Understanding self-discharge or what's going on inside a lead-acid battery when nothing happens outside

Mikael Cugnet, Florian Gallois, Angel Kirchev, Denys Dutykh

Understanding self-discharge

What's going on inside a lead-acid battery when nothing happens outside?

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Outline

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What is self-discharge?

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- Batteries that are prone to self-discharge exhibit a short shelf life and are thus disfavored in most applications.
- Self-discharge is more critical for primary batteries than secondary batteries:
  - Primary batteries ⇒ short life
  - Secondary batteries ⇒ low energy efficiency

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This feature is neglected in most battery models for simplicity!

Outline

Electrochemical reactions at each electrode

Hydrolysis of water, corrosion of the grid, and recombination of water

Positive electrode

Cathodic: $\mathrm{PbO_2 + H_2SO_4 + 2\,H^+ + 2\,e^- \rightleftharpoons PbSO_4 + 2\,H_2O}$ (discharge)

Anodic:
$$\begin{cases} \mathrm{H_2O \rightleftharpoons \frac{1}{2}\,O_2 + 2\,H^+ + 2\,e^-} & \text{(oxygen evolution)} \\ \mathrm{Pb + H_2O \rightleftharpoons PbO + 2\,H^+ + 2\,e^-} & \text{(grid corrosion)} \end{cases}$$

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Negative electrode

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Cathodic:
$$\begin{cases} 2\,\mathrm{H^+} + 2\,\mathrm{e^-} \rightleftharpoons \mathrm{H_2} & \text{(hydrogen evolution)} \\ \frac{1}{2}\,\mathrm{O_2} + 2\,\mathrm{H^+} + 2\,\mathrm{e^-} \rightleftharpoons \mathrm{H_2O} & \text{(oxygen reduction)} \end{cases}$$

liten cea tech

Redox shuttle process

Insufficiently purified water or leaching impurities from cell components

Impurities, e.g. Fe^{2+}/Fe^{3+}, lead to discharging of the cell by means of a so-called redox shuttle process:

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This process continues as long as the electrode potentials allow the oxidation and reduction of ions. The redox shuttle ions themselves are not consumed.

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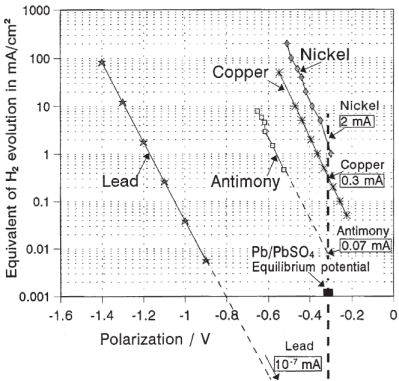

Fig. 3. Hydrogen evolution in sulfuric acid at various metal surfaces in a semilogarithmic plot vs. electrode potential (polarization). The origin of the horizontal scale is the equilibrium potential of the hydrogen electrode.

D. Berndt, J. Power Sources 95 (2001) 2-12

Some other self-discharge processes

Reactions between positive active material and separator

Lead dioxide has a very high oxidation potential and can discharge in contact with separators:

$$\mathrm{PbO_2} + \mathrm{H_2SO_4} + \text{separator} \rightleftharpoons \mathrm{PbSO_4} + 2\,\mathrm{H_2O} + \text{damaged separator} + \mathrm{CO_2}$$

The degradation of the separator must be avoided by proper choice of materials and designs.

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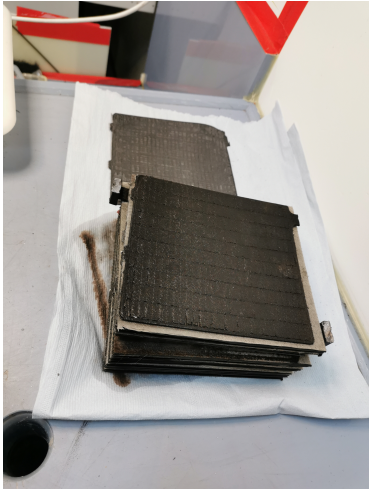
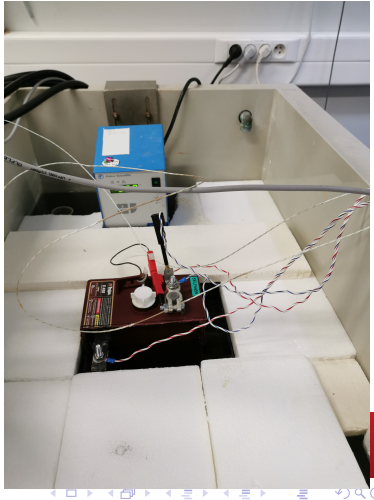
Ohmic Leakage Currents / Short Circuits

- New lead–acid batteries do not exhibit such self-discharge phenomena.
- Short circuits (e.g., formation of dendrites through the separator) can develop after long use and soon lead to cell failure, as they enable a discharging process inside the cell.
- A conductive layer of dirt on the cell container may bridge the battery terminals, but discharging caused by such fault currents can be reversed by the charging process.

Self-discharge in practice

Example of a flooded lead-acid battery for traction applications





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Tear-down of an individual electrochemical cell

- Number and dimensions of positive and negative electrodes

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- Weight of each grid (after removing active materials)

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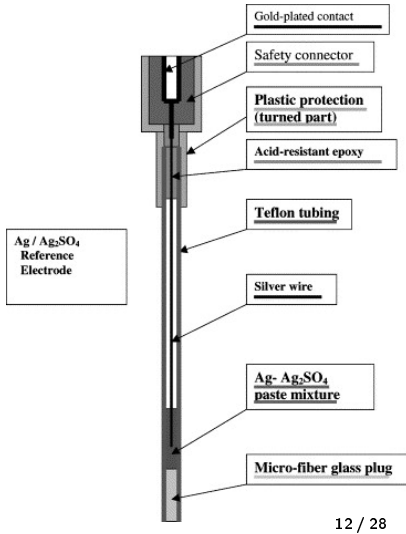
- Number and dimensions of positive and negative electrodes
- Number and dimensions of separators
- Weight of each electrode (still soaked with electrolyte)
- Weight of each electrode (after drying to remove electrolyte)
- Weight of each grid (after removing active materials)
- Estimation of the total volume of electrolyte in the cell

Reference electrode

Study of each electrochemical reaction with the silver-silver sulfate reference electrode

To measure the potential of an individual working electrode, you must combine it with a reference electrode to form a galvanic cell.



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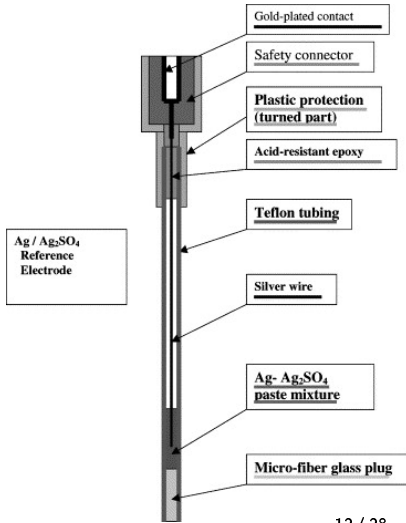
$$2\,\mathrm{Ag} + \mathrm{H_2SO_4} \rightleftharpoons \mathrm{Ag_2SO_4} + 2\,\mathrm{H^+} + 2\,\mathrm{e^-}$$



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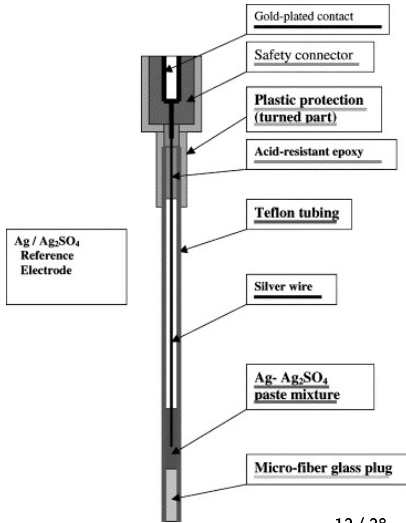
Negative electrode as working electrode

$$\mathrm{Pb + H_2SO_4 \rightleftharpoons PbSO_4 + 2\,H^+ + 2\,e^-}$$

$$\mathrm{Ag_2SO_4 + 2\,H^+ + 2\,e^- \rightleftharpoons 2\,Ag + H_2SO_4}$$



Reference electrode

Impact of the reference electrode on the Butler-Volmer model of the negative electrode

The current density of charge transfer is described by the Butler-Volmer equation:

$$i = i_0 \left\{ \exp\left[(1-\alpha) \frac{2F}{R\,T^\circ} \left(\Delta\phi - \Delta\phi^0 \right) \right] - \exp\left[-\alpha \frac{2F}{R\,T^\circ} \left(\Delta\phi - \Delta\phi^0 \right) \right] \right\}$$

with the exchange current density

$$i_0 = \frac{n\,F\,k_0}{\gamma_\ddagger} \, a_{\mathrm{H_2SO_4,ref}}^{1-\alpha} \, a_{\mathrm{H_2SO_4}}^{\alpha}$$

and the equilibrium potential at the reference temperature from the Nernst equation:

$$\Delta\phi^0_{\mathrm{Pb}}(T^\circ) = \frac{\mu^0_{\mathrm{PbSO_4}} - \mu^0_{\mathrm{Ag_2SO_4}}}{2F} - \frac{R\,T^\circ}{2F} \ln\left(\frac{a_{\mathrm{H_2SO_4}}}{a_{\mathrm{H_2SO_4,ref}}} \right)$$

Working electrode

Impact of temperature on current density and equilibrium voltage

The Arrhenius equation gives the dependence of the rate constant on T

$$k_0 = k_0^\circ \exp\left(-\frac{\Delta \bar{G}_\ddagger}{R\,T}\right)$$

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The Taylor polynomial of degree 2 for the equilibrium potential according to T°

$$\Delta\phi^0(T) = \Delta\phi^0(T^\circ) + (T - T^\circ)\left(\frac{\partial \Delta\phi^0}{\partial T}\right)_p (T^\circ) + \frac{1}{2}(T - T^\circ)^2 \left(\frac{\partial^2 \Delta\phi^0}{\partial T^2}\right)_p (T^\circ)$$

allows to estimate the equilibrium potential for any temperature value $T \neq T^\circ$ from the entropy and heat capacity at constant pressure (isobaric process)

$$\Delta\phi^0(T) = \frac{\Delta \bar{G}^0(T^\circ)}{n\,F} - (T - T^\circ)\frac{\Delta \bar{S}^0(T^\circ)}{n\,F} - (T - T^\circ)^2 \frac{\Delta \bar{C}_p^0(T^\circ)}{2\,n\,F\,T}$$

Working porous electrode

Electroneutrality and conservation of charge

The porous electrodes of lead-acid batteries are made of two phases:

- a solid phase (Pb at the negative electrode and PbO_2 at the positive electrode),
- a liquid phase (electrolyte).

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This approach is simplistic as the electrodes are also made of binders (electrical insulators) and conductive additives, but allows to consider that the whole volume of the electrode is conductive with two different types of conduction according to the phases:

- electronic in the solid phase (exclusively metallic), symbolized by the current i_s,
- ionic in the liquid phase (electrolyte), symbolized by the current i_l.

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Electroneutrality (the double layer being negligible in volume)

Charges leaving the porous matrix of the electrode must pass into the solution and reciprocally:

$$\nabla \cdot i_\mathrm{s} + \nabla \cdot i_\mathrm{l} = 0$$

Working porous electrode

Kinetics and electrostatics are two sides of the same coin

The current per unit volume of the electrode $\nabla \cdot i_\mathrm{l}$, transferred from the matrix to the solution, is involved either in faradaic reactions

$$\nabla \cdot i_\mathrm{l} = A \sum_{j=1}^{n} i_j$$

where A is the specific interfacial area (m^{-1}), $\sum_{j=1}^{n} i_j$ the sum of the current densities of all faradaic processes j involved ($\mathrm{A\,m}^{-2}$)

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$$\nabla \cdot i_\mathrm{l} = A \sum_{j=1}^{n} i_j + \frac{\mathrm{d}}{\mathrm{d}t} \left(A\, q_\mathrm{dl} \right)$$

where A is the specific interfacial area (m^{-1}), $\sum_{j=1}^{n} i_j$ the sum of the current densities of all faradaic processes j involved ($\mathrm{A\,m}^{-2}$) and q_dl the surface charge density on the electrode side of the double layer ($\mathrm{C\,m}^{-2}$).

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$$q_\mathrm{dl} = C_{dl} \cdot \frac{\mathrm{d}\Delta\phi}{\mathrm{d}t} + \Delta\phi \cdot \frac{\mathrm{d}C_{dl}}{\mathrm{d}t}$$

where C_{dl} is the double layer capacity per unit area of the electrode ($\mathrm{F\,m}^{-2}$).

Outline

Model equations

Self-discharge means no charge transferred

In open circuit, no current flows, neither electronically ($\nabla \cdot i_\mathrm{s} = 0$), nor ionically:

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Assuming two faradaic processes:

- discharge of the electrode active material with the primary current i_p
- hydrolysis of water contained in electrolyte with the gassing current i_g

and a constant double layer capacity per unit area of the electrode $\left(\frac{\mathrm{d}C_\mathrm{dl}}{\mathrm{d}t} = 0\right)$

$$\frac{\mathrm{d}\Delta\phi}{\mathrm{d}t} = -\frac{i_p + i_g}{C_\mathrm{dl}}$$

Model equations

Self-discharge means sulfuric acid consumption and dilution

Reducing self-discharge to sulfuric acid consumption works for the negative:

Negative electrode

Anodic: $\mathrm{Pb} + \mathrm{H_2SO_4} \rightleftharpoons \mathrm{PbSO_4} + 2\,\mathrm{H^+} + 2\,\mathrm{e^-}$ (discharge)

Cathodic: $2\,\mathrm{H^+} + 2\,\mathrm{e^-} \rightleftharpoons \mathrm{H_2}$ (hydrogen evolution)

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but is not sufficient for the positive, producing and consuming water:

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$$\forall\, i \in \{\mathrm{H_2O}, \mathrm{H_2SO_4}\},\ j \in \{\mathrm{p}, \mathrm{g}\},\ k \in \{\mathrm{pos}, \mathrm{neg}\},\quad \frac{\mathrm{d}n_i}{\mathrm{d}t} = -\sum_{j,k} \frac{s_{i,j,k}\, N_k\, S_k}{n_{j,k} F}\, i_{j,k}$$

Model equations

A system of 7 ordinary differential equations (2 for each electrode and 3 for the electrolytes)

Electrode k

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Bulk electrolyte

$$\frac{\mathrm{d}n_{\mathrm{H_2O}}}{\mathrm{d}t} = -\sum_{j,k} \frac{s_{\mathrm{H_2O},j,k}\, N_k\, S_k}{n_{j,k}\, F}\, i_{j,k}$$

$$\frac{\mathrm{d}n_{\mathrm{H_2SO_4}}}{\mathrm{d}t} = -\sum_{j,k} \frac{s_{\mathrm{H_2SO_4},j,k}\, N_k\, S_k}{n_{j,k}\, F}\, i_{j,k}$$

$$m = \frac{1\,000\, n_{\mathrm{H_2SO_4}}}{M_{\mathrm{H_2O}}\, n_{\mathrm{H_2O}}}$$

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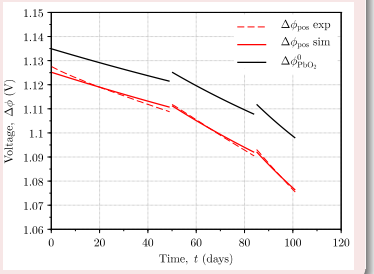
Reference electrolyte

$$\frac{\mathrm{d}m_{\mathrm{ref}}}{\mathrm{d}t} = \frac{D_{\mathrm{ref}}}{S_{\mathrm{ref}}} \left(m - m_{\mathrm{ref}}\right)$$

Model validation with experimental data

Electrode voltage and SOC during 49 days at 25 °C, 34 days at 35 °C, and 16 days at 45 °C

Positive electrode voltage



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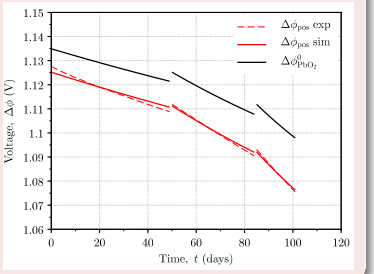
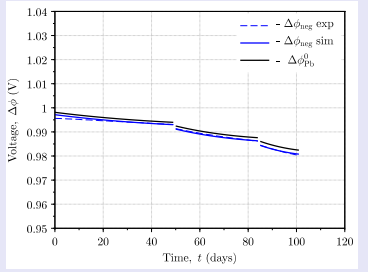


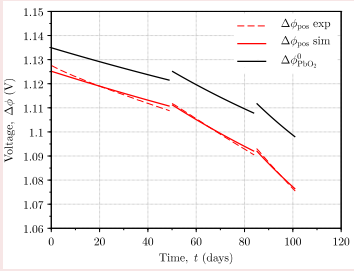
Negative electrode voltage



Model validation with experimental data

Electrode voltage and SOC during 49 days at 25 °C, 34 days at 35 °C, and 16 days at 45 °C

Positive electrode voltage



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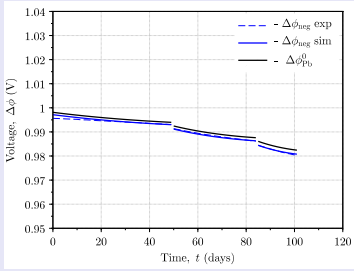
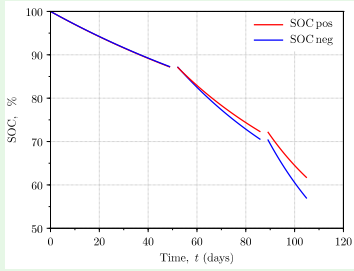


State of charge



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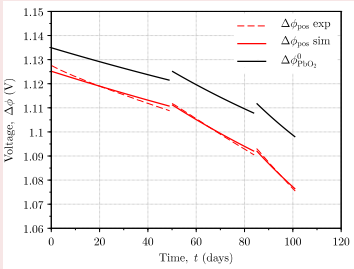

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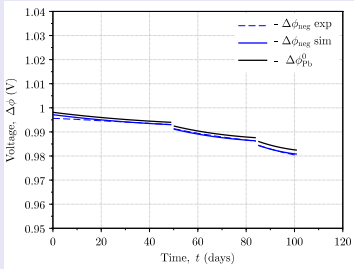

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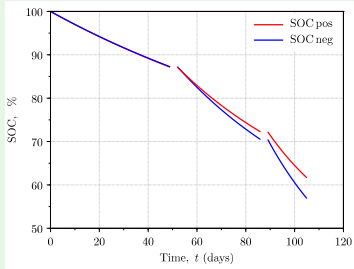

- The positive electrode polarization is much higher than the negative one.

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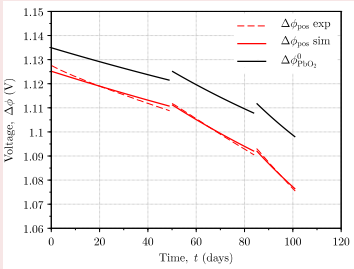

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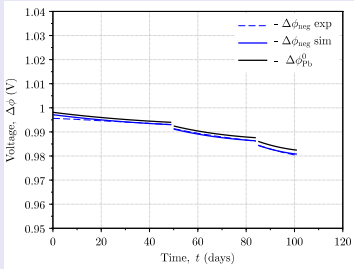

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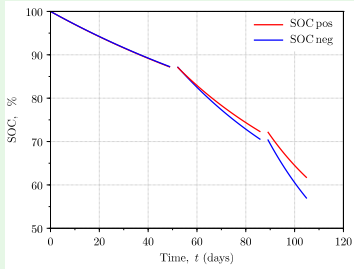

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- The positive electrode voltage decreases faster than the negative one.

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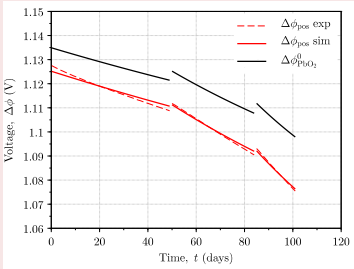

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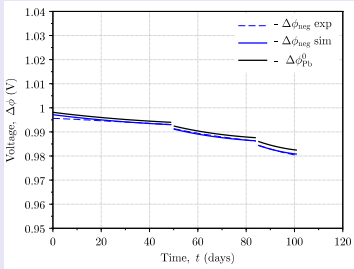

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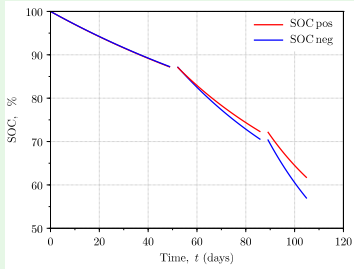
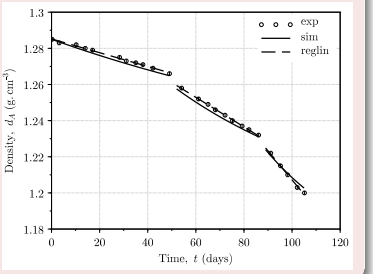


- The positive electrode polarization is much higher than the negative one.
- The positive electrode voltage decreases faster than the negative one.
- The positive electrode SOC decreases slower than the negative one.

Model validation with experimental data

Bulk and reference electrolytes during 49 days at 25 °C, 34 days at 35 °C, and 16 days at 45 °C

Bulk electrolyte density



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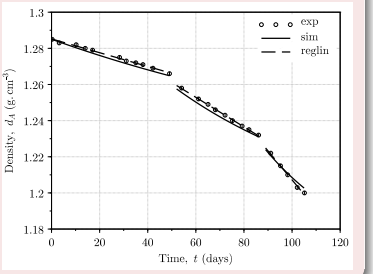

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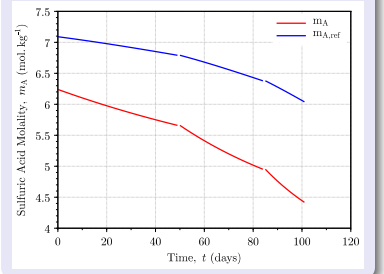

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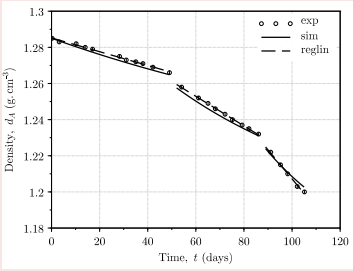

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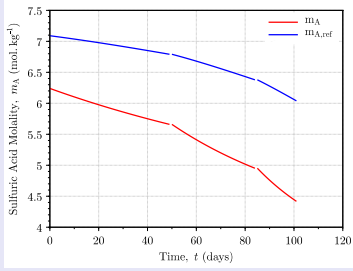
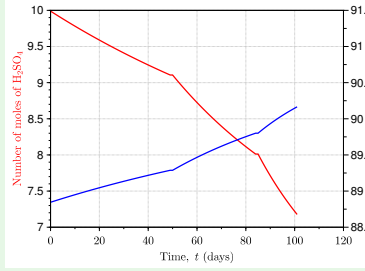


Moles of water and acid



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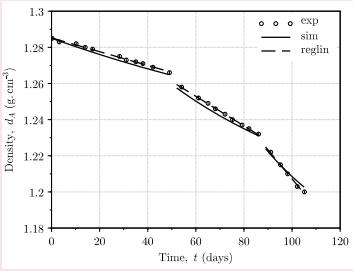

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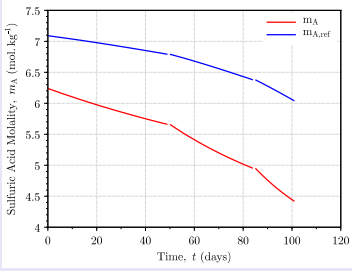

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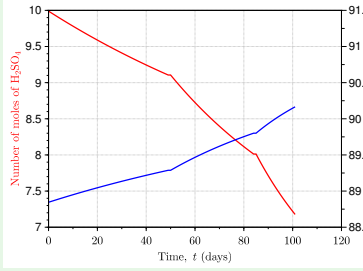

- Relative errors of density and voltages are very low ($\pm 0.3\,\%$).

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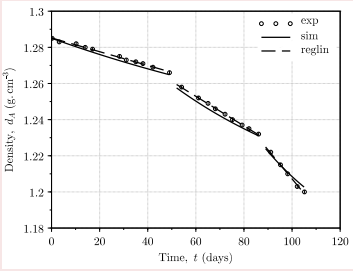

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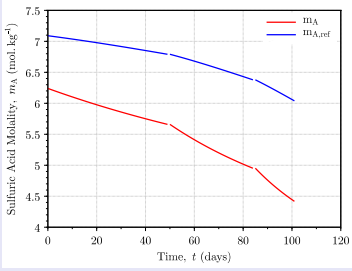

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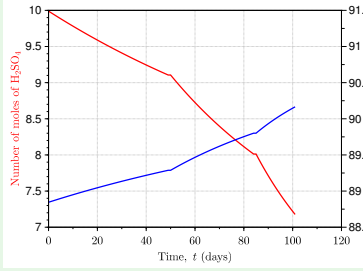

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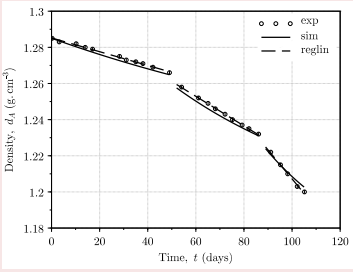

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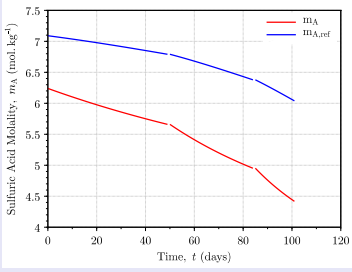

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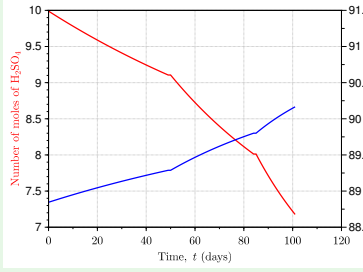
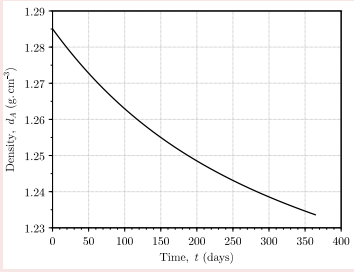


- Relative errors of density and voltages are very low ($\pm 0.3\,\%$).
- Diffusion of species from the bulk is very slow but non negligible.
- The model shows how the acid is diluted by water production.

Model extrapolation

Simulating the impact of a one-year selfdischarge at 25 °C on electrolyte density, cell voltage and SOC

Electrolyte density



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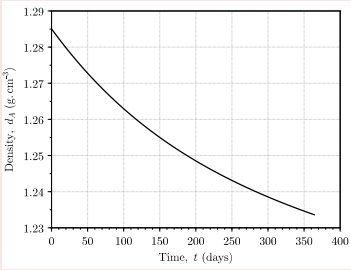
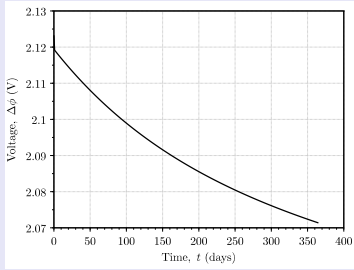


Cell voltage



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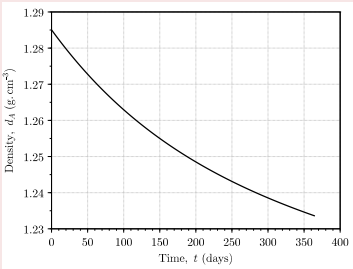
Electrolyte density



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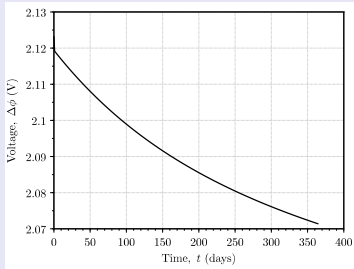
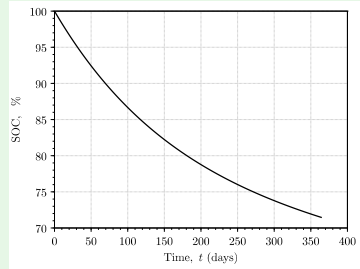


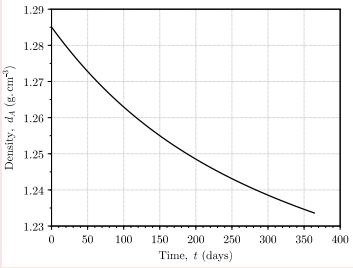
Cell SOC



Model extrapolation

Simulating the impact of a one-year selfdischarge at 25 °C on electrolyte density, cell voltage and SOC

Electrolyte density



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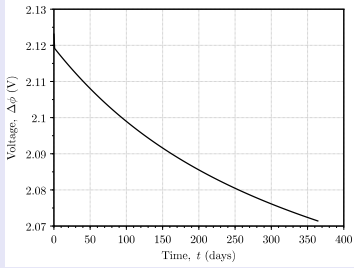

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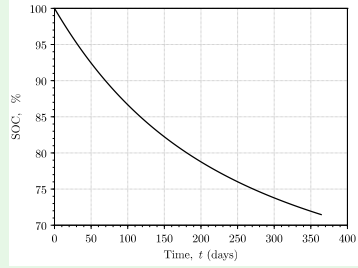

Thermodynamics and kinetics make the electrolyte density, cell voltage, and SOC decrease exponentially, showing that the lower the SOC, the lower the selfdischarge phenomenon.

Model improvements

Electrolyte density measurement issues, long-term selfdischarge at 40 °C, and sealed technologies

- Measurements from the electrolyte reserve located above the electrodes may lead to lower density values than the actual ones inside the pores.

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  - potentially add the impact of corrosion and loss of water by evaporation, if necessary.

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  - experimentally validate the model beyond one-month,
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- The model should be applied on sealed lead-acid cells as well.

Outline

What we have learned

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- Self-discharge involves many processes that are uneasy to isolate and identify.
- Self-discharge of lead-acid batteries is finally not so well-known.
- Efficient modeling of self-discharge requires to cover the complete value chain:
  - Experimental work,
  - Data collection and analysis,
  - Model development, parameter identification, and validation.

What should be done next

- If you don't know precisely what happens inside one cell, when there is no current going through it, do you sincerely believe you could drop that step and jump directly to the modeling of battery (dis)charge with more success?

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- "It is better to do the right problem the wrong way than the wrong problem the right way." R. Hamming

Richard Hamming (1915–1998)

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