Influence of recharge potential and acid concentration on the discharge behaviour of PbO_2 electrodes

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Abstract

During the recharge of PbO_2 electrodes, the electrode single potential and the acid concentration within its porous system usually changes over a wide range. A potentiostat and the Eloflux technique of forced flow-through of the electrolyte has been applied to keep these parameters homogeneous over all of the electrode for the whole period of recharge. A distinct dependence of the discharge capacity at a given rate on potential and acid-concentration conditions of the proceeding recharge has been found. Low recharge potentials and low acid concentration lead to a reversible capacity decay, while high potentials and high acid concentration may recover a previous capacity loss. This is in agreement with previous findings without forced flow-through of the electrolyte, where cycling with low initial recharge current densities induced a reversible capacity decay that was reversed (or prevented) when recharge was performed with a high initial current density. These results support the 'Kugelhaufen' model which describes the reversible insufficient mass utilization (RIMU).

Introduction

Under certain conditions, a successive capacity decrease is observed on cycling positive lead/acid battery electrodes. This is not due to corrosion of the current collector, nor to shedding of the active material, or to lack of recharge: the active PbO_2 material is still in place and fully charged, but not fully accessible for discharge, especially at high discharge rates. This effect, already known [1] in the last century (the memory effect), has been noted more and more during the past few decades, when positive electrodes containing low-antimony or antimony-free grids have come in use. As positive electrodes with grids containing antimony seem to be less prone to the effect than antimony-free types, the designation 'antimony-free effect' (AFE) had been used.

Experimental knowledge on this 'premature capacity loss' (PCL) phenomenon has been reviewed recently [2]. The experimental fact that in many cases, this capacity decay can be reversed again is taken into account by the designation 'reversible insufficient mass utilization' (RIMU) [3].

The reversible capacity decay of the PbO_2 electrode seems to be induced by certain 'unfavourable' operating conditions, such as:
- deep discharges
- cycling with low initial recharge current density [4–6]
- further overcharge of the already fully-charged electrode [5, 6]
- discharges at very high rates without rest times [7]

As a main feature of this effect, the capacity can be recovered again either successively by switching to more favourable operating conditions (which provides

permanent cycling at a high capacity level) [4–7], or immediately by special treatments of the electrode, e.g., washing free of acid and drying [4–6, 8], currentless rest times, especially at elevated temperature [8, 9], or by deep discharge at very low rates [5, 6]. These observations are true for any type of PbO$_2$ electrode (pasted, tubular, Planté), and for immobilized and liquid as well as with forced flow-through electrolyte [4, 6]. Besides antimony, tin has a noticeable influence on the PCL (cf., [10–12]) and its reversibility [13]. Also the addition of phosphoric acid, which has been used with lead/acid batteries for decades (a review is given in ref. 14), has been found to be beneficial with respect to the reversible capacity decay [15].

The decay of PbO$_2$ active-material utilization correlates strictly with a successive reduction in its electric conductivity, as has been shown by *in situ* experiments [4, 16]. The reversibility of the capacity decay is explained by the Kugelhaufen model [3, 5, 17]. Other models to describe the capacity-loss effects, especially the Barrier-layer model, are mentioned in refs. 2 and 7.

The recharge current density had been found to be one decisive parameter [4–6]. As sulfuric acid is set free during recharge within the electrode porous system, increased recharge current density with an electrode of up to several millimetres of thickness will not only lead to an increased recharge overpotential, but also to a complicated profile of current density distribution and acid concentration within the electrode. Therefore, current density, acid concentration and recharge overpotential (with respect to the very equilibrium potential) are not homogeneous within the active material, and this distribution pattern is time-dependent. Therefore, only an average over many electrode sites recharged under different conditions is seen as an influence of the overall recharge current density on capacity.

The forced flow-through of electrolyte of constant concentration perpendicular to the electrode surface (Eloflux) allows independent variation of the 'acid concentration' and 'recharge overpotential' parameters. Under these conditions, these parameters (and as a consequence, the local recharge current density) are largely homogeneous throughout the electrode.

Experimental

The experimental setup of the Eloflux technique is described in detail elsewhere [18] and has already been used in several investigations [4, 8, 19]. One pasted positive electrode and two negative counter electrodes were mounted in a cell case, together with an appropriate separation. The electrodes were sealed with respect to the case by special rubber gaskets. By an external pump and an appropriate arrangement of piping, the electrolyte was driven from a reservoir through a thermostat separately to each electrode, and flowed perpendicularly through the active material of the positive and the negative electrodes, before it returned to the reservoir. The electrolyte flow was usually 5–10 ml/min through the positive electrode at an overpressure of 0.2 bar. This setup and the excess of electrolyte of about 1 l provided a nearly constant acid gravity (change < 0.02 g cm^{-3}) within the active material. The electrodes being carefully hand pasted, cured and formed, were free of crackings to prevent an easy avenue for the electrolyte flow.

The electrode dimensions were approximately 80 mm $\times$ 76 mm $\times$ 4 mm. The weight of the formed positive active material was about 76 g. The grid alloy was Pb–3.8wt.%Sb for both polarities of plate in this experiment.

Using a thermostatic bath and a heat exchanger (cf., [18]), the electrolyte temperature was kept constant at 25 and 40 °C, respectively, for two series of experiments. Analogous

experiments at 15 °C were very difficult to perform, as the flow-through rate decreased within some cycles at this temperature to far below the value of usually 5–10 ml/min through the positive electrode. This resulted in acid depletion at the stream-out side, i.e., the electrolyte concentration was no longer homogeneous. Dissymmetry of the discharge reaction, i.e., preferential discharge at the stream-in side of the electrode, made evaluation of the results difficult and comparison impossible. Obviously, the PbO_2 material structure was changed markedly on cycling at this lower temperature, and this gave a higher flow resistance.

A Hg/Hg_2SO_4 reference electrode (in sulfuric acid, 1.20 sp. gr.), positioned in the separator near to flow-in side of the positive electrode, was used to measure and control the single electrode potential. The positive electrode was always discharged at a current of 4 A (52.6 A kg^{-1}) and with permanent electrolyte flow-through, i.e., a constant acid sp. gr. of 1.20, until the positive electrode potential reached + 500 mV versus Hg/Hg_2SO_4. This means an electrode polarization of nearly 600 mV versus the equilibrium potential in sulfuric acid of this concentration.

By comparison, the acid sp. gr. on discharge was 1.20 in all cases, even when the previous recharge had been performed with a different acid concentration. This value of acid density has been found [8] to give a maximum capacity of up to 10 Ah with healthy electrodes of this type.

After the end of discharge, the electrolyte sp. gr. was changed to 1.20, 1.25, 1.30 or 1.35. After equilibration of electrode potential and temperature, while the exchanged electrolyte was forced through the electrode, recharge was started by application of a constant potential (with respect to the reference electrode) to the positive electrode using a potentiostat. Different recharge potentials were used with flow-through of the electrolyte at controlled temperature, and the recharge current was measured. By this procedure, recharge was always performed at constant temperature, constant acid gravity, and constant potential for the positive active material. Only in case of very low recharge potentials (when the electrode could not be fully recharged within reasonable time), was the recharge potential increased by 50 mV at the very last period of recharge. Anyhow, a maximum 10% of recharge was performed under those (somewhat different) conditions. The recharge factor was at least 1.12–1.15 with respect to the previous discharge, but up to 1.8 with very high recharge potentials, when oxygen evolution was considerable.

After end of recharge, the electrolyte sp. gr. was immediately changed from the test value to 1.20 for discharge. Before the start of discharge, a rest time of about 5 h with electrolyte flow-through was applied for potential relaxation. At lower temperatures, the potential was not yet fully equilibrated at the start of discharge.

Results

Two series of experiments were performed at different temperatures (25 and 40 °C), that were kept constant during all discharges, recharges, and rest times by controlling the temperature of the permanent flow-through electrolyte. While the electrolyte sp. gr. was always the same during discharge (for comparison purposes), it was appropriately varied between 1.20 and 1.35 for recharge. The possible range of variations of recharge potential was limited by excessive oxygen evolution and poor charge acceptance, the latter also gave an upper limit to the acid sp. gr.

Changes of recharge potential and acid sp. gr. during subsequent cycles caused severe, but systematic, changes in the discharge capacity, even after only one recharge

under changed conditions. The relative capacity changes with respect to the previous discharge $(C_{i+1} - C_i)/C_i$ as a function of the two parameters, acid sp. gr. and recharge potential during recharge between the two discharges are shown in Figs. 1 and 2 for 25 and 40 °C, respectively. There was no lack of recharge of the positive electrode in either case. This can be concluded from the factor of recharge (at least 1.12) and the appearance of a 'Spannungssack' (coup de fouet) at the beginning of the discharge.
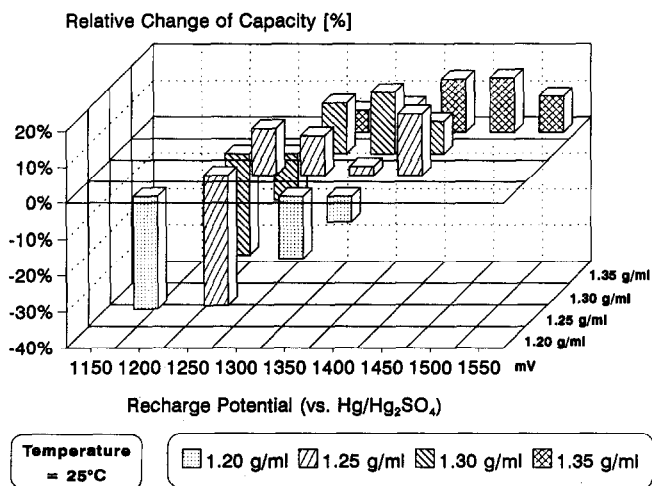

Fig. 1. Relative change in discharge capacity with respect to previous discharge of the positive electrode. Forced flow-through during discharge (electrolyte sp. gr. = 1.20) and recharge (electrolyte varied). Influence of recharge conditions (acid density and recharge potential) at 25 °C.
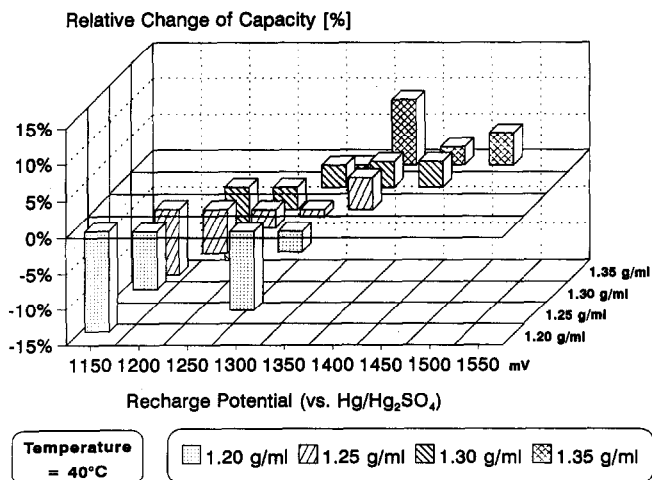

Fig. 2. Relative change of discharge capacity with respect to previous discharge of the positive electrode. Forced flow-through during discharge (electrolyte sp. gr. = 1.20) and recharge (electrolyte varied). Influence of recharge conditions (acid density and recharge potential) at 40 °C.

Discussion

Changes in recharge parameters caused corresponding changes in the discharge capacity with respect to the previous discharge by up to 20%, or more. A single experiment, that shows a capacity change after only one cycle when the recharge conditions have been changed, contains many quantitative uncertainties. This is especially true in the case where the capacity is not compared with a standard value, but with a previous discharge capacity that had been influenced by its own proceeding recharge conditions.

The systematic screening of potential and acid sp. gr during recharge gives qualitative information on the consequences of a definite acid sp. gr./recharge potential combination during recharge:
● when the recharge potential and the acid sp. gr. were both high during the preceeding recharge, an increase in capacity was found
● low recharge potential and low acid sp. gr. usually induced a considerable decrease in capacity

These observations are true at both 25 and 40 °C. Furthermore, the results obtained at 15 °C (no systematic screening, *v.s.*) support this conclusion.

Of course, several subsequent cycles with recharge potential/acid-concentration combinations, which have been found to increase electrode capacity after one cycle, would not lead to an infinite capacity movement. Increase of capacity during this examination has to be interpreted as a recovery of the capacity loss that the electrode has suffered during previous operation. If there was no previous capacity loss, nothing could be recovered. Decrease of capacity in an experiment indicates that the definite recharge potential/acid sp. gr. combination induces reversible capacity decay. By the alternate application of 'favourable' and 'unfavourable' recharge conditions during this investigation, the electrode was always kept in a state such that it could recovered again or even more deteriorated.

Possibly, both the recharge potential and the acid sp. gr. may have threshold values that have to be exceeded to prevent capacity decay. Another interpretation might be that the recharge potential has to be above a certain threshold overpotential value. This cannot be definitely decided from these experiments, as the parameter range of the study was limited by practical experimental reasons (*v.s.*).

When the relative capacity change data are plotted against the recharge overpotential (with respect to the Pb^{2+}/PbO_2 equilibrium potential at the test acid concentration) instead of against the absolute potential value (Figs. 1 and 2), the following tendencies are apparent (Figs. 3 and 4):
● increased recharge overpotential reduces capacity loss, or increases capacity recovery
● increased acid concentration makes recharge at lower recharge overpotential possible without capacity loss
● with an acid sp. gr. of 1.20, recharge was never possible without loss of capacity

These new data explain Eloflux observations that recharge at a constant cell voltage and with forced flow-through of the electrolyte lead to rapid reversible capacity decay [4]. On the other hand, when the electrolyte was not forced to flow through the electrode during the first period of recharge, the electrode could be cycled at high active material utilization for hundreds of cycles.

Forced flow-through in the first portion of the recharge has two unfavourable consequences: the acid sp. gr. is kept constant at low values (1.20 in [4]), and the positive recharge potential is lower (at constant cell voltage) than in case of non-flowing electrolyte.
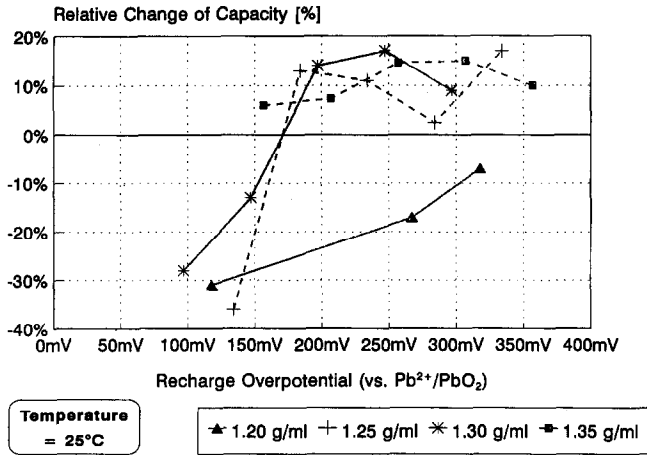
Fig. 3. Same data as in Fig. 1 (25 °C), but displayed against recharge overpotential with respect to the Pb^{2+}/PbO_2 equilibrium in the test electrolyte, instead of against absolute potential.
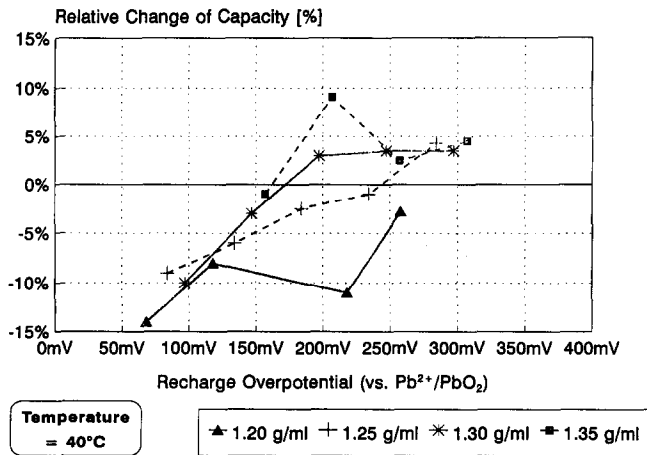

Fig. 4. Same data as in Fig. 2 (40 °C), but displayed against recharge overpotential with respect to the Pb^{2+}/PbO_2 equilibrium in the test electrolyte, instead of against absolute potential.

Comparable results have been obtained with single electrodes of different types (pasted, tubular, Planté) without forced flow, and with technical lead/acid batteries with either liquid or immobilized electrolyte (e.g., [4–6]). In such electrodes, a difficult and continuously changing distribution of local acid concentration and recharge overpotential is generated during recharge. At recharge with high (initial) current density, that quickly increases the acid concentration in the porous PbO_2 material and leads to rather high recharge potentials, the electrodes could be continuously cycled at a high capacity level, or a previous capacity decay could be reversed. By contrast, if recharge was performed with a low initial current, i.e., at low overpotential and with a less increasing acid concentration, a capacity decay was induced.

The experimental technique used here (Eloflux) enabled the influence on capacity of acid concentration and recharge potential to be investigated independently.

The Kugelhaufen model [3, 5, 17] approximates the porous PbO_2 electrode, consisting of PbO_2 crystallites of different shape and size, to an aggregate of spheres of radius R. These spheres are electrically and mechanically connected to each other by 'neck' zones that are characterized by a radius h. With this assumption, the ratio R/h determines the electric resistance of the agglomerate. This is one of the critical quantities of the model. According to the model, a high recharge overpotential leads to a high initial recharge current density, and favours formation of new nuclei with respect to further growth of existing crystallites. Altogether, PbO_2 crystallites of smaller size (represented by the radius R of the spheres in the model) are produced with a high recharge current density. Therefore, the ratio R/h may be smaller after high-rate recharge and, accordingly, the aggregate resistance is reduced. This improves the capacity on subsequent discharge (if there is already some reversible capacity decay); otherwise, the capacity is stabilized at its high level.

With increased acid concentration, the solubility of $PbSO_4$ is reduced. A diminution of Pb^{2+} ions has the same consequence as high recharge current density: formation of new nuclei is favoured with respect to the growth of existing crystallites. Thus, the Kugelhaufen model can account for the beneficial effect of both high recharge potential and high acid concentration.

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