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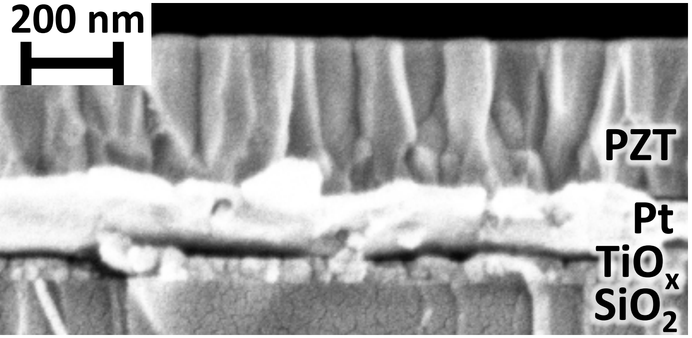

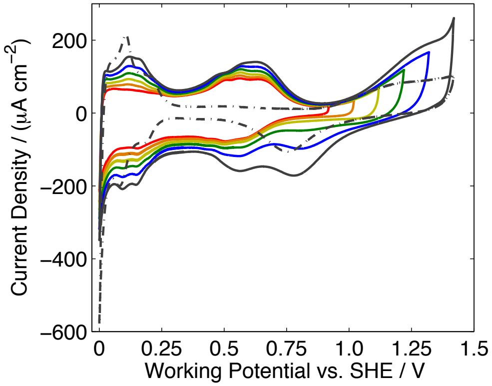

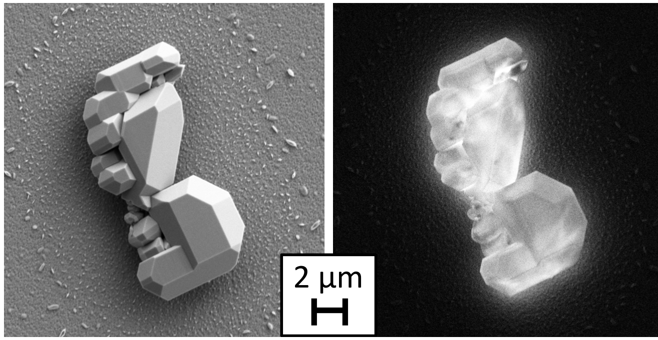

Degradation of Thin Film $Pb(Zr,Ti)O_3$ in H_2SO_4

Leo Small[1], Chris Apblett[1], Geoff Brennecka[1], Jon Ihlefeld[1], David Duquette[2]

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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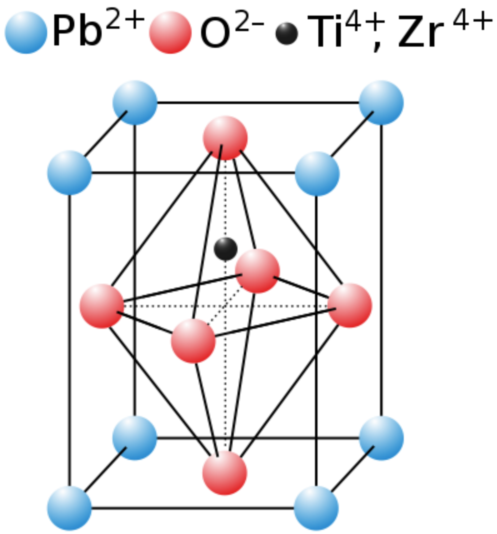
PZT in H_2SO_4: Motivation

- **Remote, self-powered sensors for extreme environments**
- Chemical processing plants, down-hole oil wells
- High pressure, high temperature, low pH: no wires!

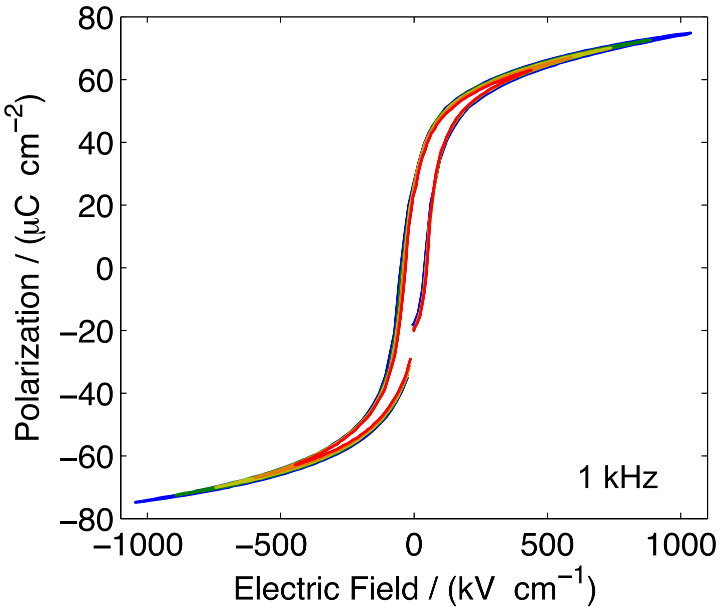
How does PZT interact with acidic, aqueous environments?

$PbZr_{0.52}Ti_{0.48}O_3$

- Ferroelectrics possess a reversible, thermodynamically stable surface charge.

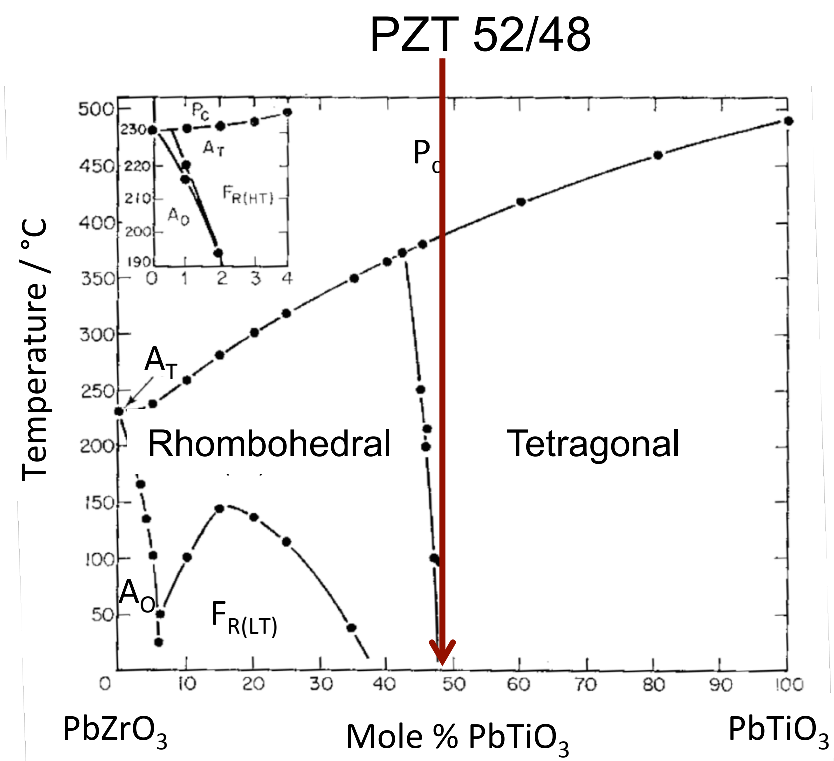


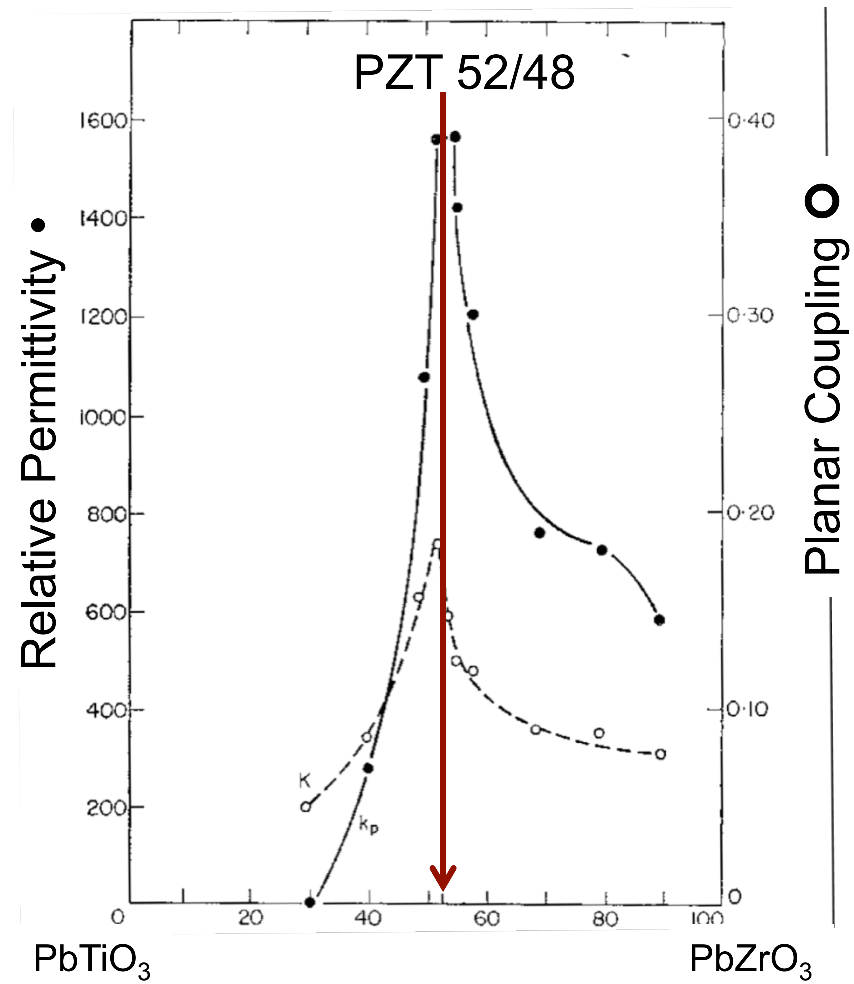
PZT perovskite crystal structure.



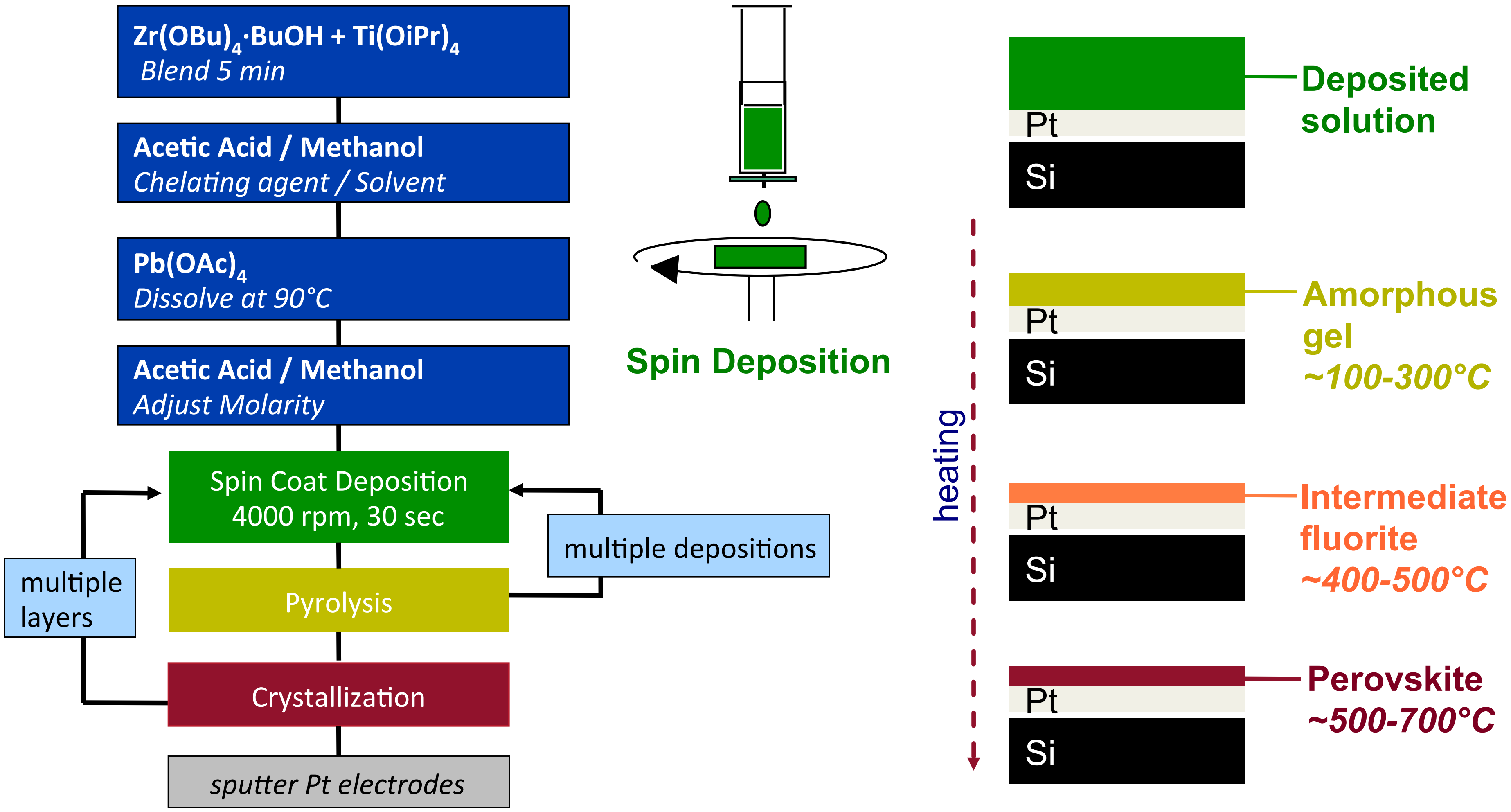
Why $PbZr_{0.52}Ti_{0.48}O_3$?

- Morphotropic phase boundary
- Increased piezoelectric performance





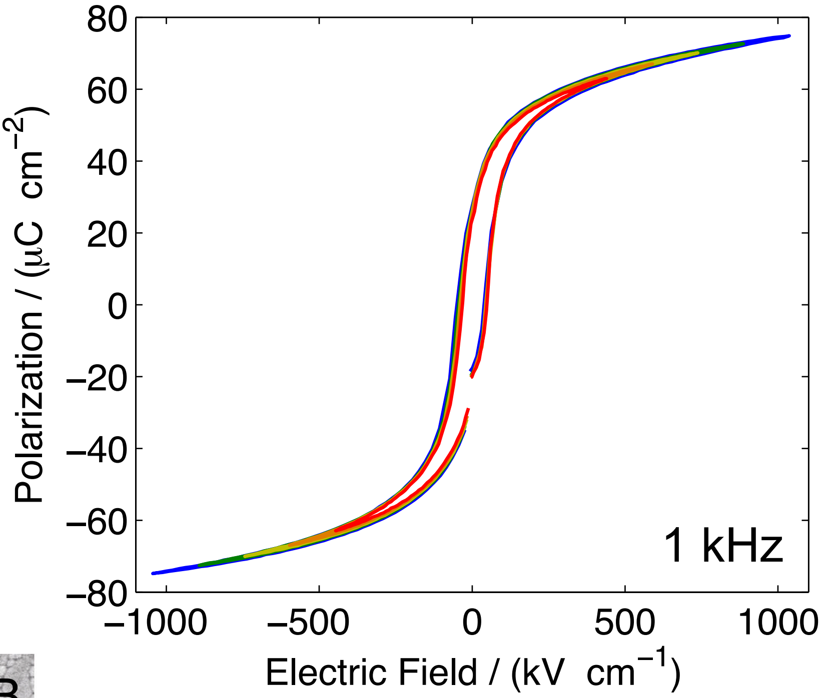
SNL Chemical Solution Deposition

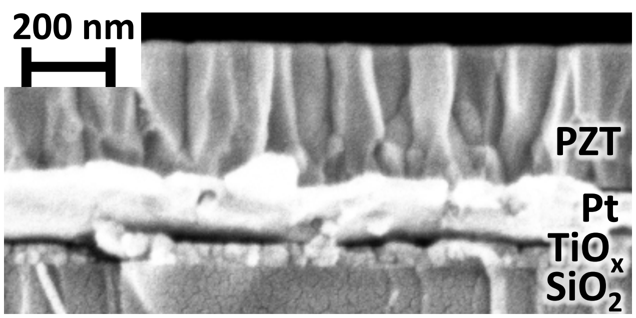


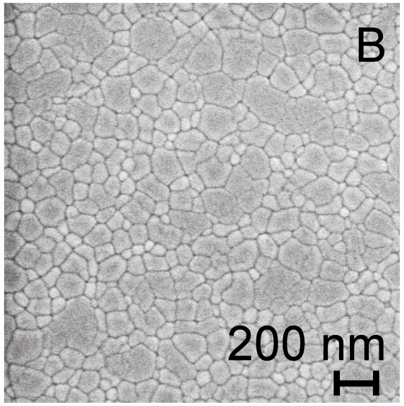
1. G. Brennecka, C. Parish, B. Tuttle and L. Brewer, **J. Mater. Res.**, **23**, 176-81 (2008)
2. B.A. Tuttle and R.W. Schwartz; ***MRS Bulletin*** (1996)

Sol-Gel PZT

- Dense columnar microstructure
- Random orientation
- Zero bias relative permittivity ~1200
- Resistivity: 10^{13} Ω•cm at 1.5 V
- Remanent polarization: 32 μC/cm^2







(A) Cross sectional and
(B) Plan-view SEM images

Microdroplet Cell

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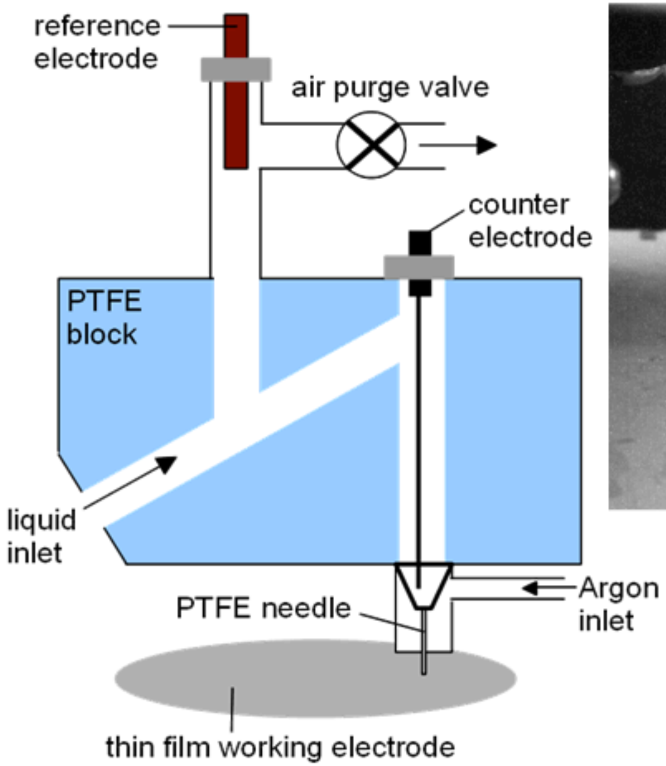
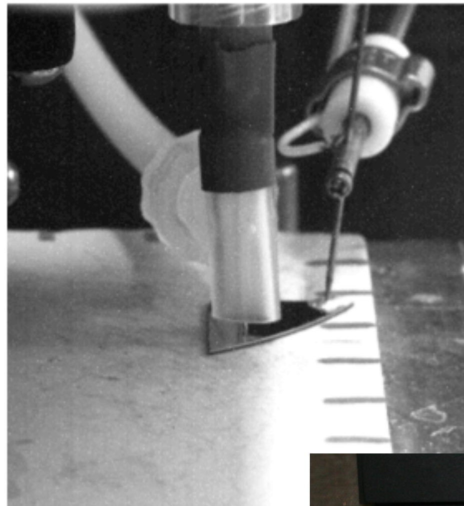
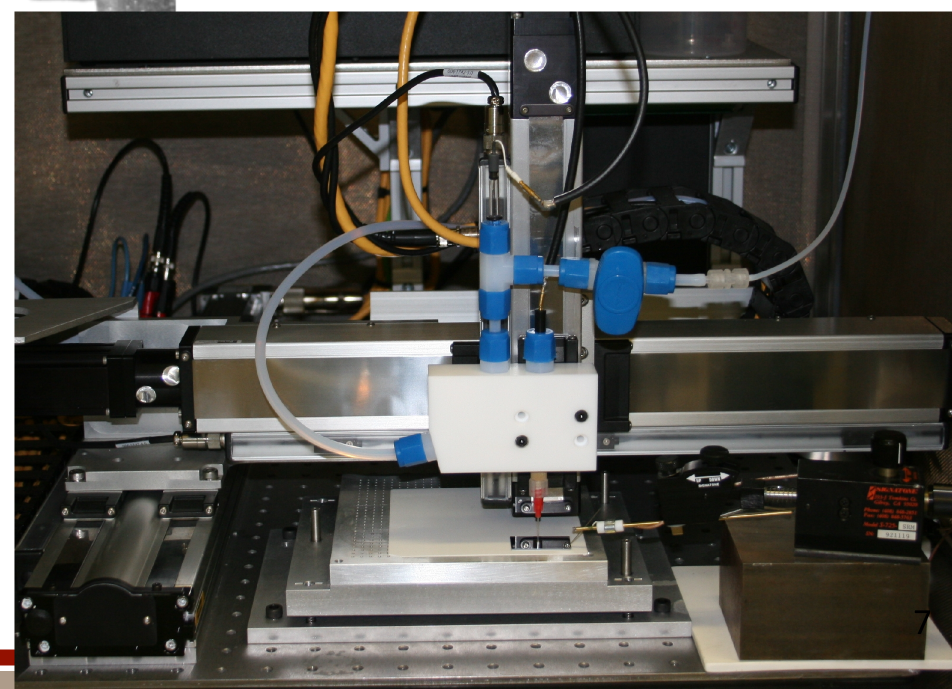


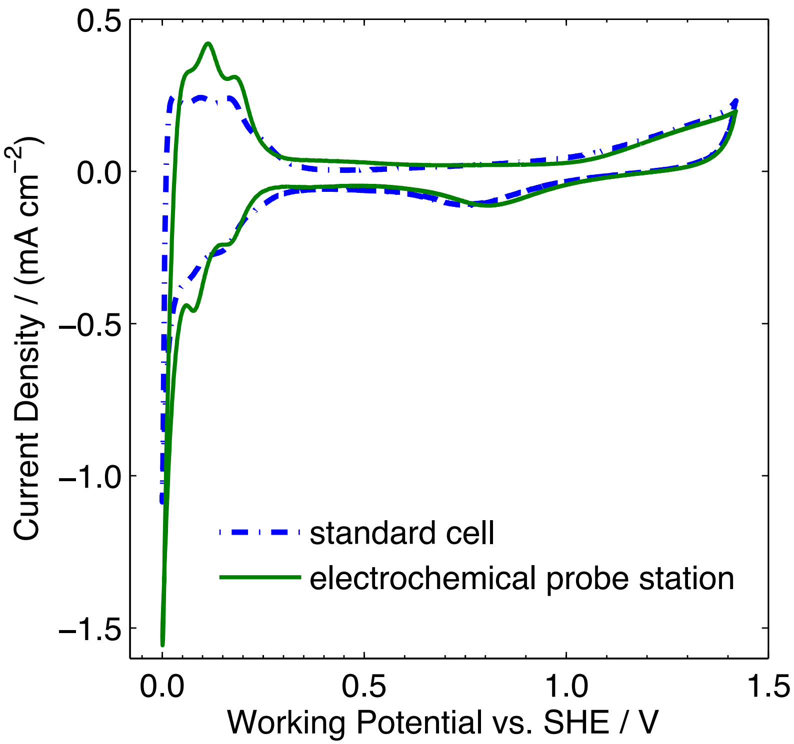


- LabView-controlled
- Automated droplet positioning, dispensing, testing
- Stage with programmable temperature control
- PTFE needle

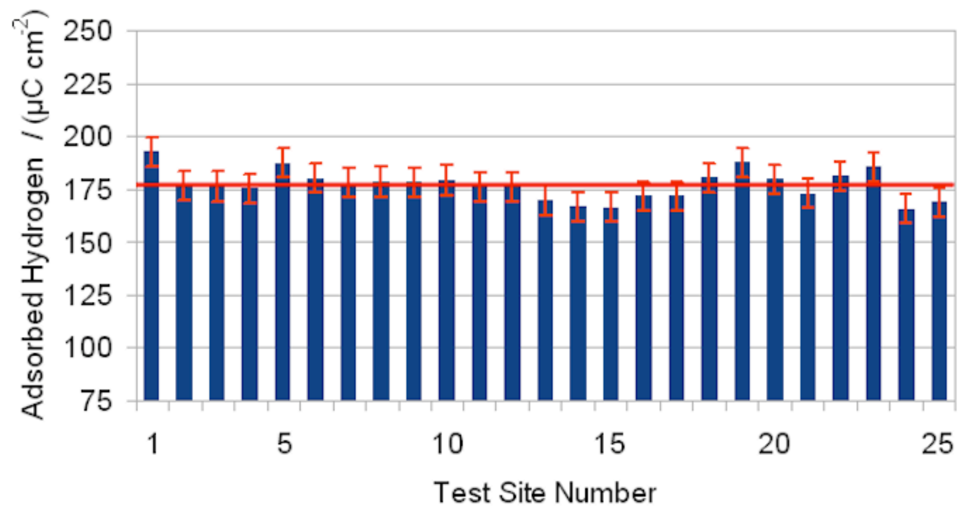


L. Small, C. Apblett, A. Cook, J.F. Ihlefeld, G. Brennecka, and D. Duquette, *J. Electrochem. Soc.*, **159** (2012) F87-F90.

Measurement Automation



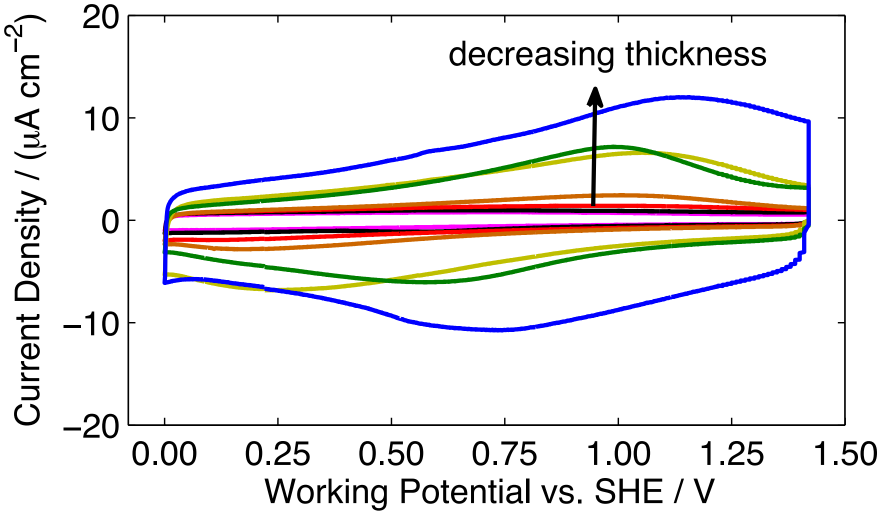
Platinum in 1 N H_2SO_4, 100 mV/s



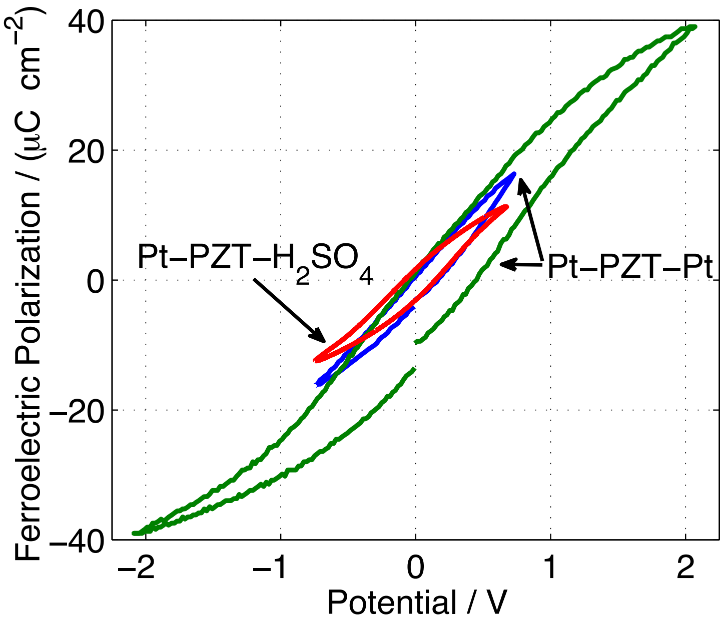
4.0% variability of hydrogen adsorbed onto thin film Pt in 1 N H_2SO_4. 0.25 mm^2 contact area.

L. Small, A. Cook, C. Apblett, J.F. Ihlefeld, G. Brennecka, and D. Duquette, *J. Electrochem. Soc.*, **159** (2012) F87-F90.

Continuous PZT: Ferroelectric Hysteresis



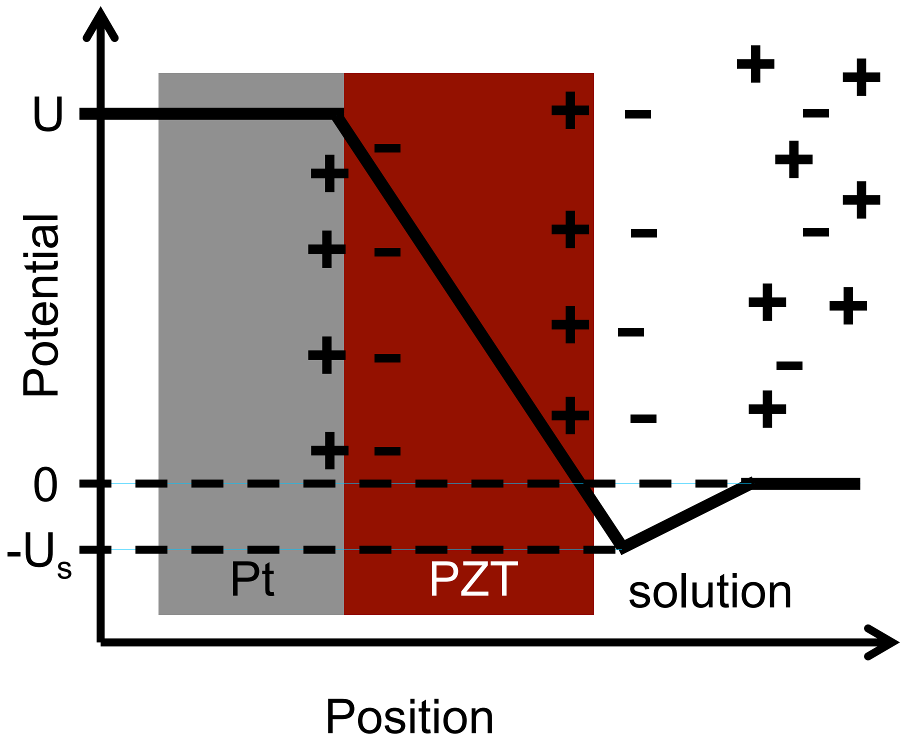
360, 300, 270, 200, 160, 100, 50 nm
PZT in 1 N H_2SO_4
100 mV/s



50 nm PZT, 3 Hz, 1 N H_2SO_4

Continuous PZT – Solution Interface

PZT controls the interface!



Ferroelectric surface charge, σ, creates potential difference across PZT-solution interface.

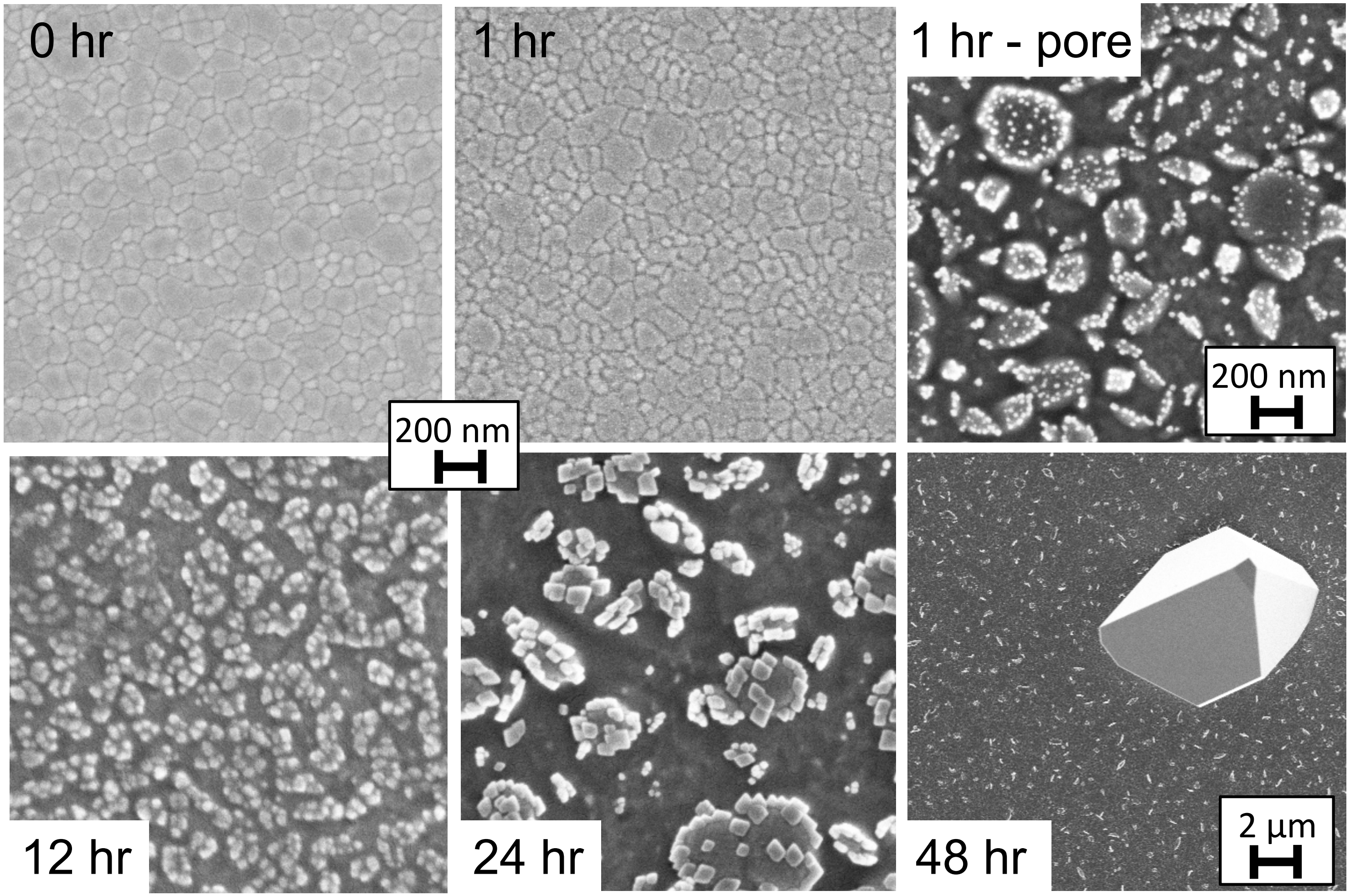
$$U_s = \frac{\sigma \varepsilon_{PZT} d}{2\varepsilon_0 \varepsilon_{H_2O}(1+\varepsilon_{PZT})}$$

U_s~55 mV for 20 μC/cm^2

ε_{H2O}= 80
d = 0.4 nm

Derived from S. Kalinin and D. Bonnell, Phys. Rev. B, **63** (2001) 125411.

Microstructural Evolution

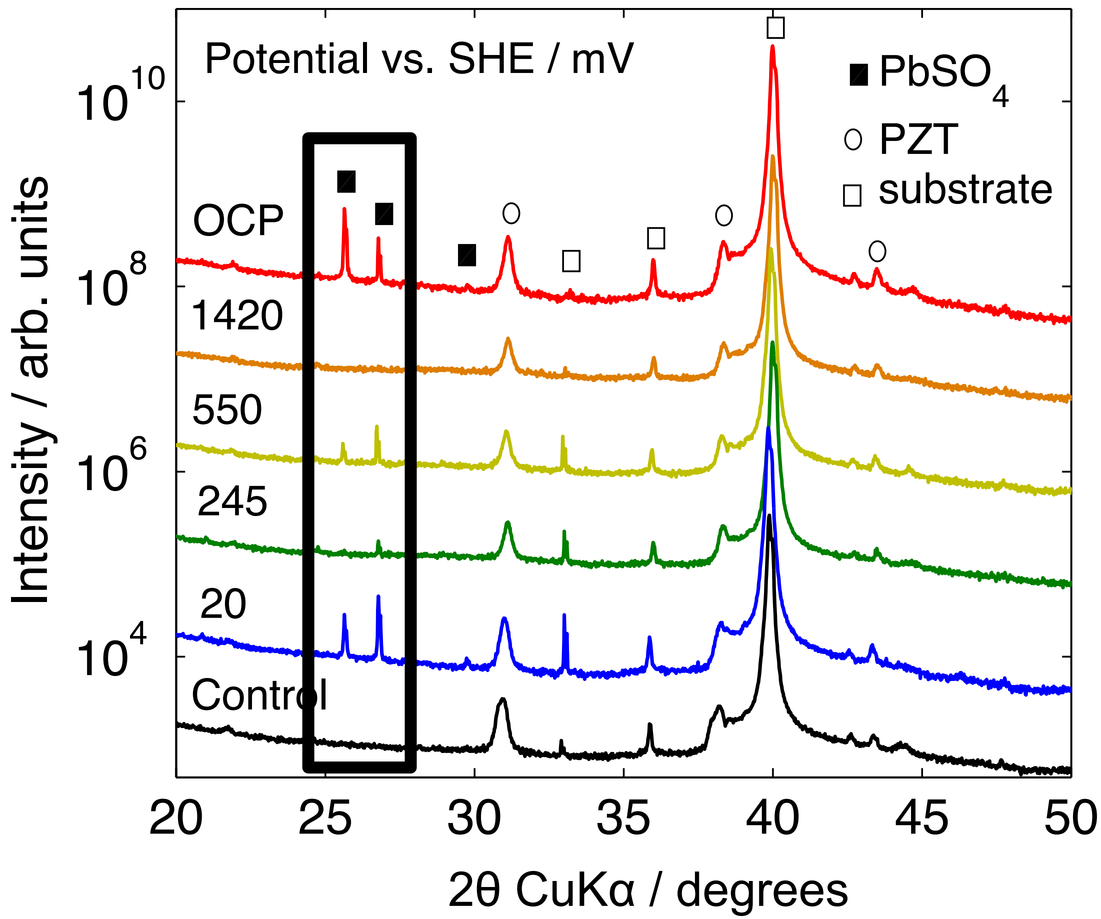


PZT film held in 0.1 N H_2SO_4 at 550 mV vs. SHE

L. Small, M. Brumbach, C. Apblett, J.F. Ihlefeld, G. Brennecka, and D. Duquette, *J. Electrochem. Soc.*, **160** (2013) C128-C135.

X-Ray Diffraction at 48 Hours

- All 48 hour samples except 1420 mV show crystalline $PbSO_4$.
- No other new phases

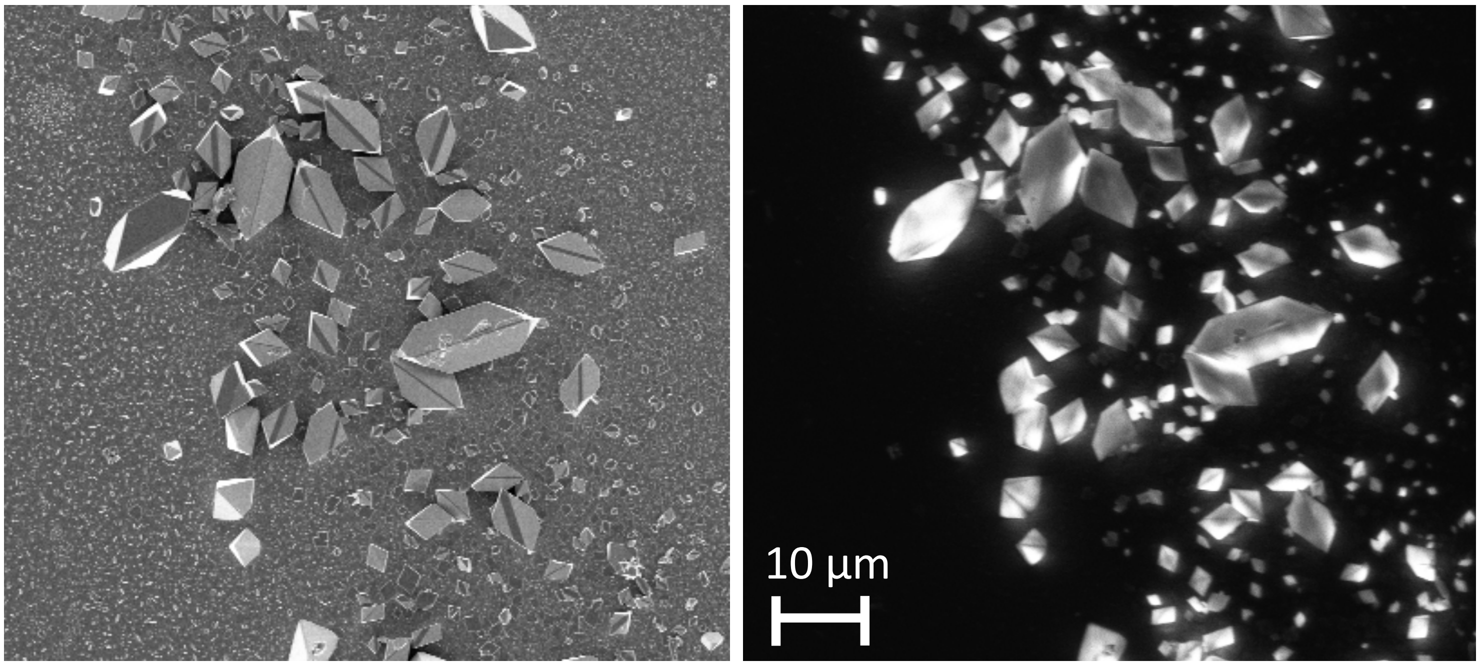


θ-2θ scans from PZT held for 48 hours in 0.1 N H_2SO_4.

L. Small, M. Brumbach, C. Apblett, J.F. Ihlefeld, G. Brennecka, and D. Duquette, *J. Electrochem. Soc.*, **160** (2013) C128-C135.

$PbSO_4$ Crystal Formation

PZT surface after 48 hours in 0.1 N H_2SO_4 at 550 mV vs. SHE

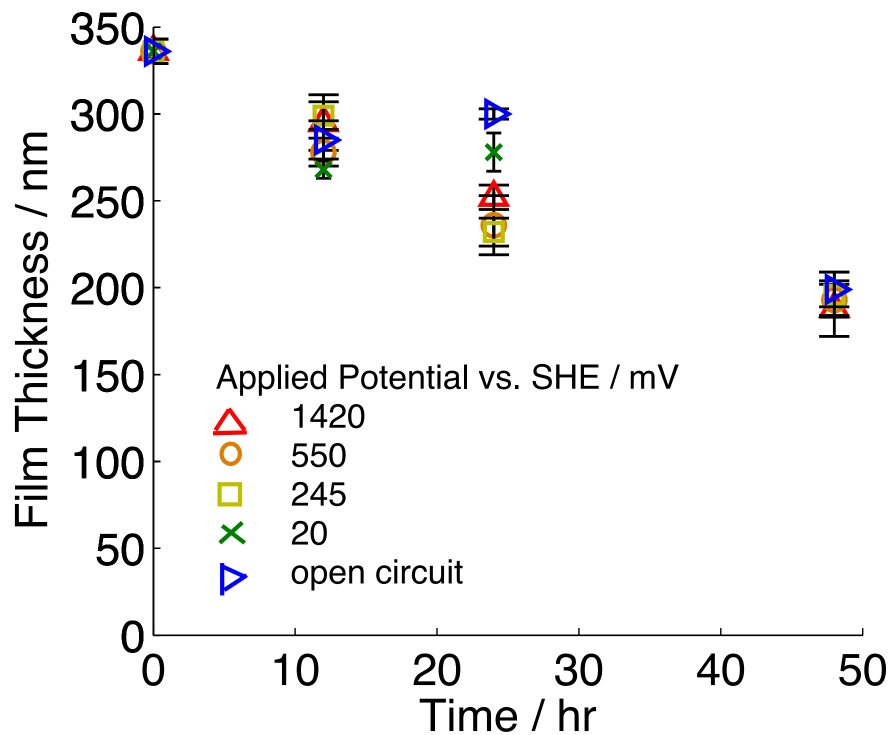


Plan-view SEM micrographs: (left) secondary electron image (right) visible light image.

L. Small, M. Brumbach, C. Apblett, J.F. Ihlefeld, G. Brennecka, and D. Duquette, *J. Electrochem. Soc.*, **160** (2013) C128-C135.

Etch Rate

- Etch rate independent of applied potential
- 2.8 nm/hr average
- No electron transfer process present



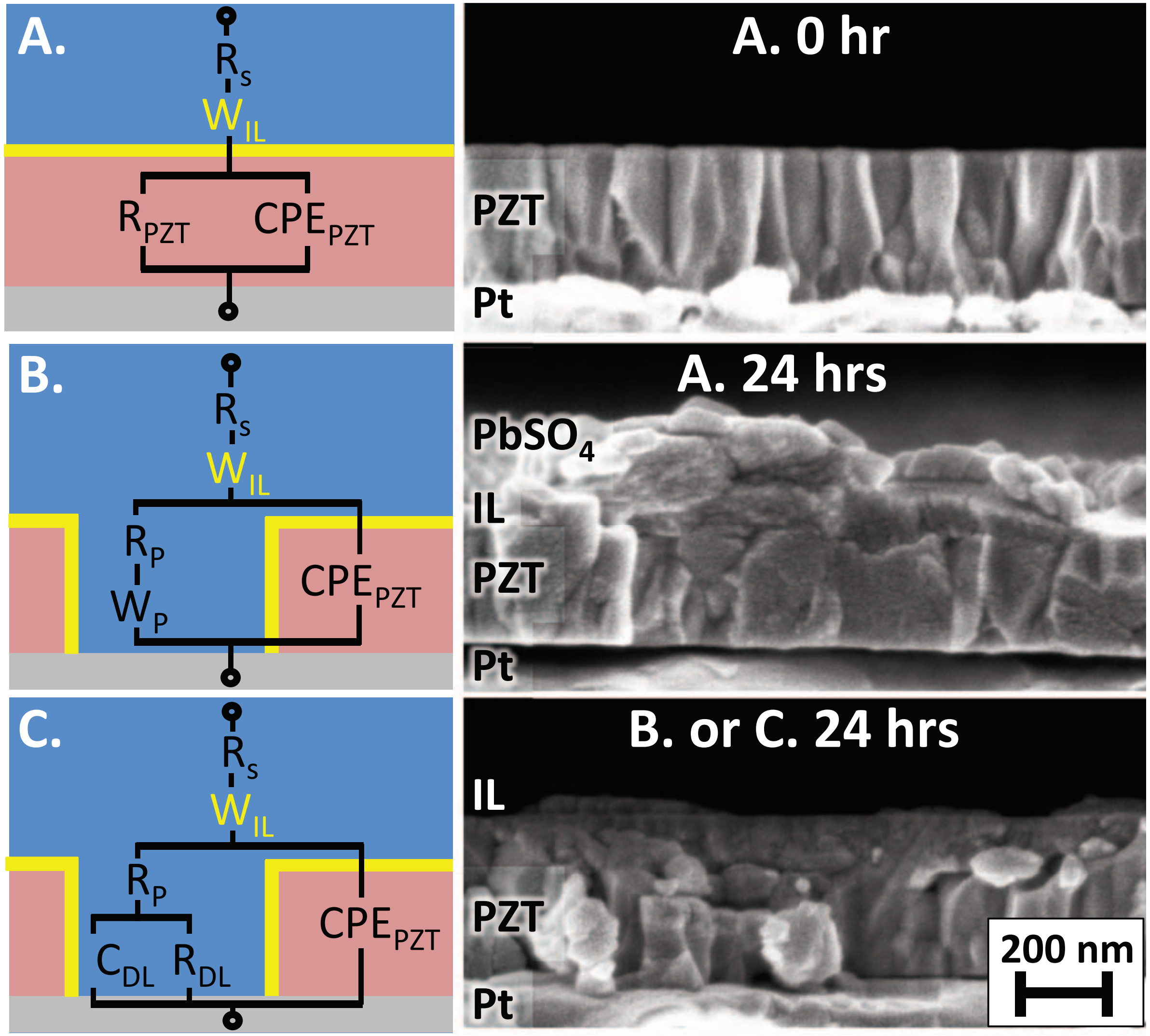
L. Small, M. Brumbach, C. Apblett, J.F. Ihlefeld, G. Brennecka, and D. Duquette, *J. Electrochem. Soc.*, **160** (2013) C128-C135.

EIS Model Development

IL Formation

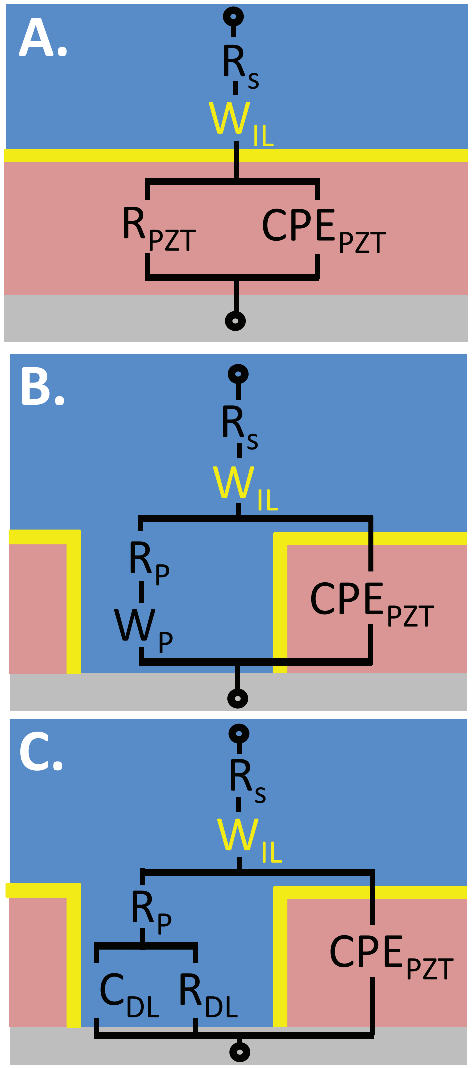
Pore growth

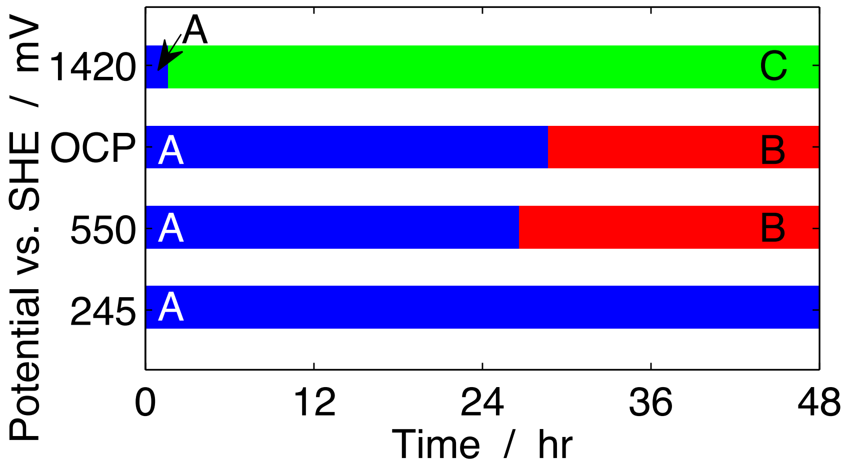
Gas Evolution



L. Small, M. Brumbach, C. Apblett, J.F. Ihlefeld, G. Brennecka, and D. Duquette, *J. Electrochem. Soc.*, **160** (2013) C128-C135.

EIS of All Samples





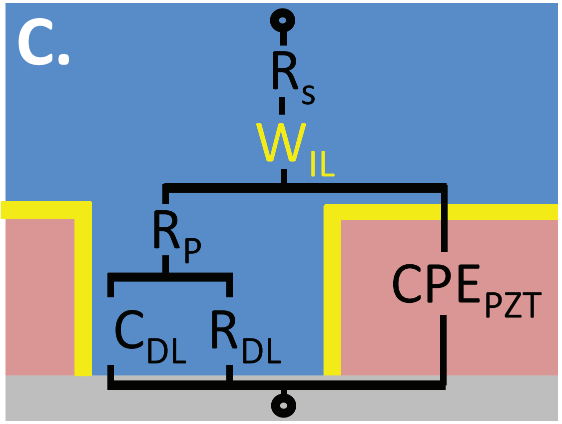
- All start as circuit A – PZT with IL growing
- Circuit B – pore growth, diffusion-limited process in pore
- Circuit C – oxygen evolution at pores/platinum

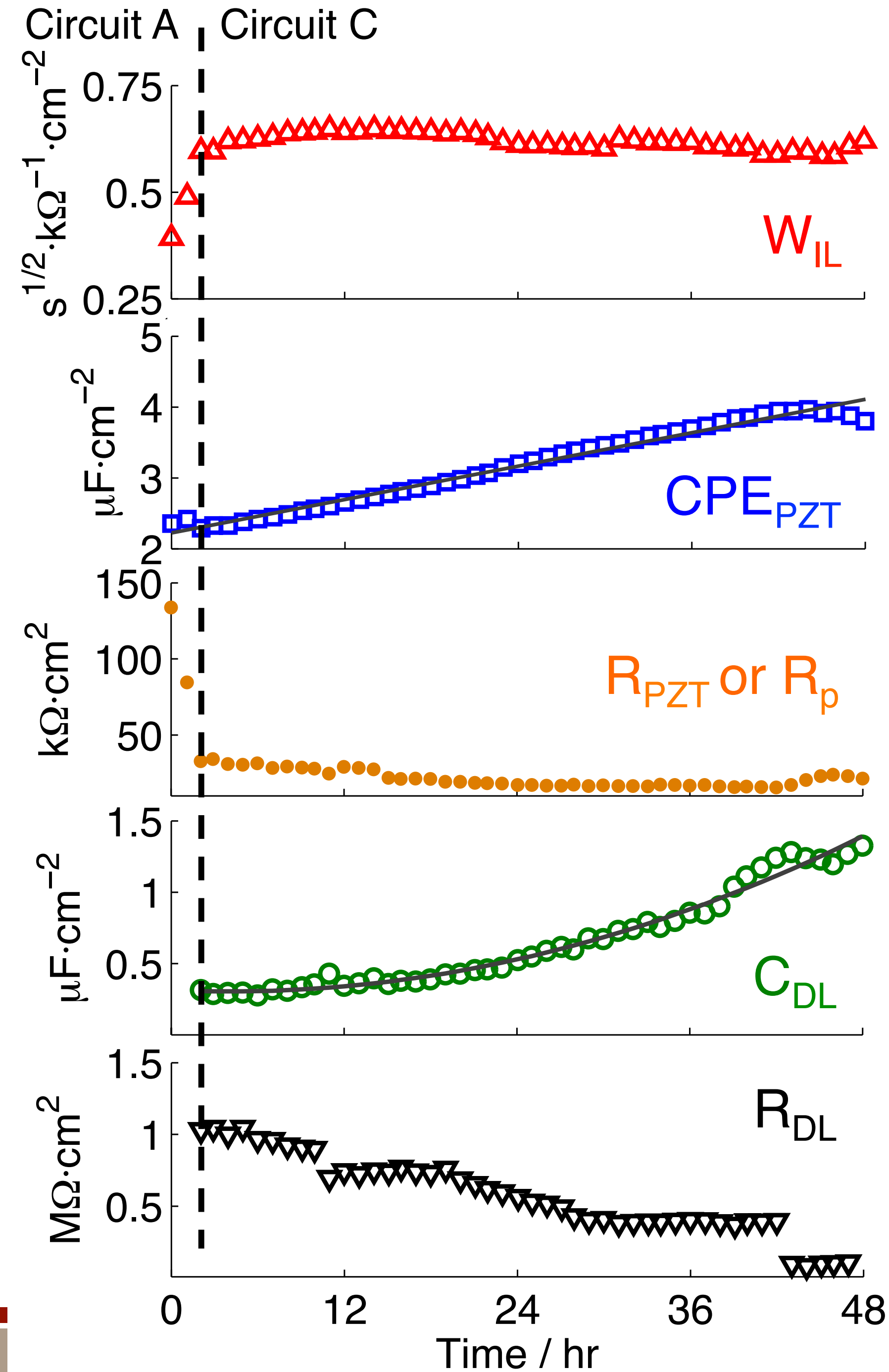
L. Small, M. Brumbach, C. Apblett, J.F. Ihlefeld, G. Brennecka, and D. Duquette, *J. Electrochem. Soc.*, **160** (2013) C128-C135.

Circuit Elements vs. Time

1420 mV vs. SHE

- W_{IL} grows over the first 2 hours, reaches stable value.
- CPE_{PZT} linearly increases with time, as expected for decreasing film thickness.
- R_p decreases with increasing pore size

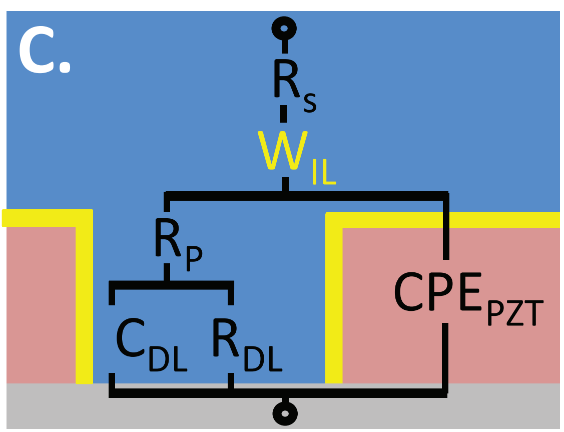


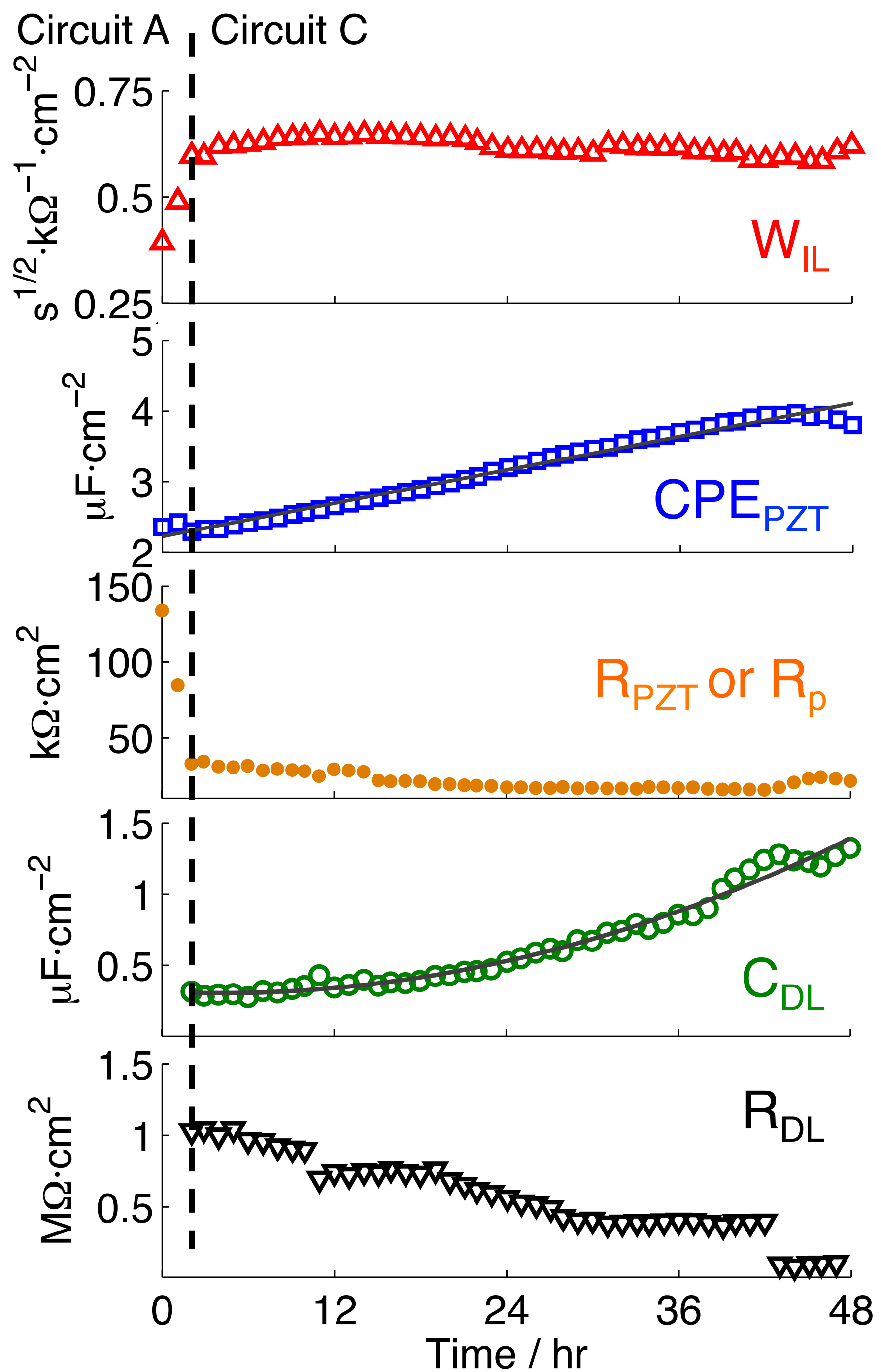


Circuit Elements vs. Time

1420 mV vs. SHE

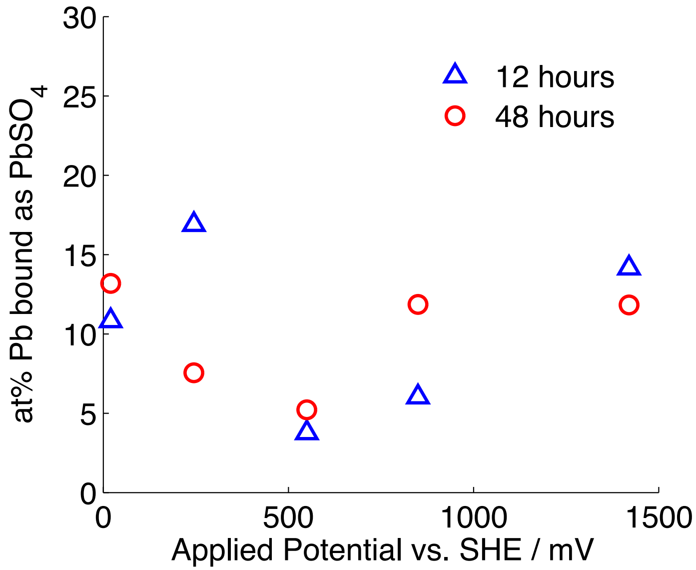
- C_{DL} is proportional to area of platinum exposed through pores.
- Quadratic fit
  → pores etched radially
  at a nearly constant rate

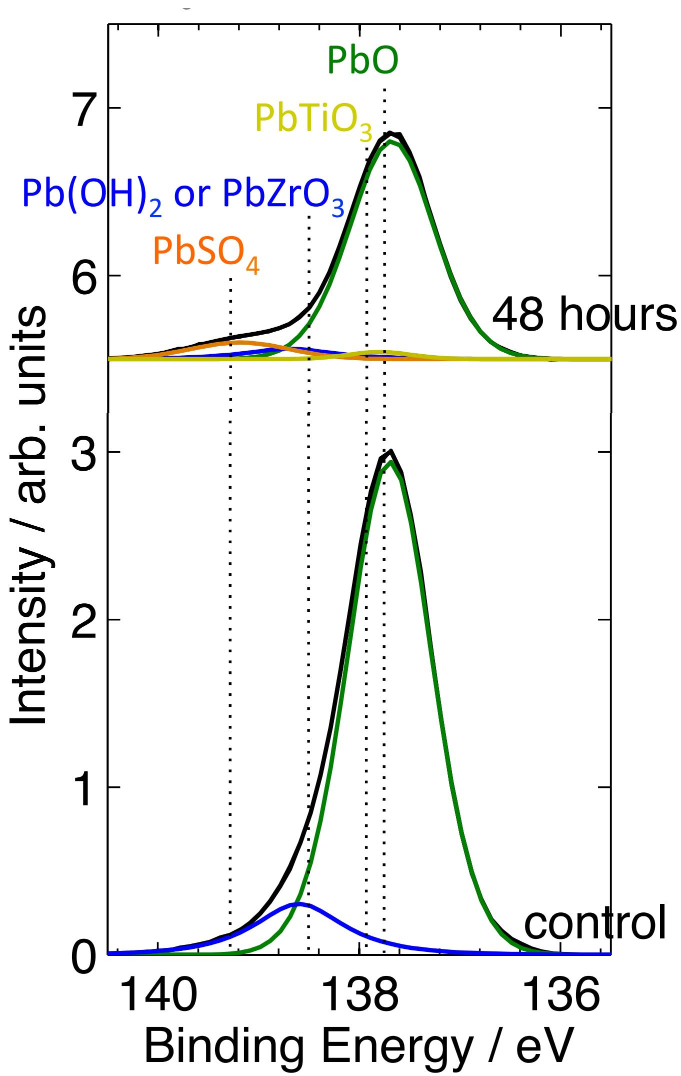




XPS Analysis: Lead $4f_{7/2}$

- $PbSO_4$ present after acid exposure
- at% Pb bound as $PbSO_4$ not strongly affected by potential or time



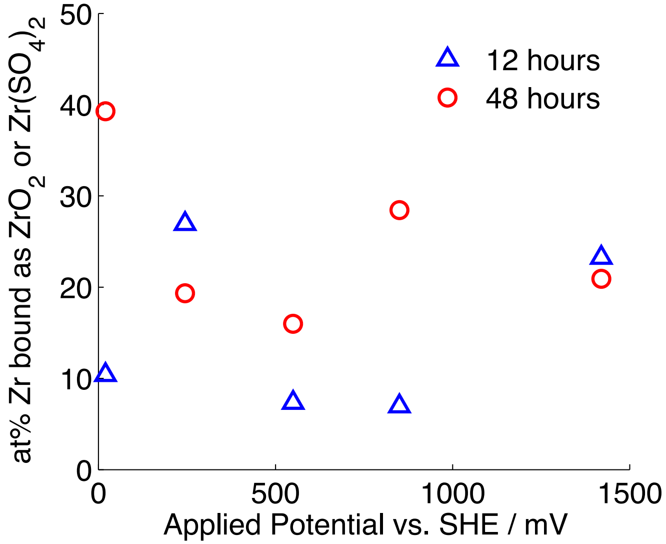


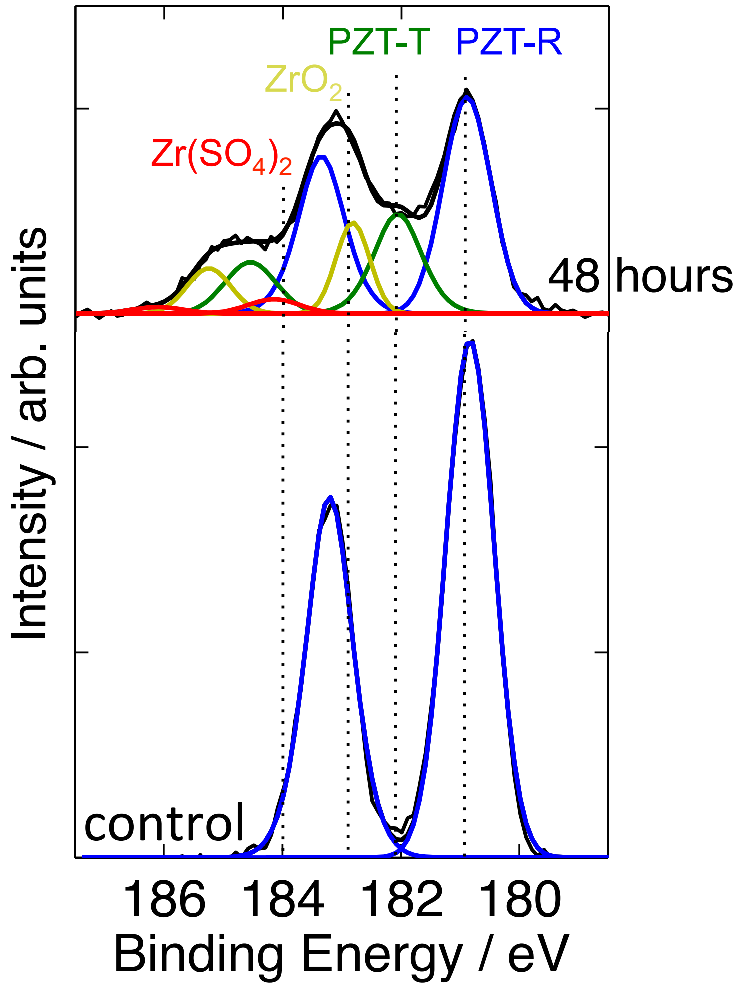
245 mV vs. SHE in 0.1 N H_2SO_4

L. Small, M. Brumbach, C. Apblett, J.F. Ihlefeld, G. Brennecka, and D. Duquette, *J. Electrochem. Soc.*, **160** (2013) C128-C135.

XPS Analysis: Zirconium 3d

- Tetragonal and rhombohedral PZT phases identified[1]
- SO_4^{2-} interacts with Zr
- at% Zr in sulfate states not affected by time or potential



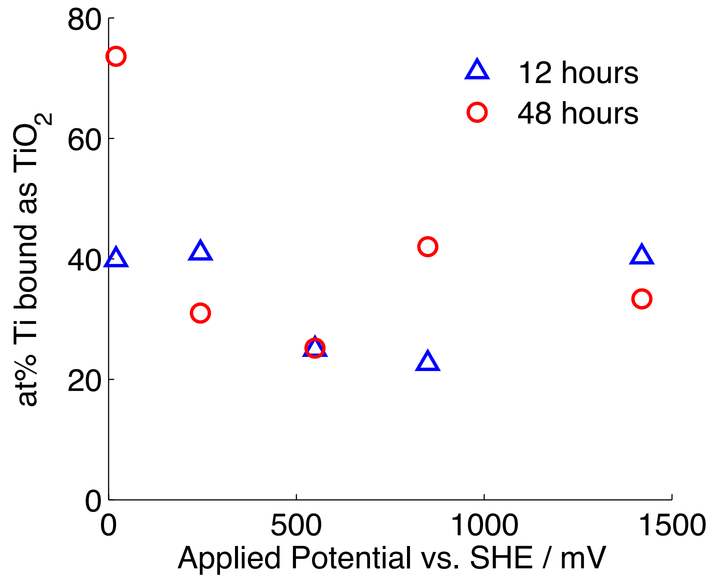


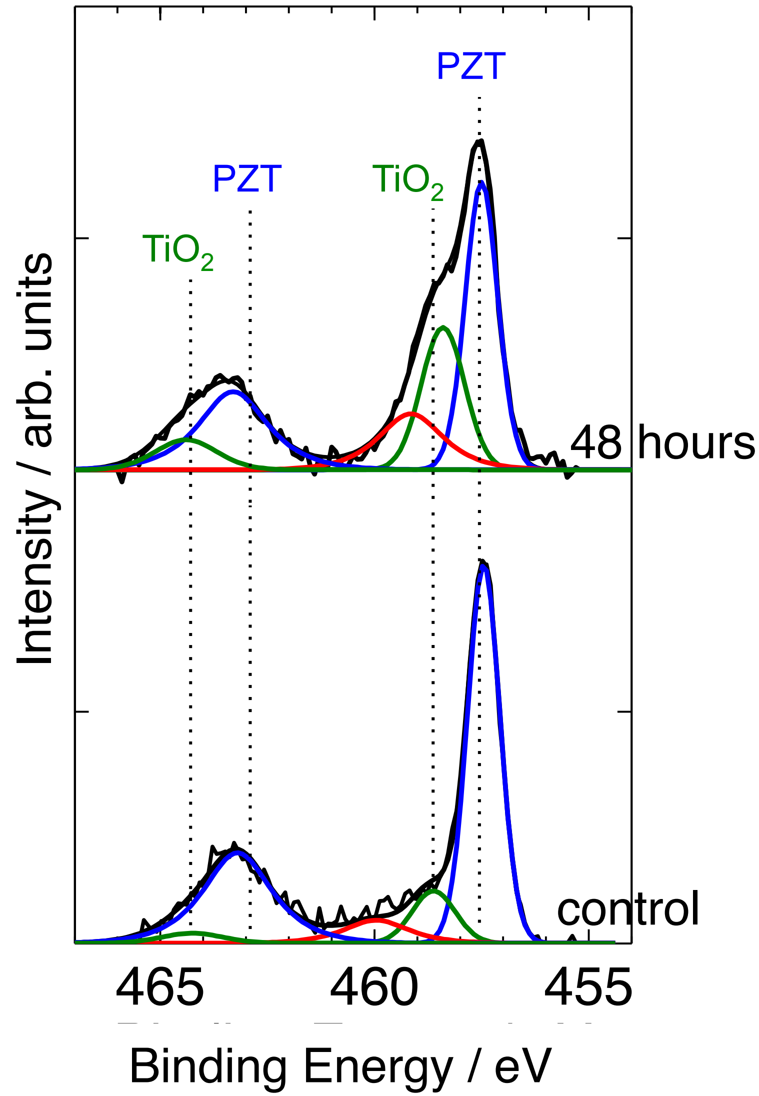
245 mV vs. SHE in 0.1 N H_2SO_4

[1]O. Sugiyama, K. Murakami, and S. Kaneko, *J. Euro. Ceram. Soc.* **24**, 1157 (2004).
L. Small, M. Brumbach, C. Apblett, J.F. Ihlefeld, G. Brennecka, and D. Duquette, *J. Electrochem. Soc.*, **160** (2013) C128-C135.

XPS Analysis: Titanium 2p

- No new phases after acid exposure
- at% TiO_2 increases upon acid exposure





245 mV vs. SHE in 0.1 N H_2SO_4

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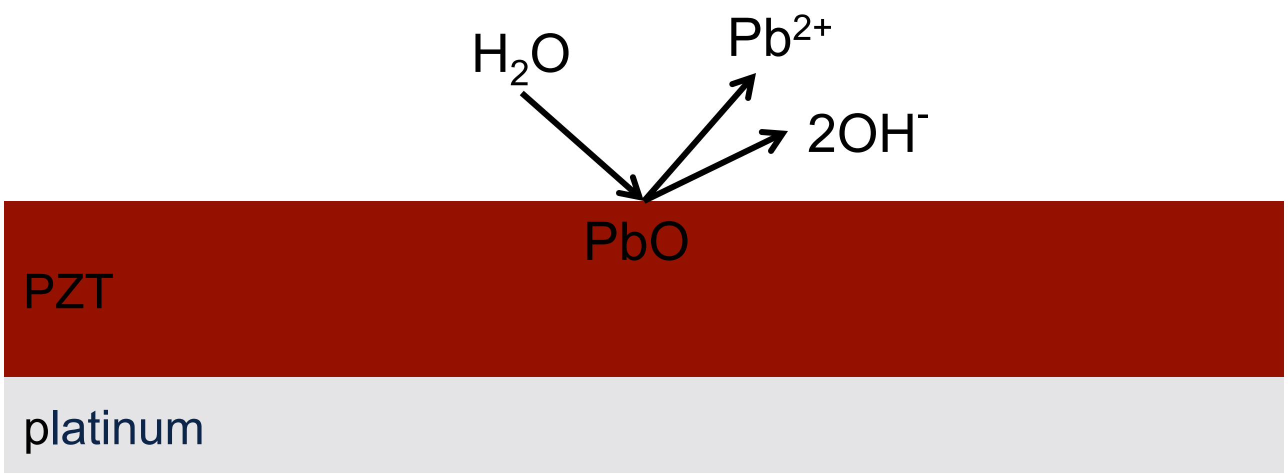
Proposed Dissolution Process

- PbO hydrolysis

$$(\mathrm{Pb}^{2+}_{Pb^{2+}})^{\mathrm{x}} + (\mathrm{O}^{2-}_{O^{2-}})^{\mathrm{x}} + \mathrm{H_2O} \rightarrow$$
$$\mathrm{Pb}^{2+}(aq) + 2\mathrm{OH}^{-} + (\mathrm{V}_{O^{2-}})^{\bullet\bullet} + (\mathrm{V}_{Pb^{2+}})''$$

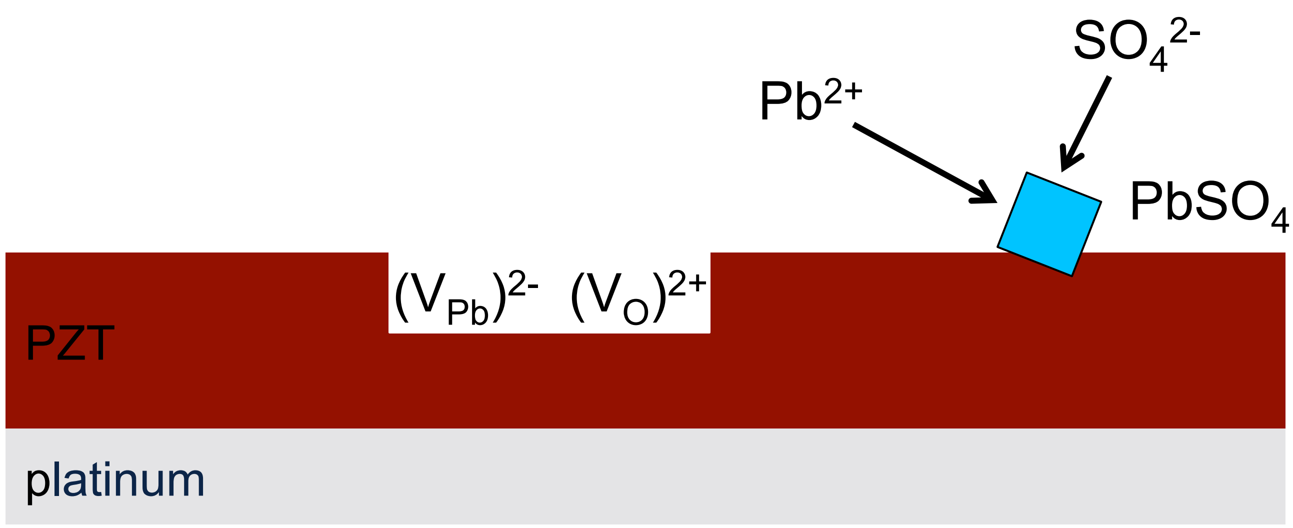


L. Small, M. Brumbach, C. Apblett, J.F. Ihlefeld, G. Brennecka, and D. Duquette, *J. Electrochem. Soc.*, **160** (2013) C128-C135.

Proposed Dissolution Process

- PbO hydrolysis
- $PbSO_4$ formation

$$\mathrm{Pb}^{2+}(aq) + \mathrm{SO}_4^{2-}(aq) \rightarrow \mathrm{PbSO}_4(s)$$



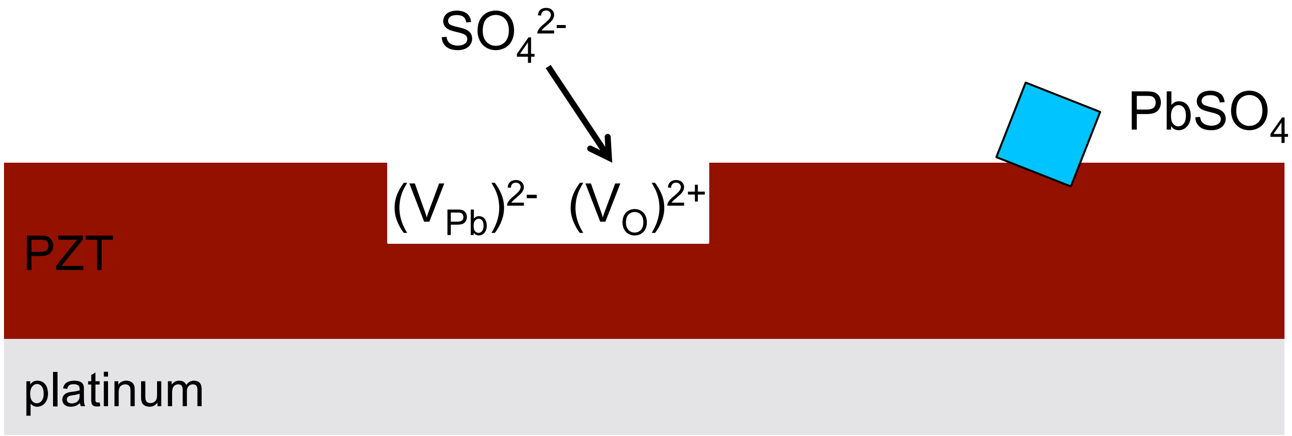
L. Small, M. Brumbach, C. Apblett, J.F. Ihlefeld, G. Brennecka, and D. Duquette, *J. Electrochem. Soc.*, **160** (2013) C128-C135.

Proposed Dissolution Process

- PbO hydrolysis
- $PbSO_4$ formation
- SO_4^{2-} attacks oxygen vacancy, bonds with Zr

$$\mathrm{SO_4^{2-}}(aq) + (\mathrm{V}_{O^{2-}})^{\bullet\bullet} \rightarrow \left((\mathrm{SO_4^{2-}})_{O^{2-}}\right)^{\mathrm{x}}$$

$$(\mathrm{Zr}^{4+}_{Zr^{4+}})^{\mathrm{x}} + (\mathrm{O}^{2-}_{O^{2-}})^{\mathrm{x}} + \left((\mathrm{SO_4^{2-}})_{O^{2-}}\right)^{\mathrm{x}} \rightarrow \mathrm{ZrO(SO_4)} + 2(\mathrm{V}_{O^{2-}})^{\bullet\bullet} + (\mathrm{V}_{Zr^{4+}})''''$$

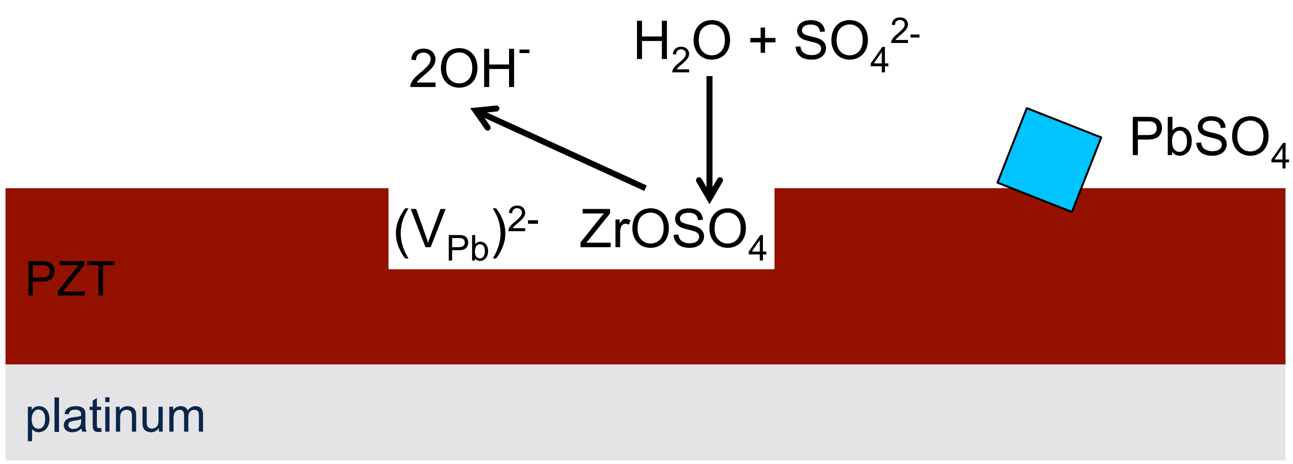


L. Small, M. Brumbach, C. Apblett, J.F. Ihlefeld, G. Brennecka, and D. Duquette, *J. Electrochem. Soc.*, **160** (2013) C128-C135.

Proposed Dissolution Process

- PbO hydrolysis
- $PbSO_4$ formation
- SO_4^{2-} attacks oxygen vacancy, bonds with Zr
- $Zr(SO_4)_2$ formation

$$\mathrm{ZrO(SO_4)} + \mathrm{SO_4^{2-}}(aq) + \mathrm{H_2O} \rightarrow \mathrm{Zr(SO_4)_2}\ (aq) + 2\mathrm{OH^-}$$



L. Small, M. Brumbach, C. Apblett, J.F. Ihlefeld, G. Brennecka, and D. Duquette, *J. Electrochem. Soc.*, **160** (2013) C128-C135.

Proposed Dissolution Process

- PbO hydrolysis
- $PbSO_4$ formation
- SO_4^{2-} attacks oxygen vacancy, bonds with Zr
- $Zr(SO_4)_2$ formation and dissolution
- TiO^{2+} dissolution

L. Small, M. Brumbach, C. Apblett, J.F. Ihlefeld, G. Brennecka, and D. Duquette, *J. Electrochem. Soc.*, **160** (2013) C128-C135.

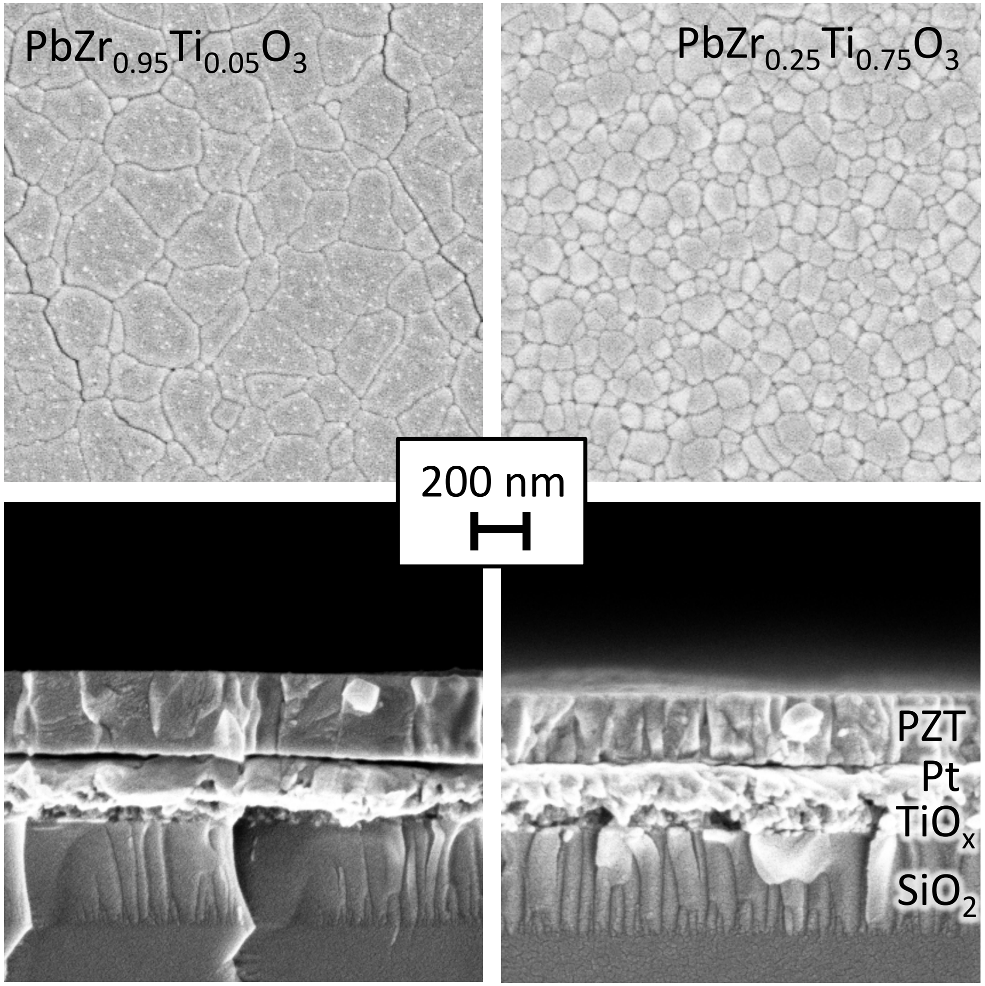
Effect of the Zr/Ti Ratio

Dense, columnar microstructure before acid exposure

Film thickness:

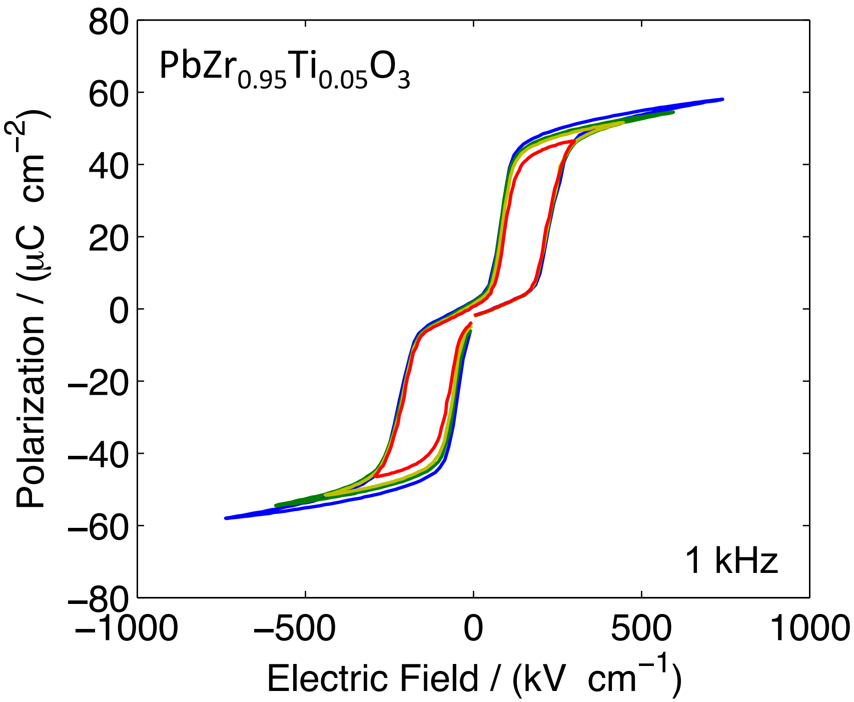
PZT 95/5:   330 nm

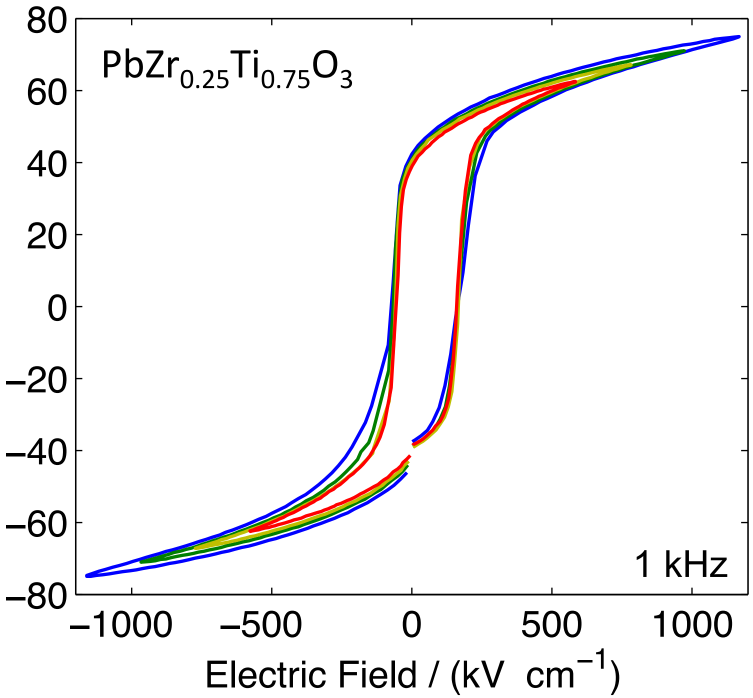
PZT 25/75: 250 nm



Effect of the Zr/Ti Ratio II

Verify electronic electronic properties – very good!





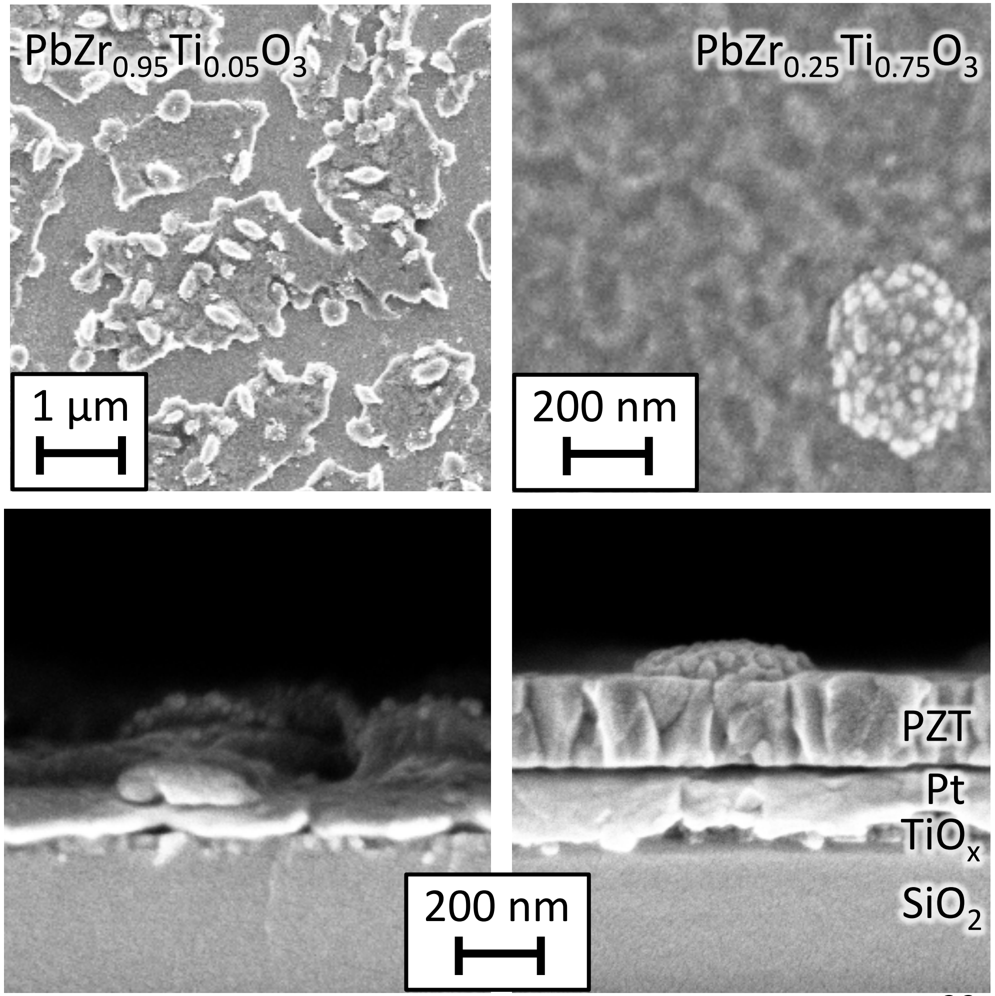
ε_r = 329 ± 18
tanδ = 0.012 ± 0.001
1 kHz, 25 mV RMS, 0 VDC

ε_r = 682 ± 36
tanδ = 0.018 ± 0.001

Effect of the Zr/Ti Ratio II

After 48 hours in 0.1 N H_2SO_4 at 550 mV vs. SHE

- Film thickness:
  - PZT 95/5: ~0
  - PZT 25/75: 220 nm
- **Increased Ti content reduces etch rate:**
  - PZT 95/5: 11 nm/hr
  - PZT 52/48: 2.8 nm/hr
  - PZT 25/75: 0.56 nm/hr

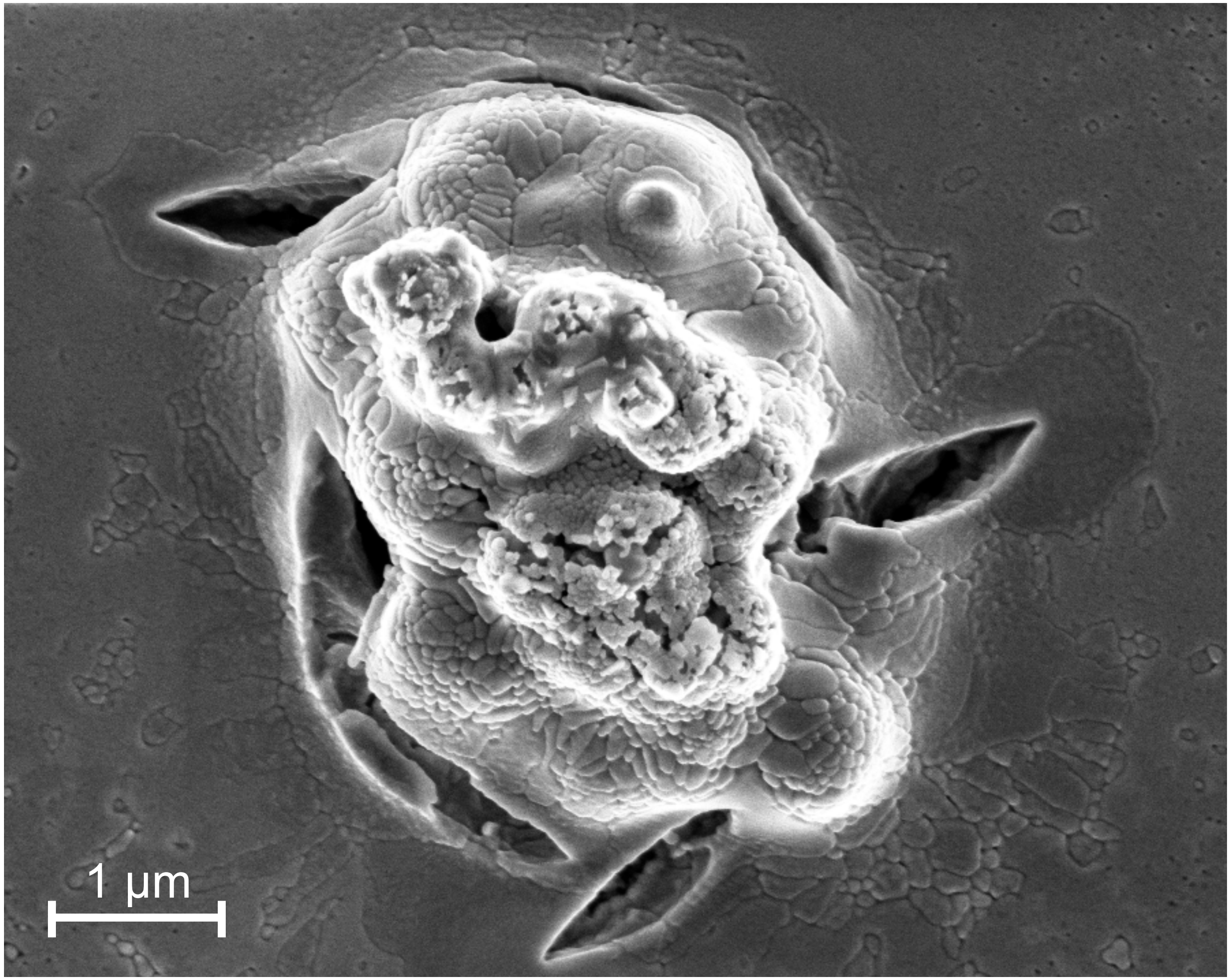


L. Small, M. Brumbach, C. Apblett, J.F. Ihlefeld, G. Brennecka, and D. Duquette, *J. Electrochem. Soc.*, **160** (2013) C128-C135.

Summary

- PZT in sulfuric acid = bad choice
- Built a fully automated microdroplet cell
- First thin film PZT ferroelectric hysteresis with liquid contact
- Used EIS, XRD, XPS, SEM to create PZT dissolution model
- Increased Ti content = reduced etch rate in H_2SO_4

Questions?



The epitaxy monster ruins a perfectly good epitaxial PZT film on $SrRuO_3/SrTiO_3$ (001).