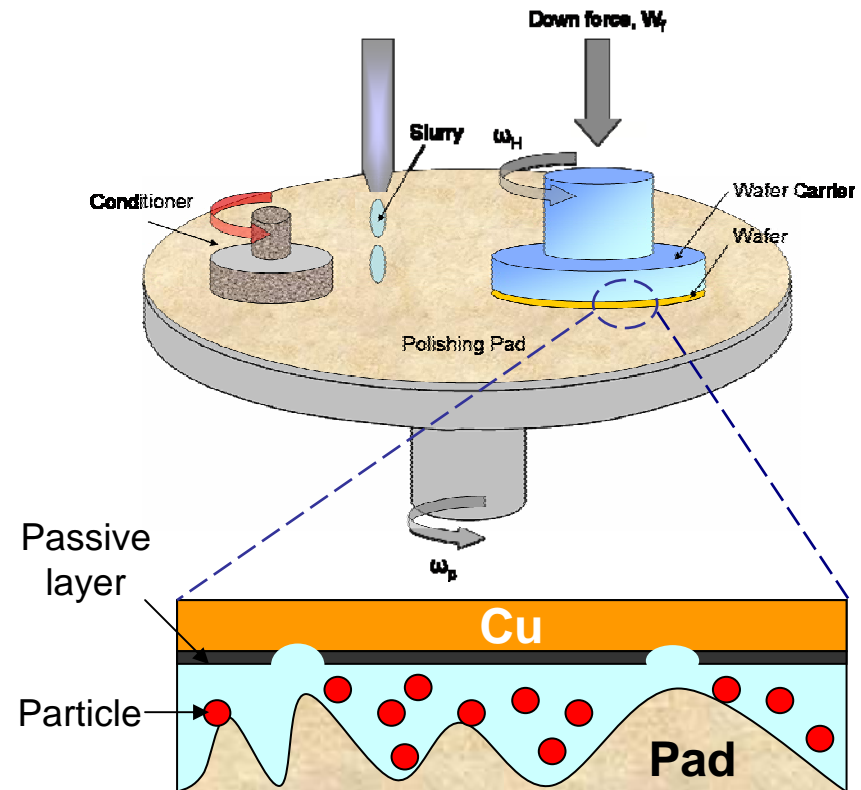# Electrochemical Reactions on Copper Surfaces with Inferences for Wafer Planarization

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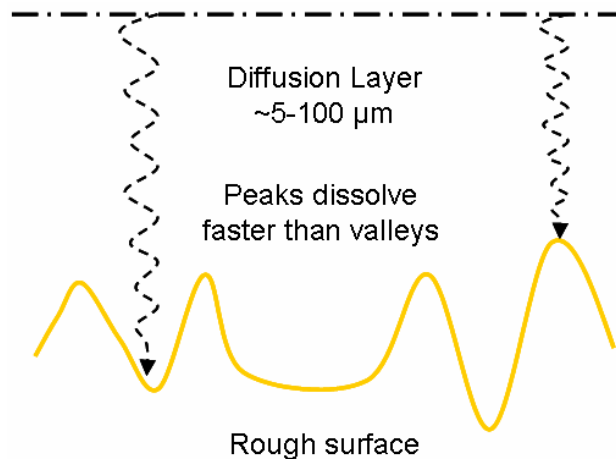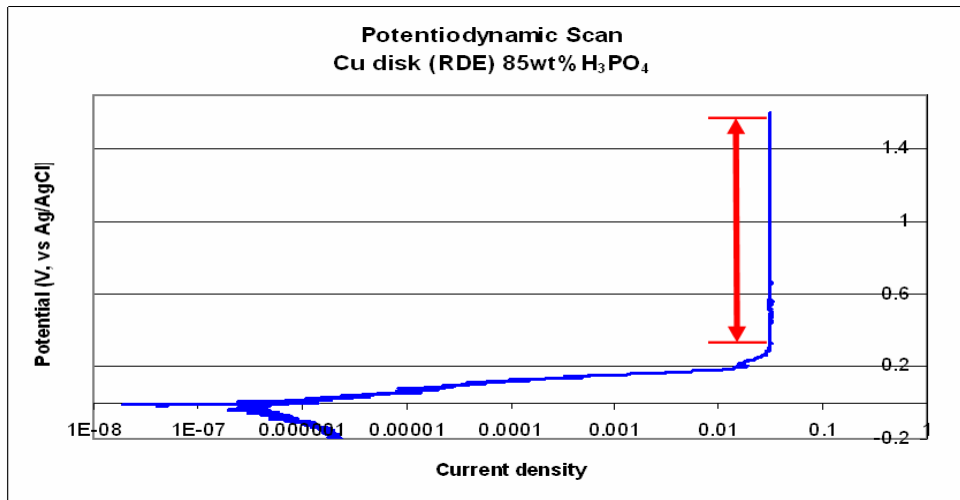
July 26, 2007

THINK **IMPACT**

Chemical Mechanical Planarization (CMP)

- Material removed by
    - Chemical dissolution
    - Mechanical abrasion
- Material removal during CMP
    1. Cu surface passivated in slurry
    2. Passivation layer and Cu scratched by particles and pad asperities
    3. Fresh Cu surface exposed
    4. Cu dissolved until passivation layer forms
    5. Concern: Cu mechanically weak – CMP can damage

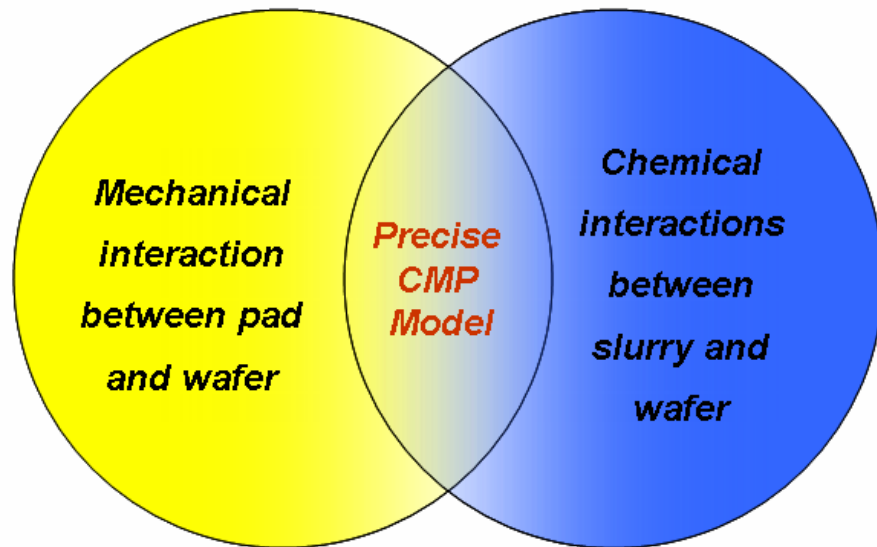# Electropolishing (EP) and Electrochemical CMP (ECMP)

Potentiodynamic Scan
Cu disk (RDE) 85wt% H_3PO_4

Potential [V. vs Ag/AgCl]

Current density

Diffusion Layer
~5-100 µm

Peaks dissolve
faster than valleys

Rough surface

- EP occurs in mass transfer controlled region

  $\rightarrow$ *limiting-current plateau* region

- Material removal in EP
  - Macrosmoothing (leveling)
  - Microsmoothing (brightening)
- ECMP
  - Combines EP, CMP
  - Addresses mechanical weakness of Cu
  - Potential is applied
    - Drives dissolution
- Reduces need for abrasion

Picture adapted from Alan West, SRC/SEMATECH ERC Tele-Seminar on 7/13/06

THINK **IMPACT**

Objectives

Mechanical interaction between pad and wafer — Precise CMP Model — Chemical interactions between slurry and wafer

- **Develop precise CMP model**
  - Allows optimization of CMP
  - Allows development of benign processes

- Mechanical interactions
  - Pad, carrier, fluid mechanics

- **Chemical interactions**
  - Surface film formation in slurry
  - Surface repassivation and dissolution
    - Electrochemical oscillations

- Slurry particle interactions with surface films

THINK **IMPACT**

Behavior of Cu in Aqueous H_3PO_4
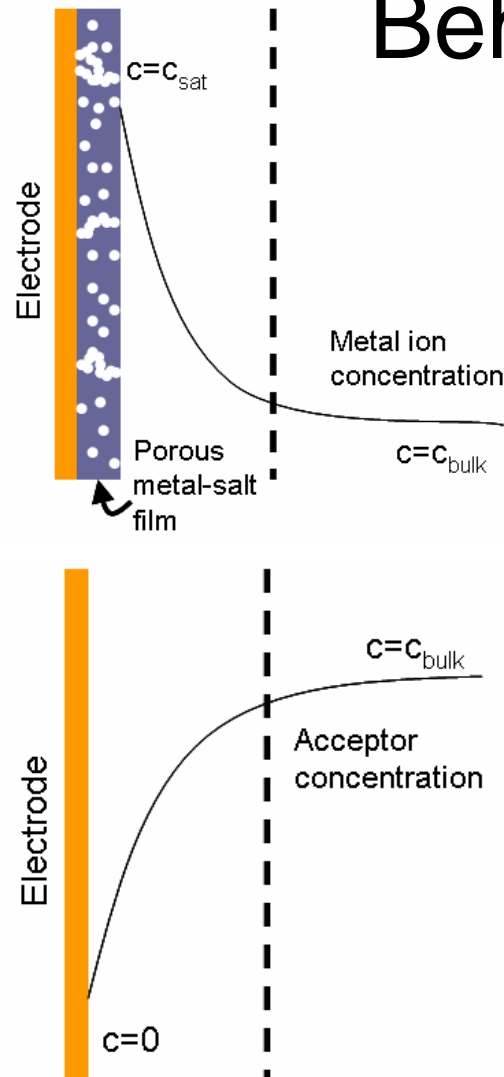
- **Nature of surface film under mass transfer control is controversial**
  - Salt film mechanism[1,2]
    - Dissolved metal ions
  - Acceptor mechanism[3,4,5]
    - Acceptors for metal ions come from bulk

- **Recent apparent agreement on acceptor mechanism in Cu-H_3PO_4 system[5]**
  - Acceptor for Cu^{2+} in H_3PO_4: Water
  - No surface film

1: Elmore, J. App. Phy. 10, p.724, 1939
2: Chang *et al.* J. Vac. Sci. Tech. B, 20(5), 2002
3: Edwards, J. Electrochem. Soc., 100(7), p.C189,1953
4: West *et al.*, J. Electrochem. Soc., 142(8), p.2689, 1995
5: Van Gils *et al.*, J. Electrochem. Soc., 154(3), p.C175, 2007

THINK **IMPACT**

Benzotriazole (BTA) and Copper

- Cu in low pH slurry
  - No native passivation layer
  - Corrosion inhibitor used
- BTA
  - Most used corrosion inhibitor
- Cu-BTA film proven
  - AFM friction study[1]
- BTA adsorption on Cu(I) at the "surface"[2]
- BTA can chelate Cu(II) in the "solution"[3]
- Inhibitory efficiency[4]
  - At pH=6, maximum efficiency
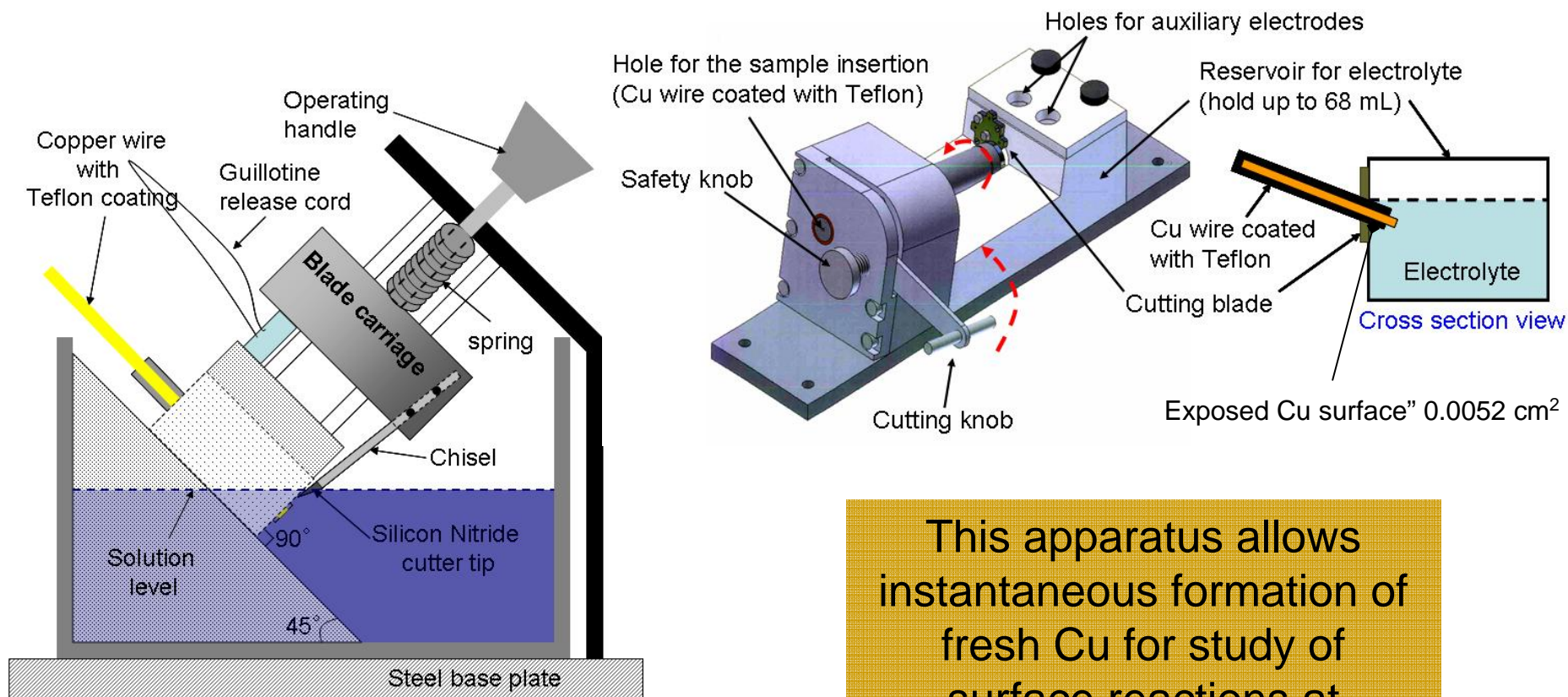 - Lower efficiency in acidic solutions
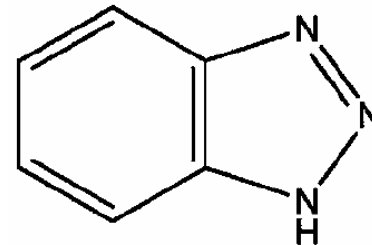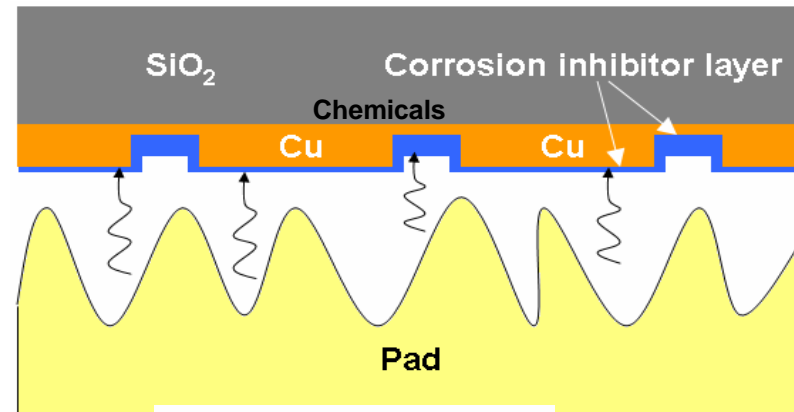
Benzotriazole

1: Lim *et al.*, Trib. Lett., 14(4), p. 261, 2002
2: Fang *et al.*, J. Electrochem. Soc., 153(1), p. G44, 2006
3: Richardson *et al.*, Dalt. Trans., 5, p.992, 2003
4: Notoya *et al.*, Proceedings (vol. 6, paper#:C076) Corrosion Science in the 21st century, 2003

THINK **IMPACT**

Guillotined Electrode

Copper wire with Teflon coating

Operating handle

Guillotine release cord

Blade carriage

spring

Chisel

Silicon Nitride cutter tip

>90°

Solution level

45°

Steel base plate

Hole for the sample insertion (Cu wire coated with Teflon)

Holes for auxiliary electrodes

Reservoir for electrolyte (hold up to 68 mL)

Safety knob

Cu wire coated with Teflon

Cutting blade

Electrolyte

Cross section view

Cutting knob

Exposed Cu surface" 0.0052 cm^2

This apparatus allows instantaneous formation of fresh Cu for study of surface reactions at different slurry conditions

Picture adapted from Burstein *et al*.
J. Elec. Soc. 148 (&) B282-B287,2001

THINK **IMPACT**

Electrochemical Impedance Spectroscopy

- Impedance
  - Generalized complex resistance
- EIS
  - Apply DC potential while superimposing small AC potential
  - Analyze resulting current
- Nyquist plot
  - Z' (Real part) *vs.* Z" (Imaginary part)
  - 100 mHz~100 kHz
  - No explicit frequency information
- Bode plot
  - Log ω vs. log |Z|

$$\omega_{max}=1/(R_pC_{dl})$$

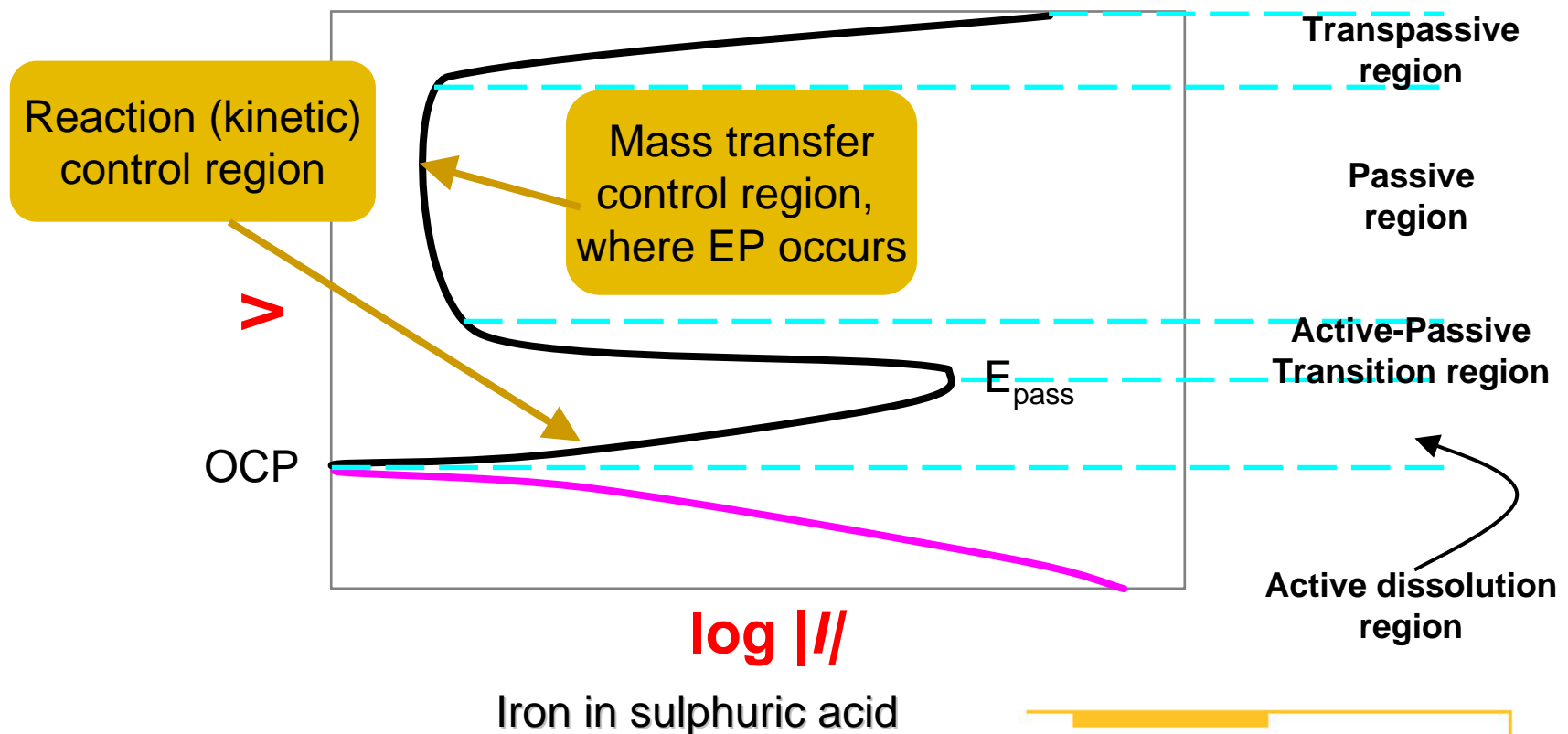Nyquist Plot

Bode Plot
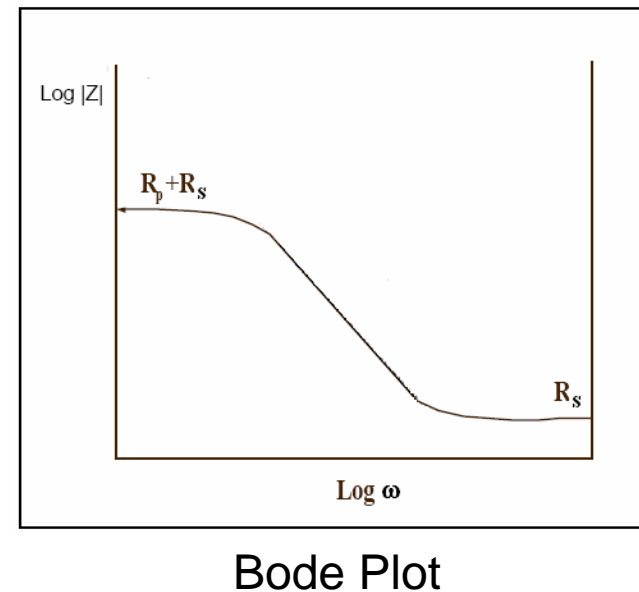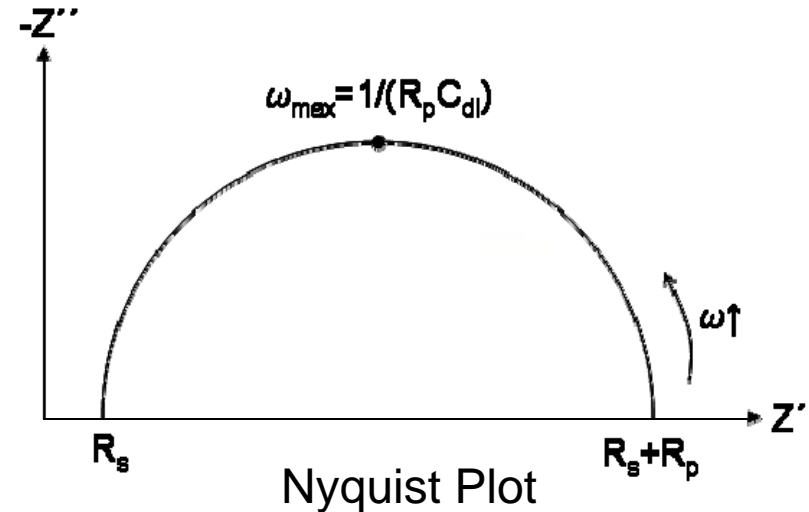
Surface Film Formation
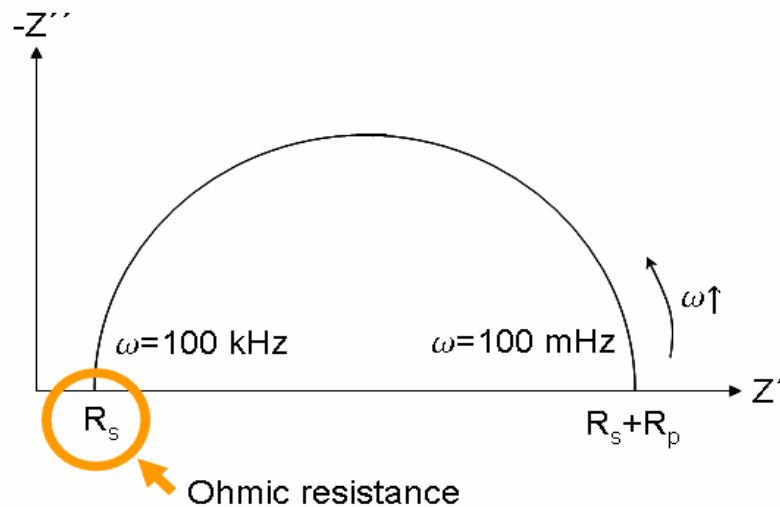
- Info from Nyquist plot
  - $R_s = R_m + R_e + R_f$ — **Constant**
  - R_p

- R_f is the resistance of the porous/viscous film

- Increase in R_s (Impedance measurement at 100 kHz)
  $\rightarrow$ **Formation of *porous or viscous liquid* layer**

- Resistance of compact solid film can be detected by changes in R_p

THINK **IMPACT**

Potentiodynamic (PD) Scan

- When a compact passive film is formed, this causes a drop in current
 - Due to the resistance of the film and its effect as a barrier to charge transfer

Reaction (kinetic) control region

Mass transfer control region, where EP occurs

Transpassive region

Passive region

Active-Passive Transition region

E_{pass}

OCP

Active dissolution region

log |I/

Iron in sulphuric acid

Systems and Conditions

- Sample
  - Teflon coated Cu wire (0.0052 cm^2)

- Systems
  - For surface film study

    1) Cu - 14 M H_3PO_4
    2) Cu - 1 wt% HNO_3
    3) Cu - 1 wt% HNO_3+ 0.02M BTA
    4) Cu - 1 wt% HNO_3+ 0.02M BTA+5 wt% H_2O_2

PTFE

Cu

- Ag/AgCl reference electrode (0.197 V *vs.* SHE)

- Superimposed AC: 5 mV

THINK **IMPACT**
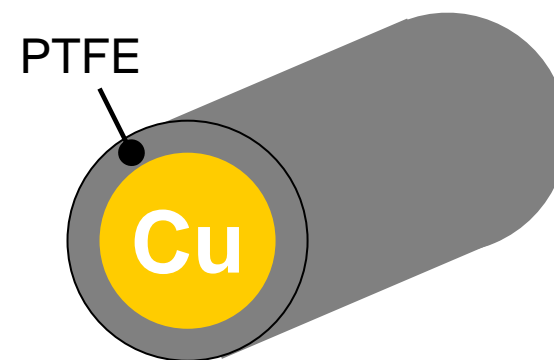
Experiments

- PD scans
  - Active/passive behavior
- |Z| *vs.* time
  - DC potential selection for |Z| measurements
    - OCP, E_{pass}, and potentials from active/passive region in a PD scan
    - DC potential holds the system at the corresponding potential (region)

- Record |Z|(t) at 100 kHz (R_s) for each system after guillotining (cutting) the Cu wire

Potentiodynamic Scan
System I
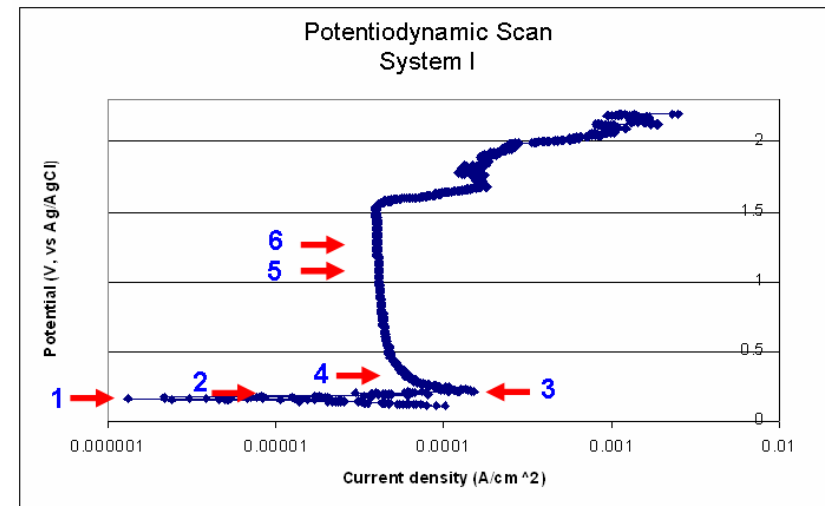
System (1): Cu - 14 M H₃PO₄

Potentiodynamic Scan
System I
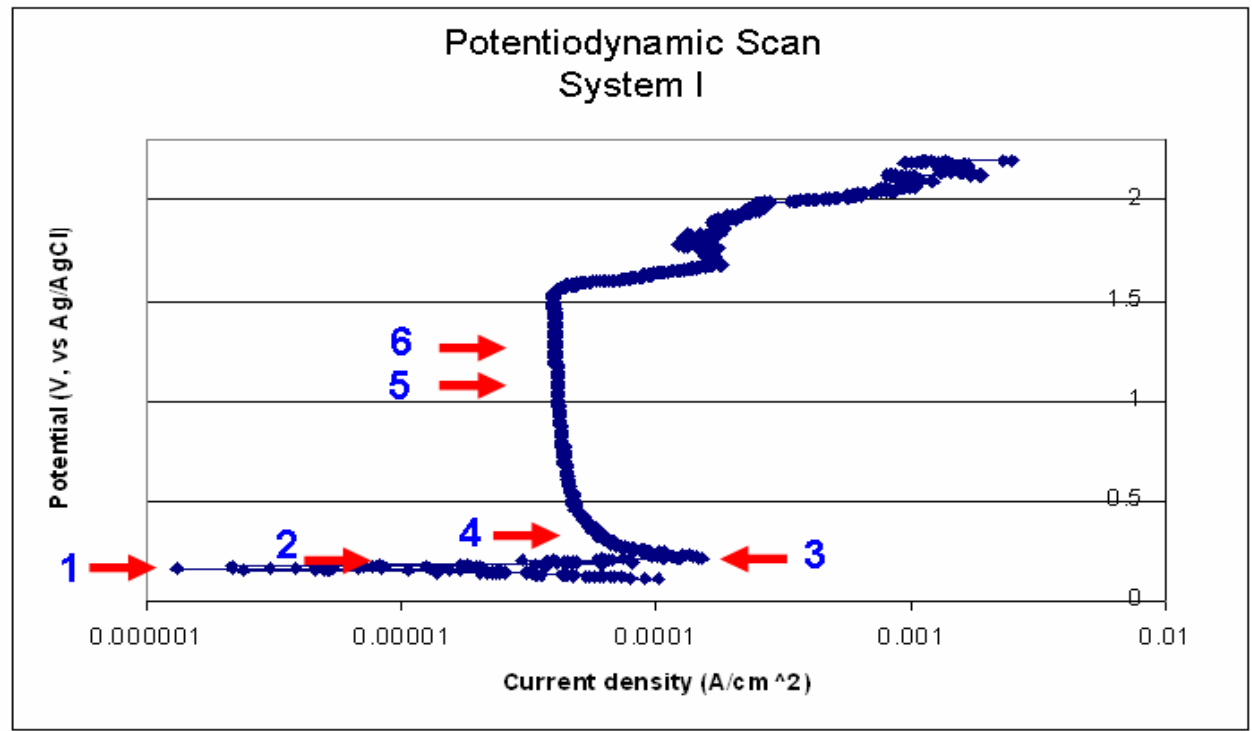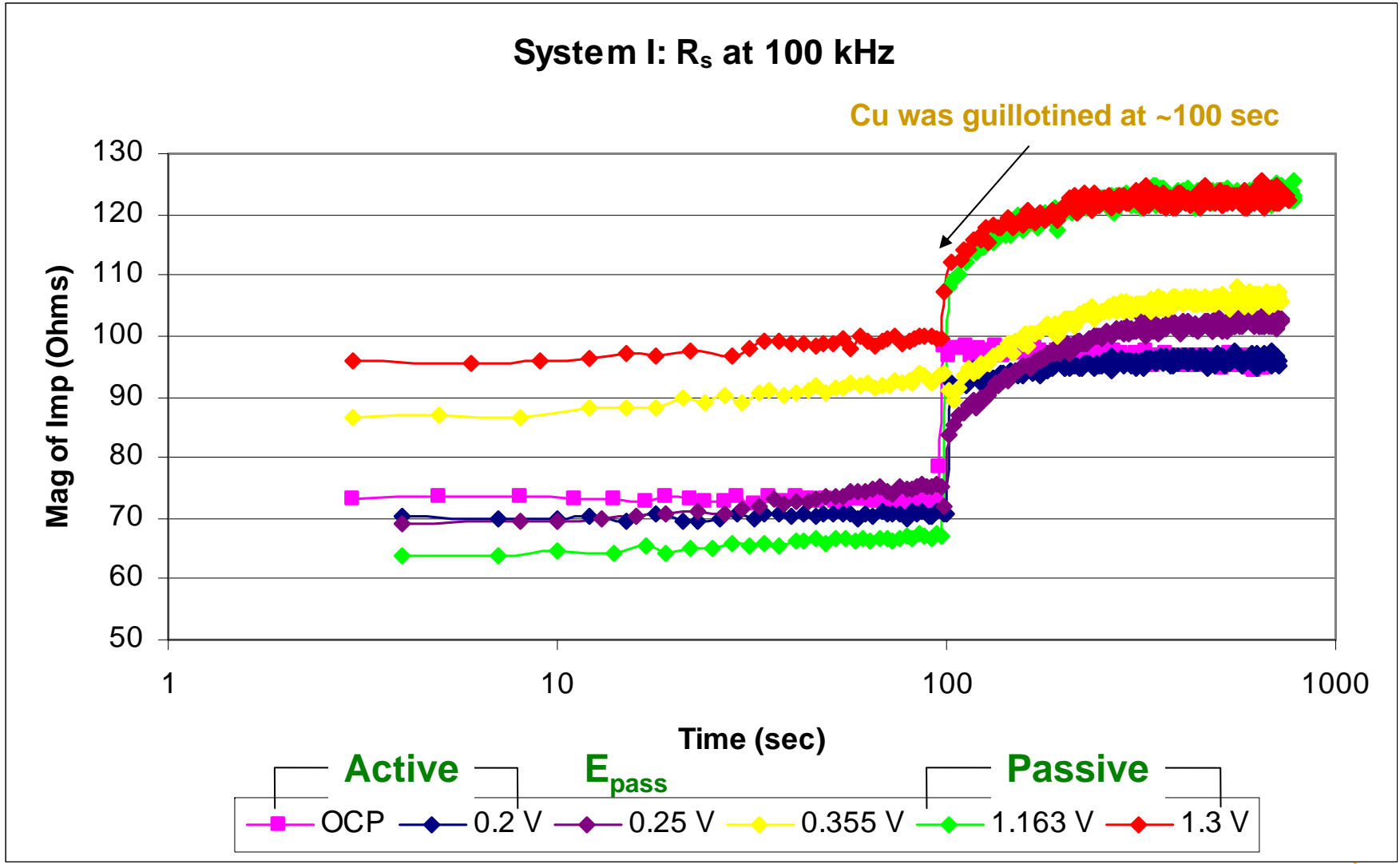
1: OCP(~0.17V), 2: 0.2 V, 3: 0.25 V, 4: 0.355 V, 5: 1.163 V, 6: 1.3 V
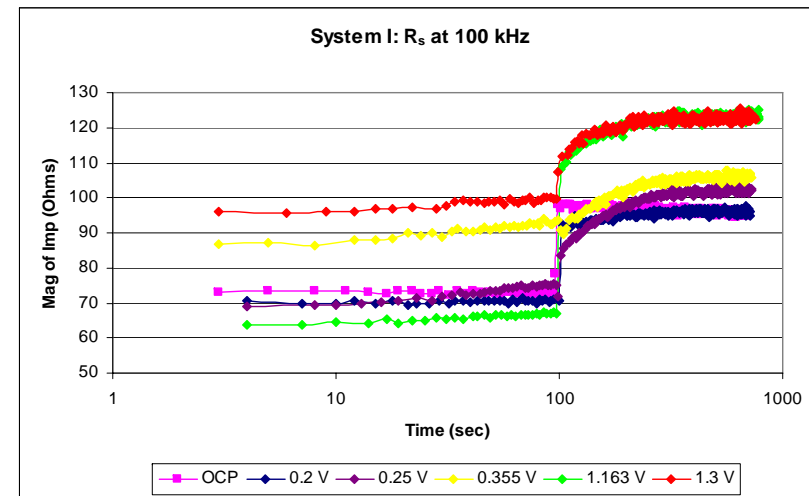
Surface Film Formation
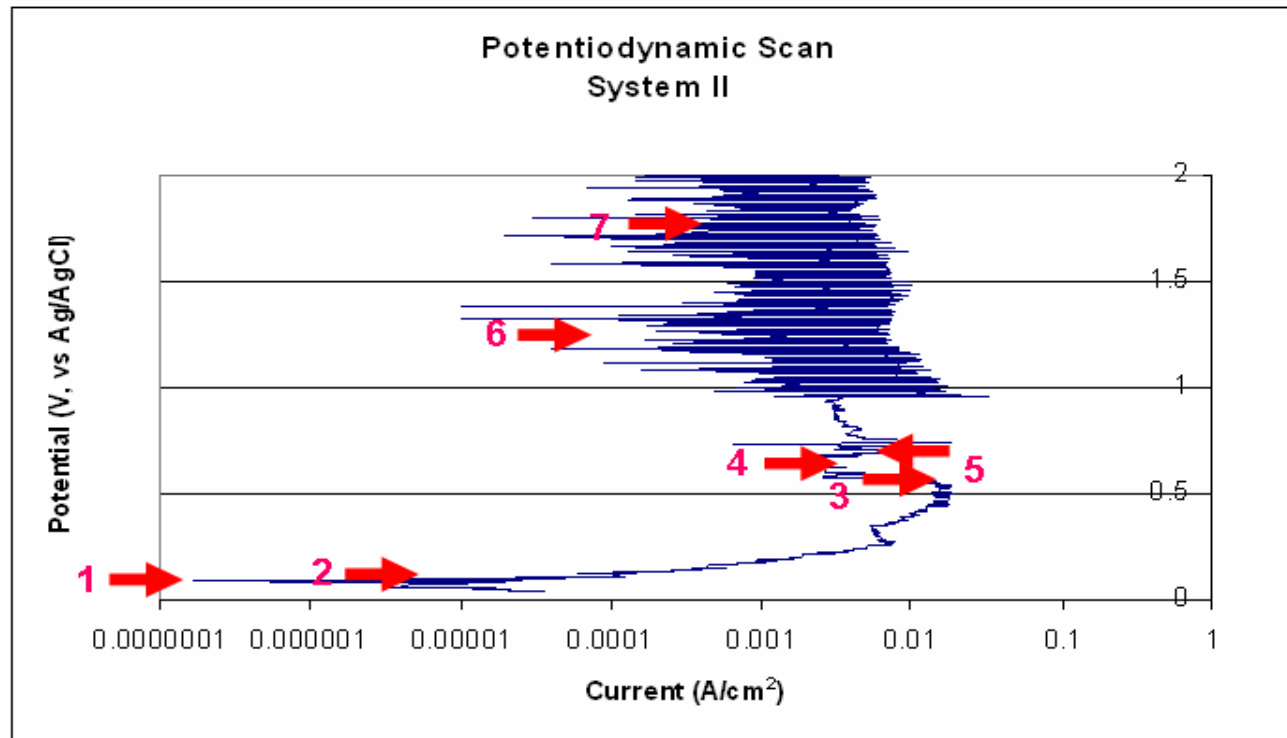
Interpretation

- Active dissolution region
  - Constant R_s
  - No porous/viscous liquid film growth

- Above E_{pass}
  - Increases in R_s to plateau
  - Viscous layer formation
    - High concentration of Cu ions and its salt
    - Viscosity increases due to the depletion of water at the surface (water acceptor)

System I: R_s at 100 kHz

Mag of Imp (Ohms) vs Time (sec)

OCP — 0.2 V — 0.25 V — 0.355 V — 1.163 V — 1.3 V

- ❖ In mass transfer control region (EP)
  - ❑ Steady state values are same
    - ❑ Consistent with literature
      - ➢ No physical film formation
      - ➢ No explanation of transient
  - ❑ This is first data showing viscous film formation in Cu-H_3PO_4 under the mass transfer control region
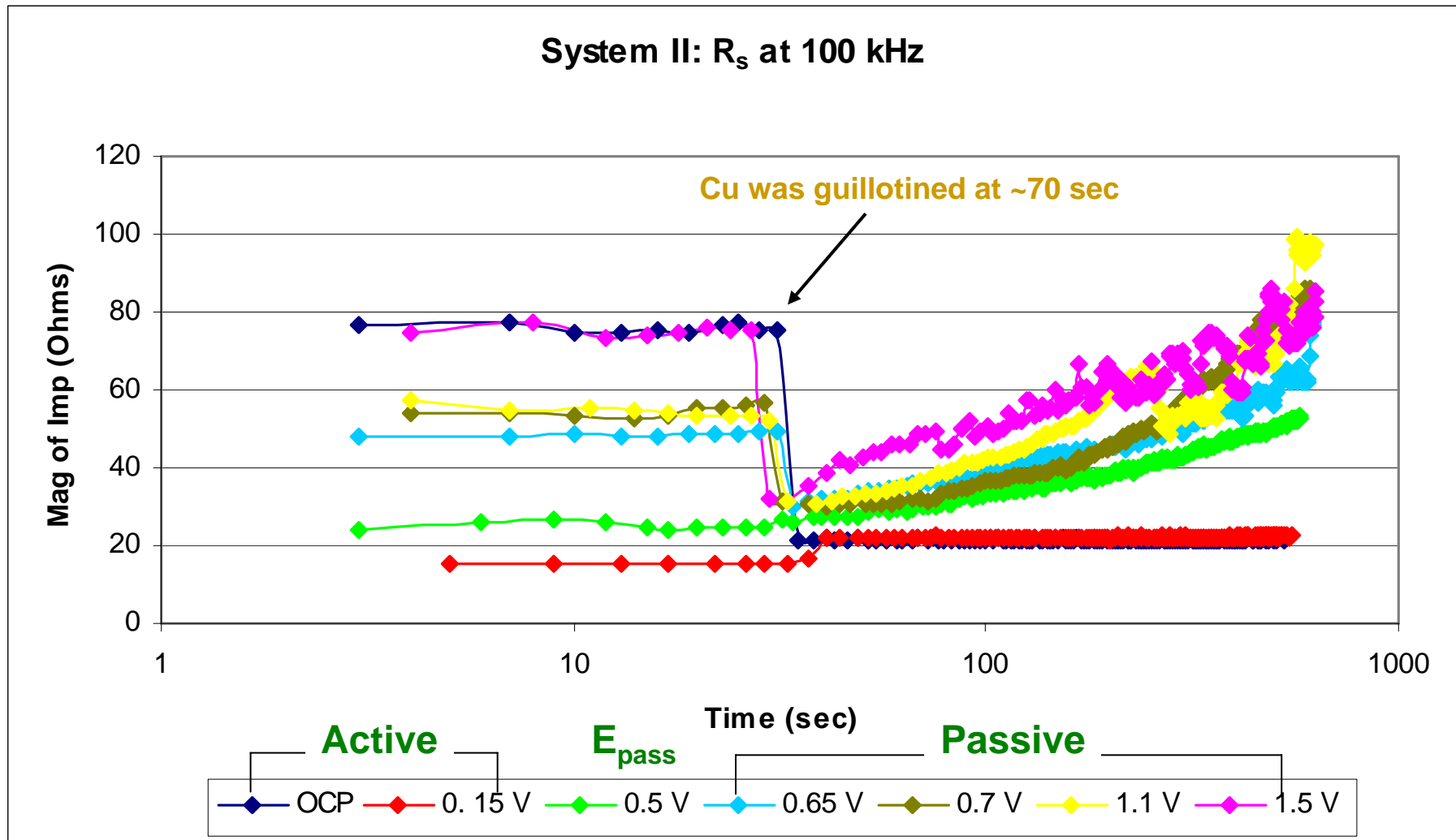
System (2): Cu - 1 wt% HNO$_3$

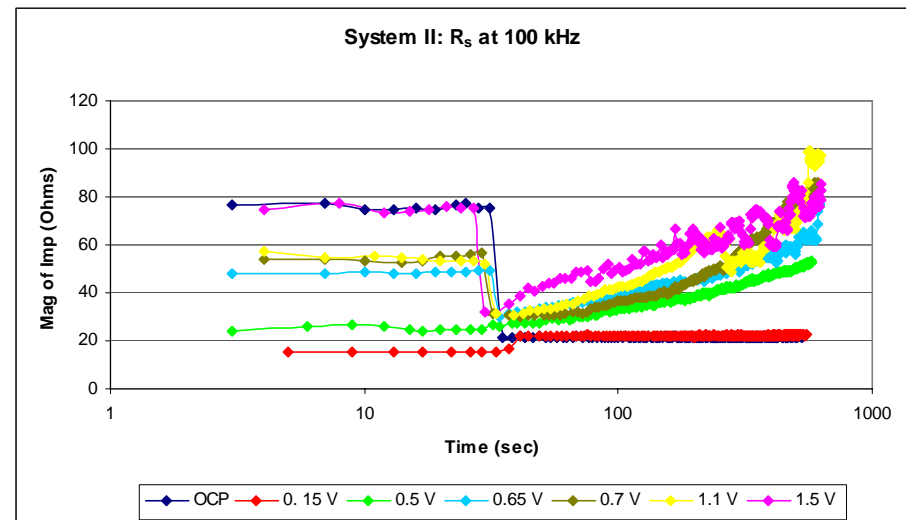1: OCP (~0.088 V), 2: 0.15 V, 3: 0.5 V, 4: 0.65 V, 5: 0.7 V, 6: 1.1 V, 7: 1.5 V

Surface Film Formation

Interpretation

- Active dissolution region
  - Constant R_s
  - No porous/viscous liquid film growth $\rightarrow$ Consistent with the literature

- Above E_{pass}
  - Increases in R_s
  - Pourbaix diagram $\rightarrow$ unstable oxide form
  - Higher potential
    - Fluctuation in R_s
    - Film formation and breakage
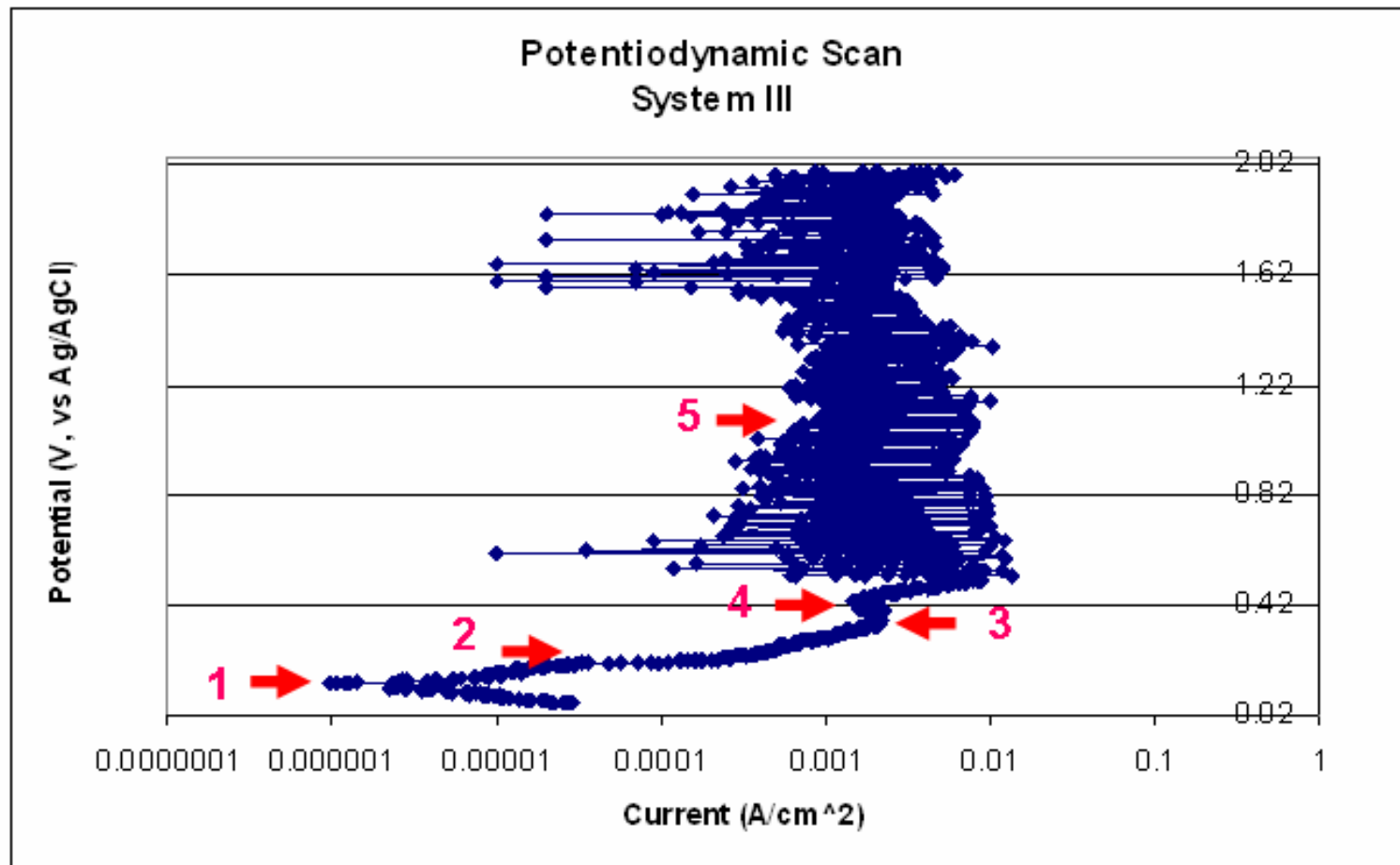

System II: R_s at 100 kHz

- Hypothesis
  - Transient copper oxide film
  - Viscous film (Cu^{2+} and its salt (water and/or NO_3^-))
  - Formation of complex
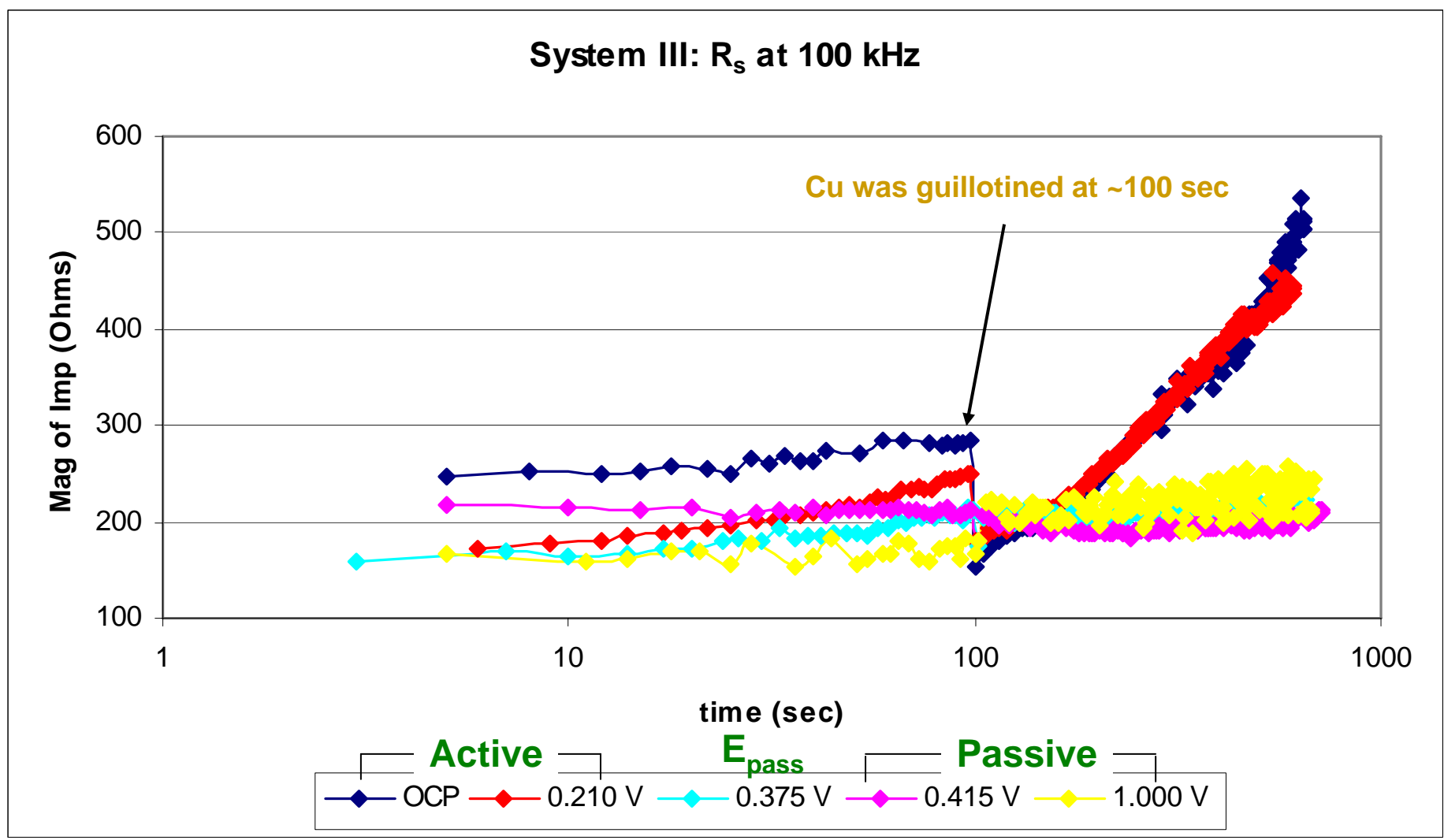   - Viscous liquid film

System (3): Cu - 1 wt% HNO$_3$+ 0.02 M BTA

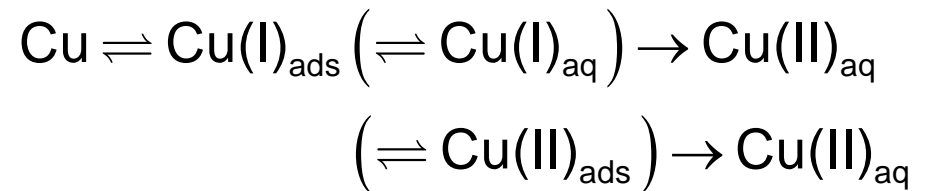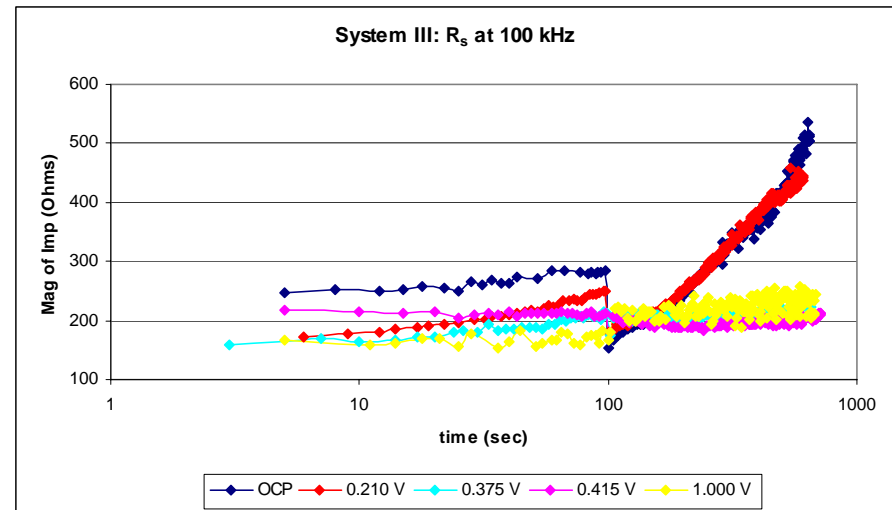1 : OCP (~0.140 V), 2: 0.21 V, 3: 0.375 V, 4: 0.415 V, 5: 1.0 V

Surface Film Formation

Interpretation

- **Active region**
  - Increases in R_s
    - Formation and precipitation of the complexes between Cu(II) and BTA, water, and nitrate
    - $\rightarrow$ Porous/Viscous film
    - Porous Cu(I)-BTA film

- **Passive region**
  - Constant R_s
    - No porous/viscous film
  - Dense Cu(I)-BTA film (not detectable by R_s, but R_p)
    - Increases in the availability of Cu(I) on the surface due to suppression of Cu dissolution

System III: R_s at 100 kHz

Legend: OCP — 0.210 V — 0.375 V — 0.415 V — 1.000 V

$$Cu \rightleftharpoons Cu(I)_{ads} \left(\rightleftharpoons Cu(I)_{aq} \right) \rightarrow Cu(II)_{aq}$$

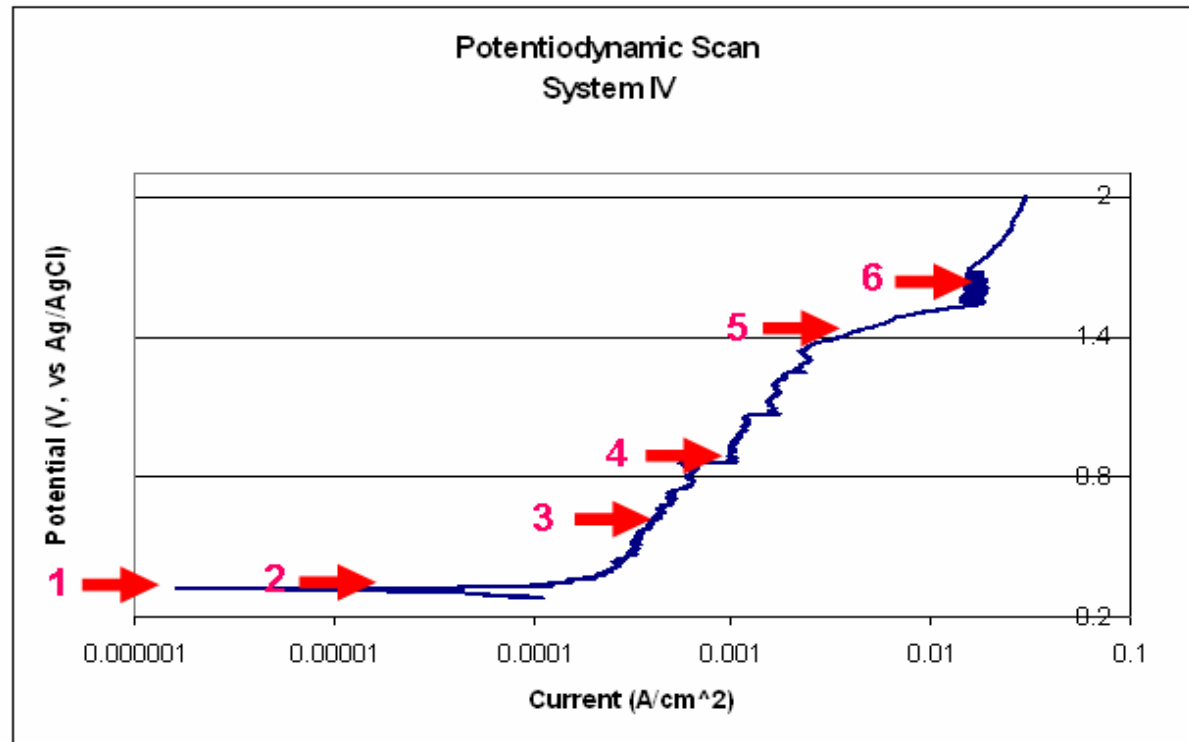$$\left(\rightleftharpoons Cu(II)_{ads} \right) \rightarrow Cu(II)_{aq}$$

$\rightarrow Cu(II)_{ads}$ is an intermediate and formed for the dissolution
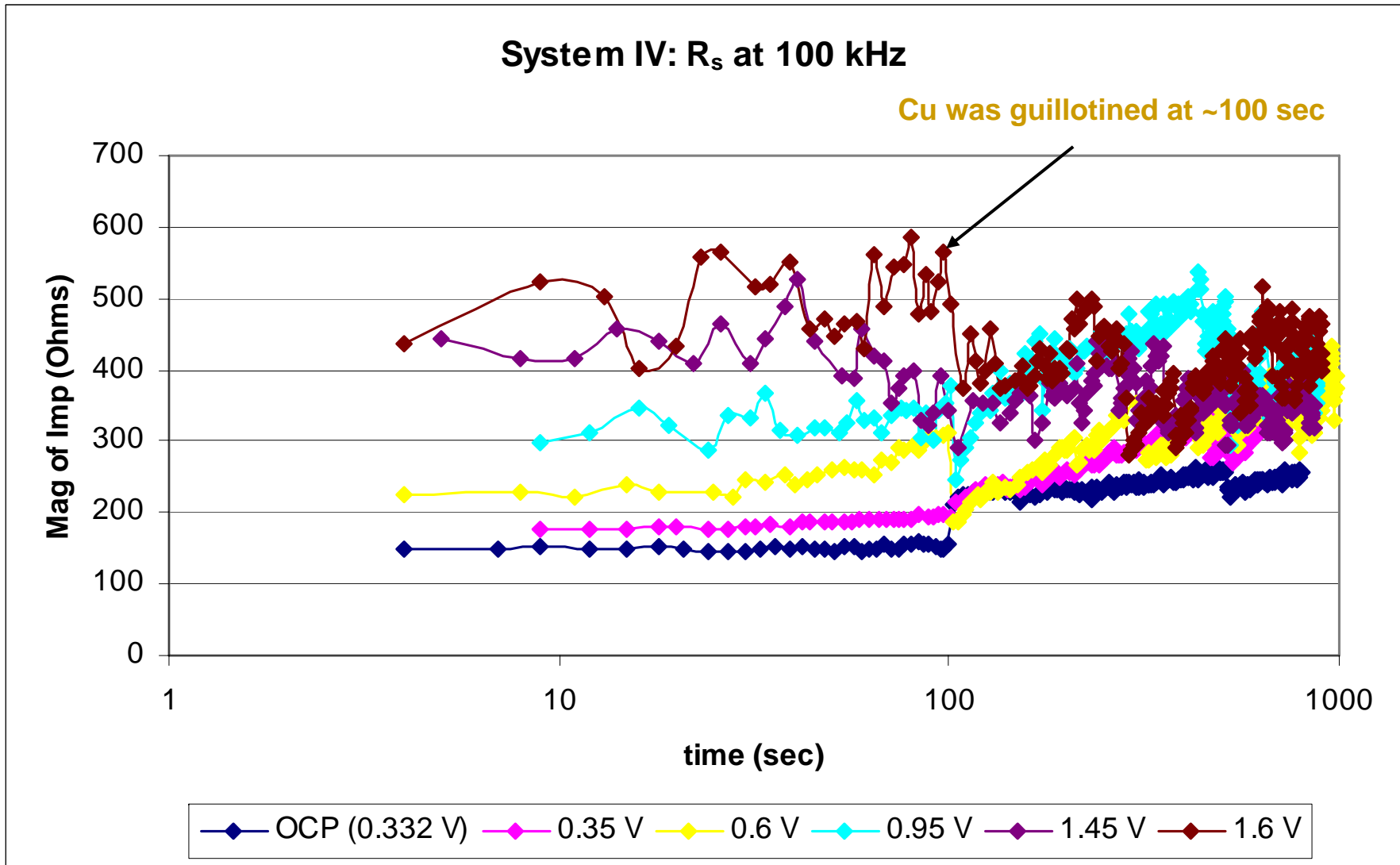
Wong, D. K. Y., Electrochim. Acta, 38(14), p.2121, 1993

THINK **IMPACT**

System (4)
Cu - 1 wt% HNO_3 + 0.02 M BTA + 5 wt% H_2O_2

Potentiodynamic Scan
System IV

1 : OCP (~0.332 V), 2: 0.35 V, 3: 0.6 V, 4: 0.95 V, 5: 1.45 V, 6: 1.6 V

Surface Film Formation

System IV: R_s at 100 kHz

Cu was guillotined at ~100 sec

Legend: OCP (0.332 V) — 0.35 V — 0.6 V — 0.95 V — 1.45 V — 1.6 V

y-axis: Mag of Imp (Ohms)
x-axis: time (sec)

Interpretation

- Strong oxidizer, H_2O_2
  - No passive region
  - Consistent with the literature

- Increases in R_s
  - Complexes between Cu(II) and BTA, water, and nitrate
  - Porous Cu(I)-BTA film

- No trends at higher potential
  - Unstable film in the presence of H_2O_2
  - Oxide film formation and breakage

System IV: R_s at 100 kHz

OCP (0.332 V) 0.35 V 0.6 V 0.95 V 1.45 V 1.6 V

THINK **IMPACT**
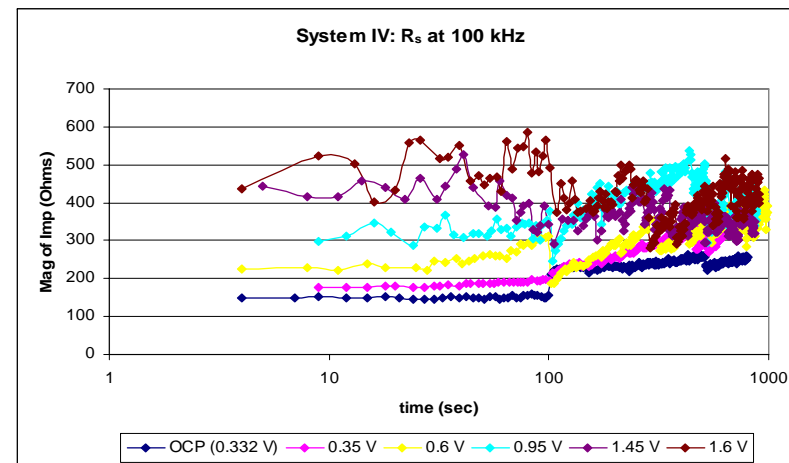
Conclusions

- Impedance at high-limit frequency
  - Can see the porous/viscous film formation
    - Cu - 14 M H_3PO_4
    - Cu - 1 wt% HNO_3
    - Cu - 1 wt% HNO_3+ 0.02 M BTA
    - Cu - 1 wt% HNO_3+ 0.02 M BTA+5 wt% H_2O_2
  - Possible hypotheses suggested

- Leads to better understanding of CMP surface reactions
  - Will be combined with particle-surface interaction studies

THINK **IMPACT**