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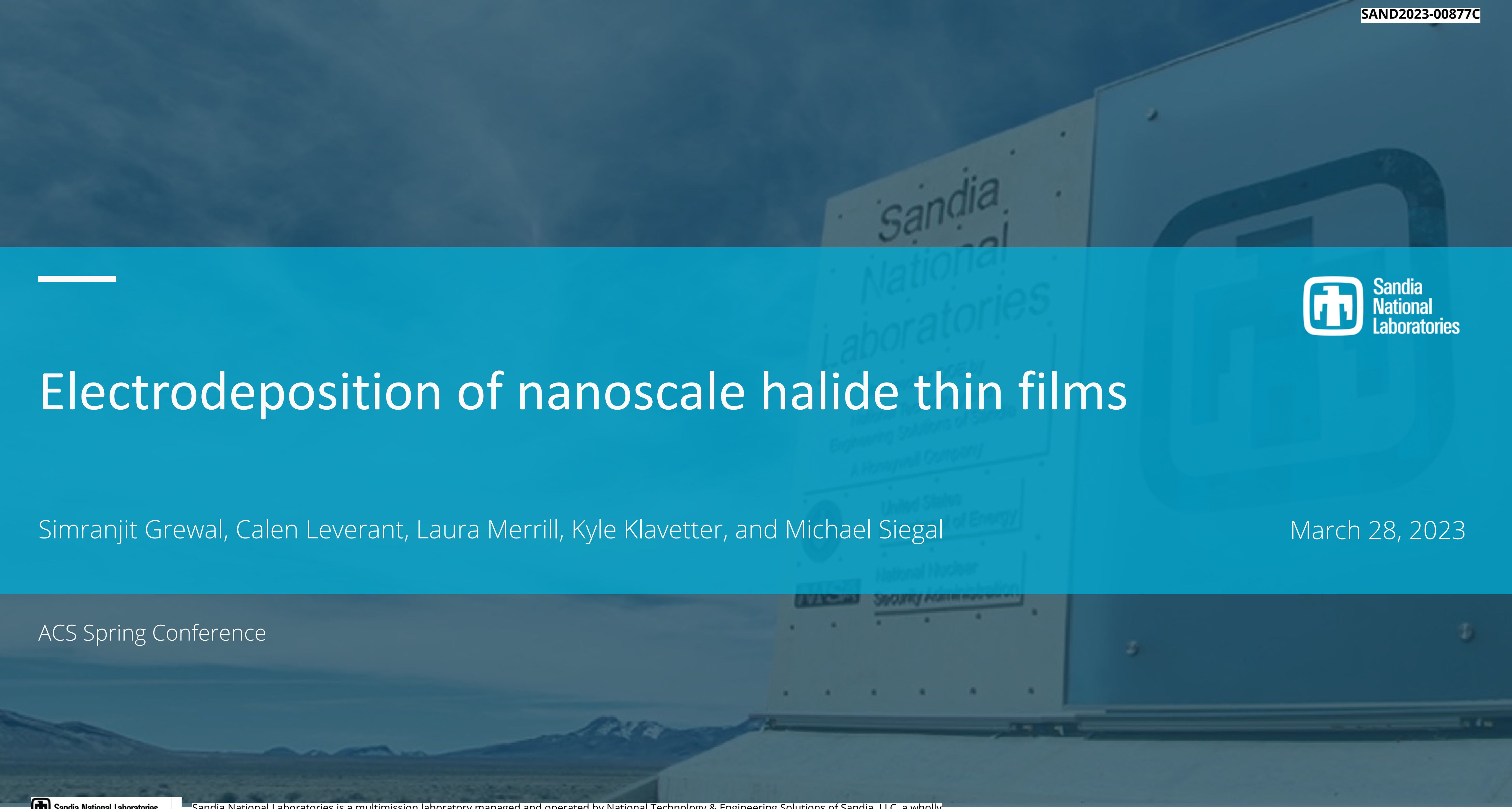

Electrodeposition of nanoscale halide thin films

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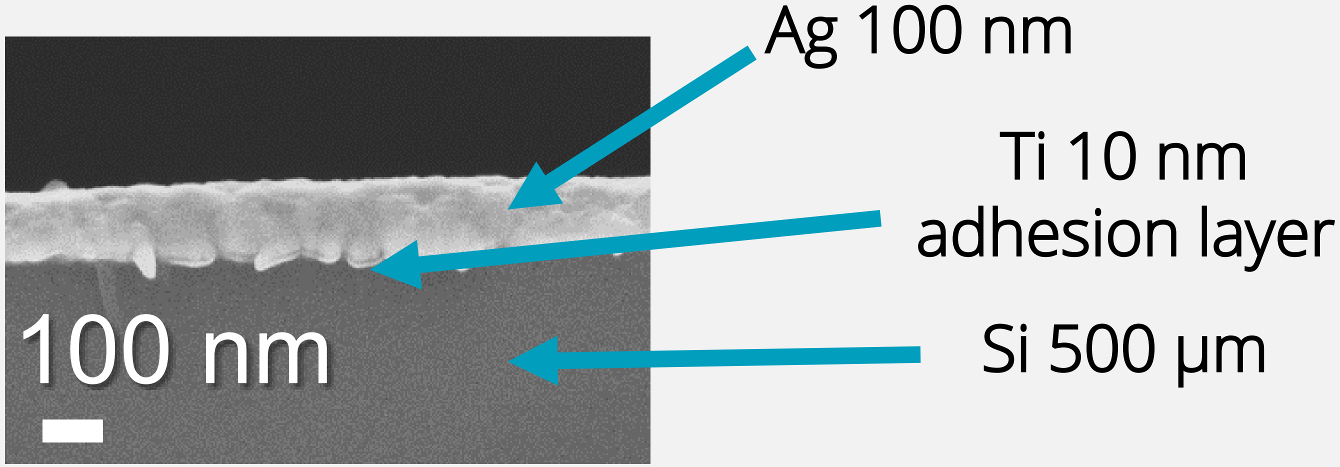
ring Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Controlling <10 at.% AgCl over a large distribution

A. Use of electrochemical and chemical methods to create <10 AgCl at.% in a Ag surface deposits have sever uniformity issues

B. Objective: Control amount and uniformity of AgCl at.% in a Ag surface using pulsed electrodeposition

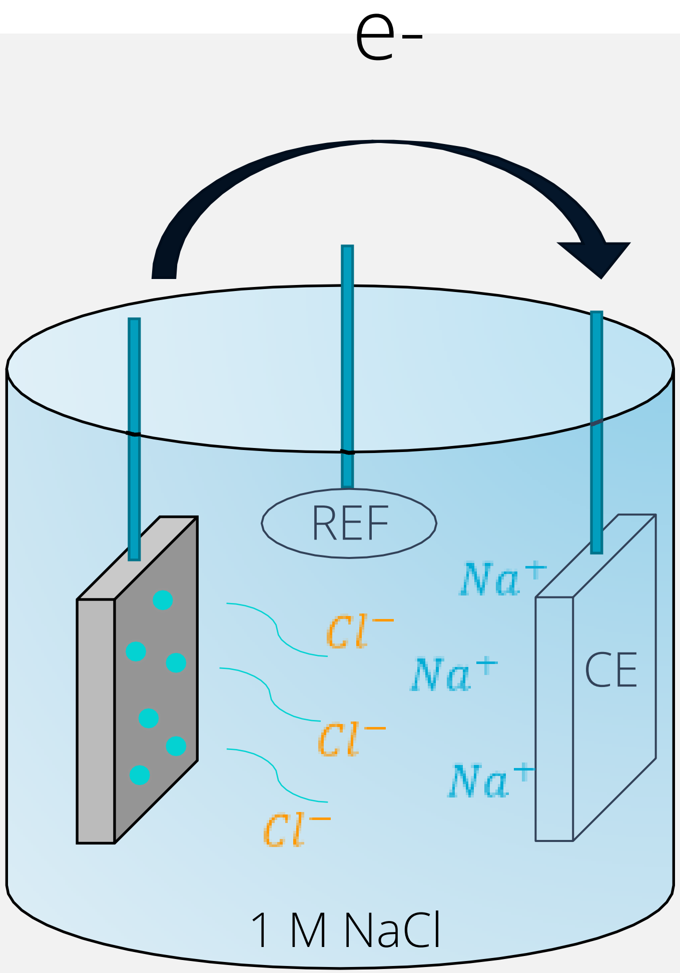
Experimental setup of electrodepositing AgCl



Ag 100 nm

Ti 10 nm
adhesion layer

Si 500 μm



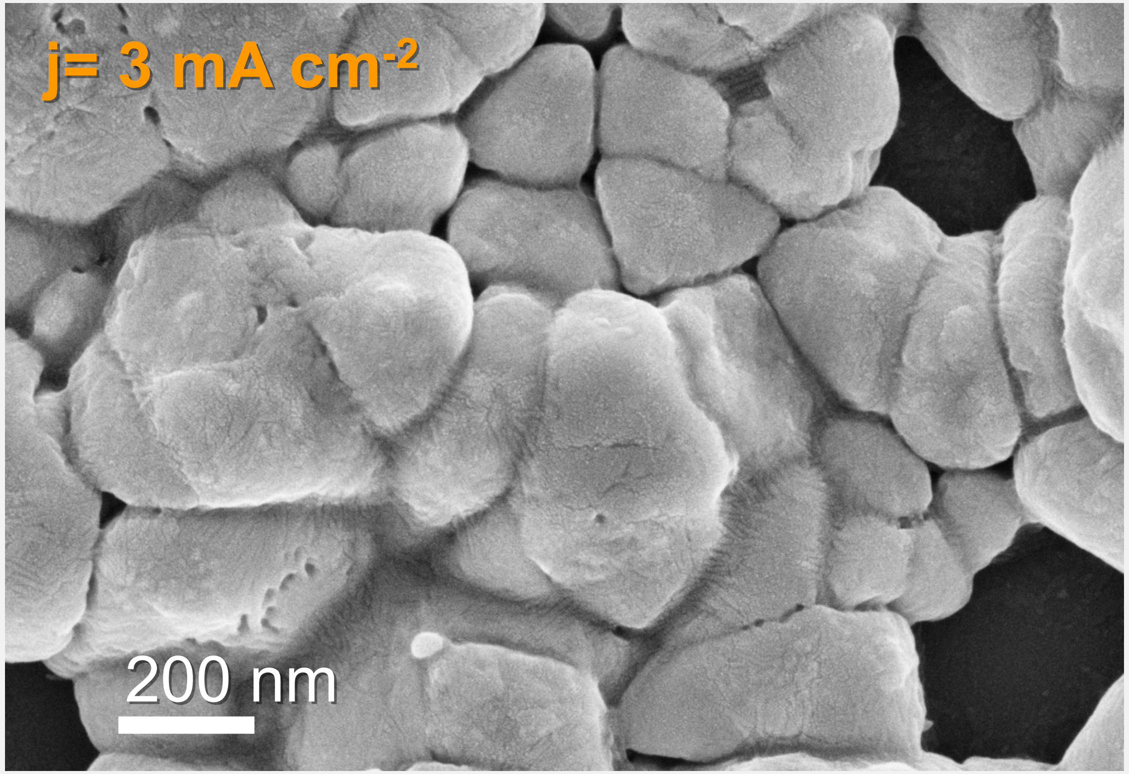
$$Cl^{-}_{(aq)} + Ag_{(s)} \rightarrow AgCl_{(s)} + e^{-}$$

$$AgCl_{(s)} = e^{-} = Q \times I \times t$$

$$\therefore Q \text{ provides "predicted" halidization } AgCl \text{ at.\%}$$

Maximizing nucleation density with pulsed electrodeposition

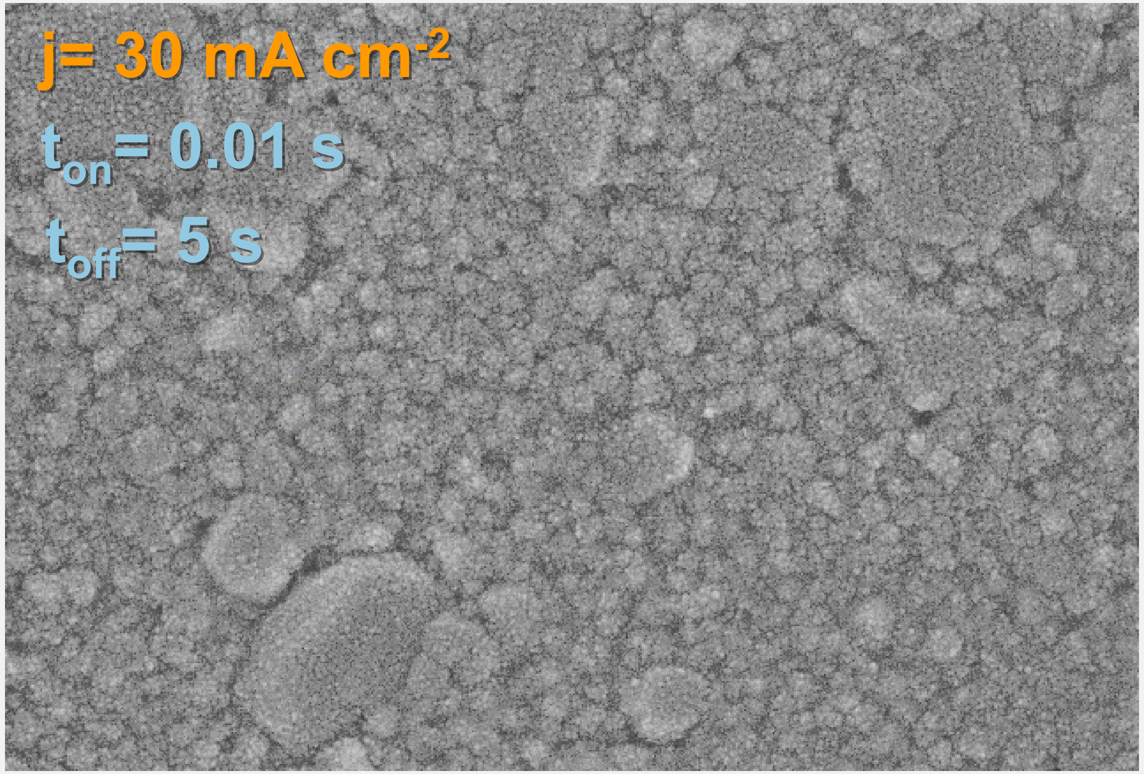
Constant Current



Inhomogenous chemically
& uniformity, why?

- Overpotential was not reached

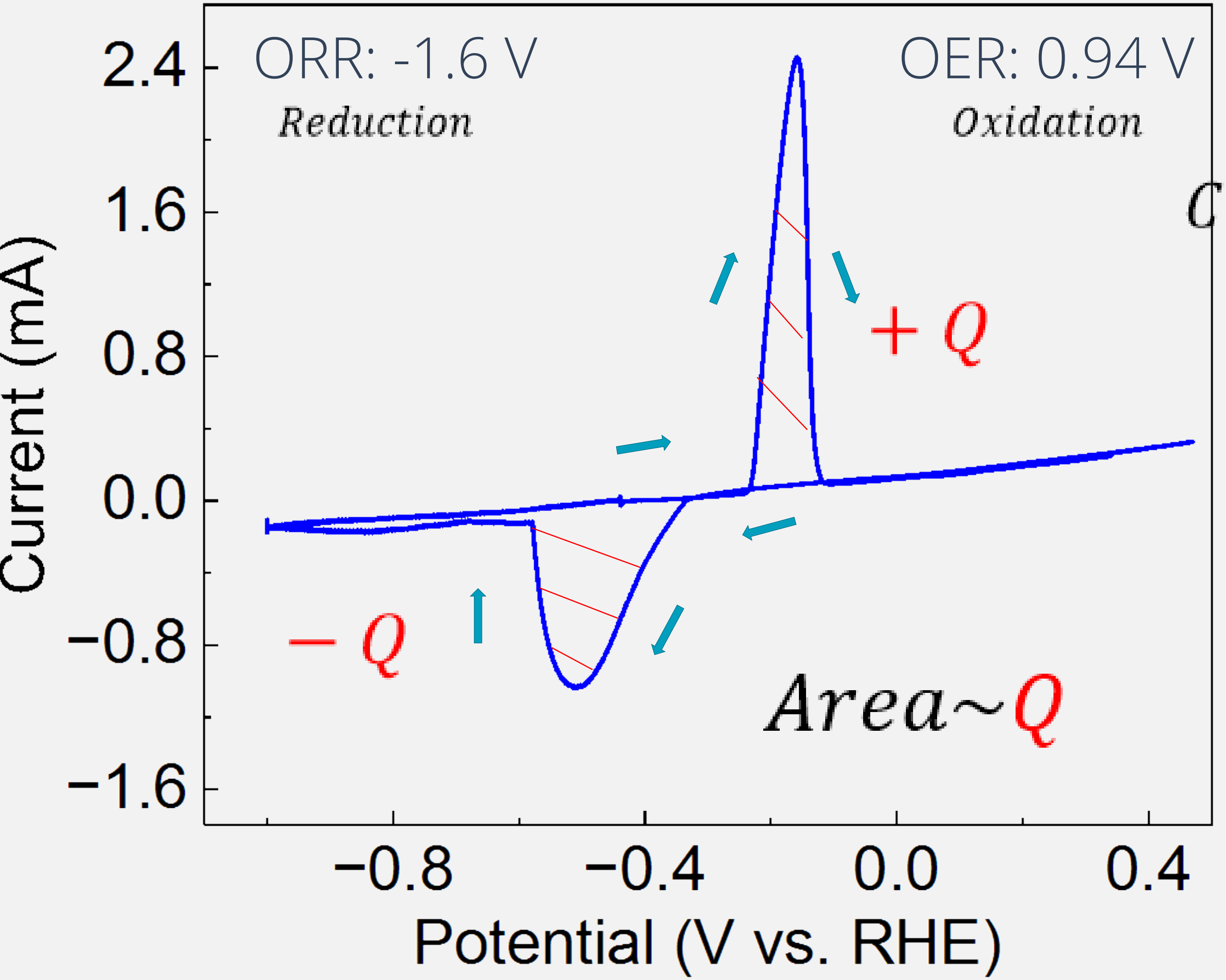
Pulsed Electrodeposition



More nucleation, why?

- More active sites
- Solubilized precursor concentration relaxation

Use of cathodic stripping to quantify AgCl



$Cl^-_{(aq)} + Ag_{(s)} \rightarrow \quad AgCl_{(s)} + e^- \qquad {\color{red}+Q}$

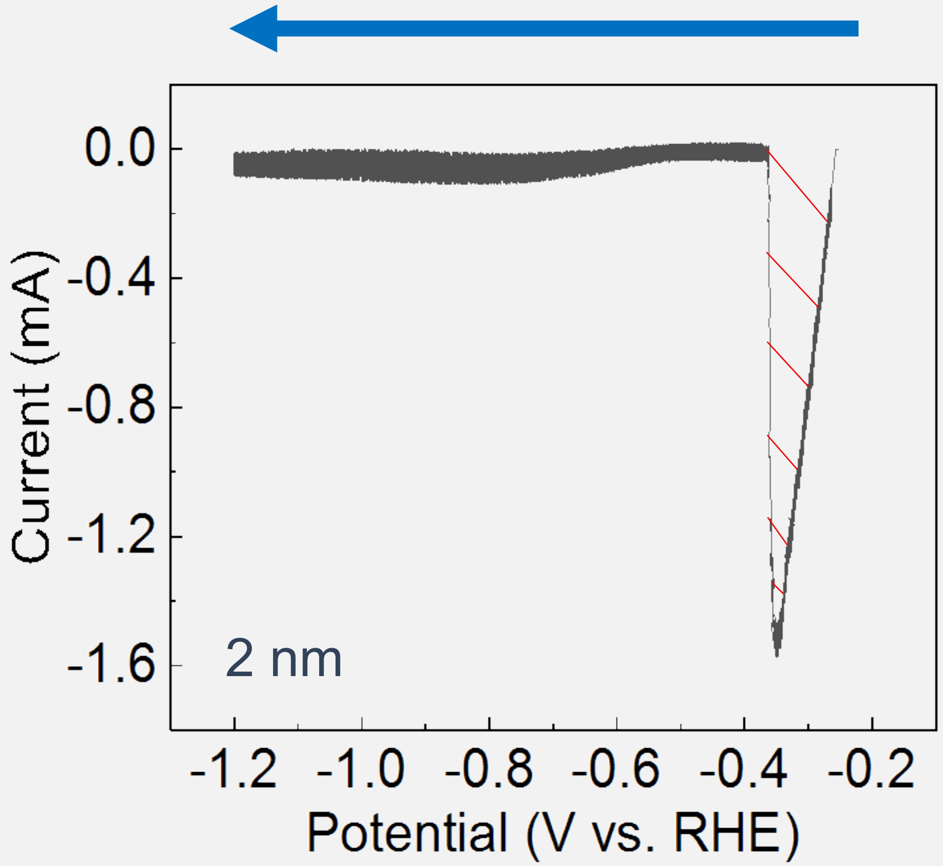
$AgCl_{(s)} + \qquad Cl^-_{(aq)} + Ag_{(s)} \qquad {\color{red}-Q}$

$\frac{-Q}{+Q} = 98.7\%\ Efficiency$

$\therefore Reversable$

Use of cathodic stripping to quantify AgCl

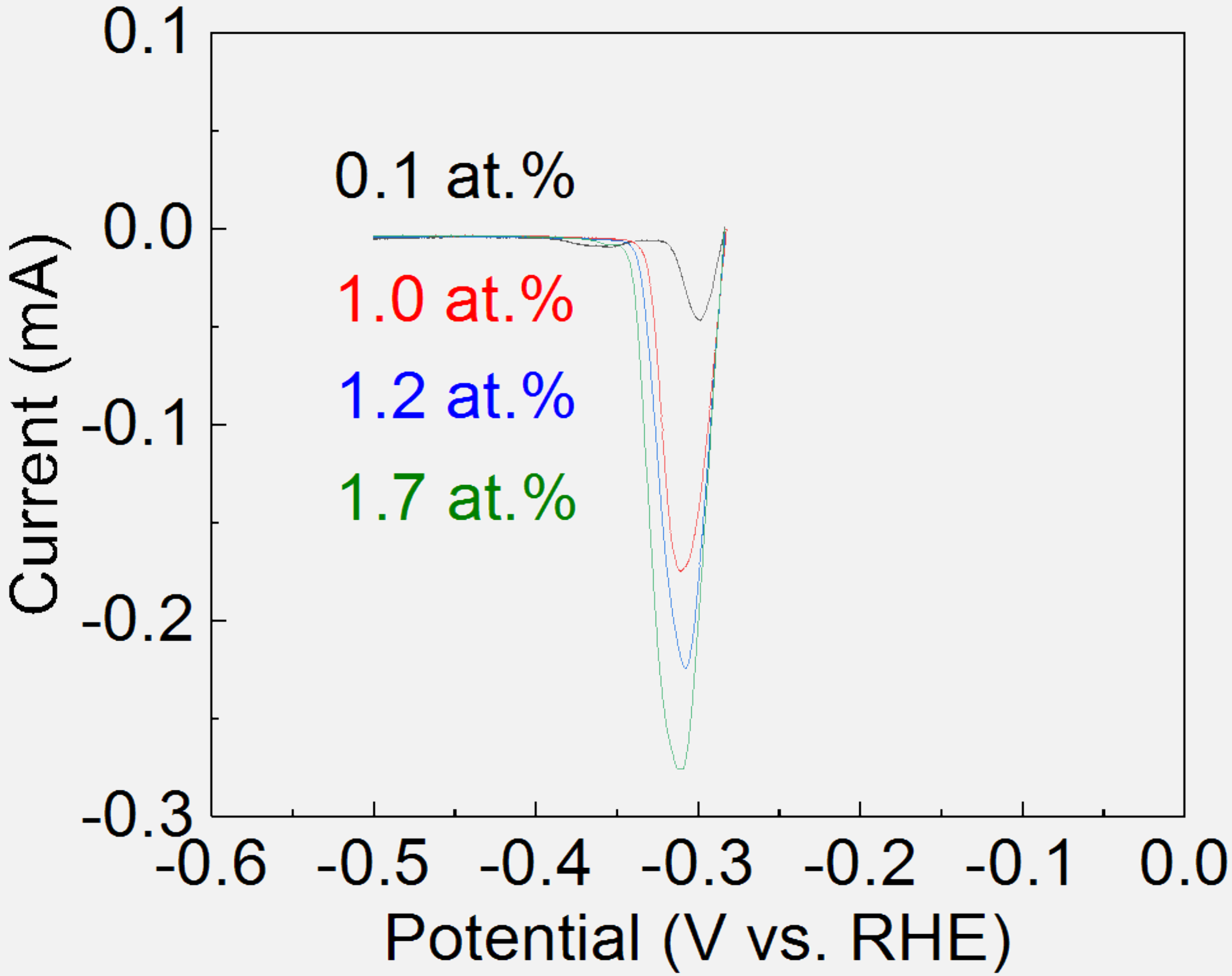
Use of linear sweep voltammetry (-0.32 to -0.8 V vs. Ag/AgCl) in 1M NaCl in water of 4 mV s^{-1} scan rate



$$AgCl_{(s)} + \qquad Cl^{-}_{(aq)} + Ag_{(s)} \qquad -Q$$

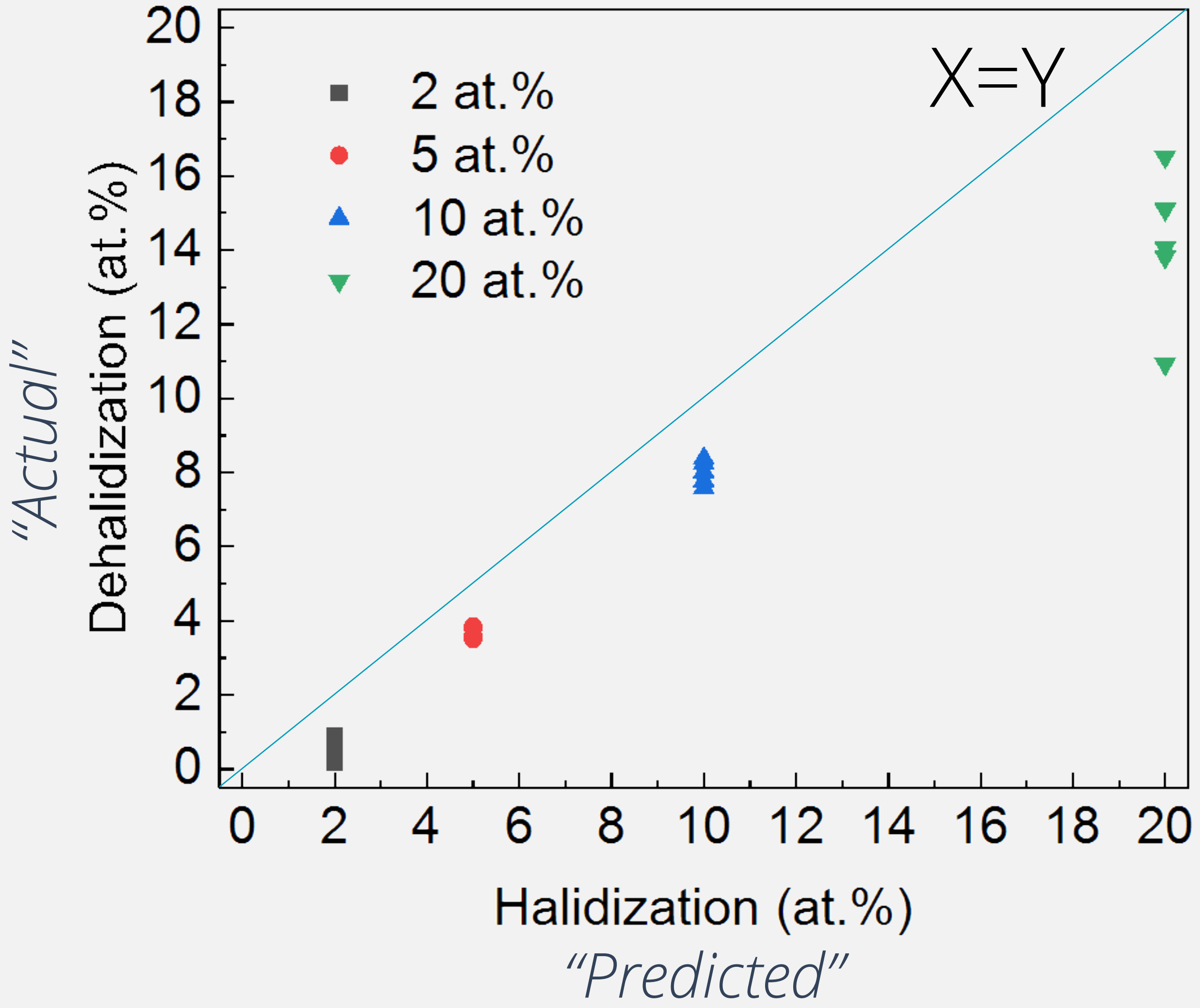
Cathodic stripping removes AgCl and correlates the charge collected to its at.%.

Detection limit of cathodic stripping



Cathodic striping can detect 0.12 at.% of AgCl

Cathodic stripping quantifies AgCl



Why such a difference between halidization and dehalidization?

1) Some of the charge applied could be going into capacitive reactions

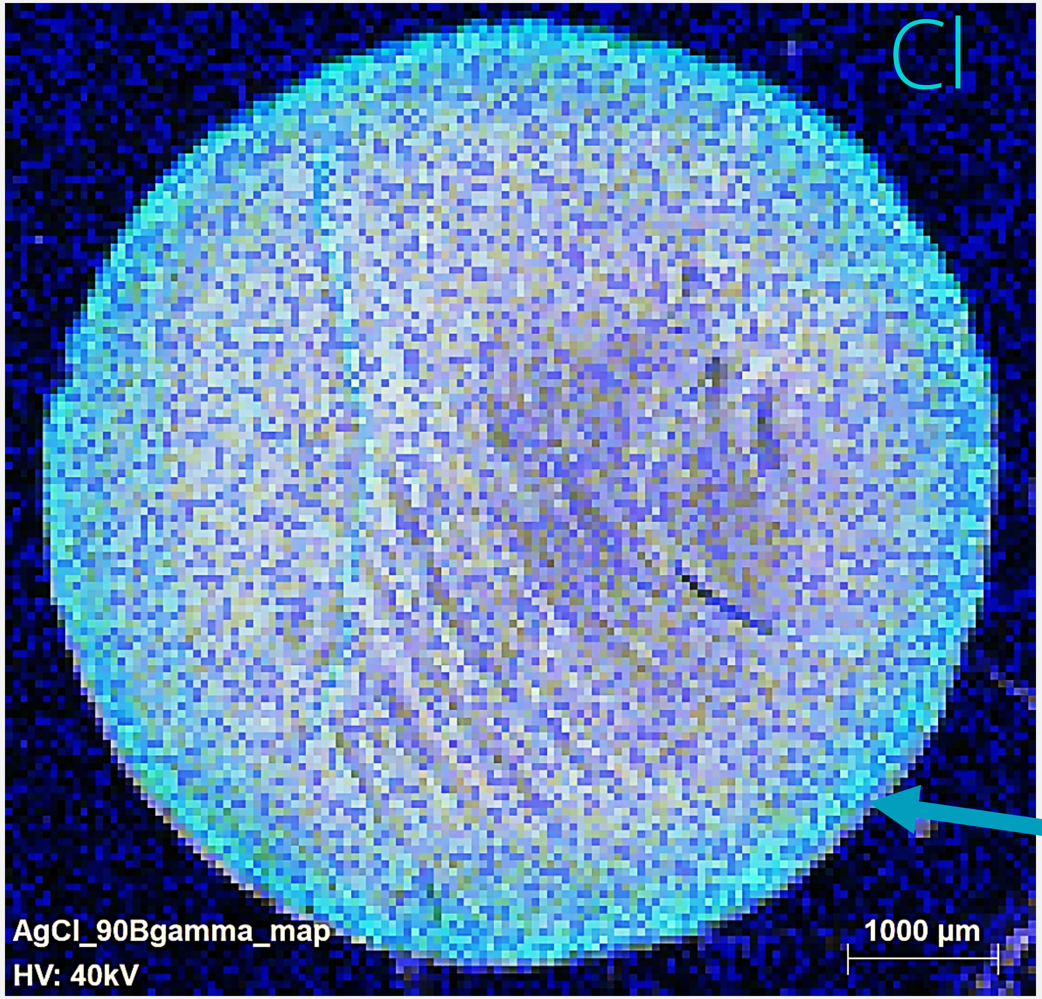
2) Hitting a limit of available Ag surface

Validating AgCl at.% from cathodic stripping using X-ray fluorescence spectroscopy (XRF)

Advantages of using XRF analysis of thin films can

1) Identify and quantify elemental data
2) Determine uniformity

Technical Challenge: Control distribution

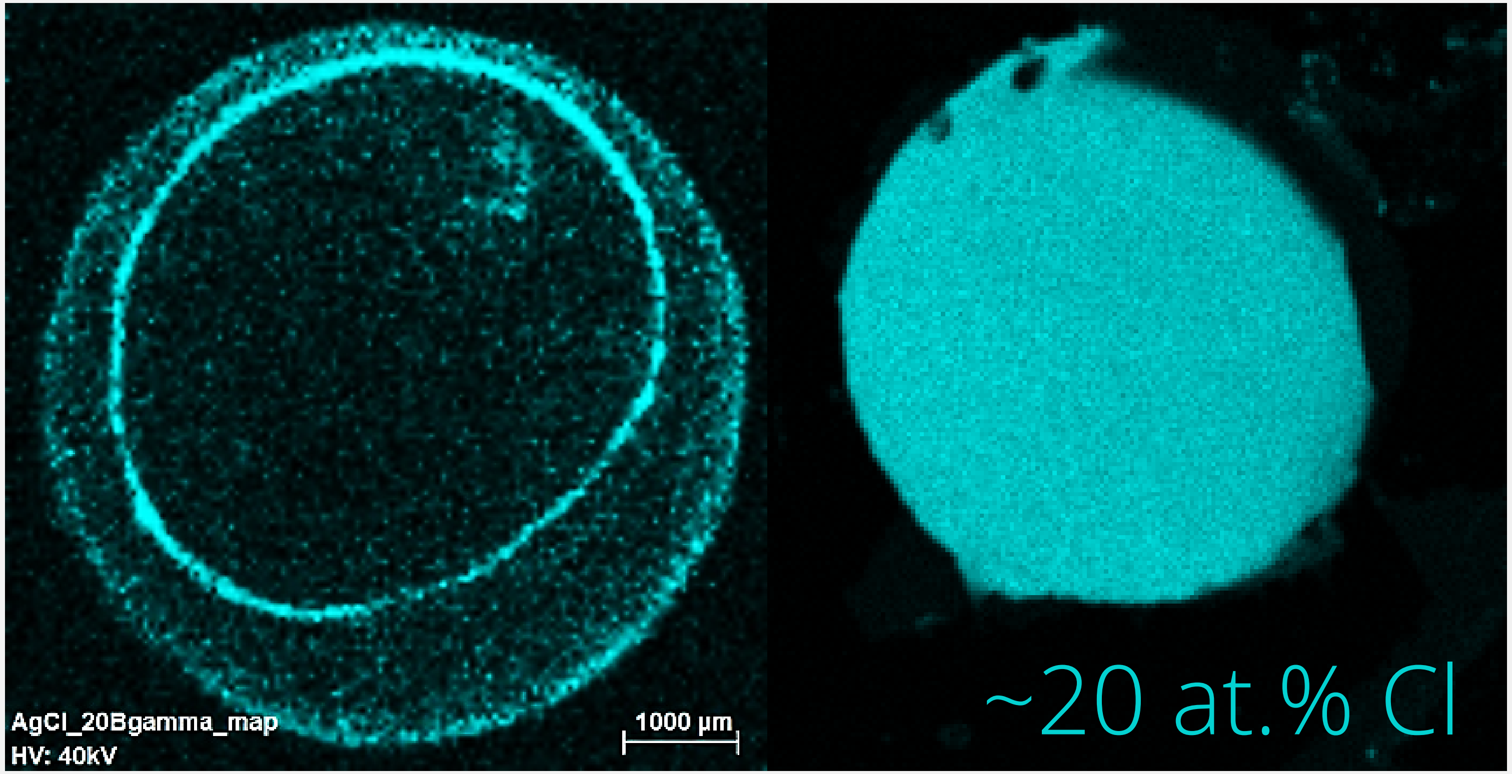


Larger amount of Cl on edges, known as edge effects, are caused by a difference in electric field strength.

Larger amount of chloride

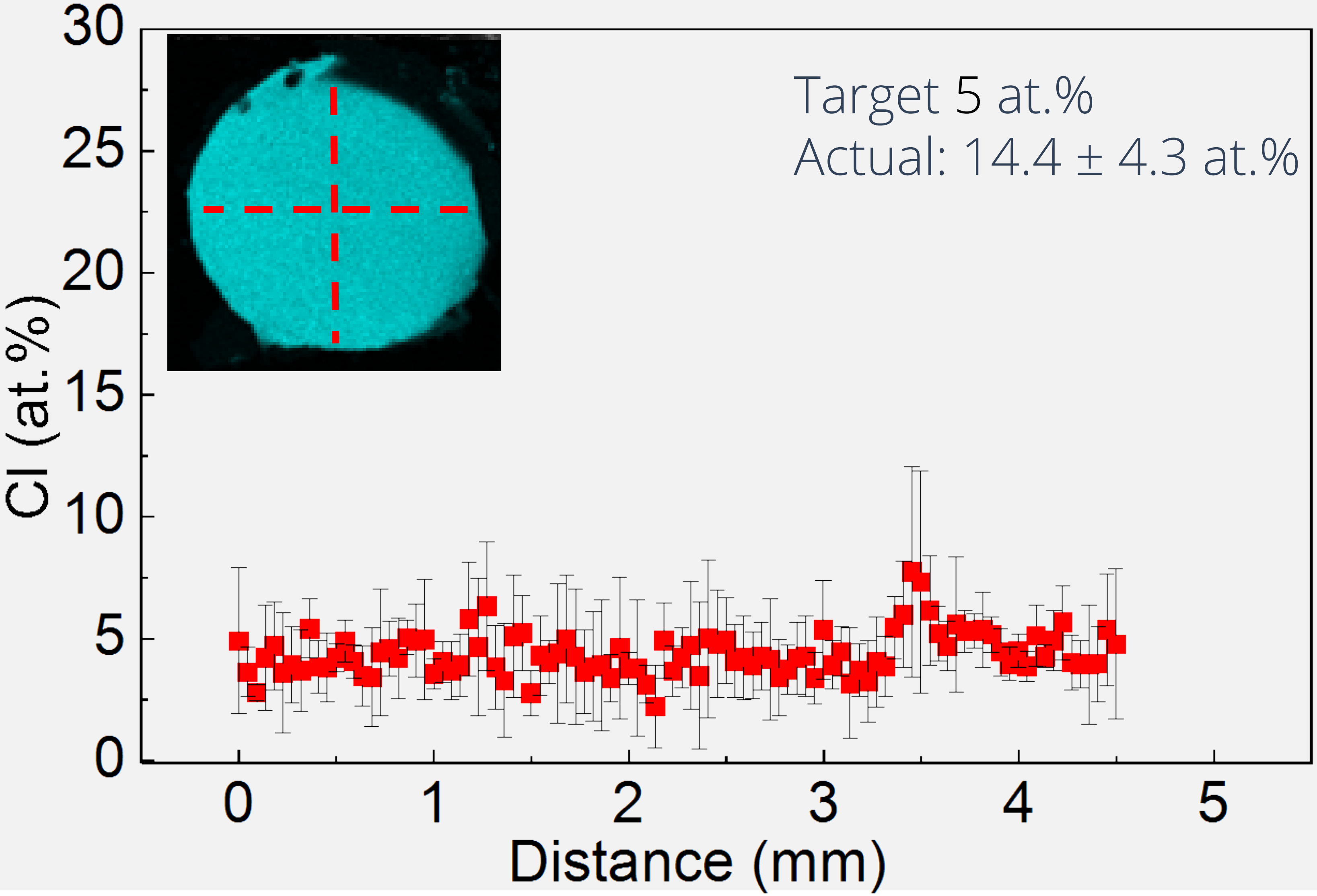
Conrad B. Diem *et al* 1988 *J. Electrochem. Soc.* 135 2524

Use of masking to evenly distribute $\vec{E}$ fields



Use of ¼ inch masking reduces edge effects on substrates and creates an even distribution of AgCl

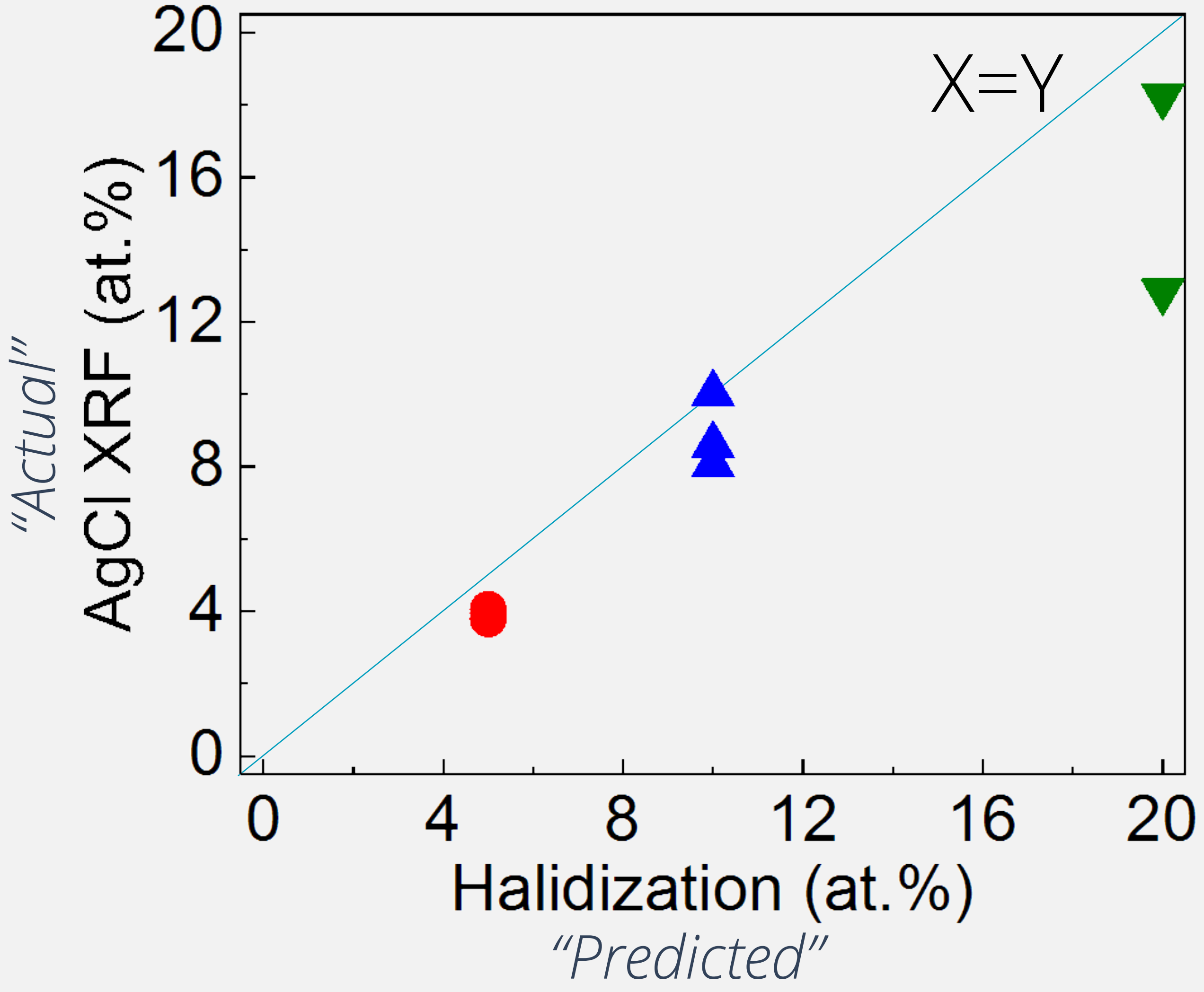
Use of XRF to determine uniform distribution of AgCl



Averaged six measurements across three samples

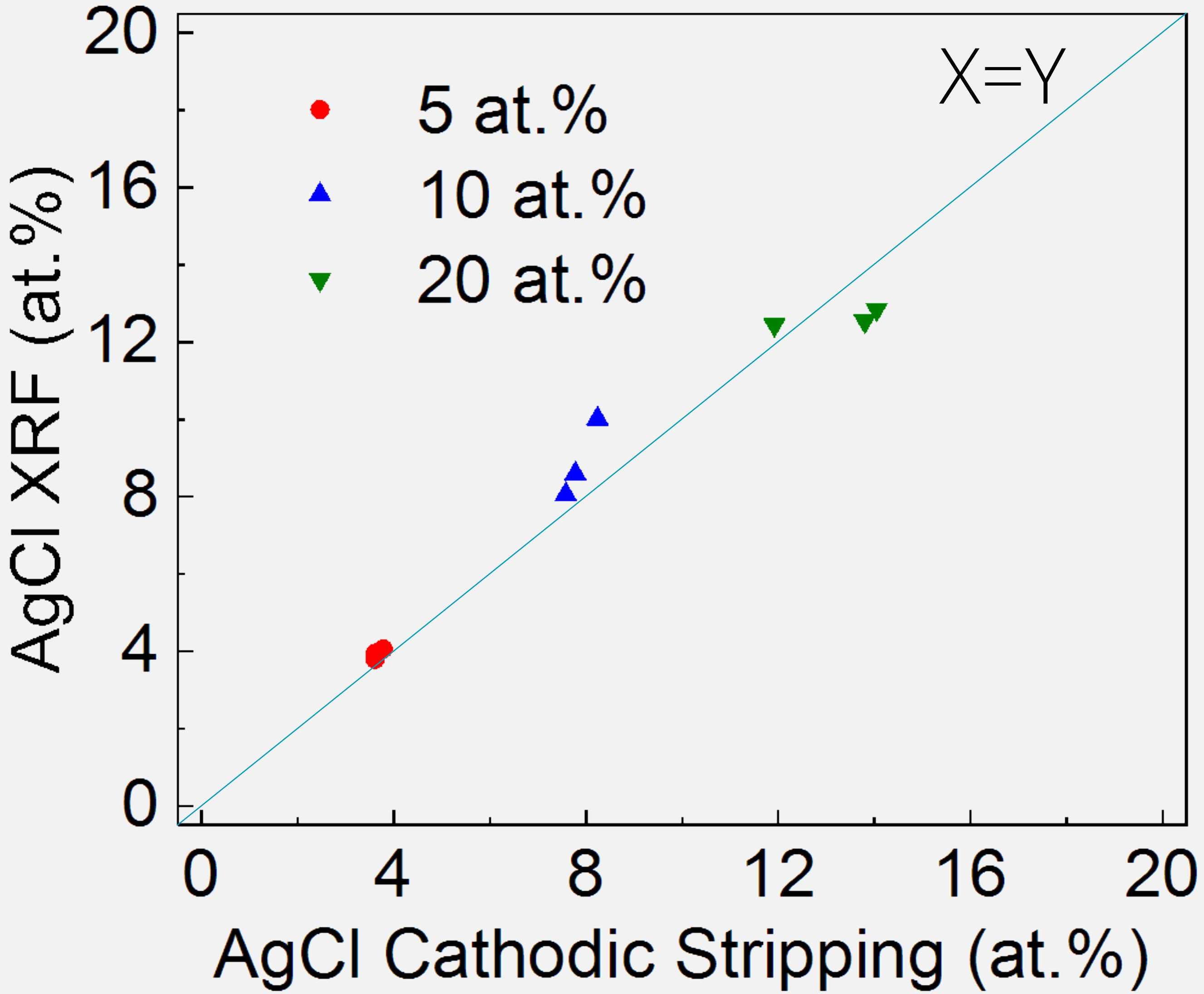
Error bars averaged from the sample.

XRF quantifies AgCl



Target 20 at.% ; Actual: 4.6 ± 1.6 at.%
Target 10 at.% ; Actual: 8.1 ± 2.7 at.%
Target 5 at.% ; Actual: 14.4 ± 4.3 at.%

Cathodic stripping and XRF measurement are in agreement of thickness for 5 &10 nm



Conclusion

A. Control <10 AgCl at.% in a Ag surface using pulsed electrodeposition

- Measure AgCl at.% using cathodic stripping (0.1at.% detection limit)
- Validate cathodic stripping measurements using XRF

B. Control uniformity of AgCl at.% in a Ag surface using masking

- Validate using SEM and AgCl XRF maps

Acknowledgement

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Thank you.

Questions?