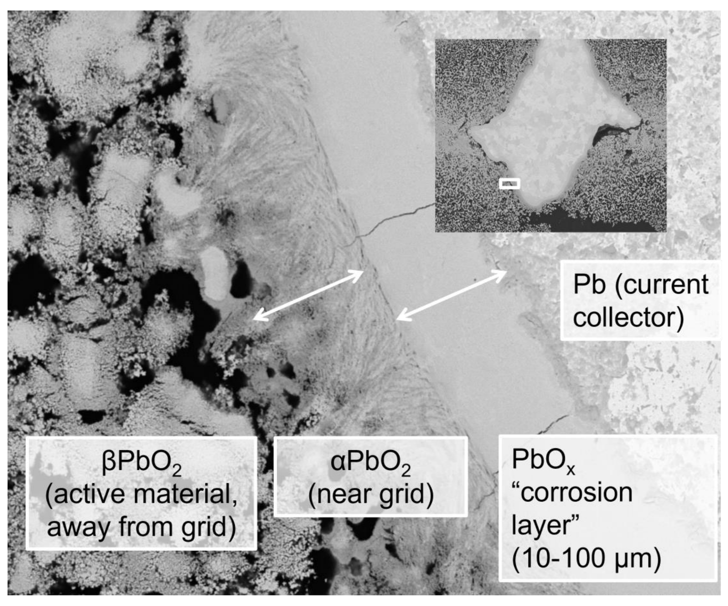
UNDERSTANDING THE STRUCTURE AND PROPERTIES OF THE NONSTOICHIOMETRIC LEAD DIOXIDE

Tiffany L. Kinnibrugh[1], Tim Fister[1], Xiaoping Wang[1], David Bazak[2], Ajay Karakoti[2], Vijayakumar Murugesan[2]
1. X-ray Science Division, Argonne National Laboratory 9700 S Cass Ave Lemont IL 60439,2. Pacific Northwest National Laboratory, Richland, WA 99354, USA

ABSTRACT

Nonstoichiometric lead oxides play a key role in the formation and cycling of the positive electrodes in a lead acid battery. These phases have been linked to the underutilization of the positive active material but also play a key role in the battery's cycle life, providing inter-particle adhesion and the connection to the underlying lead grid. Similar phases have previously been identified by mass loss or color change during thermal annealing of PbO_2 to PbO, suggesting that at least two intermediate PbO_x phases exist. Using multiple in situ analysis techniques (PXRD, XAS, XPS) and ex situ NMR measurements, the structural conversion and changes in the lead oxidation states were identified during this process. Isolation of the PbO_x phases enabled determination of Pb_3O_5 and Pb_2O_3 by diffraction and the first ^{207}Pb NMR measurement of these intermediates.

MOTIVATION

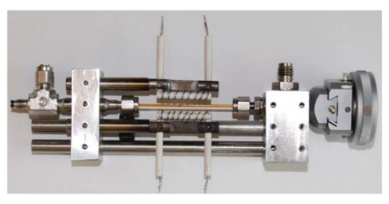


The composition of the PAM changes with formation conditions and cycling resulting in different compositions and thickness of the corrosion layer. The evolution of the nonstoichiometric lead dioxides in the corrosion layer, play a central role in the utilization of lead acid batteries[1,2].

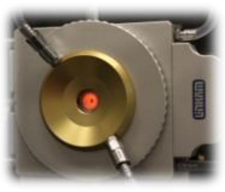
METHODS

- PXRD data was collected at 11-ID-B (in situ PXRD, flow cell furnace) and 11-BM (high resolution PXRD).
- In situ XAFS data was collected at 10-BM using the Linkam furnace.
- ^{207}Pb MAS-NMR was collected at PNNL (15 kHz MAS, Hahn Echo)
- In situ XPS/RGA was collected at PNNL

Flow cell furnace

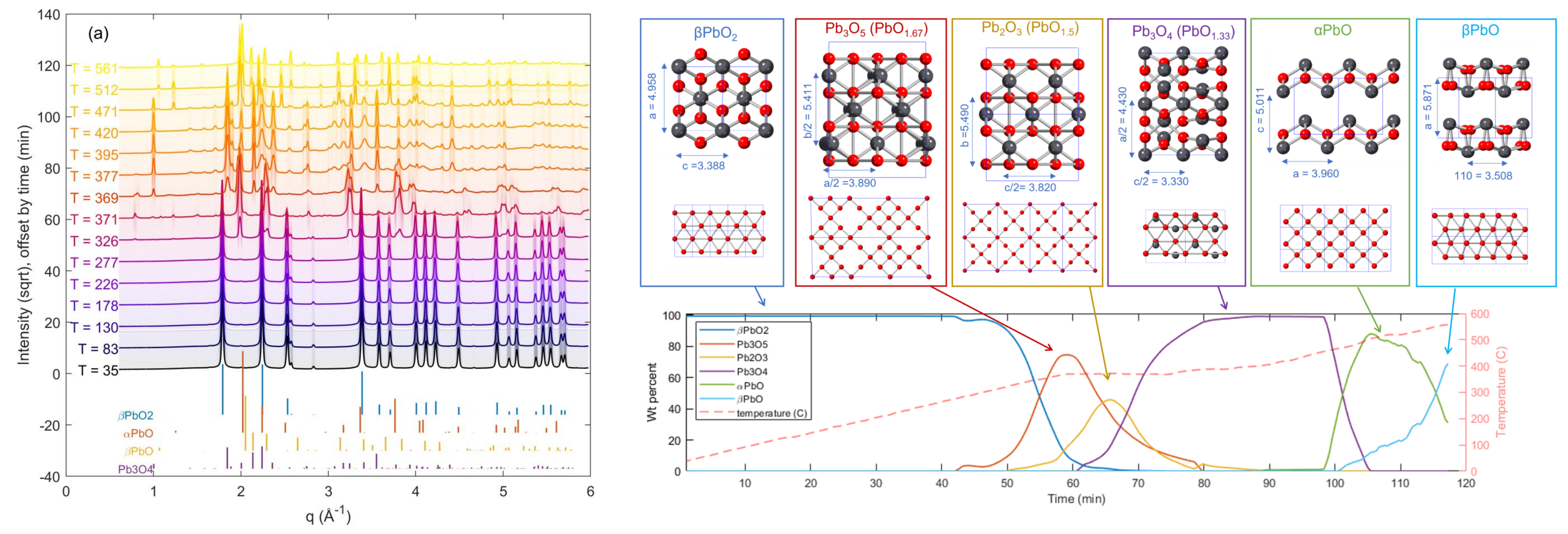


Linkam furnace



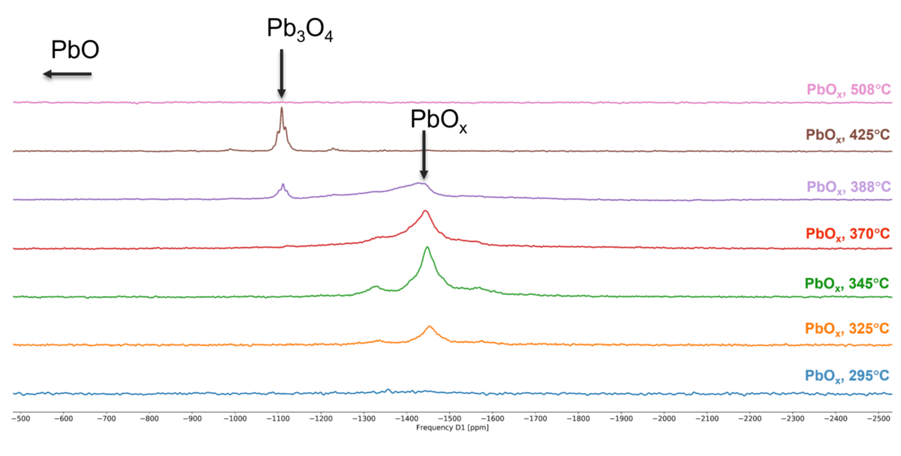
IN SITU PXRD STUDY FROM THE DECOMPOSITION OF PbO_2

The in situ PXRD study follows the decomposition of PbO_2 to PbO showing the structural evolution of the stable non-reversible lead oxide phases .



Loss of oxygen atoms drives the structural changes. Transition between nonreversible phases occur when the oxygen vacancy density reaches a maximum for the structure. Reversible nonstoichiometric phases (PbO_{2-x}, $PbO_{x-1,}$ and PbO_{1+x}) exist between these non-reversable stable lead oxides .

FIRST NMR STUDIES OF PbO_X PHASES

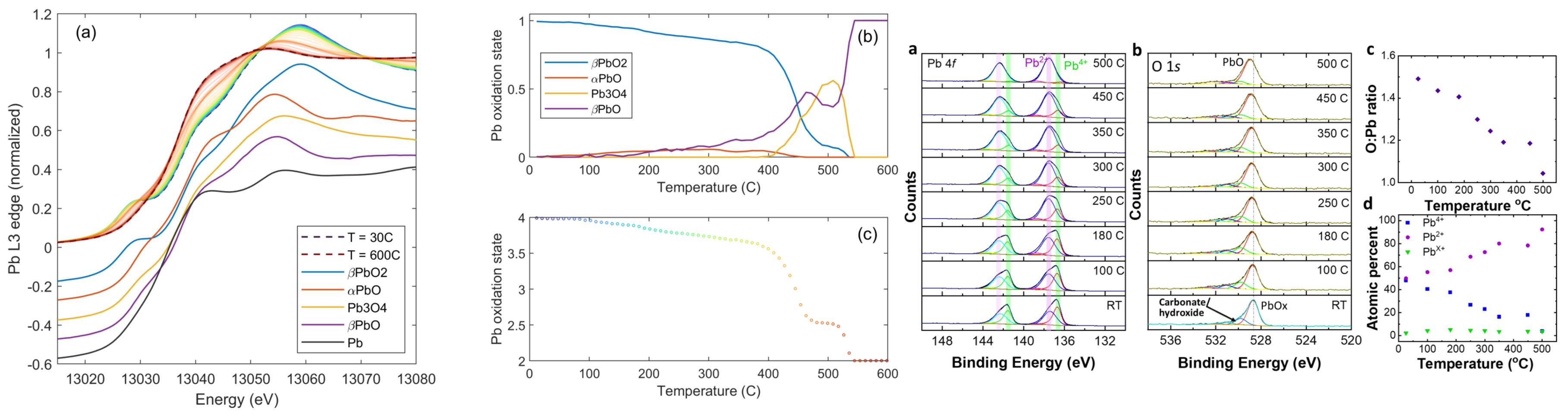


- The main PbO_x signal grows in as PbO_2 loses sufficient oxygen to become non-conductive (with the parent phase being unobservable by pulsed NMR).
- ^{207}Pb NMR technique enables the unique identification of the lead oxide phases.

EVOLUTION OF THE OXIDATION STATE AND STRUCTURE

XAFS and XPS techniques capture a continual change in oxidation state with temperature. The sensitivity of β-PbO_2 oxygen composition[3] at different oxygen partial pressures results in the different in compositional starting points for the two characterization techniques.

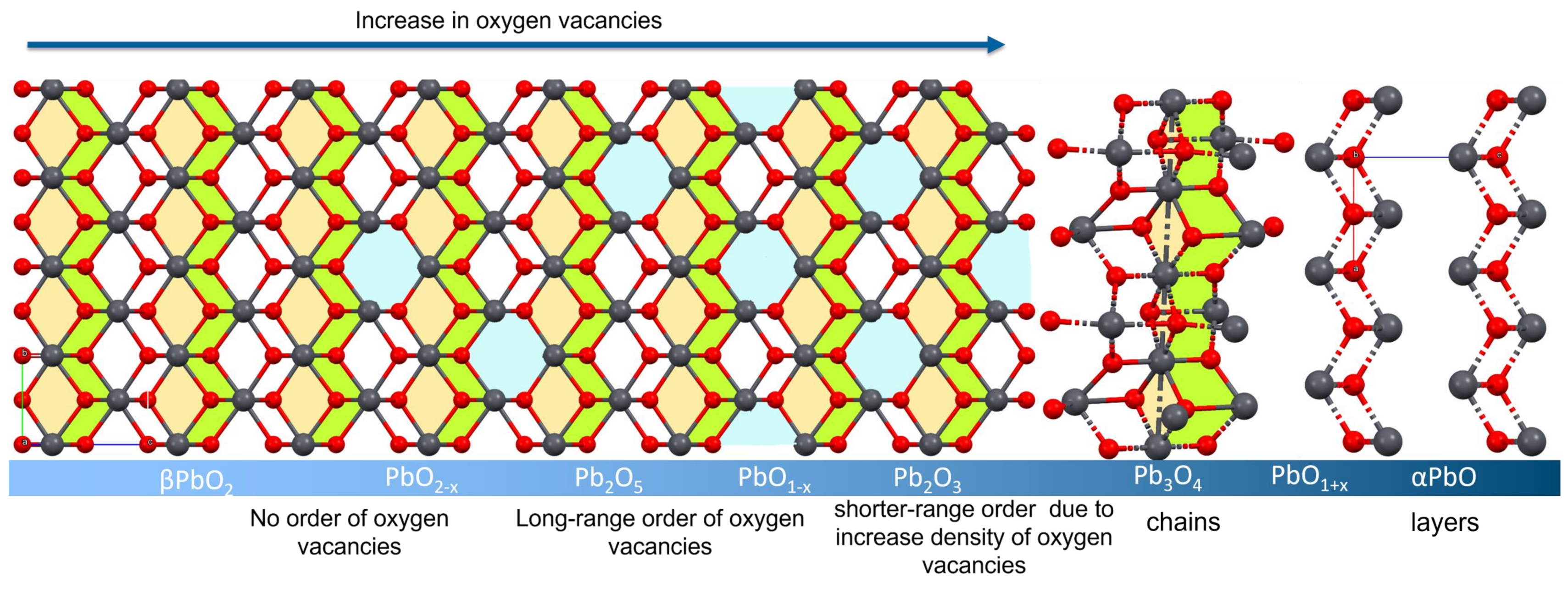
In situ XAFS *In situ* XPS



- Thermally-driven oxygen release starts at temperatures as low as 100 ^oC and progresses monotonically until reaching stochiometric PbO at 500^{o}C.
- Nonstoichiometric β-PbO_{2-x} compositions: The β-PbO_2 rutile structure is maintained till 300 ^oC as the Pb oxidation state decreases indicating oxygen vacancies in the structure.

CONCLUSIONS

- A comprehensive characterization of lead oxides and nonstoichiometric PbO_x phases from the thermal decomposition of PbO_2 has been carried out, laying the groundwork to quantify these phases in lead acid batteries.
- The Pb_2O_5 and Pb_2O_3 phases provide the key components to understand the structural transitions for the decomposition of PbO_2.
- Oxygen vacancies mobility and density control the structural transitions from PbO_2 to PbO.
- Reversible loss of oxygen result in the nonstoichiometric PbO_x phases that form between the stable lead oxide phases.



ACKNOWLEDGEMENTS

The authors would like to acknowledge financial support from the U.S. Department of Energy's (DOE's) Office of Electricity (OE) Energy Storage program (under Contract No. 57558). The X-ray data were collected at beamlines 11-ID-B, 11-BM and 10-BM at Advanced Photon Source (APS). Use of APS was supported by the U.S. DOE, Office of Science, Office of Basic Energy Sciences, under Contract DE-AC02-06CH11357 to UChicago Argonne, LLC as operator of Argonne National Laboratory.

REFERENCES

1. Moseley, P. T., Steele, I. M., T. Journal of Energy Storage 2023, 61, 106754.
2. Monahov, B., et al., Journal of Power Sources, 2003. 113(2): p. 281-292.
3. Pohl J.P. , Schlechtriemeng G. L., Journal of Applied Electrochemistry, 1984, 14 521-531