KANSAS STATE UNIVERSITY

Increasing Chemical Reaction Rates with Stochastic Heating

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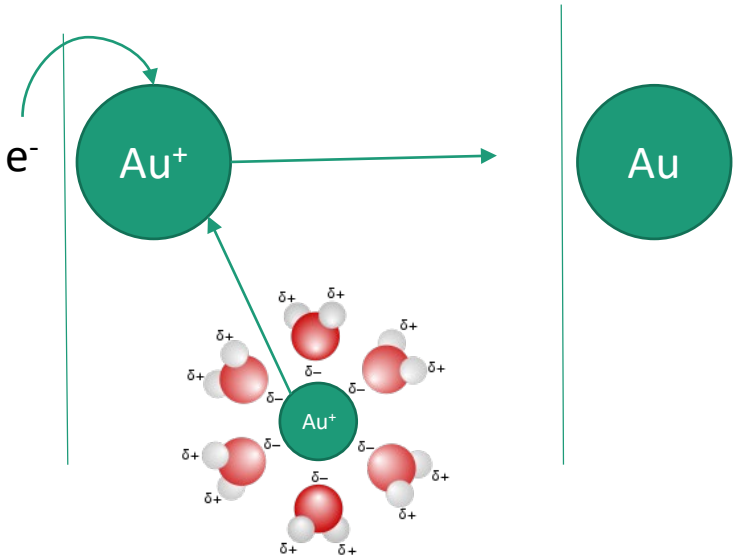
KSU REU 2019

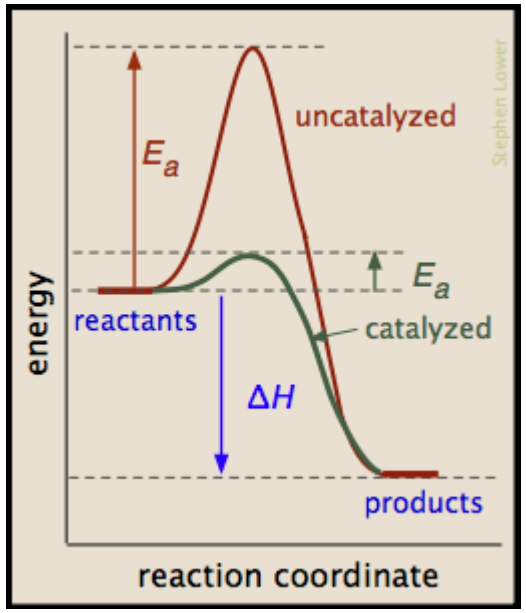
Dr. Bret Flanders

Collision Theory

$$e^- + Au^+ \rightarrow Au^0$$



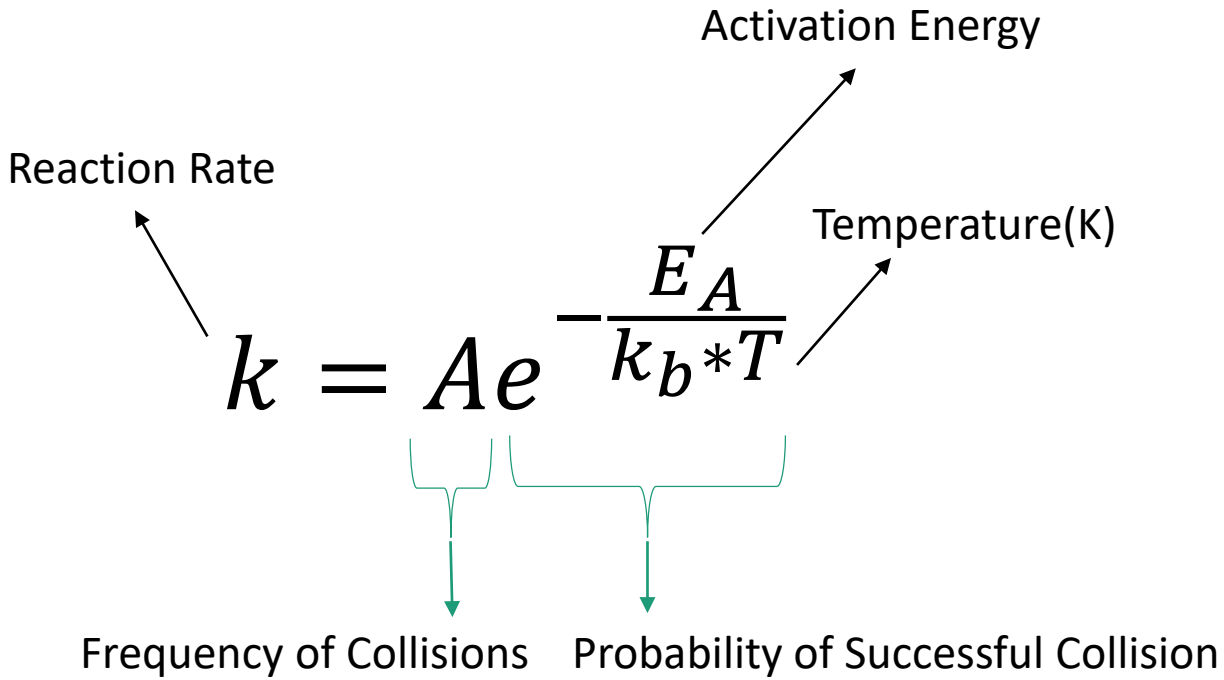
$$\dot{C_{Au}} = k[Au^+]$$



Taken from source [5]

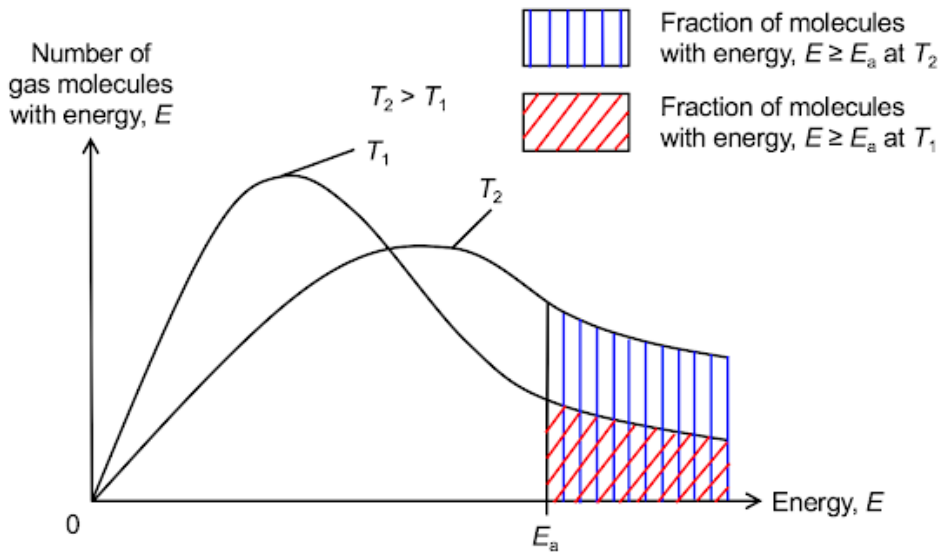
- For a reaction to occur, the reactants must interact or collide with each other.[4]
- A minimum energy must be met for the reaction to occur.
  - Bonds must break before new bonds can be made
- Sufficient energy and orientation are vital to the collision.[4]

Arrhenius Law



- Relates rate of reaction with temperature and activation energy
- Higher Temp → Faster Reaction
- Current Methods for Increasing k
  - Catalysts: Provide lower energy alternative pathway without being consumed.[4]
  - Electro-catalyst: Lower activation energy by applying potential between electrode and reaction site.[4]

Maxwell-Boltzman Distribution



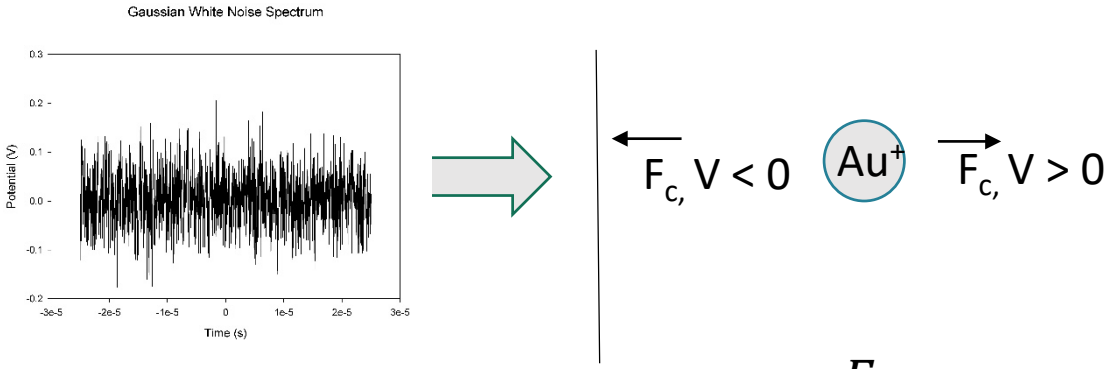
Taken from source [6]

- The rate of the reaction doubles with a 10° C rise in temperature.[4]
- More Collisions and greater momentum transfers at high temperatures

Effect of Gaussian White Noise on Charged Particles

- The voltage difference across the electrode will cause an ideally uniform electric field.
- $\mathbf{F}_c = q\mathbf{E}$ → stimulates stochastic motion in **x**
- Aqueous solution is relatively unaffected
- $T = \frac{2}{3}\frac{\langle KE \rangle_1}{k_b}$

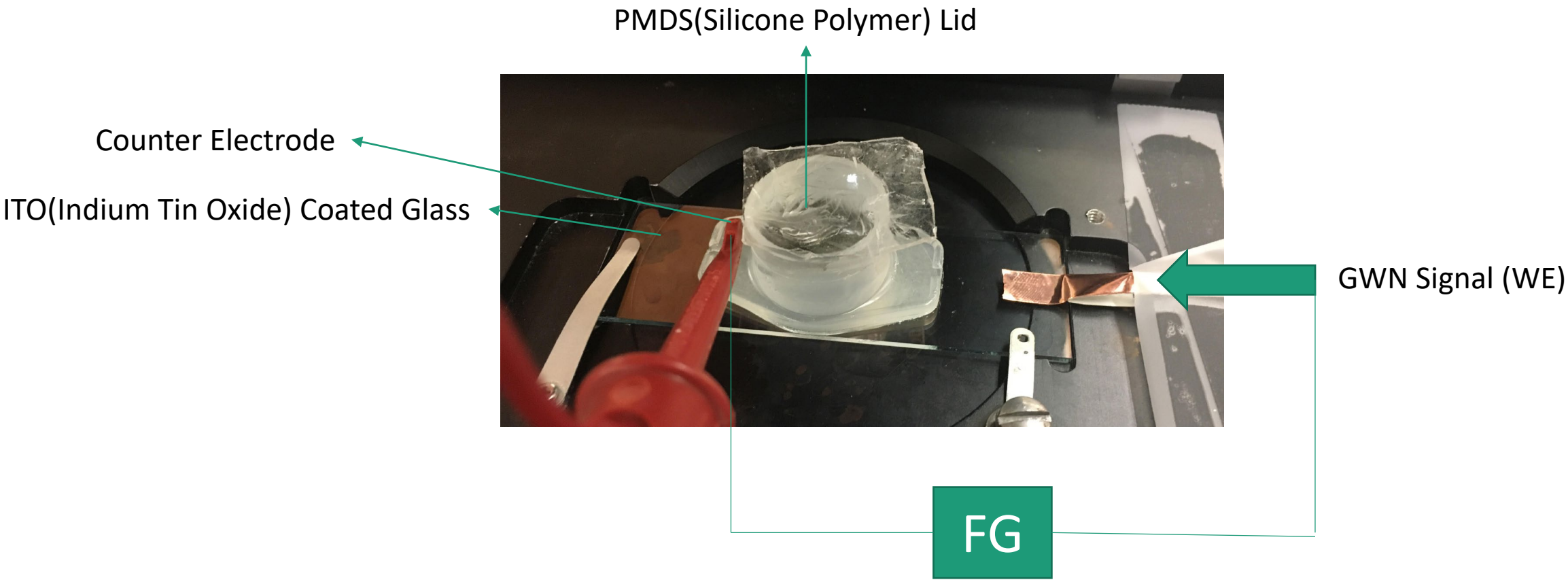
Electrode interface



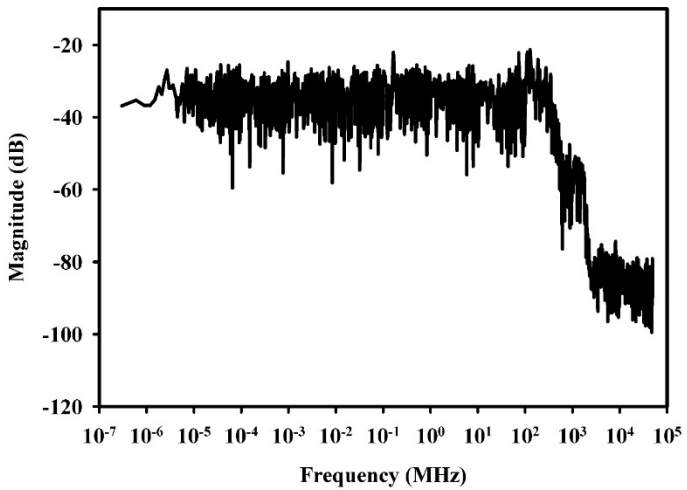
New Eqn: $k = Ae^{-\frac{E_A}{k_b * T_{eff}}}$

$T_{eff} = T + K\frac{\Gamma^2}{3*k_b}$, K = constant of proportionality

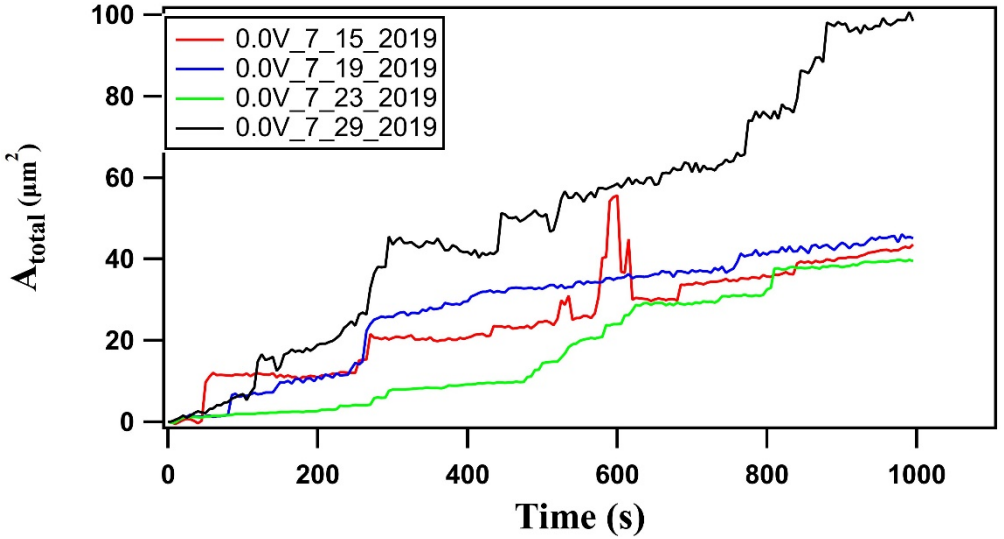
Microscope Cell for Observing Crystal Growth

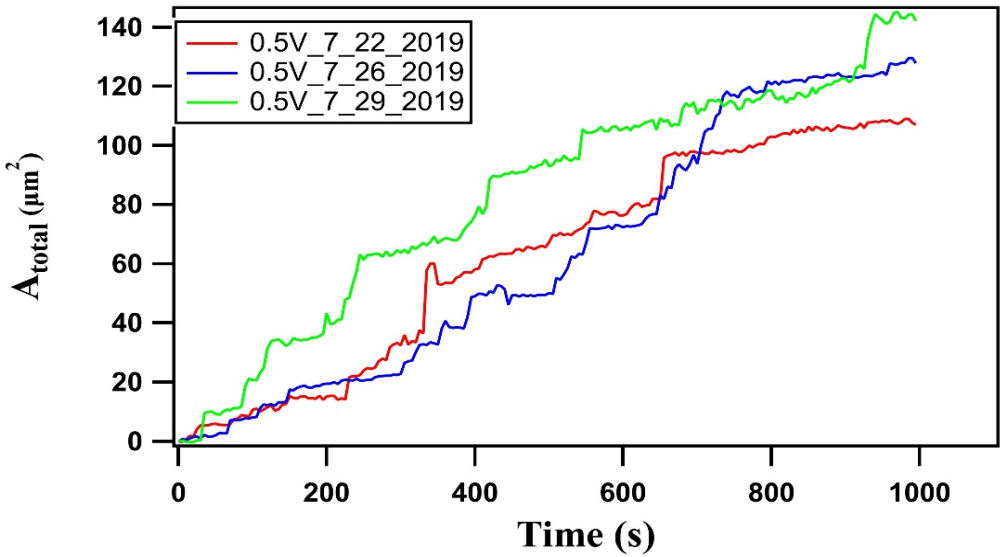


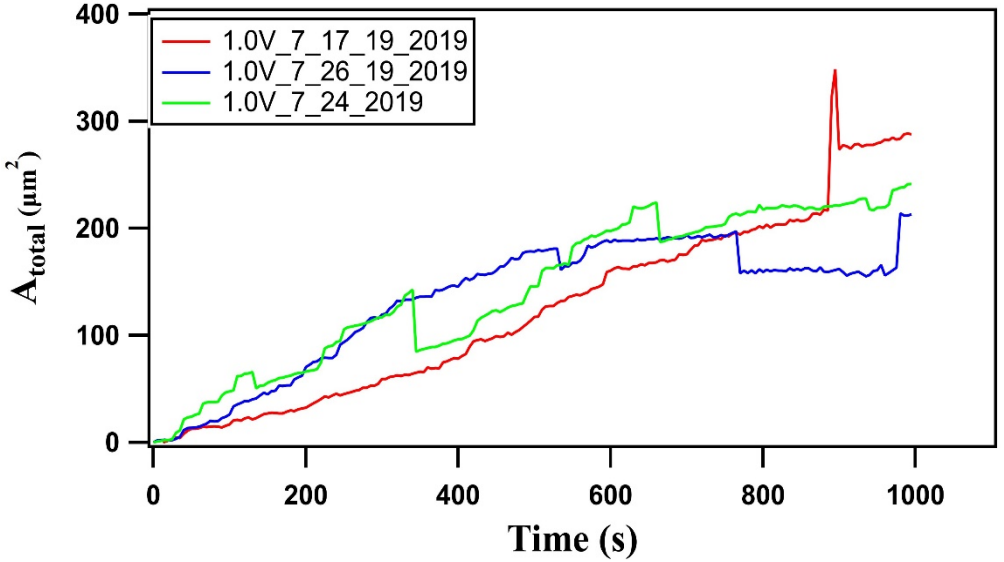
300 MHz Bandwith GWN

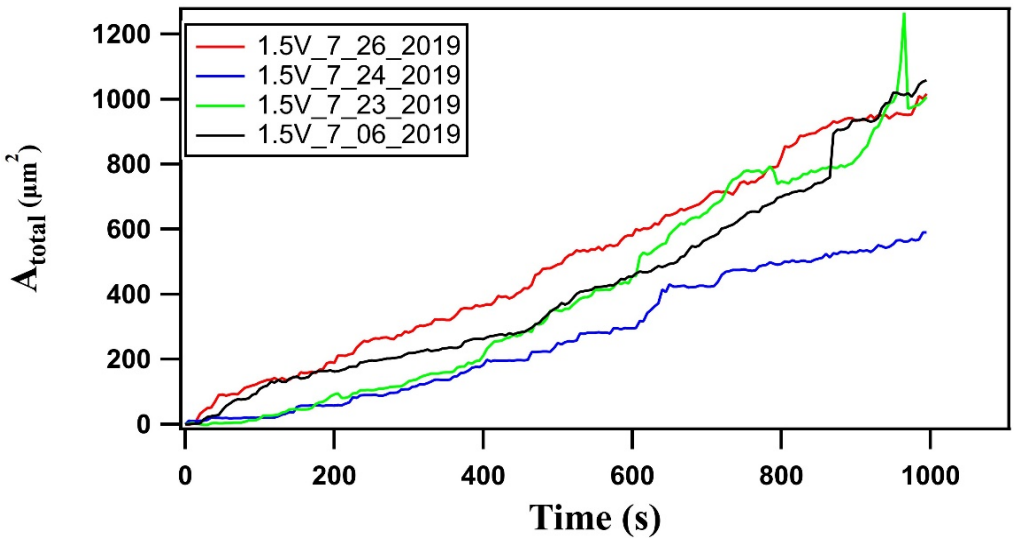


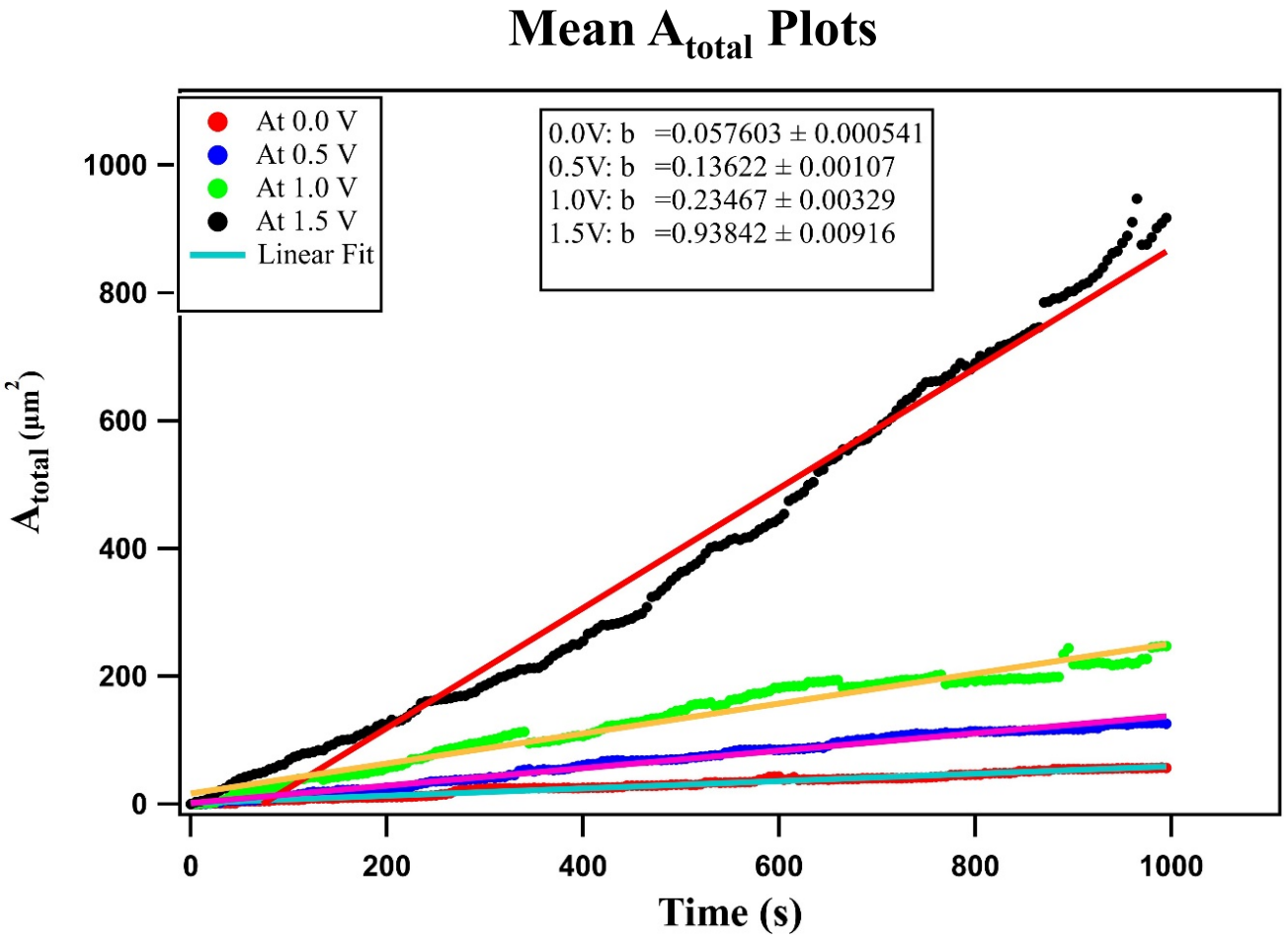
- 300 MHz GWN suppled
- 7.5 mM $NaHCO_3$, 7.5 mM $CaCl_2$
- 1 frame taken per 5 seconds
- 20 minute total time length

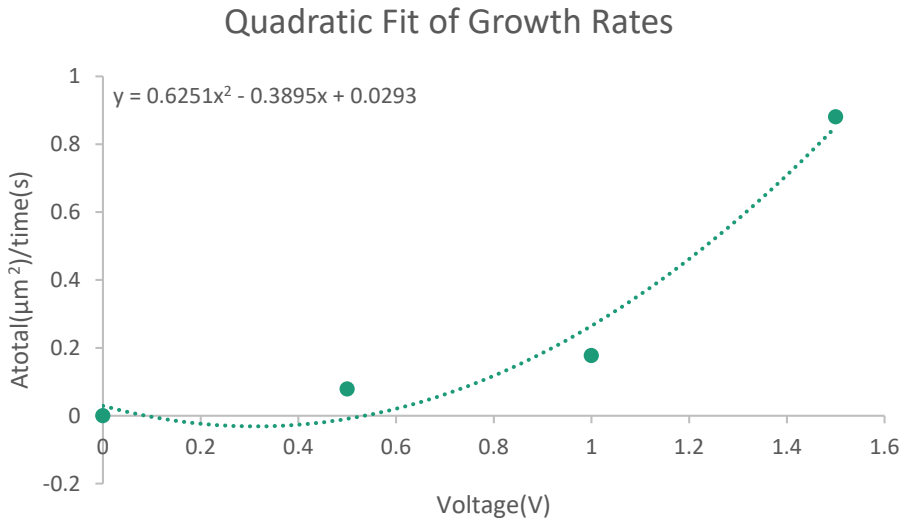

0.0V_7_15_2019
0.0V_7_19_2019
0.0V_7_23_2019
0.0V_7_29_2019
A total (µm 2)
Time (s)


0.5V_7_22_2019
0.5V_7_26_2019
0.5V_7_29_2019
A total (µm 2)
Time (s)


1.0V_7_17_19_2019
1.0V_7_26_19_2019
1.0V_7_24_2019
A total (µm 2)
Time (s)

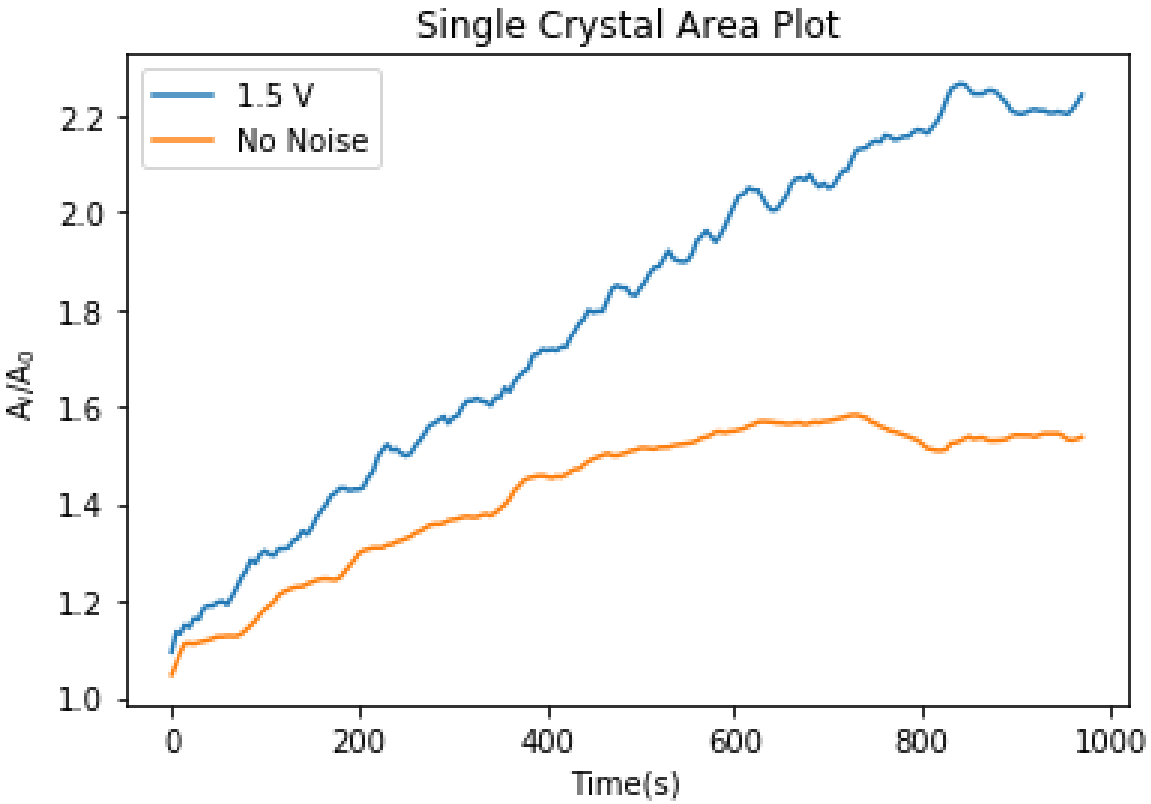

1.5V_7_26_2019
1.5V_7_24_2019
1.5V_7_23_2019
1.5V_7_06_2019
A total (µm 2)
Time (s)





$$A_{total}(\boldsymbol{t}) = a + b * \boldsymbol{t}$$

Characterizing Crystal Growth



- Linear Deposition Rae
  - Linear Single Crystal Growth with Noise
  - Linear Total Area with Noise
- Growth Rate Slows with Time for No Noise

Conclusions

- Observed Linear Relationship between Total Area and Time
- Observed increased rate of linear area growth of single cell
- Nucleation Density becomes more uniform with Noise
- Positive relationship between growth rate and RMS Voltage

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Lawrence Livermore National Laboratory

Work Cited

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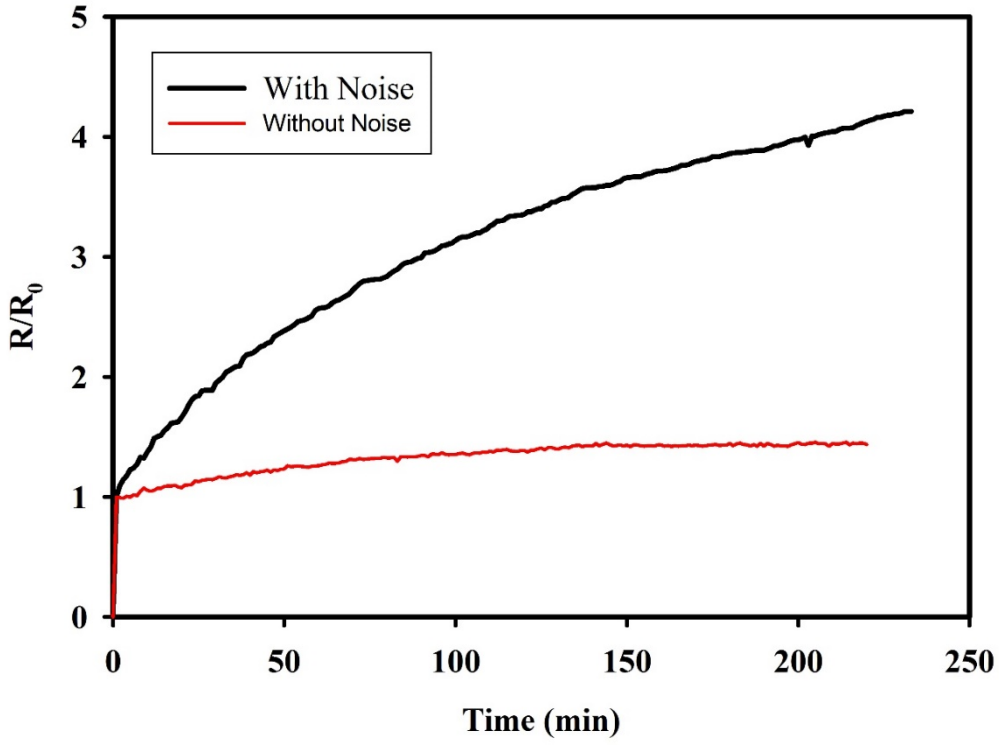
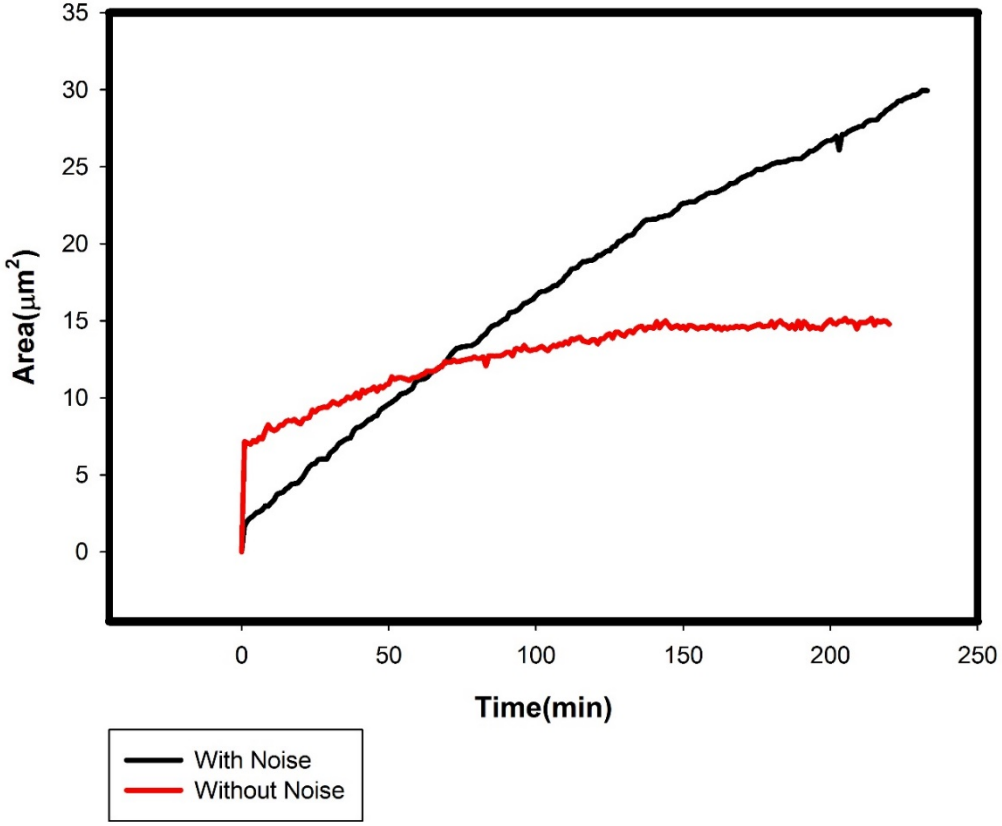
Quantifying Crystal Growth

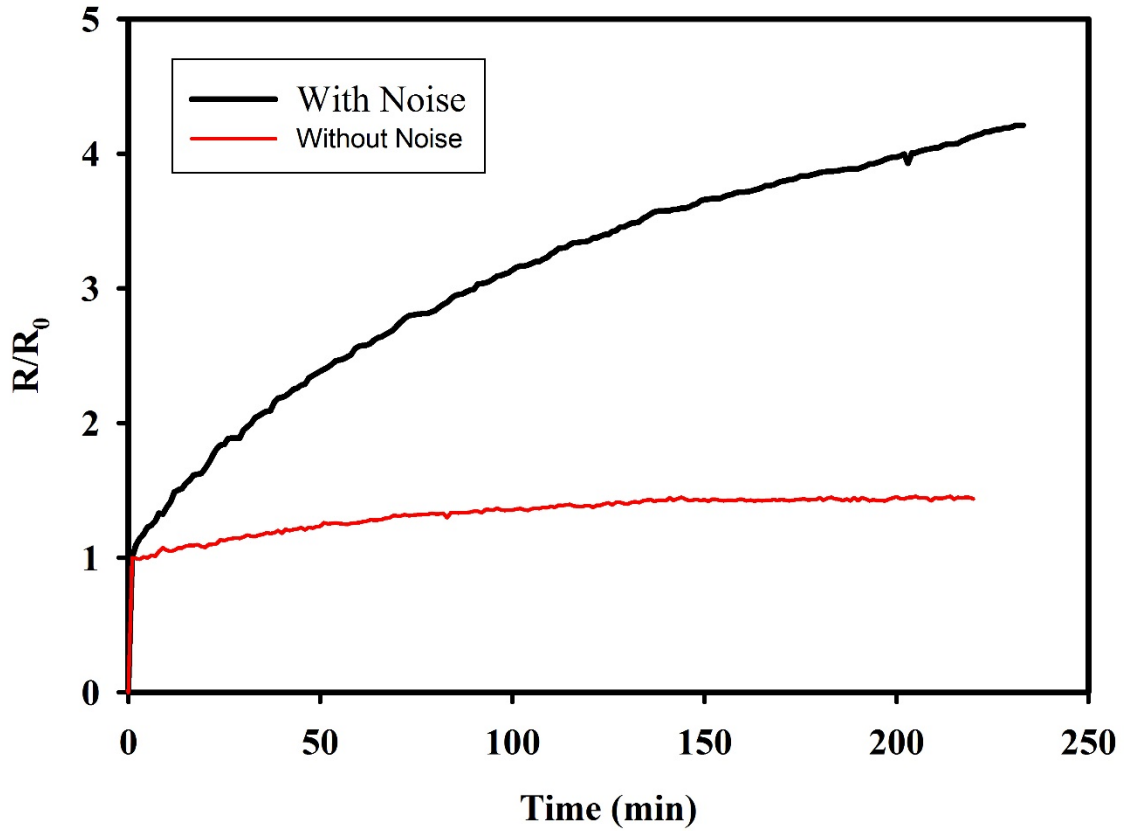
Normalized Radial Plot

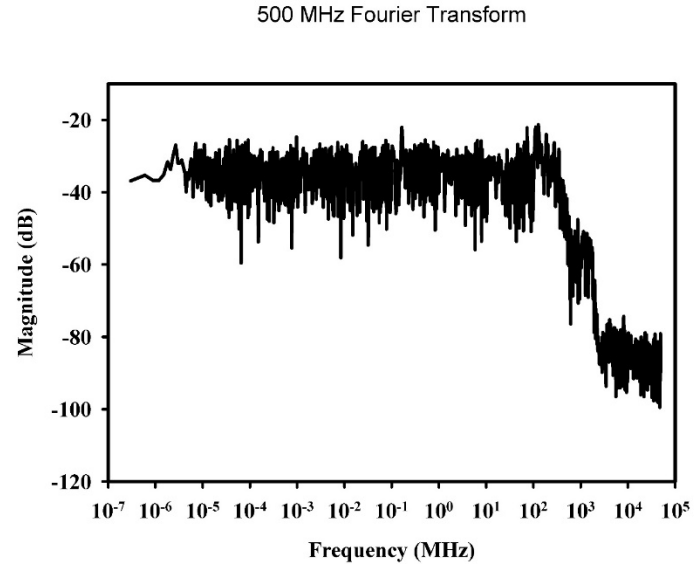


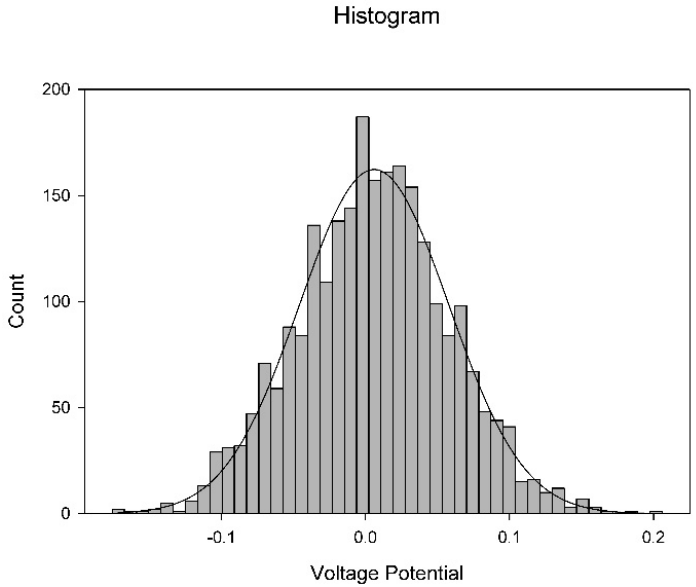
Area Plot



Normalized Radial Growth Plot





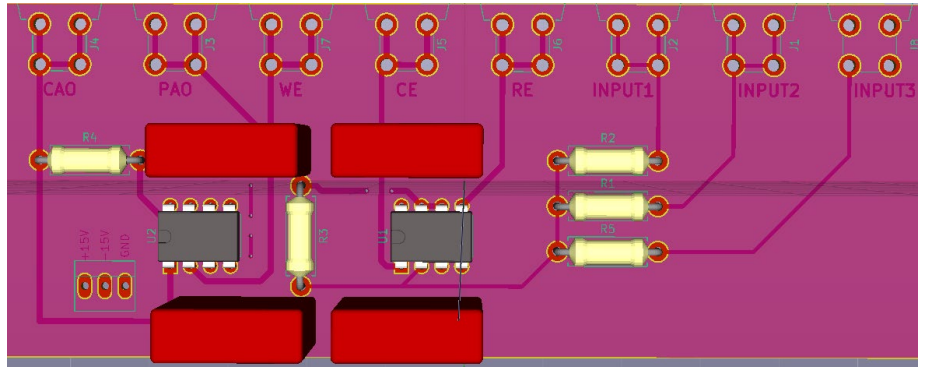


Gaussian White Noise Spectrum

- White: made from uniform frequencies across bandwidth
- Gaussian: Normally distributed in the time domain, centered at zero
- Electrical Noise spectrum with mean zero

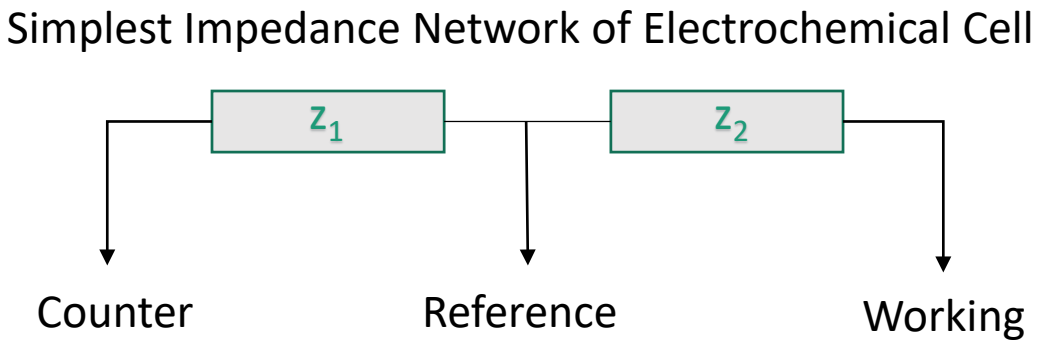
Designing Potentiostat

- Design and test circuit on breadboard
- Use KICad to generate schematic and PCB layout
- Compare PCB current and voltage outputs to breadboard design
- Use resistor values to minimize offset and maximize Bandwidth



Apparatus: Three Electrode Configuration

- Can treat electrochemical cell as electronic circuit with changing impedance.[3]
- Isolate system at working electrode.[3]
- RE held at constant potential provides control over WE potential.[3]



Moving Forward

- Generate identical electronic instruments for K-State and Lawrence Livermore NL
- Use Potentiostat to stochastically heat chemical reaction cell