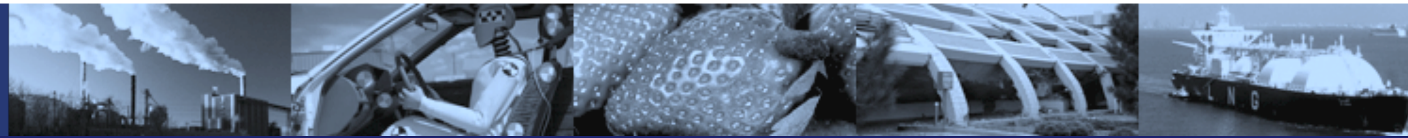
environmental • failure analysis & prevention • health • technology development

Exponent®

A leading engineering & scientific consulting firm dedicated to helping our clients solve their technical problems.

Exponent Offices



Who We Are

Exponent is a multi-disciplinary consulting firm dedicated to solving important science, engineering and regulatory issues for clients

Li-Ion Cell Cap Corrosion Monitoring

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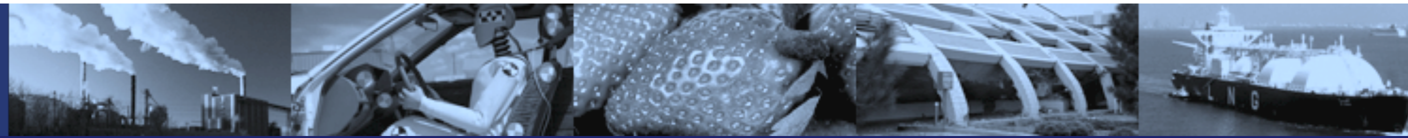
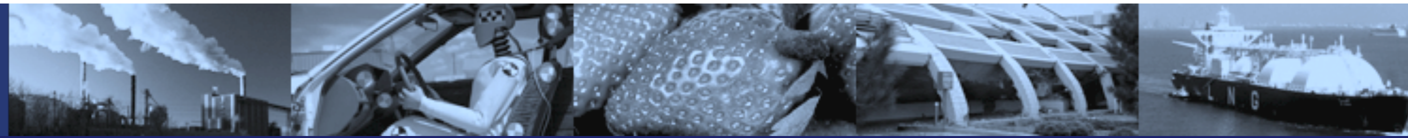


Battery Support Services

- Cell design review & assessment
- Pack design review & assessment
  - Electronics & BMU consulting
  - Thermal management
  - Structural evaluation
- Pre-compliance testing (UN, UL, BAJ, vendor specific)
- **Verification & safety evaluation testing**
- CTIA testing
- **Failure analysis & corrective action recommendations**
- Recall support
- **Manufacturing auditing**
- Cell cross-section analysis
- CT scanning
- Micro-reference electrode testing
- Accelerating rate calorimetry (ARC)
- Thermal analysis of materials (TGA/DSC)
- Materials characterization (SEM-EDS, XRD, FTIR, GC-MS)
- Custom abuse and service testing
- Fundamental electrochemical analysis
- Accelerated life testing and prediction
- Gas analysis
- Vent and CID activation



Background

- **Result of a series of projects for NASA, since 2008**
  - Assess safety and reliability of 18650 cells
  - Corrosion pitting in cell caps was detected
  - Decision was made to
    - Estimate the rate of corrosion pitting to assess expected cell aging
    - Monitor corrosion behavior to determine whether through-holes would be likely to develop over cell expected lifetime

- **Exponent would like to acknowledge:**
  - NASA JSC project team members, especially Eric Darcy, Sam Russel, Judy Jeevarajan, and John Weintritt
  - Previous Exponent project team members - Ramesh Godithi, John Harmon, Lisa Eastep, Sarah Stewart

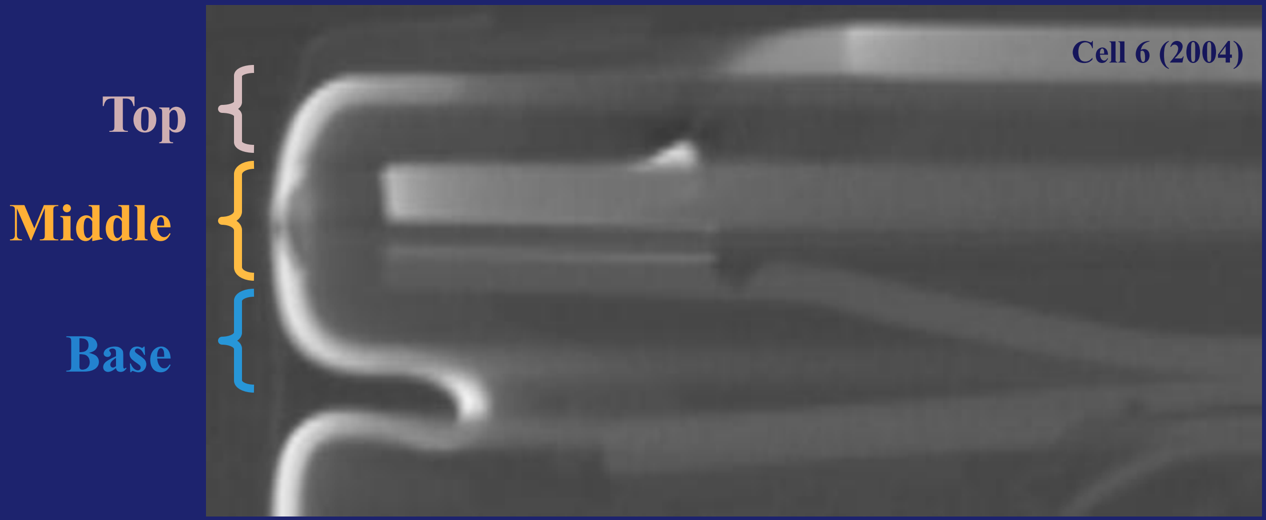
Scope of Investigation

- **Initial Destructive Cap Corrosion Investigation**
  - Evidence of pitting corrosion in cap assemblies was observed and documented
  - Metallurgical analysis (cross-sections, SEM) was performed

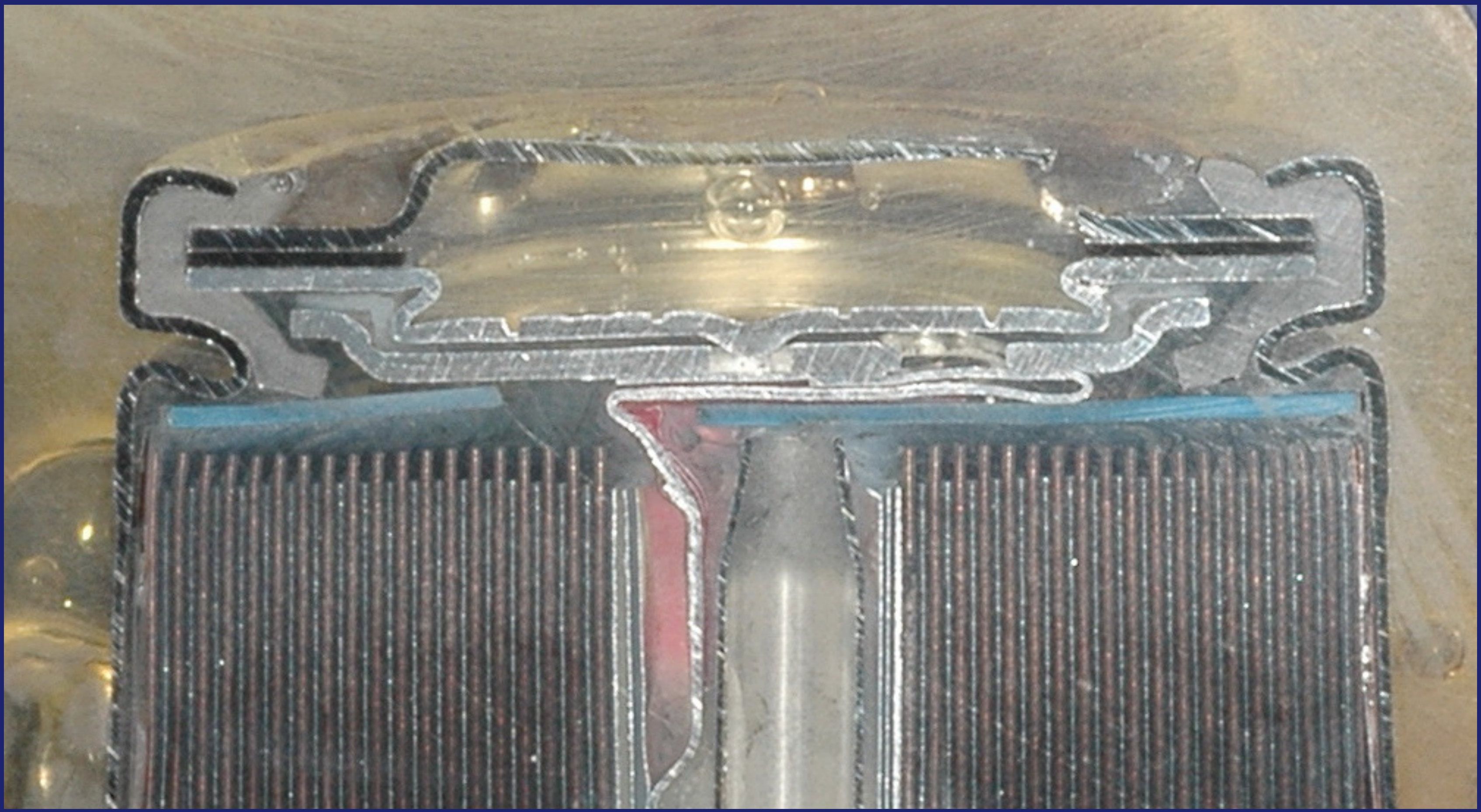
- **Long Term Cap Corrosion Monitoring**
  - Analysis of corrosion indicated that extent of corrosion correlated with age of the cell (older cells exhibited more pits, and deeper pits).
  - Cells from 4 date codes were stored in a climate controlled office environment after initial scanning
  - Cells from 3 different date codes are re-examined yearly (2009, 2010, 2011)
  - 3 Cells, year 2004
  - 3 Cells, year 2006
  - 3 Cells, year 2009

Location of Corrosion

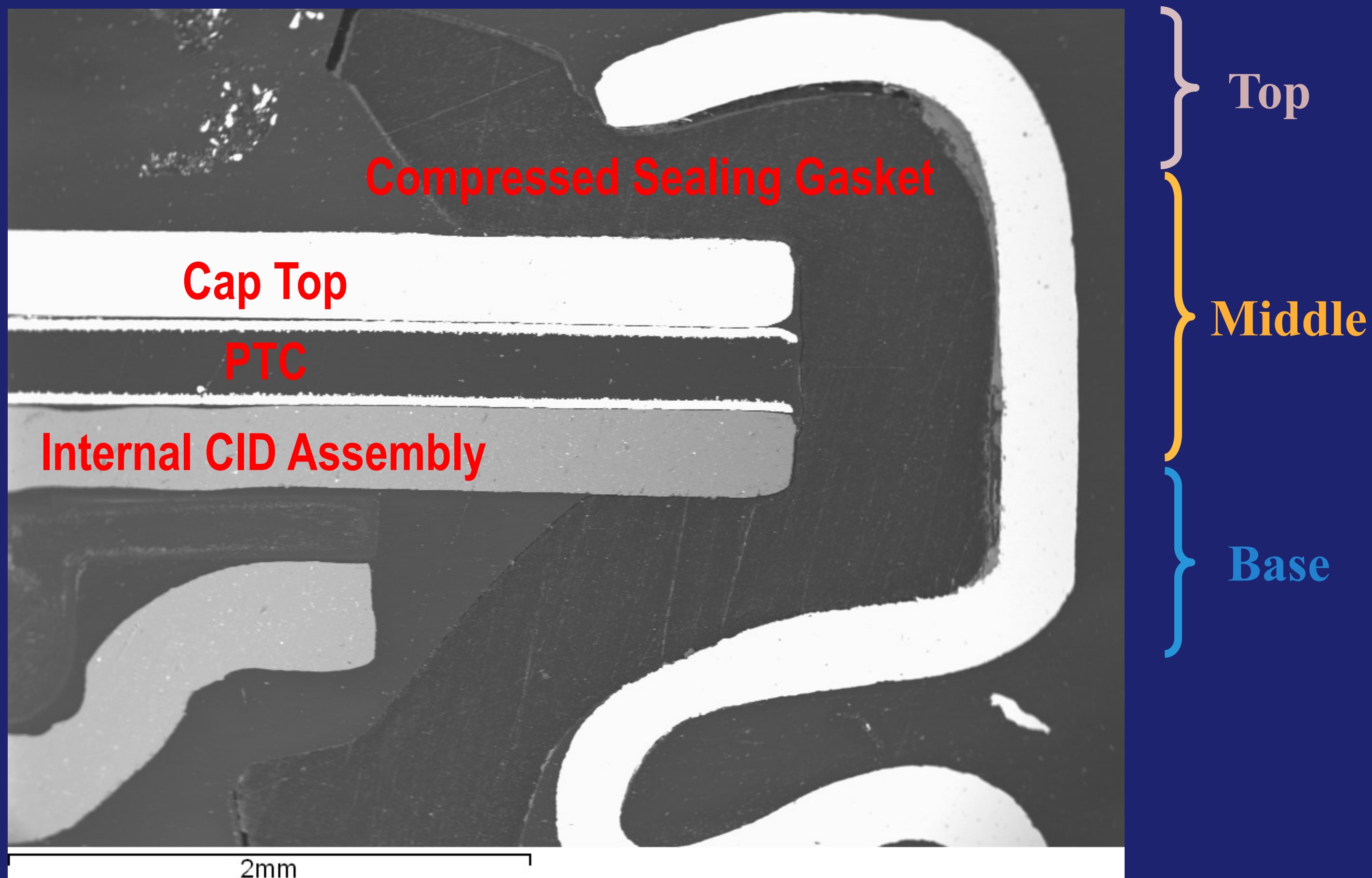
- **Corrosion in the cell caps was observed in three general locations:**
  - At the base of the seal (Base)
  - Near the middle of the seal (Middle)
  - Near the top of the seal (Top)



Location of Corrosion

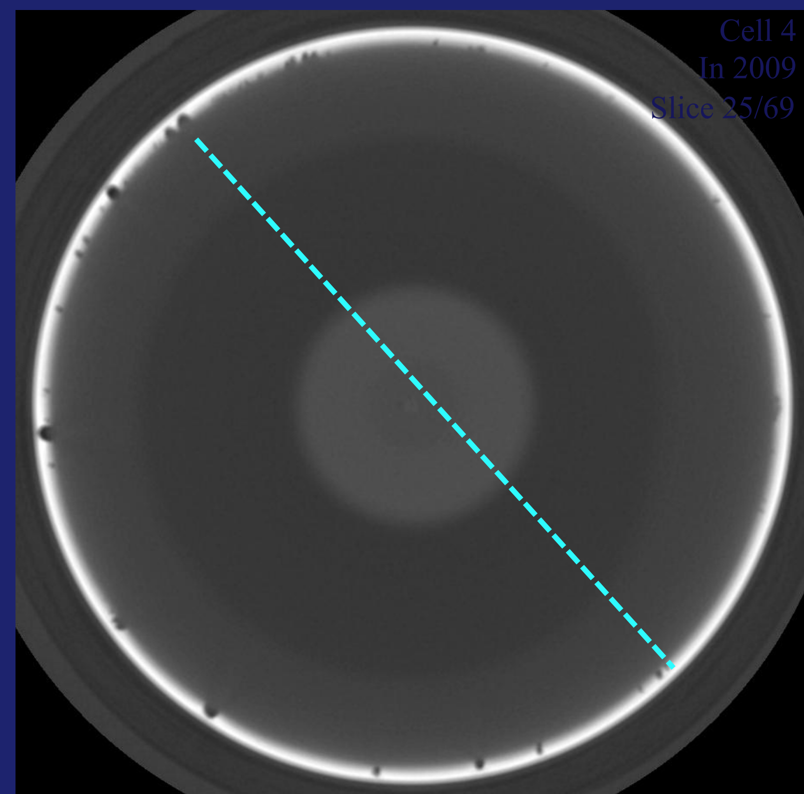


Location of Corrosion



Location of Corrosion

- Corrosion pits tend to be coplanar around cell circumference
- Consistent with tool contact to the interior of the can during neck formation

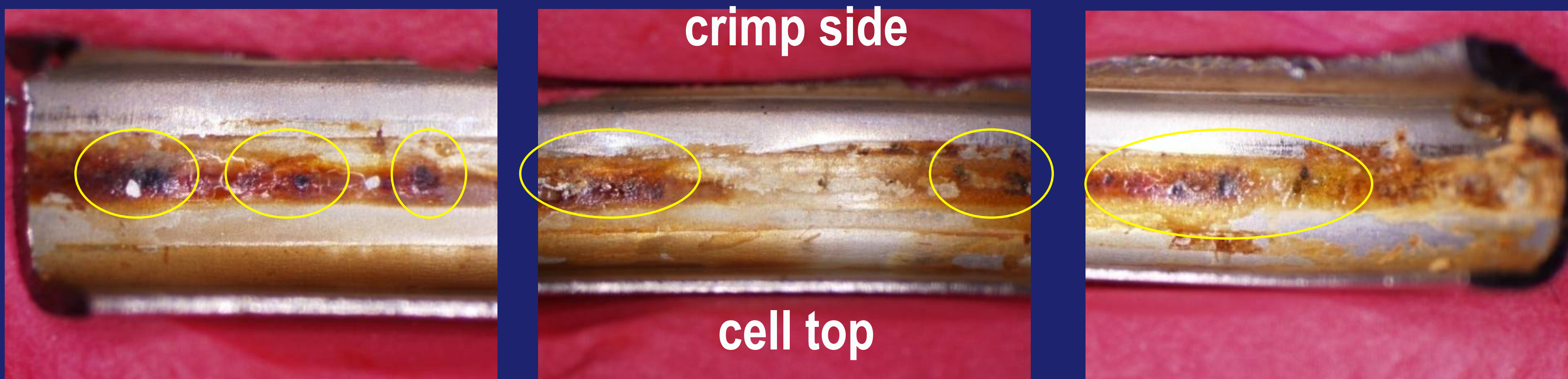


Initial Destructive Cap Corrosion Investigation

Metallurgical Examination

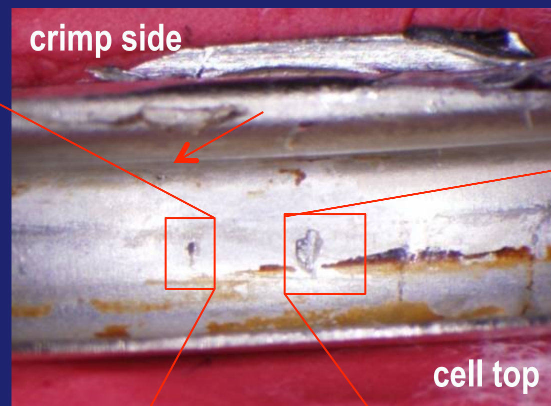
- **One selected cell was opened and the cap was examined in detail**
  - The seal was visually examined before being removed
  - The interior surface of the cap’s circumference was examined via stereo and scanning electron microscopes
  - A metallographic cross section was prepared through the center of several pits

Cap Interior Prior to Cleaning

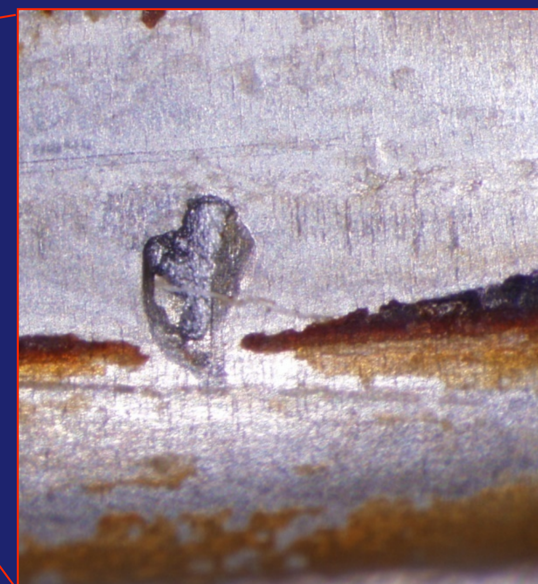


- **Several areas of dark corrosion product (circled), covering pits, were seen along the interior surface of the cap's circumference**
  - These areas were located about midway between the crimp and the cap top

After Cleaning

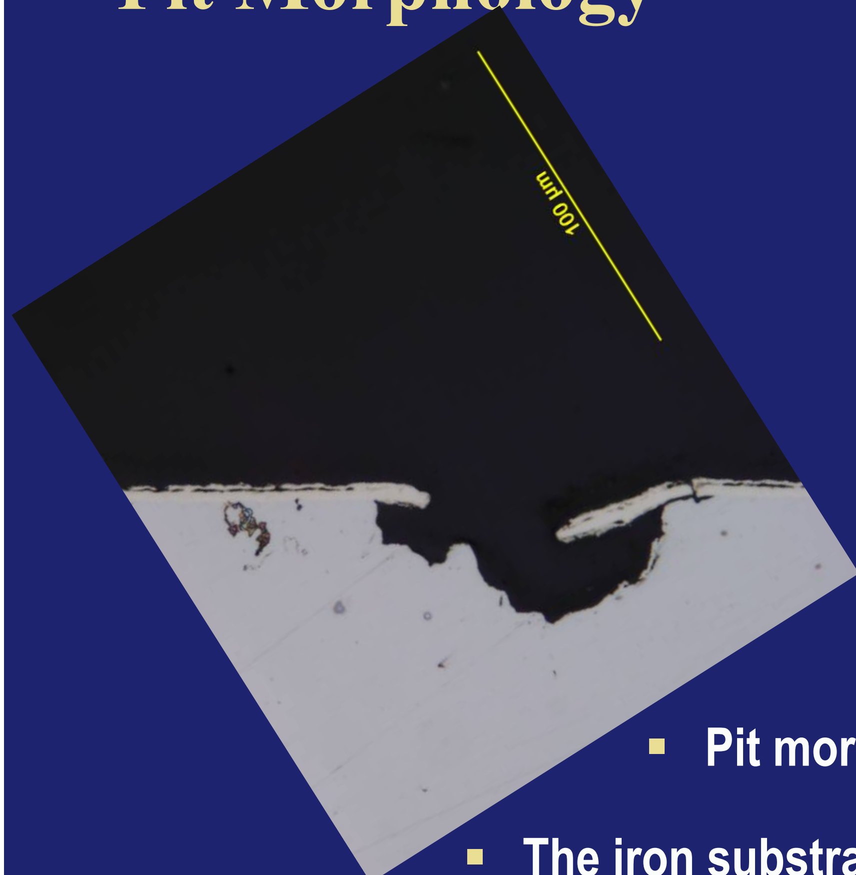


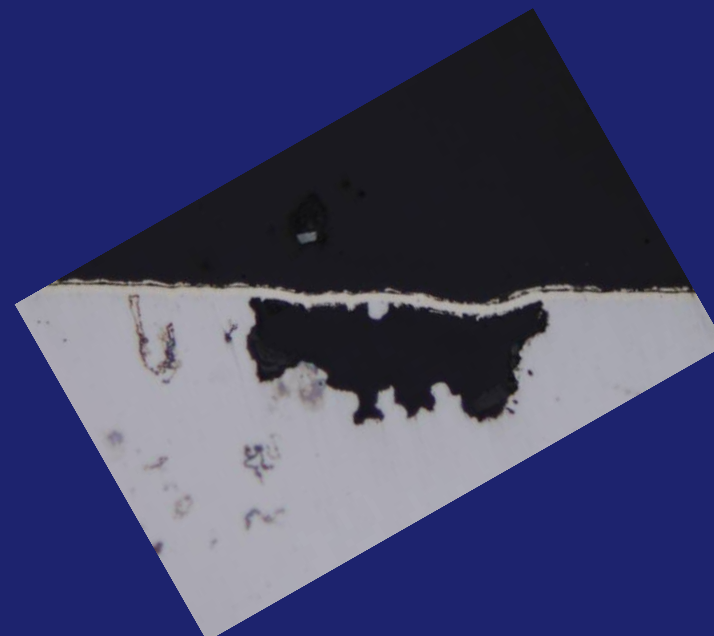
Some surface roughness, likely the precursors to pitting, was also seen on the interior surface (circled).



- After the electrolyte and corrosion product were removed, pits of varying sizes and depths could be seen
- Most pits were located approximately midway between the cap top and the crimp, though some were located closer to the crimp area (arrow)

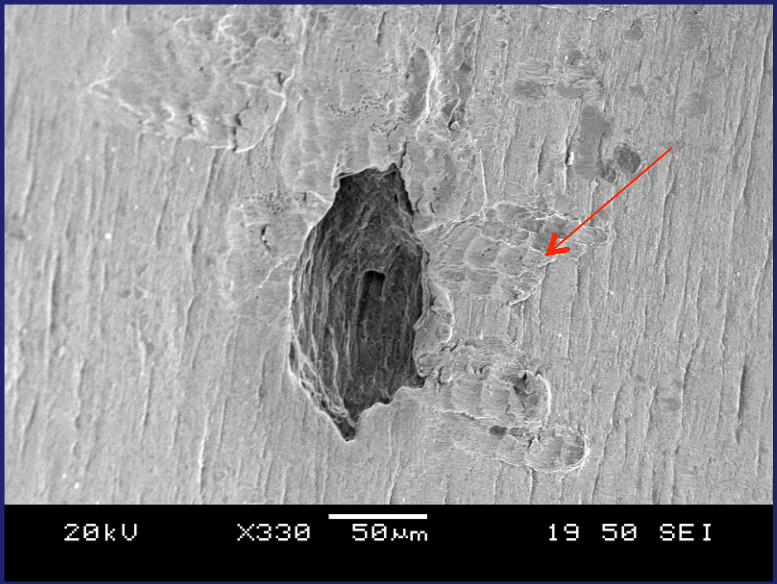
Pit Morphology





- Pit morphology is consistent with pitting corrosion
- The iron substrate is galvanically more active and would corrode preferentially to the nickel coating

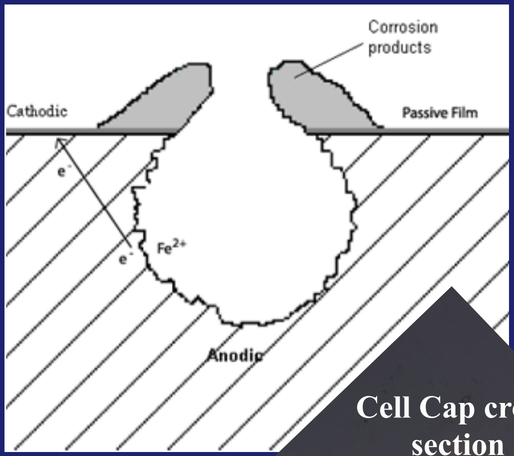
Other Surface Features

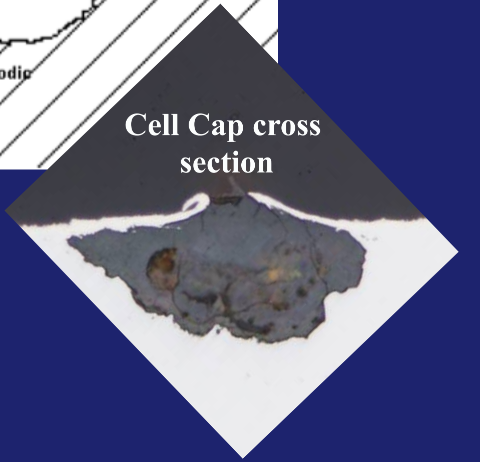


- **Rub or scrape marks (arrows) were seen adjacent to several, but not all, pits**
  - This may indicate the coating was broken or damaged, exposing the substrate material

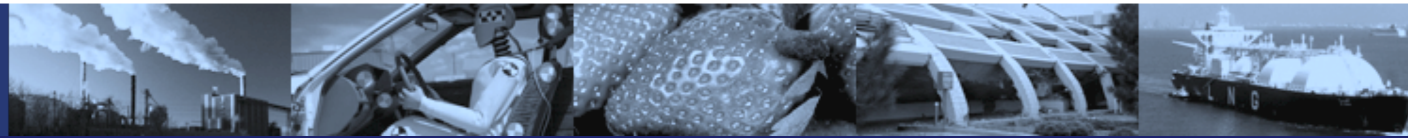
Likely Cause of Cap Corrosion

- **The Ni plating was damaged, exposing the substrate**
  - Marks surrounding pits are consistent with tool contact
  - Multiple operations during cell assembly could potentially require tool contact with top interior of cell case
- The area between the seal and the cap surface is a natural crevice, trapping moisture or other fluids
  - Electrolyte would be expected to be present in this area
- **Galvanic corrosion cell develops between nickel and iron resulting in iron dissolution**
- **Rate of corrosion will depend on multiple factors and must be determined empirically**





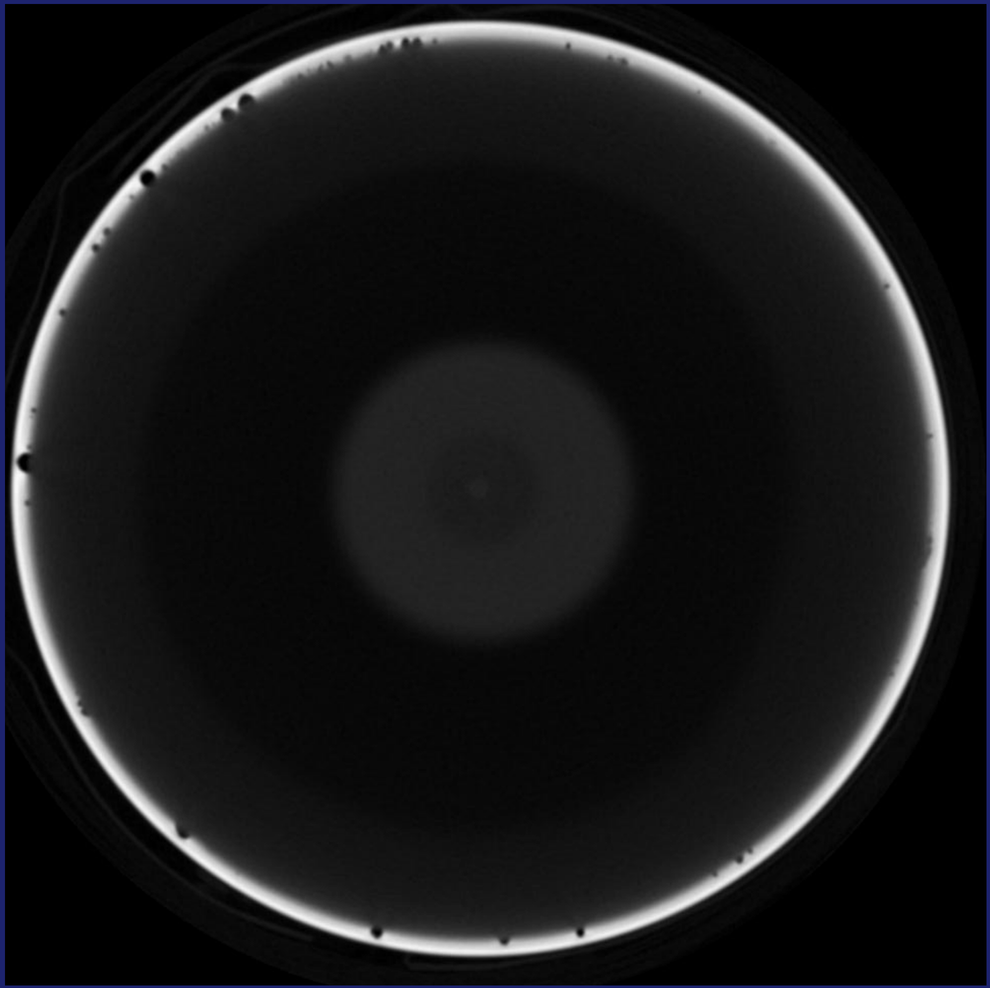
Long Term Cap Corrosion Monitoring



Long Term Corrosion Monitoring

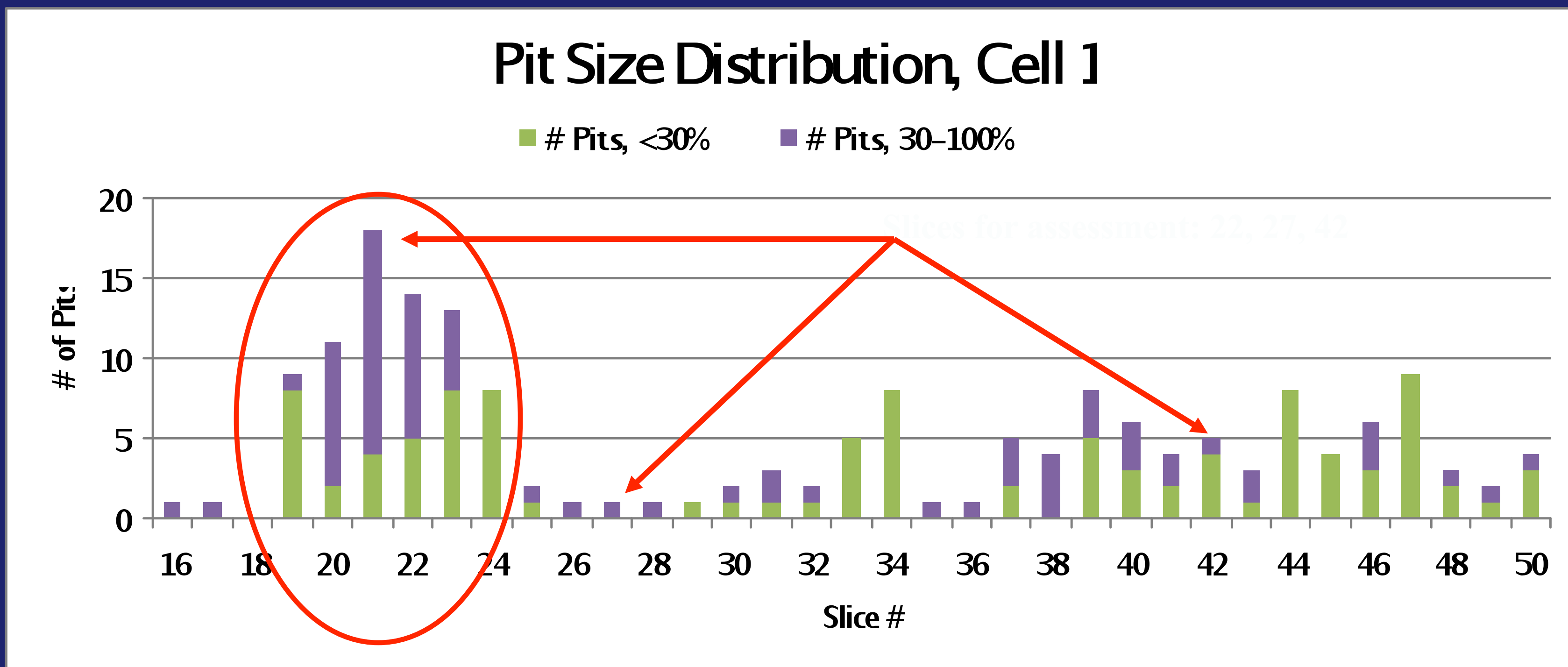
- **Yearly investigation of the pit size and growth performed**
- **Non-destructive cap cross section images obtained via CT scan allows repeated quantitative pit analysis**
- **Pit counts, location and depth of penetration recorded**
  - Individual pit depth increase is trackable
- **Pits are classified by depth of penetration (quantitative)**
  - Type A penetrates less than 50% of case
  - Type B penetrates between 50% and 75% of the case
  - Type C penetrates more than 75% of the case

Long Term Corrosion Monitoring



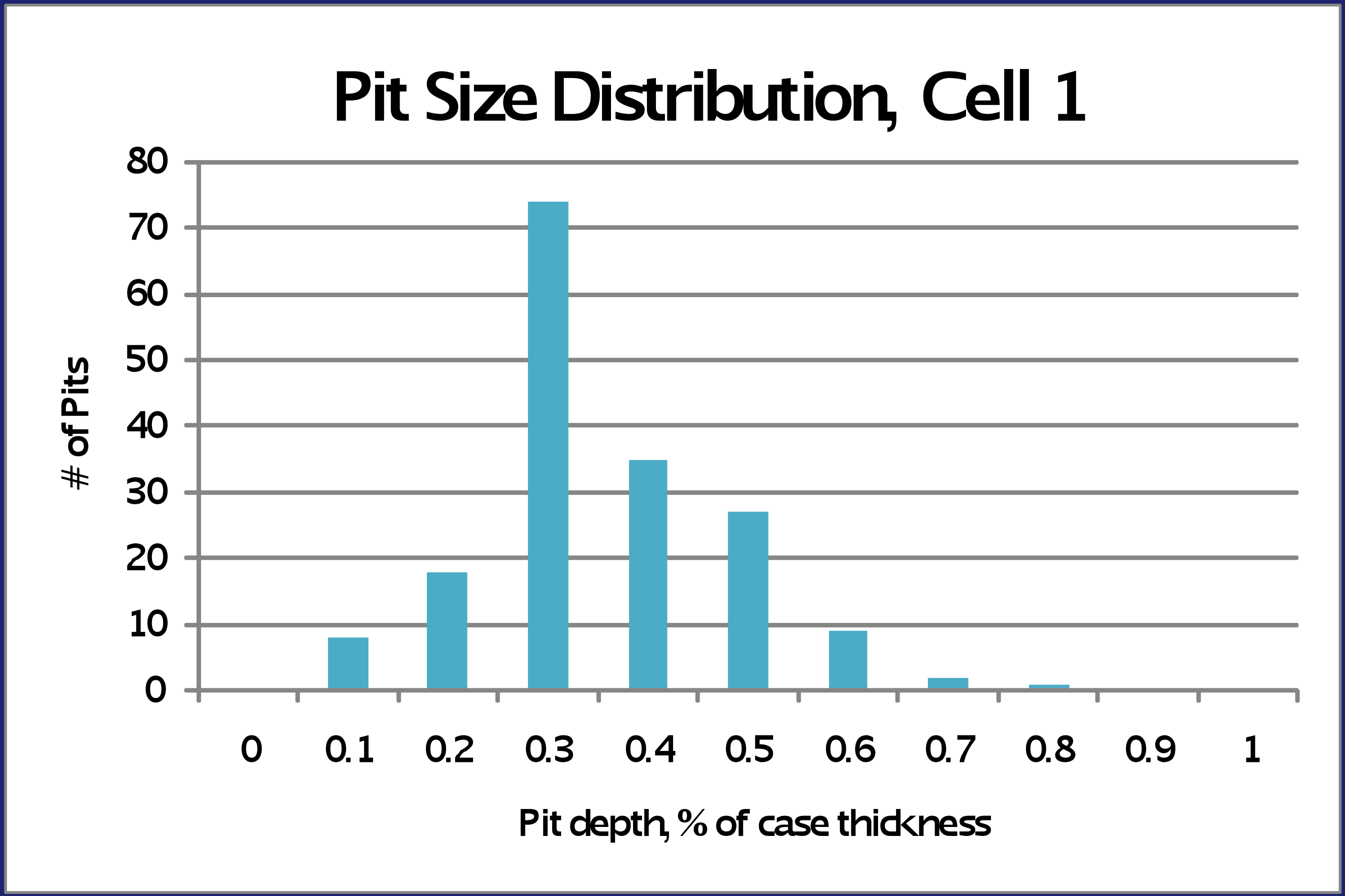
Sample of Visual Recognition Results

- Large pits appear in multiple adjacent CT slices, so slice with greatest number of pits used for assessment (in this example, pitting greatest near cell base (Slices 19-24), and Slice 22,27 and 42 used for further analysis

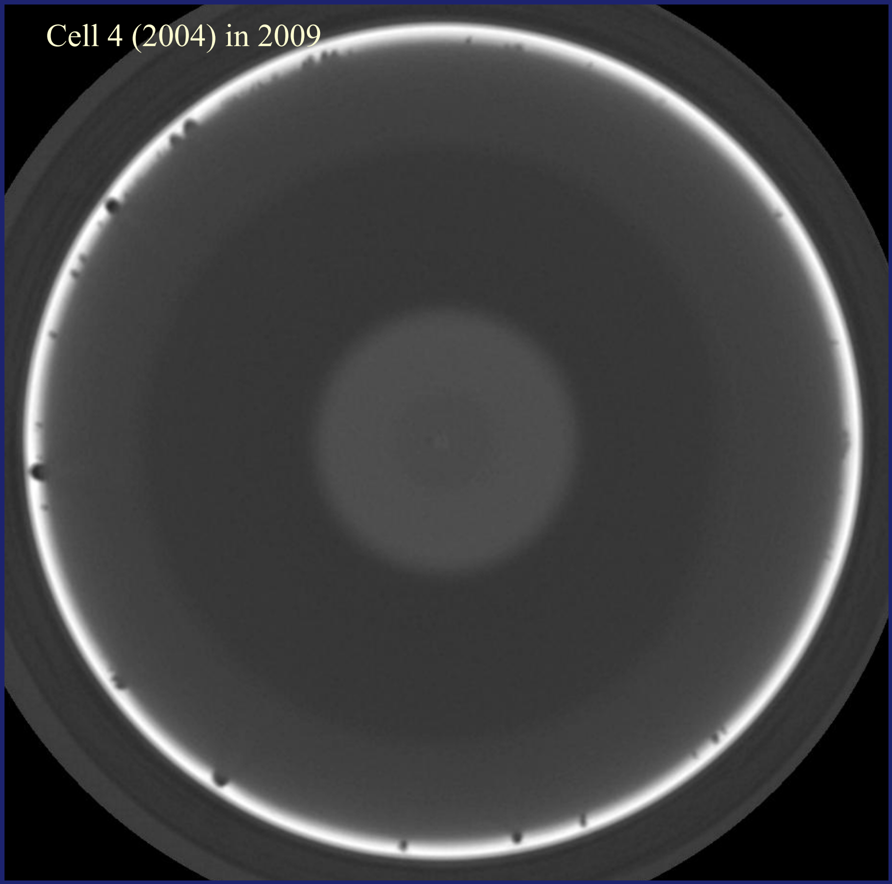


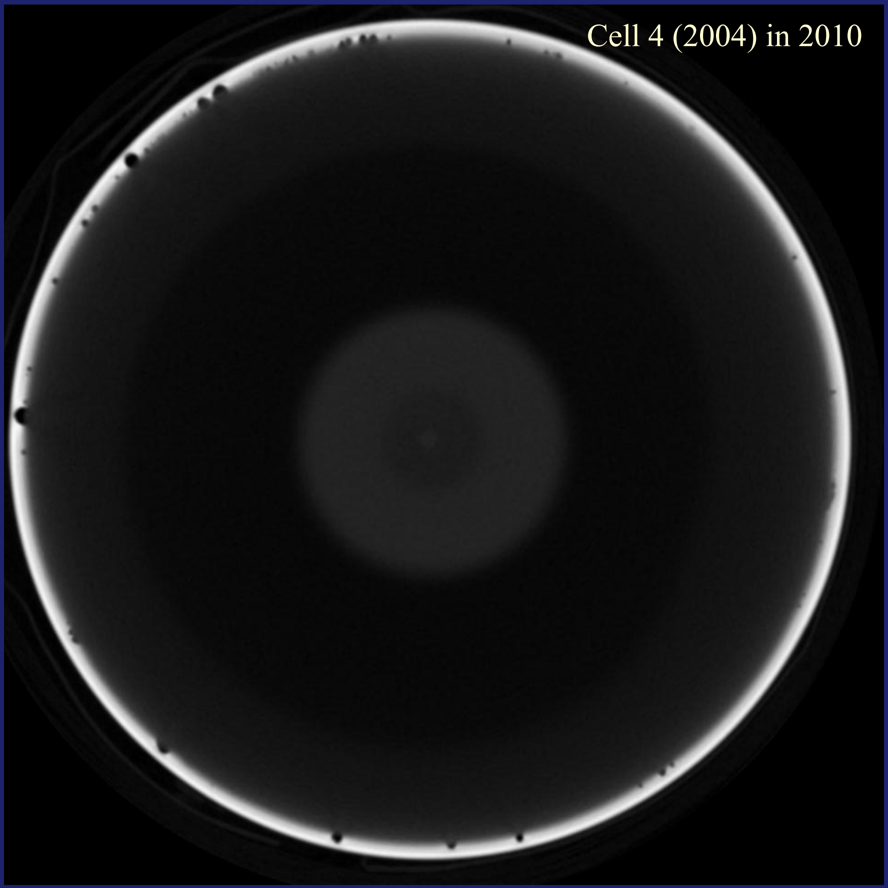
Sample of Visual Recognition Results

- Pit image size distribution for Cell 1, total of 174 pit images, corresponding to 69 actual pits.



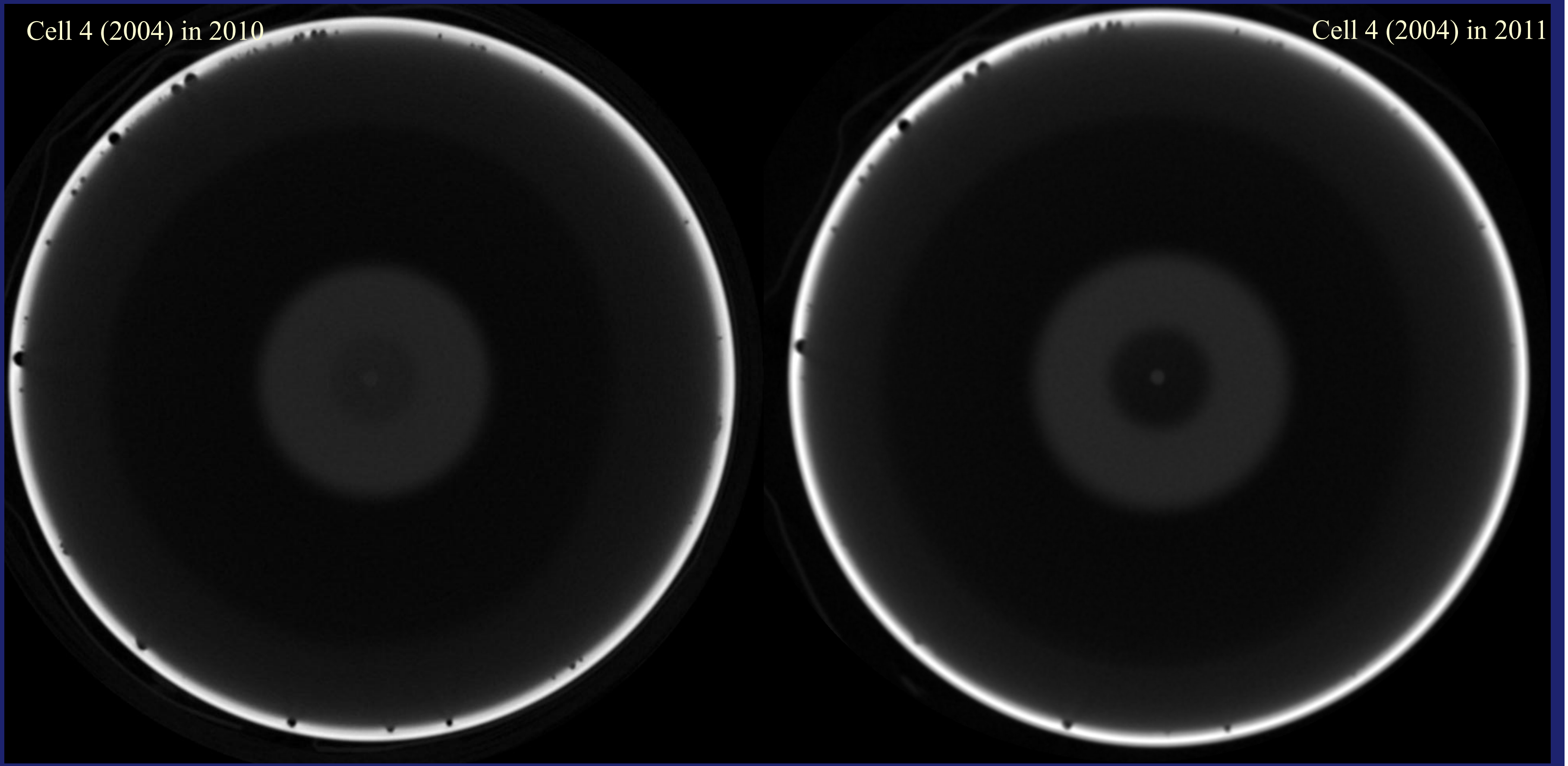
Pitting Comparison 2009 vs 2010





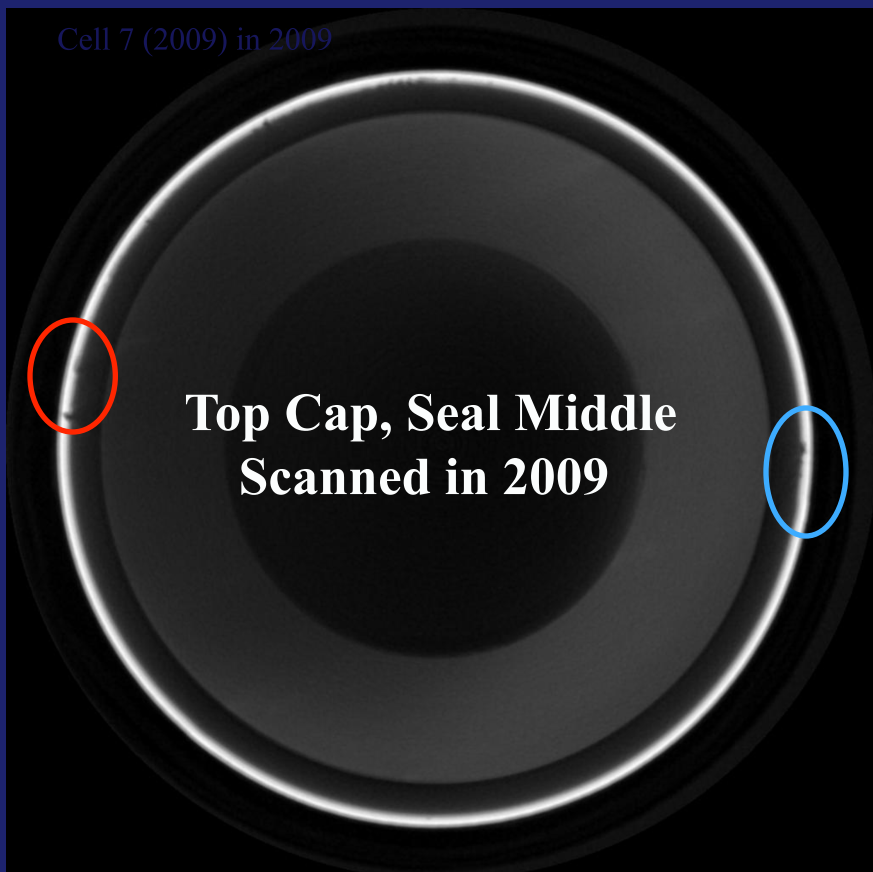
- Difficult to determine in change has occurred with a qualitative visual examination

Pitting Comparison 2010 vs 2011



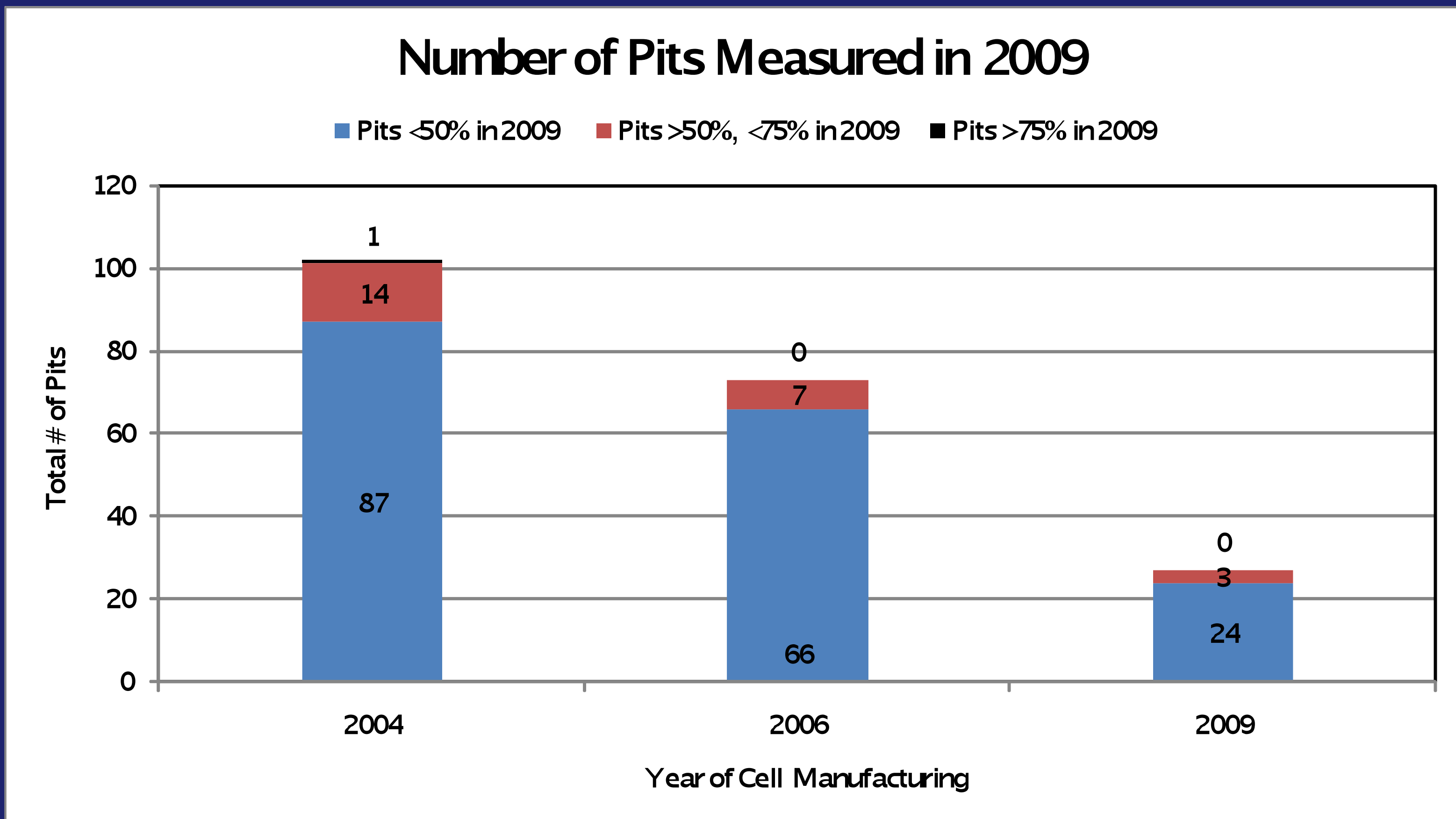
- Difficult to determine in change has occurred with a qualitative visual examination

Pitting Comparison



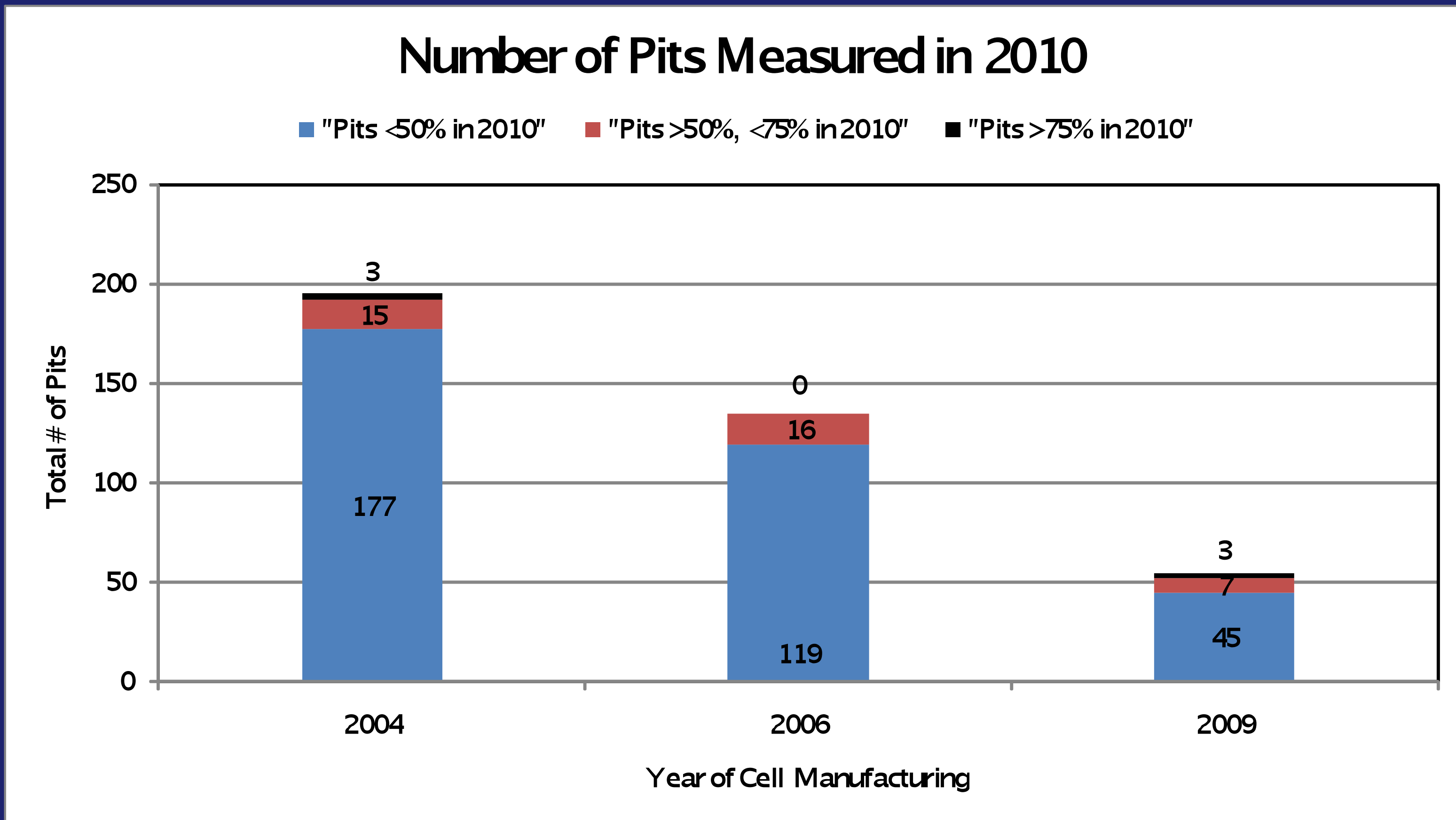
- **Small pores have become detectable via visual examination in 2010 scans due to pore growth as well as scan resolution enhancement**

Data from 2009 Measurement



- Data from top, middle, and base of cells combined

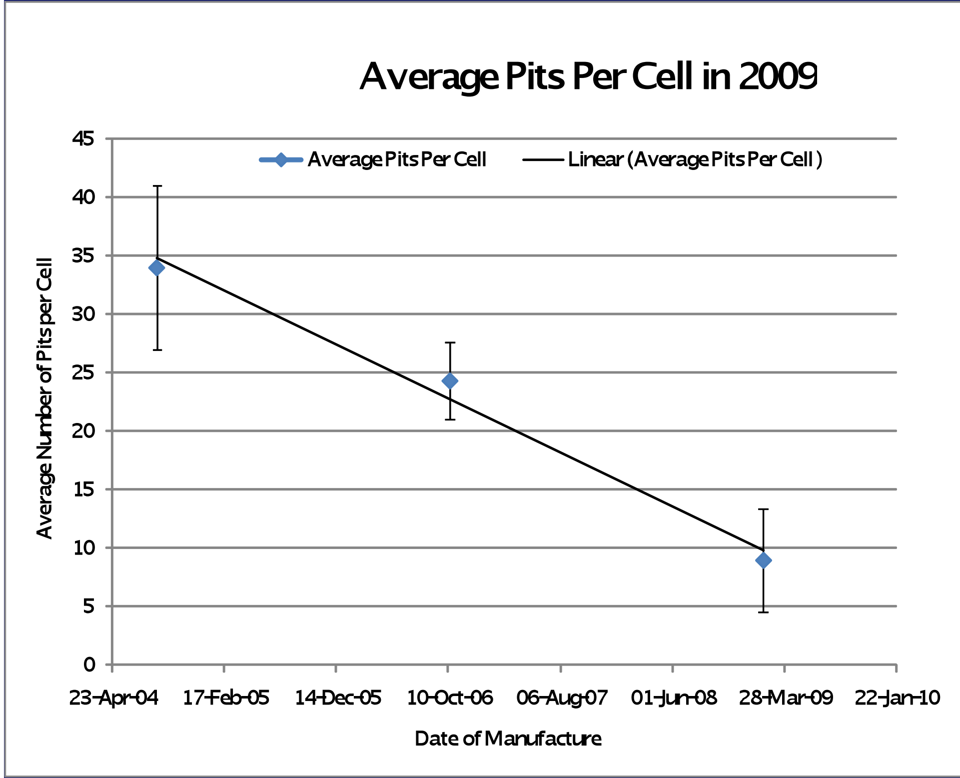
Data from 2010 Measurement

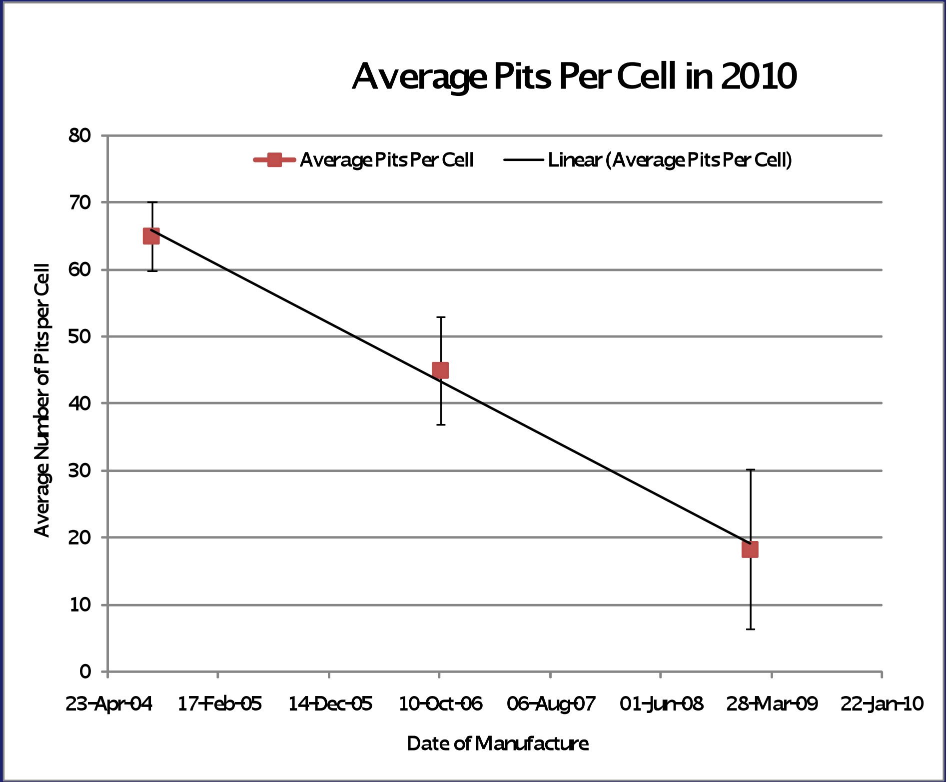


- Data from top, middle, and base of cells combined

Pit Growth

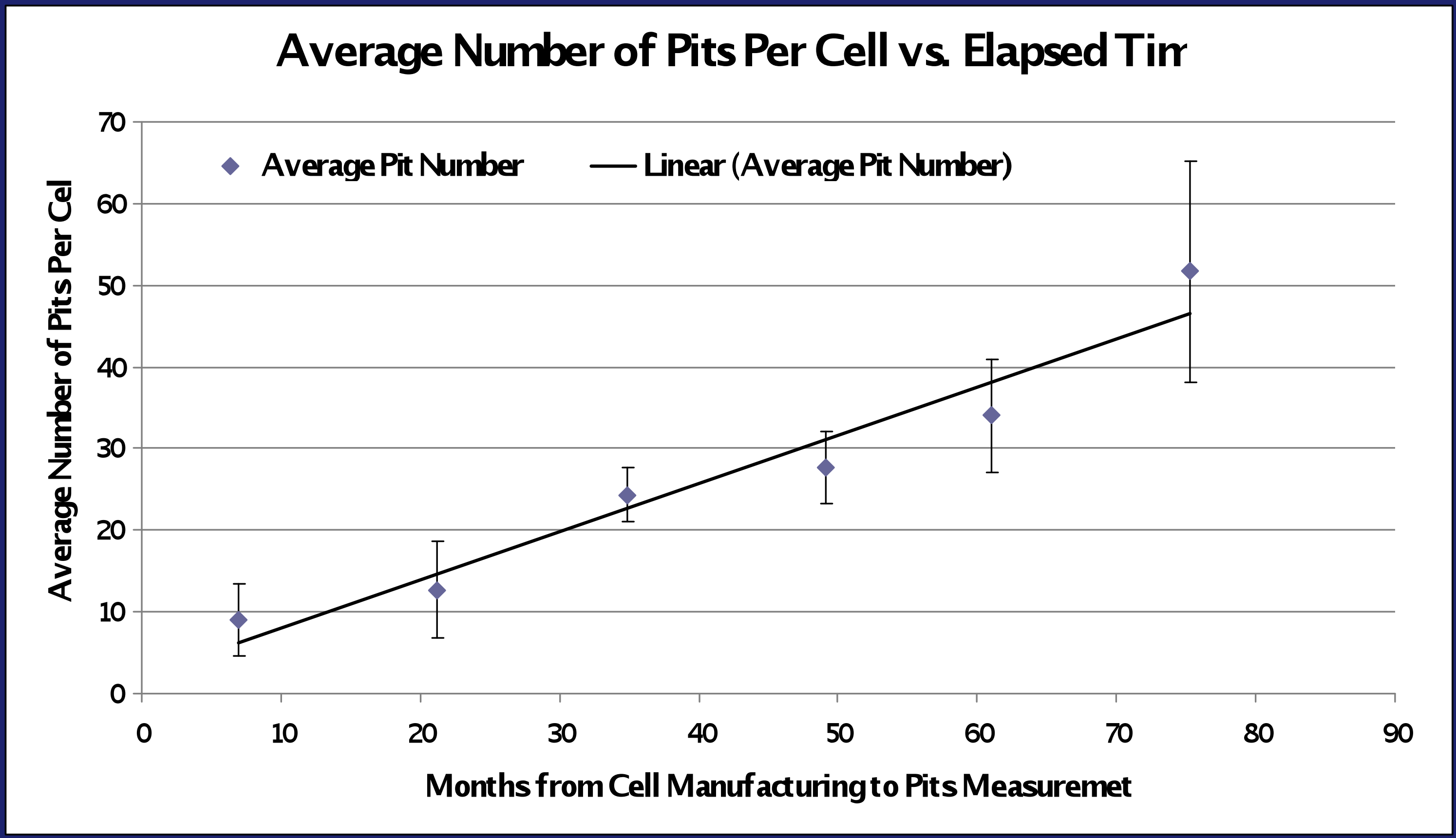
- Extent of corrosion correlated with age of the cell
  - Older cells exhibited more pits, and deeper pits
- Linear increase in average pits / cell vs date of manufacture is observed



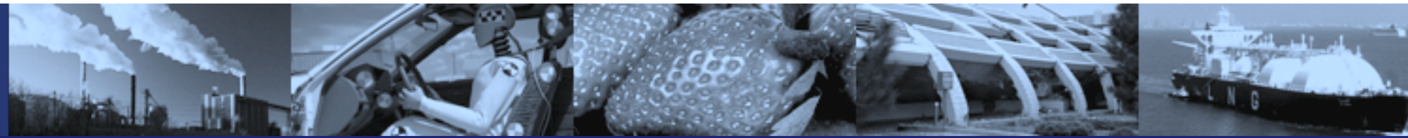


Pit Growth

- Linear increase in average pits / cell with elapsed time (2009 and 2010 data*)



*comparable scan resolutions are used



Conclusions

- **Linear increase in average pits / cell vs. date of manufacture is observed**
  - Extent of corrosion correlated with age of the cell
    - Older cells exhibited more pits, and deeper pits
    - Pits grew in number and depth in all cell years from 2009 to 2010 – new pits became visible in CT scans, and existing pits grew
  - Linear trend is observed:
    - Across cells from different date codes
    - From year to year in individual cells
- **Data from 2011 scans is currently being processed**