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The addition of red lead to flat plate and tubular valve regulated miners cap lamp lead–acid batteries

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Abstract

The study looked at the use of red lead in the manufacturing of valve regulated lead acid (VRLA) miners cap lamp (MCL) batteries that were made with either flat plate or tubular positive electrodes. A problem with using only grey oxide in the manufacture of thick flat plate or tubular electrodes is the poor conversion of the active material to the desired lead dioxide. The addition of red lead to the initial starting material improves the formation efficiency but is considerably more expensive thereby increasing the cost of manufacturing. The study showed that by carefully controlling the formation conditions in terms of the voltage and temperature of a battery, good capacity performance can be achieved for cells made with flat plate electrodes that contain up to 25% red lead. The small amount of red lead in the active cured material reduces the effect of electrode surface sulphate formation and allows the battery to achieve its rated capacity within the first few cycles. Batteries made with flat plate positive electrodes that contained more that 50% red lead showed good initial capacity but had poor structural active material bonding. The study showed that MCL batteries made with tubular positive electrodes that contained less than 75% red lead resulted in a poorly formed electrode with limited capacity utilization. Pickling and soaking times of the tubular electrodes should be kept at a minimum thereby allowing higher active material utilization during subsequent capacity cycling. The study further showed that it is beneficial to use higher formation rates in order to reduce manufacturing time and to improve the active material characteristics.

1. Introduction

Valve regulated lead acid (VRLA) batteries are used in a large range of electrical applications and their performances have been extensively studied [1–5]. A typical use of VRLA technology is found in the manufacturing of miners cap lamp (MCL) Batteries. A variety of battery designs have been suggested in the literature and the nominal designs are a 4 V/16 Ah battery, which are discharged at 1 A–3.7 V [6]. The life expectancy of such a battery is 2 years, where a typical application requires the discharge of a 0.9 A bulb for a minimum of 9 h with the possibility to operate for up to 12 h and to maintain a voltage greater than 3.7 V. Operating tem-

peratures of such batteries in their application are often above 40 °C. In the past, the service of such batteries included the replenishment of the lost water. The desire by the user of such batteries was for a sealed unit that reduces the maintenance required in a harsh mining environment, where acid spill and the addition of unknown impurities to the battery can result. A completely sealed unit would allow for only one external maintenance application, such as the charging sequence after use.

Due to the fact that the battery is primarily used in deep discharge applications, many designs made use of tubular positive electrodes that would reduce the shedding of the positive active material and give extended life cycle capacity. However, this design has a higher manufacturing cost and requires more active material per electrode when compared to similar positive flat plate design batteries. Many tubular

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design cells such as those used in vehicle traction applications and MCL VRLA are assembled in their unformed state, which is followed by jar formation of the completed cell. In this process, factors such as the formation acid concentration, formation rate, temperature during formation and the final electrolyte density become important. The addition of red lead (Pb_3O_4) to the positive active material is known to improve the formation efficiency of batteries that have relatively thick flat plate or tubular positive electrodes [7]. Pb_3O_4 is made by a batch process where α-PbO is further oxidized by air at about 400 °C and is currently 56% more expensive by mass that the normal grey oxide. The addition of red lead to the positive active material during manufacturing is considered to be useful when initial low capacities of batteries are obtained which are due to the positive electrode's incomplete formation. Red lead results in the formation of β-PbO_2 as shown in Eq. (1), during the soaking or paste-mixing stage and indirectly during the formation stage [7]. The presence of β-PbO_2 increases the conductivity of the active material before formation and allows for seed crystals to develop that would increase the conversion efficiency to the final formed active material (PbO_2).

$$Pb_3O_4 + 2H_2SO_4 \rightarrow \beta\text{-}PbO_2 + 2PbSO_4 + 2H_2O \qquad (1)$$
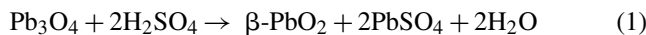
After filling tubular electrodes with dry lead oxide, the plates are subjected to a process known as soaking, dipping or pickling in a low-density acid [8–10]. This process has a number of advantages. It eliminates the loose dust that coats the exterior of the tubes thereby making the plates easier to work with during the assembling stages of manufacturing. However, if the dipping time is too long, or the concentration of the acid used is too high, the lead oxide in the tubes would convert entirely to lead sulphate, from which it is then more difficult to form lead dioxide. In practice, this process of dipping can vary from a few minutes up to a few hours [9–12].

One of the advantages of using flat plate electrodes in VRLA MCL batteries, rather than tubular, is the reduction of material and manufacturing cost per positive electrode. This includes the fact that the flat plate positive electrode requires less active material for the same Ah capacity and that a more automated pasting process could be used as compared to the tubular electrode. Batteries made with flat plate electrodes have better oxygen recombination efficiencies, which results in lower water loss during the recharge cycle. However, flat plate batteries have comparatively much lower life cycle capabilities when compared to similar batteries made with tubular electrodes. Due to the flat plate thickness and VRLA cell type assembly, the efficient conversion of active material is often low when only grey oxide is used during manufacturing. It is therefore, necessary to investigate the effect of adding red lead to the flat plate manufacturing process and to optimise the formation process in order to obtain a reliable product without compromising its final performance.

The following is a comparative study between the two types of positive electrode manufacturing technologies used with variations in red lead addition to the active material in the manufacture of VRLA MCL batteries.

2. Experimental

Batches of active material for tubular and flat plate MCL electrodes were prepared by, respectively, adding 25, 50, 75 to grey lead oxide that was made from a Barton Pot process and 100% Pb_3O_4. The cells were assembled with the different ratio oxides and were tested using two different formation sequences. The procedures for preparing the two types of electrodes with variation in red lead content are described as follows.

2.1. Flat plate

The correct ratio of grey oxide and red lead was prepared in a Mullen wheel paste mixer and pasted by a single-sided belt paster and pasted onto a 112 mm × 55 mm × 4 mm cast grid current collector. The paste was prepared by adding 24 L of 1.24 g cm^{-3} sulphuric acid and 32–40 L of water to 300 kg of oxide mix containing 0.1% of floc-fibre. The paste was mixed until the correct paste properties were obtained with a density between 136 and 144 g/(2 in.^{3}) and a plasticity of 27–29 using a Globe Pentometer. The characteristics of the red lead and grey oxide used are summarized in Table 1. The pasted flat plates were allowed to cure in a humidity chamber set at 25 °C and 85% humidity for 48 h. The cured plates were allowed to air dry completely before being assembled into cells or used for further analysis.

2.2. Tubular electrodes

A 6 spine current collector with rectangular profiled non-woven acrylic tubes as active material support was used to make the positive tubular electrodes. The correct ratio of grey oxide and red lead was prepared and the plates were vibration-filled containing 0.012% Syloid. The average packing density of the tubular plates was 3.4 g cm^{-3} and the characteristics of the red lead and grey oxide used are summarized in Table 1. The filled tubular plates were dipped in sulphuric acid with a density of 1.1 g cm^{-3} for 5–15 s only, since previous work

Table 1
Characteristics of the red lead and grey oxide

	Grey oxide	Red lead
Free lead	27.3%	–
β-PbO	15.4%	11.8%
α-PbO	57.3%	4.4%
Pb_3O_4	–	83.9%
Acid absorbance	152.3 mg g^{-1} oxide	–
Apparent density	28.64 g in.$^{-3}$	–
BET surface area	0.686 m^2 g^{-1}	0.536 m^2 g^{-1}
Particle size mean, D [4,3]	9.55 μm	8.31 μm
Particle size median, D (v, 0.5)	6.16 μm	4.49 μm

Table 2
Sequences used in the formation of flat plate and tubular MCL batteries

Electrode type		Rest (h)	Charge (A)	Rest (h)	Charge (A)	Rest (h)	Charge (A)
	Low rate	1	1.5 for 22 h	1	2 for 21 h	1	1 for 21 h
Flat plate			2 for 2 h		4 for 3 h		2 for 6 h
	High rate	1	9 for 3 h	1	3 for 3 h	1	1.5 for 10 h
			5 for 3 h				
	Low rate	1	1.5 for 26 h	1	2 for 27 h	1	1 for 27 h
Tubular			2 for 4 h		4 for 5 h		2 for 6 h
	High rate	1	9 for 4 h	1	3 for 4 h	1	1.5 for 10 h
			5 for 5 h				

had shown this to be sufficient for tubular electrodes [10]. The dipped plates were subsequently washed with water in order to remove any excess acid and were allowed to cure in a humidity chamber set at 25 °C and 85% humidity for 48 h. The cured plates were allowed to air-dry completely before being assembled into cells or used for further analysis.

The flat plate grids used for the negative electrodes were made by pasting with a standard mixture of grey oxide and expander. The same negative plates were used in the assembling of batteries using the tubular or flat plate positive electrodes that were made with the various ratios of red lead to grey oxide.

The cells were assembled into polycarbonate containers with three negative flat-plates and two positive tubular or flat-plates wrapped with AGM glass matt separator. The average compression of the cells was determined to be about 12 kPa. The cells were filled with excess formation acid with a density of 1.26 g cm^{-3} and formed using an "open" system [14]. All cells were formed with excess electrolyte ensuring that no drying out of the electrodes would occur during the duration of the sequence. At the end of formation, all cells showed that sufficient electrolyte remained and the electrolyte was adjusted to a density of 1.31 g cm^{-3}. The cells were allowed to "soak" for 1 h in the acid before commencing the formation sequence. The formation was done using a common multi-step constant current formation profile until 250% [8] of the theoretical active material capacity was achieved and this is referred to as the low rate sequence (Table 2). The high rate sequence was only optimised after completing the studies using the low rate sequence (Table 2). The voltage and temperature profiles of the different batteries were simultaneously recorded during their formation process using the Maccor battery tester.

The cells were rated at 16 Ah at the 1 A rate. After formation, an initial 1 A discharge test to 1.75 V cell^{-1} was done followed by a constant voltage (2.65 V cell^{-1}) recharge where 140% of the discharged capacity was returned. This was followed by a 10 cycle test at the 1 A rate. All discharge capacities and cycling tests were carried out at room temperature. The active material of duplicate formed cells was removed from the batteries, washed with water and dried for their respective XRD phase composition [13], BET surface area and Hg porosimetry analysis. All discharge capacity

results are recorded as Ah and the Ah kg^{-1} of active cured material was also determined and averaged over the set of cells studied.

The Hg porosimetry analyses of the tubular electrodes were carried out by using a complete 10 mm length section of a single spine containing the active material and acrylic gauntlet. The sides of electrode sample were sealed in order to ensure that the Hg intrusion would flow through the outer gauntlet section of the sample and not through the two open sides of the sample. The flat plate electrodes were analysed by removing complete sections of the active material from the grid wire current collector.

3. Results and discussion

3.1. MCL batteries made with flat plate electrodes

The XRD phase composition of the various flat plate electrodes' cured active material are summarized in Table 3.

The results show that the 0, 25 and 50% addition of red lead to the cured active material of the flat plate contained about 40% T3 in the final mixture. This T3 is formed from the reaction of PbO with sulphuric acid and is an important component in the binding of the active material during curing and formation [15]. The tri-basic lead sulphate material would be finally converted to lead dioxide during the formation process, but is considered to give the formed PbO$_2$ its structure and rigidity, that allows the electrode to undergo chemical phase changes that occur during discharge and charge capacity cycling, with limited shedding [15,16]. The results show that small amounts of PbO$_2$ had formed during the curing process for the cured electrodes that contained 25, 50 and 75% added Pb$_3$O$_4$, which had come from the reaction of red lead with sulphuric acid. This shows that the predominant reaction during the curing process is the reaction of free lead and PbO to tri-basic lead sulphates.

The cured material made from 100% red lead was included for comparison purposes only and showed poor active material structural bonding to the grid and to itself after curing. The reaction of the red lead with sulphuric acid would be according to Eq. (1) giving rise to no tri- or tetra-basic lead sulphates, which form part of the precursor to the active mate-

Table 3
XRD phase analysis of the cured active material of the flat plate electrodes with various additions of red lead to the grey oxide

Cured sample (% Pb_3O_4)	Flat plate					
	α-PbO (%)	β-PbO (%)	Pb_3O_4 (%)	T3 (%)	$PbSO_4$ (%)	β-PbO_2 (%)
0	42	15	–	43	–	–
25	37	10	17	34	–	2
50	11	11	35	38	–	5
75	10	8	60	19	–	3
100	–	–	76	–	11	13

T3: tri-basic lead sulphate.
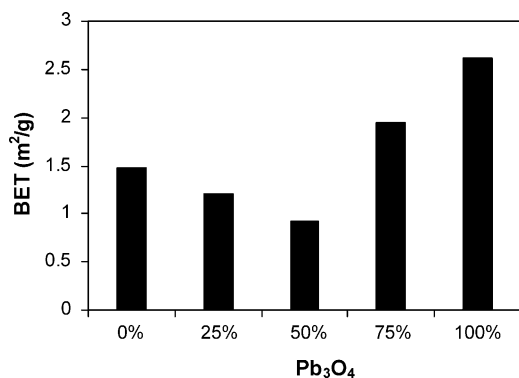
Fig. 1. BET surface area of cured active material for flat plate electrodes made with different concentrations of red lead.

rial structure, which is needed to give the electrode its rigidity and bonding capability.

The low percentage yield of the lead sulphate and lead dioxide was due to the fact that the pasting recipe was kept the same for all the electrodes manufactured, and that a minimal amount of sulphuric acid was used.

The change in the BET surface area of the cured flat plate electrodes with various additions of red lead is shown in Fig. 1. The results show that there is at first a slight decrease in surface area in the range from 0 to 50% added Pb_3O_4, followed by an increase to above $2\,m^2\,g^{-1}$ for the cured material made from 75 and 100% Pb_3O_4. Hence, this implies that the cured active material might have a high surface area (above $2\,m^2\,g^{-1}$), but the structural integrity of the material could

Table 4
XRD phase analysis of the formed active material of the flat plate electrodes with various additions of red lead to the grey oxide

Formed sample (% Pb_3O_4)	Flat plate electrode		
	α-PbO_2 (%)	β-PbO_2 (%)	$PbSO_4$ (%)
Low rate formation			
0	21	51	28
25	15	68	18
50	9	70	21
75	25	53	22
100	23	51	24
High rate formation			
0	28	50	22
25	28	58	14
50	23	56	21
75	18	57	25
100	19	67	14

be poor due to low bonding of particles as was observed for the electrodes made with 100% Pb_3O_4.

For each battery tested, one cell of a duplicate pair was removed for analysis after formation and the other cell was further tested for its discharge capacity. The phase composition of the formed active material for the various cells studied using flat plate electrodes are summarized in Table 4.

The XRD phase composition analysis of the formed material for the additions of Pb_3O_4 in the range 0–50% showed only relatively small differences. However, visually the electrode having no Pb_3O_4 showed significant amounts of lead sulphate still present on the surface of the electrode (Fig. 2a).

2a: 0%   **2b:** 25%   **2c:** 50%   **2d:** 75%   **2e:** 100%
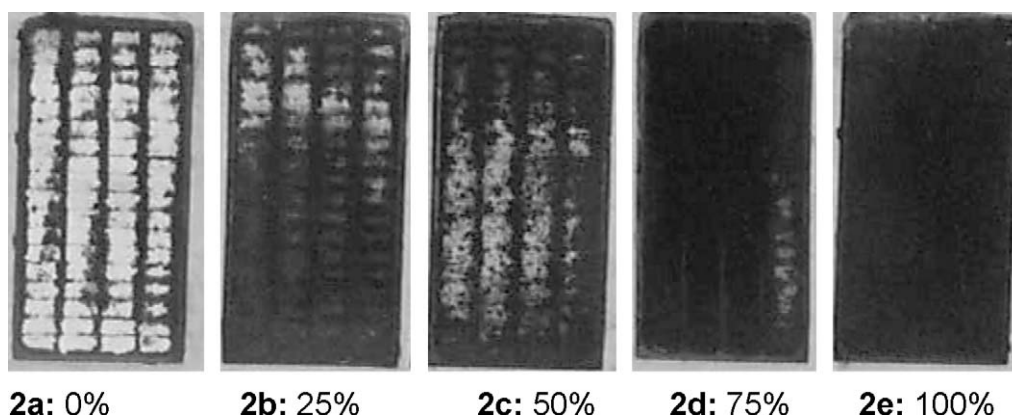
Fig. 2. Positive electrodes formed using the low rate procedure with various additions of Pb_3O_4 added to the initial cured material.
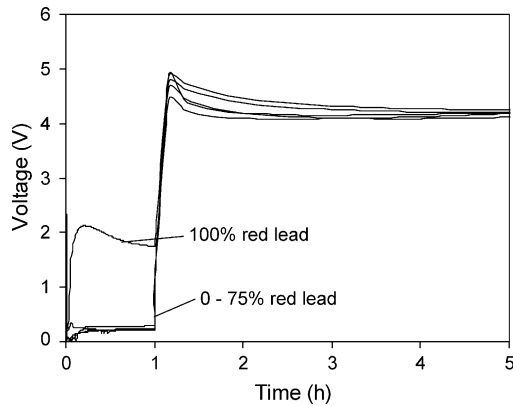
Fig. 3. Voltage formation profile for flat plate electrodes formed at the low rate with various additions of red lead showing the first 5 h only.

Fig. 4. Temperature profile for selected cells made with 100% Pb_3O_4 flat plate electrodes formed with the low and high rate sequences.

The white lead sulphate on the surface would decrease as the Pb_3O_4 content increased in the initial cured material (Fig. 2b–e).

The effect of the non-conducting lead sulphate on the surface would detrimentally influence the discharge capacity of the electrode by inhibiting the underlying active material (PbO_2) that is used in the discharge reaction. The electrode made with 100% Pb_3O_4 showed a high conversion of active material to PbO_2; however, the structural integrity was relatively low, since the active material pellets in the grid support were easily removed showing poor adhesion properties.

The advantage of the Pb_3O_4 addition can also be seen in the initial formation voltage profiles of the cells. Fig. 3 shows the formation voltage change during the first 5 h of formation.

The voltage change during the first hour (open circuit) shows that there was an increase in the cell potential for the 100% Pb_3O_4 added electrode. During the rest period, the acid is allowed to "soak" into the active material that converts the Pb_3O_4 to PbO_2 and $PbSO_4$. There was an initial increase in the voltage, followed by a gradual decrease after about 0.5 h. This can be explained by the fact that the acid available during the rest period, converted firstly the active material to PbO_2 and then with time, converting it further to $PbSO_4$. The increase in voltage during the rest period was not observed for the other batteries made with lower Pb_3O_4 addition. The slight increase in the initial formation charge voltage would imply better conversion efficiency.

The temperature of the battery during formation is considered to be critical in terms of efficiency and active material conversion [3,14]. If the temperature is too high, excessive gassing and damage of the electrode's active material would occur. Low temperatures would indicate a poorer manufacturing efficiency in terms of unnecessary time spent for the formation stage. There was no significant difference in the temperature profiles between the batteries made with different concentrations of red lead. The temperature profiles of the cells made with 100% Pb_3O_4 were selected for comparison purposes and are shown in Fig. 4.
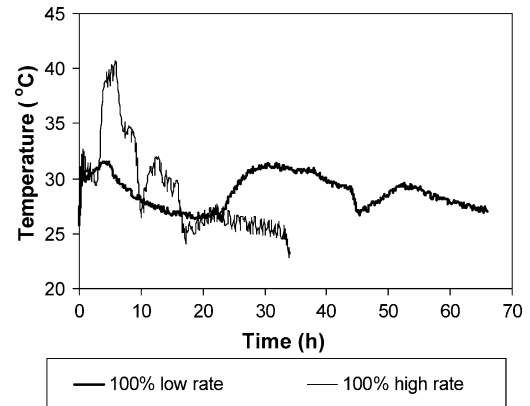
The temperature profiles show that the initial stage during formation sequence had a rise in temperature mainly due to the conversion of lead oxide, red lead and basic lead sulphates to lead sulphate. This reaction is exothermic and depending on the size of the battery, the increase in temperature can cause the battery to have temperatures above 50 °C before formation [1]. In order to reduce the initial increase in temperature after the addition of the acid, most manufacturers add "chilled" acid to the batteries (about 5 °C). Due to the size of the MCL batteries and the amount of active material in this study, it was not necessary to add "chilled" acid.

The temperature during the first few steps of formation for the low rate sequence was relatively low showing that a "too-low" current parameter was used. Even though the conversion process to form lead dioxide continued during this step, it would not be beneficial in terms of unnecessary time taken to complete the formation sequence. After careful consideration of the temperature profiles recorded during the low rate formation, a new profile labelled as "high rate" was developed that would reduce the time of formation and optimise the conversion of the active material.

The current rates for the subsequent steps in using the high rate sequence were increased, where a significant increase in temperature to 40 °C was observed. This is beneficial in increasing the conversion rates of the active material, where Dimitrov and Pavlov [17] have also reported that there are added benefits in using high rate formation currents to improve the final conversion and properties of the active material. The temperatures of the cells were limited by keeping the high charge currents for a short period of time only. It was subsequently beneficial to start decreasing the current towards the end of formation in order to reduce the effect of water loss at a lower cell temperature and charge voltage. A significant reduction in the overall formation time from 66 h (low rate) to 33 h (high rate) was achieved.

The BET surface area results for the positive active material with different red lead additions formed with the two different formation procedures are shown in Fig. 5. The surface area of the active material straight after formation and
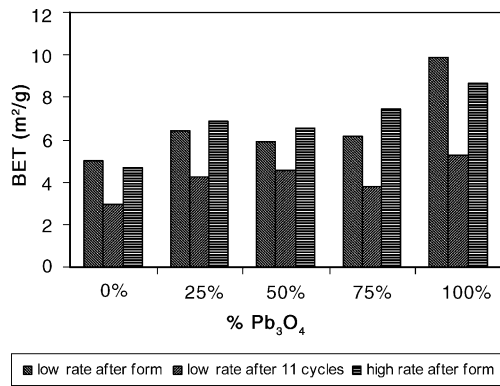
Fig. 5. BET Surface area of formed active material for flat plates with low and high rate procedure for various additions of red lead. Analysis was done on duplicate samples after formation and after 11 capacity cycles for the low rate cells only.

after completing 11 capacity cycles showed that there was a decrease in surface area after capacity cycling. This phenomenon is common and has been reported elsewhere [10]. A slight increase in the surface area of the formed active material was observed as the initial percentage Pb_3O_4 content increased; in particular, the electrode that contained 100% Pb_3O_4 showed a high surface area. However, the structure integrity of active material was low, giving it poor adhesion characteristics to the electrode grid and to itself.

Only slight differences in the surface area of the formed active material were observed between the use of the high and low rate sequences. The surface area of the electrodes that were formed with the high rate procedure for the 25 and 75% Pb_3O_4 were slightly higher than those formed with the low rate procedure, whereas the electrode that contained 100% Pb_3O_4 had a comparatively lower surface area. There seems to be no significant influence on the surface area of the active material of the electrodes when using the two different formation rates.

The porosity results for the formed active material from the flat plate electrodes made with different concentrations of red lead in the initial cured material are summarized in Fig. 6. The porosity results show only slight differences between the electrodes formed with the two different rates, where the
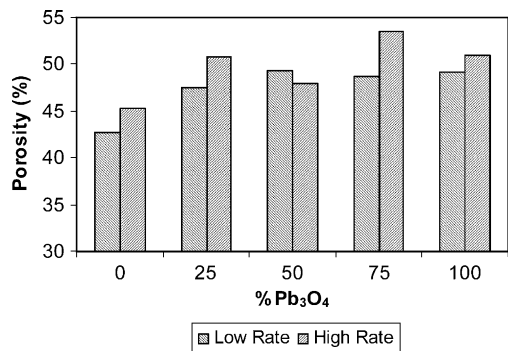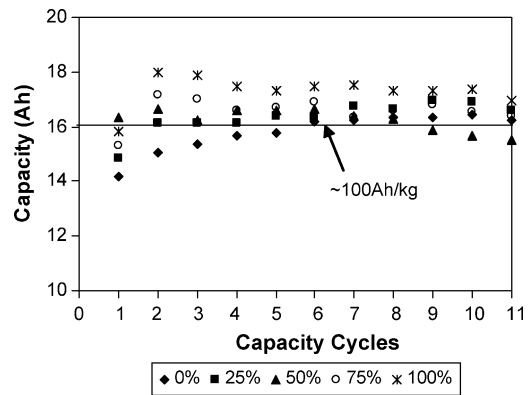

Fig. 7. Capacity cycle (Ah) of flat plate electrodes made with various concentrations of red lead formed at the low rate.

active material that formed with the high rate had slightly higher porosity than the corresponding samples formed with the low rate sequence. Noticeably, the active material that had initially no Pb_3O_4 in it, had about a 10% lower porosity than the material that contained 25% or more Pb_3O_4. This might play a role in the subsequent capacity tests, where the availability of the electrolyte to the active material would be influenced by the respective porosity and available surface area of the active material.

The MCL battery is nominally rated at 4 V/16 Ah and discharged at 1 A–3.7 V [6]. For most applications, the capacity of a battery is reported in terms of Ah at a specified discharge rate. However, it is often of interest to report electrochemical investigations of battery material utilization in terms of the $Ah\,kg^{-1}$ of active cured material. Since there are slight variations in the active mass between the cells studied, an average $Ah\,kg^{-1}$ capacity of the cells is shown, respectively. The variation in capacity over 11 cycles for the different batteries made from various concentrations of Pb_3O_4 in the initial active material are shown in Figs. 7 and 8, respectively for the cells formed with the two different formation procedures.

The cells formed with the low rate procedure showed that the electrodes made with 0 and 25% Pb_3O_4 had a very low

Fig. 6. Porosity of active material for flat plates formed at the high and low rate for various concentrations of red lead.
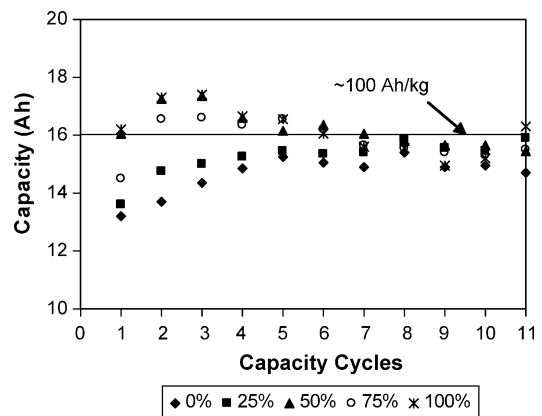

Fig. 8. Capacity cycle (Ah) of flat plate electrodes made with various concentrations of red lead formed at the high rate.

Table 5
XRD phase analysis of the cured active material of the tubular electrodes with various additions of red lead to the grey oxide

Cured sample (% Pb_3O_4)	α-PbO (%)	β-PbO (%)	Pb_3O_4 (%)	T3 (%)	$PbSO_4$ (%)	β-PbO_2 (%)
Tubular (gauntlet and spine removed)						
0	80	6	–	7	7	–
25	53	7	26	10	4	–
50	32	–	53	7	7	1
75	15	–	70	8	6	1
100	–	8	76	–	14	2
Tubular (surface of the gauntlet)						
0	39	11	–	50	–	–
25	37	11	16	36	–	–
50	7	5	47	18	14	9
75	4	4	60	15	11	6
100	4	4	49	–	36	7

T3: tri-basic lead sulphate.

1st capacity. The subsequent capacity increased slowly with cycling, where only after the 5th cycle did the cells obtain a discharge capacity of 16 Ah. Noticeably, the cells that contained 25% Pb_3O_4 achieved the rated capacity after three cycles.

The cells formed using the high rate procedure showed that the average capacity of all cells was lower than the corresponding capacities using the low rate procedure. The cells made with 50 and 100% Pb_3O_4 achieved 16 Ah after the 1st capacity test. The cell made with 75% Pb_3O_4 achieved 16 Ah after the 2nd capacity cycle. All three cells showed a slight increase in capacity after a few more cycles, with a gradual decrease during the 11 cycles to below 16 Ah. The decrease in capacity towards the end of the 11 cycle tests shows that there is a deterioration of the active material support, which is, encouraged by the decrease in surface area of the active material (Fig. 5). The cells made with 100% Pb_3O_4 showed a fair amount of active material shedding after the 11 cycle test, once the electrodes were removed from the cell containers. The cells, made with 0 and 25% Pb_3O_4, that were formed with the high rate procedure did not achieve the 16 Ah after the 1st cycle and showed a gradual increase in capacity so that only after the 9th cycle 16 Ah was obtained.

The Ah kg^{-1} showed the cells on average achieved almost 50% of the theoretical active material utilization of 224 Ah kg^{-1} [1,2]. These results show good utilization efficiencies and the importance of determining the correct mass balance of the active material in designing the expected rated capacity (Ah) of a battery. This shows that the rated capacity of the MCL battery can be achieved with a higher rated formation procedure where it would be beneficial to use a multi step formation procedure with careful temperature control.

3.2. MCL batteries made with tubular electrodes

The phase analysis of the active material was carried out with the external gauntlet and inner spine removed. The phase analysis of the tubular cured material showed a relatively low percentage of corresponding PbO_2 and $PbSO_4$ when compared to the flat plate electrodes (Table 5). This was pri-

marily because the filled tubular electrodes were only dipped for a short time in 1.1 g cm^{-3} acid and the reaction product remained primarily in the gauntlet outer fabric. This can be observed by the immediate change in colour of the electrodes that contained Pb_3O_4, when the outer layer of the gauntlet of the electrodes changed from a red colour to dark brown that is typical for lead dioxide.

The XRD phase analysis of the surface of the gauntlet material was carried out by aligning a section of a filled tube specimen into the sample holder and rotating it at 20 rpm during analysis. This was done in order to allow for a relatively large representative sample of the surface to be exposed to the X-rays, thereby eliminating any effects due to preferred orientation of the crystals or uneven surface concentration (Table 5).

The results show that there is a significant difference in the phase composition of the active material on the surface of the gauntlet as compared to that of the bulk inner core. The dipping of the filled tubular electrodes in dilute sulphuric acid for short periods of time leaves the inner core material largely un-reacted. The tubular electrode with 0% Pb_3O_4 had up to 50% tri-basic lead sulphate (T3) in the gauntlet material. The T3 concentration would decrease as the red lead addition increased. No lead sulphate was formed on the electrodes that had 0 and 25% Pb_3O_4. However, the lead sulphate concentration on the surface of the gauntlet increased as the red lead concentration of the electrode increased from 50 to 100% Pb_3O_4 and this can be described by Eq. (1). The formation of β-PbO_2 was relatively low. This shows that in spite of using a relatively shorter dipping time and a relatively low concentrated acid, a considerable amount of lead sulphate does already form on the surface of the tubular electrodes that contain Pb_3O_4. In order to aid the formation process, it would be beneficial to have a larger amount of the conductive β-PbO_2 present, rather than the non-conducting lead sulphate.

Cross-sections of selected tubes filled with 0 and 100% Pb_3O_4, were examined after acid dipping and curing under a stereo microscope and show the effect of the acid penetrating the active material (Fig. 9). The white basic lead sulphate layer near the gauntlet, extending slightly into the grey oxide,
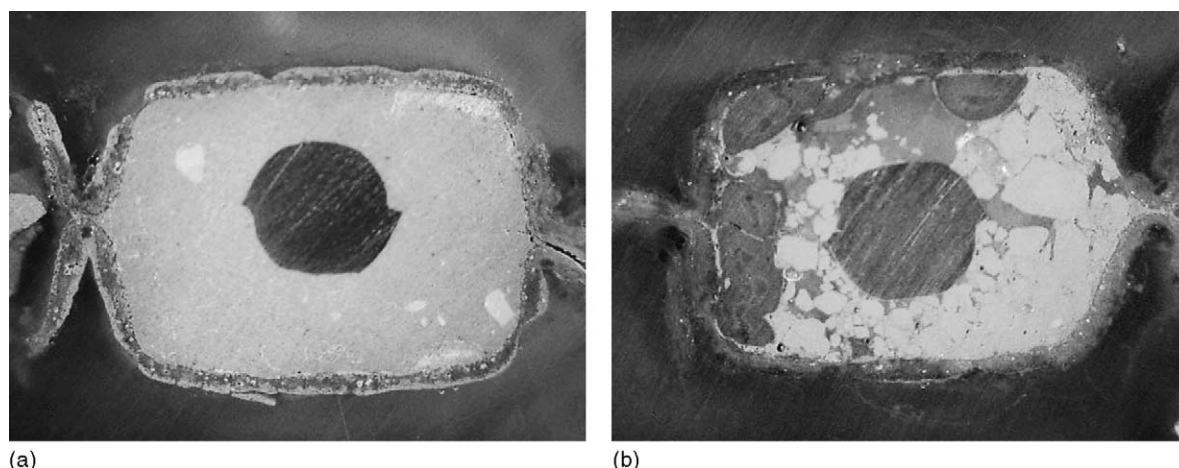
Fig. 9. Stereo microscope pictures of a cross-sectional view of a MCL tubular electrode for 0% (a) and 100% (b) red lead addition, after dipping in acid and curing.

is evident in the electrode containing no Pb_3O_4 (Fig. 9a). The darker patches of lead dioxide that occur when red lead reacts with sulphuric acid are observed for the electrodes filled with the 100% Pb_3O_4 (Fig. 9b). However, the distribution of the brown PbO_2 is not uniform and is of relatively low concentration as shown by XRD analysis (Table 5).

The small amounts of PbO_2 and $PbSO_4$ at the surface of the electrodes are sufficient to reduce the effect of loose dust that coats the tubes after filling. The advantage of reducing the "pickling" time of tubular electrodes was discussed previously [10]. In particular, if red lead is used in the filling oxide, excessive pickling would convert all the material to PbO_2 and finally to $PbSO_4$. The phase analysis shows that the conversion to lead sulphate seems to be the dominating reaction. Further, excessive pickling would encourage the $PbSO_4$ to grow and thereby reduce the effective surface area of the active material and inhibit efficient conversion to the active PbO_2 and reduce the penetration of the acid during formation. Once the electrodes are assembled into batteries and allowed to "soak" before formation, further lead dioxide would form thereby encouraging the formation process. The tubular electrodes consisting of 0 and 25% Pb_3O_4 would form only the basic lead sulphates during the pickling and soaking steps, which would have a higher resistance during the formation process.

The change in the BET surface area of the cured tubular electrodes with various additions of Pb_3O_4 is shown in Fig. 10. The results show that the cured active material with no Pb_3O_4 in the tubular electrodes, has a surface area very similar to that obtained for the starting material of the grey oxide ($0.69 \, m^2 \, g^{-1}$). However, upon addition of Pb_3O_4, followed by the short pickling and curing process, the surface area increased significantly up to a maximum of $1.7 \, m^2 \, g^{-1}$ for the active material that contained 100% Pb_3O_4, even though the surface area of the initial Pb_3O_4 added was only $0.54 \, m^2 \, g^{-1}$ (Table 1). This effect shows significantly that the short period of "pickling" in acid and curing increases the surface area of

the starting material, which becomes important during the subsequent formation procedure.

After formation, one cell of a duplicate pair was removed for analysis, while the other cell was further tested for its discharge capacity. The phase composition results of the formed tubular electrodes show that there are significant differences between the electrodes made with different amounts of Pb_3O_4 and are summarized in Table 6. The electrodes that contained 0–50% Pb_3O_4 in the initial cured material had up to 30% $PbSO_4$ remaining in the final formed active material when using the low rate sequence. Similar electrodes that were formed with the high rate sequence had between 40 and 47% $PbSO_4$ remaining. The unformed $PbSO_4$ reduces the effective utilization of the active material during capacity cycling and inhibits the achievable capacity by acting as a resistive barrier between the electrolyte and the available PbO_2. However, cells made with 75 and 100% Pb_3O_4 had between 10 and 24% $PbSO_4$ remaining in the active formed material for the cells that were formed using both the low and high rate sequences. The cells that were formed with the higher rate sequence showed slightly better conversion of the
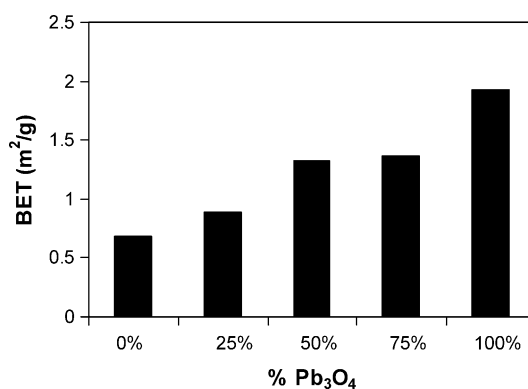

Fig. 10. BET surface area of cured active material for tubular electrodes made with different concentrations of red lead.

Table 6
XRD phase analysis of the formed active material of the tubular electrodes with various additions of red lead to grey oxide

Formed sample (% Pb$_3$O$_4$)	Tubular electrode		
	α-PbO$_2$ (%)	β-PbO$_2$ (%)	PbSO$_4$ (%)
Low rate formation			
0	8	62	30
25	13	58	29
50	9	63	28
75	24	66	10
100	21	63	16
High rate formation			
0	16	37	47
25	14	43	43
50	6	55	39
75	7	69	24
100	5	82	13

Fig. 12. Temperature profile for selected cells made with tubular electrodes formed at the low and high rates.

active material to PbO$_2$. This implies a better conversion of the active material to lead dioxide for the tubular electrodes that contain predominantly Pb$_3$O$_4$ and which are formed with a faster formation sequence.

Fig. 11 shows the formation voltage change during the first 5 h of formation. The results show that during the initial rest period in the acid, an increase in cell voltage for the 100 and 75% added Pb$_3$O$_4$ batteries was observed. This shows that some of the Pb$_3$O$_4$ is converting to lead dioxide which would act as "seeding" crystals for the initial stages of formation to effectively convert the bulk material to the active lead dioxide. This was not observed for the cells that contained lower amounts of Pb$_3$O$_4$ in the starting material.

After carefully considering the formation voltage and temperature profiles when using the low rate procedure, a new procedure (high rate) was developed that would reduce the time of formation and still maintain a good conversion to the desired active material. There was no significant difference in the temperature profiles between the batteries made with different concentrations of red lead. Fig. 12 shows the temperature profiles recorded during formation of the 100% added Pb$_3$O$_4$ batteries using the two different formation procedures.
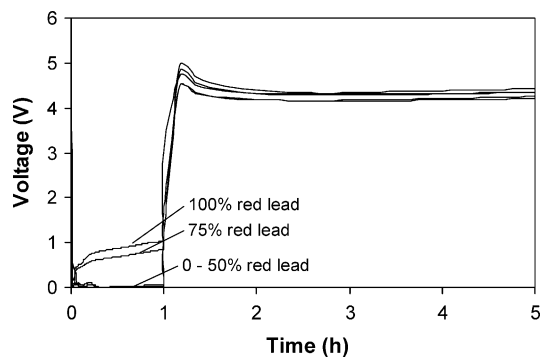

Fig. 11. Voltage formation profile for tubular electrodes formed at the low rate with various additions of red lead showing the first 5 h only.
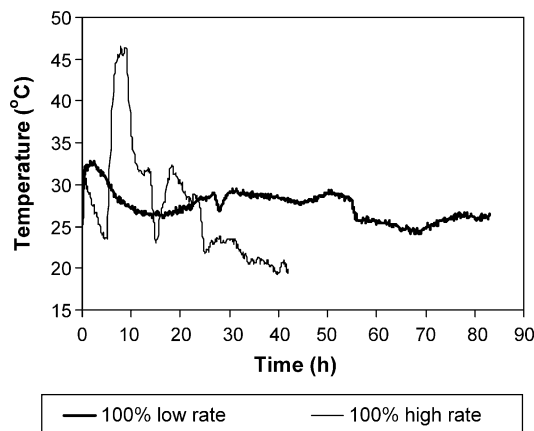
The formation times used for the batteries with tubular electrodes were longer than for those made with the flat plate electrodes. This was primarily due to the fact that more active material in the tubular electrode has to be converted and that the conversion process is less efficient than for the flat plate electrodes.

The increase in the charging currents during the initial stages of the formation sequence also showed an increase in temperature to about 45 °C. This step was done for a short period of time in order to prevent excessive water loss and possible damage to the active material on the electrodes due to high temperatures. However, tubular positive electrodes are less susceptible to damage due to high temperatures because of the protective gauntlet used. The temperature towards the end of formation decreased significantly, showing that possible further reduction in the formation time could be achieved with an increase in the current for those steps, however, care needs to be taken to prevent excessive water loss and the possibility of drying out the cells before the formation cycle is completed. A significant reduction in formation time from 83 h (low rate) to 41 h (high rate) was achieved and there was still sufficient electrolyte in the cells after the formations were completed.

The BET surface area for the formed positive active material from the tubular electrodes made with different concentrations of Pb$_3$O$_4$, formed at the low and high rate is shown in Fig. 13. The corresponding BET surface area results for the electrodes that were subjected to 11 capacity discharge and charge cycles are included in the figure.

The surface areas of the formed material, using the low rate procedure, increased considerably with increasing the Pb$_3$O$_4$ content of the initial active material. The increase covered the range from 4.4 (0%) to 8.4 m^2 g^{-1} (100%), respectively. Similarly, the formed material, using the high rate procedure, covered a surface area range from 3.5 (0%) to 8.7 m^2 g^{-1} (100%), respectively. This difference can be primarily ascribed to the better conversion of the active material in the cells that contained Pb$_3$O$_4$, where factors such as PbO$_2$ seeding crystals encourage efficient active material conversion and that the
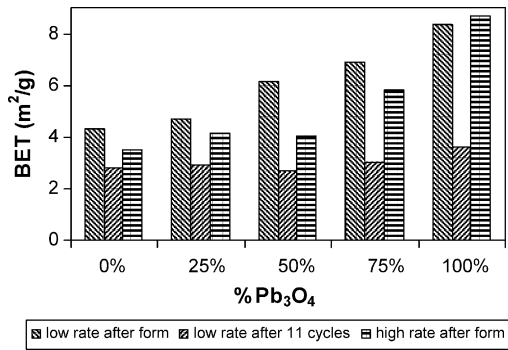
Fig. 13. BET Surface area of formed active material for tubular electrodes at the low and high rate for various concentrations of red lead.

cured material already had a comparatively larger surface area.

The surface areas of the active material after the 11 capacity tests were lower than the corresponding cells that were evaluated after formation. Noticeably, the surface areas for all the cells after capacity cycling were approximately $2.8 \, m^2 \, g^{-1}$. This implies that the surface area of the various tubular electrodes, after 11 capacity cycles, becomes relatively similar, irrespective of the amount of initial Pb_3O_4 in the cured material. However, the surface area, straight after formation, is significantly influenced by the amount of Pb_3O_4 present in the initial cured material.

The characteristic property of the formed active material, having a higher surface area after formation, is important for the utilization of the active material during the subsequent capacity testing. The greater the surface area, the more active sites are available for reactions to take place.

Fig. 14 shows the change in percentage porosity of the electrode materials formed with the low and high rate procedure. The results show that the percentage porosity of the formed active material increased significantly as the Pb_3O_4 content of the tubular electrodes increased. There was only a slight difference in the percentage porosity of the active material between the low and high formation procedures. An electrode with a higher porosity allows more electrolyte to
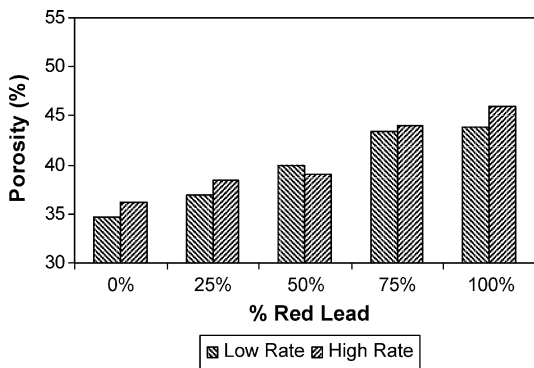
penetrate the active sites, thereby increasing the discharge capacity during cycle testing.

The discharge capacity (Ah) results of 11 cycles for the various cells made with positive tubular electrodes formed under the different conditions are shown in Figs. 15 and 16, respectively. The cells consisting of positive electrode material with 0–50% Pb_3O_4 did not achieve the rated capacity of 16 Ah after the first discharge capacity, whereas the cells consisting of positive electrode material made with 75–100% Pb_3O_4 achieved capacities above 16 Ah, after the first discharge cycle. The respective capacity increased gradually over the 11 cycle test.

The capacity cycle results of tubular electrodes that were formed with the high rate procedure showed on average a lower active material utilization when compared to the cells formed with the lower rate. The cells made with electrode material that contained 0–75% Pb_3O_4 had very low 1st capacity values. The capacities increased during the 11 capacity cycles, where the cells obtained capacities just below 16 Ah after the 8th cycle. This shows that a lot of unformed material remained in the electrode and only through repetitive cycling, did the unformed material convert to active lead dioxide. The cell that contained positive electrode material made
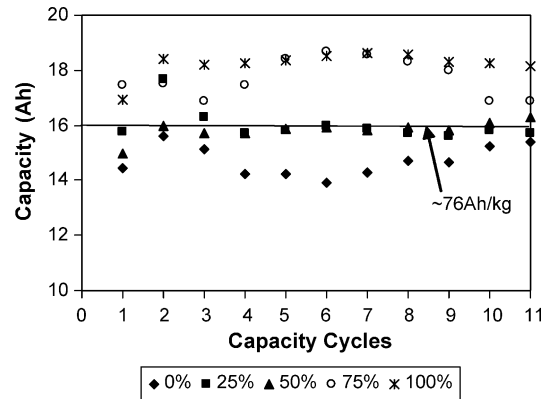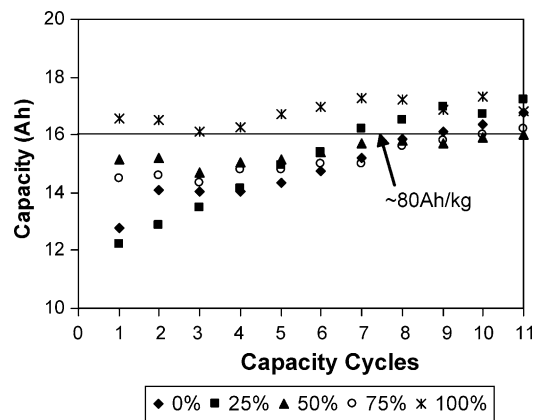

Fig. 15. Capacity cycle of tubular electrodes made with various concentrations of red lead formed with the low rate formation procedure.

Fig. 14. Porosity of formed active material for tubular plates formed at the high and low rate for various concentrations of red lead.

Fig. 16. Capacity (Ah) cycle of tubular electrodes made with various concentrations of red lead formed the high rate formation procedure.

with 100% Pb_3O_4 achieved a discharge capacity above 16 Ah after the first discharge test. This value remained relatively consistent throughout the 11-cycle test.

These results show that a higher rate formation sequence can be used for cells consisting of electrode material made with Pb_3O_4 only, where the surface area and porosity of the formed material was initially high, thereby encouraging efficient active material utilization.

4. Conclusion

The addition of red lead to the positive active material for flat plate electrodes has been compared with tubular electrodes for VRLA MCL batteries. The following are the most important experimental findings:

1. The addition of red lead improves the formation efficiency of both types of batteries by producing lead dioxide seeding crystals during the initial soaking stage before applying the formation current.
2. The results show that tubular electrodes were on average 30% less efficient than flat plate electrodes in terms of utilizing the active material per Ah kg^{-1} of active material. Hence, more active material in the tubular electrode is required with longer formation times.
3. The formation procedure used to electrochemically form the two types of MCL batteries made with flat plate or tubular electrodes can be optimized by using multi step formation sequences and controlling the temperature. The time was reduced by half, when compared to the existing process and still maintaining a relatively good first discharge capacity.

Furthermore, the following points apply specifically to the batteries made with flat plate electrodes.

1. It is beneficial to add small amounts of red lead (25%) to the paste preparation of the flat plate, since this improves the formation efficiency and results in first discharge capacities that are close to the rated capacity of the battery. Increasing the red lead content further, might increase the first capacity, but would result in a weaker active material in terms of its structural strength, which would start shedding during capacity cycling due to the lack of tri-basic lead sulphate formation during curing.
2. An important parameter is the visual presence of surface sulphates that remain on the formed electrodes, which was especially observed for plates containing no Pb_3O_4. The layer of surface sulphate inhibits the utilization of the underlying lead dioxide active material. Even the use of only 25% Pb_3O_4 decreases the effect of the surface lead sulphate considerably. Although the average lead sulphate content in these formed electrodes was above 20%, reasonably quick conversion of the material was observed during subsequent capacity cycling.

Regarding the use of tubular electrodes, the following important points can be noted:

1. There was no significant benefit in using lower amounts of Pb_3O_4 in the manufacturing of tubular MCL electrodes. The results show that they should contain at least 75% Pb_3O_4.
2. The results show that active material of electrodes that contain 75 and 100% Pb_3O_4, had a higher surface area for both cured and formed cells than the electrodes containing lower amounts of Pb_3O_4, and that the higher formation rate showed better utilization of the active material. However, with subsequent capacity cycling, the surface areas of all samples decreased and were very similar in value, irrespective of the initial amounts of Pb_3O_4 present in the cured material.

Acknowledgment

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