Operation of thin-plate positive lead-acid battery electrodes employing titanium current collectors

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A B S T R A C T

One of the root causes for the limited lifetime or the restricted high power performance of the lead-acid batteries is the corrosion of the positive current collectors. These barriers can be overcome using titanium as an attractive alternative of the lead and the lead alloy grids, due to a combination of excellent mechanical strength, corrosion resistance and great abundance. This article presents a new technological route to simultaneous decrease of the electrode thickness and weight, and a replacement of the classic grids with titanium substrates like tin dioxide coated foil or expanded mesh. The new electrodes are studied electrochemically and physically revealing that the reduction of the electrode thickness promotes the formation of positive electrodes composed of pure beta lead dioxide with high crystallinity. The latter induces an initial partial capacity loss, which can be avoided by lowering the depth of discharge, positive plate oversizing or changes in the paste mixing and curing processes.

1. Introduction

The lead-acid batteries remain preferred electrochemical system in many domains due to their affordable pricing, safety of operation, and recycling rates exceeding 99% [1,2]. However, in most of the emerging applications like hybrid electric vehicles and grid-connected/renewable energy storage, the lead-acid batteries are less competitive due to either short lifetime or insufficient efficiency at high rates of charge and discharge cycling or micro-cycling. The main phenomenon limiting the durability of this system is the corrosion of the positive current collectors transforming progressively the metallic lead into lead dioxide [3]. Since the corrosion process proceeds in direction normal to the surface of the current collector (or the grid), the lifetime of the battery can be extended through the increase of the grid thickness. The result is thicker electrodes, which reduces the battery power and efficiency due to diffusion limitations, as well as penalizing charge transfer and ohmic polarization effects. The replacement of lead or lead-alloy with titanium is a very attractive alternative route to simultaneously increase lead-acid battery lifetime, specific power and specific energy [4–6]. The latter allows also to reduce the electrodes thickness without taking the risk of premature corrosion failure. In the same time, it has been found that the titanium-based thin-plate positive electrodes remain

susceptible to capacity loss due to a drop of the active material utilization despite the use of absorptive glass-mat (AGM) separators and stack compression [7]. Thus, the objective of this work is a further, more detailed electrochemical study of the thin-plate electrode system $Ti/SnO_2/PbO_2/PbSO_4/H_2SO_4$ in the context of its application in advanced lead-acid batteries.

2. Experimental

The titanium-based thin-plate electrodes have been prepared according to the procedure described in a previous publication [7]. Four types of pure titanium materials have been used as alternative current collectors – titanium foil with a thickness of 250 μm (VWR, France) and three different types (type A, B and C) of expanded titanium mesh provided by Dexmet Corporation (USA). The specifications of the expanded mesh can be found in the supplementary information together with their digital microscope images (S0). The current collectors have been coated with 2 μm thick Sb-doped SnO_2 (ATO) using thermal decomposition method [8]. One of the current collectors was subsequently electroplated with 17 μm thick PbO_2 coating using lead methanesulfonic bath [7].

The electrochemical cells have been assembled with one titanium-

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Table 1
Specifications of the cells used for the study of the positive thin-plate lead-acid battery electrochemistry.

Cell reference	Ti/SnO$_2$ positive current collectors		Positive electrode EC equivalent	Surface loading	Theoretical PAM Thickness @ 50% PbO$_2$ porosity	ratio PAM : grid	Electrolyte specific gravity
	[g]	[type]	[Ah]	[g cm^{-2}]	[mm]	[g : g]	[g cm^{-3}]
S03P02	3.478	Foil	0.48	0.078	0.17	0.6 : 1	1.24
S03P03	3.487	Foil	0.54	0.088	0.19	0.7 : 1	1.24 + 2% SiO$_2$
S04P16	0.433	A	0.92 (0.8*)	0.597	0.32	9.5 : 1	1.24 + 2% SiO$_2$
S05P03	0.850	B	0.78	0.169	0.27	4.1 : 1	1.20 + 2% SiO$_2$
S05P04	0.879	B	0.88	0.190	0.30	4.5 : 1	1.20 + 2% SiO$_2$
S06P01	0.401	A	0.86	0.558	0.30	9.6 : 1	1.22 + 3% SiO$_2$
S06PP	3.357	Foil	0.84	0.136	0.29	1.1 : 1	1.22 + 3% SiO$_2$
S06PF	0.299	C	0.78	0.506	0.27	11.6 : 1	1.22 + 3% SiO$_2$
S06P02	0.400	A	1.54	1.000	0.53	17.2 : 1	1.15 + 2% SiO$_2$
S06P03	0.400	A	1.68	1.091	0.58	18.8 : 1	1.15
S05P05	0.830	B	0.86	0.186	0.30	4.6 : 1	1.15

* paste only.

based thin-plate positive electrode having a height of 5.5 cm and width of 5 cm, a thick dry-charged negative electrode cut to the same size from negative plates extracted from a traction lead-acid battery Trojan T-105, and Ag/Ag$_2$SO$_4$/H$_2$SO$_4$ reference electrodes. The positive and the negative electrodes have been separated by AGM separators (220 g m^{-2} / 1.3 mm @ 10 kPa) provided by Bernard Dumas (France). The electrochemical cells have been housed in flexible polyethylene envelops allowing the application of external compression. The electrolyte level has been kept constant by periodic top-up with demineralized water. Table 1 presents the detailed characteristics of the electrochemical cells used in this study in terms of nominal capacity, nominal thickness, surface loading (gamma-coefficient), positive active material to current collector ratio, and electrolyte composition.

3. Results and discussion

3.1. Initial performance of the thin-plate positive electrodes

After the end of the formation process, the cells have been subjected to a short charge/discharge cycling with depth of discharge (DOD) equal to 100%. The discharge current density was equal to 5.6 mA g^{-1} for all cells. This discharge regime corresponds to a 20 h-rated current considering 50% utilization of the lead dioxide. The charge algorithm was made up of constant current / constant voltage / constant current (IUi) steps starting with different initial constant current densities allowing to evaluate the impact of the charge algorithm on the positive plate electrochemistry. Fig. 1 presents the evolution of the current, voltage, and half-cell potentials of three cells with different thickness of positive plate and different electrolyte compositions during the initial cycling, when the positive active material utilization is close to its maximum value. The comparison of the positive electrodes with smaller thickness and higher electrolyte concentration (Fig. 1a and c) reveals nearly identical discharge behavior, despite the significant difference in the γ-coefficient, the active material thickness, and the current collector pretreatment (presence or absence of electroplated PbO$_2$ coating the Ti/ SnO$_2$ current collector). The observed maximum of the lead dioxide utilization is in the range of 65–67 % (145–150 mAh g^{-1}), which coincides well with the results from a recent theoretical study published by Vargonen using the percolation theory and a Monte-Carlo model [9]. Further increase of the electrode thickness and decrease of the electrolyte concentration leads to a lower utilization of the lead dioxide down to 48% (108 mA h.g^{-1}), and 44% (99 mA h.g^{-1}) in the case of electrolyte doped with 2% fumed silica (the results are summarized in Table 2). The positive electrode discharge transient (Fig. 1f) undergoes also significant change in this last case – it becomes less flat, without the distinct "knee" in the end, which indicates clearly the end of the discharge process in the first two cases. These results show that the diffusion of the sulfuric acid from the separator to the pores of the

positive electrode is amongst the main phenomena limiting the active material utilization. The achieved rates of lead dioxide utilization can be compared also with some state of the art cases, the AGM-VRLA battery for automotive SLI applications being the most appropriate example. According to Pavlov et al. [10], the utilization of the active material in conventional positive plates with a thickness of 1.6 mm reaches a maximum value of about 55 +/- 0.5% in electrolytes with a density starting from 1.24 to 1.33 g cm^{-3} and applying a discharge current equal to C$_n$/10 h (3.37 mA g^{-1}). A decrease of the electrolyte density down to 1.15 g cm^{-3} leads to a decrease of the active material utilization down to 32% [10]. This comparison shows that the thin-plate design allows to increase the active material utilization from 12 to 16% keeping the same electrolyte concentration at state of charge equal to 100%.

The comparison of the cell voltage and the positive electrode potential transients during the charge of the cells S04P16, S03P03 and S06P03 shows that the presence or the absence of electroplated outer layer of PbO$_2$ on the surface of the Ti/SnO$_2$ current collector impacts strongly the beginning of the charge process. It can been seen that when the Ti/SnO$_2$ current collector is pre-coated electrochemically with a dense layer of PbO$_2$, the charge voltage and potential transients do not differ from those observed at the state of the art positive plates [11]. In contrast, when the Ti/SnO$_2$ current collector is used directly without any further modification, the charge process starts with a sharp spike of the positive electrode potential. Such kind of spike in the begging of the charge is typical for lead-acid batteries with positive grids composed of pure lead and it is ascribed to the oxidation of non-stoichiometric lead oxides (PbO$_n$ with n varying between 1 and 1.6) with high electric resistance [12,13]. Similar phenomenon has been observed also during the cycling of PbO$_2$/Pb^{2+} electrodes in methanesulfonic acid electrolytes, where it has been suggested that the formation of resistive non-stoichiometric lead oxides is a result from the solid state reduction of PbO$_2$ [14]. The insets in Fig. 1b, d and e present a zoom view of the potential transient in the beginning of the charge. It can be seen that the settling time is rather independent on the electrode type and the applied charge current. On the other hand the spike duration can be evaluated as peak full width at half its maximum (FWHM value). In the case of cell S03P03 (Fig. 1d), the FWHM value is equal to 6.1 s and its coulometric equivalent is equal to 0.03% of the total PbO$_2$ content of the electrode, while at the positive electrode S06P03 (Fig. 1f) the corresponding values are 7.5 s and 0.05% of the total PbO$_2$ content. The comparison of these results, taking into account the absence of the spike at the cell S04P16, allows to conclude that the formation of the resistive non-stoichiometric lead oxides is focused at the interface between the porous lead dioxide from the positive active material and the SnO$_2$ coating the titanium current collector. The height of the spike and the applied charge current can be used to calculate the electric resistance related to the presence of the non-stoichiometric lead oxides formed in