Scanning Electrochemical Cell Microscopy as a Probe for Crystal Dissolution

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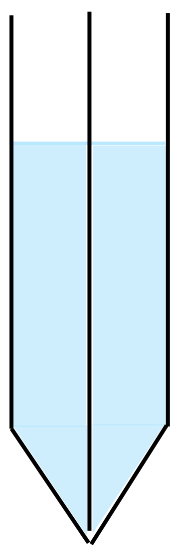
Summary

* Scanning Electrochemical Cell Microscopy (SECCM)
* Crystal dissolution
* Experimental setup
* Crystal etching rates
* Further work

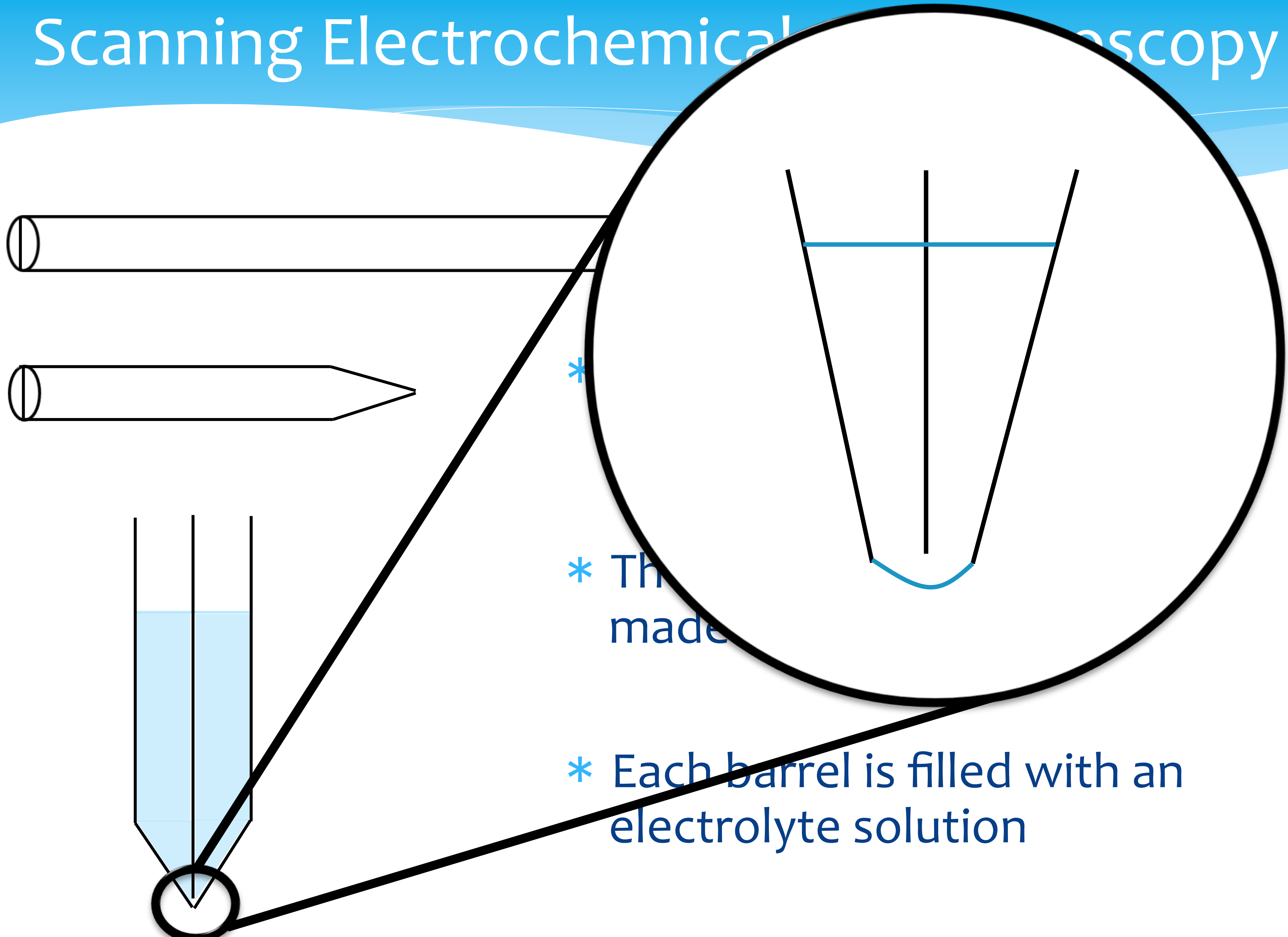
Scanning Electrochemical Cell Microscopy

* Tapered glass theta capillary is used as a probe



* The glass is silanized to be made hydrophobic
* Each barrel is filled with an electrolyte solution

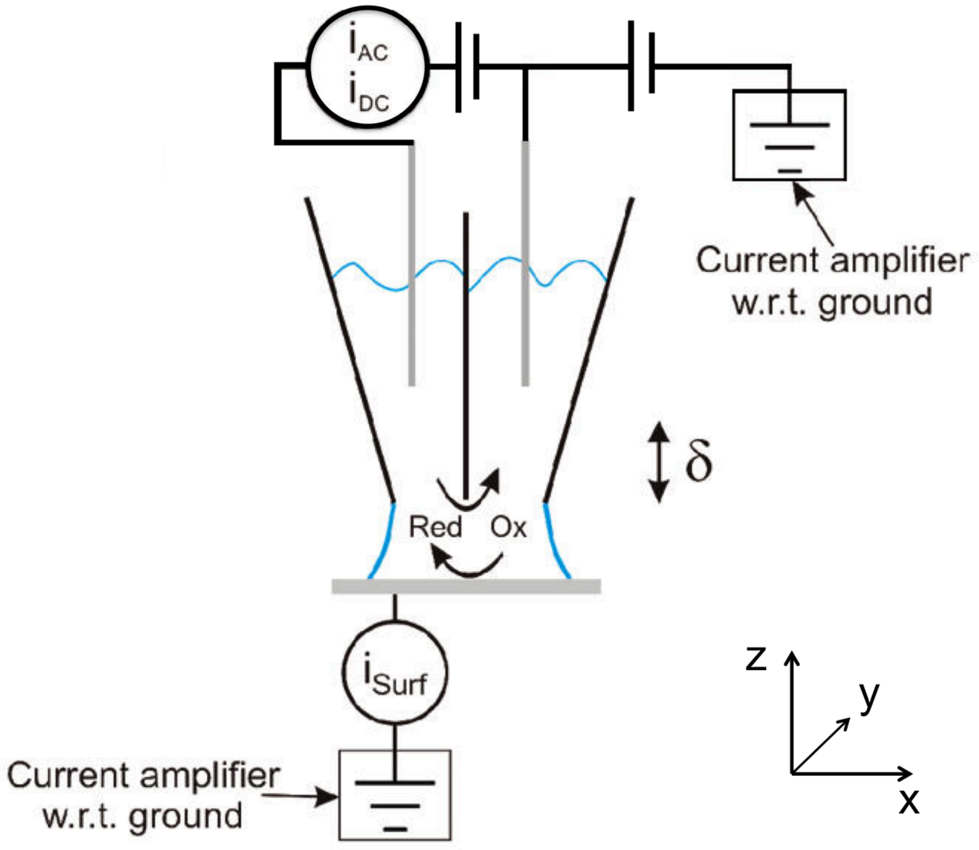
Scanning Electrochemical [...]scopy



* Th[...]
  made[...]

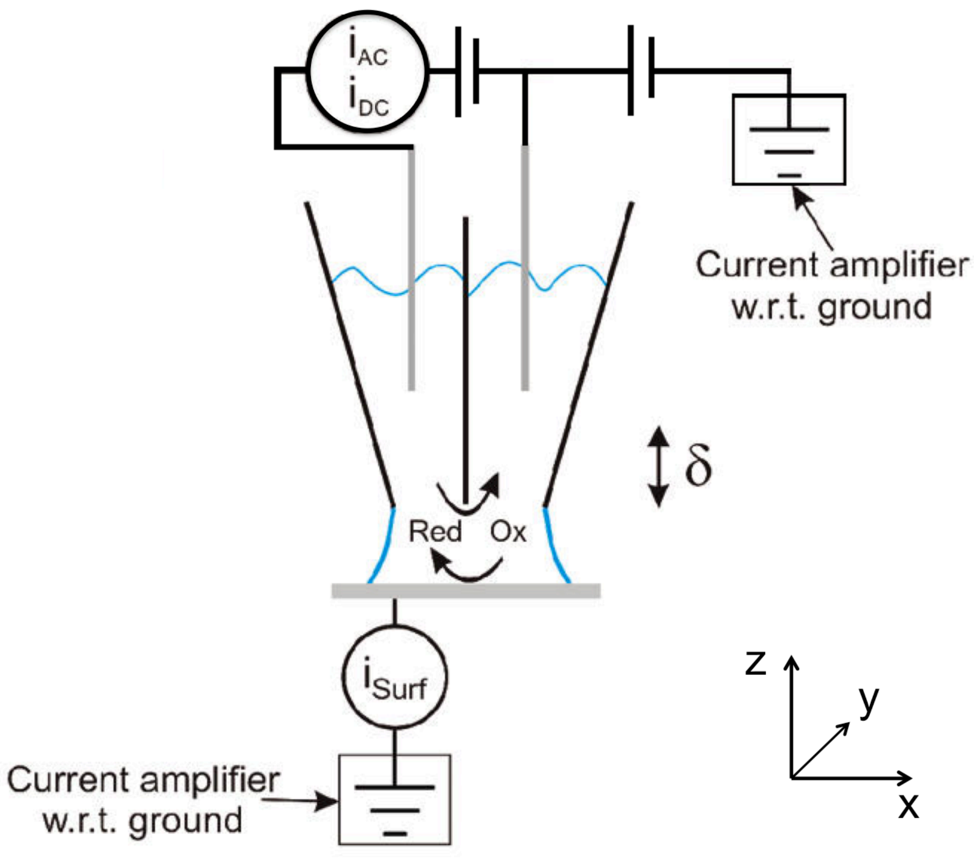
* Each barrel is filled with an electrolyte solution

Scanning Electrochemical Cell Microscopy



- Silver-Silver Chloride wire electrode placed in each barrel
- A potential is applied between the two electrodes
- The probe is held perpendicular to the substrate
- The pipet is oscillated normal to the substrate

Scanning Electrochemical Cell Microscopy



* Meniscus is deformed when it touches the substrate
* Oscillation in the z position periodically changes the resistance in the meniscus causing an alternating current

Crystal Dissolution

* Simple ionic solution:

$$A^{+}_{(aq)} + B^{-}_{(aq)} \rightleftharpoons AB_{(s)}$$

* Solubility product:

$$\{A\}\{B\} = K_{sp}$$

Crystal Dissolution

* Saturation:

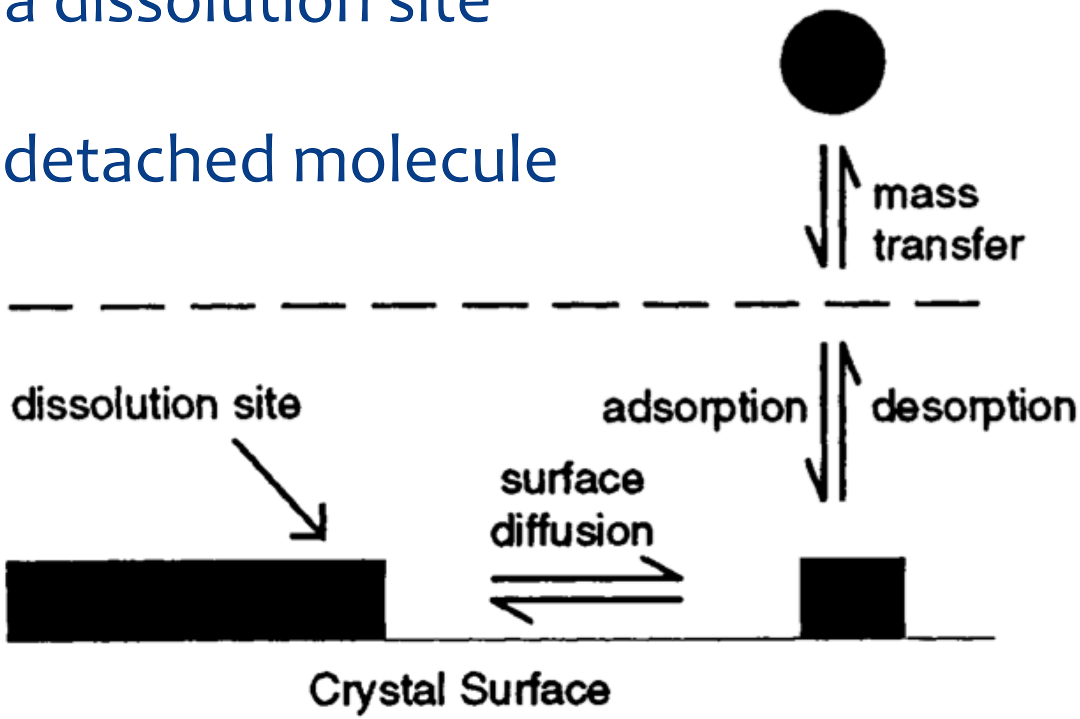
$$\mathrm{S} = \frac{\{A\}\{B\}}{K_{sp}}$$

* For crystal dissolution, the activity of the solutes must be less than the solubility product, i.e. an UNDERSATURATED solution is required

Crystal Dissolution

Crystal dissolution occurs in 4 stages:

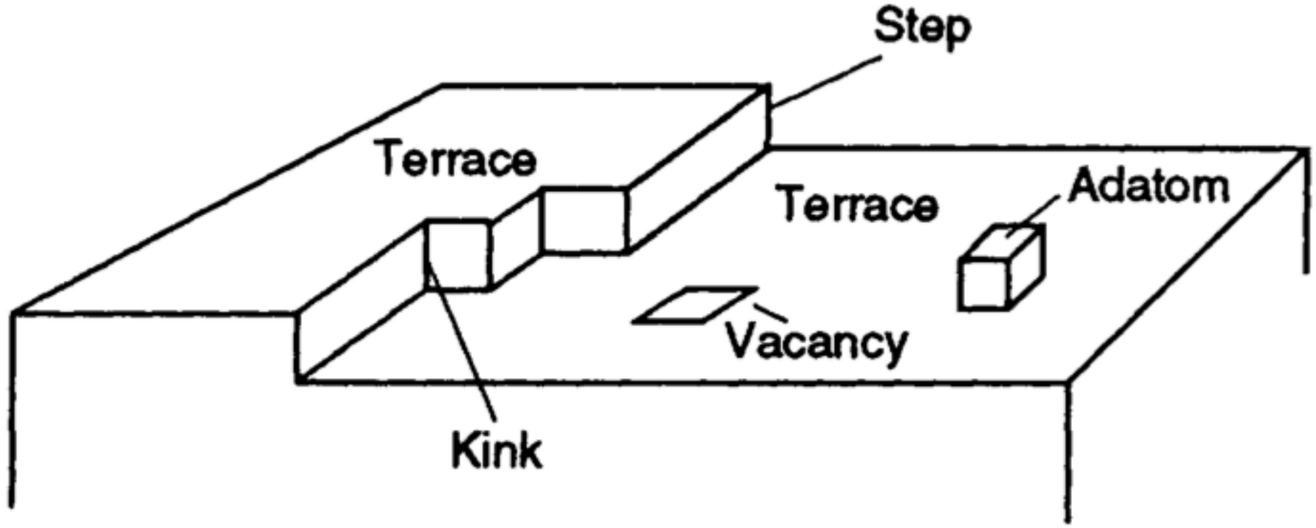
* Ions are detached from a dissolution site
* Surface diffusion of the detached molecule
* Desorption
* Mass transfer of the ion away from the crystal



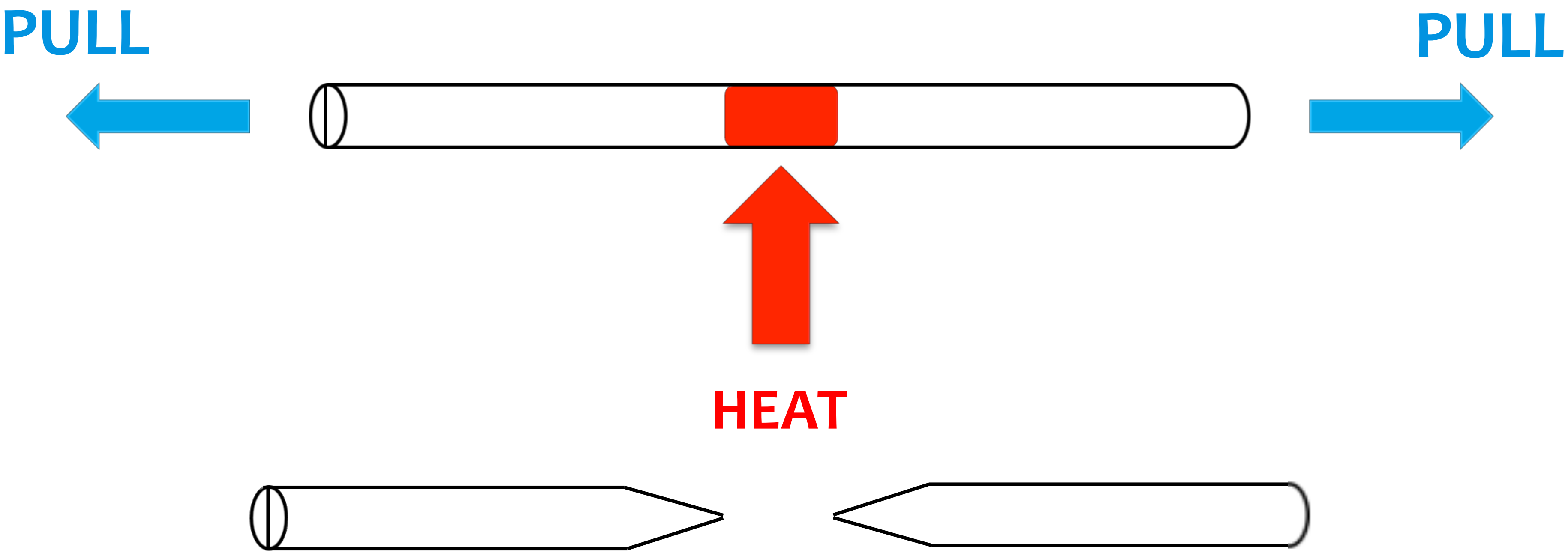
Crystal Dissolution

* Ions move across the crystal surface to the most energetically favourable position

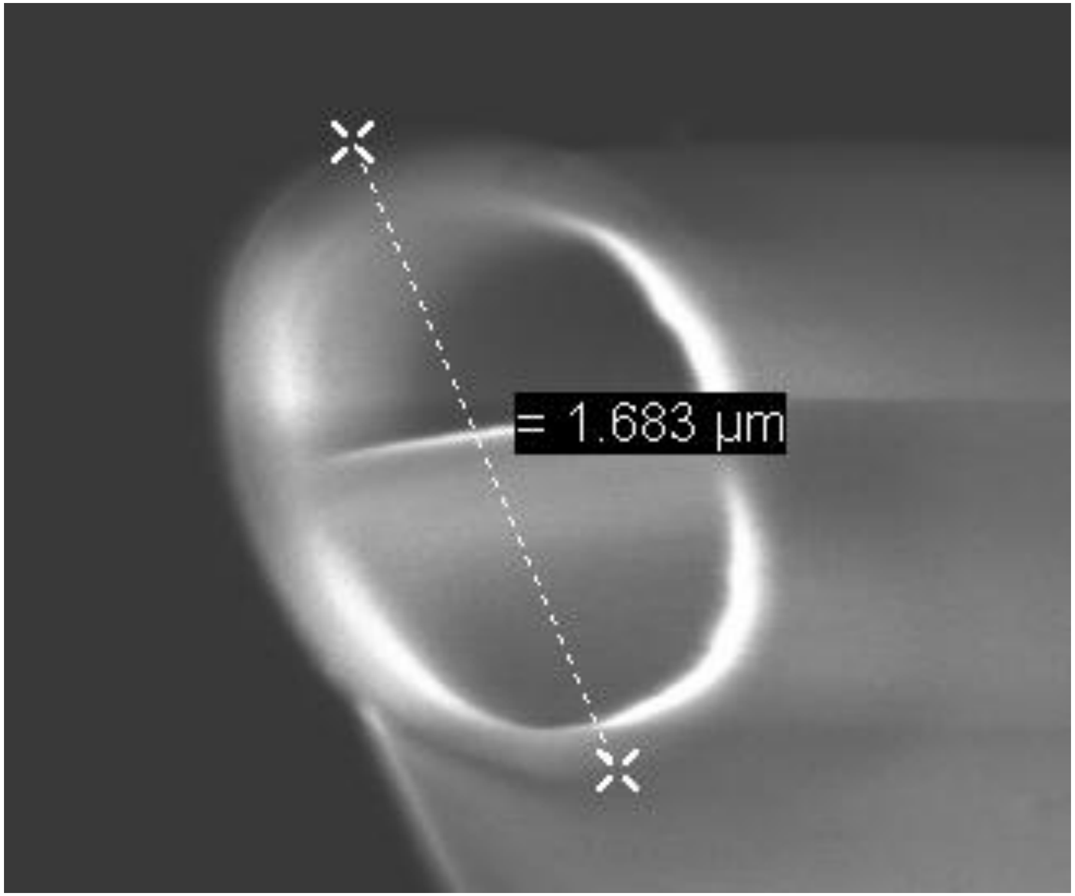
* Atoms gain a degree of freedom and are lost from the crystal



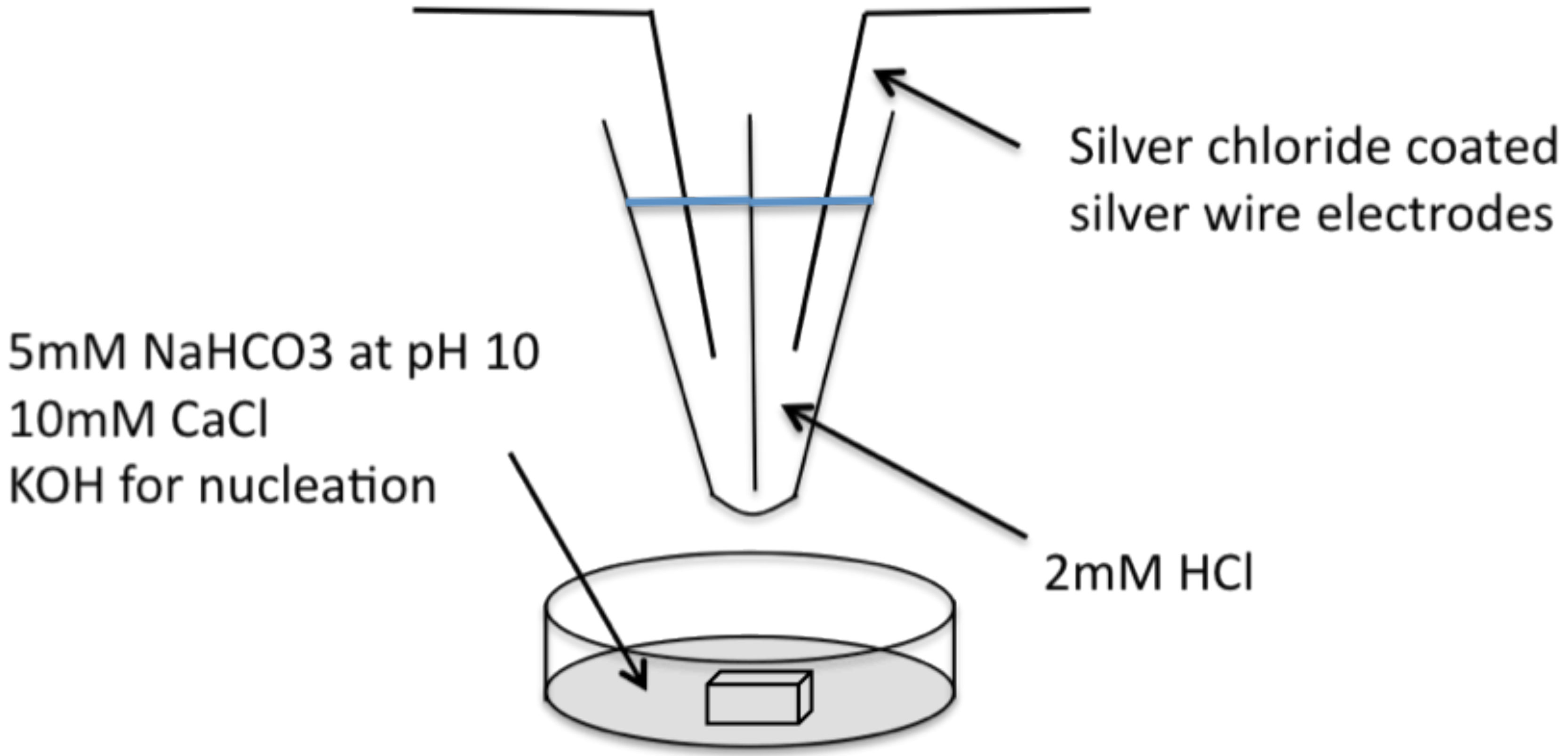
Experimental Setup



Experimental Setup



Experimental Setup

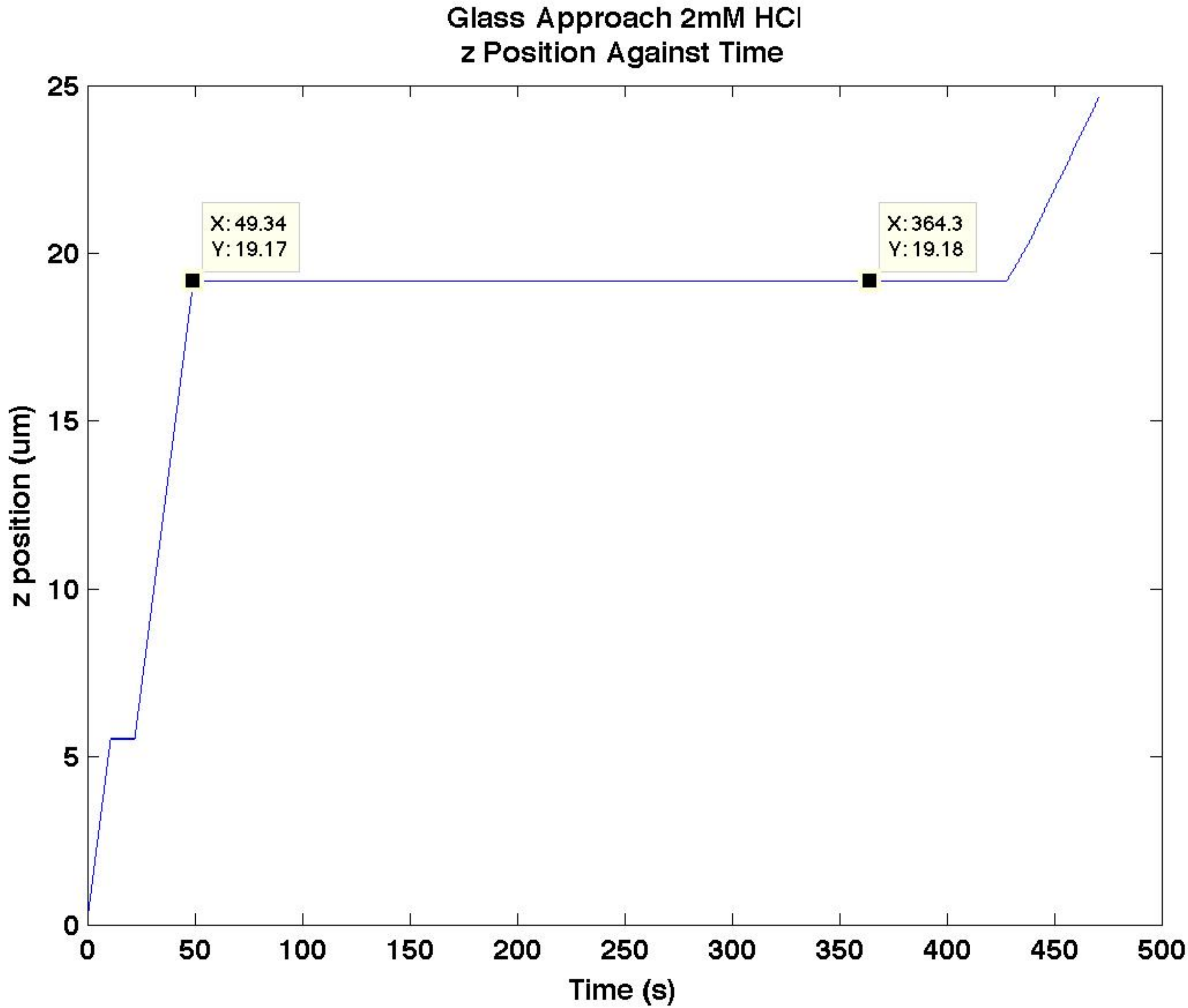


Experimental Setup

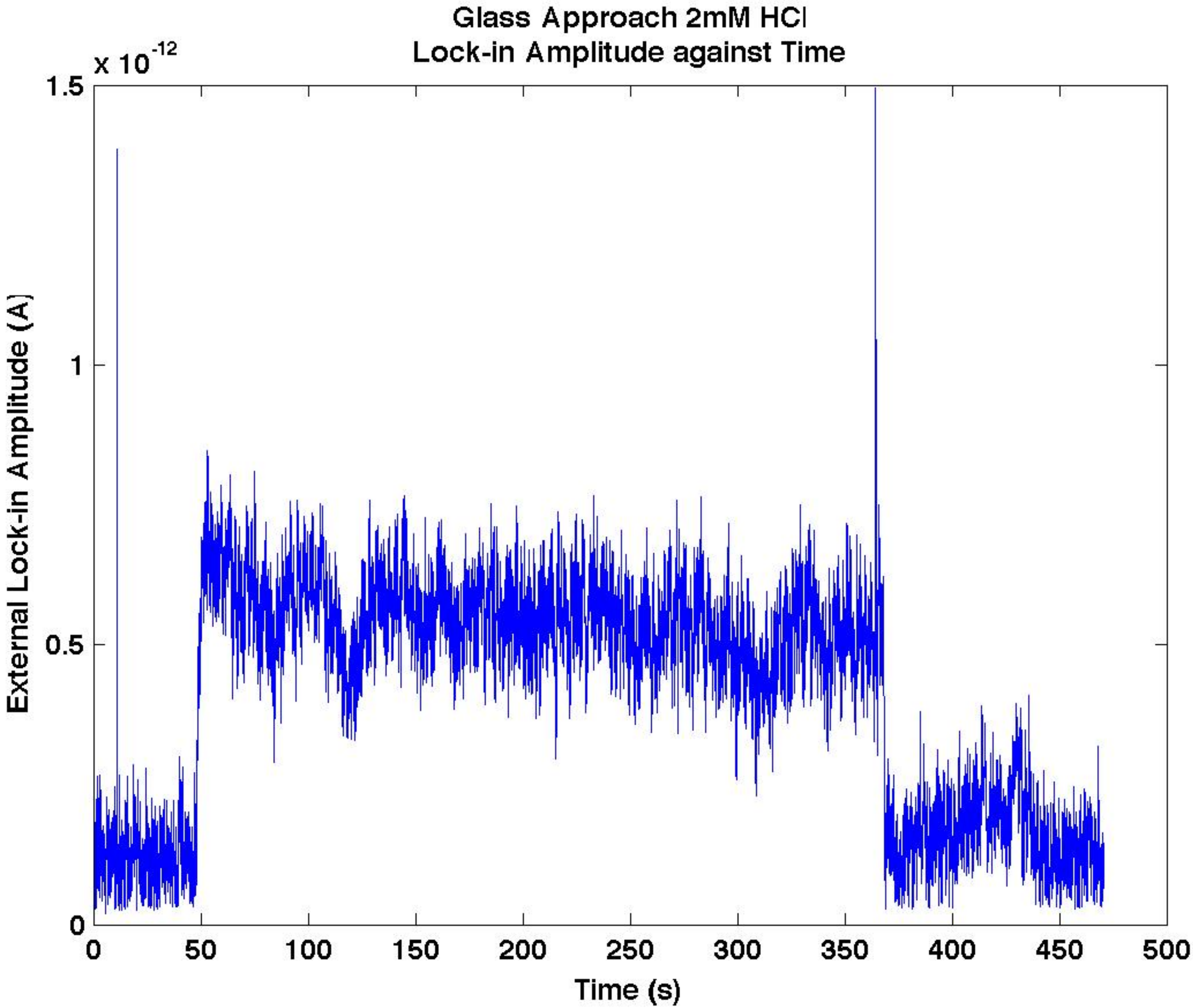
Results – Glass Approach

* The SECCM method worked reliably on glass

* The probe could be suspended for many minutes

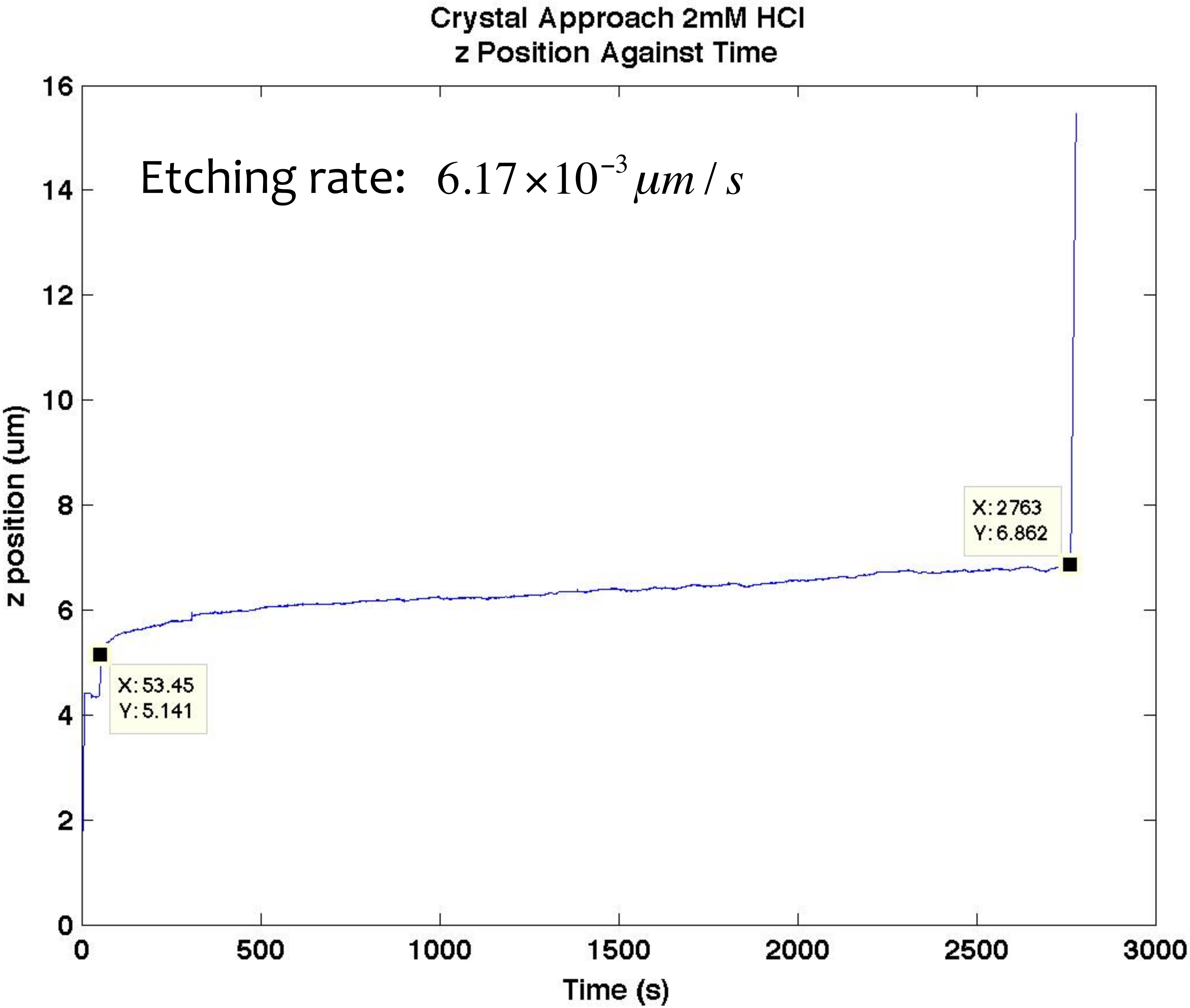


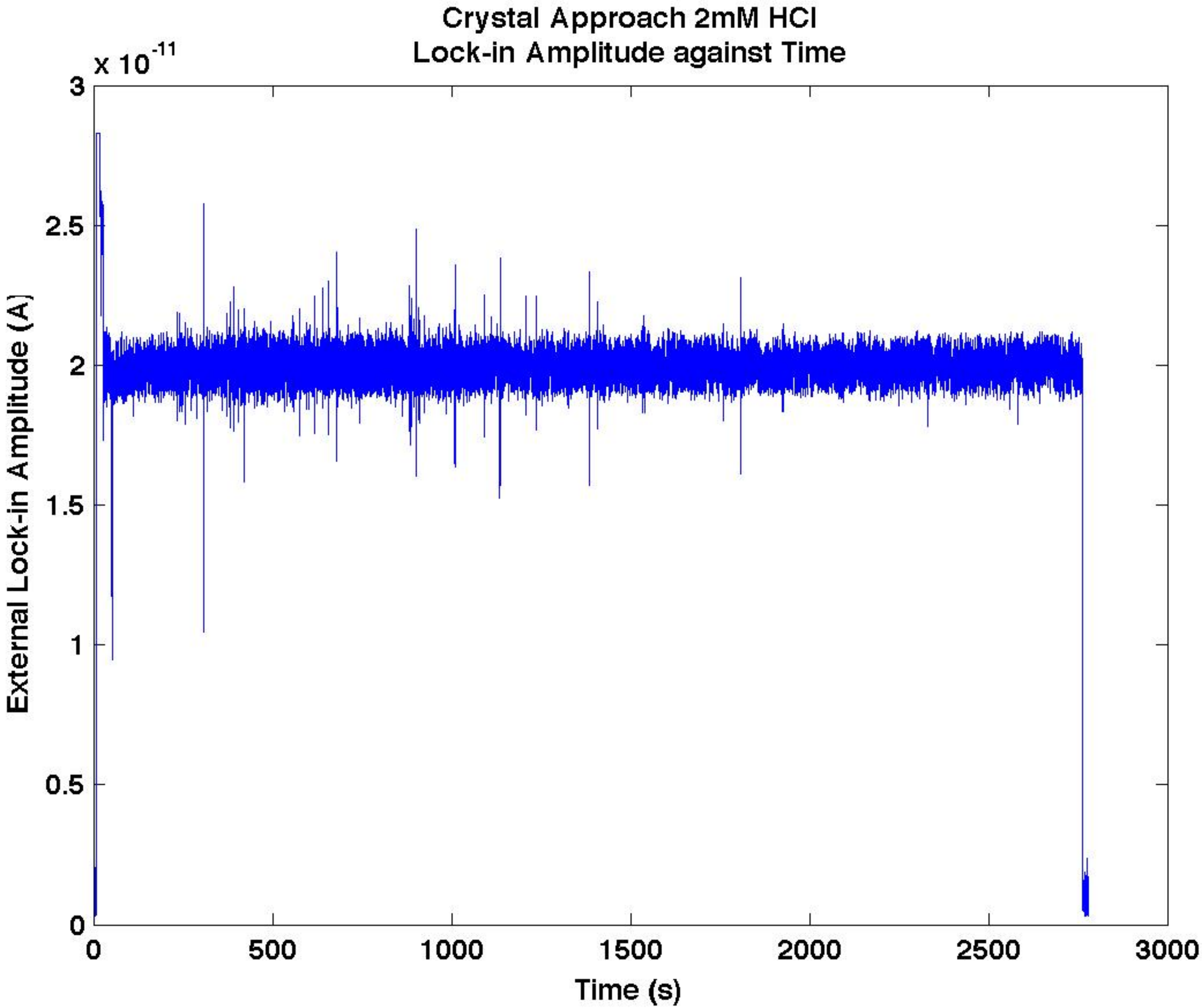
Glass Approach 2mM HCl
z Position Against Time
X: 49.34
Y: 19.17
X: 364.3
Y: 19.18
z position (um)
Time (s)
0
5
10
15
20
25
0
50
100
150
200
250
300
350
400
450
500


Glass Approach 2mM HCl
Lock-in Amplitude against Time
x 10^-12
1.5
1
0.5
0
External Lock-in Amplitude (A)
0
50
100
150
200
250
300
350
400
450
500
Time (s)

Results – Crystal Approach

* The method was less reliable on crystal surfaces
* Unsuccessful approaches may have been caused by the meniscus not properly wetting the surface
* Successful approaches saw an increase in z position extension while the probe was hovering over the surface

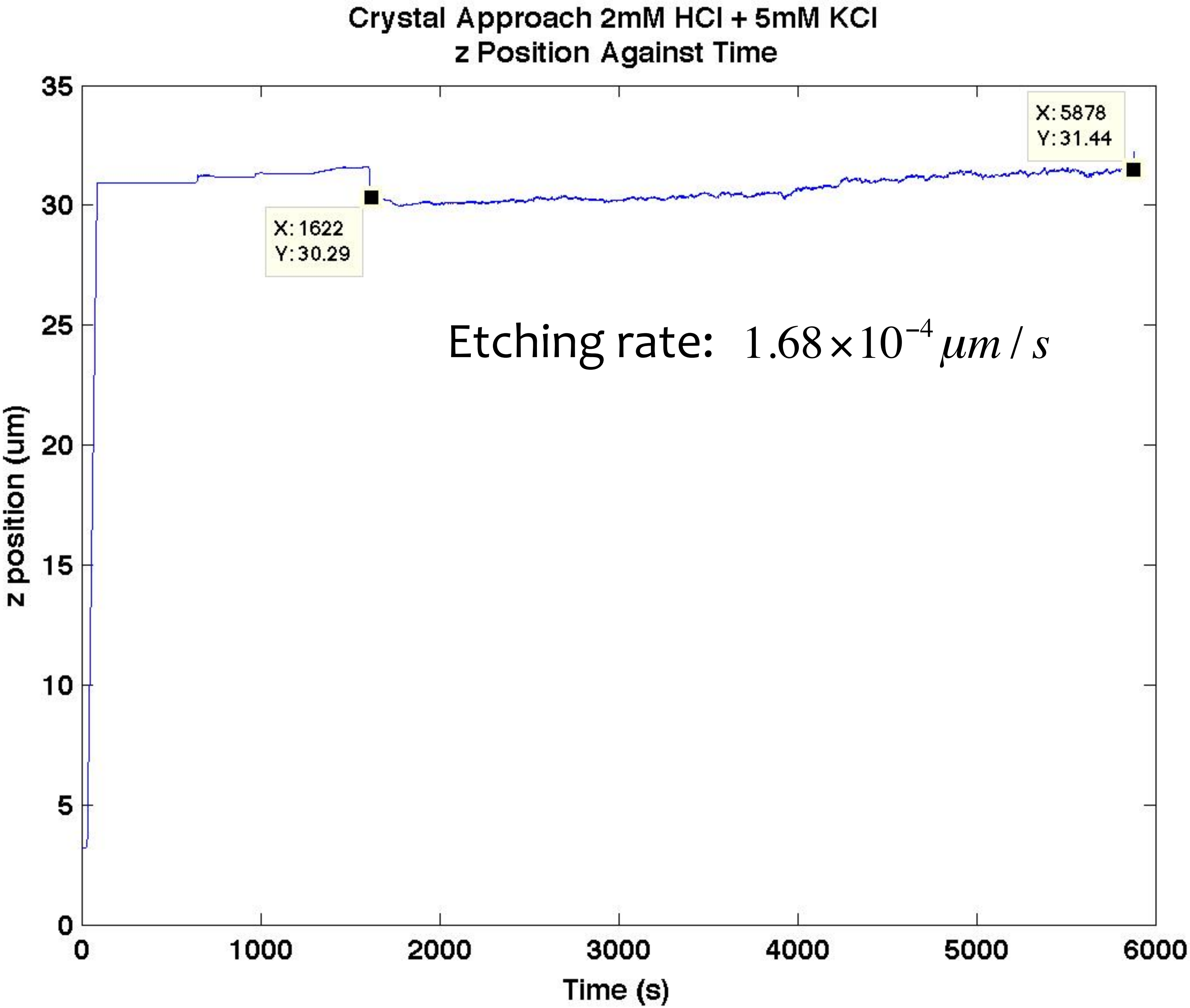

Crystal Approach 2mM HCl
z Position Against Time
Etching rate: $6.17 \times 10^{-3} \mu m / s$
z position (um)
Time (s)
X: 53.45
Y: 5.141
X: 2763
Y: 6.862
0
2
4
6
8
10
12
14
16
0
500
1000
1500
2000
2500
3000



Crystal Approach 2mM HCl
Lock-in Amplitude against Time
x 10^-11
3
2.5
2
1.5
1
0.5
0
External Lock-in Amplitude (A)
0
500
1000
1500
2000
2500
3000
Time (s)

Results – Crystal Approach with KCl

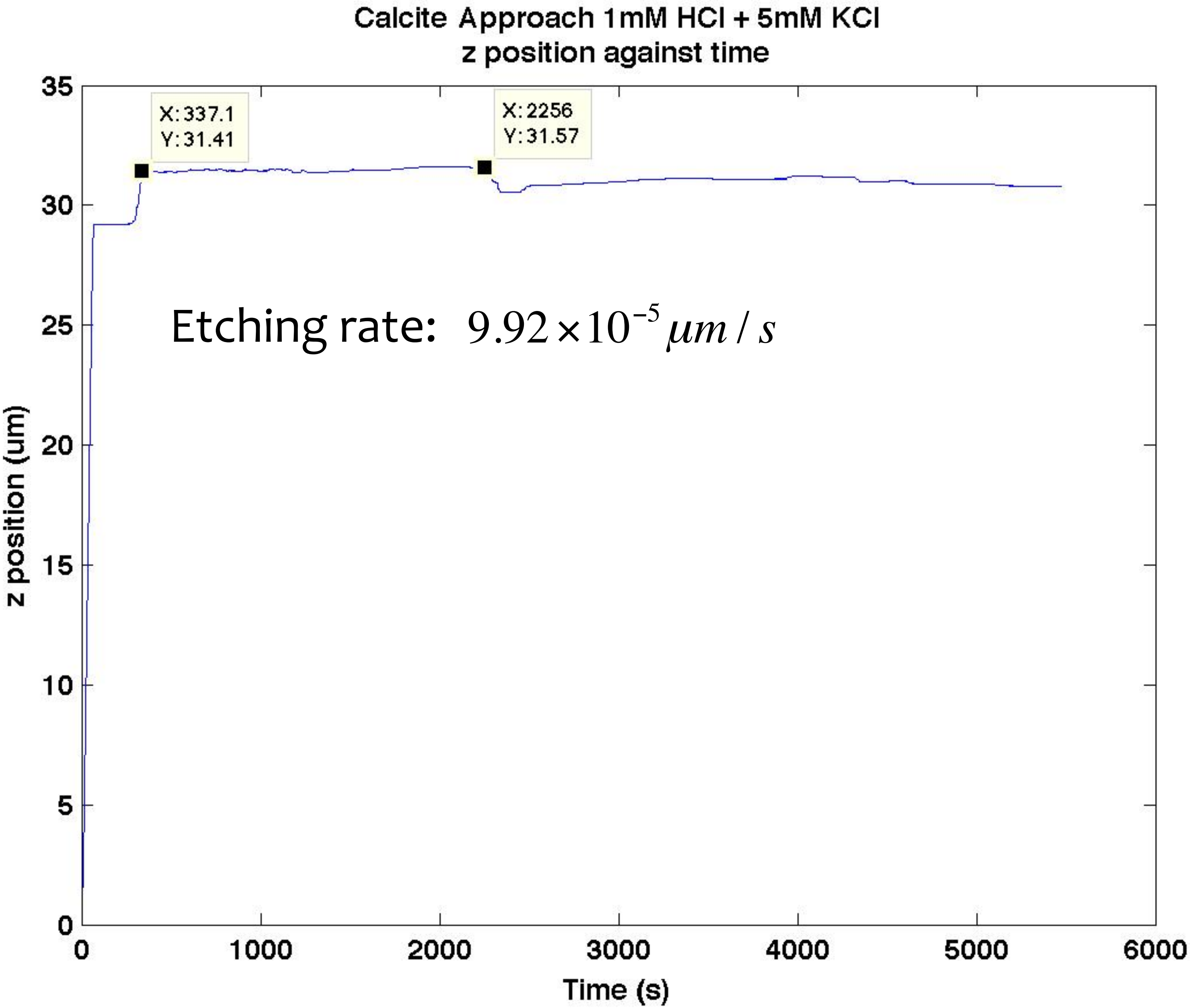
* A 5mM KCl support was added to the HCl electrolyte
* Having more ions in the solution gives a higher migration current, providing a greater signal to noise ratio



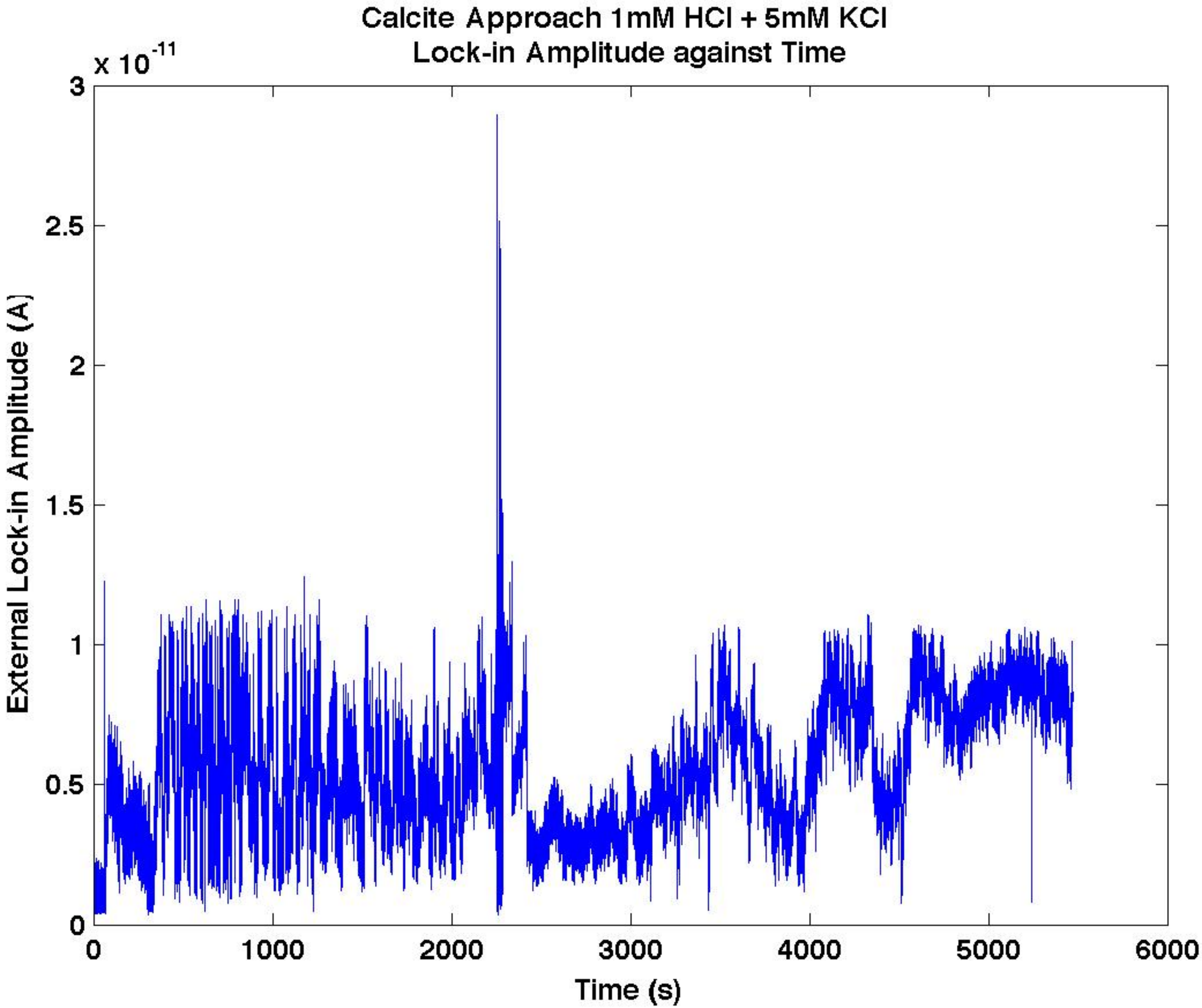
Etching rate: $1.68 \times 10^{-4} \mu m / s$

Results – Crystal Approach with KCl (1mM HCl)

* The concentration of HCl was halved
* A decrease in the etching rate was observed
* More measurements of a variety of concentrations are needed to confirm the results



Etching rate: $9.92 \times 10^{-5} \mu m / s$



Calcite Approach 1mM HCl + 5mM KCl
Lock-in Amplitude against Time
x 10^-11
3
2.5
2
1.5
1
0.5
0
External Lock-in Amplitude (A)
0
1000
2000
3000
4000
5000
6000
Time (s)

Further Work

* Experiments need to be done on a range of acid concentrations to examine the etching rate trend

* Nanoscale tips – smaller tips would further reduce the noise and allow the electrolyte to be delivered to the surface slower and over a smaller area

* Crystal growth would next be examined

Thanks!

* Pat Unwin
* Michael Snowden
* University of Warwick Electrochemistry and Interfaces group
* MOAC
* EPSRC

erc

MoAC

EPSRC
Pioneering research and skills

References

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