

The influence of the pickling and curing processes in the manufacturing of positive tubular electrodes on the performance of lead-acid batteries

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Abstract

The effects of changing the dipping and curing times of tubular positive electrodes on the discharge capacity were investigated. The comparative study showed that longer dipping and curing times do not necessarily result in electrodes with better first capacity performance. Acid adsorption studies of tubular plates filled with lead oxide showed that about one-third of the acid, that would have been adsorbed after 15 h, was already adsorbed after 5 s of dipping. The optimum surface area and porosity of the cured active material was obtained after 15–60 min of dipping. This is equivalent to the rest period used in the formation process where the plates are kept in the acid just before charging. Curing times should be kept around 24 h in order to reduce the free lead in the oxide. The study showed that the pore size distribution of the formed active material influenced the high current discharge ability more than the available surface area of the positive electrode. However, the surface area and pore size distribution changed dramatically during capacity cycling and the continuous capacity performance of the tubular electrode was partially influenced by the initial characteristics of the cured active material.

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1. Introduction

Lead-acid batteries that are assembled with tubular positive electrodes are used in a wide range of applications such as vehicle traction and stationary standby power (UPS). The robust structure of the cell and in particular the tubular design of the positive electrode have resulted in a battery that can undergo deep discharge life cycles with limited active material shedding that causes cell failure.

One way of manufacturing stationary type batteries is to assemble dry-charged cells, where both the positive and negative electrodes are assembled in their fully formed state. The electrolyte would be added just before application. During the manufacturing process, it is possible to optimize the formation conditions for the tubular design outside the assembled cell. Many authors have investigated tubular cell designs with their variables in manufacturing and formation in order to optimize the performance of the active material [1–4]. They have found that the formation acid should be at a specific gravity (S.G.) between 1.05 and 1.15 for optimal utilization of the active material. Optimal formation can be easily achieved during the dry charge process where the S.G.

of the formation acid can be easily controlled in a bath. However, many tubular design cells such as those used in vehicle traction applications 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, temperature during formation and the final electrolyte S.G. become important. One way of overcoming problems is to use a two-stage formation process. The cells are allowed to start their formation in a lower S.G. acid. This is then followed by emptying the jars and filling them with a higher S.G. acid before the finishing stages of the formation [5]. However, the additional step required in the process becomes costly. In order to aid the formation process of the active material in the tubular plates, red lead (Pb_3O_4) is frequently added to the oxide during the filling process of the tubes. This can vary from 10 to 80% and is considerably more expensive than the normal filling oxide [4].

After filling the tubes with dry lead oxide, the plates are subjected to a process known as soaking or dipping in a low S.G. acid. This is also described by some authors as pickling [3]. This process has three main advantages. Firstly, it eliminates the loose dust that coats the exterior of the tubes thereby making the plates easier to work with for assembling purposes. Secondly it would aid in the formation of mono-basic and tri-basic lead sulphates during the curing

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stage and thirdly, it would reduce the free lead that was present in the filling oxide. Free lead that remains in the active material can lead to lower formation efficiencies and possible self-discharge in the final product. Higher formation temperatures are usually observed when the active material contained a high concentration of free lead [4]. In practice, this process of dipping can vary from a few minutes up to a few hours. A number of authors have investigated the relationship between the formation efficiency and curing times [2,6].

Battery manufacturers are always looking at improving their production processes in order to become more efficient. It was necessary to investigate the possibility of reducing the production process time in the manufacturing of tubular jar-formed cells without decreasing the performance of the final product. The following study will investigate the influence of varying dipping and curing times of tubular plates that are jar-formed, without compromising the final cell capacity performance.

2. Experimental

The positive tubular plates chosen for the study were 14 spine plates with rectangular profiled non-woven tubes. The plates were vibration-filled with an industrial grade grey oxide that contained 0.012% Syloid (amorphous silica). The average packing density of the spines was 3.9 g/cm^3 . The characteristics of the grey oxide used are summarized in Table 1.

The phase analysis of the oxide and active material was determined by X-ray powder diffraction (XRD) and the data was analyzed using the method developed by Hill [7]. The BET surface area was determined by nitrogen gas adsorption on the active cured or formed material that was carefully removed from the fabric tube and inner Pb-spine. The absolute density of formed active material was determined by using a Helium pycnometer. The Hg porosimetry pore volume distribution and porosity was carried out on a complete 12 mm length section of a single spine containing the active material.

The oxide-filled tubular plates were dipped in 1.1 S.G. sulphuric acid for 5 s, 15 min, 60 min, 5 h and 15 h, respectively. The dipped plates were subsequently washed with water in order to remove any excess acid and were allowed

to cure in a humidity oven set at 25°C and 85% humidity. Selected plates from the different batches were removed after 12, 24 and 48 h curing time. The plates were allowed to air-dry completely and reweighed before being assembled into cells. The cells were assembled with one negative flat plate on either side of the positive tubular plate. The cells were rated at 22.5 Ah at the C_5 rate and contained an excess amount of acid. The formation acid used had an S.G. of 1.24 that was adjusted to 1.25 after formation. The assembled plates were allowed to soak for 1 h in the acid before commencing with the formation.

The formation conditions for all cells were kept the same and were done at constant current (4 A) until 250% of the theoretical active material capacity was achieved [1]. An initial C_5 discharge test to 1.75 V was done followed by a constant voltage (2.6 V) recharge of 140% of the discharged capacity. This was followed by a high current (50 A) discharge test and a 10 cycle test at the C_5 rate. Once the 10 cycle test was completed, another 50 A discharge test was done. All discharge capacities and cycling tests were done at room temperature. The active material of duplicate cells of the different dipping and curing times were analysed for their respective phase composition, BET surface area, absolute density, porosity and pore volume distribution after the curing, formation and capacity cycling steps. All discharge capacity results are recorded in Ah/kg of active cured material.

3. Results and discussion

The relationship between the acid adsorption and the different dipping times show that a significant amount of acid had been adsorbed after only 5 s of dipping (Fig. 1). The amount of acid adsorbed within the first 5 s was approximately one-third of the acid that would be adsorbed after 15 h. Lin et al. [2] reported that an acid adsorption of 170 mg/g oxide should be achieved for optimal formation. However, in this study an acid adsorption of only 130 mg/g

Table 1
Characteristics of filling oxide

| | |
|---|-------|
| Free lead (%) | 15.2 |
| α -PbO (%) | 13.5 |
| β -PbO (%) | 71.3 |
| Acid adsorption (mg/g oxide) | 153.0 |
| Apparent density (g/in.^3) | 29.42 |
| BET surface area (m^2/g) | 0.71 |
| Particle size mean D [4,3] (μm) | 5.51 |
| Particle size median D (v, 0.5) (μm) | 4.44 |

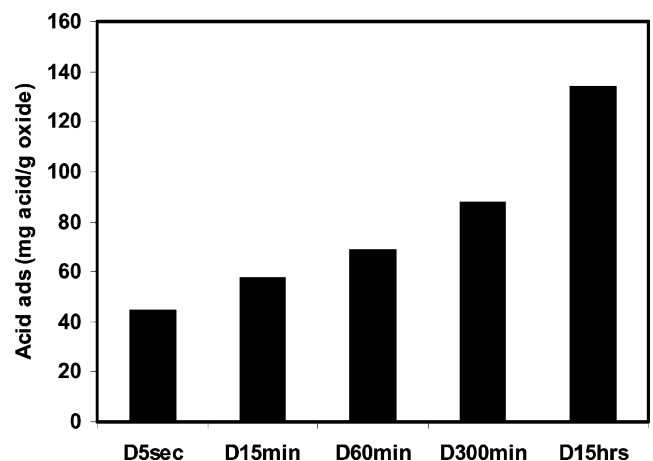


Fig. 1. Relationship between the acid adsorption and dipping time for tubular positive plates.

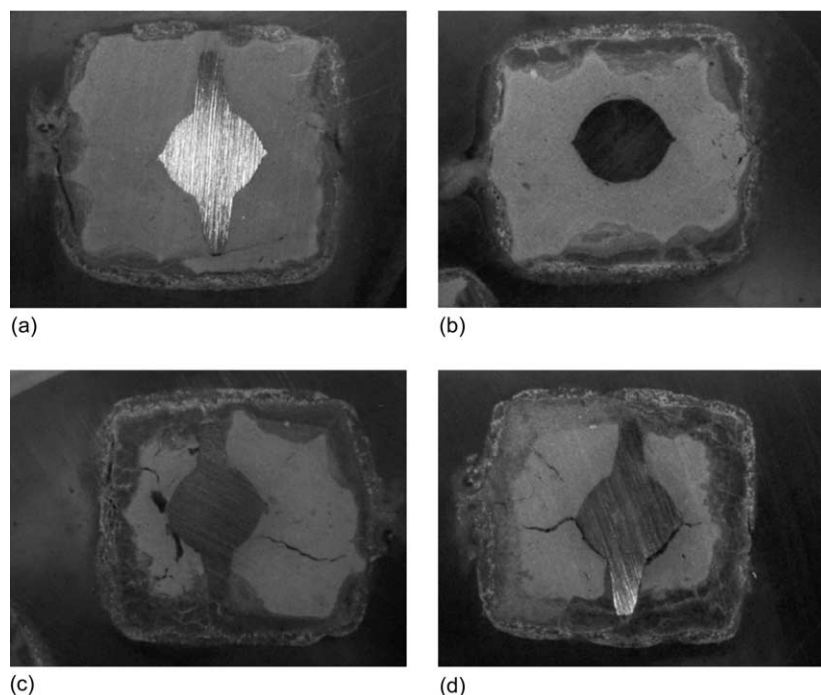


Fig. 2. Stereo-microscope view of cross-sections of spines that were dipped for various times and cured for 48 h. (a) Spine dipped for 15 min; (b) spine dipped for 60 min; (c) spine dipped for 300 min; (d) spine dipped for 15 h.

oxide could be achieved after 15 h of dipping. The cross-sectional stereomicroscope pictures (Fig. 2a–d) show the depth to which the acid penetrated after the various dipping times. Leaving a plate in acid for 15 h did not result in the acid to penetrate all the way through the oxide to the middle Pb-spine. Instead, a thick crust of lead sulphate was formed on the exterior surface of the spine. Table 2 summarizes some of the XRD phase analysis results for the cured and formed active materials after the 12 and 48 h of curing. The total sulphate content of the cured material was considerably lower than the results indicated in Fig. 1. This was because a

lot of the sulphate material would have remained on the non-woven outer tube that was removed before analysis. The results showed that there was an increase in lead sulphate and mono-basic lead sulphate for the samples that were dipped for longer periods of time in acid. However, there was no significant difference in phase composition for the various samples that were cured for 24 or 48 h, nor was there any significant increase in the tri-basic lead sulphate for samples that were cured for a longer time.

The changes in the surface area of the cured active material with dipping and curing times are shown in

Table 2

XRD phase analysis of the cured and formed active material of tubular spines that were dipped in acid for various times and cured for 12 and 48 h, respectively

| Sample | Cured active material (%) ^a | | | | | Formed active material (%) | | |
|---------------------|--|--------------|----|----|-------------------|----------------------------|---------------------------|-------------------|
| | α -PbO | β -PbO | T3 | T1 | PbSO ₄ | α -PbO ₂ | β -PbO ₂ | PbSO ₄ |
| D: 5 s; C: 12 h | 65 | 12 | 0 | 8 | 8 | 8 | 68 | 24 |
| D: 5 s; C: 48 h | 74 | 12 | 0 | 4 | 6 | 10 | 70 | 20 |
| D: 5 min; C: 12 h | 65 | 11 | 4 | 8 | 4 | 8 | 72 | 20 |
| D: 5 min; C: 48 h | 66 | 10 | 7 | 7 | 4 | 9 | 66 | 25 |
| D: 60 min; C: 12 h | 59 | 11 | 0 | 13 | 8 | 9 | 69 | 22 |
| D: 60 min; C: 48 h | 57 | 10 | 4 | 14 | 12 | 10 | 66 | 24 |
| D: 300 min; C: 12 h | 60 | 10 | 4 | 8 | 10 | 10 | 66 | 24 |
| D: 300 min; C: 48 h | 61 | 12 | 4 | 11 | 9 | 7 | 66 | 27 |
| D: 15 h; C: 12 h | 52 | 11 | 4 | 0 | 26 | 9 | 59 | 32 |
| D: 15 h; C: 48 h | 44 | 11 | 4 | 10 | 27 | 7 | 68 | 25 |

D: various dipping times; C: various curing times; T1: mono-basic lead sulphate; T3: tri-basic lead sulphate.

^a The free-Pb values are shown in Fig. 4.

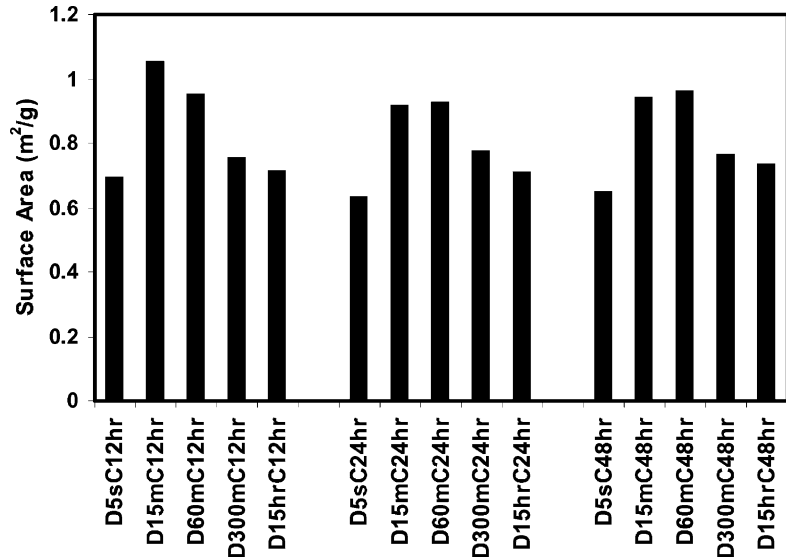


Fig. 3. Relationship between the BET surface area and various dipping and curing times of cured active material.

Fig. 3. These results show that there was a sharp increase in the surface area for the cured active material in going from a dipping time of 5 s to 15 and 60 min, respectively. A gradual decrease in the surface area of the active material was observed for samples that were dipped for 5 and 15 h, respectively. This trend was the same, irrespective of the curing times. During the initial stages of dipping, the lead oxide would react with the acid to form lead sulphate. If the oxide remained in the acid for longer periods of time, the lead sulphate crystals would start to grow and fuse together to form larger crystals. This in turn would cause a decrease in the surface area of the active material.

The changes in the free-Pb of the cured active material with dipping and curing times show that the free-Pb decreased considerably between the 12 and 24 h of curing (Fig. 4). The decrease in free-Pb after 12 h of curing was

only 6%, whereas the decrease after 24 h was almost 11%. The free-Pb after 48 h of curing was only slightly lower than that after 24 h of curing. Literature recommended that the free-Pb after curing should be kept low in order to eliminate possible Pb in the final formed active material [8]. No Pb was observed in the final formed material and higher formation temperatures, due to the higher free-Pb in the cured active material, were not noticed because the cells used had an excess amount of electrolyte and would allow the transfer of any excess heat. The scale-up effect of using more plates per cell could result in higher formation temperatures, but this could be overcome by using an initial low temperature filling acid.

The surface area of the formed plates that were dipped for 5 s showed a greater surface area when compared to the plates that were dipped for longer periods of time (Fig. 5). It would seem that the increase in surface area takes place

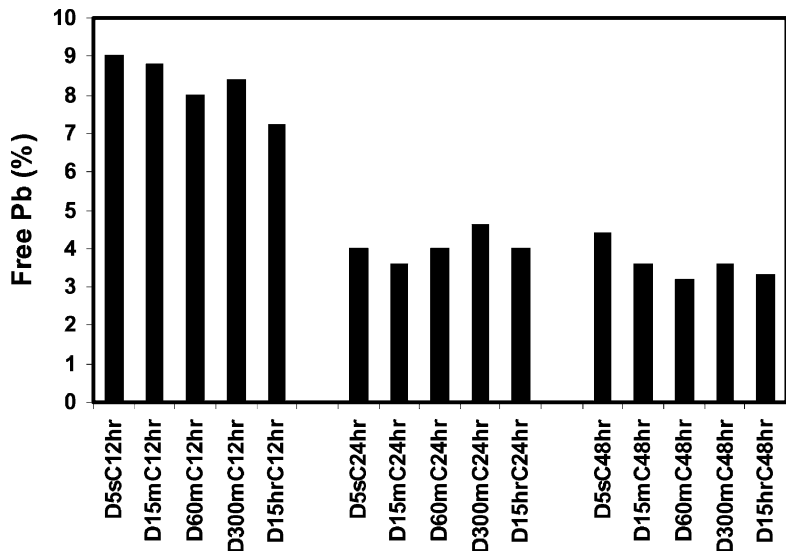


Fig. 4. Relationship between the free-Pb and various dipping and curing times of cured active material.

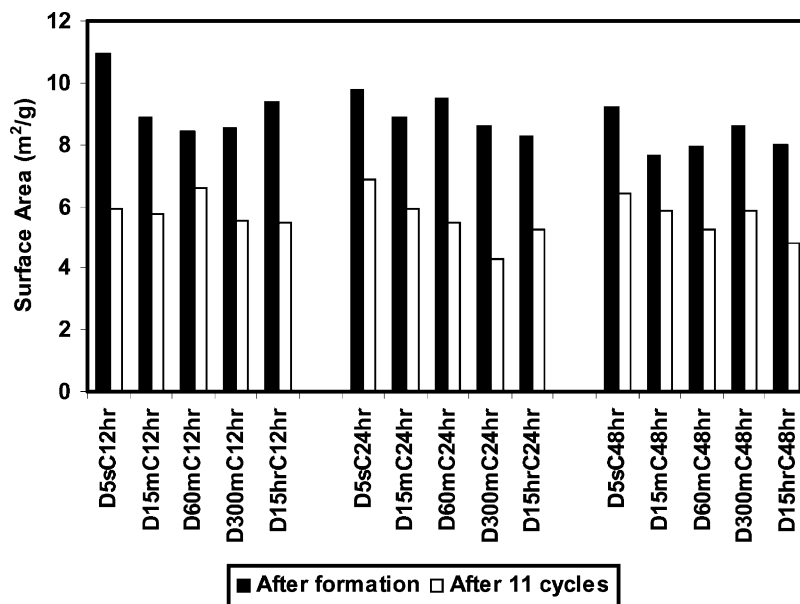


Fig. 5. Relationship between the BET surface area and various dipping and curing times of formed active material after formation and after 11 cycles.

during the initial stages of formation, thereby allowing more active sites to develop. The crystal growth and size of the lead sulphates crystals during this time would be critical and could increase considerably in size as the soaking time increases [5]. The results in Fig. 3 showed that the largest surface area of the cured active material was obtained for a dipping time between 15 min and 1 h. Even though the surface area after 5 s of dipping was not optimal, the surface area would increase during the 1 h soaking time before formation. The plates that were dipped for the longer times (5 and 15 h) before curing, showed a decrease in surface area of the final formed active material when compared to the plates that were dipped for shorter times. This could be due to the non-conducting sulphate crystals that were already present in the active material, especially concentrated near the exterior layer of the tubular spine (Fig. 2d). These crystals would increase in size during the pre-formation soaking time and thereby decrease the available surface area and reduce the effective penetration of electrolyte to the core of the spine during formation. Hence, a high concentration of large lead sulphate crystals would reduce the formation efficiency. This can also be seen in the slightly higher sulphate content of the formed active material for the plates that were initially dipped for 15 h (Table 2). There was a considerable decrease in surface area of the active material after 11 capacity cycles (Fig. 5). The surface area of the active material that was initially dipped for longer times (300 min and 15 h), showed a lower surface area after the 11th discharge cycle when compared to the samples that were dipped for shorter periods of time. Hence, the effect of a relatively lower surface area after formation is still evident after 11 capacity cycles, although changes in the morphology of the active material had taken place during cycling where most of the active material would be lead dioxide.

Only slight variations were observed in the absolute density of the active material after formation between the samples that were dipped and cured for different times (Fig. 6). However, all samples showed a slight decrease in the absolute density of the active material after 11 capacity cycles, except for the samples that were dipped for 15 h before curing, where a slight increase in absolute density was observed. These trends were irrespective of the length of curing time used.

The porosity, determined by Hg porosimetry, of the cured, formed and capacity cycled plates are summarized in Fig. 7. The samples studied were taken from the plates that were dipped for different times and cured for 48 h only. In order to evaluate the porosity of the active material effectively, a 12 cm complete section of spine with the outer fabric and active material still in one piece, was used. This caused the results of the porosity to be slightly lower than the porosity of the active material only, which was reported in the literature to be about 50% on average [9]. The results for the cured plates showed a decrease in porosity with increasing dipping time. The cumulative pore volume distributions determined by Hg porosimetry for the cured samples show that the mean pore diameter for the cured active material was about 1 μm (Fig. 8). The results also show that the cured plates that were dipped for 15 h had a lower pore volume penetration than the other spines that were dipped for shorter times. These results can be largely attributed to the large amount of sulphates that formed a crust layer on the surface of the spine (see Fig. 2d), reducing the penetration of the Hg into the sample and ultimately reducing the effective penetration of the electrolyte during formation.

The increase in porosity after formation was the lowest for the 5 s dipped plates, with an increase to the 60 min dipped

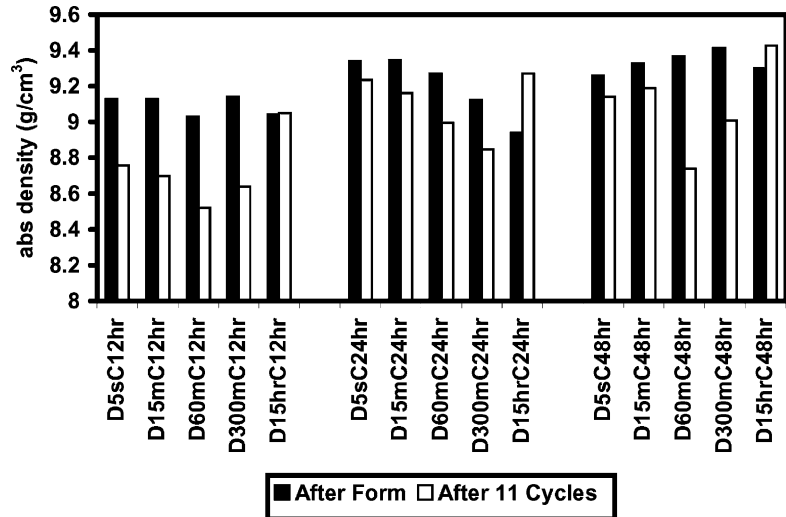


Fig. 6. Variation of the absolute density between the formed active material and after 11 capacity cycles for the different curing and dipping times.

plate and followed by a slight decrease for the longer dipped plates (Fig. 7). However, after capacity cycling, all plates showed a decrease in porosity, with the 60 min dipped plate the lowest. The incremental intrusion volume of the formed plates (Fig. 9) show that pore size distribution varied between the various dipping times. After formation, all samples show two peaks of pore sizes at 1 and 0.05 μm , respectively. The plates that were dipped for 5 s showed a slightly larger pore volume at the pore size of 0.05 μm , whereas the plates dipped 300 min and 15 h showed a larger pore volume at 1 μm , respectively. The pore size distribution after 11 capacity cycles (Fig. 10) show that the pore sizes are spread over a wider region between 5 and 0.05 μm with an increase in the median pore diameter. A noticeable decrease in total intrusion volume was also observed when compared to the results from the formed plates only. The Hg porosimetry results are based on intrusion pressure only. For all the samples studied, no extrusion results were obtainable. The

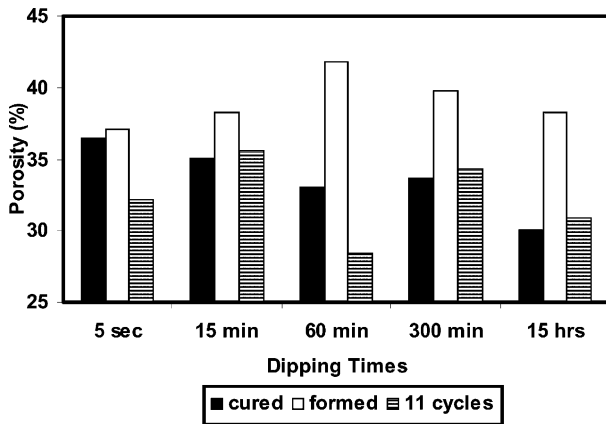


Fig. 7. Relationship between the porosity (%) and the various dipping times of the cured, formed and the after 11 capacity cycled active material. The curing time was 48 h.

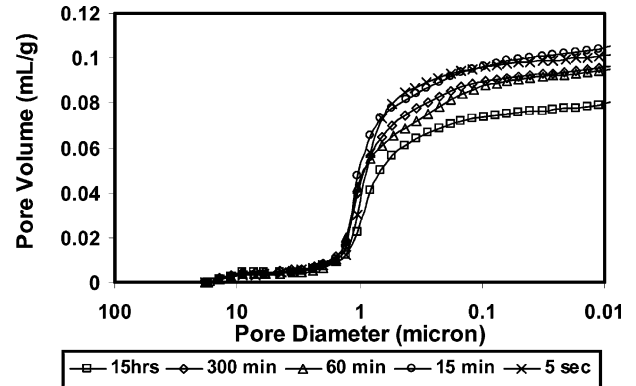


Fig. 8. Relationship between the cumulative pore volume distribution and the pore diameter for the various dipping times of the cured active material. The curing time was 48 h. Pore volume: ml Hg per mass of 12 mm complete spine.

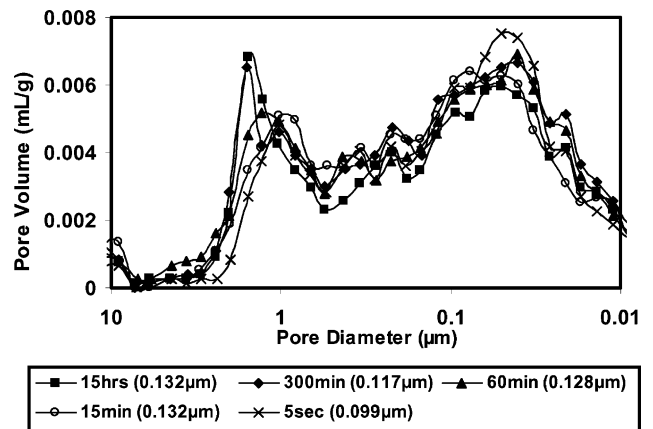


Fig. 9. Relationship between the incremental pore volume distribution and the pore diameter for the various dipping times of the formed active material. The curing time was 48 h. Pore volume: ml Hg per mass of 12 mm complete spine. The median pore diameter in brackets is shown for each respective sample.

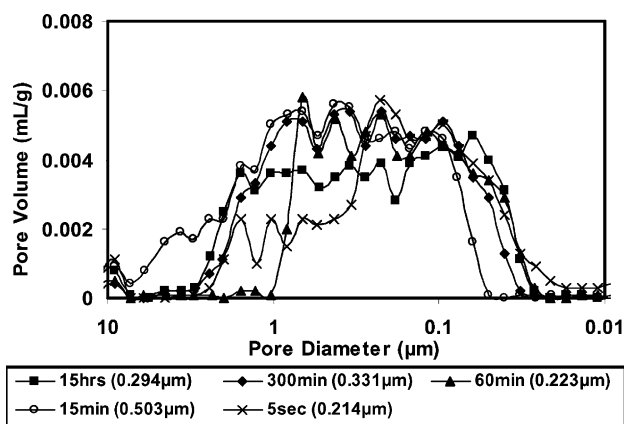


Fig. 10. Relationship between the incremental pore volume distribution and the pore diameter for the various dipping times of the formed active material after 11 capacity cycles. The curing time was 48 h. Pore volume: ml Hg per mass of 12 mm complete spine. The median pore diameter in brackets is shown for each respective sample.

reasons for this could be that the intrusion of Hg caused the internal pores and voids to collapse during the high pressures, or the pores have “ink bottle” type structures preventing the Hg from extruding during the decrease in pressure.

The first C_5 discharge capacity for the plates that were dipped for 5 s was similar to the capacity obtained for the plates that were dipped for 15 h (Fig. 11). However, for the plates dipped for 15, 60 and 300 min, respectively, a slightly lower first capacity performance was obtained. This trend was observed irrespective of the curing times. The trends of the first capacity are very similar to the trend observed for the surface area of the formed plates (Fig. 5). During the subsequent capacity cycling, the capacities of the cells increase significantly for the next 2–3 cycles and would start to plateau at a relative consistent discharge capacity until the 11th cycle. After this, some cells started to show a

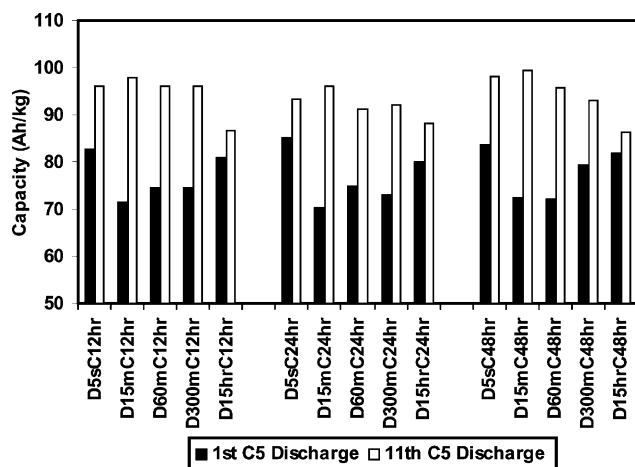


Fig. 11. Relationship between the first and 11th C_5 discharge capacities and various dipping and curing times for tubular positive cells.

slight decrease in their respective discharge capacities. On average, all cells showed similar capacities (Ah/kg) after 11 cycles except for a slightly lower value for the plates that were dipped for 15 h, where the increase in capacity was the lowest during cycling when compared to the electrodes that were dipped for shorter periods of time. This trend was similar for the various curing times and was similar to the trend observed when comparing the surface area of the active material after the 11th capacity cycle (Fig. 5). A noticeable decrease in surface area was observed between the first and 11th cycles. The initial increase in capacity during the cycling can be mainly ascribed to the conversion of unformed active material to lead dioxide. The maximum discharge capacity is reached when all of the active material would then have been converted. With continuous cycling, other factors start to contribute to the decrease in discharge capacity. These include a decrease in active material porosity, available surface area and loss of contact between lead dioxide particles. Active material shedding in tubular plates is not as common as in flat plate automotive batteries and would only be noticeable after many more capacity cycles. The main contributing factors to a decrease in discharge capacity during cycling can be attributed to the decrease in porosity and surface area of the active material.

The results of the high current discharge (50 A) tests after the first and the 11th C_5 discharge capacity tests are shown in Fig. 12. The first high rate capacity for the plates that were dipped for 5 s and 15 h were lower than the capacities for the plates dipped for 15, 60 and 300 min. This trend is almost the opposite of that observed for the first C_5 capacity test. The high rate capacity that was repeated after 11 cycles was considerably lower than the first one, except for the plates that were dipped for 15 h. Similarly, the absolute density determined for the formed and cycled active material showed a similar trend (Fig. 6). These results show to what extent the pore size and surface area of active material would influence the cell potential through either a diffusion-controlled reaction (concentration gradient) or through a resistance-controlled reaction (potential gradient). During the high rate discharge the reactions are primarily concentrated at the surface of the active material and are dependent on the rate and ability for the acid to penetrate to the active sites. The decrease in high rate capacity after 11 cycles can be linked to the decrease in surface area. The slight increase in capacity for the 15 h dipped sample can be due to the increase in active material (lead dioxide) that became available during continuous cycling. Even though the 5 s dipped plates showed a high surface area and an initial larger first C_5 capacity, the high rate (50 A) discharge was comparatively lower. The lower capacity would be due to the smaller pore size that would limit the available acid to diffuse to active sites rather than available surface area. The lower discharge rate (C_5) is more dependent on the pore volume available for the conversion of active material than just on the surface area of the active material as is the case for high rate discharging.

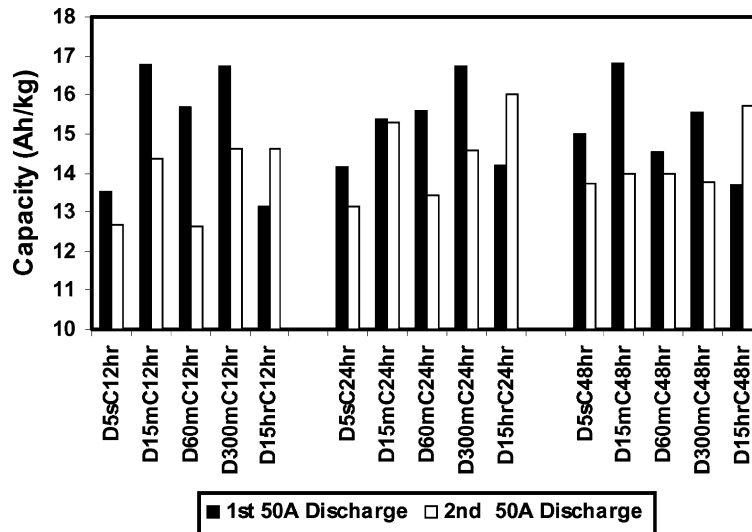


Fig. 12. Relationship between the first 50 A discharge and after the 11 capacity cycle testing for the various dipping and curing times for tubular positive cells.

4. Conclusion

During manufacturing, the positive electrodes are usually not completely formed to lead dioxide as active material. As much as 30% of the unformed material, which is mainly made up of lead sulphate, can remain in the tubular plates [3]. This study showed that there was no significant difference between the first capacity of tubular positive plates that were dipped for 5 s or 15 h. The cell's capacity improved with capacity cycling until it would plateau to a relatively constant capacity value for the first 11 cycles. The study showed that the length of time for which the positive tubular plates were dipped in acid prior to curing and formation does have an influence on the surface area and pore volume distribution of the active material even after subjecting the active material to a number of charge and discharge cycles. The study also showed that it would be sufficient to dip tubular positive plates for 5 s before curing. This would eliminate any loose oxide on the surface of the tubes and would give the plate enough rigidity for assembling purposes. About one-third of the acid that would have been adsorbed after 15 h is adsorbed during this step. Increasing the dipping time before curing, did convert more lead oxide to lead sulphate but reduced the surface area and formed a hard crust of lead sulphate near the surface of the spine reducing the effectiveness for electrolyte to penetrate to the core of the electrode. The optimal surface area on the active material required for optimum formation would be achieved during the 15–60 min soaking stage prior to applying the

formation current. The respective 50 A and C_5 discharge capacity study of the cells showed that multiple diffusion and potential reaction mechanisms take place during the discharge of tubular plates. These depend on the active material conversion, surface area, porosity and pore size distribution. These parameters change considerably during the life cycle of the plates and depend on the requirements of a particular application (low or high current rates).

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References

- [1] H.W. Yang, Y.Y. Wang, C.C. Wan, *J. Power Sources* 15 (1985) 15.
- [2] M.T. Lin, Y.Y. Wang, C.C. Wan, *Electrochem. Acta* 31 (5) (1986) 565.
- [3] H. Bode, *Lead-Acid Batteries*, Wiley, New York, 1977.
- [4] L. Prout, *J. Power Sources* 41 (1993) 163.
- [5] N.E. Hehner, *Storage Battery Manufacturing Manual*, 3rd ed., IBMA Inc., USA, 1986.
- [6] A.T. Kuhn, J.M. Stevenson, *J. Power Sources* 10 (1983) 389.
- [7] R.J. Hill, *J. Power Sources* 9 (1983) 55.
- [8] L. Prout, *J. Power Sources* 41 (1993) 107.
- [9] I. Dreier, F. Saez, P. Scharf, R. Wagner, *J. Power Sources* 85 (2000) 117.