

EPSRC Centre for Doctoral Training in Industrially Focused Mathematical Modelling



Modelling Lead-acid Batteries for Off-grid Energy Storage Systems in Sub-Saharan Africa

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BBOXX Home Systems power 70,000 homes in Eastern Africa

1. Introduction

Background

BBOXX designs, manufactures and distributes “plug & play” solar systems to improve energy access across Africa. These provide charge to a range of devices such as lights, televisions or phone chargers through a lead-acid battery that is charged during the day by a solar panel. A unique feature of these systems is the SMART Solar system, which records current, voltage and temperature of the battery up to every ten seconds. This enables remote monitoring and management of the battery.

BBOXX have the ambition to produce the best product in the sub-100W category. To do this, it is important to understand why batteries fail and how their lifetime can be increased. Mathematical modelling is an important tool to help to achieve this. By developing mechanistic models of the physical and chemical processes occurring at the micro-scale within a battery, we can gain insight into its behaviour, which then allows us to improve our understanding of the physical meaning of the observed current, voltage and temperature readings.

We can use this improved intuition to help the development and management of the product in three ways. Firstly, we can optimise the battery design, for example to improve the efficiency of the battery or reduce its degradation. Secondly, we can derive more efficient charge profiles to improve battery life. Thirdly, we can use the mechanistic models to derive simple relationships between current and voltage, which can then be used to analyse the SMART Solar data.

There are two important processes to model in rechargeable batteries. The first is the regular process of charge, rest and discharge, occurring on the relatively short timescale of a day. This process is measured in terms of the “State of Charge”. The second, much slower, process is degradation of the battery, which occurs over several years and is measured in terms of the “State of Health”.

Project Aim

The main aim of this project is to lay a solid foundation for future work by developing a simple model that can later be extended into a more complex one. In particular, we focus on modelling a single discharge of a planar cell.

An advantage of mathematical modelling is that we are not limited by the chemistry of the battery, and we can draw on research on models of many different batteries. We will adapt the model by Liu and Monroe [2] to the case of a lead-acid battery; additional difficulties arise in the lead-acid chemistry from the fact that the reactions are different at the two electrodes. This simple model gives great insight and allows us to qualitatively reproduce the response of electrolyte concentration and specific gravity and battery voltage to a discharge at constant current.



Figure 1: A single lead-acid cell (Photo: Ashley Grealish, BBOXX). Alternating positive and negative electrodes; soldered together in parallel to make two large electrodes. A (12V) battery is made up of six (2V) cells connected in series.

Chemical Background

In a lead-acid cell (Figure 1), different reactions occur in the positive and negative electrodes (Figure 2). During a discharge, in the negative (lead) electrode the lead reacts with hydrogen sulfate ions to form hydrogen ions and deposits a layer of solid lead sulfate, releasing electrons in the process. Meanwhile, in the positive (lead dioxide) electrode, lead dioxide reacts with hydrogen sulfate ions and hydrogen ions and consumes electrons to produce water and solid lead sulfate. As a result, the solution level drops, and the electrolyte becomes less concentrated; further, the electrolyte is less concentrated at the positive electrode than at the negative electrode.

More solution (electrolyte + water) is consumed than produced during a discharge, so both the volume and the concentration of the solution decreases.

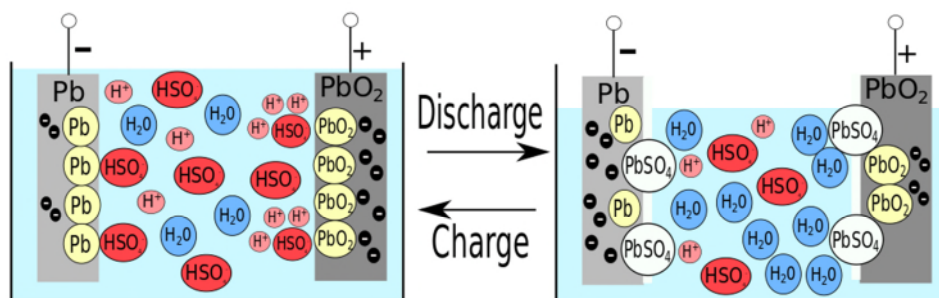


Figure 2: Idealised chemistry of a lead-acid battery. Left is charged state, right is discharged state. Solid species: Lead (Pb), Lead dioxide (PbO_2), Lead sulfate (PbSO_4). Liquid species: Hydrogen ions (H^+), Hydrogen sulfate ions (HSO_4), Water molecules (H_2O).

When the electrodes are connected, the electrons released at the negative electrode flow through the external circuit to the positive electrode, and thus provide charge to the external circuit. The battery is recharged by externally driving electrons the flow of electrons back from the positive electrode to the negative electrode, reversing the electrode reactions.

2. Model

Glossary of terms

- **Current density:** The ratio of current to electrode surface area, measured in Amps/ cm^2 .
- **Capacity:** Amount of charge available in the battery, i.e. time taken for a complete discharge multiplied by the current, measured in Amp-hours (Ah)
- **Electrode:** Electric conductor used to make contact between the external circuit and the electrolyte.
- **Electrolyte:** The electrically conducting liquid in the battery, containing ions (sulphuric acid for lead-acid batteries). Together with water, the electrolyte forms the solution in the battery. A binary electrolyte contains only two species: positively charged particles (hydrogen ions) and negatively charged particles (hydrogen sulfate ions). We can show that these must have equal concentrations in the bulk; we refer to this concentration as the electrolyte concentration, measured in moles/ cm^3 . A simple binary electrolyte is assumed to have concentration-independent properties (e.g. molar volume).
- **Potential/Voltage:** The difference in electric potential energy between the negative and positive electrode. The potential of a (12V) battery is six times the potential of a single (2V) cell. The aim of a battery is to produce a high, constant potential.

- **Specific gravity:** The density of the electrolyte relative to the density of water. Often used to measure of State of Charge.

Mathematical Model

Real electrodes are porous, so the reactions take place within the pores. However, we model the electrodes as non-porous sheets, and assume that all reactions occur on the planar electrode-electrolyte interface. This gives some initial insight while avoiding some mathematical difficulties

We initially derive a fully general model for the thermodynamics and transport in a multispecies electrolyte, at constant temperature and pressure. This model is explicitly thermodynamically consistent, unlike many models in the literature. By specialising to a simple binary electrolyte, we then simplify the general model to a single advection-diffusion equation for the concentration.

Applying our model in a simple one-dimensional planar (not porous) geometry, we find that the potential is equal to a reference potential of 2V minus losses from three effects. Firstly, potential is lost due to resistance in the electrolyte (Ohmic losses). Secondly, there is a loss from the difference in concentration between the negative and positive electrode (concentration losses). Finally, there is a loss due to the energy required for reactions to occur at the electrode-electrolyte interface (overpotentials). Note that we ignore the resistance of the electrodes in this model.

Comments

- Our one-dimensional model uses the full set of equations for transport in a concentrated electrolyte. This gives insight into the physical behaviour of the battery.
- With our one-dimensional model, we replicate the fact that the liquid level decreases during discharge (Figure 2) by allowing the positive electrode to move.

3. Results

We investigate results for a range of currents. Typically, BBOXX batteries are discharged at currents between 0.2A (e.g. to power a light) and 2A (e.g. to power a TV). We investigate discharges at those two currents, as well as at 10A and 20A to gain more insight into the behaviour of our model.

Concentration of Electrolyte

First, we study the change in concentration during discharge at various currents. In Figure 3, we compare a 0.2A discharge with a 20A discharge.

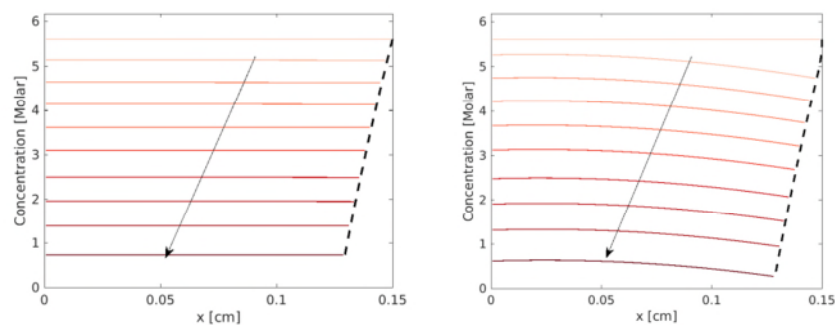


Figure 3: Snapshots of concentration profiles during discharge. Red lines are the concentration, with time increasing linearly as the line darkens (as indicated by the arrow). Dotted black line is the position of the positive electrode. Left: 0.2 A discharge; Right: 20 A discharge.

The electrolyte is more dilute at the positive (right) electrode than at the negative (left) electrode, as expected.

At both 0.2A and 20A, the average concentration decreases with time and the concentration at the positive electrode (at the right-hand side of the plot) is slightly lower than the concentration at the negative electrode, as expected from our discussion of the chemistry. The position of the positive electrode, shown by the black dotted line, decreases with time; this reflects the fact that the liquid volume is decreasing. At both currents, the concentration is almost spatially uniform; this is because diffusion is much faster than convection. The rate of convection is proportional to the current, so the concentration is slightly less uniform at higher currents (right-hand graph).

The specific gravity of the electrolyte is directly proportional to its average concentration. In Figure 4, we show that the specific gravity decreases linearly with time at all currents, as is expected (see [1]).

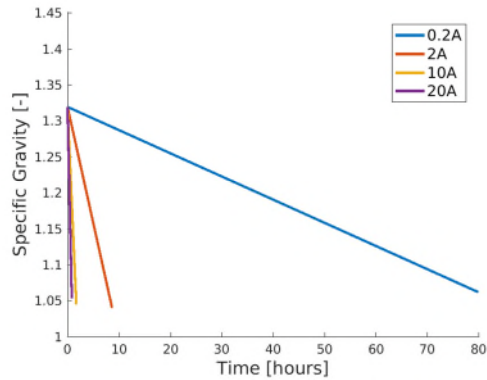


Figure 4: Specific gravity during discharge at 0.2A, 2A, 10A and 20A.

Specific gravity decreases linearly with time.

Potential/Voltage

Finally, we investigate the potential across a single cell, comparing discharges at 0.2A, 2A, 10A and 20A (Figure 5).

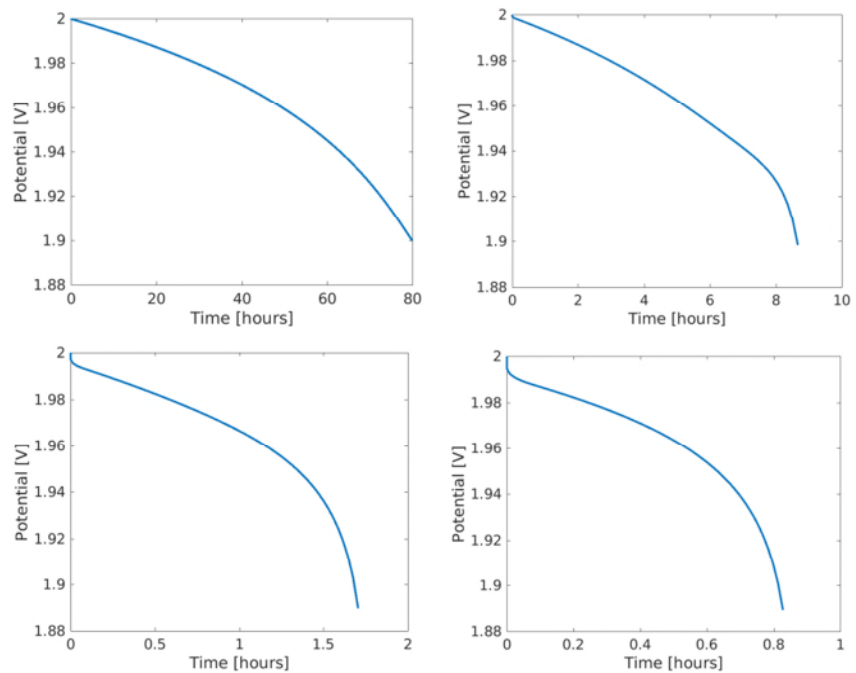


Figure 5: Potential across a single cell during discharge at various currents. Top left: 0.2A. Top right: 2A. Bottom left: 10A. Bottom right: 20A.



The profile of the potential is qualitatively similar in all four cases, and resembles the potential that we would expect to see. First, there is an initial, rapid drop (sometimes referred to as the *coup de fouet* effect), proportional to the current. Then, the potential decreases roughly linearly with time. Finally, there is a relatively rapid drop to the cut-off potential.

The potential drop is due to Ohmic losses, concentration losses and overpotential.

When we investigate the sources of potential loss at different currents, we observe that there are some important differences (Figure 6). At lower currents, the overpotential is almost entirely responsible for the total potential drop. As we increase the current, Ohmic losses and concentration losses become more important. This is because ohmic and concentration losses are proportional to the current, while overpotential depends only on the concentration, which decreases by the same magnitude at all currents as shown by Figure 4.

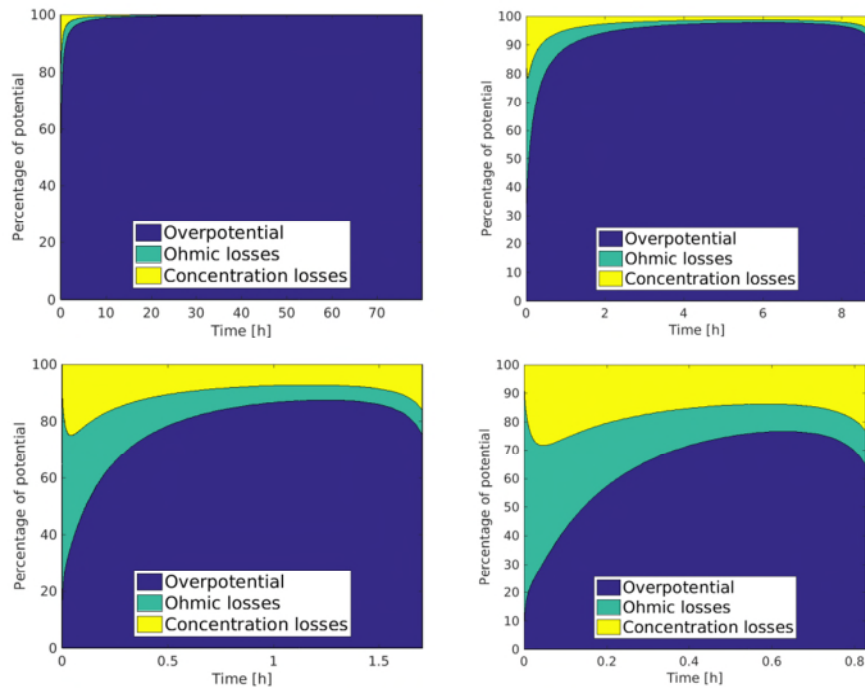


Figure 6: Causes of drop in potential from 2V, during discharge at various currents. Top left: 0.2A. Top right: 2A. Bottom left: 10A. Bottom right: 20A.

Note that there is a difference in time scale in the four discharges in Figures 4 and 5. In all four cases, we find the capacity of the battery to be 17 Ah, which is the same as the value given by the manufacturer. However, in reality we expect the capacity to be higher at lower current discharges and lower at higher currents. Our model does not capture these effects, as they are related to the extent to which the porous electrode is used.

Extending the model

There are several extensions to consider as next steps:

- To capture the effect of the decreasing solution level, we can extend our one-dimensional model to a two-dimensional one.
- As well as considering discharge, we will adapt the model to investigate the behaviour of the battery during charge and at rest.
- We use our simple model as a microscale building block for a model of a cell with porous electrodes. A key to the systematic generation of our new model will be a mathematical technique called *homogenisation*.

- Later, we will include effects that lead to degradation of the battery, such as corrosion of the electrodes.

4. Conclusions and Future Work

We have developed important insights into the both the modelling and the behaviour of the batteries.

Battery understanding

We have understood the models used to describe transport in general concentrated electrolytes, and how these can be specialised to describe simple binary electrolytes. Our simple model provides us with a solid base from which to create more accurate models – in particular taking into account the porosity of the electrodes. We will then be able to compare our improved model with the existing literature.

Voltage drop

We have investigated constant-current discharges at a range of currents and found good qualitative agreement with the expected profile of the potential. Our model predicts the right capacity for the batteries. Further, we can quantitatively identify three distinct sources of potential loss: overpotential, Ohmic losses and concentration losses. This gives an insight to ways in which to manufacture more efficient batteries in which these losses are reduced.

Future work

The initial aim of future work will be to make improvements to the simple model, such as solving the two-dimensional extension. After this, our main focus will be to develop a model for a porous cell. This will allow us to quantitatively observe the behaviour of the cell, and thus compare our model with both experimental data and the BBOXX Smart Solar data. Consequently, we can suggest better battery design or better management techniques.

Later in the future, it will be important to consider effects that lead to degradation of the battery, such as corrosion of the electrodes. This will allow us to further optimise battery properties and management in order to minimise degradation and maximise battery life.

A porous cell model is necessary to obtain quantitatively accurate results and compare our model with real world data.

5. Potential Impact

Chris Baker-Brian, Co-founder and CTO of BBOXX, commented:

“Over the next 24 months, BBOXX expects to deploy close to 250,000 solar home systems across the developing world, bringing electricity to millions of people for the first time. As part of this deployment, it is critical for the company that we understand the behaviour of the systems over time and are able to put in place appropriate measures to manage the performance of the battery in the field. In the short term, this piece of work will allow BBOXX to better predict how our battery units degrade over time, allowing us to accurately forecast our maintenance requirements. In the longer term, this work will potentially allow better batteries to be manufactured, improving the lifespan even further”.

References

1. David Linden and Thomas B Reddy. *Handbook of batteries*. 2002.
2. J Liu et al (2014) *Solute-Volume Effects in Electrolyte Transport*. *Electrochimica Acta*. 135, 447-460.