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Understanding Ageing in Li-ion Cells: an Enabler for Effective Grid Interaction Strategies

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1. Abstract

Due to the large upfront expenditure of a battery pack, usage lifetime optimisation is an important objective both for battery pack design and control system. In this work we aim to review the physical and chemical ageing mechanisms, the impact on cell performance and the factors that accelerate them. This knowledge is essential both for the battery pack design and the battery management system, and the way in which they can minimise the effects of cell ageing through controlling factors such as temperature, current and Voltage limits in an intelligent approach. This work is also the first step towards the design of an advanced cell ageing model that can be used to inform both the design of battery packs but also the battery management system. This can then be used to assess the ageing impact of usage from both vehicle and energy storage applications, in particular vehicle-to-grid interactions, 'powerwall' type applications and large scale energy storage. Our study was confined to Li-ion cell chemistries bounded to ageing under normal cycling conditions. As a result, we did not investigate abuse conditions such as impact and short circuiting.

2. Introduction

Li-ion battery cells are in increasing demand for automotive, home, and large scale energy storage systems [1] because of their high energy density, good operating temperature range and long lifetime. Like all battery chemistries, Li-Ion cells degrade in performance over time. Due to their large initial cost, it is important to understand this process, both to accurately estimate performance reduction, and to control their usage for optimal lifetime. This project approaches this complex, multi-dimensional problem by investigating the physical degradation mechanisms within Li-ion cells and their sensitivity to usage conditions. This poster explains the conclusions of this review, and the implications this has on the usage of Li-ion cells.

3. Ageing in Li-Ion Cells

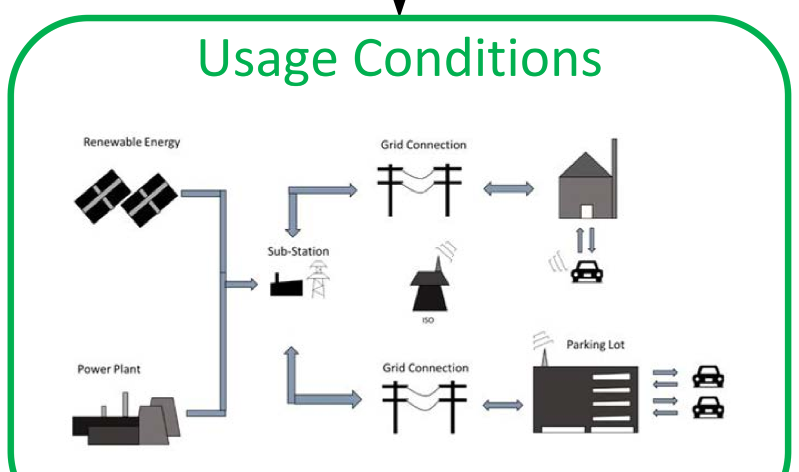
- Two main ageing symptoms of battery cells: Capacity decrease and impedance increase.
- Combined, these reduce both energy and power capability of the cell.
- Both factors are intertwined in a reciprocal relationship.

Ageing during early cell life is dominated by the formation of a Solid Electrolyte Interphase (SEI) layer on the graphite anode. Li-ion cells work at a potential in which the electrolyte and anode are unstable, causing reactions at their interphase. The products of these reactions settle on the electrode surface, forming a layer between the electrode and electrolyte. As these products include lithium, capacity is reduced with SEI layer formation and growth [2]. An initial capacity loss with cycling is seen as the layer forms [3]. Because the layer is never completely hermetic, there is a slow continual capacity loss throughout cell lifetime [4].

Steep capacity degradation towards end of life is caused by lithium plating. When the rate of lithium transport through the electrolyte during charge exceeds the maximum acceptance rate of the anode, lithium deposits on the anode surface. This has a compound effect, reducing capacity through lithium loss, and increasing anode impedance. As electrode impedance rises, acceptance rate decreases, making this mechanism self-accelerating [4].

There are several other Li-ion cell ageing mechanisms. While these have small direct influence on capacity loss, they accelerate SEI layer formation, indirectly reducing cell lifetime.

Figure 1: A modern EV, a home energy storage system, and a large scale energy storage system



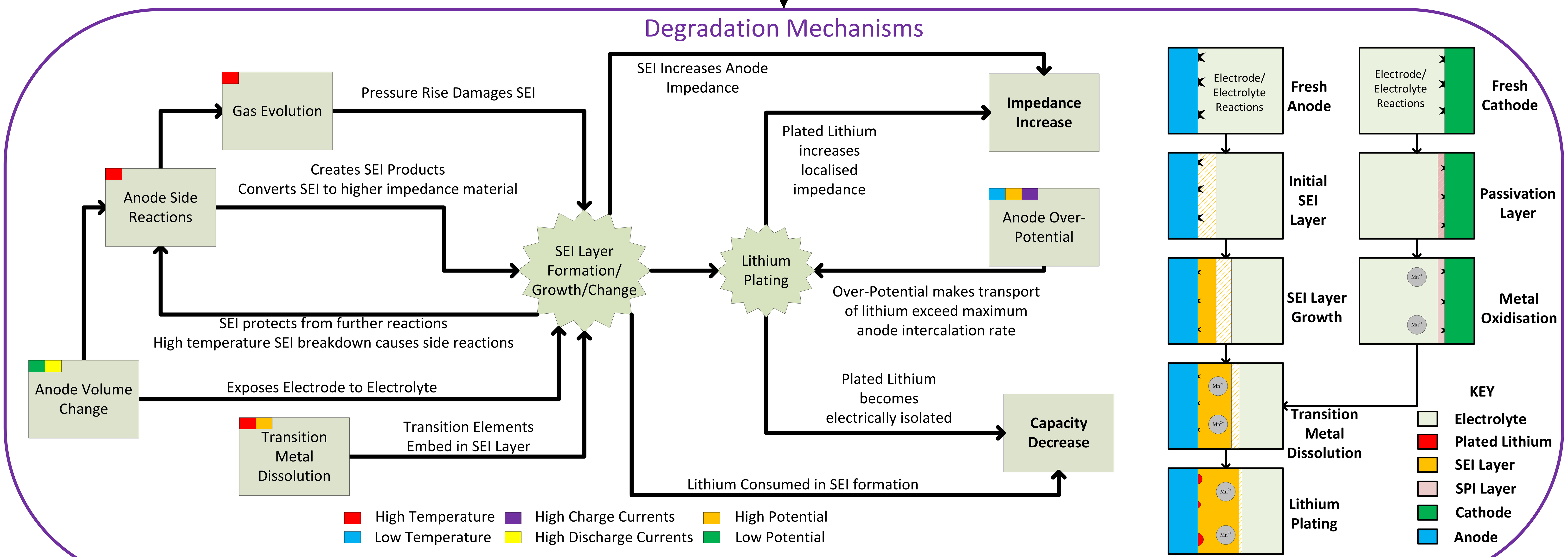
Vehicle/Grid Interfacing [12]

Cell size variation

Module construction

4. Influence of Usage Conditions on Cell Lifetime

- SEI layer formation, and therefore cell degradation, is inevitable as a function of Ah throughput.
- The rate of formation is influenced by several factors, such as temperature and SoC.
- Lithium plating is avoidable under the right conditions.
- Cell usage should be controlled to minimise SEI layer formation while preventing lithium plating.
- The most influential factor is temperature.
- High temperatures increase SEI layer formation rate.
- Cells age during storage due to SEI layer formation, particular at high temperature and SoC [5].
- Low temperature increases risk of lithium plating [6].
- The ideal temperature to balance these factors is 15-25 ºC, with ageing rate increasing either side of this [7] [8].
- Thermal gradients across the cell reduce lifetime in a similar way to high temperature conditions [9].
- Lithium plating only occurs during charge, and is sensitive to charge current.
- Lithium plating is likely to occur in high current, low temperature and high SoC charging due to the resultant over-potential of the anode [10] [11].
- This makes cells much more sensitive to temperature during charge than discharge.
- The main risk during discharge is low SoC cycling, as anode volume change during the bottom 20% of the capacity range damages the SEI layer.
- Pulse charging does not show to have a negative effect on lifetime, meaning intermittent power delivery such as wind and solar should not cause accelerated ageing.

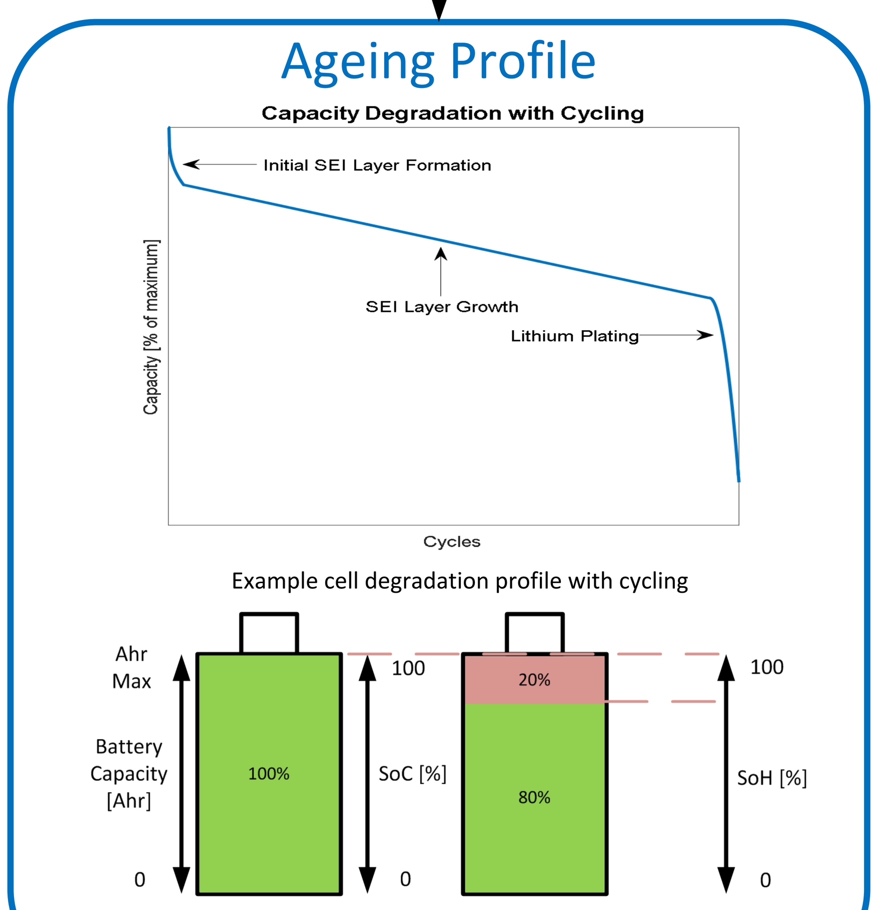


Degradation mechanism impacts, and the usage factors that affect them

Evolution of degradation mechanisms on each electrode

5. Implications on Energy Storage Applications

- As ageing is unavoidable, a cost function must be included to account for the cost of ageing in designs.
- Ageing should be considered in the system design.
- Excess capacity could be incorporated to reduce average current and SoC swings, avoiding extremes of the Voltage curve.
- Long periods of charge should be avoided to reduce over-potential, particularly at high SoC
- Temperature control should be considered at system design level.
- Temperature is more important during charge, so temperature profiles during expected cycling times should be considered.
- Temperature control should be costed for, particularly in very warm or cold climates. Location of home storage should consider this i.e locate indoors rather than in a garage or outside.
- Size packs so that not more than 80% of maximum capacity is used during cycling, ideally 70% if cost allows.



Example cell degradation profile with cycling

Illustration of capacity fading

6. Future Work

- Use knowledge to build an ageing model
- Use model to test for ageing sensitivity to different usage conditions.
- Explore how a cell ages when subjected to typical vehicle-to-grid, home and large scale energy storage profiles.
- Incorporate model into process to design for optimal lifetime
- Investigate future changes in cell chemistry and their effect on ageing mechanisms.

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