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Studies of the pulse charge of lead-acid batteries for PV applications
Part II. Impedance of the positive plate revisited

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Abstract

In the second part of this publication series, dedicated to the pulse charge of the lead-acid battery, a special attention is paid to the impedance spectrum of the positive plate as a source for estimation of the electrostatic capacitance of the double layer (C_{dl}) on the surface of the positive active mass. The impedance spectra were measured at open circuit for different states of charge (SoC) in H_2SO_4 with specific gravity 1.24 and 1.28 g ml^{-1}. A substantial difference was observed in the impedance spectra of partially charged and partially discharged positive plates keeping the same value of the SOC. The impedance data were subjected to inductance error correction, followed by differential impedance analysis (DIA). Considering the results from DIA, the recently published equivalent circuits of the positive plate in charged and in discharged state and the gel-crystal model of the lead dioxide, we proposed a model of the positive plate in partial state of charge (PSoC). The analysis of the obtained experimental results using this model and DIA show that the double layer capacitance is not frequency distributed. The influence of the state of charge and state of health on the model parameters is discussed. One of the most interesting results is the dependence of C_{dl} on SOC—it features a hysteresis at which the values of C_{dl} during the charge are 5–6 times higher than the corresponding ones during the discharge. This result was discussed in terms of changes in the double layer structure considering the gel-crystal model of the lead dioxide. During the discharge in H_2SO_4 with specific gravity 1.28 g ml^{-1} a passivation process was detected as a high frequency pseudo-inductive loop in the Nyquist plots in PSoC. The passivation time constant is higher at 50–60% SOC and decreases to zero in the end of the discharge. During the charge in both electrolytes, pseudo-inductive time constant was observed too. It was attributed to the phenomena of the dehydration of $Pb(OH)_4$, an intermediate in the reaction scheme of the $PbSO_4$ oxidation. The state of health influences mostly the ohmic resistance R_Ω, the charge transfer resistance R_{ct} and the parameters of the constant phase element accounting the diffusion in the pores (CPE_{diff}), when the plate is well charged.

Keywords: Lead-acid batteries; Positive plate; Gel-crystal model; Impedance spectroscopy (EIS); Electrochemical double layer (EDL); State of health (SoC); State of charge (SoH)

1. Introduction

In the first part of this work it was found that the electrochemical double layer (EDL) on the surface of the lead dioxide, constituting the positive active material (PAM) of the lead-acid battery, plays a very important role in the mechanism of the pulse charge [1]. Using the concept of the average double layer current, it was demonstrated that during the “ON” periods of the pulse charge, in some cases more than a half of the energy introduced in the charge of the positive plate can be used to charge the double layer instead of faradic processes like lead sulphate oxidation or oxygen evolution. The electrochemical impedance spectroscopy (EIS) is one of the best methods to study the EDL properties, especially in the case of high porosity systems like PAM, where methods like the linear sweep cyclic voltammetry are hardly applicable because of the high currents and the simultaneous proceeding of faradic processes. In addition, the impedance spectroscopy provides an opportunity for an *in situ* microstructural characterisation of the positive plate, and more

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particularly the PbO_2/electrolyte interphase. EIS is also widely used as a tool for estimation of the state of charge (SoC) and state of health (SoH) of the battery [2–10].

The first studies of the EDL on the surface of the lead dioxide have been published more than half a century ago by Kiseleva and Kabanov [11]. The measured potential of the zero charge (PZC) in 0.05 M H_2SO_4 is about 1.8 V versus normal hydrogen electrode (NHE), which is more than 300 mV above the equilibrium value of the $PbO_2/PbSO_4$ electrode in 5 M H_2SO_4 (1.464 V versus NHE). The same authors estimate also a strong adsorption of sulphuric acid species (H_2SO_4, HSO_4^- and SO_4^{2-}) [12]. Later, Carr and Hampson extend the studies on the EDL of lead dioxide electrode towards less concentrated H_2SO_4 and estimate the presence of surface reactions with the participation of H^+ ions [13]. Recently Munichandraiah, using cyclic voltammetry, showed that the EDL capacitance increases substantially with the rise of the PbO_2 electrodeposition current density—from 10 mF cm^{-2}, the EDL capacitance increases to 20 mF cm^{-2} when the current density increases from 2 to 20 mA cm^{-2} (geometrical electrode surface) [14,15]. No matter that most of these results are obtained by alternative current (ac) methods they are not “classical” EIS experiments considering a large band of ac frequencies and corresponding equivalent circuit model fitting. Other very important detail in the above-mentioned studies is the maximum H_2SO_4 concentration for which the EDL is studied—it is about 0.05 M, and the electrodes are of “model” type, i.e. PbO_2 electrodeposited on smooth (polished) Pt or Au surface. These conditions are not close to the typical ones for the lead-acid cell—highly porous PbO_2 electrode immersed in 5 M H_2SO_4, frequently with a considerable amount of $PbSO_4$ deposited in the PAM pores when the case of partial state of charge (PSoC) is considered.

The aim of this work is to study the impedance behaviour of the positive plate at different SoC and SoH (state of health) during both the charge and the discharge of the plate, to propose and confirm an equivalent circuit of the positive plate in PSoC and to estimates the dependence of the circuit elements on SoC and SoH.

2. Experimental

The experiments were carried out in three-electrode electrochemical cells consisting of:

- *working electrode*: dry-charged flat positive plate with 3 mm thickness, 8 Ah nominal capacity at 50% PAM utilization, produced by CEAC-EXIDE (France), with grid composition Pb–2.8%Sb. The plates where cut from bigger 40 Ah plates;
- *counter electrode*: two dry-charged CEAC-EXIDE (France) negative plates, with nominal capacity 8 Ah and thickness 3 mm. The plates where also cut from bigger 40 Ah plates;
- *reference electrode*: Ag/Ag_2SO_4 (1.28 s.g. H_2SO_4), +38 mV versus Hg/Hg_2SO_4 in the same solution [16,17].

The electrolyte was H_2SO_4 solution, with a specific gravity (s.g., density) 1.24 g ml^{-1}. The cells were tested on SOLARTRON Multistat 1470 instrument supplied with Frequency Response Analyzer.

After 30 min of soaking in the electrolyte the cells were subjected to a 20 h charge-up at $I = 0.25$ A in order to oxidize the residual quantities of $PbSO_4$ unconverted into PbO_2 or Pb during the formation. After this conditioning of the cells a following cycling regime was applied:

- *Discharge*: $I = -0.8$ A down to $\varphi^+_{\text{cutoff}} = 0.75$ V; open circuit 120 min; constant current charge: $I = 0.8$ A up to $\varphi_i^+ = 1.38$ V (interruption potential). The pulse current charge was performed with $I = 0.8$ A until a 15% of the nominal capacity was introduced. The applied frequency f and duty cycle $r = ft_{\text{on}}$, where the t_{on} is the duration of the charge during one square-wave period, were, respectively $f = 1$ Hz and $r = 1$. After the end of the charge the cell was subjected to 120 min open circuit stay [18].

All impedance measurements were carried out after 120 min open circuit stay in order to be sure that the positive plate has reached steady state conditions. The ac amplitude was 5 mV, keeping the dc potential equal to the one measured in the end of the open circuit stay. The frequency band was between 50 kHz and 0.1 Hz (or lower), with a spectral density of 20 points per decade.

When studying the positive plate impedance in PSoC, the charge or the discharge was interrupted by 2 h open circuit periods for each 1 h of charge or discharge with 0.1 C_{10} rate (0.8 A), at the end of which the EIS was performed. Similar series of experiments were performed also with pulse charge with 0.05 C_{10} rate combining 2 h charge period with 2 h open circuit stay.

Separate experiments with a constant current cycling have been done also in 1.28 s.g. sulphuric acid, after 1 h open circuit stay with ac amplitude 10 mV and 10 points per decade. In the discussion of these results, it will be mentioned specially that they were performed in more concentrated acid.

3. Results and discussion

3.1. Strategy of the analysis of the impedance spectra

In order to analyze the obtained impedance spectra, the following strategy was employed: first the parasitic inductance high frequency “tail” was partially corrected according to the procedure listed below (Section 3.1.1), then a differential impedance analysis (DIA) of the spectra was used in order to recognize the number of the time constants in the system. A brief description of DIA is given in Section 3.1.2. The third step was to propose an equivalent circuit model of the positive plate and to perform a fitting with *Z*-View2 software in order to obtain the values of the equivalent circuit parameters. Using the values of the equivalent circuit parameters, the simulated impedance spectra was subjected to DIA in order to be compared with the DIA data of the experimental spectra. This comparison was used as an addi-