JOURNAL OF APPLIED ELECTROCHEMISTRY 9 (1979) 381–387

The formation of Planté cells using a nitrate process

W. H. EDWARDS

Chloride Industrial Batteries Ltd, Exide Works, Clifton Junction, Manchester, UK

N. A. HAMPSON

Chemistry Department, Loughborough University of Technology, Leicestershire, UK

Received 13 June 1978

The results are presented of a study of the fundamental and technological aspects of a new process for the production of Planté cells. In this process the classical use of the perchlorate ion is replaced by the nitrate ion.

1. Introduction

A very large number of electric power stand-by batteries are manufactured using the Planté process. The original process of Planté [1] involved a repetition of cycles of oxidation

$$Pb + H_2SO_4 \rightarrow PbSO_4 + 2H^+ + 2e \qquad (1)$$

$$PbSO_4 + 2H_2O \rightarrow PbO_2 + H_2SO_4 + 2H^+ + 2e \qquad (2)$$

and reduction applied to pure lead electrodes in sulphuric acid. This process was continued until a thick layer of porous PbO_2 was formed on one electrode and a corresponding layer of porous lead was formed on a second. The conventional 'modern' process [2] employs perchloric acid as a 'forming agent' which accelerates Reactions 1 and 2 in the sense that considerable thicknesses of active materials can be built up in quite short times. The forming agent acts via the high solubility of lead perchlorate so that passivating layers of lead sulphate are avoided. The form of the pure lead electrode (blank) is a parallel array of lamells forming a closely spaced rib structure in order to increase both the surface area and the adhesion of the formed layer. After a cathodic cleaning process in sulphuric acid (1 M containing the forming agent) the positive plate is anodically attacked and then cathodically reduced in the formation electrolyte. For completion the 'positives' are fully oxidized (to PbO_2). However, before this is carried out all traces of perchlorate forming agent must be rigorously removed by washing. This washing is crucial if the useful life of the final product is to be satisfactory and must be carried out with the electrode in the reduced state. If traces of perchlorates are left behind in service continued attack rapidly consumes the base lead and the cells fail due to short circuiting.

We have already confirmed [3] that other ions may be useful forming agents. There has been no large scale application [4] although a related process involving nitric acid was used for the production of the now obsolete 'Manchester' plates [2].

It is an attractive goal to seek a forming agent which would not detract from life performance if it remained in the finished cell. Not only would this avoid the tedious process of washing but the 'forming' process could be performed in the cell, i.e. jar formation. It is clear that the key properties of the forming ion sought would be the existence of a corresponding soluble lead(II) salt and either the rapid transformation of the ion to a passive (non-aggressive) state or its elimination as gaseous products from the cell.

Of the ions examined by us previously [3] only two, nitrate and sulphamate, appeared to possess these properties. Of these the nitrate ion appeared to be more attractive because of the cheapness and greater commercial availability. This paper is concerned with the development of a Planté process based on the nitrate ion.

Printed in Great Britain.

2. Experimental

Preliminary experiments on microelectrodes ($\phi = 2$ mm) of lead (99·999% supplied by Johnson Matthey) shrouded in Teflon were made under potentiostatic control (Chemical Electronics potentiostat type TR70-2A). The electrode could be rotated at a strictly controlled speed (Chemical Electronics, type RD1) monitored by a stroboscope (Dawe Instruments type 1200 E). The potential of the working electrode was measured via a conventional Luggin system using a multimeter (Hewlett–Packard type 3409 A).

Galvanostatic measurements were made using conventional Planté cells with conventional resistance-controlled circuits. The cells used consisted of parallel arrays of four positive and five negative electrodes separated by sintered PVC. When fully processed these cells delivered nominally 26·25 A h in 5 h at a potential greater than 1·82 V. The negative electrodes in these cells consisted of lead–antimony alloy grids pasted with a mixture of 'leady' oxide (grey oxide) and sulphuric acid. On reduction these were transformed to porous (spongy) lead.

Nitrate and ammonium analyses were made using ion selective electrodes. For NH_4^+ a meter (EIL model 7050) was used in conjunction with a suitable dual reference electrode (EIL model 8002-2). The potential of this electrode was found to conform to

$$E(\text{mV}) = 103{\cdot}02 - 55{\cdot}27 \log_{10} [NH_4^+] \ (\text{mg dm}^{-3*})$$

For NO_3^- ion a dual electrode (Orion model 93-07) was used which had a potential response

$$E(\text{mV}) = -263{\cdot}3 - 54{\cdot}4 \log_{10} [NO_3^-] \ (\text{M}^*)$$

Morphological examinations of electrode sections were made using the SEM (JEOL JSM 35) and the technique already described [5, 6].

3. Results and discussion

3.1. *Potentiostatic experiments*

Fig. 1 shows the current–time curve corresponding to a potentiostatic experiment in which the lead electrode was maintained at 1·35 V measured against a Hg_2SO_4/Hg electrode in the same solution (4·0 M H_2SO_4). The magnitude of the current flowing across the electrode is quite small and can be explained by the need to replace $PbSO_4$ removed by dissolution in the electrolyte solution ($PbSO_4$ solubility ~ 3·0 mg dm^{-3} in this concentration of H_2SO_4). The addition of nitric acid to the solution produces a marked increase in current flow which increases with time until a steady state is achieved after about 20 min. These data also are shown plotted in Fig. 1. There was no rotation speed dependence of these curves indicating that the controlling factor was the passage of electricity through a $PbSO_4$ layer on the electrode. The increase in current with time is probably connected with the development of centres of localized attack (pitting corrosion) on the base metal. Initially the surface is covered with a layer of $PbSO_4$, the current at the start of the experiment reflects the enhanced solubility of Pb^{2+} ions due to the presence of nitrate ion. As the reaction proceeds localized corrosion causes an increase in current; however, this increase tends to a limit due to control of the reaction by the metallurgical characteristics of the metal when adequate nitrate ion is available. The proportionality between steady state current and nitrate concentration observed initially in Fig. 1 is lost as the nitrate concentration is increased.

A choice of concentration of added nitrate ion was made on the basis of the argument that the additive concentration should be in the region where the steady current was controlled by this addition. Thus, a value of 0·16 mol dm^{-3} was chosen as the optimum concentration. (From the practical cell production time standpoint this proved to be an excellent choice.)

3.2. *Galvanostatic experiments*

A group of seven cells each of which contained initially 0·16 mol dm^{-3} HNO_3 added to 1·200 specific gravity H_2SO_4 were charged galvanostatically at 4 A for a period of 48 h. Cells were removed periodically for examination electrochemically, analytically and morphologically. The development of electrical capacity is shown in Fig. 2. The formed capacity of the cell is initially quite low but after about 24 h charge ~ 80% of the required electrical storage capacity has been realised. Over the final 24 h the formed capacity increases only slightly.

---

* The difference in units is due to convention.

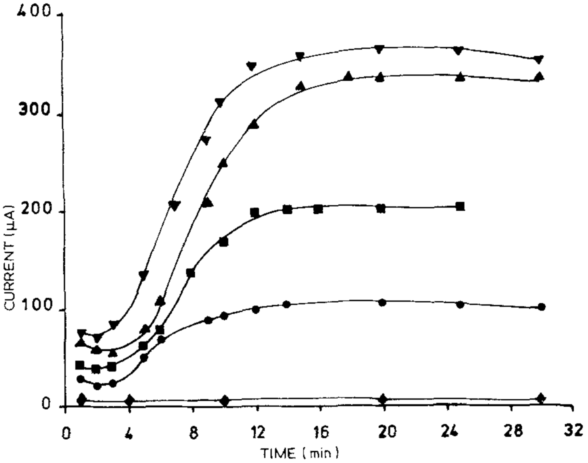

Fig. 1. Current–time characteristics of lead electrodes in H_2SO_4 (4·0 M) containing HNO_3. 23° C, 1·35 V versus Hg/Hg_2SO_4 (PbO_2 region). ◆, no HNO_3; ●, 0·08 M HNO_3; ■, 0·16 M HNO_3; ▲, 0·24 M HNO_3; ▼, 0·32 M HNO_3.

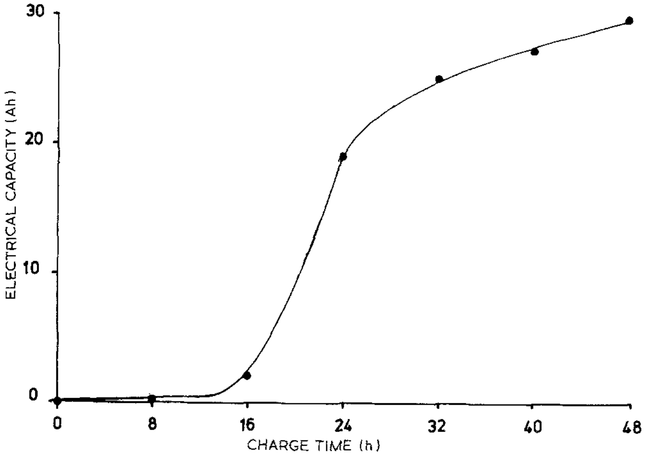

Fig. 2. The development of electrical storage capacity with charge at 4 A for a cell of 26·25 A h nominal storage capacity.

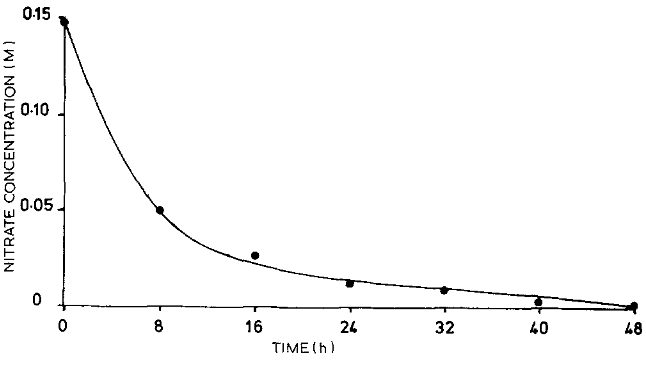

Fig. 3. The removal of NO_3^- ion from cells corresponding to Fig. 2.

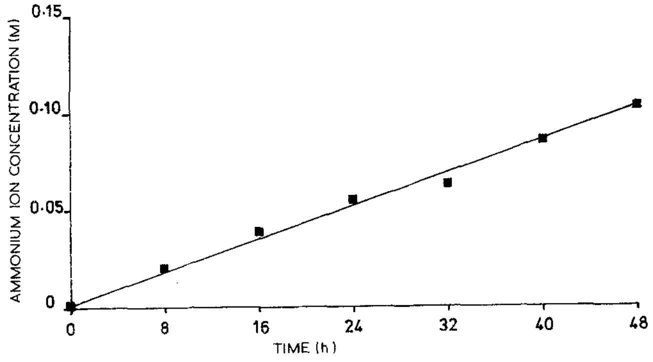

Fig. 4. The development of NH_4^+ ion in cells corresponding to Fig. 2.

Fig. 3 shows the removal of nitrate ion from the cell electrolytes during the charging period and Fig. 4 shows the concurrent formation of NH_4^+ ion over this period. It is clear that the ultimate product of the electrolysis of the nitrogen species is ammonium ion, which does not affect the subsequent cycle life of the cell. This is clear from a number of investigations recorded in the literature.

Morphological studies of the development of PbO_2 and $PbSO_4$ showed a great similarity to previously reported systems [5, 6] and confirm that the structure of the surface lead sulphate and lead dioxide is similar to that prepared by the oxidation of massive lead and lead oxide pastes in sulphuric acid. We can conclude, therefore, that the nitrate ion is not modifying the formed electrode structure.

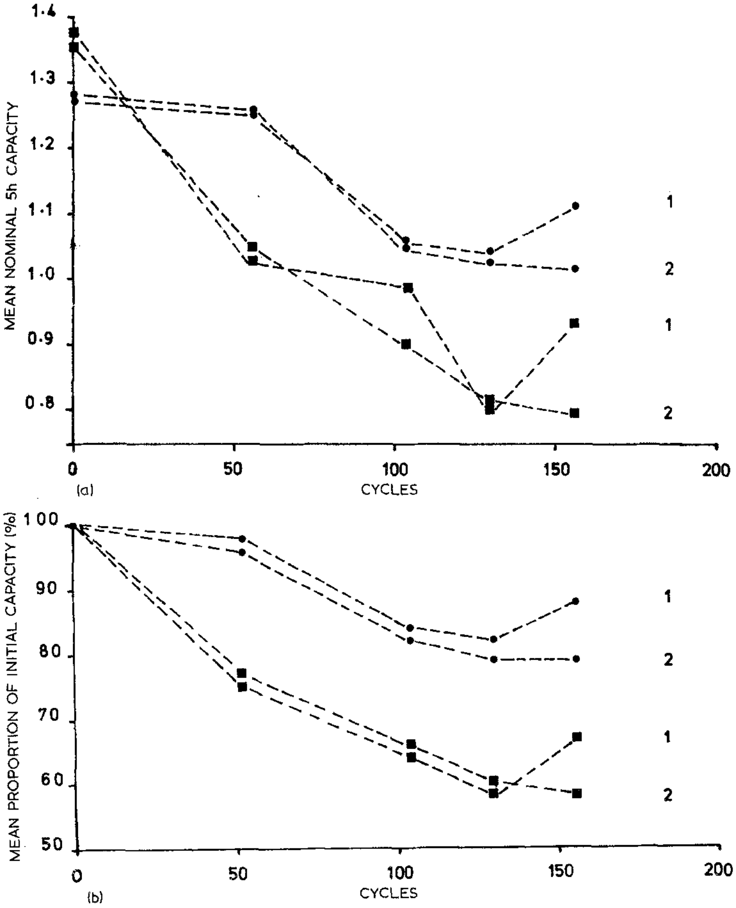

Fig. 5. Comparison of cycle life test of 'nitrate' and 'perchlorate' formed cells. (a) nominal capacity; (b) proportion of initial capacity; ●, 'nitrate'; ■, perchlorate. Cells discharged 4 h at 5 h rate (5·25 A); recharged 8 h at 3 A. Capacities determined as data points at 5 h rate. 1 and 2 denote different batches of cells.

3.3. *Small scale industrial trial*

Groups of 36 cells, each with four positive electrodes and five negative electrodes (26·25 A h in 5 h nominal capacity), were prepared by charging (48 h at 4 A) after filling each cell with H_2SO_4 (1·200 sp. gr.) containing various added concentrations of HNO_3. Groups of cells of similar capacity prepared by the perchlorate process were 'first-charged' in a parallel circuit.

At the end of charge a conventional brown ring test [7] showed the electrolyte solutions free of nitrate or nitrite ion and in the specific gravity range 1·205–1·215. The capacities of the cells were all above the nominal 26·25 A h in 5 h.

The cells were tested for failure in the following modes: cycle life, open-circuit specific gravity loss, overcharge. Fig. 5 shows the relationship between cell capacity and cycle life for the case of batches of cells prepared using either perchlorate or nitrate as the forming agent.

Fig. 6 shows the relationship between the concentration of nitric acid added to the electrolyte solution and the fractional nominal capacity in 5 h. These data were measured on the second cycle in order to eliminate any initial variability connected with the metallurgical condition of the electrode. (This procedure accords with the usual commercial practice.) The correlation coefficient of 0·76 for 48 degrees of freedom indicates that the relationship is linear over the range considered. Line fitting to a 95% confidence limit gave a best estimate of linear dependence of

$$\frac{C_2}{C_n} = 0{\cdot}0265\,[HNO_3]\,[g(cell)^{-1}] + 0{\cdot}769 \quad (3)$$

where C_2 is the capacity at second discharge, and C_n the nominal capacity (A h). This equation can be used to predict the capacity of the cell when the relationship readily becomes

$$C_2(A\,h) = 0{\cdot}696\,[HNO_3]\,[g(cell)^{-1}] + 20.2$$
$$[HNO_3] > 5\,g(cell)^{-1}. \quad (4)$$

It is clear from Fig. 6 that the optimum nitric acid addition would be 15 $g(cell)^{-1}$ which is equivalent to 0·16 mol dm^{-3} (1% wt/vol).

The lives of the cells to a cycling test consisting of a 4 h discharge at the 5 h rate (5·25 A) followed by 8 h recharge at 3 A (114% overcharge) are shown in Fig. 5. These data suggest that the lives of Planté cells manufactured by the nitric acid process are at least equal to that of cells made using the 'perchlorate' process.

Fig. 7 shows the results of overcharge experiments in which cells are charged galvanostatically at 0·9 A (conventionally a current rate of 3% of the nominal A h capacity expressed in A). Initially it was observed that the rate of material loss from the positive electrode was greater in the case of the 'nitric' cells. This may be due to the significant processing difference of complete cathodic reduction of the formed positive electrode (which is imperative if all traces of ClO_4^- are to be removed) before a final oxidation stage in the cell itself. It is likely that the reduction step provides a highly retentive sub-structure on which the PbO_2 is subsequently formed. The relatively greater loss of deposit observed in the case of the 'nitric' cells rapidly decreased, however, and Fig. 7 shows quite clearly that satisfactory lives are obtainable.

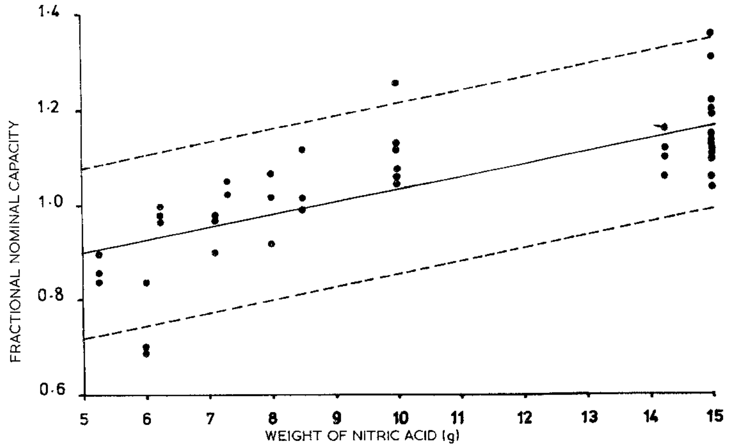

Fig. 6. The relationship between nitric acid addition and nominal 5 h capacity achieved for 26·25 A h cells.

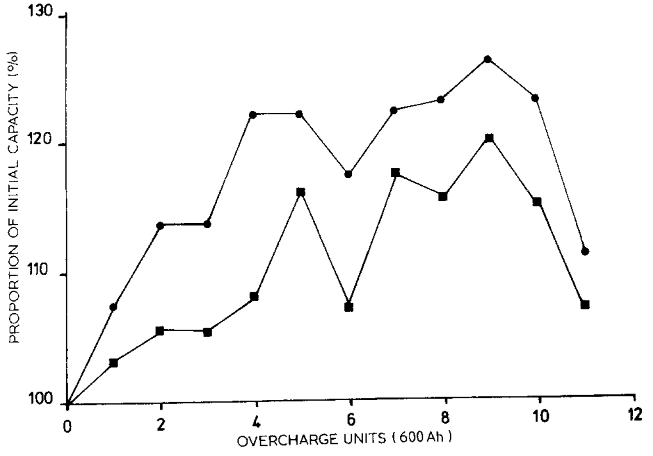

Fig. 7. Comparison of overcharge life test of 'nitrate' and 'perchlorate' formed cells corresponding to Fig. 5.

Fig. 8 shows the rate of loss of charge of the cells due to the hydrogen evolution reaction. This reaction is usually ascribed to the influence of the low hydrogen overpotential metal, antimony, a necessary alloying ingredient for the support grid of the negative electrode. It is quite likely that carrying out the in-depth oxidation step in the cell itself would free some antimony from the negative electrode and thus facilitate the h.e.r. Fig. 8 shows this loss in capacity expressed as a density fall to be no more serious with the 'nitric' cells than with the 'perchlorate' cells. For cells

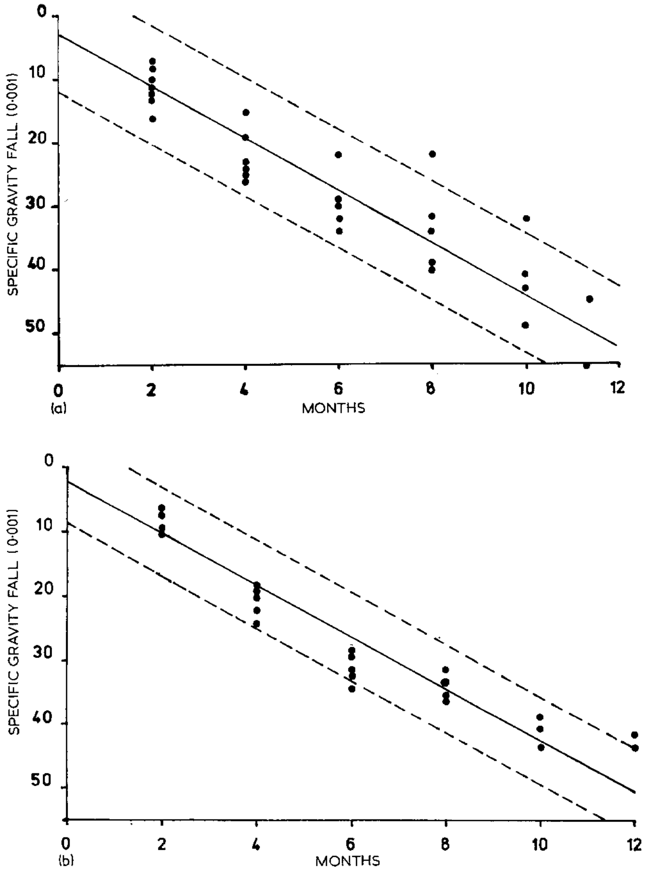

Fig. 8. Loss in acid specific gravity on open circuit for (a) cells prepared by the 'perchlorate' process (b) cells prepared by the 'nitrate' process.

prepared by the classical method the data conformed to

$$\delta = 4{\cdot}164t + 2{\cdot}69 \qquad (5)$$

(standard error 4·5895) where δ is the fall in specific gravity (1 unit = 0·001) and t the time (months), invoking a 95% confidence limit. (53 degrees of freedom; correlation coefficient = 0·954) compared with

$$\delta = 4{\cdot}012t + 1{\cdot}88 \qquad (6)$$

(correlation coefficient, 0·974; standard error 3·2571).

It is clear from these results that the attack on the negative electrode in contact with nitrate ion must be quite negligible.

4. Conclusions

The 'nitrate' promoted formation of lead dioxide from lead is a satisfactory alternative to the 'perchlorate' process.

The quality of cells produced by the nitrate process is equivalent to that of 'perchlorate' cells.

Acknowledgement

We thank the Directors of the Chloride Group for permission to publish this work.

References

[1] G. Planté, 'Recherches sur l'électricité', Gauthier-Villars, Paris (1883).

[2] E. J. Wade, 'Secondary Batteries', The Electrician Publishing Company, London (1902).

[3] S. E. Afifi, W. H. Edwards and N. A. Hampson, *Surface Technol.* 4 (1976) 173.

[4] R. Albrecht, 'Elektrische Akkumulatoren', 3rd edition Janecke–Verlag, Leipzig (1944).

[5] P. Casson, N. A. Hampson, K. Peters and P. Whyatt, *J. Appl. Electrochem.* 7 (1977) 257.

[6] *Idem*, *J. Electroanalyt. Chem.* in press.

[7] A. I. Vogel, 'Textbook of Macro and Semimacro Qualitative Inorganic Analysis', Longman Green and Co., London (1962) p. 363.