The lithiation and delithiation of PbS was studied. Below 1.0 V vs. Li/Li⁺, lithiation produced a series of Li–Pb alloys and Li2S. The Li–Pb alloys were reversibly lithiated and delithiated, but at a 1 C rate their capacity faded through 100 cycles. Above 1.5 V vs. Li/Li⁺, Li2S is electrooxidized to Li⁺ and soluble polysulfides, and the sulﬁde is irreversibly depleted.

Presently, 86% of lead consumed in the U.S. is used in conventional automotive lead-acid batteries. However, hybrid and electric vehicles do not use these conventional lead-acid batteries, and so as these alternative vehicles are more widely adopted, an excess lead production capacity is likely to develop. Because lead forms a series of lithium alloys, the excess lead could be diverted for use in a different type of battery chemistry such as lithium-ion batteries. Li–Pb alloy anodes have a theoretical capacity advantage over the commonly-used graphite, 582 mAh g⁻¹ for Pb vs. 372 mAh g⁻¹ for graphite. Prior research into Pb as an anode material for lithium-ion batteries, along with PbO⁺14 and other Pb-based materials,8–13 has not resulted in particularly attractive candidate materials. Men et al. achieved over 200 mAh g⁻¹ for 200 cycles with Pb-sandwiched nanoparticles.2 With spray-pyrolyzed PbO films, Martos et al. were able to attain capacities of nearly 500 mAh g⁻¹ for 40 cycles.3 Wang et al. reached a capacity of 250 mAh g⁻¹ after 50 cycles with Pb(NO₃)₂/C.14 Our previous study of PbTe nanoparticles showed that the combination of Li–Pb alloys and Li2Te formed during the first lithiation cycled stably at a PbS mass loading of approximately 0.5 mg cm⁻². A black precipitate appeared immediately. The resultant PbS particles were collected by centrifugation and washed twice with DI water and once with acetone. They were then dried under vacuum at 70 °C overnight.

X-Ray Diffraction (XRD) measurements were performed on a Spider R-axis diffractometer with a Cu Kα radiation source at 40 kV and 40 mA. Scanning Electron Microscopy (SEM) micrographs were obtained using a Hitachi S-5500 electron microscope.

Electrochemical measurements.— A slurry of PbS nanoparticles (60 wt%), polyacrylonitrile (20 wt%) binder, and Super P Li conduc-

Experimental

Synthesis and characterization.— All chemicals were purchased from Sigma-Aldrich, unless otherwise noted, and used as received. Based on a procedure by Zhang et al., PbS nanoparticles were prepared as follows.10 10 mmol of elemental sulfur was added to 100 mL of deionized water with magnetic stirring. 0.2 mol of NaOH was added in order to dissolve the sulfur. The solution was heated to ~80 °C to facilitate dissolution of the sulfur. The solution was dark yellow, but still transparent. A second solution was created by dissolving 10.2 mmol of Pb(Ac)₂ in 10 mL of DI water. The first solution was allowed to cool to room temperature, and the second solution was added all at once. A black precipitate appeared immediately. The resultant PbS particles were collected by centrifugation and washed twice with DI water and once with acetone. They were then dried under vacuum at 70 °C overnight.

The XRD spectrum of the synthesized black powder is shown in Fig. 1a, and it matches with the galena reference spectrum (JCPDS 01-077-0244), confirming that the material was phase-pure galena PbS. An SEM micrograph (Fig. 1b) shows that the synthesized particles were roughly 50–100 nm in size with a rough texture and nonspherical shape.

The first two cyclic voltammetry cycles for a PbS electrode are shown in Fig. 2, conducted at a scan rate of 0.1 mV s⁻¹. The pairs of reduction/oxidation peaks at potentials positive of 1.0 V vs. Li/Li⁺ correspond to sequential formation of polysulfides and Li2S according to Eqs. 1 and 2.18 The reduction/oxidation peaks negative of 1.0 V correspond to the sequential formation of Li–Pb alloys: LiPb, Li1.3Pb, Li1.4Pb, and Li1.5Pb.2,11 The overall lithium-lead alloying reaction is given in Eq. 3.

\[
PbS + (2/n) Li \leftrightarrow Pb + (1/n) Li2Sn \tag{1}
\]
\[
Pb + (1/n) Li2Sn + (2 - 2/n) Li \leftrightarrow Pb + Li2S \tag{2}
\]
\[
Pb + 4.5 Li + Li2S \leftrightarrow Li1.5Pb + Li3S \tag{3}
\]

The reduction peaks positive of 1.0 V vs. Li/Li⁺ shift toward a more positive potential after the first cycle, indicating an activation step in which there is an overpotential associated with nucleation during the initial lithiation.25,26 These peaks’ magnitudes also shrink going from cycle 1 to cycle 2 due to irreversible dissolution of lithium polysulfide, a problem common in sulfur and sulfur-based electrodes.25,28 The reduction peaks negative of 1.0 V vs. Li/Li⁺ do not shift potentials in going from cycle 1 to cycle 2, but the magnitude of the current density is larger for the first cycle due to the initial solid electrolyte interphase (SEI) layer formation at potentials lower than about 1.1 V.31 According to the reactions above, there are two different theoretical capacities depending on the voltage cutoff. Negative of 1.0 V the lead is lithiated/delithiated. With 4.5 Li ions reversibly reacting as in Eq. 3, the theoretical specific capacity is 504 mAh g⁻¹. If the upper cutoff is extended to 3.0 V and if the reaction remains reversible (i.e.

Results and Discussion

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sulfur is not irreversibly extracted from the electrode by formation of lithium polysulfides), then 2 more Li ions react as in Eqs. 1 and 2, providing a total theoretical specific capacity of 728 mAh g\(^{-1}\).

The results for galvanostatic cycling in the potential ranges 0.01 V ↔ 1.0 V and 0.01 V ↔ 3.0 V are shown in Fig. 3. The electrodes were first cycled at a C/20 rate for a single conditioning cycle, and then at a 1 C rate for 100 cycles. The electrodes approached their theoretical capacities on the C/20 cycle, reaching 455 mAh g\(^{-1}\) for the 1.0 V cutoff and 689 mAh g\(^{-1}\) for the 3.0 V cutoff. After 10 cycles, cycling to either 1 V or 3 V provided nearly identical capacities for the 11\(^{th}\) through 100\(^{th}\) cycles. Through the 20\(^{th}\) cycle a capacity of around 400 mAh g\(^{-1}\) was maintained. After the 20\(^{th}\) cycle the capacities faded, dropping to about 140 mAh g\(^{-1}\) at the 100\(^{th}\) cycle.

The capacity-voltage profiles in Fig. 4 reveal why cycling to the different cutoff potentials provided similar capacities after the 10\(^{th}\) cycle. The large plateau in cycle 2 at 1.4 V is associated with the reversible reaction of lithium with PbS, as in Eqs. 1 and 2. This plateau rapidly decreased throughout the first ten cycles (shown by the arrow in Fig. 4) and was nearly absent by the tenth cycle. Its fading is consistent with the loss of sulfur through lithium polysulfide dissolution.\(^ {30}\) After ten cycles, electrodes cycled only to 1.0 V contain both Pb and Li\(_2\)S, whereas those cycled to 3.0 V contain only Pb. The lower potential lead-lithium alloying features persist, irrespective of the presence or absence of Li\(_2\)S.

Fig. 5a shows that the 0.4–0.5 V reduction peak shifts toward lower potentials during cycling, and Fig. 5b tracks this peak as a function of cycle index. The peak’s potentials became more positive for both systems for the first few cycles, which is indicative of an activation step after which this lithium insertion reaction becomes more facile. The peak then begins to shift toward more negative potentials for both systems. Upon cycling only to 1.0 V the peak-potential downshift...
is much slower than upon cycling to 3.0 V. One possible reason the peak may shift negative during cycling is that the particles undergo massive expansion and contraction during cycling (323% in going from Pb to Li$_4$Pb),

experiencing significant strain and fracture. This destruction sometimes electrically isolates particle fragments, making them unavailable to participate in the lithiation reactions. When this occurs, the remaining electrically connected particles experience a higher current density (i.e., the same current is now being applied to a smaller mass). Higher current densities cause higher overpotentials and a negative shift of the reduction peak. Upon cycling to 3.0 V in our system, the 0.4–0.5 V reduction peak shifts negative more quickly and earlier in cycling, indicating a higher current density and thus a larger loss of active material via this mechanism. The lack of Li$_2$S to help prevent sintering in the system cycled to 3.0 V could explain its more rapid peak downshift.

Fig. 6 shows the accelerated loss of capacity as the C-rate is increased after a single C/20 conditioning cycle (not shown). The electrodes were sequentially cycled ten times each at rates of C/10, C/5, C/2, 1 C, 2 C, 1 C, and C/5. Capacity loss was observed for both the 1.0 V cutoff and the 3.0 V cutoff. For cycling to 1.0 V, the capacities were 469, 453, 395, 294, and 190 mAh g$^{-1}$ after 10 cycles at C/10, C/5, C/2, 1 C, and 2 C, respectively. For cycling to 3.0 V, the capacities were 461, 427, 343, 248, and 159 mAh g$^{-1}$. Upon returning to the slower C/5 rate, the electrode cycled to 1.0 V recovered more of its initial capacity than that cycled to 3.0 V.

Conclusions

The lithiation/delithiation of electrodes made with slurry-cast galena PbS particles was studied. When cycled in the 0.01–1.0 V range, the electrodes did not lose their sulfur; when cycled in the 0.01–3.0 V range, they lost their sulfur through lithium polysulfide dissolution. Following the dissolution of sulfur, the specific capacities were similar for 100 cycles whether the cutoff was 1.0 V or 3.0 V. The overpotentials were smaller when sulfur was retained, possibly due to contamination of the electrolyte and/or lithium counter electrode with dissolved polysulfides or from the Li$_2$S preventing electrochemical sintering of the Pb particles. At higher rates, the presence of sulfur provided for higher capacities of Li alloying and de-alloying with Pb. The PbS electrode was clearly inferior to the earlier-studied PbTe electrode, as its capacity faded substantially and rapidly through 100 cycles.

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