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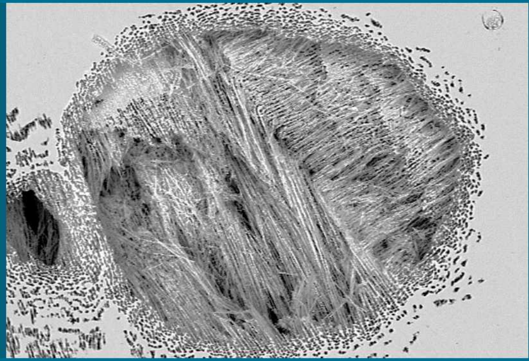
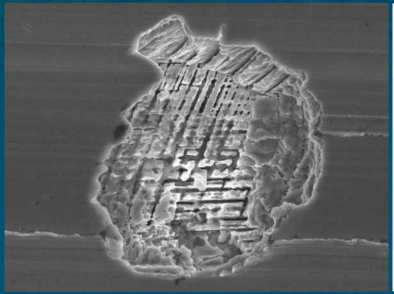
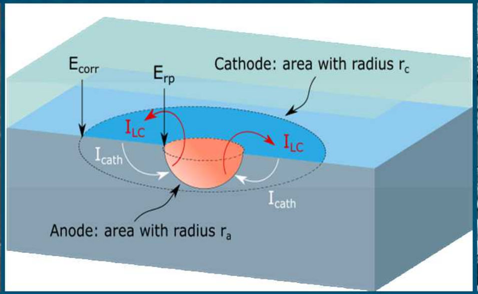
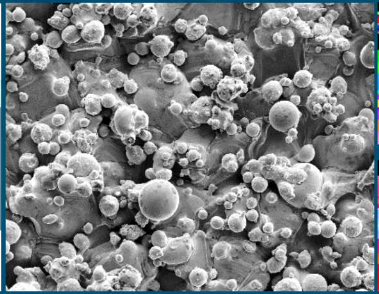
SAND2020-9841C

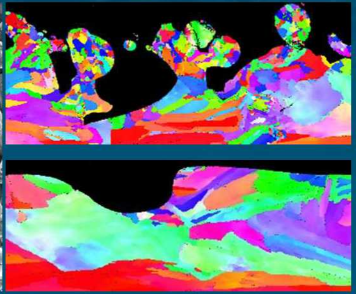
Corrosion kinetics and pit morphology of pure aluminum during atmospheric corrosion by in-operando microtomography











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Co-authors: Philip Noell (SNL) and Eric Schindelholz (OSU)

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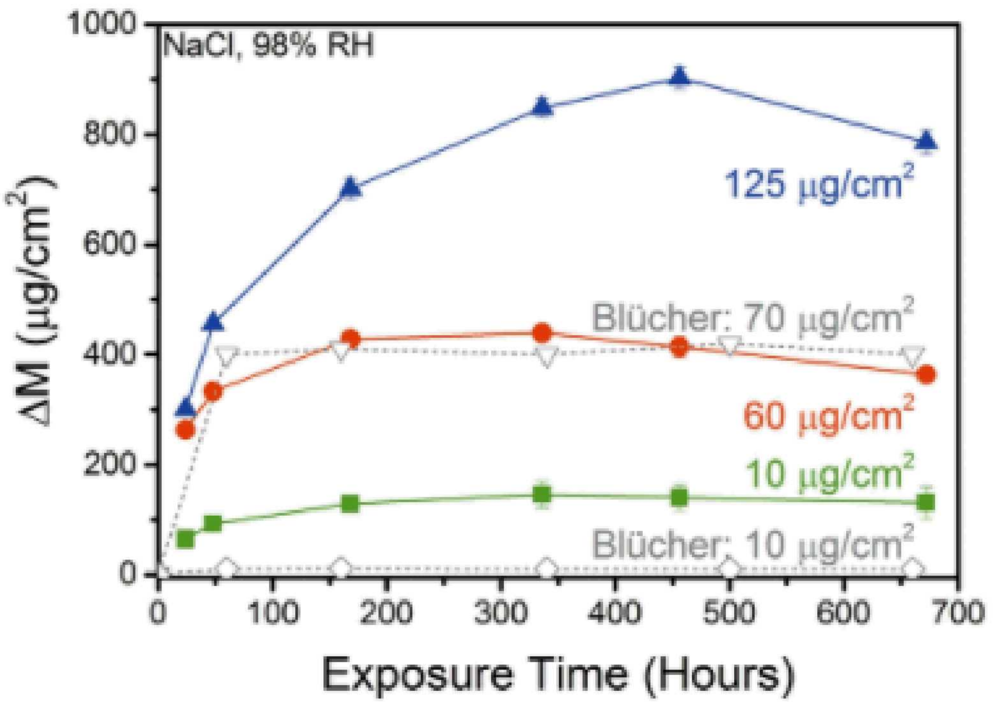
Motivating Questions

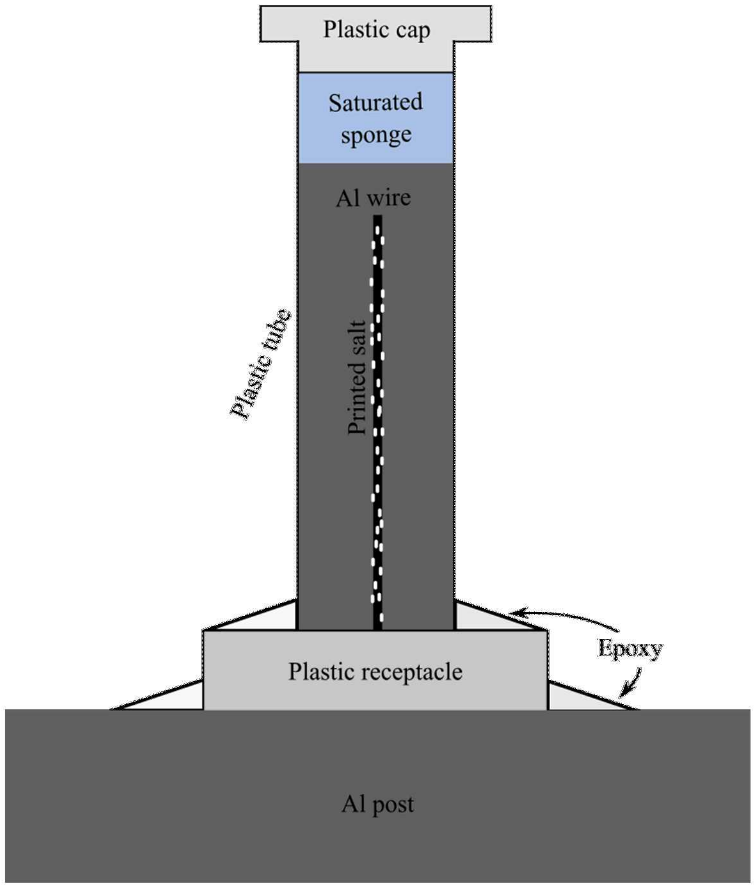
1. What are the growth kinetics of individual pits?
2. How does this compare to mass-loss studies of growth kinetics?
3. How does pit morphology evolve during growth?



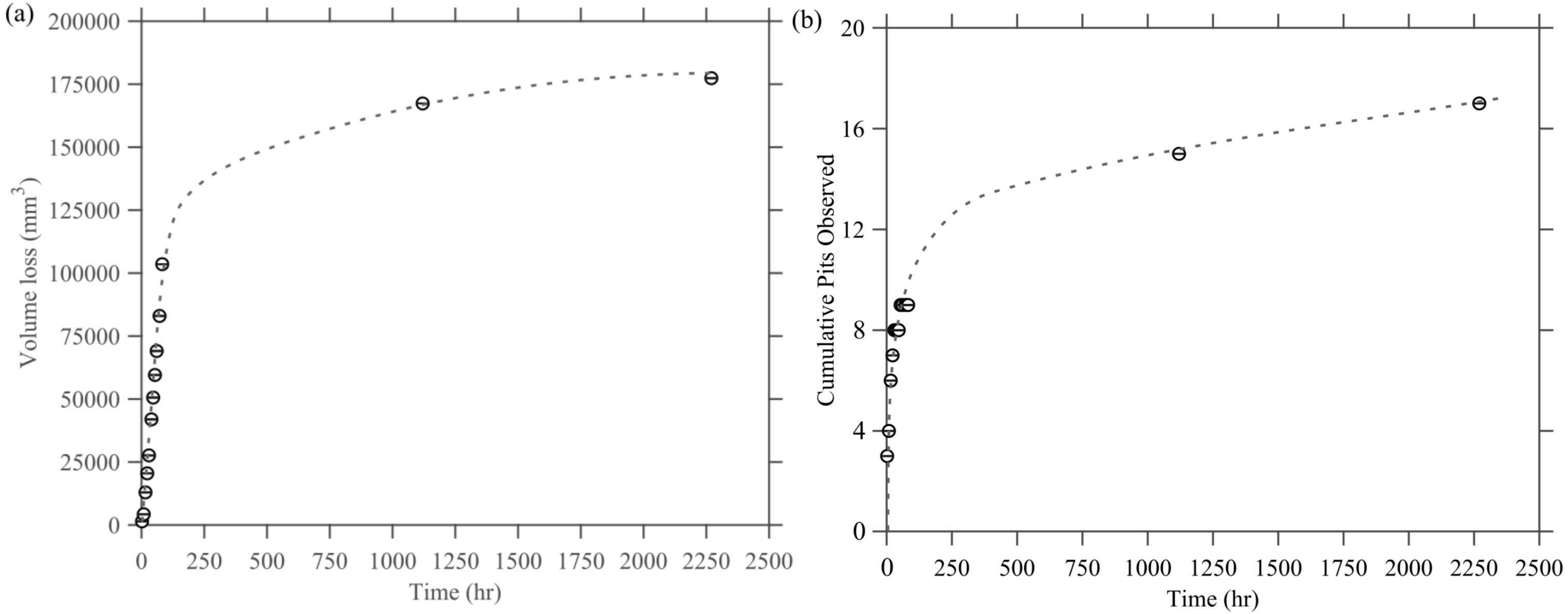
Schaller, Rebecca F., et al. "The controlling role of sodium and carbonate on the atmospheric corrosion rate of aluminum." npj Materials Degradation 1.1 (2017): 1-8.

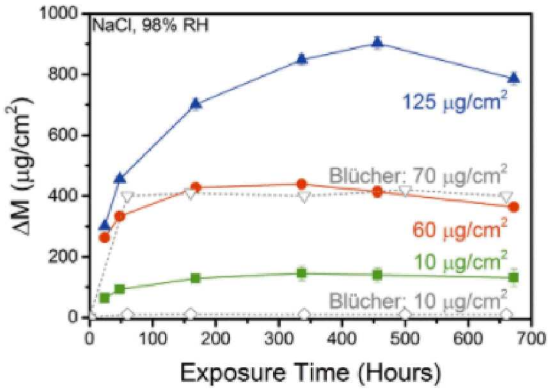
Methods

1. Material – 99.9% pure Al wire containing Fe-rich impurities.
2. Salt loading - Printed with NaCl at 60 $\mu g/cm^2$.
3. Humidity – 84% RH.
4. 15 x-ray computer tomography (XCT) datasets collected, 13 within first 88 hours of exposure. Final scan after 2270 hours of exposure.
5. Spatial resolution – 27 μm^3.
6. Time between scans was typically 7 hours, 3.5 hours in some cases.



Overall volume loss and nucleation rate





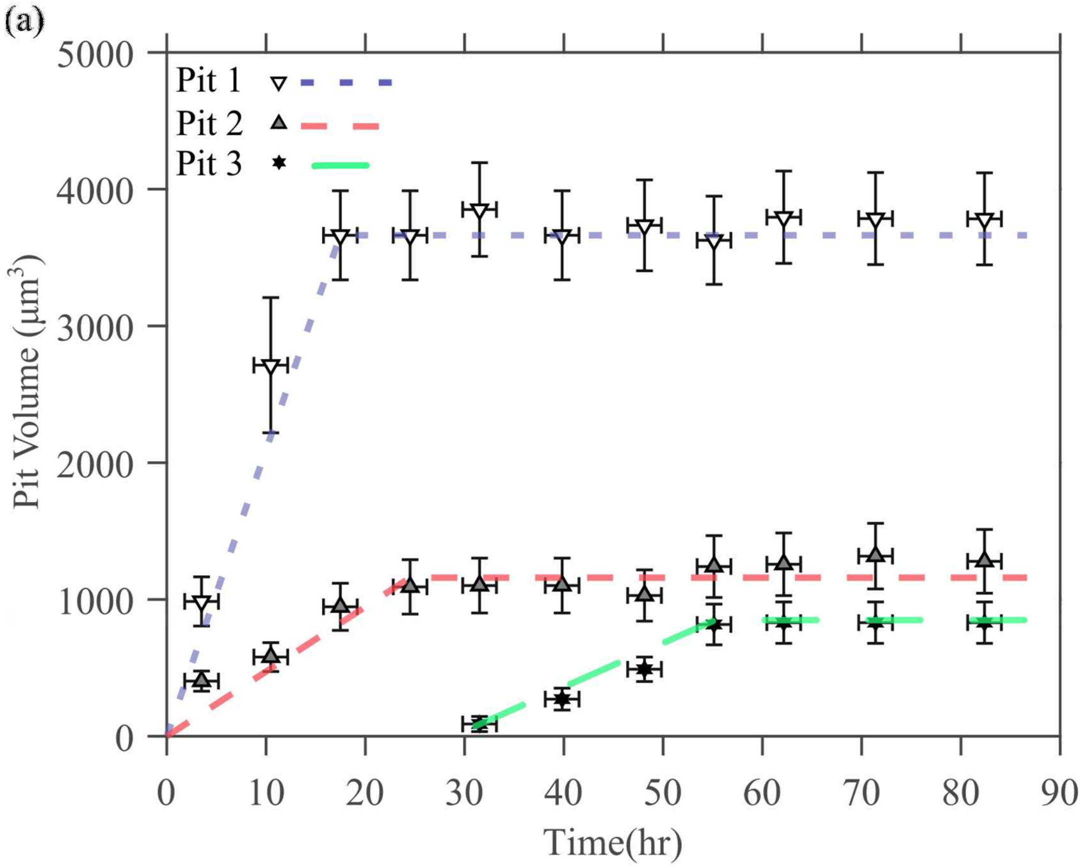
Schaller, Rebecca F., et al. (2017).

Total volume loss trend (left) similar to that observed by others.

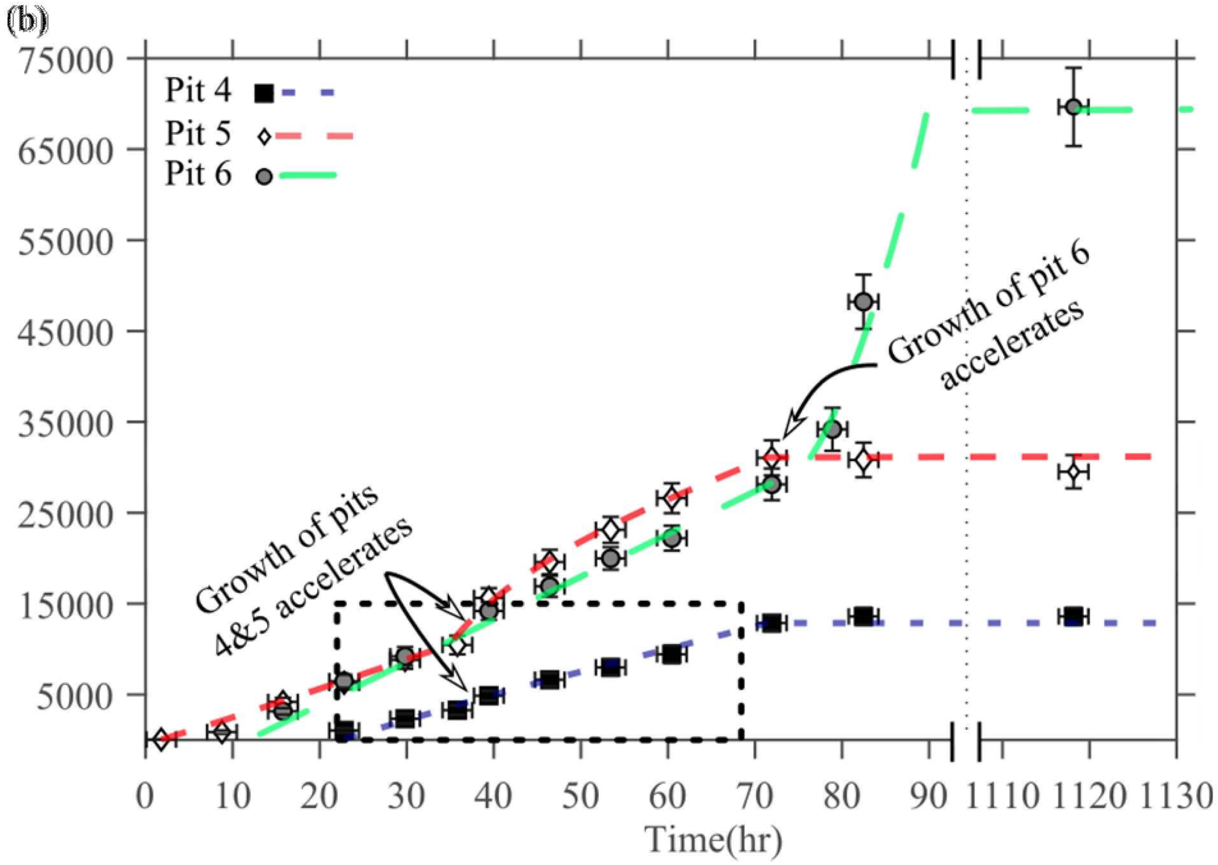
Nucleation rate (right) slowed over time.

Growth rates of individual pits

Small pits (< 5,000 μm³)



Large pits (> 5,000 μm³)

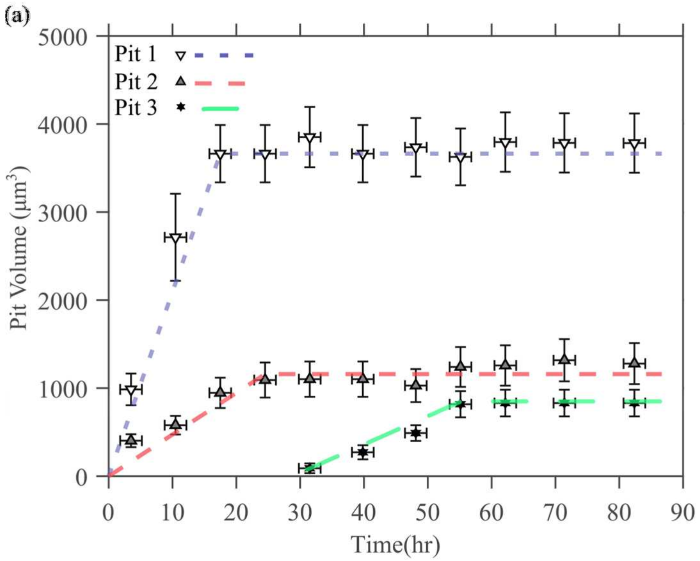


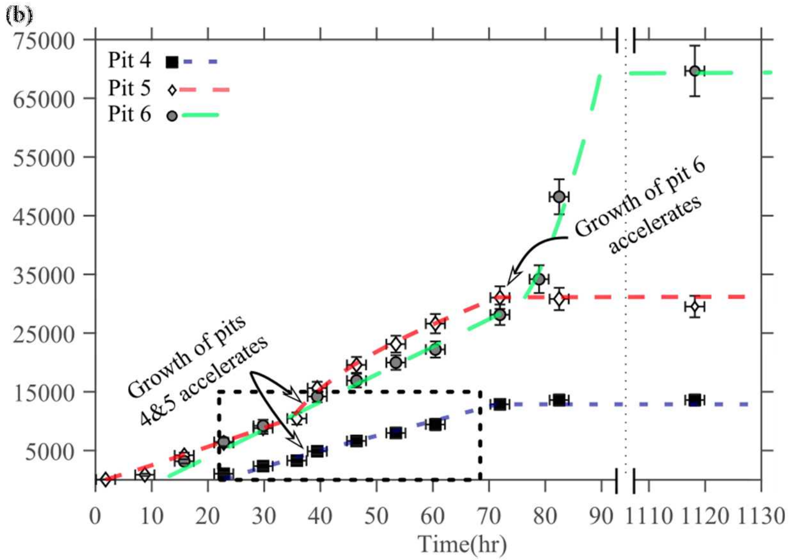
9 pits for which we have kinetic data (nucleated in first 88 hours), separated into two general categories:

- **Small pits:** six of the nine pits ceased observable growth less than 25 hours after nucleation and had final volumes less than 4000 μm³ and
- **Large pits:** three of the nine pits grew for 46 or more hours and reached final volumes greater than 13,000 μm³.

Growth rates of individual pits

Small pits





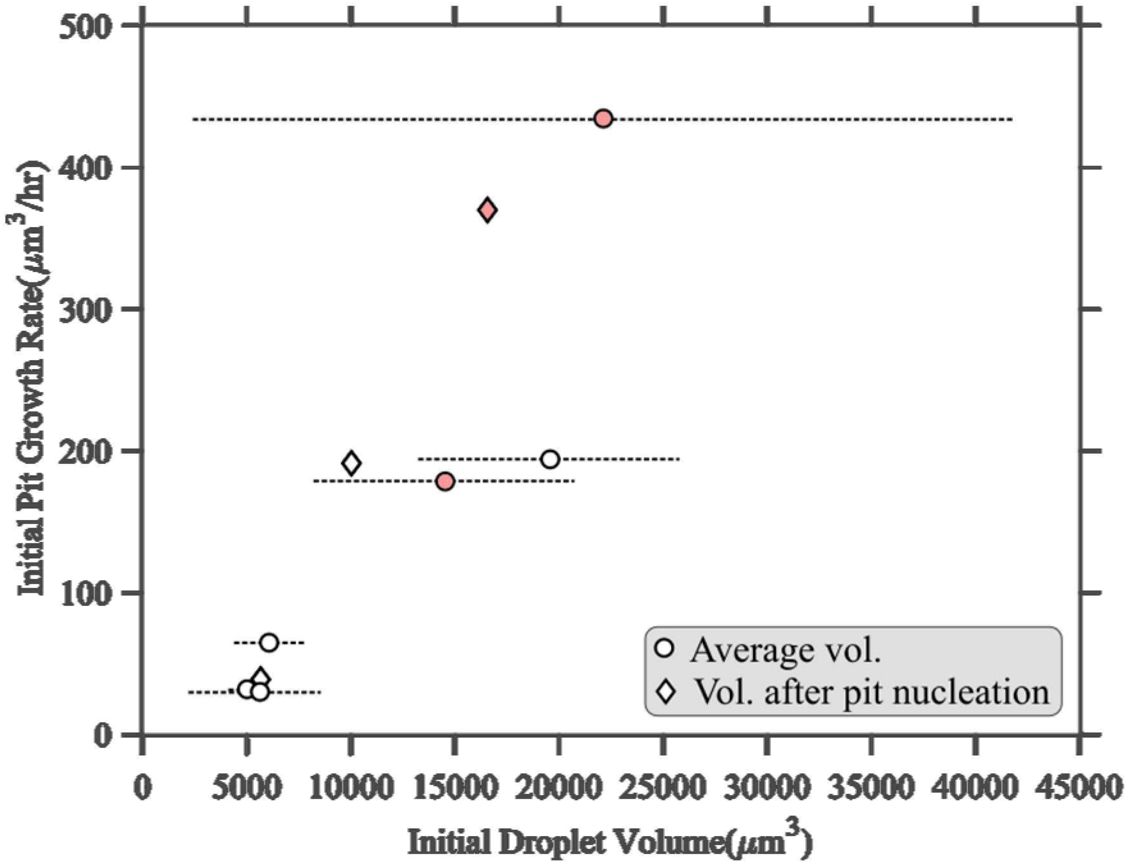
Large pits

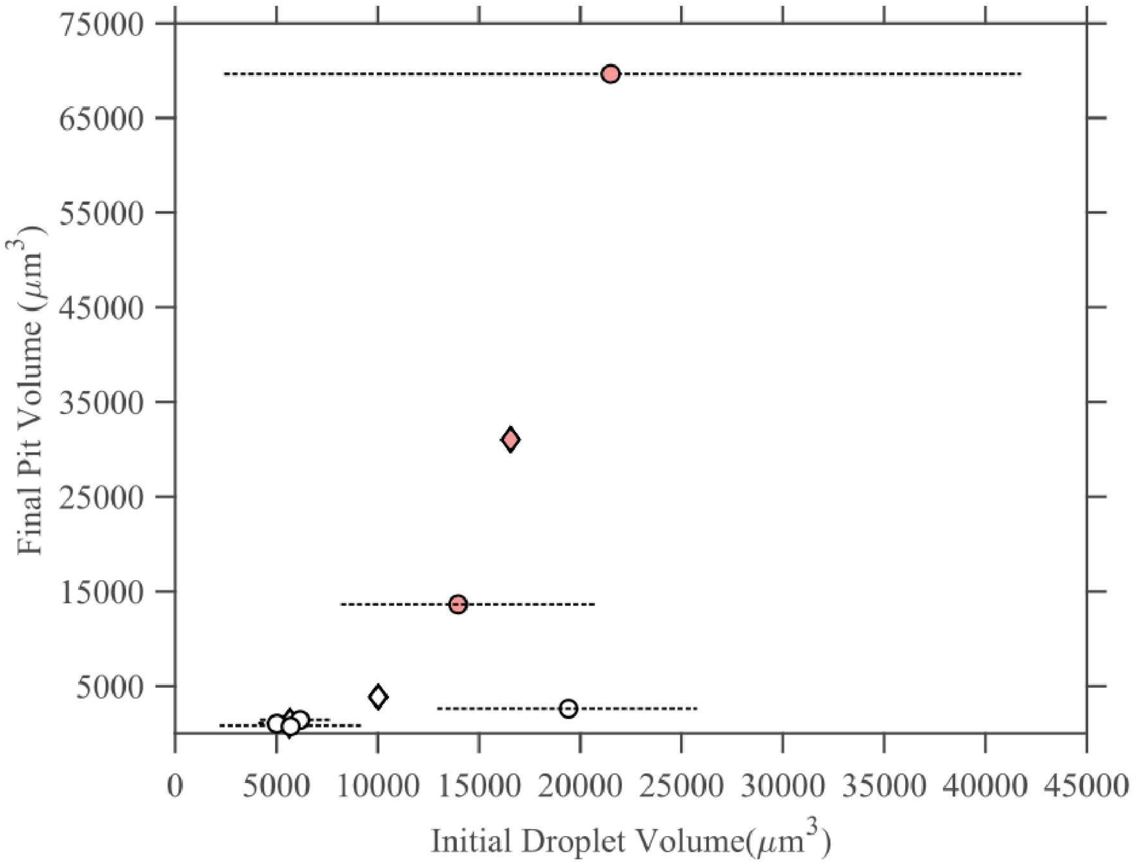
	Pit 1	Pit 2	Pit 3	Pit 4	Pit 5	Pit 6	Pit 7	Pit 8	Pit 9
Final volume (μm^3)	3800	1300	800	13600	30900	69700	800	1440	2800
Initial Growth Rate (μm^3/hr)	194	39	30	172	370	439	32	65	194
Secondary Growth Rate (μm^3/hr)	-	-	-	240	475	3930		-	-
Time Growing (hr)	12	19	24	46	72	>65	14	14	15
Maximum Depth (µm)	26	13	12	30	22	44	14	16	22

9 pits for which we have kinetic data (nucleated in first 88 hours), separated into two general categories:

- **Small pits:** six of the nine pits ceased observable growth less than 25 hours after nucleation and had final volumes less than 4000 μm^3 and
- **Large pits:** three of the nine pits grew for 46 or more hours and reached final volumes greater than 13,000 μm^3.

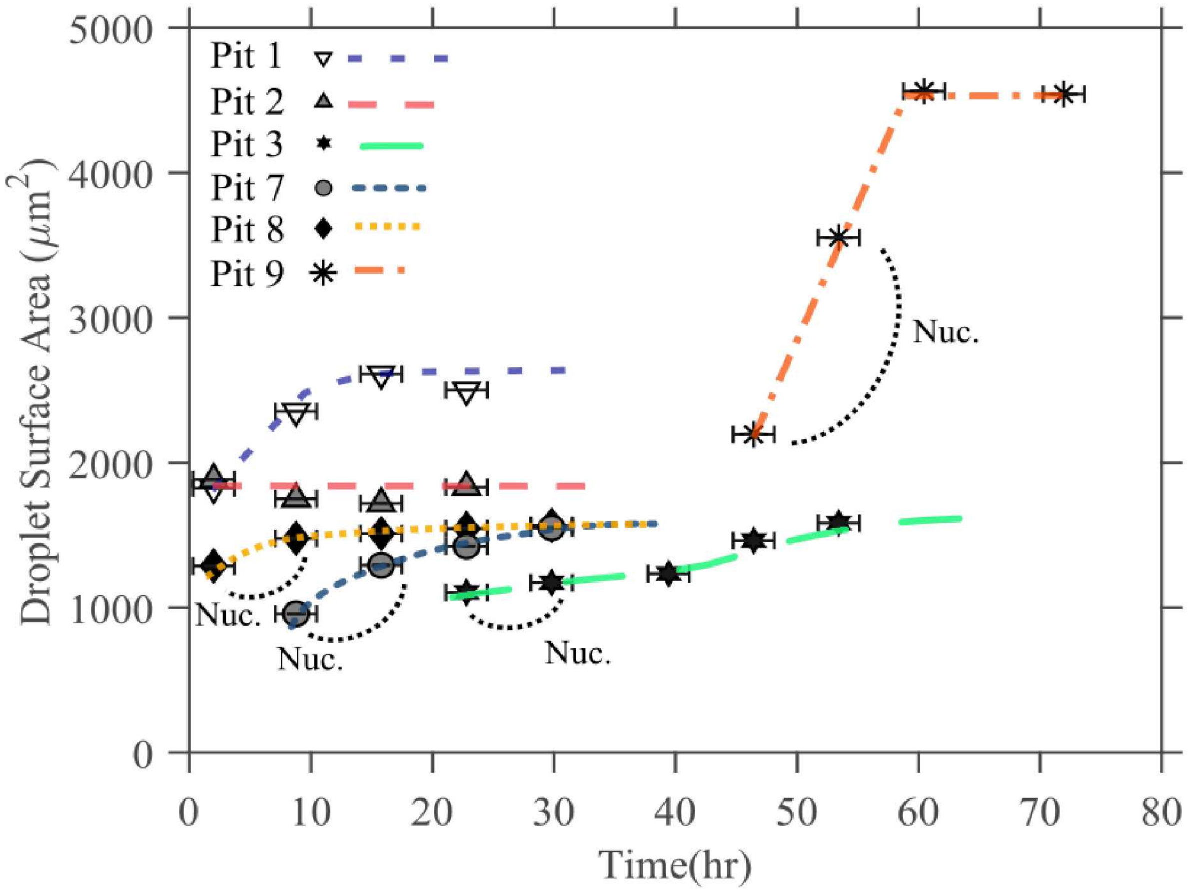
Why do some pits grow faster (initially) and end up being bigger than others?





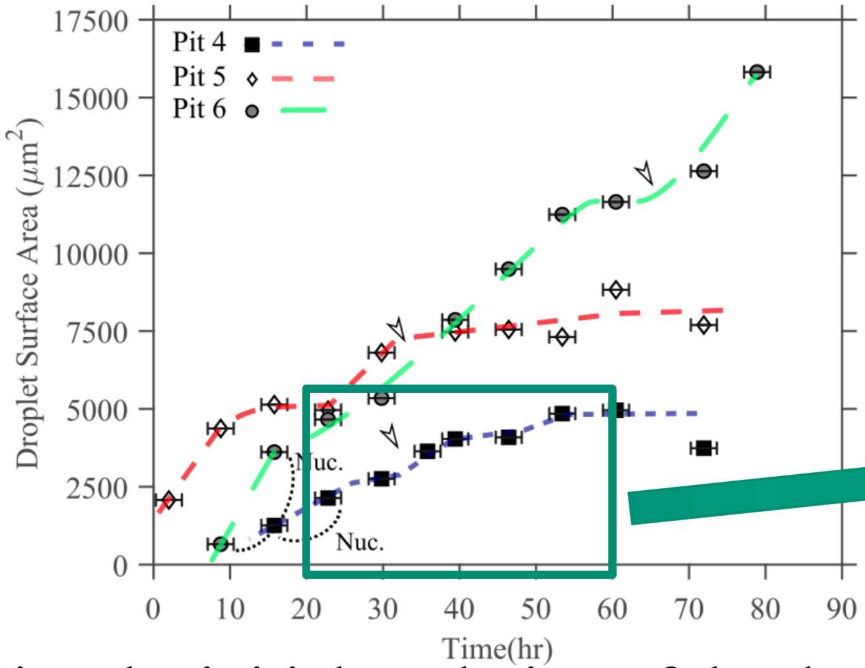
Is it all about cathode size? Initial droplet size?

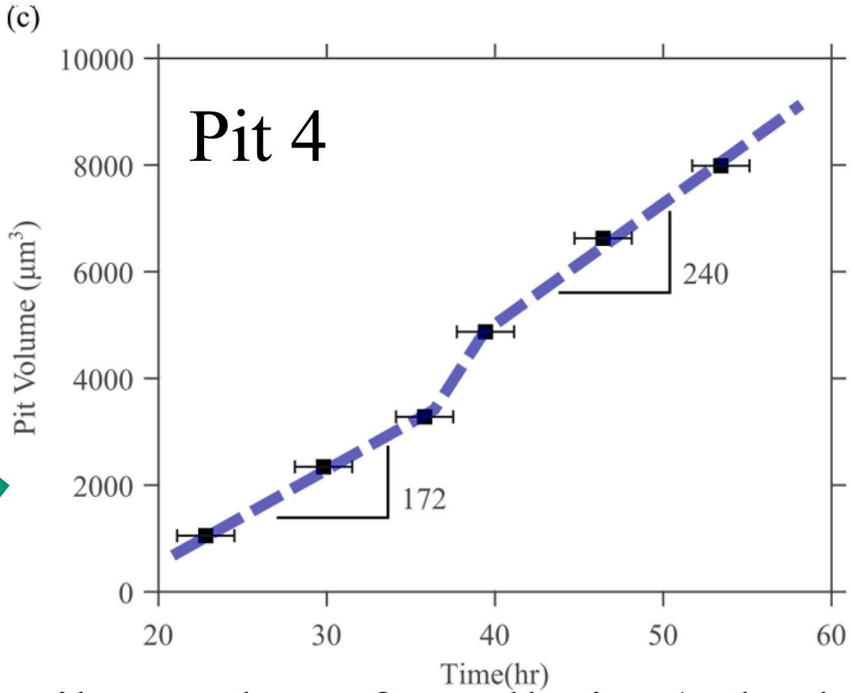
Why do some pits keep growing for a (relatively) long time and have a jump in growth rate? – **Small pits**



For small pits, droplet surface area typically increases slightly initially. This is likely because XCT data doesn't allow corrosion product and droplet to be clearly distinguished. Expansion of surface area is hypothesized to primarily be due to more corrosion product.

Why do some pits keep growing for a (relatively) long time and have a jump in growth rate?





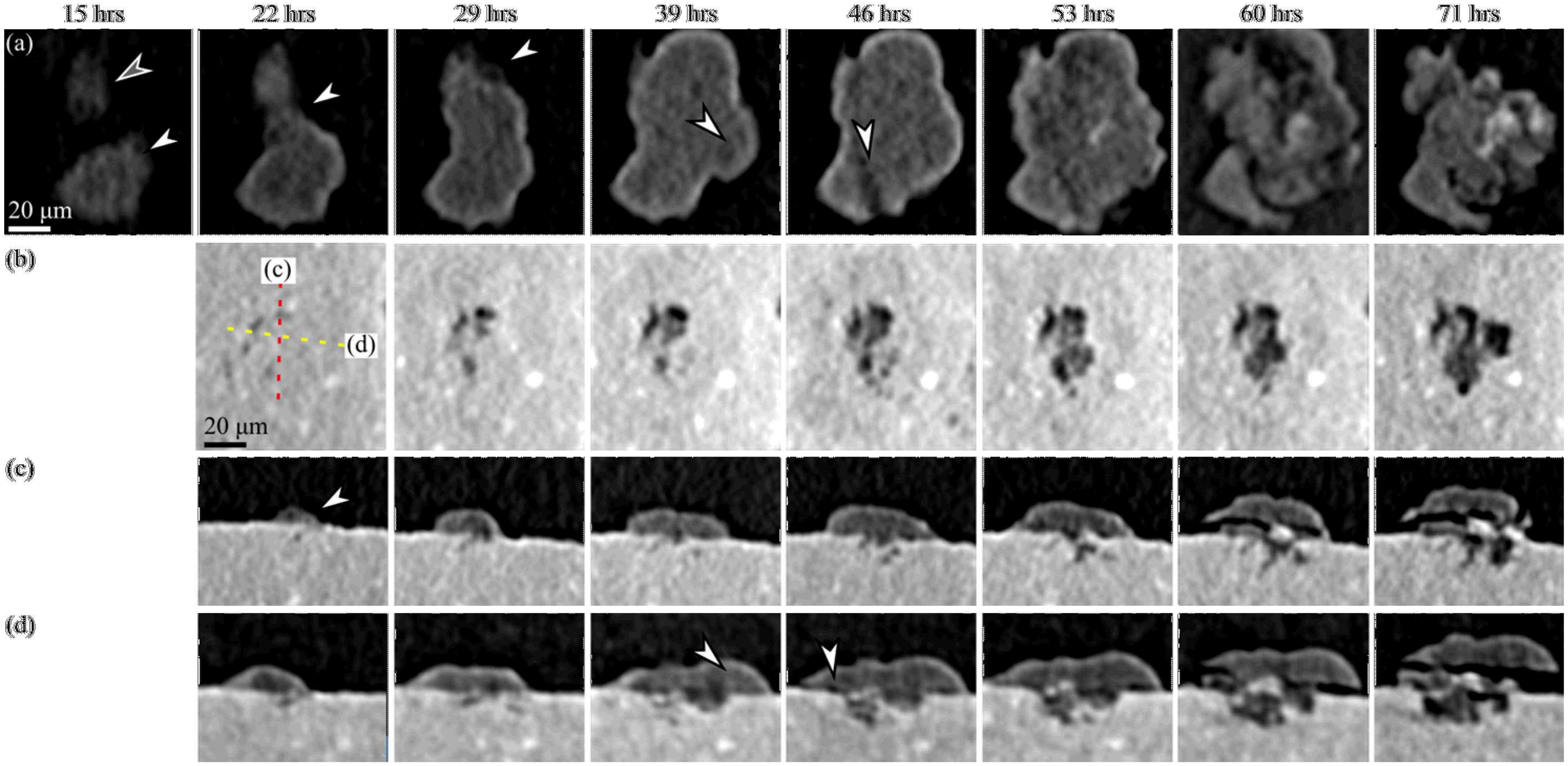
For big pits, the initial evolution of the droplet is similar to that of small pits (~doubles in size) - The one exception is pit 6.

Big jump in droplet coverage area happens at about the same time a jump in pit volume happens. **Why?**

1. Faster corrosion = more corrosion product in droplet = XCT measures a larger "droplet".

2. Droplet surface area gets bigger, then corrosion speeds up.

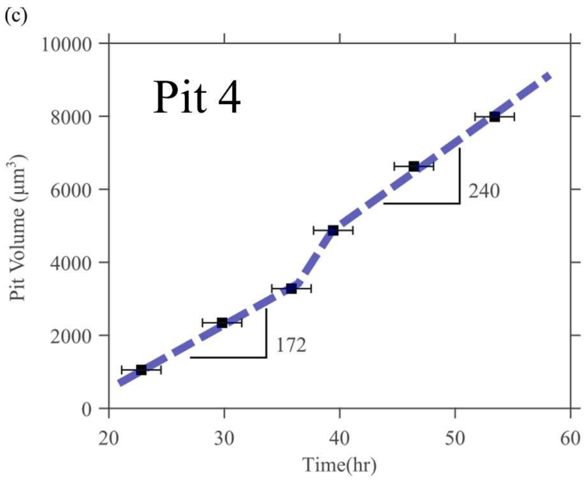
XCT let's us answer that question



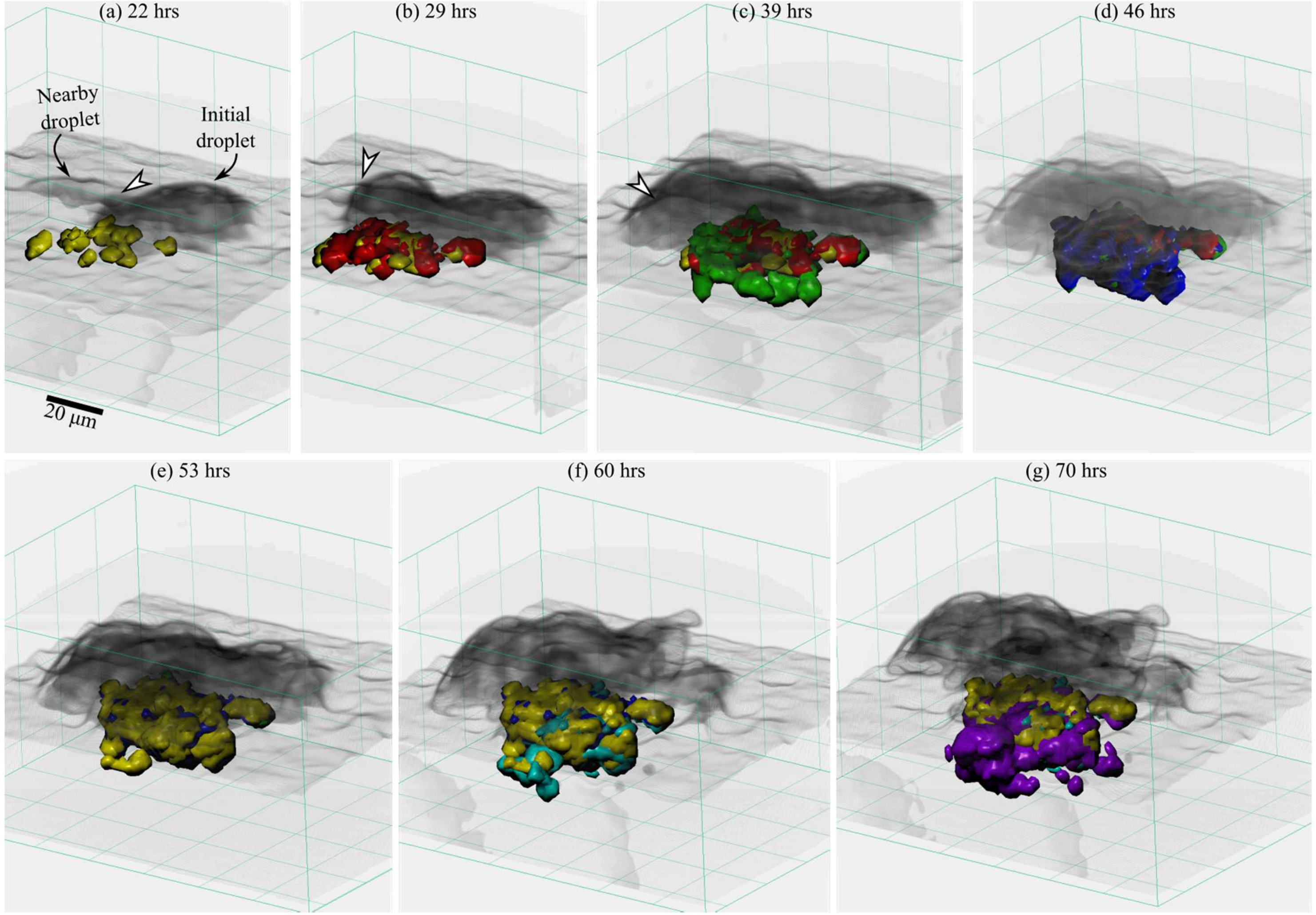
Shows solution spreading ~30-40 hours.

2D renderings of Pit 4 **(typical of large pits)** shows that jump in growth rate is preceded by droplet spreading.

Bigger droplet = larger cathode **(pit grows faster)** and impedes droplet drying **(pit grows longer).**

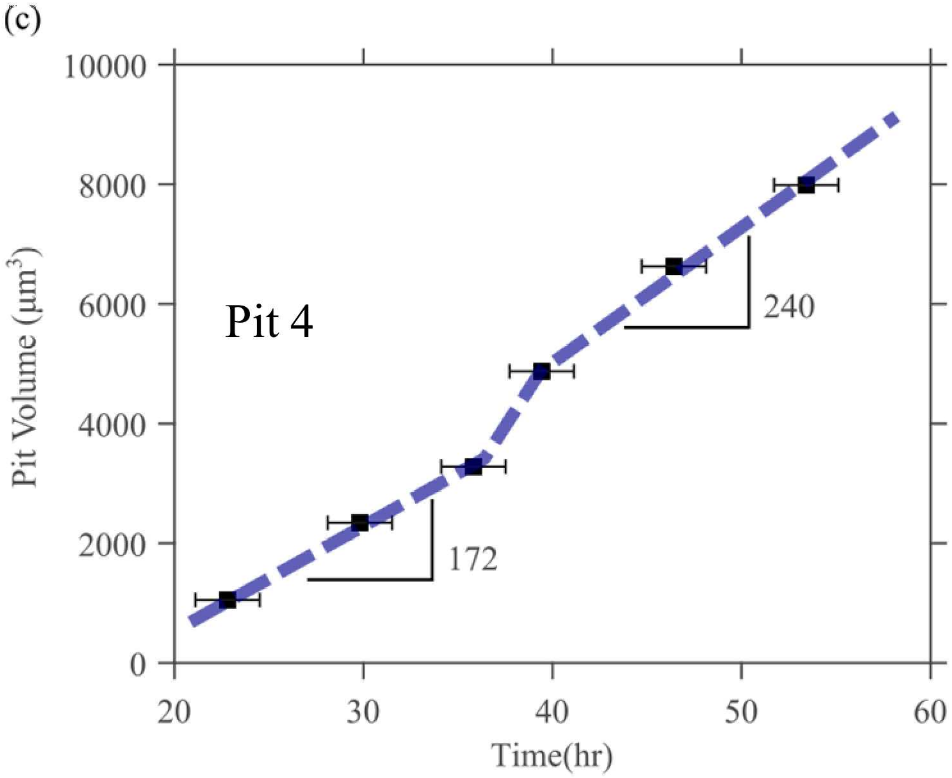


XCT let's us answer that question

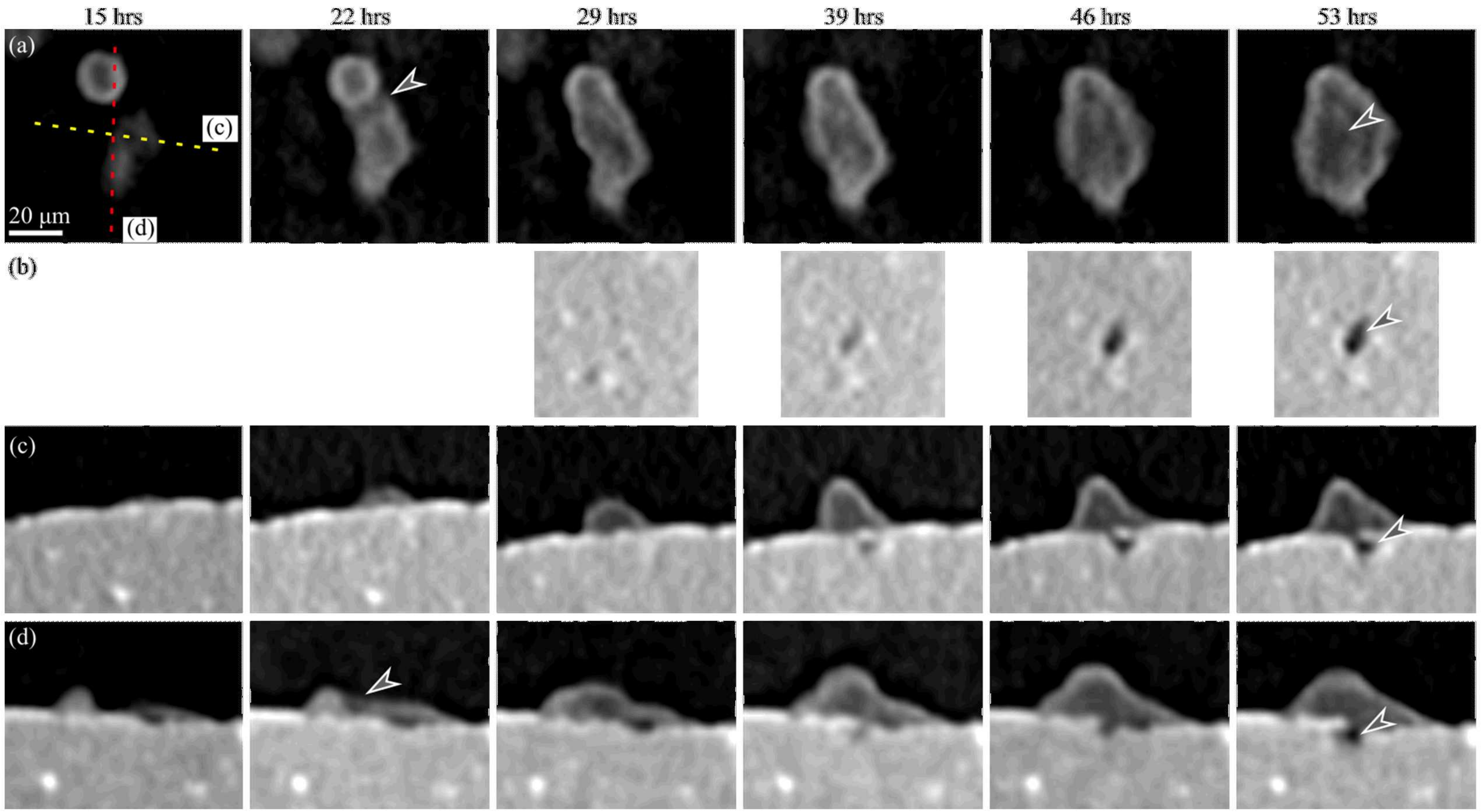


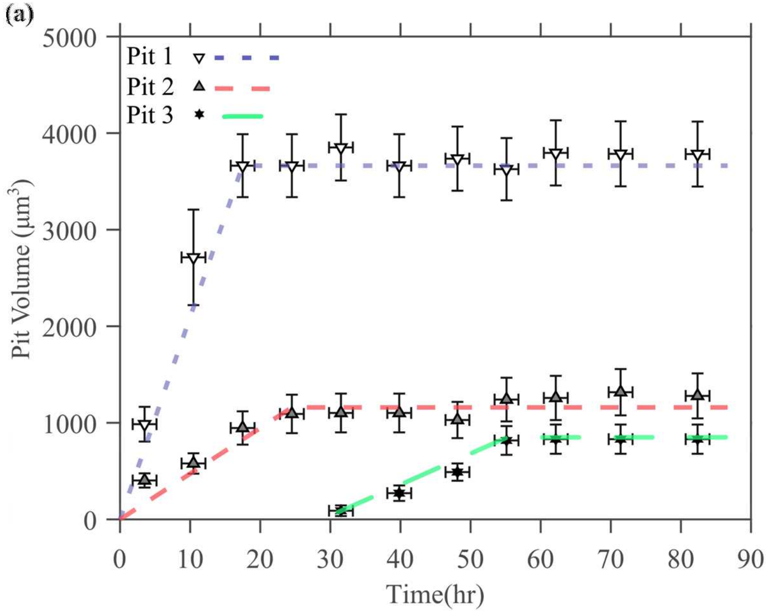
3D renderings of Pit 4 **(typical of large pits)** shows that jump in growth rate is preceded by droplet spreading

Bigger droplet = larger cathode **(pit grows faster)** and impedes droplet drying **(pit grows longer)**



Small pits don't have droplet spreading



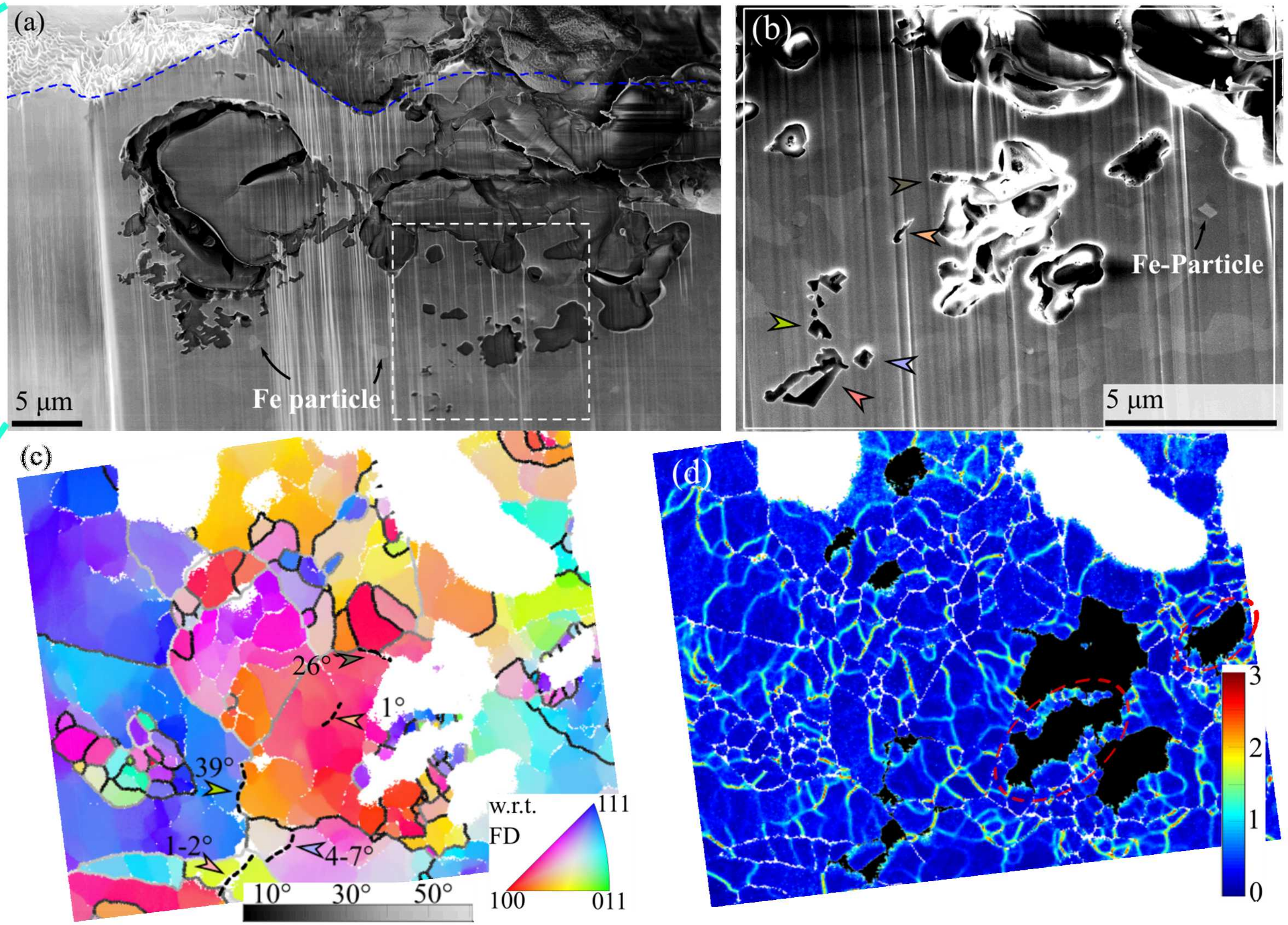


Typical small pit (pit 3) doesn't exhibit droplet spreading

There's more… pit morphology

Pit 4 – XCT 2D rendering

Plasma FIB and EBSD of specific pits (Pit 6 in this case)



How does the pit interact with:

- **Secondary phase particles**
- **Grain boundaries**
- **Dislocations network?**

Conclusions and Questions

Mass-loss trends seem to be related to nucleation rate slowing over time rather than growth rate changing of the individual pits.

Suggests that, for constant salt loading, short (months) studies of mass loss are indicative of long-term behavior.

Questions this study (at least somewhat) answers:

- Why do some pits grow significantly larger and for significantly longer times than others? – droplet spreading
- What accounts for jump in growth rate? – droplet spreading

Remaining questions

- How does the growth rate remain constant for 10s of hours despite evolving conditions?
- What is the relationship between initial droplet size and pit growth rate? Is it linear?
- Why do some droplets spread and not others?

Acknowledgements

Laboratory Directed Research and Development (LDRD) Programs funded this work.

Many people to thank…

Luis Jauregui, Daniel Perry, Joe Michael, and James Griego.

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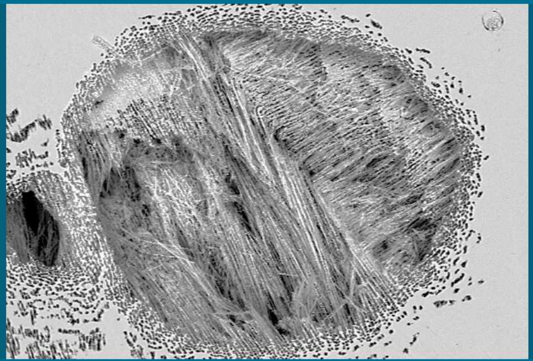

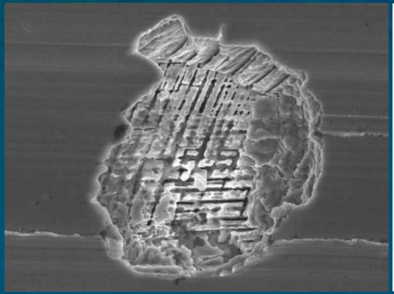

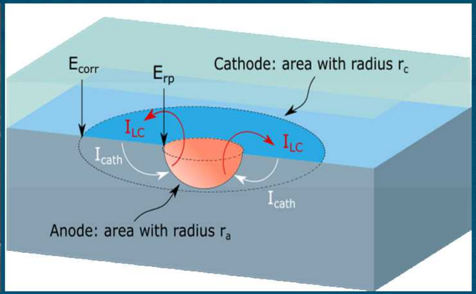

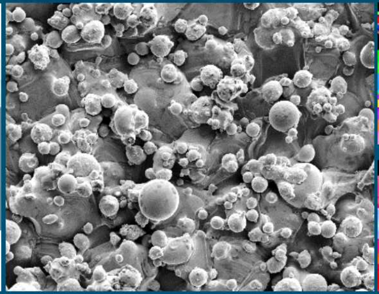

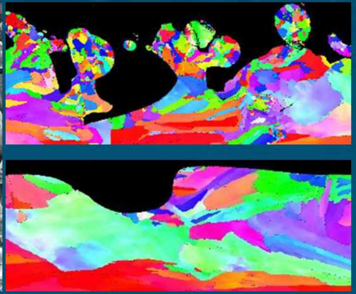

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