Advanced Technologies Reliant on the Properties of Lead

Timothy Ellis, Travis Hesterberg and Mark Drezdzon

Abstract Over the past several years, great strides have been made in the fundamental understanding of the processes at play in a lead (Pb) battery. Using modern analytical opportunities such as high energy X-rays available at the Advanced Photon Source at the Argonne National Laboratory and Scanning Laser Mass Spectrometry, new features of Pb battery processes are being uncovered. And though the Pb battery is the largest application of Pb in the modern economy, other technologies take advantage of the unique properties of Pb. New battery types such as Li/PbS and solar cells/thermoelectrics based on the perovskite structures on materials contain Pb which are emerging as important technologies. These applications not only represent new opportunities for Pb in the economy, but also will motivate the industries continued need to maintain its societal license to operate through continuous improvement to sustainability.

Keywords Batteries · Solar cells · Thermoelectric · Perovskite · Lithium ion

Introduction

RSR Technologies (RSRT), a member of the ECOBAT group, is a research and development company engaged in the non-ferrous smelting and refining industries. The company provides services to battery, mining, and smelting companies. RSR Technologies is focused on achieving innovations in material science to help companies develop batteries achieving the highest standards for health, safety, and the environment. The company provides R&D services to its worldwide secondary lead producers and is headquartered in Dallas, Texas.

RSRT has been engaged in lead alloy developed for the active material of Pb-acid batteries in three areas, active material utilization, dynamic charge acceptance, and cycle life. Batteries tested with the new alloy can approach the performance level of some lithium batteries, while keeping low costs and maintaining recyclability. With

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the aid of real-time X-ray imaging, technology has gone into commercial production following tests that show it doubles the cycling life of lead batteries.

Pb batteries offer a unique cross section of performance, cost, and sustainability. These advantages are accessed because of the very materials that make up lead batteries, mainly lead, plastic, and electrolyte. However, performance enhancement in lead batteries must keep pace with the added requirements demanded by an increasingly energy storage dependent world. RSRT's view of this issue is the best way to change how lead batteries perform is to start from the very beginning: lead.

Experimental Program for Batteries

The role of common elements found in lead alloys on the growth and crystal habit of the many species ($PbSO_4$ and PbO_2 for instance) in Pb batteries is not understood. Each element has an effect, and we are studying how each can benefit or limit the dynamic charge acceptance and cycle life of lead active material. For instance, electron microscopy has shown that the $PbSO_4$ crystal behavior can change drastically based on the elements present in the active material or electrolyte (Fig. 1).

The slow dissolution behavior of $PbSO_4$ is of key importance due to its negative effect on charge acceptance and cycle life. The focus on $PbSO_4$ crystal behavior has been fruitful, yielding a new alloy for higher performing lead battery active material, SUPERSOFT-HYCYCLE®. Trace elements in this alloy help govern the crystallization of $PbSO_4$ in the positive and negative electrode. Smaller $PbSO_4$ crystallites with a more easily dissolved crystal habit are formed using SUPERSOFT-HYCYCLE®. The

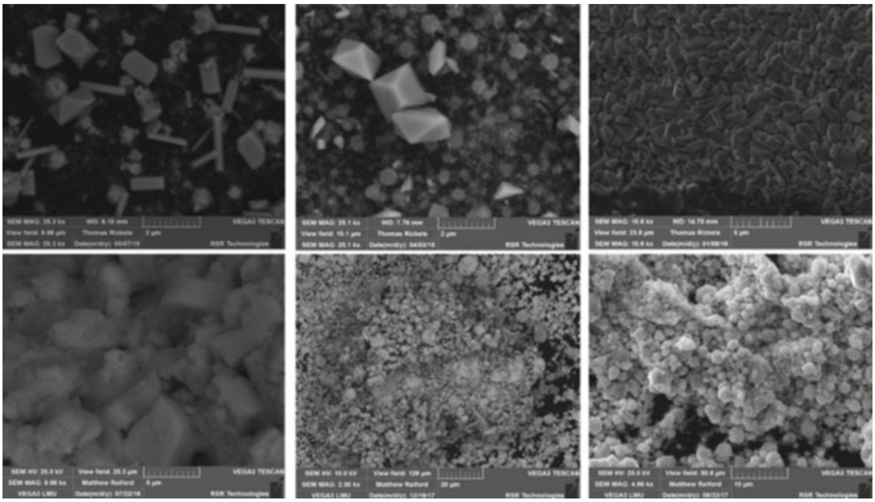

Fig. 1 $PbSO_4$ morphological change due to minor element contaminate variation

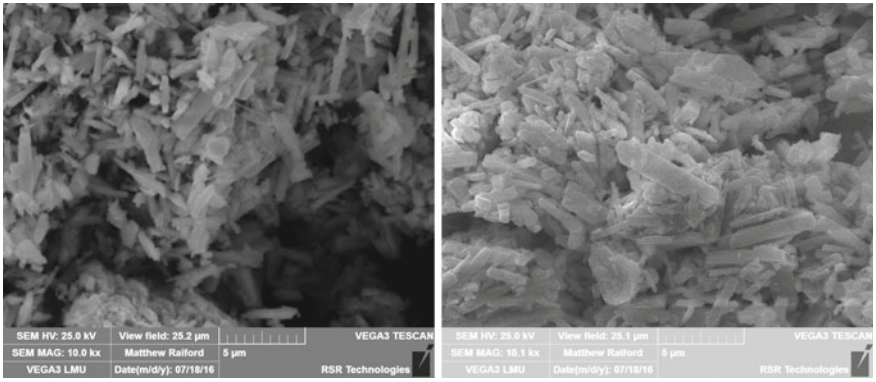

Fig. 2 Morphological differences between convention active material (left) and SUPERSOFT-HYCYCLE® micro-alloy active material (right)

faster dissolution in turn facilitates high charge acceptance and cycle life provided they remain in electrical contact within the active material (Fig. 2).

The breakthrough SUPERSOFT-HYCYCLE® material contains a carefully engineered suite of micro-alloying additions which have been shown to enhance the cycling and charge acceptance of the active material in a Pb-acid battery combination of antimony, arsenic, and lead. The effect of the micro-alloying addition on the micro-structure of the active material was determined with the use of the Advanced Photon Source at the Argonne National Laboratory (ANL), a synchrotron used in a wide range of scientific disciplines. This has allowed far more accurate analysis of dynamics of crystallization phenomena that occur in the battery during charge/discharge cycling, Fig. 3.

When the SUPERSOFT-HYCYCLE® alloy was placed against a "control" lead element typical of standard lead batteries, careful selection of antimony (~100 ppm) and arsenic (~100 ppm) micro-alloying additions and removal of specific contaminants were found to directly aid in changing the $PbSO_4$ to a more easily solubilized crystal form, thus prolonging battery life shown in Fig. 3. For reference, the control is oxide produced with standard 99.9% Pb, SUPERSOFT-ULTRA® is refined control material with Cu < 2 ppm, Ni < 1 ppm, and Te reduced to <0.3 ppm, and SUPERSOFT-HYCYCLE® as stated is micro-alloyed. This test was done under the EN 50342 Micro-Hybrid Test (MHT) protocol (Fig. 4).

An interesting new technology is the use of Pb based materials as anode in a lithium (Li) ion battery [1]. Li–Pb alloy anodes have a theoretical capacity advantage over the commonly used graphite, 582 mAh g^{-1} for Pb versus 372 mAh g^{-1} for graphite. Cycling at C/20 cycle of the electrodes reached 455 mAh g^{-1} using a 1.0 V cutoff close to the theoretical maximum which increases to 689 mAh g^{-1} for the 3.0 V cutoff. Research in this arena may lead to interesting new opportunities for Pb in electrochemical storage.

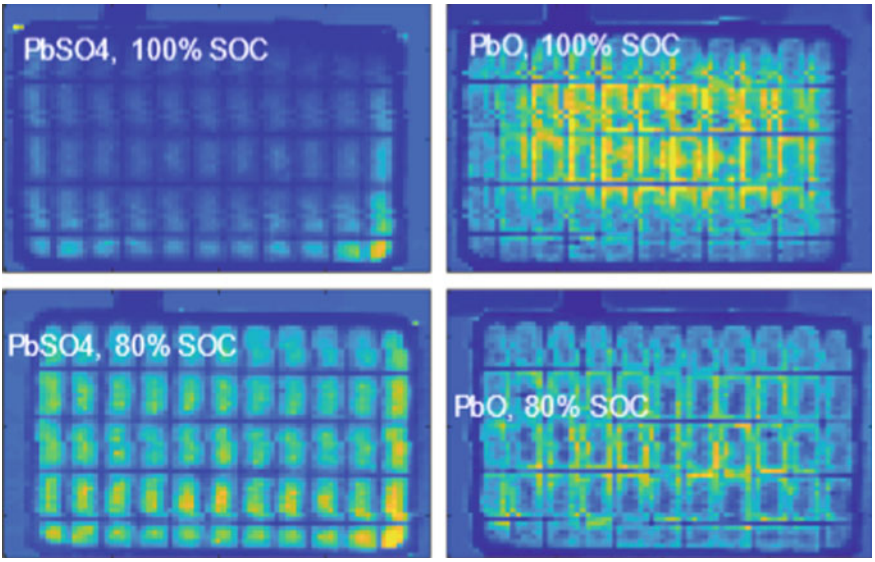

Fig. 3 X-ray diffraction imaging of Pb battery plates on cycling

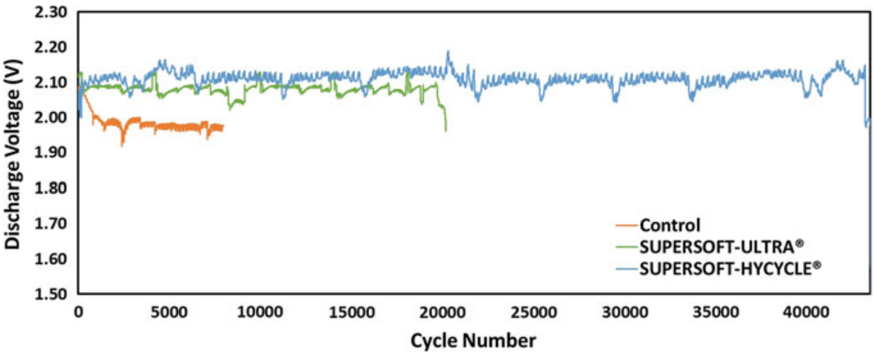

Fig. 4 Cycle life comparison of three active material Pb's

Applications of Pb in Energy Harvesting

One cannot over-emphasize the importance of the Pb based battery to the overall Pb market. And though Pb is still used for roofing, cable sheathing, electrowinning anodes, and other fabricated products, the 150-year history of the Pb battery is of paramount importance to the industry. However, several new applications have emerged based on the unique properties of the Pb atom with its relativistic effects which make it somewhat unique. In truth without relativity, lead would be expected to behave much like tin, but calculations indicate that 10 V of a 12 V are due to relativistic effects [2]. The relativistic properties of Pb have been used in the development of organic–inorganic hybrid perovskite materials to produce solar cells. Generally, these materials have a chemical formula of AMX_3, where A=Cs, CH_3NH_3; M=Pb, Sn; X=Halide, for example. One great attribute of this chemistry is the band gap 1.15–3.06 eV, and one great advantage of the methylammonium Pb iodide is its band gap 1.55–1.62 eV which is ideal for single junction photovoltaic solar cells [3, 4].

For quite a while, Pb chalcogenides, e.g. PbTe, PbSe, PbS, have been known to have interesting properties for thermoelectric device for heating or cooling [5]. Thermoelectrics are rated by their figure of merit, ZT, which helped determine the thermodynamic efficiency of the material. The value of ZT is a ratioing of the Seebeck coefficient which is the thermopower, *r* the electrical resistivity, *k* the thermoconductivity, and the temperature of the device *T*. Since these devices are band gap materials with the thermal gradient across them, which generates the electron/hole carrier distribution across the material. Carrier concentration may also be tuned by doping or alloying the materials to form molecular composites to tune them to the temperature range of operation. Of interest to Pb producers is that tellurium (Te), selenium (Se), and sulfur (S) are all very common elements in the smelters. Particularly in the case of Te and Se finding, an outlet for these elements may be interesting as modern specifications for Pb active materials in batteries remove these to very low levels.

Conclusion

The unique chemistry of Pb opens many new opportunities for technical innovation in the realm. As Pb has an already established recycling industry in the support of the drive for a circular materials economy, Pb will continue to be a vital part of the energy portfolio.

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