Electrochemical properties of lead oxide films obtained by spray pyrolysis as negative electrodes for lithium secondary batteries

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Abstract

Lead(II) oxides in bulk and thin film form were assessed as electrodes for lithium rechargeable batteries. Films were prepared by spray pyrolysis of aqueous solutions of Pb(CH\textsubscript{3}–COO\textsubscript{2})\textsubscript{2}·2H\textsubscript{2}O and deposited onto lead substrates at 175°C. Films heated at 250°C were found to consist of well-crystallized tetragonal PbO and evolve to the orthorhombic polymorph with prolonged heating. Cycling of the cells at a current density of 0.25 mA/cm\textsuperscript{2} over the range 1.0–0.0 V led to the formation of various Li\textsubscript{y}Pb alloys. Cells made from bulk oxides, whether tetragonal or orthorhombic, were found to exhibit poor performance (their capacity rapidly faded with cycling). By contrast, PbO film electrodes exhibited reversible capacity above 500 mA h/g beyond 40 cycles. The lead substrate must thus appreciably influence the electrochemical properties of the cell by facilitating adhesion of Li\textsubscript{y}Pb microcrystals to its surface, thereby favoring alloying/de-alloying processes. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The announcement by Fuji Photo Film Celltec. Co. (Japan) of its Stalion lithium ion cell [1] opened up new prospects in the search for anodic materials for lithium ion batteries. The Stalion cell employed a LiCoO\textsubscript{2} cathode but used an amorphous tin based composite oxide as anode instead of carbon. This outstanding discovery led to intensive research in the last few years aimed at elucidating the behavior of tin, tin-based intermetallics and composites in lithium cells [2,3]. Their improved gravimetric and volumetric specific capacities relative to carbon are a result of a reversible alloying reaction between Li and tin.

Other metals such as Pb, Al, Zn, Cd, Ag and Mg also alloy with Li [4–7]. Special attention was given to the use of some of these lithium-based alloys as alternatives to elemental lithium in the 1970s. Authors working on batteries with molten salt electrolytes that operated at temperatures above the melting point of lithium were especially interested in this possibility and reported the electrochemical characterization of various lithium alloys [8].
Today, the use of lithium alloys as anodic materials in Li-ion batteries is an interesting field of research on account of the promising results provided by tin-based compounds. Our group has focussed on the ability of lead to form lithium alloys. This paper reports on the potential of lead oxide as an anodic material. The toxic effects of this element can be avoided by strictly adhering to lead-acid battery collection and recycling regulations currently in force in most countries. This system was selected for two reasons, namely: (i) the low cost of lead; and (ii) the commercial significance of the lead-acid battery. A lead-based material usable in both lead-acid and Li-ion batteries would be attractive for manufacturers wishing to complement or replace the role of lead-acid batteries on its traditional market (viz. the automotive industry).

We used a spray pyrolysis method to prepare lead oxide electrodes. This method is a simple, inexpensive choice with the added advantage that it allows the deposition of large thick films and can be adapted for on-line manufacturing processes. This paper reports the characterization of PbO films using different physical techniques, and their performance in Li cells.

2. Experimental

In the proposed method, compressed air is used to atomize a solution containing the precursor compounds through a spray nozzle over the heated substrate [9]. Air is directly compressed from the atmosphere, using filters to remove water and oil waste in order to obtain films of large surface areas at a reduced cost. The precursor is pyrolyzed on the heated substrate. The substrate holder is equipped with thermocouples and heating elements the latter of which are monitored via a temperature controller. The substrate is moved forward and backward at a fixed frequency by an electronically controlled step motor. An aqueous solution of 0.05 M Pb(CH_3COO)_2·3H_2O is used as precursor. The solution is pumped into the air stream in the spray nozzle at a rate of 50 ml/h for a preset time by means of a syringe pump. Air stream of 140 l/h, measured under atmospheric conditions, is used to atomize the solution. High-purity lead sheets (Goodfellows, 0.25 mm thick) kept at 175°C, are used as substrates. The substrate size uniformly coated in this way is 2 cm long by 1 cm wide. X-ray diffraction (XRD) patterns were recorded on a Siemens D5000 X-ray diffractometer, using Cu-Kα radiation and a graphite monochromator. For identification purposes, intensities were collected at 0.04° intervals using 0.06 s per step. For the evaluation of broadening in the diffraction lines, intensities were recorded in the same scan step at 3.6 s per step. Scanning electron microscopy (SEM) images were obtained on a Jeol JMS 6400 microscope.

Electrochemical experiments were carried out by using two Swagelock-type electrode cells with lithium as counter and reference electrode. Two types of working electrodes (viz. thin films and powdered PbO samples) were tested. The thin film of active material deposited onto the Pb foil substrate was cut into 4 × 4 mm² squares. Powdered PbO pellets were prepared by presssing in an stainless steel grid ca. 3 mg of active material with acetylene black (10% wt.) and PTFE (5% wt.) at 4 ton. Lithium foil was cut into circles 7 mm in diameter. The electrolyte used was 1 M anhydrous LiPF₆ (supplied by Strem Chem.) in a 1:1 mixture of ethylenecarbonate (EC) and dimethylcarbonate (DMC) (both supplied by Merck). Cells were assembled under an argon atmosphere in an M-Braun glove-box the water content of which was less than 3 ppm. Electrochemical measurements were made with a MacPile II potentiosstat-galvanostat. Galvanostatic charge/discharge curves were obtained at a current density of 0.25 mA/cm². Potentiostatic intermittent titration techniques (PITT) were also applied. Cells were allowed to initially relax until the condition ΔV/Δt < 2 mV/h was attained. Spectra were recorded at 10 mV/h. Diffusion coefficients (D) were obtained from these PITT measurements, using the current–time relationship. At long times, the current decays exponentially to zero and, provided the condition t ≫ δ²/D (δ, cathode thickness) is fulfilled, D can be determined from the slope of a log i versus time plot since

$$i(t) = 2QDδ² \exp\left(-\pi²Dt/4δ²\right)$$

where Q is the total charge passed through the cell. In order to ensure reproducibility in the measurements, all were made at least in duplicate.

3. Results and discussion

One of the aims of this work was to obtain highly pure PbO coatings with a well-tailored morphology. To this end, an aqueous solution of Pb(CH_3–COO)_2·3H_2O was used as precursor. By using carefully controlled times and substrate temperatures, uniform prism-like particles of also uniform size (about 10 µm wide) were deposited (see Fig. 1a). The XRD patterns reveal that, at the selected temperature (175°C), the films are crystalline and identified as undecomposed lead acetate (Fig. 2a). A post-deposition heat treatment at 250°C for 4 h, (hereafter named film A), resulted in the formation of well-crystallized tetragonal PbO (Fig. 2b). Although particle size was significantly reduced from about 10 to 1 µm, the films retained a highly homogeneous size distribution. Moreover, particle shape underwent significant alterations and changes to pseudo-octahedral forms, as shown by the micrograph of Fig. 1b. Increasing the heating time to 24 h led to film B, which
essentially preserved the particle shape of film A but had a slightly greater particle size: ca. 3 μm (Fig. 1c). However, the diffraction spectrum exhibited new peaks at 15.14, 29.20, 32.72 and 37.96° (2θ) that can be assigned to the orthorhombic polymorph, highly oriented along the 00l direction (Fig. 2c). The retention of the initial particle shape resulted from the topotactic nature of this phase transition. No peak corresponding to the underlying Pb-substrate was detected in the course of these thermal treatments. This is consistent with uniform coating of the whole substrate surface by PbO (the film thickness as estimated from the SEM images was about 10 μm). The X-ray photoelectron spectroscopy analysis of the films revealed a symmetric Pb 4f photoemission signal (binding energy 138.9 eV Pb 4f7/2; 143.7 eV Pb 4f5/2), as expected for PbO.

Before the electrochemical behaviour of the films is described, it may be highly illustrative to comment on the behaviour of bulk massicot and litharge in lithium cells, taking into account that both polymorphs were present in the films. The influence of PbO polymorphism on the Li/PbO cells was examined in experiments where cells containing pure commercial PbO (tetragonal, litharge) and PbO (orthorhombic, massicot) as positive electrodes were subjected to a deep discharge and subsequent cycling over the range 1.0–0.0 V. The galvanostatic discharge curves for the PbO polymorphs are compared in Fig. 3A. The orthorhombic form profile is essentially consistent with previous results of Bicelli et al. [11] over the potential range 3.0–0.5 V; also the amount of lithium inserted into PbO during this reaction is roughly the same as that of Li predicted by the reaction

\[ 2\text{Li} + \text{PbO} \rightarrow \text{Pb} + \text{Li}_2\text{O} \quad (2) \]

This is followed by various steps that can be better visualized by analysing the differential specific capacity plots as discussed below. The discharge profile for the tetragonal form exhibits the same features; the plateau accounting for reaction (2), however, is not so well defined as that for the orthorhombic form. The differential specific capacity curves of Fig. 3 exhibit four peaks at ca. 1.5, 1.3 (less symmetric for the tetragonal form), 0.55 and 0.38 V. The origin of the peak at about 1.5 V is unclear. A short quasi-plateau near the initial potential drop was previously reported [11] that was ascribed to the presence of PbO₂ impurities, otherwise not detected in our polymorphs. The low voltage peaks obtained can be ascribed to electrochemical alloying of Li with Pb if one assumes the absence of side reactions such as decomposition of the electrolyte. Based on this assumption, Li₄₅Pb and Li₄Pb alloys will be formed at the end of the first few electrochemical discharges for the orthorhombic and tetragonal forms, respectively. In fact, a number of Li–Pb alloys have so far been reported. Thus, Pearson [12] suggested the presence of at least six intermetallic compounds (LiPb; Li₁.₅Pb; Li₂Pb; Li₃.₃₃Pb; Li₃.₅Pb and Li₄Pb). On the other hand, Huggins et al. [5] described the system in terms of composition ranges, LiₚPb, and their respective voltage plateaux. This author identified four potential plateaux at 0.601, 0.449, 0.374 and 0.292 V over the composition range 0 < y < 4.5. The curve of Fig. 3 exhibits only two of such plateaux at voltages similar to those reported

Fig. 1. SEM images of the precursor deposited at 175°C, before (a) and after heating at 250°C for 4 (b) and 24 (c) h.

by Huggins et al. [5]. Kinetic contributions inherent in the galvanostatic procedure used might account for the discrepancy. In fact, better agreement was observed in PITT experiments. The measurements for both polymorphs are shown in Fig. 3B. As expected, there was a close relationship between the two profiles. Below 0.7 V, two well-defined peaks at 0.50 and 0.35 V, in addition to a weaker one at 0.25 V, are observed. These peaks must correspond to the last three plateaux reported by Huggins et al. [5]. The plateau at 0.601 V is difficult to confirm from PITT measurements. Also, the peak in the differential capacity plots at 1.3 V, which is essentially ascribed to the conversion of Pb(II) into Pb(0), is split into at least three (at 1.35, 1.15 and 0.9 V). This suggests that the apparently simple reduction process defined by reaction (2) indeed occurs through a more complex mechanism. In this context, the explanation proposed by Ohzuku et al. [13] regarding the conversion of Pb(II) to Pb(0) through Pb(I) as intermediate, although poorly documented, cannot be discarded.

The cycling properties of both polymorphs over the voltage range 0.0–1.0 V are illustrated in Fig. 4. The first anodic wave corresponding to both polymorphs (Fig. 4a,b), exhibits four peaks at 0.16, 0.39, 0.48 and 0.64 V. Only 2.5 Li+ ions can be removed in this charging process; the electrode composition at 1.0 V must range from LiPb to Li2.5Pb, with a greater proportion of the latter. Although the dealloying process is incomplete, its reversibility is apparent from the pres-
ence of the four peaks at 0.53, 0.38, 0.18 and 0.05 V in the cathodic wave. By analysing the faradaic composition of the charge–discharge curves and, consistently with the potential plateaux designed by Huggins et al. [5] for the formation of Li$_x$Pb alloys, the first two cathodic peaks must correspond to the formation of Li$_{2.5-3.0}$Pb and Li$_{3.2}$Pb alloys. More difficult is the assignation of the last two cathodic peaks, which must correspond to Li$_x$Pb alloys with higher lithium content (Li$_{3.5}$Pb, Li$_{4}$Pb and Li$_{4.5}$Pb).

Both polymorphs exhibit similar changes in their anodic and cathodic wave profiles. The multiple alloying/de-alloying processes undergone by the electrodes result in a rapid decrease in the peaks at 0.64 (anodic wave) and 0.53 V (cathodic wave), which reveals the difficulty of returning from high to low lithium alloys. Both cells exhibited a poor capacity (see Fig. 4c) that is worse for the orthorhombic polymorph. In fact, the intensity of the two main peaks for this polymorph decreased fast relative to the litharge; by the tenth cycle, the specific capacity of the cell fell below 40 A h/kg. By contrast, the litharge cell exhibited a better capacity retention and, although this also faded on cycling, the loss was less marked (110 A h/kg at the tenth cycle).

The way changes in PbO polymorphs that affect the capacity retention can be better understood by considering two complementary facts, namely: (i) the crystalline state of PbO as examined from broadening in the diffraction lines; and (ii) the Li chemical diffusion coefficients obtained from PITT measurements.

Crystallinity was analysed from the three strongest peaks for each polymorph [viz. (111), (002) and (200) for massicot, and (101), (110) and (002) for litharge]. In

![Fig. 3. First-discharge galvanostatic (A) and potentiostatic (B) curves for Li/PbO [orthorhombic (a) and tetragonal (b) polymorph] cells. Inset: differential capacity plots for Li/PbO [orthorhombic (a) and tetragonal (b) polymorph] cells.](image-url)
Fig. 4. Differential capacity plots [orthorhombic (a) and tetragonal (b) polymorph] and (c) changes in specific capacity [orthorhombic (●) and tetragonal (○) polymorph] for Li/PbO cells cycled over the range 0.0–1.0 V.

order to resolve the crystallite size and distortion components, the expression for the integral breadth method was used in the following form [14]:

\[
(\delta 2\theta)^2 = 16\langle \varepsilon^2 \rangle \sin^2 \theta + k^2 \lambda^2 / L^2
\]

where \((\delta 2\theta)\) is the integral breadth after correction for the instrumental broadening obtained from a highly crystalline \(x\)-quartz, \(\langle \varepsilon \rangle\) denotes local strains (defined as \(\Delta d/d, d\) being the interplane spacing), \(L\) is crystallite size and \(k\) is a near-unity constant related to crystal shape. Local strains and crystallite size can be calculated from the slope and intercept, respectively. The plots of Eq. (3) for the different samples studied are shown in Fig. 5. One common feature of these plots is a near-zero slope. Both polymorphs therefore possess too low a microstrain content to be detected. However, commercial oxides exhibit a greater crystallite size and massicot tends to possess a greater crystallite size than litharge, particularly in commercial oxides (see Table 1). The lower crystallinity of litharge may account for an increased capacity retention, similarly to related systems such as SnO and SnO\(_2\) in lithium cells [15,16].

Evaluating diffusion coefficients from Eq. (1) has the inherent problem that this equation is based on a semi-infinite linear diffusion model, so the equation cannot be applied to a two-phase reaction, where the voltage composition-independent. Thus, diffusion data must be calculated at compositions relating to a non-zero gradient. For this reason, Li chemical diffusion coefficients were calculated at a faradaic yield \(> 2.5\) F/mol; otherwise, the region where the material can be cycled. The composition dependence of the chemical diffusion coefficients is illustrated in Fig. 6. In both

<table>
<thead>
<tr>
<th>Sample</th>
<th>(L) (Å)</th>
</tr>
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<tbody>
<tr>
<td>Litharge</td>
<td>712</td>
</tr>
<tr>
<td>Massicot</td>
<td>3640</td>
</tr>
<tr>
<td>Litharge (film A)</td>
<td>490</td>
</tr>
<tr>
<td>Massicot (film B)</td>
<td>550</td>
</tr>
</tbody>
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polymorphs, $D$ exhibits a similar trend, viz. it increases slightly with increasing faradaic yield, particularly over the range where low-lithium content alloys are formed. Moreover, the $D_{Li}$ values for Li/PbO (litharge) are somewhat higher than those calculated for massicot. The higher mobility of Li$^+$ ions found in litharge can be understood by taking into account the lower crystallinity of this polymorph, which must facilitate the transport of Li through the structural framework.

Fig. 7a shows the first discharge of the cells made from film A. The amount of active material was calculated by weighing the powder scraped from the substrate. The curve, like those for bulk oxides, exhibits a sharp potential drop at the beginning of the discharge process due to the ohmic cell resistance. Subsequently the voltage decreases very gradually with increasing depth. Unlike the bulk material, no plateau is observed at 1.3. The origin of this difference is unclear at present;
one possible explanation is diffusion of lithium throughout the porous film and reaction with pure lead. However, the fact that powder scraped from the substrate and pelletized with carbon black and binder exhibits a well-defined plateau (see Fig. 7b), should be consistent with weak adherence of PbO particles to the substrate, which has an adverse effect on the electrode conductivity. On further cycling between 0.0 and 1.0 V (Fig. 8), additional plateaux appear, the charge–discharge depth of which increases with cycling. This suggests closer contact of the active material with the substrate on cycling, which decreases the resistivity of the active material–substrate interface. Direct evidence that these features really correspond to the PbO coating is provided by the discharge curve for the uncoated substrate (Fig. 7c), the electrochemical performance of which is indeed very poor. In this case, the potential drops abruptly, which suggests that lithium is scarcely prone to react with the Pb substrate.

Fig. 9a,b show the dq/(ndV) versus potential plots for the first, fifth, tenth and twentieth charge–discharge sequence of the cells between 0.0 and 1.0 V. Although the two main peaks for the cells made from bulk oxides are also prominent and the reversibility of the oxidation–reduction process is apparent from the symmetric anodic and cathodic waves obtained, there are some differences worth noting. Thus, significant polarization is observed from the discharging to the charging process. This is often the case with thin-film electrodes, as shown by other anodic materials deposited on metal substrates [17–19]. As a result, the weak peaks at the lower voltages are barely discernible. This means that the alloys with the higher lithium contents play a less prominent role and result in simpler alloying/de-alloying processes. Moreover, peak intensity increases on cycling, probably as a result of improved reversibility in the processes.

Fig. 9c shows the variation of the specific capacity of the cells as a function of the number of cycles. Again, significant differences between this plot and that for bulk PbO (Fig. 4c) are observed. Whereas the capacity of the latter system fades on cycling, irrespective of the polymorph structure and the synthesis procedure, the cells made from PbO films tend to gain capacity on cycling, thus reflecting an increased peak intensity. Also, better, reversible capacity retention of the films is observed relative to the bulk material. In fact, the capacity for film A is close to the theoretical value (540
A h/kg based on the formation of the Li$_{4.5}$Pb alloy. The lead substrate must significantly influence the electrochemical properties of the cell in spite of its low reactivity towards Li. Thus, the gradual increase in cell capacity on cycling must reflect improved adherence of the particles to the substrate once alloying/de-alloying processes have taken place. The electrode must go through a process similar to curing in lead-acid battery plates, one purpose of which is to promote adhesion of active particles to the grid. With Li cells, adhesion of the active material to the substrate must be favoured by the attack of Li itself to the Pb substrate, with formation of a Li$_x$Pb thin film on the substrate surface. This layer should help alloyed particles cement to the substrate. This model is consistent with the poorer electrochemical performance of Li cells made from bulk oxides (particularly that formed from PbO particles deposited on the substrate and mixed with acetylene black and binder, Fig. 9c). The poor cycling properties of this cell, similar to those of cells made from commercial oxides, provides direct evidence of the favorable effect of the Pb substrate.

One plausible alternative explanation for the cycling properties of thin films involves assuming that the outer lead substrate surface is activated upon cycling and that this helps maintain or even increase cell capacity (this is quite feasible since excess lithium is present). One way to avoid this problem is by using an ion-lithium cell and monitoring its capacity retention. The following cell composition was tested for this purpose: Li$_{1.01}$Fe$_{0.3}$Mn$_{1.7}$O$_4$/PbO. The selection of an Fe–Mn spinel as lithium source was based on its good cycling properties as reported elsewhere [20,21]. The positive electrode (containing 8.7 mg of active material) was prepared by following the same procedure as that for the negative electrode (containing 1 mg of PbO). Cells were cycled at a current density of 0.5 mA/cm$^2$ over the voltage range 2.8–4.2 V. The voltage–composition curves for the first few cycles of the cells made from thin film A and commercial PbO electrodes are shown in Fig. 10a,b. The amount of Li extracted in the first charge was ca. 4.8 atoms per Pb atom, and thus led to the formation of low-lithium content alloys (upper limit Li$_{2.8}$Pb). Although the cell delivered only a 64% of its theoretical capacity in the first discharge, it retained a reversible capacity of ca. 200 mA h/g over the next 15 cycles tested (see Fig. 10c). By contrast, the capacity of the cell made from commercial PbO not only was smaller but also declined steeply on cycling. These results are thus better explained by the role of the lead substrate than by the presence of excess lithium used in the cell configuration.

Once it reaches its maximum capacity, the cell formed by film A possesses good capacity retention. On the other hand, the cell made from film B gradually loses capacity on cycling. Various models can be used to account for this differential performance. As shown above, based on composition, the cycling properties of litharge are somewhat better than those of the massicot polymorph. Thus, the excellent capacity of film A is consistent with the presence of litharge as the sole phase. The presence of massicot in film B must be responsible for the slight decrease in capacity with increasing number of cycles. One alternative interpreta-

![Fig. 10](image-url)
tion is based on the particle size of the films, film B being formed by particles of greater size than film A. A model based on the formation of large aggregates has been used to explain the capacity fade observed in tin oxides formed by large particles [22]. The formation of large crystals of Li,Pb alloys must favor the coexistence of crystallites of different structure and Li/Pb ratios within the particles, which results in the presence of multiphase regions whose differences in molar volume may cause fragmentation and a subsequent loss of contact between fragments. The increased in electrode resistivity may hinder reversion of the lithium insertion–extraction process.

4. Conclusions

Crystalline PbO films deposited on pure Pb substrates were prepared by heating at 250°C precursor films obtained by spray pyrolysis with aqueous solution of Pb(CH$_3$–COO)$_2$·3H$_2$O. SEM images revealed thorough coating of the substrate and a uniform particle size distribution. Electrochemical lithium insertion into bulk PbO in two different polymorphs (litharge and massicot) up to 0.0 V versus a lithium electrode, resulted in the formation of various Li,Pb alloys. The de-alloying process was incomplete, its irreversibility increasing on cycling. The initial behavior of the films used as electrodes in lithium cells revealed poor adherence to the metal substrate, which, however, increased with alloying. On the other hand alloying/de-alloying in films was complete and reversible. The small particle size, the presence of litharge as the dominant component and the use of the Pb substrate are responsible for the good electrochemical properties of these electrodes, which exhibit a specific capacity of 540 A h/kg and excellent capacity retention.

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References