Communication—Stages in the Dynamic Electrochemical Lithiation of Lead

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The intermediates and final phase in the dynamic electrochemical lithiation of lead at ambient temperature were determined by ex situ XRD. The phases and their corresponding potentials matched well with coulometric data. The detected phases were LiPb, Li3Pb, Li5Pb, and Li3Pb.

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Lead has been studied as a potential anode material in lithium-ion batteries.1−13 Wang et al. chemically synthesized a series of Li-Pb alloys and measured the equilibrium electrochemical potentials of electrodes made thereof, proposing the intermediates shown in Eqs. 1−4 with a corresponding fully-lithiated phase of Li34Pb.14 However, Goward et al. reported that the most lithium-rich phase of lead is actually Li17Pb4 rather than Li34Pb. Additionally, X-ray diffraction (XRD) studies of the Li-Pb alloys formed from materials such as Pb(NO3)2/C,16 PbGeO3/graphene,17 and PbSe18 suggested different intermediate phases.

\[
Pb + Li \leftrightarrow LiPb \quad E^0 = 0.601 \text{ V} \quad [1]
\]

\[
LiPb + 2Li \leftrightarrow Li_3Pb \quad E^0 = 0.449 \text{ V} \quad [2]
\]

\[
Li_3Pb + 0.2Li \leftrightarrow Li_3Pb \quad E^0 = 0.374 \text{ V} \quad [3]
\]

\[
Li_{1.3}Pb + 1.3Li \leftrightarrow Li_4Pb \quad E^0 = 0.292 \text{ V} \quad [4]
\]

In the present study, the various Li-Pb phases were synthesized by dynamic electrochemical lithiation of pure Pb in 1M LiPF6 in 1:1 fluoroethylene carbonate (FEC)/diethyl carbonate (DEC, 1:1 w/w) at room temperature. The compositions of the Li-Pb phases were determined by ex situ XRD measurement and compared to the coulometric data. Notably, the most lithium-rich compound of the phase diagram, Li34Pb, was not reached during dynamic electrochemical lithiation.

A similar discovery was made about the lithiation of silicon, which had historically been thought to have a final lithiation phase of Li22Si5 but was later found to only have an electrochemically-reachable phase of Li17Si4.19

Experimental

Lead electrodes were prepared by mixing 83% of -100 mesh Pb powder (Alfa Aesar), 7% of polycrylonitrile (Sigma Aldrich, 150 kDa) binder, and 10% of Super P Li conductive carbon (Timcal) with enough dimethylformamide to form a viscous slurry, which was coated onto copper foil and dried in a vacuum oven at 120 °C for at least 6 h. The resulting composite film was punched into disks that formed the working electrodes of CR 2032 coin-type cells. Each electrode had an average Pb mass loading of 2.4−2.6 mg cm−2. Prior to assembly into coin cells, each electrode was soaked in a 1 wt% aqueous solution of disodium ethylenediaminetetraacetic acid (EDTA) for approximately five minutes to remove any surface oxide. The electrodes were then rinsed with deionized water and ethanol and immediately transferred into an argon-filled glove box to prevent re-oxidation. Cells were assembled with Li foil as the counter/reference electrode and Celgard 2400 polypropylene membrane as the separator. A solution of 1M LiPF6 in fluoroethylene carbonate (Solvay Fluor)/diethyl carbonate (1:1 w/w) was used as the electrolyte. Electrochemical measurements were performed on an Arbin BT 2143 multichannel battery testing system.

For the ex situ XRD, electrodes were discharged or charged to a particular potential vs. Li/Li+ in a series of coin cells. Open circuit potentials were measured after allowing cells to relax for 48 h. Each coin cell was opened in the glove box, and the electrode was extracted and rinsed lightly with DEC to remove any residual LiPF6 salt. The electrode was taped to a glass slide using air- and humidity-impermeable Kapton tape, and its XRD spectrum was measured using a Rigaku MiniFlex 600 diffractometer with a Cu Kα radiation source at 40 kV and 15 mA. To correct for height errors introduced by securing the electrode to the glass slide, all XRD spectra were shifted using the Cu (1 1 1) peak as an internal reference, aligning it to a 20 value of 43.342° (JCPDS Card #01-070-3039).20

Results and Discussion

Lead electrodes were lithiated and delithiated at a rate of 30 mA g⁻¹ (~C/15) to generate the voltage profiles seen in Figure 1. During lithiation, two flat voltage plateaus were seen at 0.55 V and 0.40 V vs.

![Figure 1](https://example.com/figure1.png)
Figure 2. Ex situ XRD spectra of lead electrodes extracted at the points indicated in Figure 1.

Li/Li$^+$, indicative of two-phase transitions. Below 0.30 V, a sloping voltage profile was seen. During delithiation, two sloping voltage plateaus were seen between 0.30 V and 0.45 V, and two flat voltage plateaus were seen at 0.47 V and 0.62 V.

The XRD spectra of the electrodes extracted at each of the red points in Figure 1 are shown in Figure 2. The points were chosen during delithiation in the voltage plateaus that were well-defined. The pristine electrode exhibited only the expected pure lead and copper substrate peaks. When lithiated to 5 mV (which relaxed to a potential of 0.24 V vs. Li/Li$^+$), two lead compounds were present: Li$_3$Pb and Li$_7$Pb$_2$; there was no Li$_{4.5}$Pb or Li$_{17}$Pb$_4$ detected. Therefore, the phase that was richest in lithium was Li$_7$Pb$_2$. One potential reason for the discrepancy between the presently observed phases and those of Wang et al. is that their Li-Pb compounds were synthesized chemically followed by electrochemical measurement of their potentials, all of which was performed at equilibrium conditions. Conversely, the compounds discussed in the present study were synthesized in situ under dynamic electrochemical conditions that may be more characteristic of those found in lithium-ion batteries. We believe that the different synthesis methods are the root cause of the disparate reaction sequences and observed phases.

When the electrodes were delithiated to 0.39 V and 0.46 V (which relaxed to potentials of 0.34 and 0.44 V, respectively), the observed phases were LiPb, Li$_7$Pb$_2$, and Pb, their ratio varying slightly at the two potentials. The mixed phases and unexpected early presence of Pb were most likely caused by the different sizes of the Pb particles used to make the electrodes. Tin particles of different size have been shown to lithiate/delithiate at different rates, leading to a non-uniform distribution of varying Li$_x$Sn phases.$^{21,22}$ In our Li-Pb system, the smallest particles may also delithiate completely before the larger particles, leading to the presence of phases that are not at their reversible potentials.

Upon further delithiation to 0.61 V, all of the Li$_7$Pb$_2$ was absent from the spectrum, leaving only LiPb and Pb in similar amounts. During the final delithiation to 1.00 V (which relaxed to a potential of 0.60 V), nearly all of the LiPb disappeared. The residual LiPb may remain because of either a) incomplete delithiation due to sluggish kinetics or b) fracturing of the particles caused by the massive volume change during delithiation/lithiation which leaves portions of particles electrically isolated and unavailable for further reaction. When lithiated to its final phase of Li$_7$Pb$_2$, the Pb volume increases by 177%.

Based on these XRD spectra, we propose the series of reactions for the lithiation of lead shown in Eqs. 5–8. In Figure 3, these reactions were incorporated into the charge/discharge curves from Figure 1, showing good agreement of our proposed steps with the experimental data both in terms of the potentials of the observed plateaus and the coulometrically-reached final phase. Using these reactions, the theoretical capacity of lead as a lithium-ion battery anode material is 453 mAh g$^{-1}$, and it has an average lithiation potential of 0.45 V vs. Li/Li$^+$.

Figure 3. Lithiation/delithiation potential profiles for a lead electrode cycled at a 30 mA g$^{-1}$ (~C/15) specific current. The green line shows the proposed (de)lithiation sequence.

$$\text{Pb} + \text{Li} \leftrightarrow \text{LiPb} \quad E^0 = 0.60 \text{ V} \quad [5]$$

$$\text{LiPb} + (5/3) \text{Li} \leftrightarrow \text{Li}_3\text{Pb}_3 \quad E^0 = 0.44 \text{ V} \quad [6]$$

$$\text{Li}_3\text{Pb}_3 + (1/3) \text{Li} \leftrightarrow \text{Li}_7\text{Pb}_2 \quad E^0 = 0.34 \text{ V} \quad [7]$$

$$\text{Li}_7\text{Pb}_2 + (1/2) \text{Li} \leftrightarrow \text{Li}_7\text{Pb}_2 \quad E^0 = 0.24 \text{ V} \quad [8]$$

**Summary**

The intermediates and end phase in the dynamic electrochemical lithiation of lead in 1 M LiPF$_6$ in 1:1 FEC/DEC (w/w) at room temperature have been re-determined using ex situ XRD measurements:
LiPb, Li3Pb3, Li2Pb, and Li7Pb2. From these phases and their relaxation potentials, a new set of reaction stages was proposed which agreed well with the electrochemical data. The resulting theoretical capacity of lead as a lithium-ion battery material is 453 mAh g⁻¹.

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