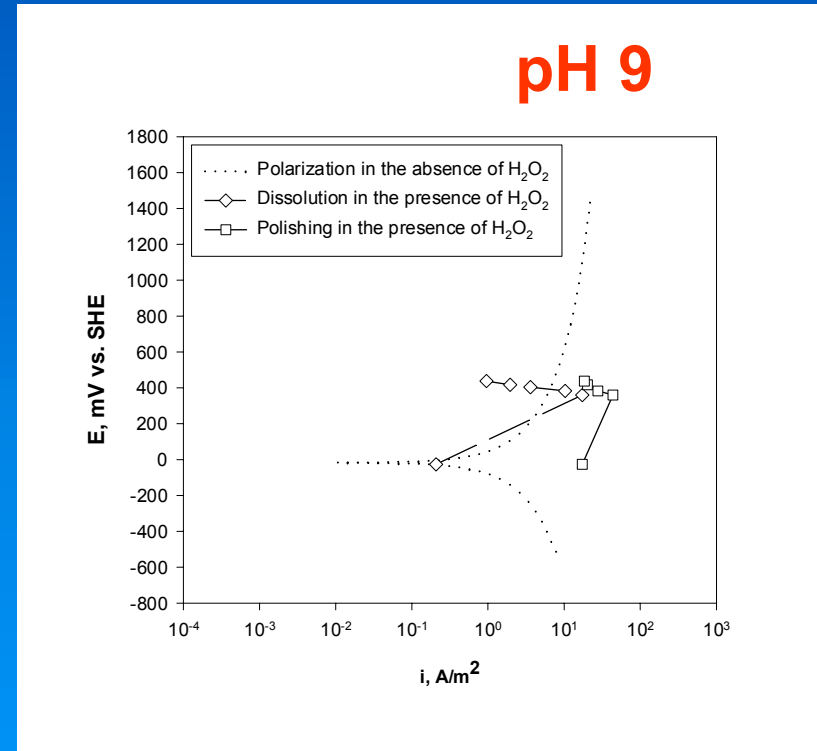
$y = 59.31\log(x) + 395.801$

$R^2 = 0.996$

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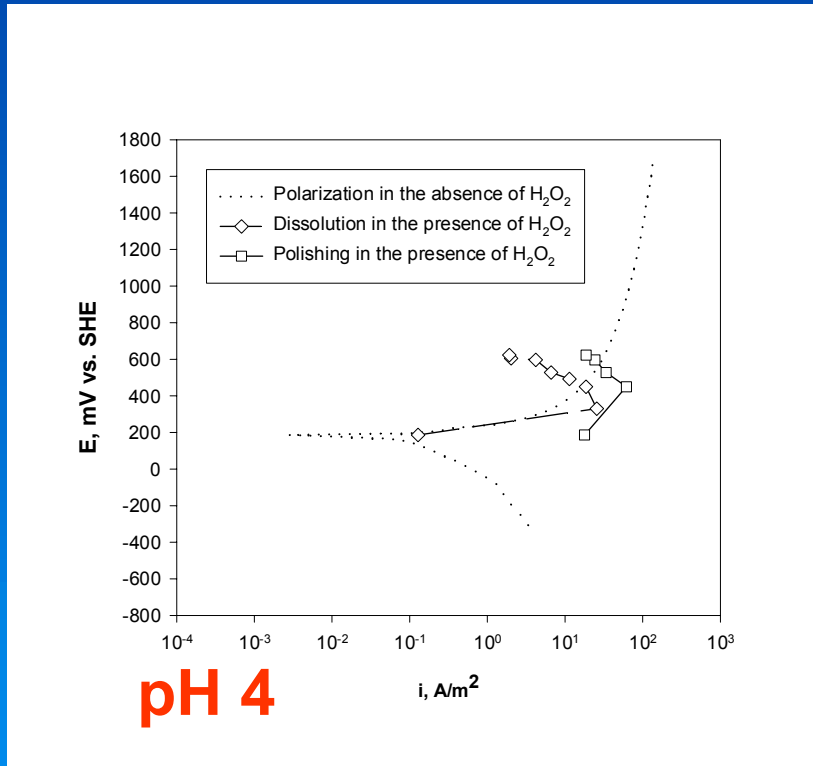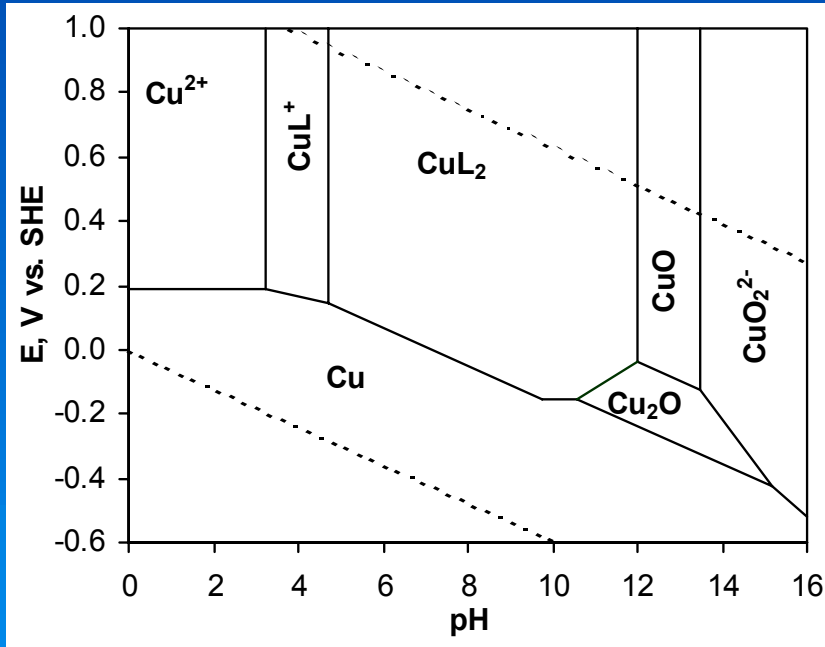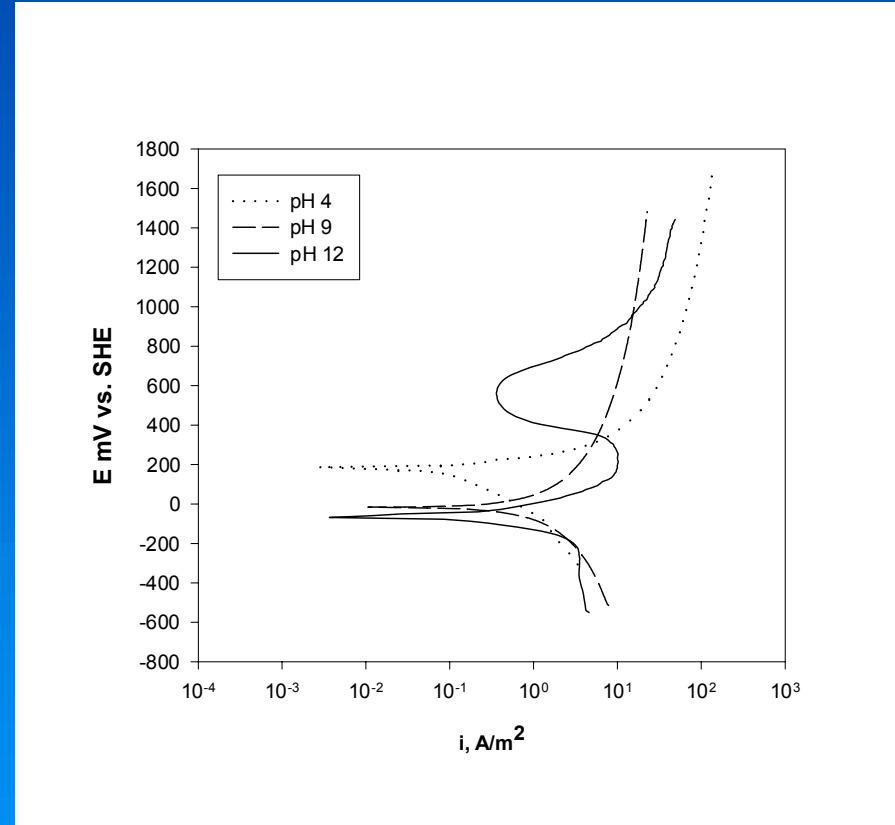# Equivalent Polarization Curves

Polarization Curves in Cu-Glycine-H$_2$O

$\{Cu_T\} = 10^{-5}$, $\{L_T\} = 10^{-2}$

$\{L_T\} = 10^{-2}$

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Formation of Metastable Films

- **Passivation induced by H_2O_2 at moderate concentations cannot be due to colloidal effects altering abrasive-substrate interactions, because this effect is seen for dissolution, in the absence of abrasives**

- **Not due to a thermodynamically stable phase**

- **Cu_2O (*Hernandez, Wrschka, and Oehlein, J. Electrochem. Soc., 148, G389, 2001*)**

- **Cu_2O_3 or CuO_2 (*Pourbaix, 1965*)**

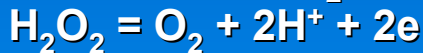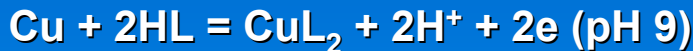# Do the different gradients provide insight into the films forming at pH 4 and pH 9?

- **Dominant cathodic reaction**
  - ◆ $H_2O_2 + 2H^+ + 2e = 2H_2O$

$$E = 1.776 + \frac{0.0591}{2} \log \frac{\{H_2O_2\}\{H^+\}^2}{\{H_2O\}^2} V$$

- **Anodic reactions**

$Cu + HL = CuL^+ + H^+ + 2e$ (at pH 4)
$Cu + 2HL = CuL_2 + 2H^+ + 2e$ (pH 9)
$H_2O_2 = O_2 + 2H^+ + 2e$

$$E = 0.682 + \frac{0.0591}{2} \log \frac{\{O_2\}\{H^+\}^2}{\{H_2O_2\}} V$$

- **The different copper complexation reactions at pH 4 and 9 are likely to yield different films**
- **The kinetics of gas evolution (anodic decomposition of H_2O_2) are strongly substrate dependent**

Cathodic

Net

Potential, V (SHE)

E_{oc}

$H_2O_2 = O_2+2H^++2e$

$Cu+HL=CuL^++H^++2e$

log i
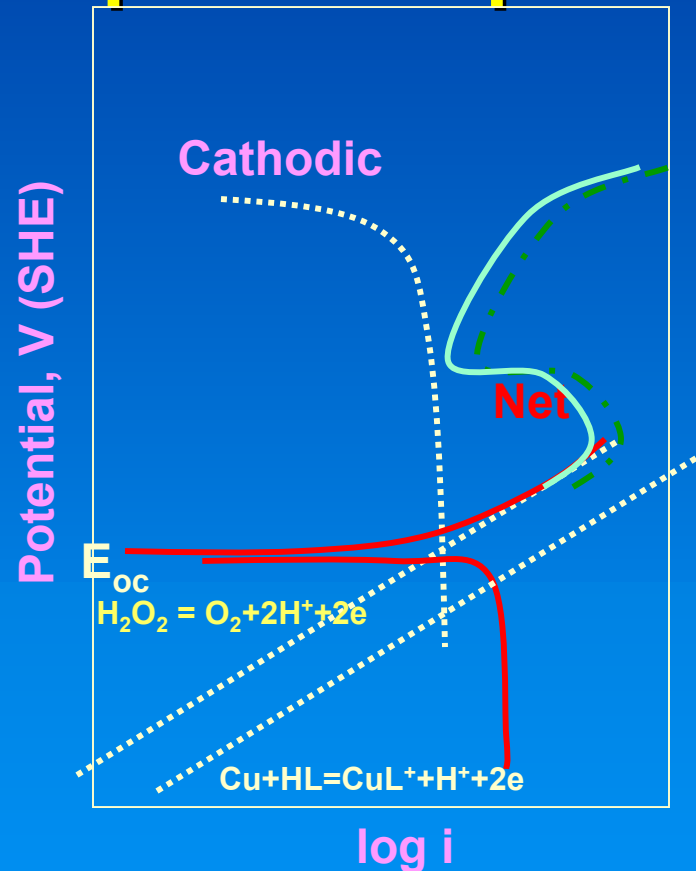
The mixed potential reached in peroxide solutions is expected to be strongly pH dependent

Weight loss and copper release rates
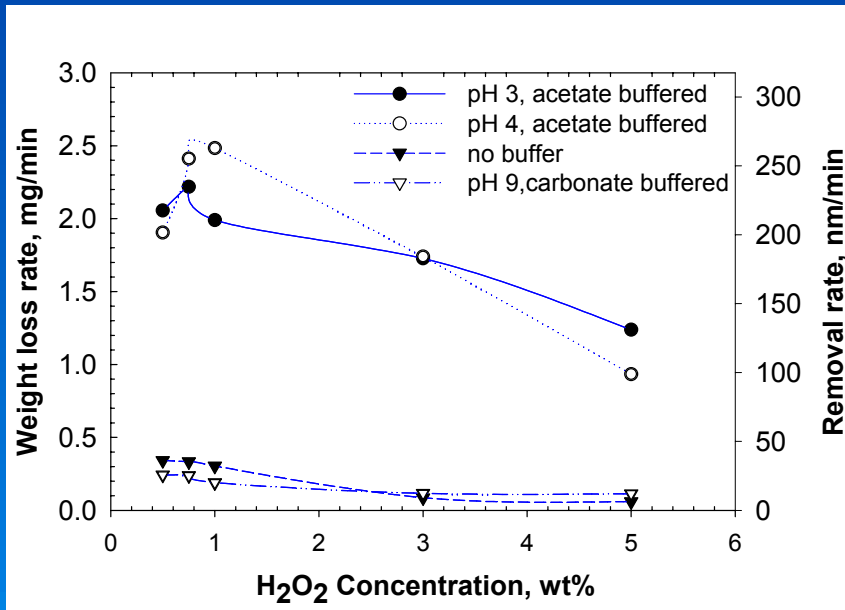
23x23 mm copper coupons

200 ml solution, 10^{-2} M glycine

50 min contact

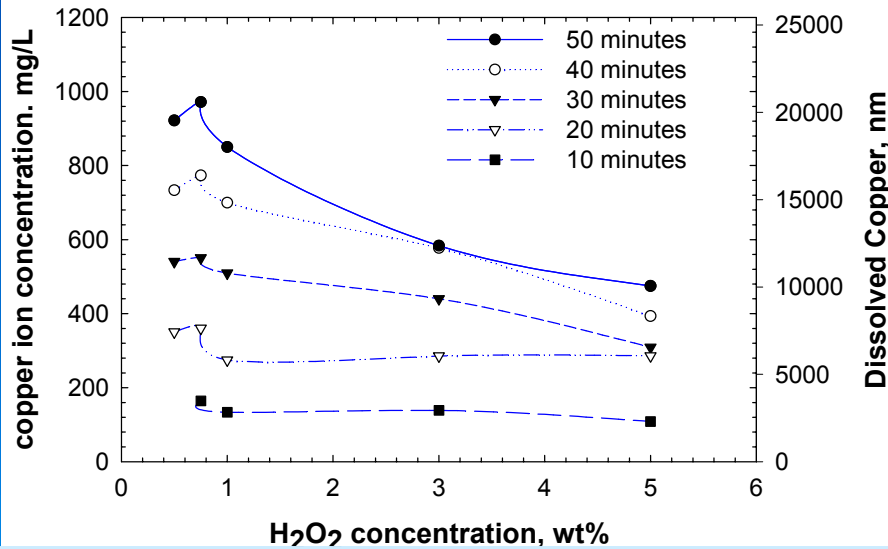Weight loss and copper release rates converted to corrosion rates, nm/min

See that at acidic pH, weight loss measurements suggest lower rate of reaction than do copper concentrations in solution

At higher pH, two measurements fairly consistent

Suggests that surface films formed at low pH contain more oxygen/water/glycine than films formed at high pH

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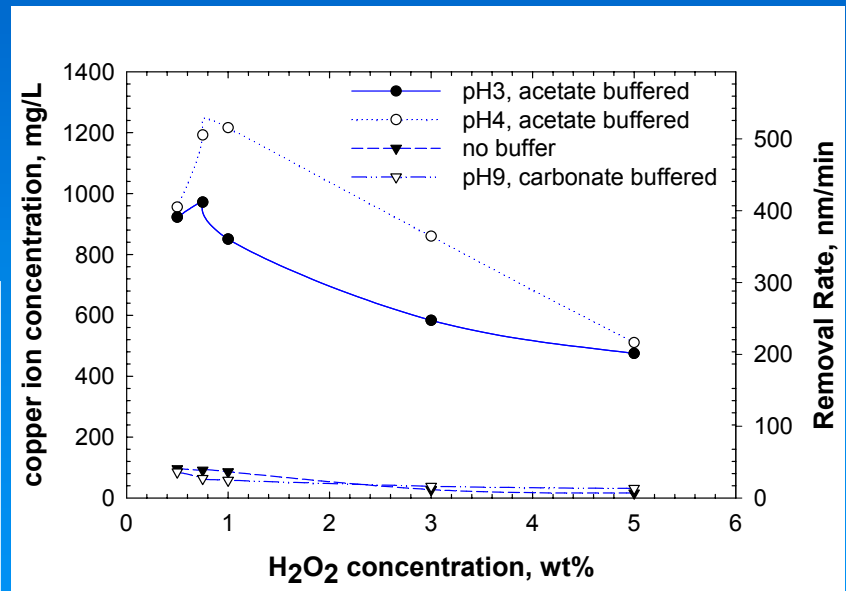
Copper dissolution at pH 3, 10⁻² M glycine

23x23 mm copper coupons

200 ml solution

Samples withdrawn periodically and analyzed for dissolved copper

At 3% and 5% H_2O_2, copper surfaces turn black

At short contact times, dissolution rates insensitive to amount of H_2O_2

After longer contact times, see non-linearity in dissolution rates at high H_2O_2 concentrations
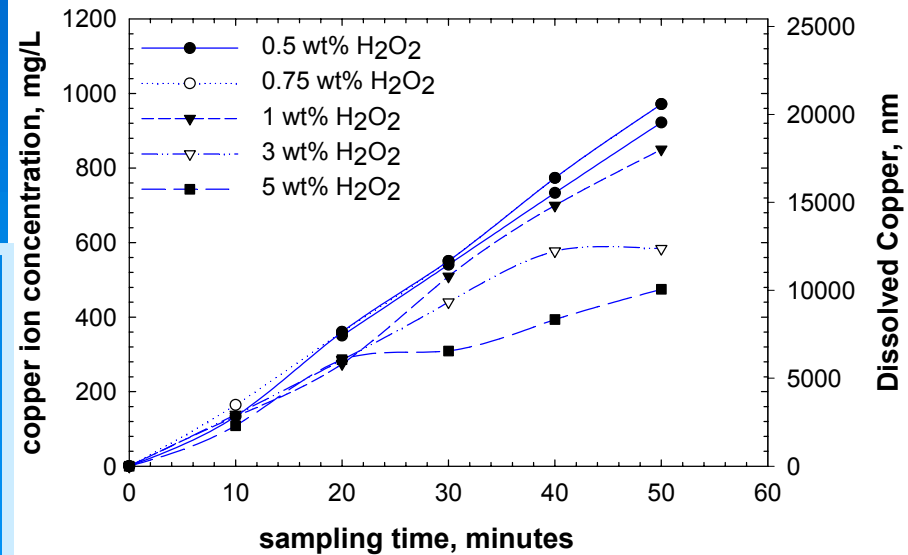
Consistent with progressive thickening of a protective layer, rather than with adsorption of an inhibiting species from solution

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Copper dissolution at pH 4, 10^{-2} M glycine

23x23 mm copper coupons

200 ml solution

Samples withdrawn periodically and analyzed for dissolved copper

At 3% and 5% H_2O_2, copper surfaces turn black

Even at short contact times, dissolution rates more sensitive to amount of H_2O_2

After longer contact times, see more pronounced non-linearity in dissolution rates at modest and high H_2O_2 concentrations

Consistent with progressive thickening of a protective layer, rather than with adsorption of an inhibiting species from solution

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Copper dissolution in 10^{-2} M aqueous glycine (no buffer, pH ~ 4.5)

- 50 minutes
- 40 minutes
- 30 minutes
- 20 minutes
- 10 minutes

concentration of copper ion, mg/L

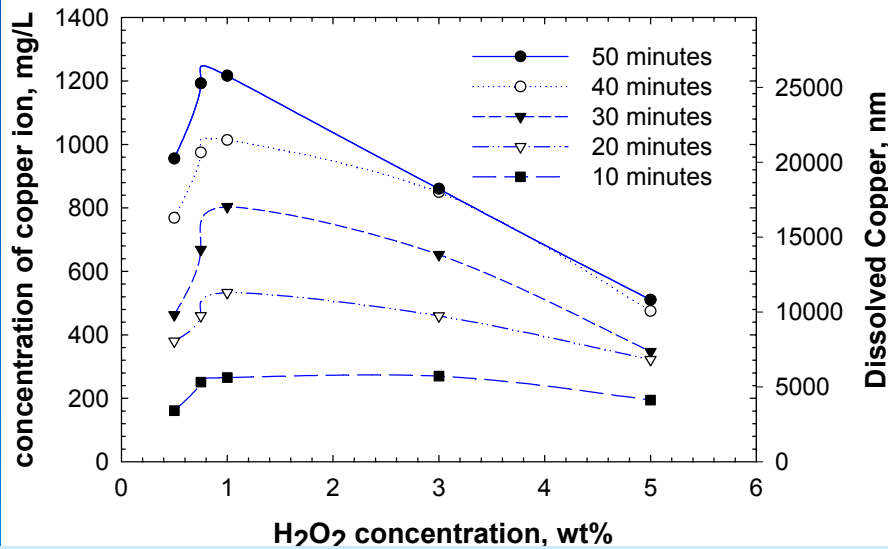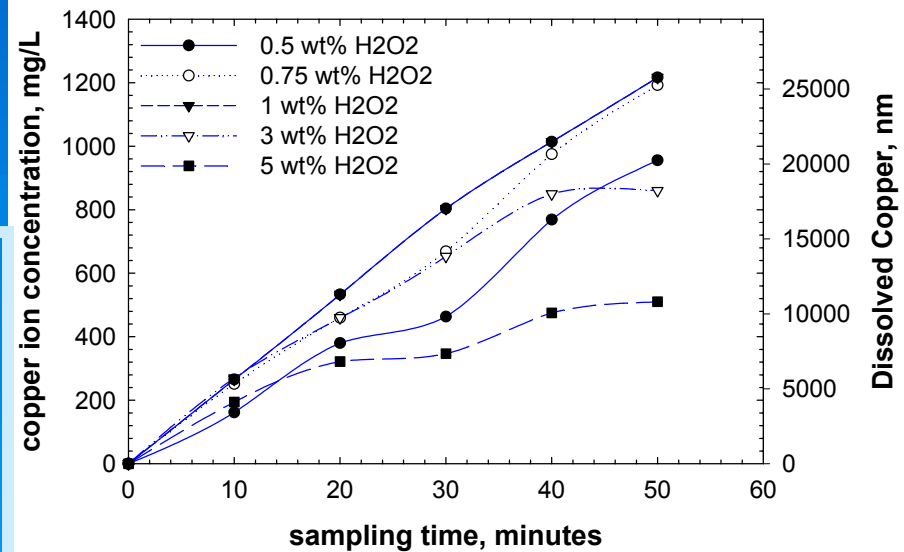Dissolved Copper, nm

H_2O_2 concentration, wt%

23x23 mm copper coupons
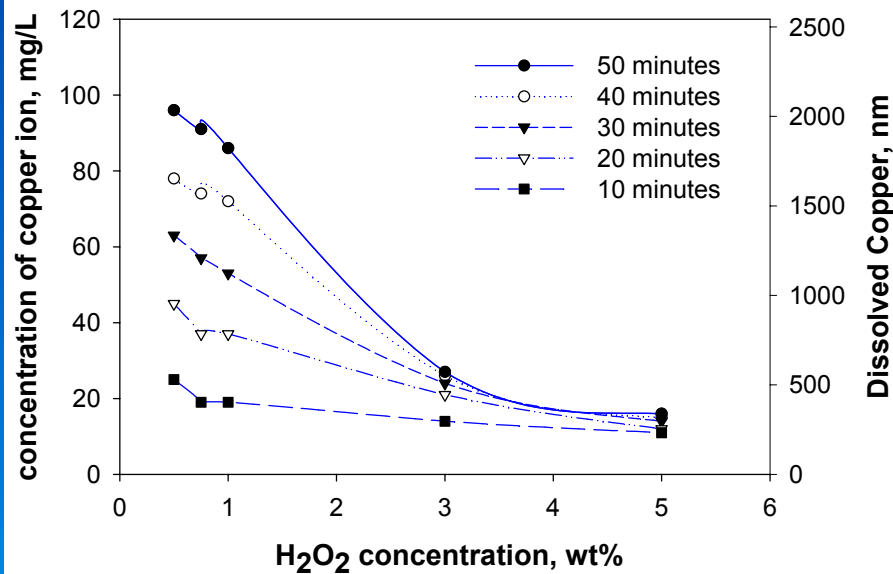
200 ml solution

Samples withdrawn periodically and analyzed for dissolved copper

At 3% and 5% H_2O_2, copper surfaces turn black

- 0.5 wt% H_2O_2
- 0.75 wt% H_2O_2
- 1 wt% H_2O_2
- 3 wt% H_2O_2
- 5 wt%H2O2

copper ion concentration, mg/L

Dissolved Copper, nm

sampling time, minutes

Rates an order of magnitude lower than at pH 3 or 4

Even at short contact times, dissolution rates more sensitive to amount of H_2O_2

After longer contact times, see pronounced suppression of dissolution at high H_2O_2 concentrations

Although films contain less oxygen/water/glycine than those formed at pH 3 or 4, highly protective

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Copper dissolution at pH 9, 10^{-2} M glycine

23x23 mm copper coupons

200 ml solution

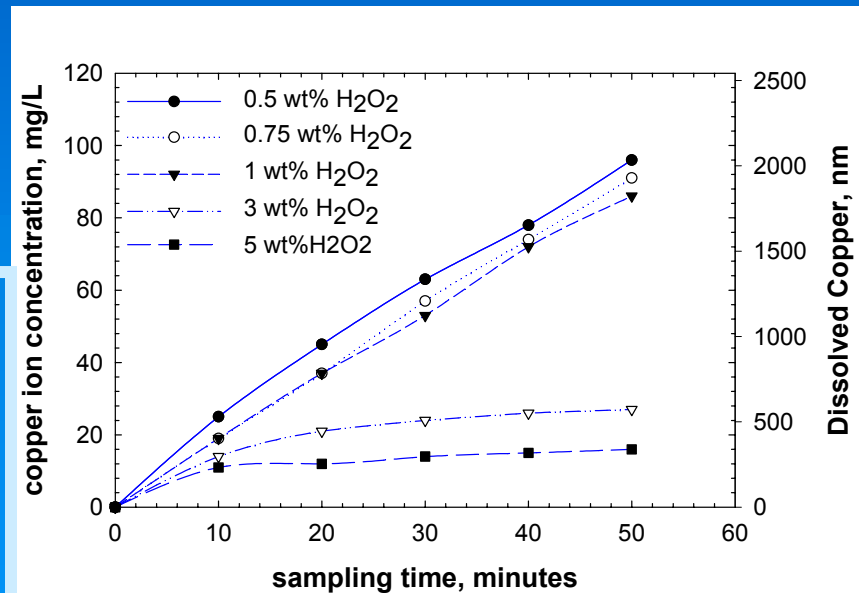Samples withdrawn periodically and analyzed for dissolved copper

Copper surfaces turn black at all H_2O_2 concentrations
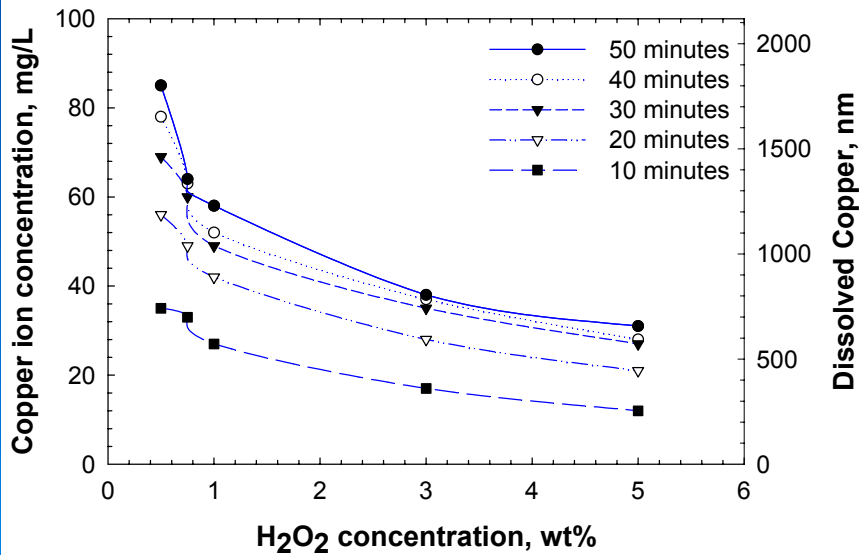
Rates an order of magnitude lower than at pH 3 or 4

Even at short contact times, dissolution rates sensitive to amount of H_2O_2

After longer contact times, see pronounced non-suppression of dissolution at all H_2O_2 concentrations

Although films contain less oxygen/water/glycine than those formed at pH 3 or 4, highly protective

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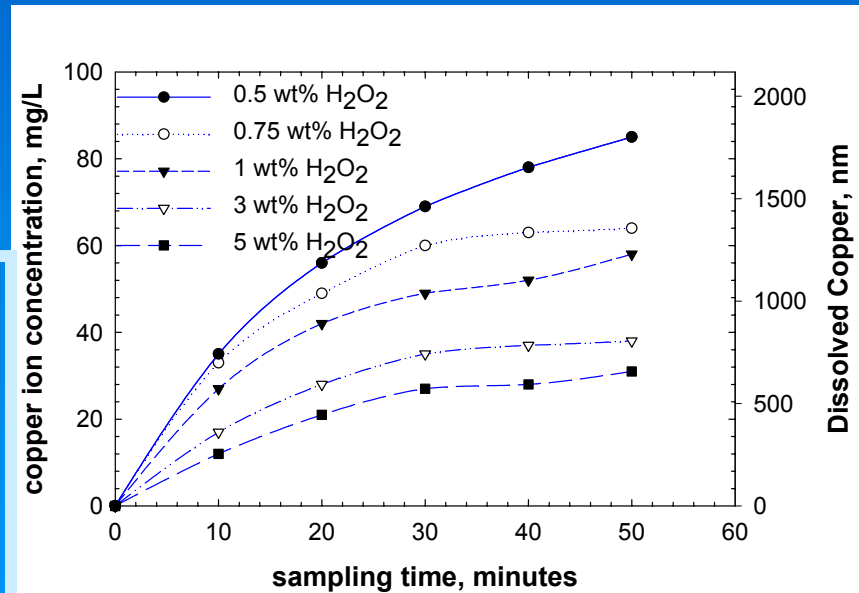
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Conclusions

- **Electrochemistry provides useful, quantitative information on behavior of metals in CMP**
- **However, see that specific oxidants, in this case peroxide, induce unexpected passivation**
- **Mechanism for passivation**
  - **Formation of higher oxides**
  - **Surface perturbation of pH due to peroxide decomposition**
  - **Does not appear to be sorption of inhibiting species**
- **For CMP, this passivation is highly desirable**
  - **Even with passivation, high rates seen at pH 3 and 4 *with acetate buffer*. Possible that acetate plays an active role**
- **Emphasizes the need to couple electrochemical studies with chemical studies**
- **Future work to characterize physical nature of films**