ACOUSTIC CHARACTERIZATION OF LEAD ACID BATTERIES

Ultrasonic Markers for Local State of Charge and State of Health

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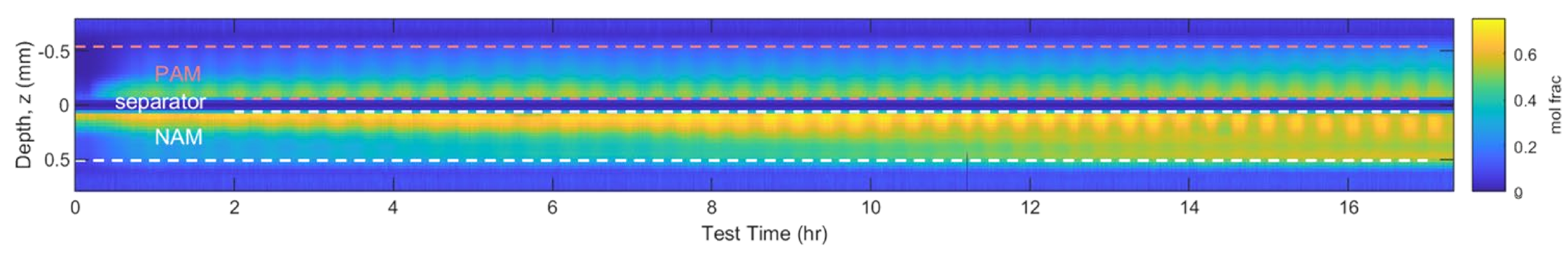
1. ABSTRACT

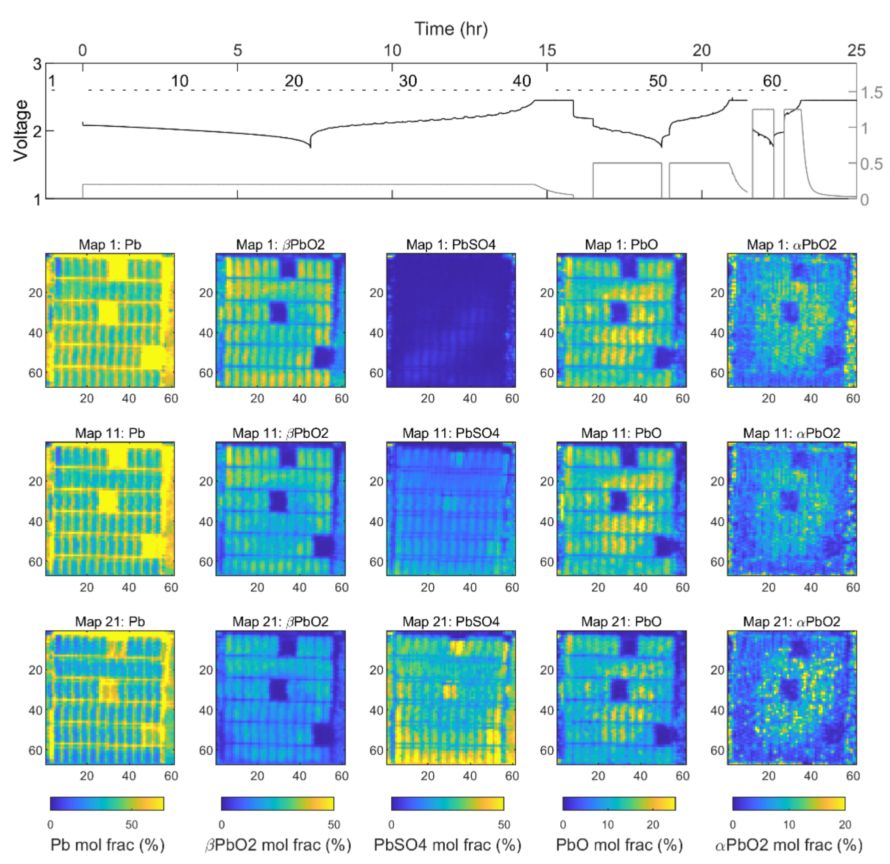
Lead acid batteries are prone to heterogeneous state of charge:

- High-rate cycling: local consumption of SO_4 and buildup of lead sulfate at interface with separator
- Low-rate cycling: electrolyte stratification and lead sulfate accumulation at bottom and sides of electrodes

This heterogeneity accumulates during cycling and can lead to common failure mechanisms. Previously we have used synchrotron x-ray methods to characterize species contributing to variation in state of charge (SOC) and state of health (SOH), but alternative, routine techniques are needed to achieve higher cycle life.



Example of x-ray depth profiling: note accumulation of $PbSO_4$ near the separator with extended, high rate PSOC cycling.

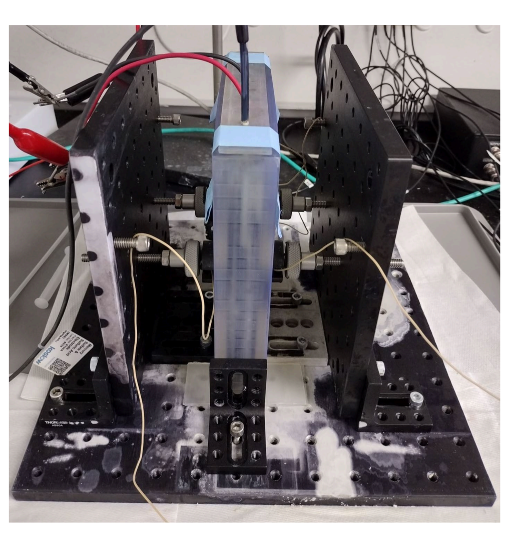


Accumulation of $PbSO_4$ at bottom and sides of VRLA cell at high depth-of-discharge (low-rate): an example of lateral heterogeneity.

Acoustics are now being used for characterization and quality control in a variety of applications, including Li-ion batteries. Initial results show that ultrasonics are highly sensitive to changes in speciation in lead acid batteries and could be used to correlate changes in electrode speciation with swings in acid specific gravity.

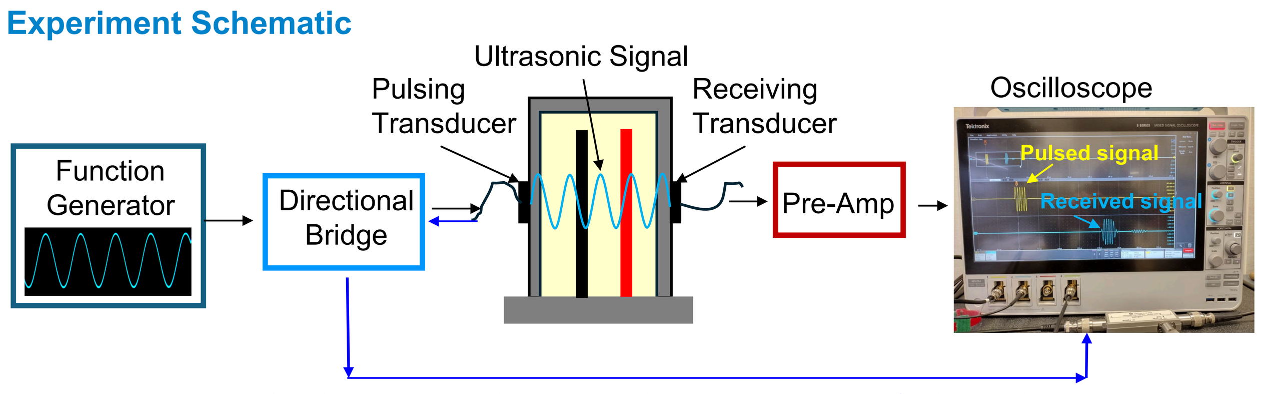
2. SETUP

Single-channel and multi-transducer arrays are currently used for Li-ion as a diagnostic during manufacture and cycling. Active and passive acoustics were also previously used at APS to study rock deformation and fracture. During APS Upgrade, we borrowed a two-channel setup from GSECARS to adapt ultrasonics to lead acid.



Above: Initial test cell. Transducers are used to generate and measure sound propagation through commercial electrodes

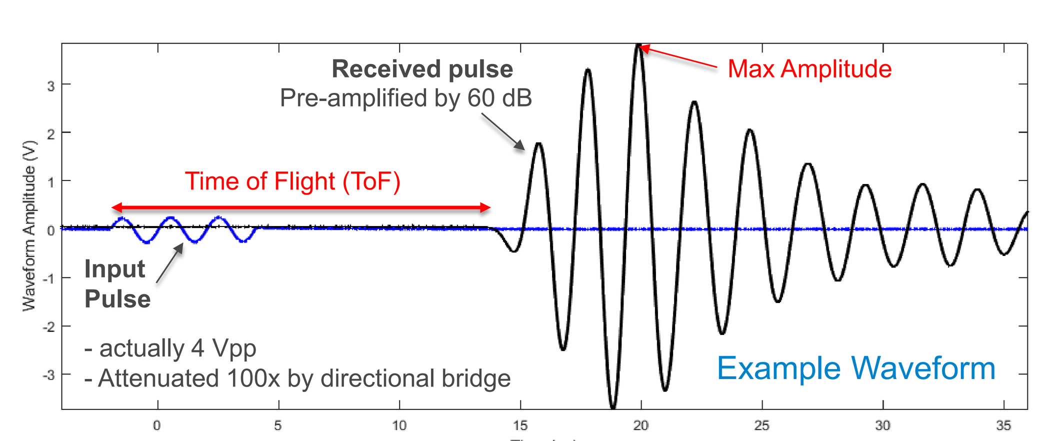
Experiment Schematic



Directional bridge distinguishes between incoming and reflected electrical signals. Allows for pre-amplification of pulsing sensor without affecting input pulse

- Up to 6.25 GHz sampling rate
- Can condition pulses -voltage, frequency, # of cycles, wave shape
- Can measure reflection and transmission (but porous electrodes have poor refection signal).

Most important parameters:
Signal Amplitude and **Time-of-Flight (ToF)**



3. MEASURING STATE OF CHARGE BY TIME-OF-FLIGHT (TOF)

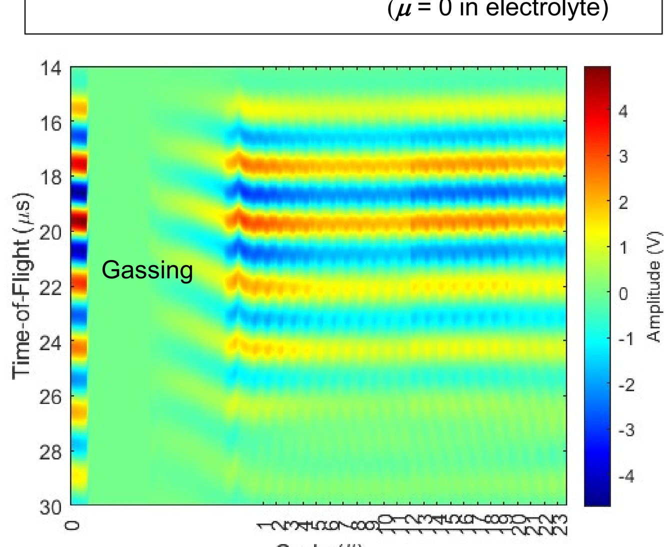
Initial studies using commercial AGM plates (Clarios) showed that bubbles greatly attenuate 500 kHz sound waves (lower frequency transducers will have better transmission).
Cycling in a partial state of charge window displays repeatable changes in time-of-flight and amplitude, but response was nonlinear.

P-wave velocity

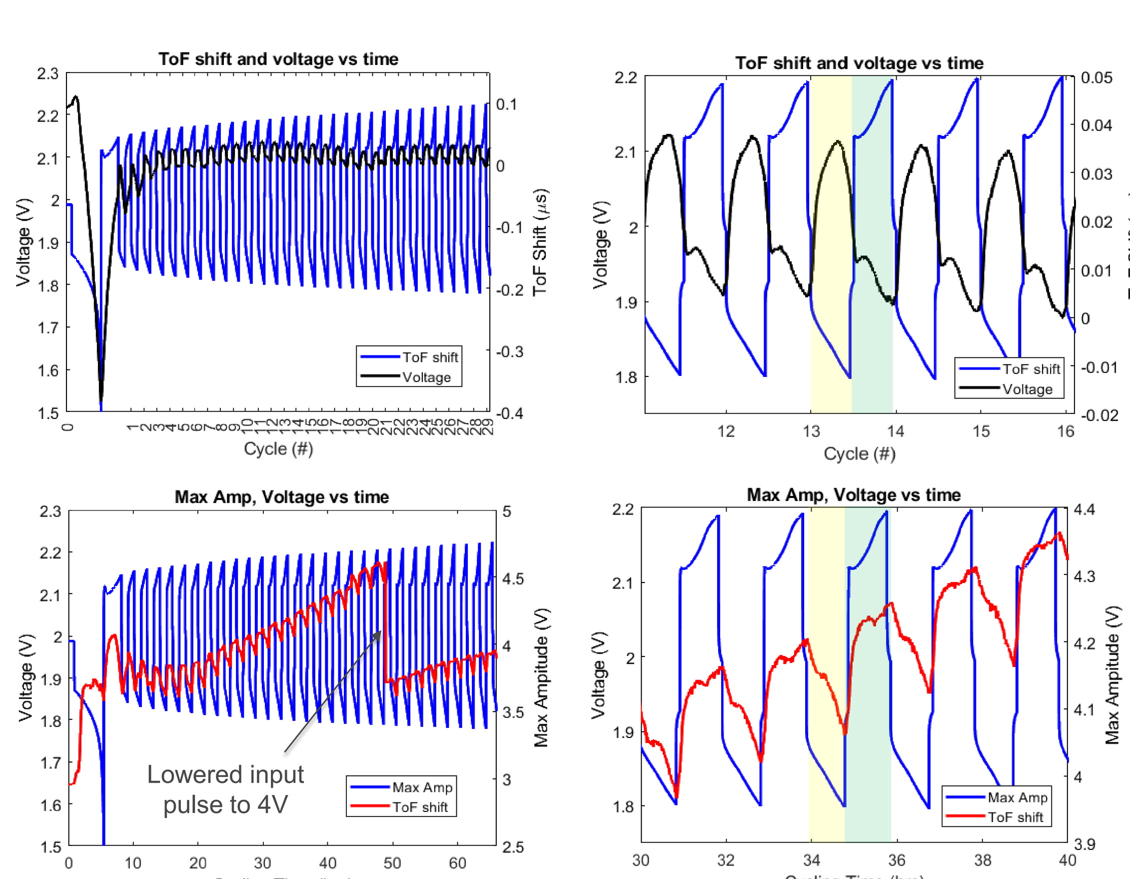
$$V_P = \sqrt{\frac{K + \frac{4}{3}\mu}{\rho}}$$

K = bulk modulus
μ = shear modulus
ρ = density

(μ = 0 in electrolyte)

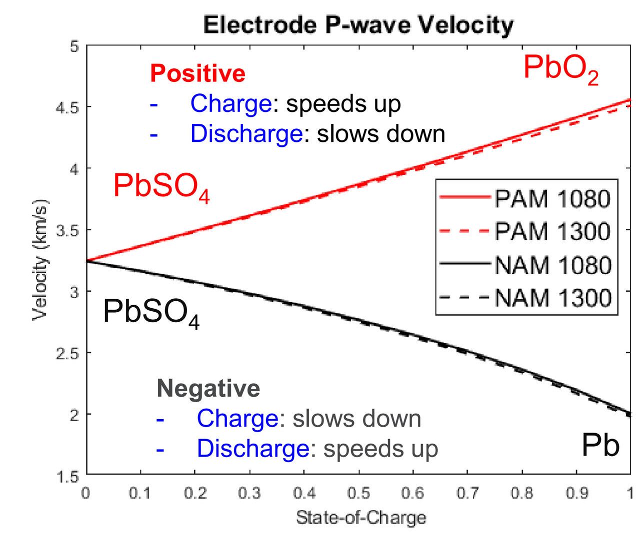


Heatmap of waveforms during 30-70%SOC cycling



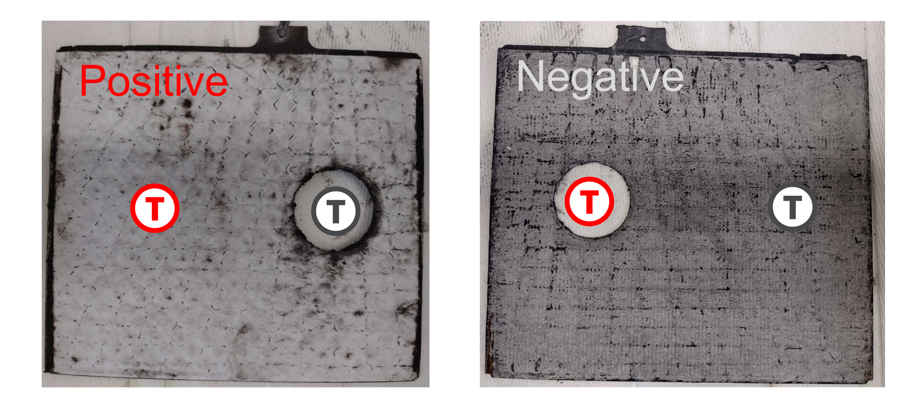
Change in ToF and amplitude during 40-60%SOC cycling

4. DIFFERENTIATING BETWEEN CONTRIBUTIONS FROM PAM VS NAM

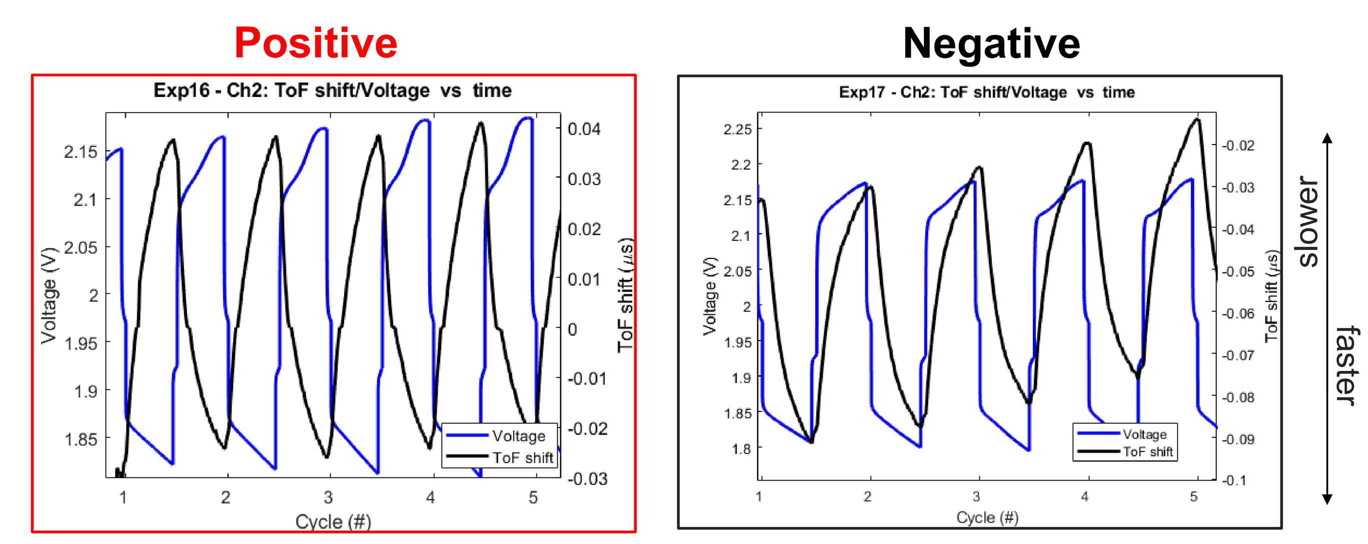


Theoretical P-wave velocity of PAM and NAM during charge/discharge

To better understand the response of each electrode, acoustic "windows" were made to isolate sound through positive and negative electrodes.



Electrode 'windows' were used to isolate individual plates.



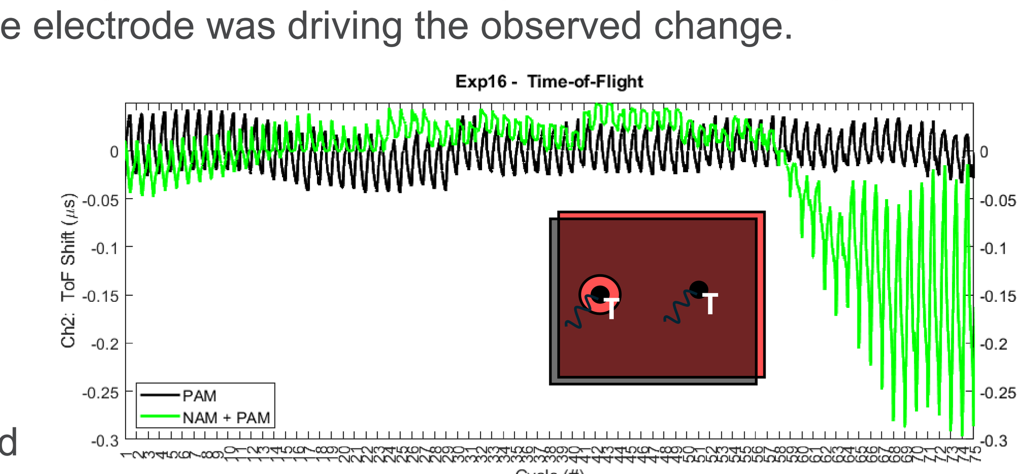
Positive electrode: sound speeds up during charge (PbO_2 is hard!)

Negative electrode: sound slows down during charge (Pb is soft!)

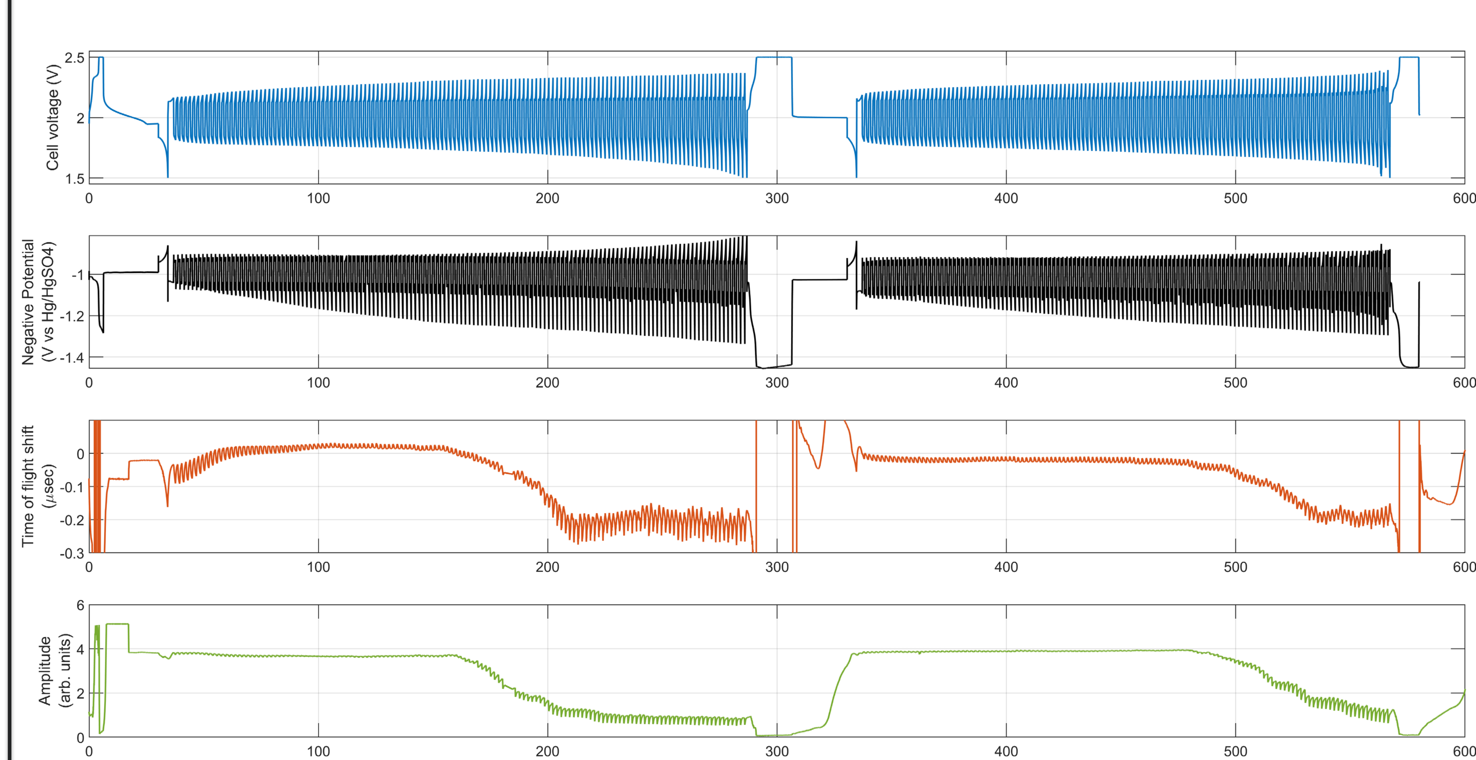
5. STATE OF HEALTH EXAMPLE NEGATIVE SULFATION DURING HIGH RATE PSOC CYCLING

Extended cycling was measured for 40-60%SOC @ 2C. This high-rate PSOC regime is known to lead to negative irreversibility due to surface sulfation. Initial tests (right) compared the ToF response of the cell vs. the positive. After ~50 cycles, the overall signal shifted dramatically. The lack of change in the positive electrode suggested that the negative electrode was driving the observed change.

Ultrasonics on just the negative electrode confirmed this effect. The decrease in ToF is consistent with the buildup of $PbSO_4$. The reduced amplitude is driven by hydrogen evolution, which occurs near the end of the charging step. While further modeling is necessary, these effects could be tied to the overall state-of-health of the battery and could be used to predict failure.

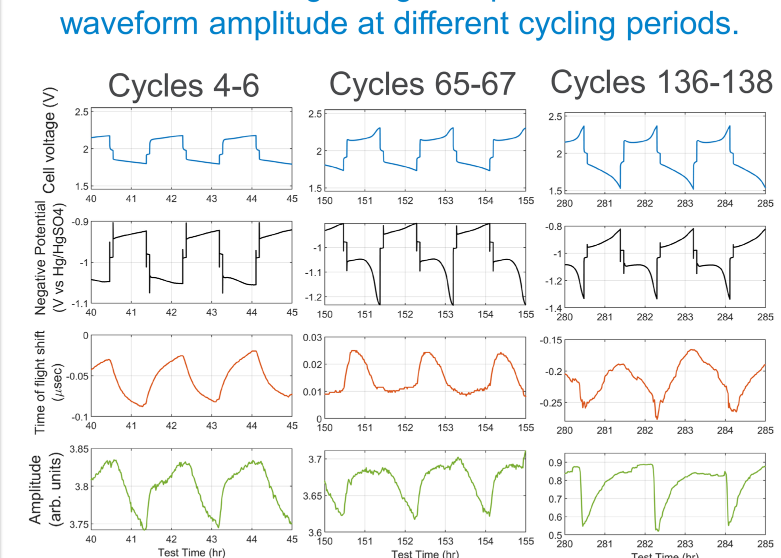


Measurements in 40-60%SOC window for cell and positive-only channels.

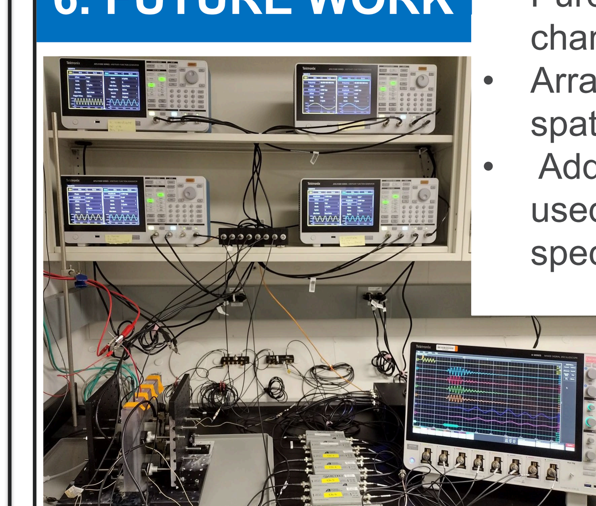


Comparison of cycling data with negative electrode ToF shifts and amplitude changes. The changes in acoustic data after ~100 cycles is consistent with negative sulfation.

Evolution of voltage, negative potential, ToF and waveform amplitude at different cycling periods.



6. FUTURE WORK



- Purchased new equipment with 8 channels and higher sampling rate
- Array of sensors to investigate spatial variation in SOC
- Additional channels will also be used to study stratification in acid specific gravity
- Testing sensors with different frequency response (Can we get through bubbles and more plates?)
- *In operando* studies coupled with x-ray diffraction at APS

7. CONCLUSIONS

- Ultrasonic characterization is a powerful tool for **diagnosing local state-of-charge** of individual electrodes.
  - Changes in density and elastic moduli drive changes in acoustic signals (ToF and signal amplitude) allowing us to estimate local SOC to an accuracy of ~1%.
  - Lateral variations can be measured by multiplexing the measurement
  - Depth dependent information may be encoded in the overall waveform
- Changes in composition, morphology, and gassing all are manifested in the acoustic signal. This information can be used to help **diagnose state-of-health**.
- Acoustics could be used for **feedback during cycling or quality control** during manufacture of lead acid batteries.

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