

Understanding the problem



**University of
Sheffield**

**Implamenting multistage constant-current charging
methods in lithium based batterys to reduce
degredation**

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1 Introduction

There are currently over 7 billion people with access to electricity [1], the global consumption of energy is rising by 4.5×10^{16} Joules every year; 77% of which is from utilising non-renewable sources. With the affects of non-renewables on the environment still not fully realised, coupled with the concern of their finite-life nature, poses a constant need to increase usage of renewable sources. However, a large set of renewable generation methods fall under the category of variable renewable energy (VRE) sources [2], thus requiring a robust form of energy storage to solve the intermittent availability - methods of storage do exist and suitable solutions depend on the specifics and locations; as battery technology increases, the use of battery as a storage medium for the energy sector are ever more increasing. There is also the rapid increase in electric vehicle production, with a push to increase the adoption of EV's, 17.3 million cars were produced in 2024 [3] alone with a recent 20% average year-on increase. Lithium Ion batteries (LIB's) are the most common currently used batteries due to their desirable characteristics in energy density, aging properties, cost and more.

EV's and the energy sector account now account for 90% of the total lithium ion battery demand since 2016, the total lithium-ion battery demand is 10-times larger [4] since 2016. Different resources predict different forecasts of total battery growth [5, 6], regardless, it appears the rate of demand will not be decreasing in the near future.

LIB's, like all batteries and decrease in performance and capacity [7] until they are deemed unsuitable for their current use. This means eventually, all current batteries in use today will need to be disposed of, given that over 660,000 tonnes of earth metals were mined in 2023 alone, a strong case for slowing down the need for mining new materials is made, whilst keeping up with the demand (cite the iea thing). It's noted that battery chemistry is still a developing field, thus newer batteries may use less scarce materials, thus hard to truly predict the sustainability of mining these materials, for example, some reports (cite faraday) say cobalt supplies could be used entirely by 2040. Solutions do exist, recycling methods have been developed in order to extract the materials, termed battery metal recycling (BMR), however there are widely different sources suggesting how much of current batteries actually are recycled (one showing 5%), (other showing 90%), and the technology to do so is still a developing field, there are many different methods (cite issurs), since most of the rare earth elements are within the batteries cathode, methods such as hydrometallurgical process can extract these, but at the cost of severe reduction in lithium yield (cite enji) - although there are

promising methods with some proposing a lithium recovery needing less than 40% the energy compared to mining the virgin material (cite enji yoo) whilst still recovering nickle and cobalt. There is also the rising interest in reusing the batterys before recyling, these batterys are ferrerd to as second-life batteries (SLB's); in the EV use-case, the majority of the batteries are deemed finished once their usable capacity drops below 80% (cite), but often, due to the other parameters of the batteries needing to be of high standards for EV use, the 'dead' batteries can still provide a very usefull serivce in less demanding applications, a common one being energy storage systems (ESS) [8], with claims resuing can reduce CO2 emmisions by 56% as apposed to using natural fuel gas in situe. However there are again challanges associated, for saftey there is the need for robust testing, asorting the batteries based on their current health states, non automised methods of extracting cells from their original pack. These additional steps mean the price of SLB's could become at a point where they are not much cheaper than new batteries, making the solution less attractive to many sectors [8].

In summary, there are methods that are developping to reduce the need for mining new materials and decreasing recyling emrgy, but ultimately, providing methods to increase the usable life of the current batteries serves as a direct way reduce the impacts of batteries themselves and to meet their growing demand. If just 1 extra life cycle could be added to all EV's currently on the road (60 million (citr)), this could power all of the UK's energy needs for one day (cite govengy); as most batterys cycle life are well over 1000, any incament in cycle life can be greatly beneficial.

Much research has been done into both modeling LIB's and optimising their usage from both an energy and aging perspective.

What is this project? the general apprach

1.1 Project Aims

Its would be good to see how the ecm parts change over degredation to see future behaviour

Look at new ways to parameterise batteries, allowin

1.1.1 Objectives

- Analyse ICLOCS2 and other methods in parameterising batteries during realtime use

- Modify previously developed charging methods for running in a lab to rest actual results
- See how affective adaptive methods are in the charging process as the battery ages
- Feed results to a data driven model to see if predictions in battery degradation can be made

2 Literature Review

2.1 Lithium based battery degradation modes

Basic Background of Lithium Ion Batteries

Lithium-ion based batteries are favorable largely due to the highly reductive nature of Lithium, taking the potential relative to hydrogens reduction, lithiums half-reaction is -3.01V (cite gregg), meaning lithium can release its outershell electron relatively easy. Any cells potential difference is the difference in potentials of the negative and positive electrodes ($V_t = \phi_s^+(t) - \phi_s^-(t)$), so having a very negative potential like the lithium reduction, allows a variety of positive electrodes (where the oxidation occurs), to yield a high battery voltage. Coupled with Lithium's low molecular weight, a high energy density cell can be achieved to. The force produced by the potential difference between the electrodes drives the electrons via the external circuit, providing useful work, allowing lithium batteries to act as an energy storage medium.

Lithium batteries all follow the same basic principle of operation, as shown in They consist of a positive and negative electrode, electrolyte a separator and current collectors. Unlike many other battery chemistries, where the metal ions undergo chemical reactions at the electrodes which change the composition of the electrodes, lithium ions intercalate and deintercalate within the electrodes - they are in essence absorbed to and from the electrode structures (cite greg p), forming as loosely bonded lithium atoms within the electrodes. The electrodes for the negative side is usually a graphite based structure, allowing up to 1 lithium atom to be stored per 6 carbon atoms, whilst the positive electrode can vary greatly between different lithium batteries; the most common positive electrodes are often composed of transitional metal oxides such as LCO, LMO, NMC, NCA (cite Alex K Hoech et al). The lithium state in the graphite is similar to that of individual lithium atoms, thus the electrode potential of the negative electrode is very similar to that of pure lithium (-3V) (cite liquin), although its lithium storage abilities are usually lower than the positive electrodes.

The lithium ions within the positive electrodes are in a much lower energy state, thus their reaction potential ranges from $-1 - 2V$, therefore, overall there is a large potential difference created by the want of the positive electrode gaining electrons and the lithium ions, and the want of the lithium within the carbon of the negative electrode to give up the lithium ions and electrons (relative to each other). In general, the negative electrodes used currently are carbon based, their capacity to hold the lithium (per unit volume) is greater than the positive electrodes used today as shown in figurexx (cite Alex), but as discussed later in this section the negative electrode is often the key limiting factor in degradation. The positive electrode materials vary greatly in material, but since this electrode has the biggest electrode potential, it has a largest impact on the overall cell voltage, and thus energy density of the cell, in addition since per volume it holds less lithium, electrode material with higher lithium capacity will be of greater affect than improving the negative electrodes capacity. The two reactions with lithium with the battery electrodes chosen for this project are shown below (during discharge, the reactions proceed from left to right, for the charging process, it's right to left):



The electrolyte is a medium in which the lithium ions can be transported via diffusion to the electrodes, the electrolyte does not however allow electrons to flow, only via an external circuit can they flow, . The separator acts as a structural barrier to prevent the opposite electrodes from touching, which would allow both electrons and ions to flow, causing major fire risks from the uncontrolled reactions. During the discharging process, a path for electrons is provided externally across the current collectors, (these collectors are not part of the reactions and are just a means to electrically connect the electrolytes to a useful surface for soldering) the lithium stored within the negative electrode deintercalates, released as the positive lithium ion, whilst the electron leaves the electrode, traveling across the external circuit to the positive electrode, whereby the lithium ions meet the electrons. During charging, the applied voltage at the terminals will be above the difference of the electrode potentials, this applied overpotential causes the lithium ions within the positive electrode to deintercalate, traveling across the electrolyte to the negative electrode, where they intercalate within the graphite structure as the ions combine with electrons. The speed at which the ions flow is far slower than the electron transfer (cite greg), which contributes to the behaviour of lithium batteries.

Mention diffusion differences between charge and discharge (cite Micheal J. Whiney well)

2.1.1 Degredation methods

Lithium plating - During discharge, the lithium ions intercalate into the positive electrode. Under certain conditions,

Causes increased ageing and safety risks, it's the deposition of metallic lithium on the anode surface, happens at high charging currents and low temperature. Since during charging, the lithium ions move, through the SEI into the anode, if the ions cannot intercalate fast enough, they deposit and can become metallic lithium. Especially when charging is forced, local overpotential can cause the lithium plating, can cause dendrites

- SEI layer growth via pores \approx not really solvable, grows square root over time and cycle number

- Lithium plating

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- Active material loss (from parts mentioned above)

- SEI Breakages

Charging too **high** of a temperature causes mechanical stress on the SEI layer, causing it to crack and reform, consuming more lithium ions in the process. Loose SEI material can also float in the electrolyte, causing further issues.

- Electrolyte decomposition

2.2 Equivalent Circuit Model

This S2352152X2400584X nicely shows the overpotential of the battery relating to the difference of the output of the battery to the equilibrium potential of the battery. Shown as the summation of electrolyte overpotential, Li concentration overpotential, kinetic overpotential. Attempts to estimate the anode voltage based off reduced order electrochemical models and by use of a state estimator. In the electrochemical models, the anode potential is equal to the kinetic overpotential, anode equilibrium potential and the electrolyte potential, (cite) shows the solid-phase electrode potential is equal to $U_{eq} + \mu_{ct} + \Phi_{electrolyte}$ (cite).

and resistive overpotential. This are equated within the ECM model as the polarizing RC, and R. 0378775313020880 bib5 gives the

Just say, that there are models for overpotential which can cause the dendrite formations, these are caused by too fast of charge and overcharging.

Polynomial fit

$$mCp \frac{dT}{dt} = \underbrace{I^2 R_0 + IV_1}_{irreversible} - \underbrace{IT \frac{\partial U}{\partial T}}_{reversible} - \underbrace{hAT}_{dissipation} \quad (3)$$

Capturing temperature models can be challenging in order to achieve high accuracy, often methods of measuring temperature can have high levels of noise, alongside the thermocouples themselves often detaching from the batteries. There is then the modeling of the batteries themselves. (Talk about the irr and rev heat complications). There's the paper explaining the irr and rev, link to electrochemical model. Then there's the paper that gives a rough value of the du/dt .

2.3 Charging methods

There was a paper comparing them in general, talk about the advantage of the different ones etc.

2.4 Optimal control

Fmincon stuff

- Fmincon
- Greyest
- ICLOCS

- **2.4.1 Machine Learning**

- General Understanding
- LSTM
-

3 Plans for Remaining Work

4 Self Review

5 Project progress

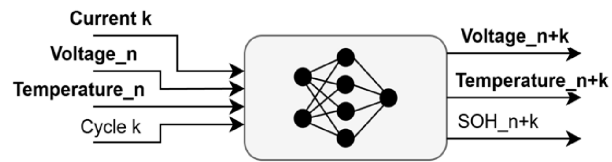


Figure 1: Initial end objective: Black Box Battery

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