



Electrolyte depletion control laws for lead-acid battery discharge optimisation



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HIGHLIGHTS

- We maximise both the discharge current and duration.
- Battery control prevents electrolyte depletion.
- Battery controls are 1) proportional controls and 2) integrated past controls.
- The controls are exponentially stabilising controls.

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ABSTRACT

The technique described in this paper balances the power and energy withdrawn from a battery in galvanostatic discharge control that aims for stabilisation of the electrolyte concentration above the depletion level. This aim is achieved with relatively simple proportional feedback controls that are exponentially stabilising controls for a simple diffusion process that is the core part of battery processes. Although the full mapping of the proposed controls to state is rather complex, it has shown that the transformation works. In practice, these controls can be approximated either with the integrated past controls or with a simple exponential function that depends on a few parameters adjusted to the electrochemical processes in a battery under consideration. The battery control is tested in simulation on a detailed model developed for a lead-acid electrochemical cell.

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1. Introduction

Backup batteries are a source of power in many energy systems. On demand, the batteries should supply the largest current possible while withdrawing the maximum amount of chemical energy. These objectives are contradictory and hence difficult to achieve because ion depletion of the electrolyte emerges, always, when the discharge current is large.

This paper maximises both the discharge current and duration. The objectives are achieved using appropriate boundary controls that stabilise the depletion process. These controls are proportional feedback controls that, in a practical application, can be either approximated with a simple time-dependent function with a few parameters adjusted to a battery or represented as integrated past controls. The proposed depletion process controls are asymptotically stabilising controls; to some extent, they can be compared with a simpler potentiostatic control if the reference point for the

desired voltage is selected in a close and safe distance from the cut-off voltage.

Widespread current interest in discharge control arises from safety issues in powerful lithium ion batteries that should be controlled in the dependence on the state of electrochemical processes in batteries. Monitoring and control of the electrochemical processes in batteries would allow their safe use. For example, the lack of safe control is a primary obstacle for use in the important application area of the automotive sector.

In contrast to lithium ion batteries, lead-acid batteries are well understood and are an excellent facility for simulation of cell controls.

Significant research efforts related to modelling of lead-acid batteries have been carried out by several groups over a long period. Although numerous other and significant contributions to the topic have been made, the work of Newman and Tiedemann [1], Hiram Gu, Nguyen, White [2], Nguyen, White, Hiram Gu [3], Gu, Wang, Liaw [4], Newman and Thomas-Alyed [5], Boovaragavan et al. [6], Cugnet et al. [7], Kashkooli et al. [8] are some that should be mentioned, as they have strongly influenced the work behind

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this paper. We also build on work related to the modelling of maintenance-free, valve-regulated lead-acid batteries by Berndt [9], Tenno et al. [10–13].

The control research of batteries at the electrochemical cell level has seen less attention in the literature. However, the depletion control has been considered in other electrochemical processes (electrodeposition, via fill) using deterministic [14–17] and stochastic [18] models.

2. Battery model

The lead-acid batteries can be modelled in single dimension as a sandwich of electrochemical cell represented in Fig. 1. The model of the cell is well established and varies only slightly in the literature. In this work, one of the models [2] is selected for the basis and modified for the computational and control needs. The modified model is explained in Sections 2.1–2.7.

The concern of this paper is a discharge process that can be explained with the four primary reactions in the spatial domain (regions 1–4 in Fig. 1) and with the boundary conditions at the collector (centrum) $x = 0$ of positive electrode and at the collector $x = l_4$ of negative electrode. In discharge, the secondary reactions (the water decomposition and oxygen/hydrogen recombination and the double-layer effect) are insignificant [19–21]; we omit them.

For brevity and simpler understanding, the model is explained in conceptual terms. All the details required for building of the computational model in the 4 subdomains and on/at the 5 boundaries are explained and given in the Appendix, Table 1. For the computational needs, the model can be extended most simply if the interested reader starts from the model in the literature [2] and then updates this model using our modifications explained in Section 2.7.

The battery model includes many physical processes. For streamline reading and brevity, the explanation of most symbols (that are more or less standard) is omitted from the text, and symbols along with their explanation are compiled in the Appendix, Table 2. The parameters used in simulation are taken either from the literature [6–8] or from our previous study [10,11]; they are given in Table 1.

2.1. The positive electrode

The primary processes (1)–(3), (5) in the positive electrode (region 1 in Fig. 1) are coupled with each other and with the related processes (6), (8)–(11) as follows.

Model of the porosity of electrode

$$\frac{\partial \varepsilon}{\partial t} = D_e \frac{\partial^2 \varepsilon}{\partial x^2} + (V_{\text{PbSO}_4} - V_{\text{PbO}_2}) \frac{Aj}{2F} \quad (1)$$

Ohm's law in solid porous matrix

$$\delta_e \frac{\partial \phi_s}{\partial t} = \frac{\partial}{\partial x} \left(\varepsilon^{\beta_1} \sigma_{\text{PbO}_2} \frac{\partial \phi_s}{\partial x} \right) - Aj \quad (2)$$

Ohm's law in electrolyte

$$\delta_e \frac{\partial \phi_l}{\partial t} = \frac{\partial}{\partial x} \left(\varepsilon^{\beta_2} \kappa \frac{\partial \phi_l}{\partial x} \right) - \frac{RT}{F} (1 - 2t_0^+) \frac{\partial}{\partial x} \left(\varepsilon^{\beta_2} \kappa \frac{\partial \ln(c)}{\partial x} \right) + Aj \quad (3)$$

In Eq. (3), the conductivity coefficient $\varepsilon^{\beta_2} \kappa$ depends on the porosity [1,15] and on the concentration of the electrolyte $\kappa(c)$; we use an empirical formula in Table 1 for the latter relationship.

The electric field and diffusion potential drives the ion current in the electrolyte [5].

$$\frac{i_l}{\varepsilon^{\beta_2} \kappa} = -\frac{\partial \phi_l}{\partial x} + \frac{RT}{F} (1 - 2t_0^+) \frac{\partial \ln c}{\partial x} \quad (4)$$

In Eq. (4), the first component on the right is the ion migration-related current in the electric field, due to the conductivity of electrolyte and the second component is the diffusion-related current, due to the concentration gradient that creates diffusion potential, which prevents substantial separation of binary charges with different diffusivities (slower and faster).

Mass balance in the electrolyte depends on three main processes: diffusion, convection and electrode kinetics, shown in the same order from right to left in Eq. (5).

$$\varepsilon \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} D_e \varepsilon^{\beta_2} \frac{\partial c}{\partial x} + u_V \frac{\partial c}{\partial x} + \left((3 - 2t_0^+) (1 - cV_e) + 2cV_o \right) \frac{Aj}{2F} \quad (5)$$

Here the diffusivity coefficient $D_e \varepsilon^{\beta_2}$ depends on the porosity of the electrode [1,5] and on the concentration of the electrolyte $D(c)$; we use an empirical formula in Table 1 for the latter relationship.

For a large discharge current, the convection of the electrolyte out of the electrode is substantial [8]; its dependence is on the variable porosity as the volume average velocity of convection [1].

$$u_V = (V_{\text{PbSO}_4} - V_{\text{PbO}_2} - (3 - 2t_0^+) V_e + 2V_o) \frac{i_l}{2F} \quad (6)$$

Conservation of charge requires that the charge entering the solution phase equals the charge leaving the solid matrix phase. Hence, the current densities for solid i_s and liquid i_l phases satisfy the continuity Eq. (7).

$$\frac{\partial i_l}{\partial x} + \frac{\partial i_s}{\partial x} = 0 \quad (7)$$

The total current transferred from the liquid phase to the matrix phase is equal to the net rate of electrochemical reaction per unit volume of electrode.

$$\frac{\partial i_l}{\partial x} = Aj \quad (8)$$

The electrochemical reaction is a specific property that depends on electrode kinetics. In this work, the two-directional Butler–Volmer equation (9) is applied to describe the electrode kinetics

$$j = i_0 \frac{c}{c_{\text{ref}}} \left(\exp \left(\alpha_a \frac{F}{RT} \eta \right) - \exp \left(-\alpha_c \frac{F}{RT} \eta \right) \right) \quad (9)$$

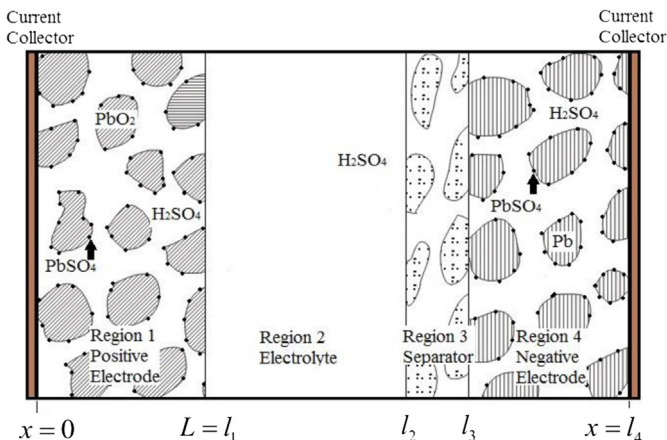


Fig. 1. The electrochemical cell represents a lead-acid battery in a single dimension.

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