Numerical algorithm for optimization of positive electrode in lead-acid batteries

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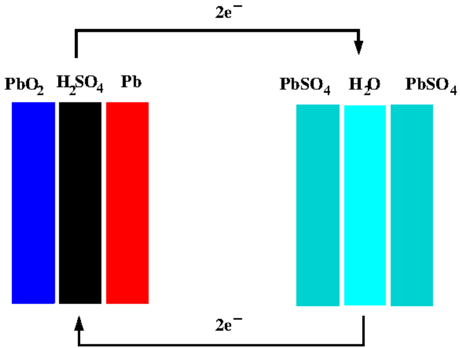
Contents

1. Lead acid battery
2. Software structure
   - Image analysis
   - Mathematical model
   - Current propagation
3. Data analysis. Results
4. Summary

Lead-acid battery



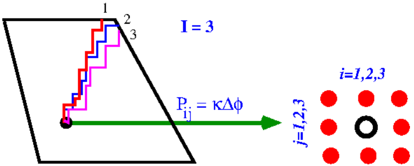
- Fully charged: 2.14 V
- Reactions are reversible up to $\approx$ 1.75 V

Electrode's structure

Electrode = metallic (Pb) support & porous active mass

The model

- hopping model: electrons are localized to specific sites; at each time step we have a probability of jump between current position and neighbours
- the jump probability $\mathcal{P}_n$ is direct proportional to the potential gradient in the given point
- $$\mathcal{P}_n = k\nabla\phi(\vec{r}) \qquad (1)$$
- n is the temporal index, k is a random number with uniform distribution between 0 and 1 and $\nabla\phi(\vec{r})$ the gradient of the electric potential.



Software structure

What to do:

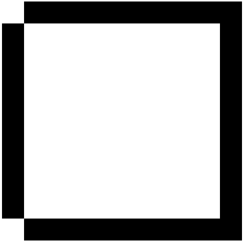
- Image analysis
- Poisson equation solver
- Time propagation
- Data analysis

How to do:

- Use of the XPM format
- Relaxation method on grid
- Monte-Carlo subroutine
- Average values for pellets

Software: handling the XPM format

```
/* XPM */
static char *noname[] = {
/* width height ncolors chars_per_pixel */
"11 11 2 1",
/* colors */
"  c black",
". c white",
/* pixels */
".          ",
" ......... ",
" ......... ",
" ......... ",
" ......... ",
" ......... ",
etc
};
```



Mathematical model: potential during discharge

The potential distribution is extracted using the continuity equation for the electric density during the discharge

$$\vec{\nabla} j = -\frac{\partial \rho(\vec{r})}{\partial t} \tag{2}$$

j is the current density while ρ is the charge density. Ohm's law in differential form:

$$j = \sigma\epsilon \; \epsilon = -\frac{d\phi(\vec{r})}{d\mathbf{n}} \tag{3}$$

ϵ is the intensity of the electric field and σ is lead electric conductibility.

This leads to

$$\sigma \Delta \phi(\vec{r}) = -I \tag{4}$$

where $I = \frac{\partial \rho}{\partial t}$ is the current generated by charge fluctuation (i.e. electrochemical reaction)
In a plane parallel to the electrode (no charge is crated/destroyed) we get

$$\Delta \phi(\vec{r}) = 0 \tag{5}$$

Mathematical model: potential during discharge

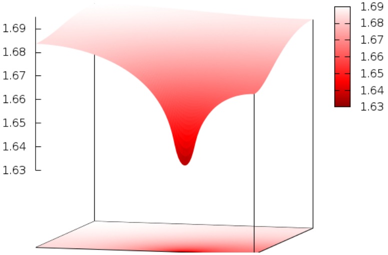
The boundary conditions for the equation are:

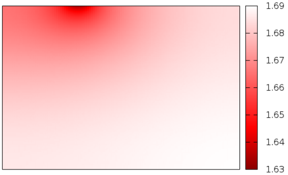
$$\frac{d\phi(\vec{r})}{d\mathbf{n}} = 0 \qquad (6)$$

at any edge points of the electrode, different form the collector, and

$$j_0 = -\sigma \frac{d\phi(\vec{r})}{d\mathbf{n}} \qquad (7)$$

for the collector region, and where σ is the lead conductibility (i.e. $\sigma = 4550$ S / mm)





Mathematical model: Poisson-Laplace equation

The relaxation method: $\phi(x, y)$ is the potential at the coordinates (x,y) a Taylor expansion allows us approximate the values

$$\phi(x + h_x, y) = \phi(x, y) + h_x \frac{\partial \phi}{\partial x}(x, y) + \frac{1}{2!} \frac{\partial^2 \phi}{\partial x^2}(x, y) h_x^2 \qquad (8)$$

By summing up the similar equation for the $\phi(x - h_x, y)$ we get:

$$\phi(x + h_x, y) + \phi(x - h_x, y) = 2\phi(x, y) + h_x^2 \frac{\partial^2 \phi}{\partial x^2}(x, y) \qquad (9)$$

A similar expression holds for $\phi(x, y \pm h_y)$.

Mathematical model: Poisson-Laplace equation

If we use a grid representation for $\phi(x, y)$ the $h_{x/y}$ are defined by grid steps in discreet (grid) form we have

$$\frac{\phi(x+h_x, y) + \phi(x-h_x, y) - 2\phi(x, y)}{h_x^2} + E(y) = 0 \tag{10}$$

Next, $\phi(x, y)$ is expressed as a function of the values of its neighbors points

$$\phi(x, y) = \beta(\phi(x+h_x, y) + \phi(x-h_x, y) + \alpha(\phi(x, h+h_y) + \phi(x, y-h_y))) \tag{11}$$

where

$$\alpha = \frac{h_x^2}{h_y^2} \beta = \frac{1}{2(1+\alpha)} \tag{12}$$

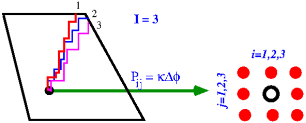
Mathematical model: Poisson-Laplace equation

The equation:

$$\phi(x,y)^{(n+1)} = (1-p)\phi(x,y)^{(n)} + p\phi(x,y) \tag{13}$$

is iterated until the convergence is reached. Here $\phi(x,y)^{(n+1)}$ is the potential at iteration $n+1$ while $\phi(x,y)^{(n)}$ is the potential at iteration n. Parameter p controls the convergence, typically taking values between 0.5 and 1.

Software: Monte Carlo time propagation



- At each iteration, n for each point/pelet the charge is propagated with probability $\mathcal{P}_n$
-
$$\mathcal{P}_n = k\nabla\phi(\vec{r}) \tag{14}$$
- k is a random number with constant distribution, ranging from 0 to 1 and $\nabla\phi(\vec{r})$ is the gradient of the potential.
- if the gradient is negative, no jump takes place
- if the metallic part is reached, we add $+1$ at total charge generate by the pellet.

Geometrical models

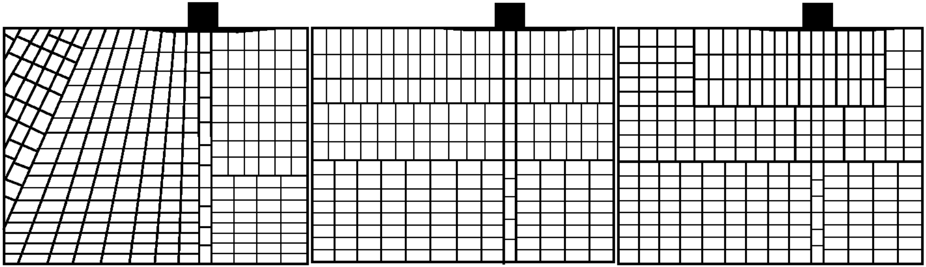


Figure: Geometric shapes of the grids studied: from left to right we note them as G1, G2 and G3.

- All models were drawn using Xfig (vectorial format fig, export to xpm)
- The same size for the electrode is used in all cases
- The same potential file is used for propagation
- Results are given in pixels - for the electrode drawings and iterative cycles, respectivelly

Time to collect charge

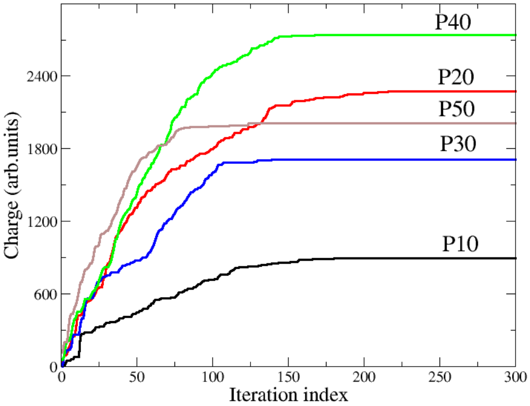


Figure: Example: time dependence of the current for selected pellets in G1.

Time to collect charge

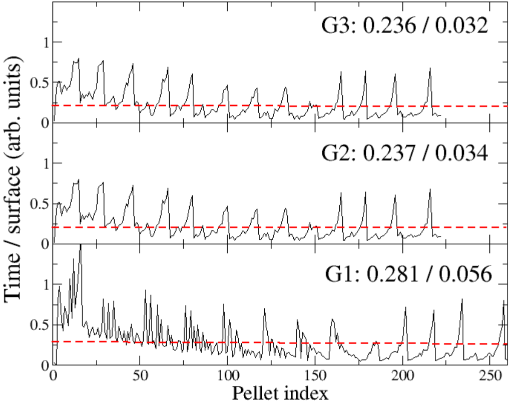


Figure: Time needed to collect the charge for grids G1, G2 and G3: average and MSQ for all pellets

Pellet usage at discharge

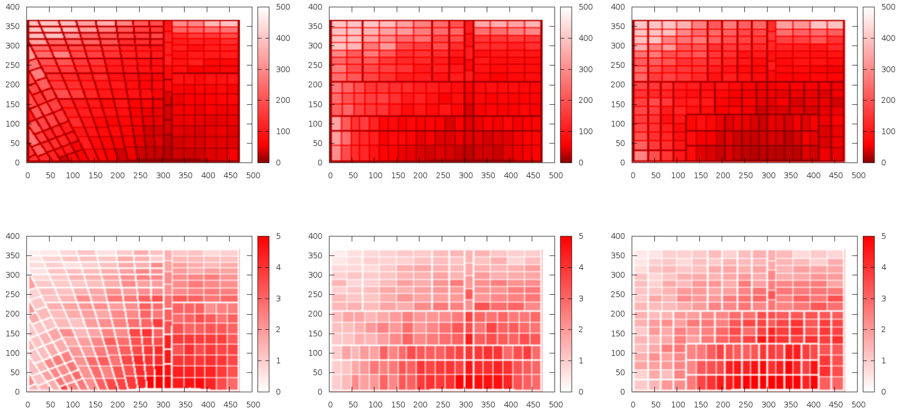


Figure: Top: time needed to collect the charge for grids G1, G2 and G3. Bottom: Percent of usage for each pellet after 1/10 of the discharge time for grids

Summary

- We propose and algorithm to analyse the quality of the lead-acid collector in the pozitive electrode of lead-acid battery
- The idea is to use a hopping model and a Monte-Carlo procedure to analyse the system's state during battery discharge
- A dedicated software was developed to implement all the features
- This includes image analysis, Poisson solver and Monte Carlo time propagation of the charge generated by electrochemical reaction.
- Data analysis is complex
- A "qualitative index" may be assigned to each support of the positive electrode

Thank you!