

Scanning Electrochemical Cell Microscopy as a Probe for Crystal Dissolution

Rachel Sheldon

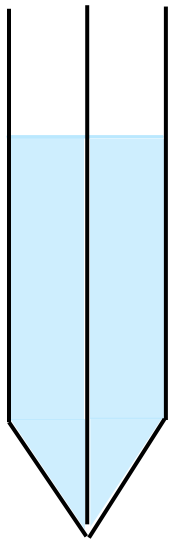
Summary

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

Scanning Electrochemical Cell Microscopy

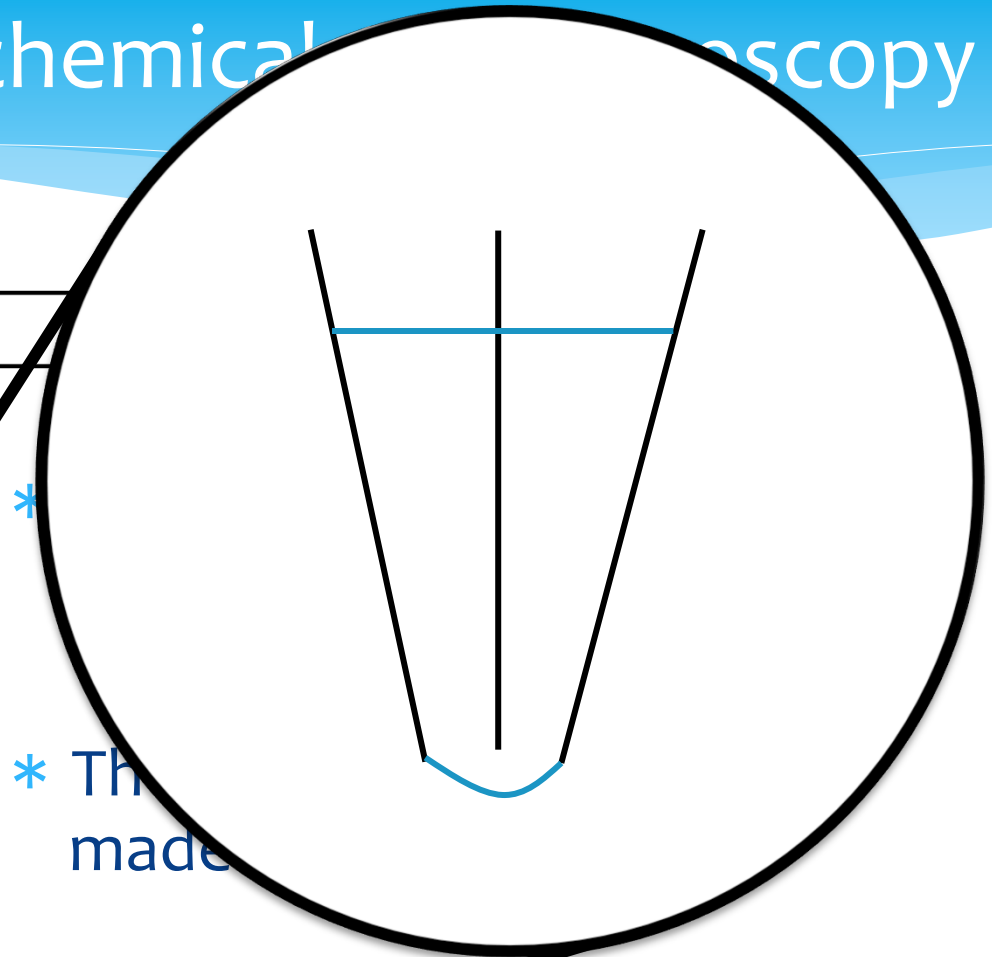
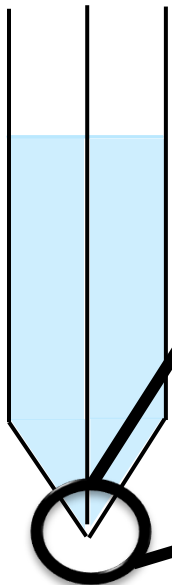
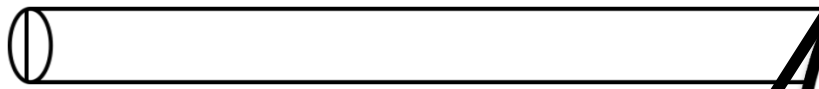


- * Tapered glass theta capillary is used as a probe



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

Scanning Electrochemical Microscopy

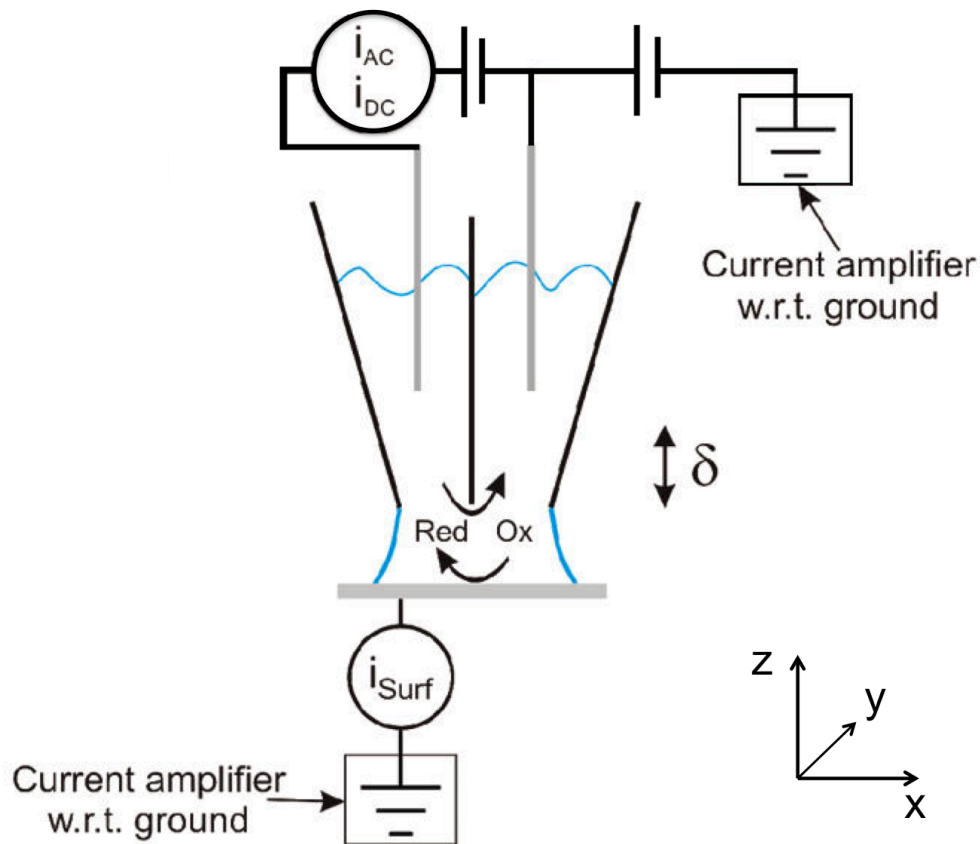


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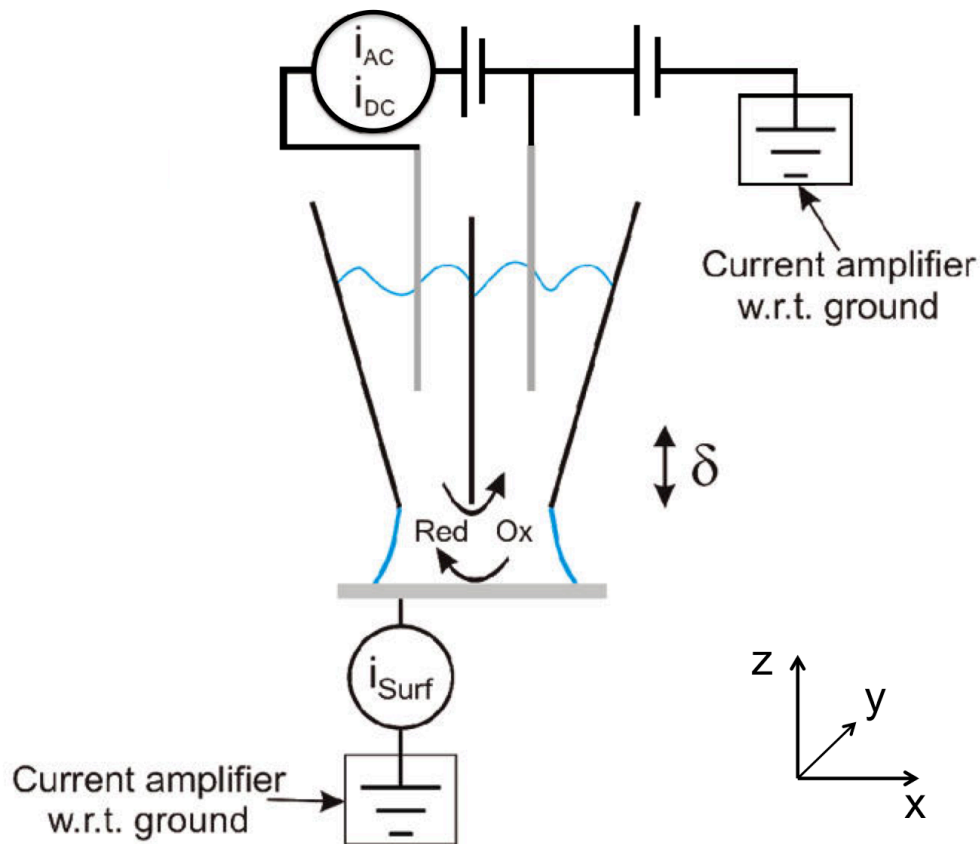
* Each barrel is filled with an electrolyte solution

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

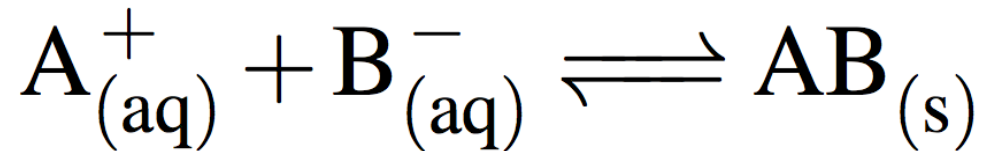
Scanning Electrochemical Cell Microscopy



- * 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:



* Solubility product:

$$\{\mathbf{A}\}\{\mathbf{B}\} = \mathbf{K}_{sp}$$

Crystal Dissolution

* Saturation:

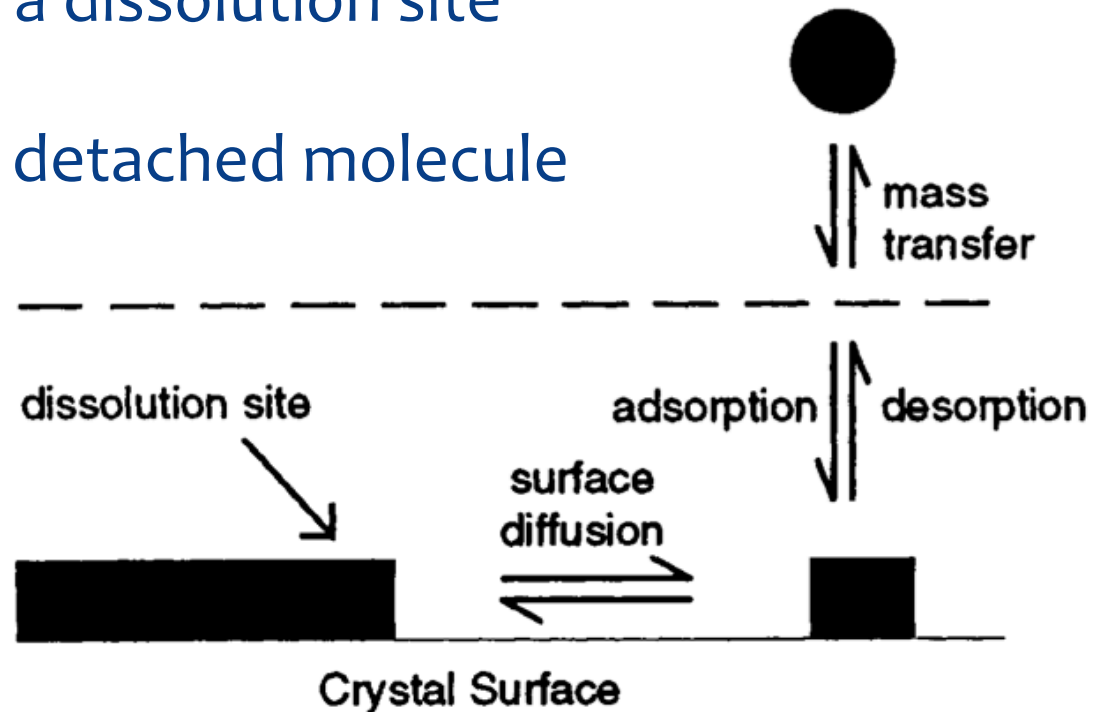
$$S = \frac{\{A\}\{B\}}{K_{sp}}$$

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

Crystal Dissolution

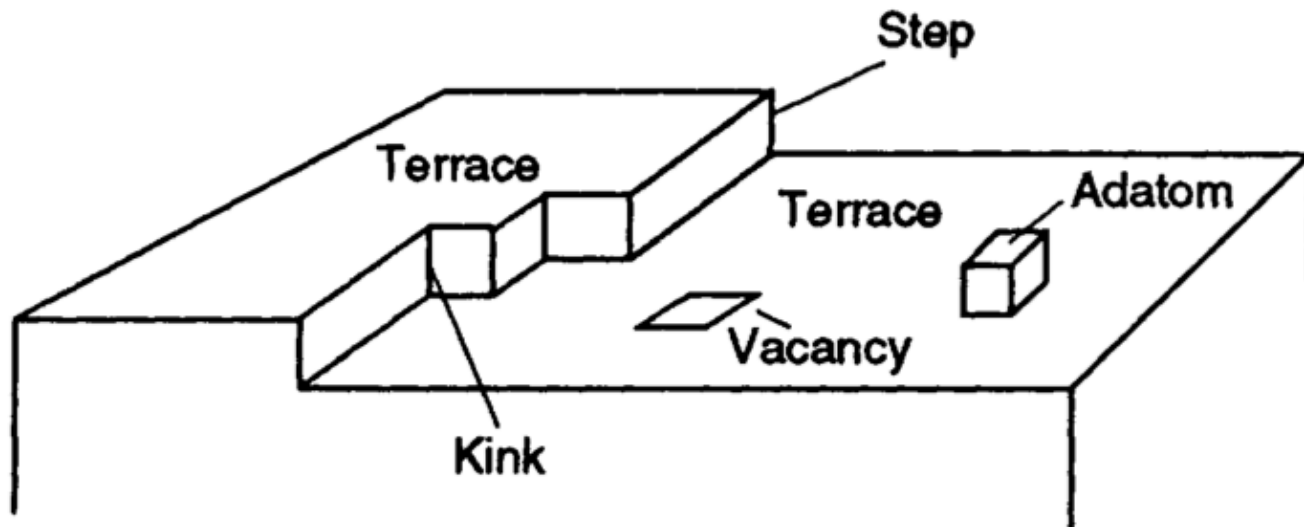
Crystal dissolution occurs in 4 stages:

- * 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

PULL



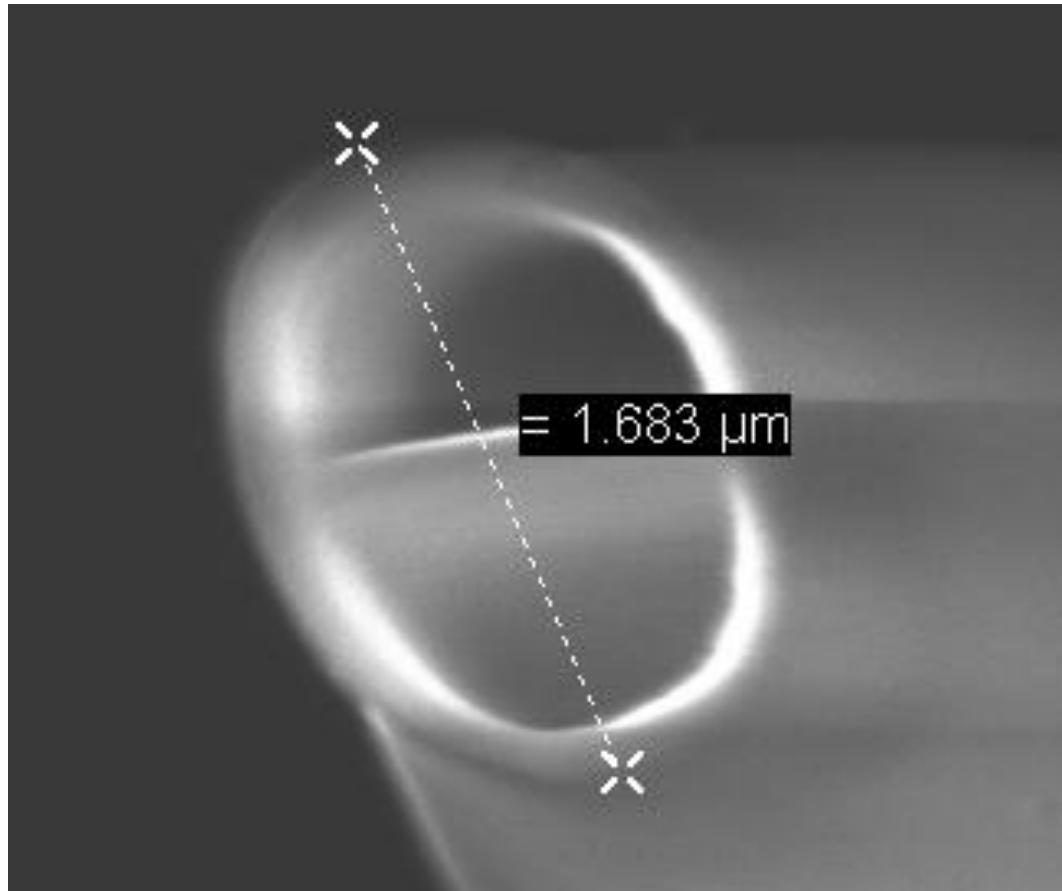
PULL



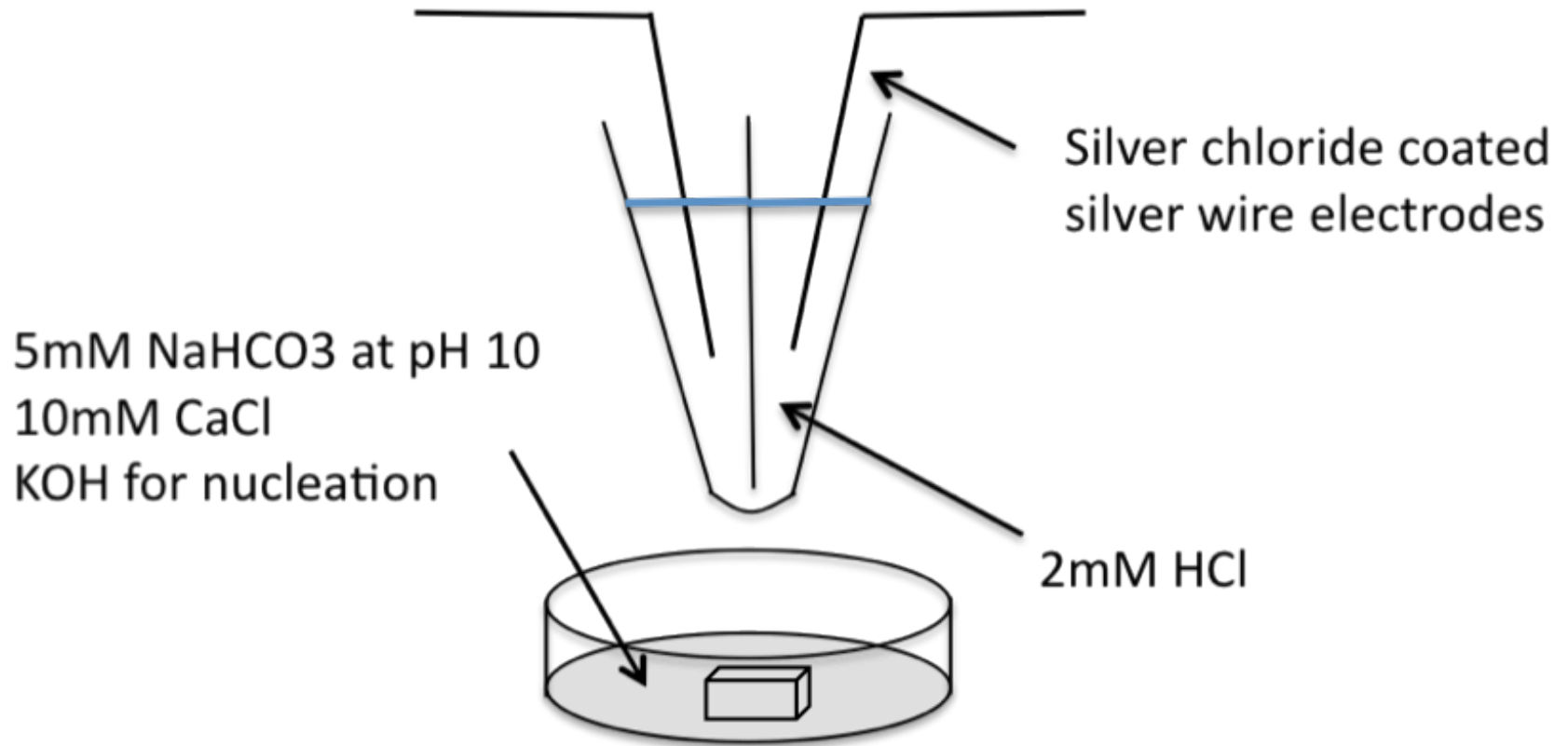
HEAT



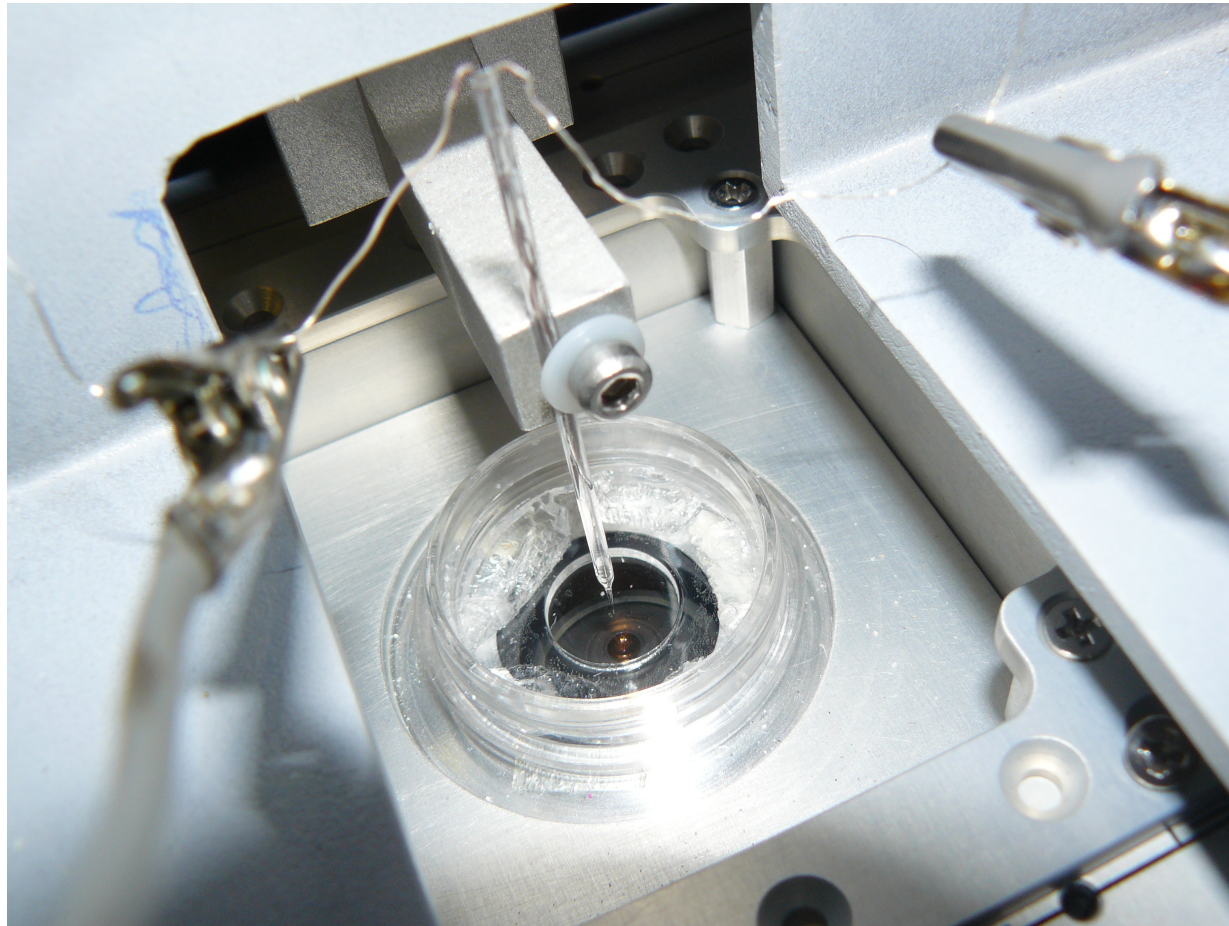
Experimental Setup



Experimental Setup



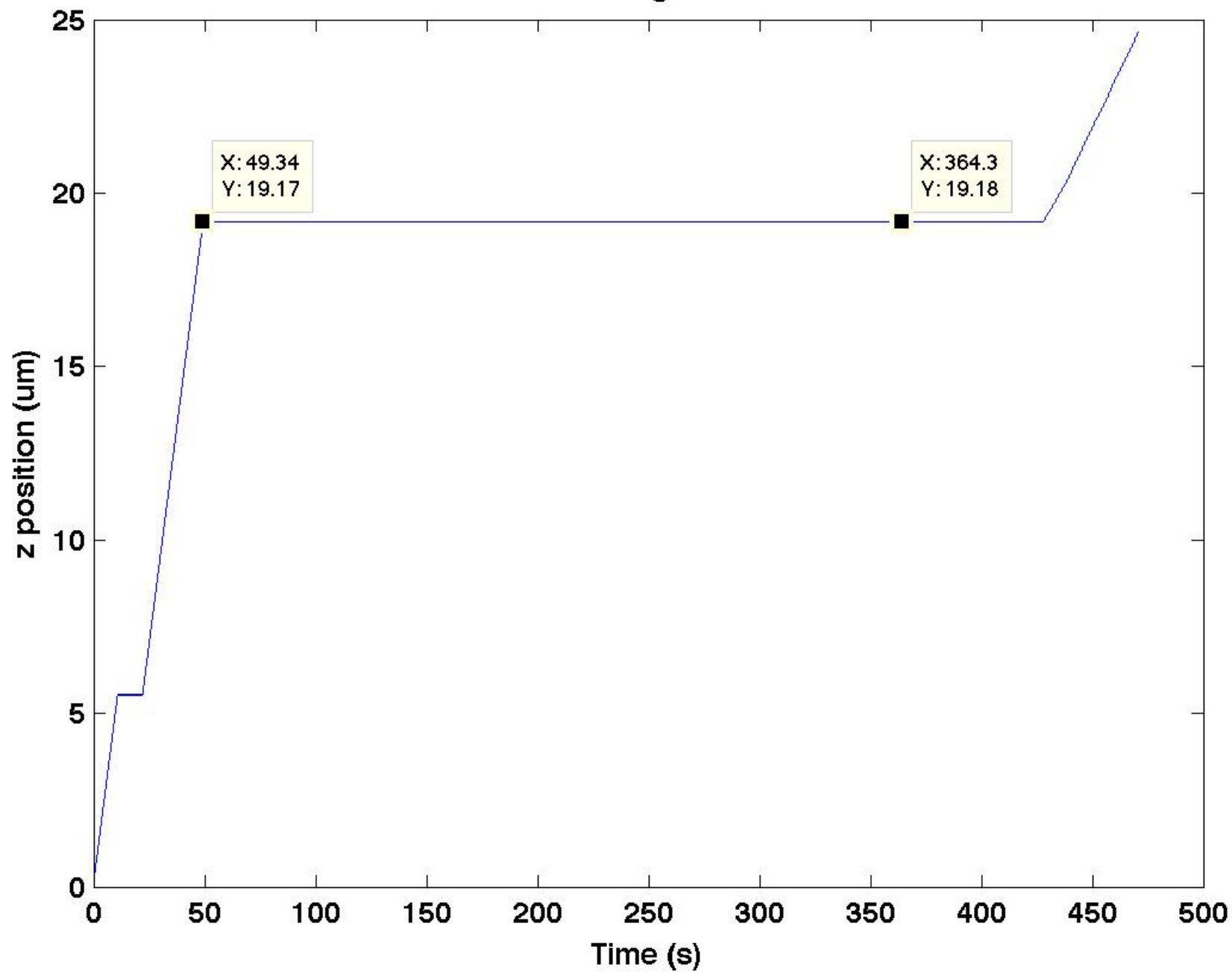
Experimental Setup



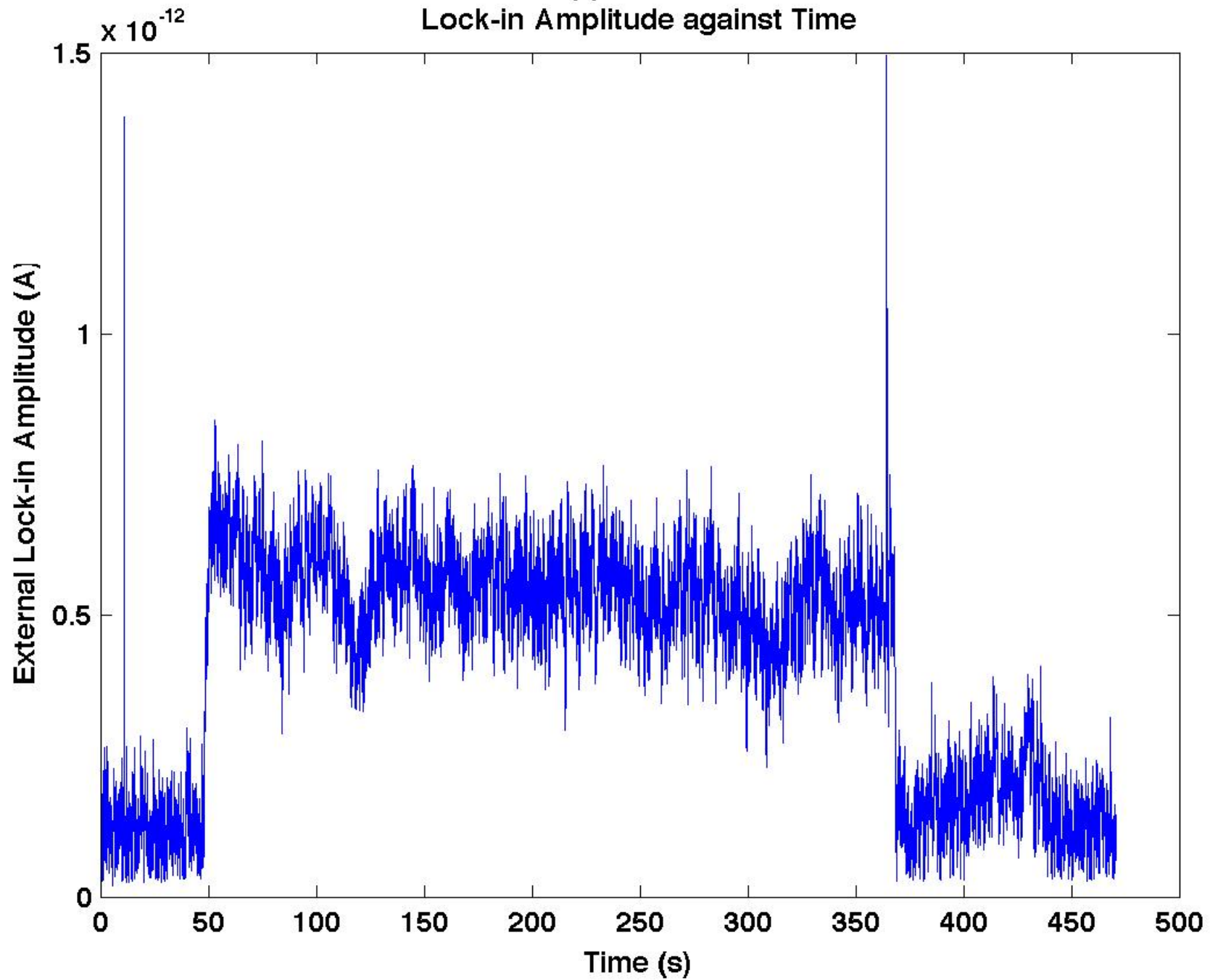
Results – Glass Approach

- * The SECCM method worked reliably on glass
- * The probe could be suspended for many minutes

Glass Approach 2mM HCl
z Position Against Time



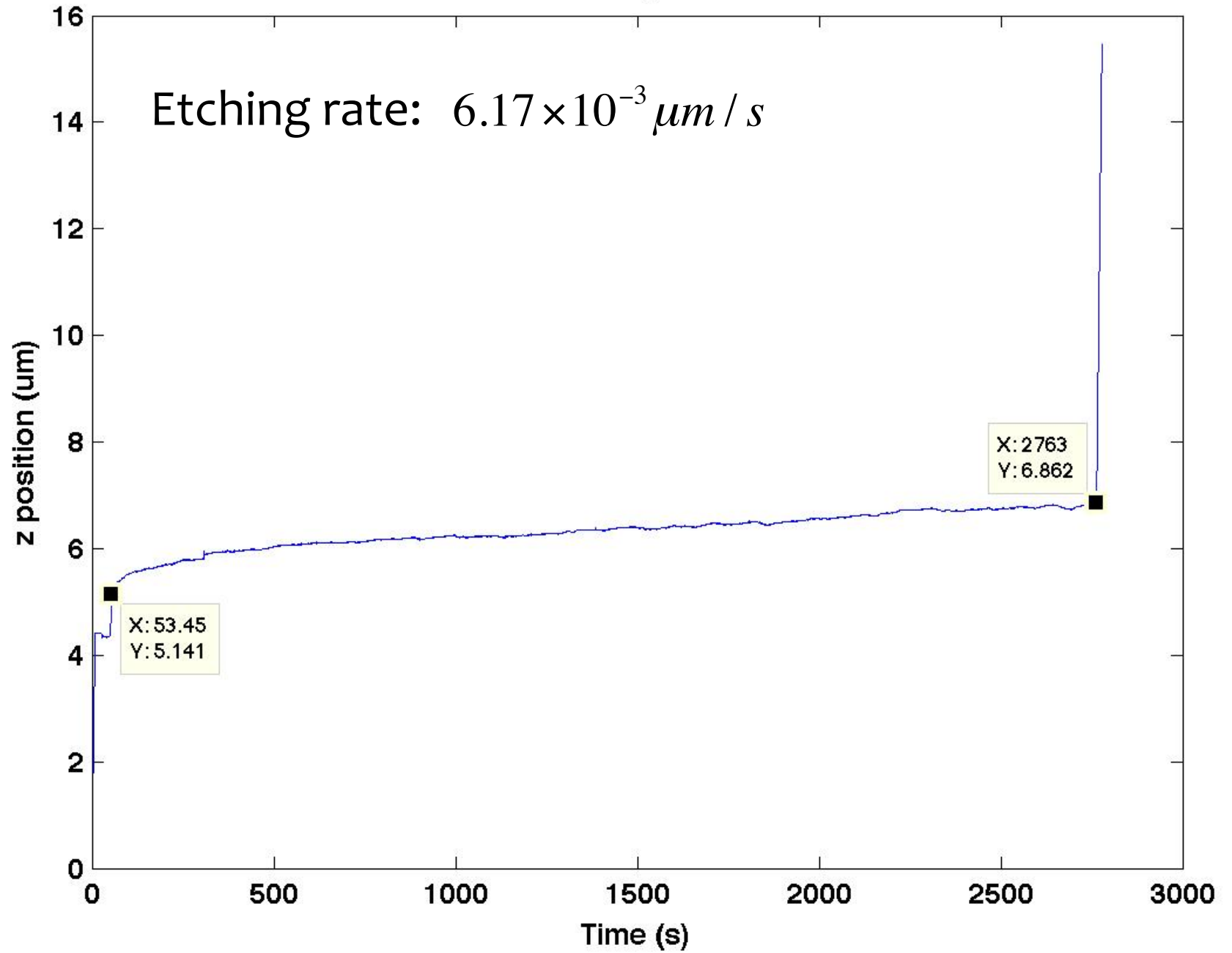
Glass Approach 2mM HCl
Lock-in Amplitude against Time



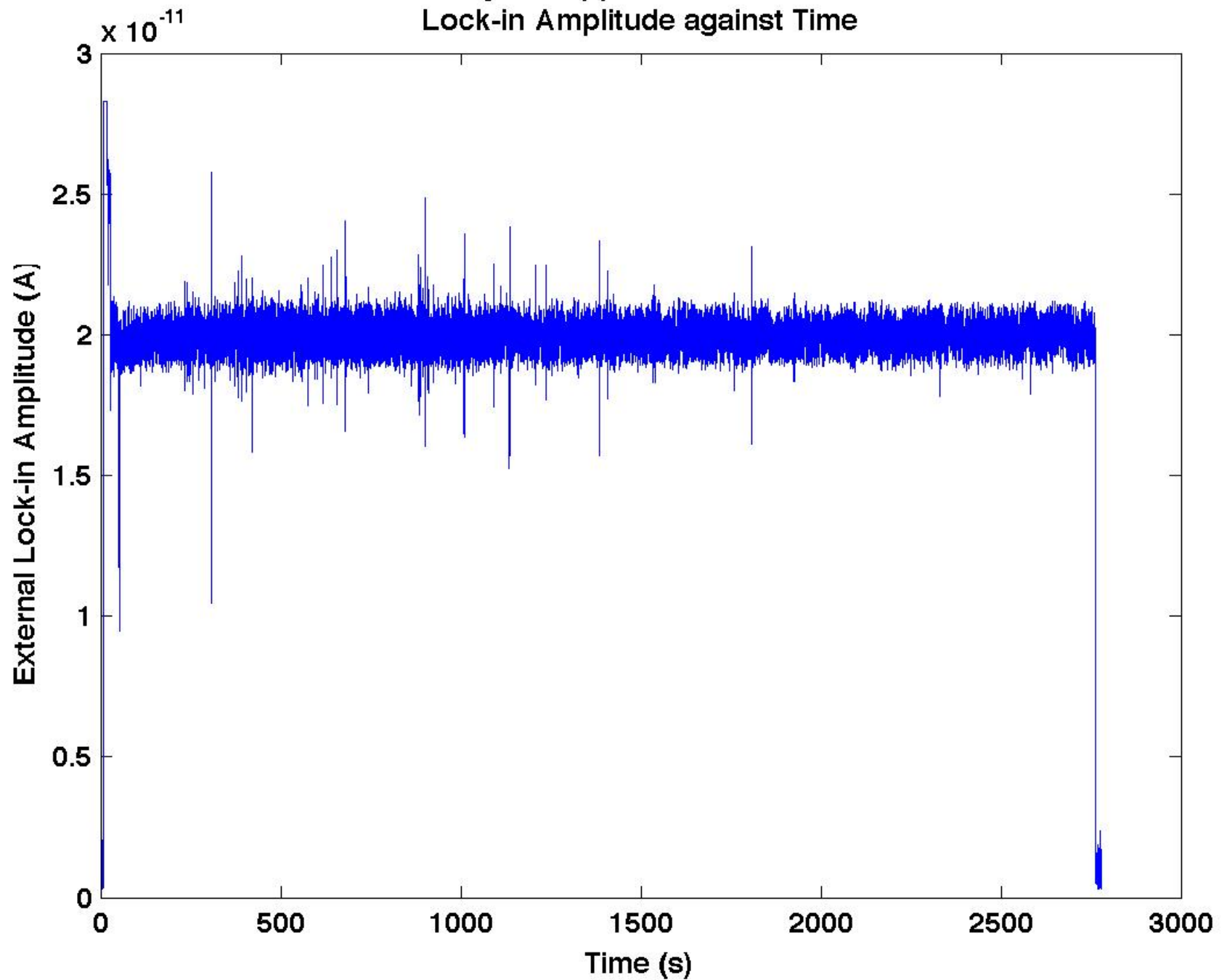
Results – Crystal Approach

- * 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



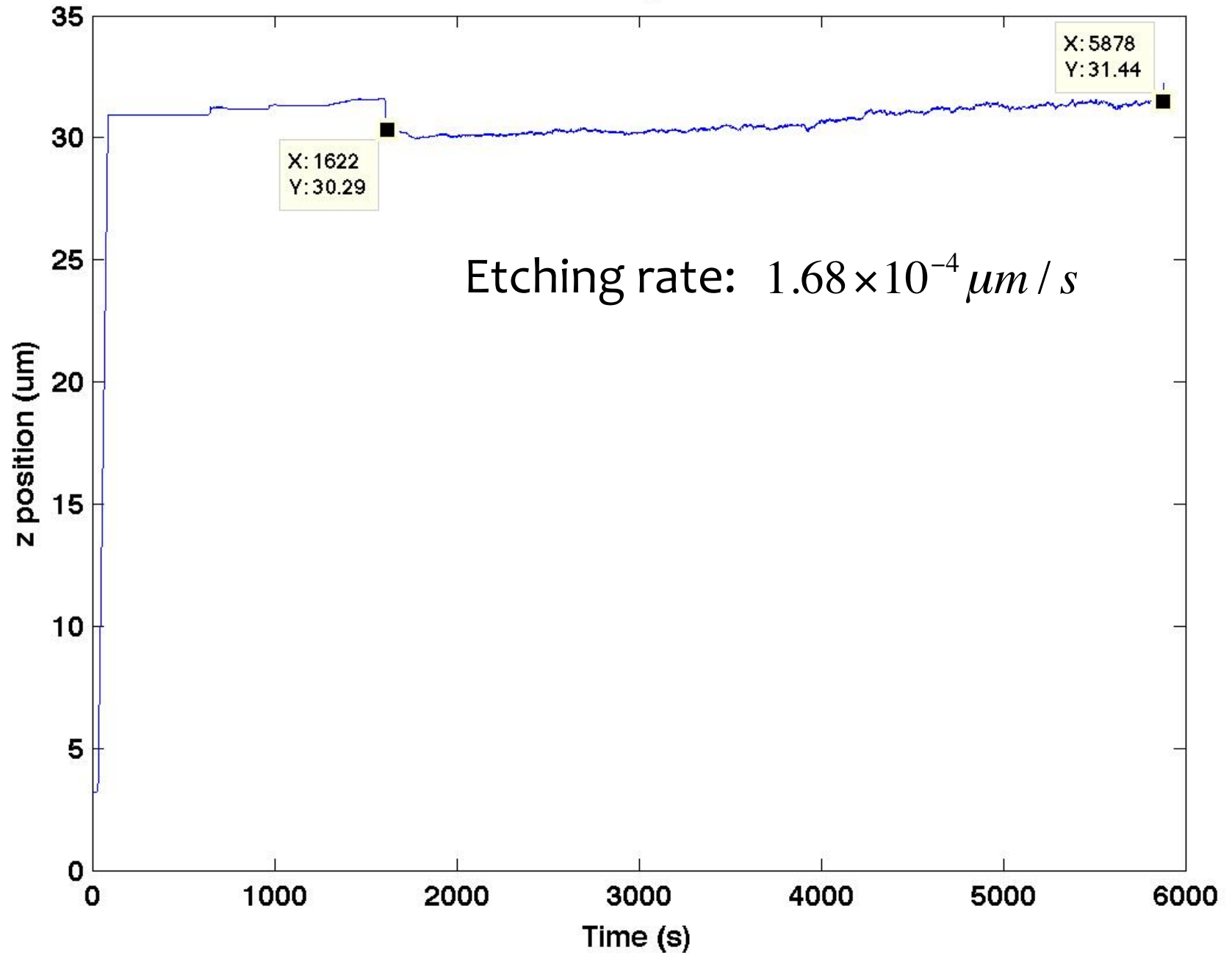
Crystal Approach 2mM HCl
Lock-in Amplitude against Time



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

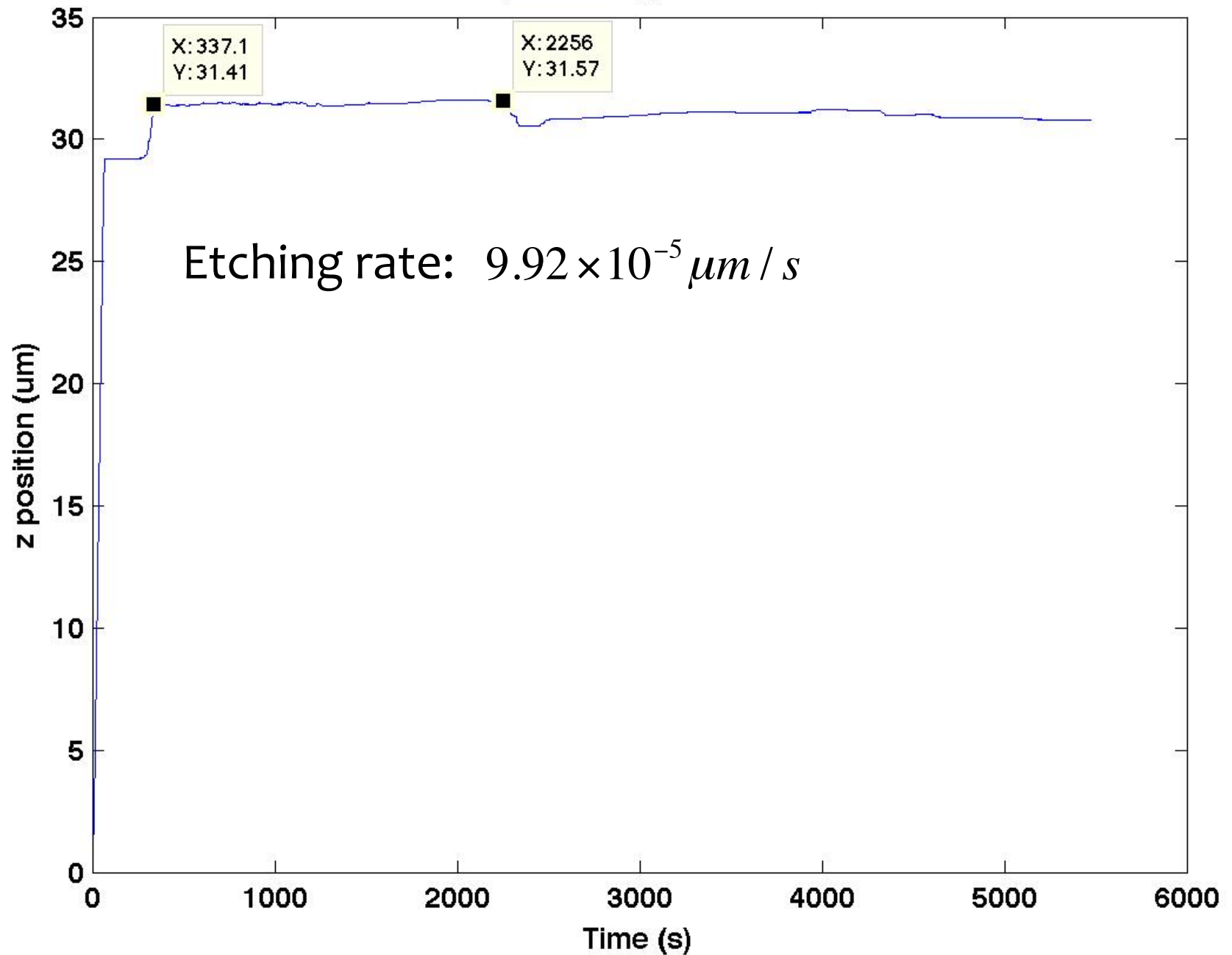
Crystal Approach 2mM HCl + 5mM KCl
z Position Against Time



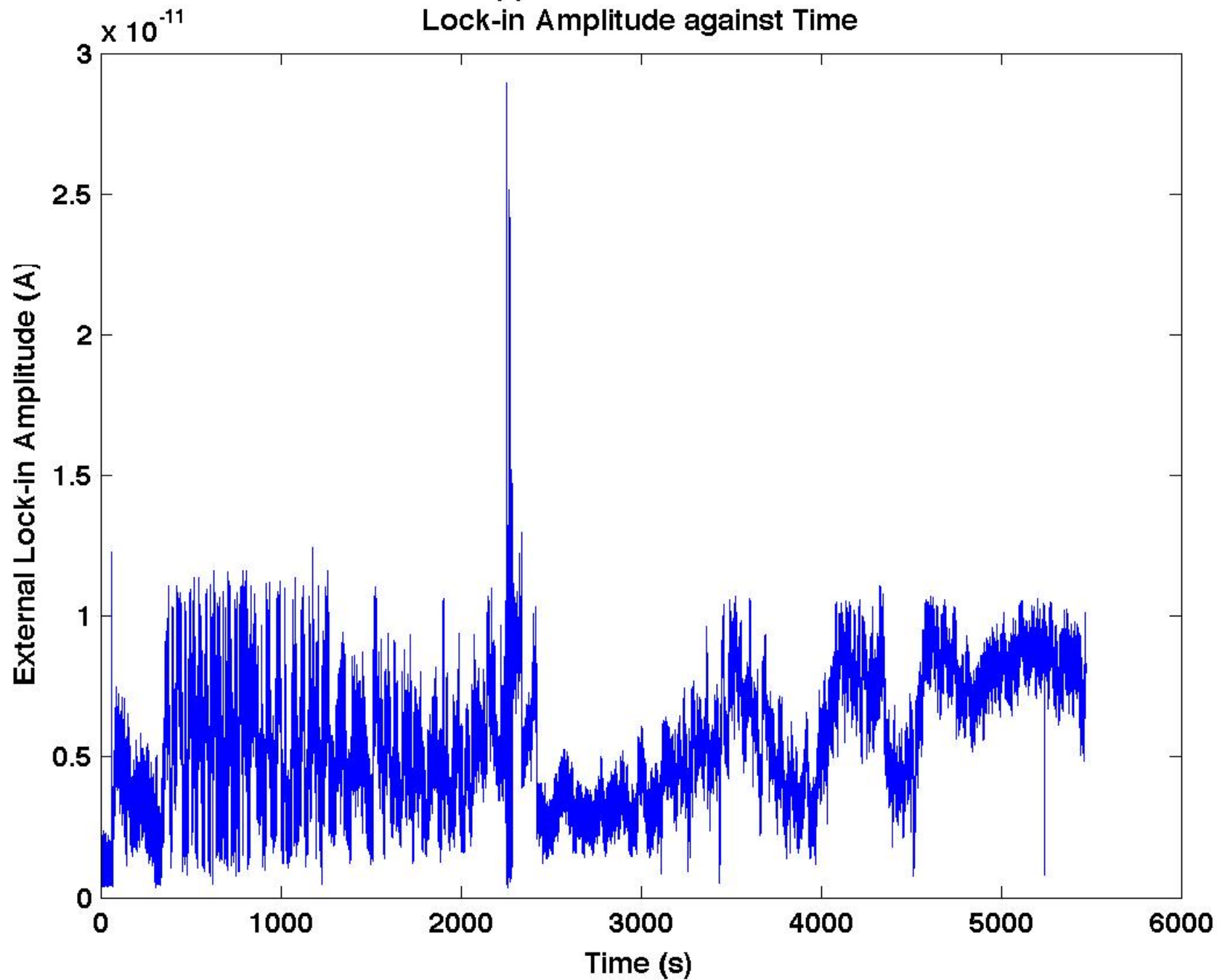
Results – Crystal Approach with KCl (1mM HCl)

- * 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

Calcite Approach 1mM HCl + 5mM KCl
z position against time



Calcite Approach 1mM HCl + 5mM KCl
Lock-in Amplitude against Time



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



References

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