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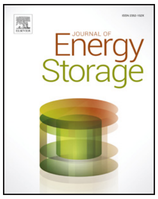

Deterministic models of Li-ion battery aging: It is a matter of scale

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ABSTRACT

Due to the increasing interest on the Li-ion battery aging studies among researchers, there are numerous battery degradation models presented in literature. However, they are either focused on a single technology, form factor or scale. This can be challenging for researchers that typically have to bridge multiple technologies and are interested in crossing multiple scales, from material-level, to cell and module/pack level. This paper explores the models presented for Li-ion battery degradation in different scales from the material level to the application level. In each scale, the main aging variables are summarized, the mathematical presentation of models are analyzed and the merits and disadvantages of each scale is discussed. This review aims at bringing together methods and results for multiple technologies, form factors for the most common Li-ion battery technologies.

1. Introduction

As batteries are found in increasingly more devices, from portable to transportation and grid, battery aging remains as a challenging factor for manufacturers and users. Batteries, and in particular Li-ion, show high energy density, but limited lifetime [1]. Up to this point, batteries have mainly been used for single tasks, but this scenario is moving towards multiple tasks [2–4]. An example is an electric vehicle driving, recharging and providing grid services. As each task has a different priority, aging cost and economical cost or benefit, all these factors need to be considered when scheduling the tasks during the life of the battery.

It can become even more relevant when batteries are repurposed for second life. For example, in transportation, due to the high power and energy demands, the battery end of life is reached when the capacity degrades to an 80% of the original capacity. Therefore, there is still available capacity that can be repurposed as a second life in less demanding applications [5]. In this second life, the battery starts from a degraded point due to its first life and will increase in degradation. Therefore, modeling and identifying the causes of degradation is highly relevant. However, approaches are spread out at different scales due to the dichotomy of aging taking place at the material level, but decision making and control taking place at the system level [6].

Other challenges add to this scenario, namely considering different Li-based technologies, form factors and cycling characteristics that affect the aging observed. Other available review papers [7–9] focus either on a single application, single technology or on a single scale. However, most researchers have to bridge scales and technologies and consider multiple aging phenomena. The objective of this paper is to analyze the current approaches to the battery aging modeling in each scale, and its application across Li-ion technologies. This review will help the researchers to identify the main aging factors and variables in each scale, mathematical aging models and their strength and weaknesses to be able to simulate the models for their own purpose. Fig. 1 provides the graphical illustration of this paper's perspective. This paper is outlined as follows: Section 2 explains the aging in the material and electrode level and presents the related models in this scale, Section 3 scales up the aging models to the cell level, Section 4 explores how to use the aging models in module and pack level.

2. Material and electrode level models

Before discussing the aging phenomenon inside the battery cell, a brief overview on the Li-ion battery cell performance will be helpful. A Li-ion battery cell presents negative electrode, positive electrode, a separator in between electrodes and electrolyte permeating throughout the battery (Fig. 2). During discharge, Li ions de-intercalate from the negative electrode, passing through the electrolyte, and intercalate in the positive electrode. At the same time, electrons travel in the same direction through the external circuit. The opposite reactions take place during the charging process.

Material scale models are based on the phenomenological approach developed by Doyle [10] to mathematically describe the movement of ions in the battery. This model was based on Newman's porous

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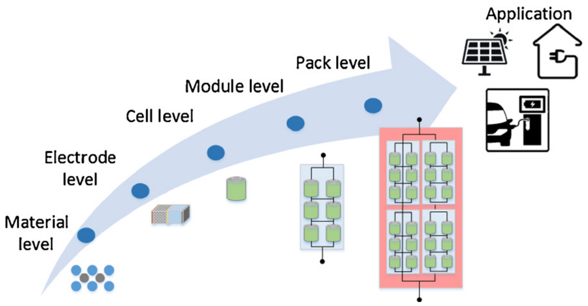

Fig. 1. Trend of the aging models analyses in the paper.

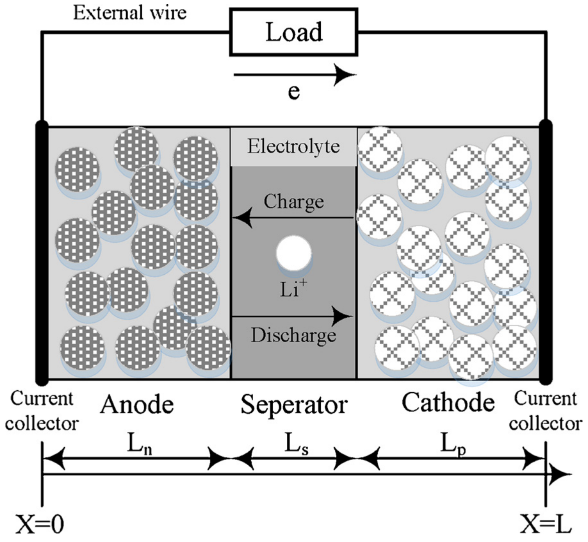

Fig. 2. Li-ion cell schematic.

electrode theory [11]. However it did not include a thermal model, which was added to the porous electrode model [12].

Inside a Li-ion battery cell, aging starts in the electrodes/ electrolyte interface. The degradation in the positive and negative electrodes follows different mechanisms [13]. The negative electrode is commonly carbon-based and is made of graphite, titanate or silicon [14]. The major source of aging in the negative electrode is the formation of a resistive layer between the electrode and electrolyte surface due to the side reactions named solid electrolyte interface (SEI) [15]. The SEI is normally formed during the initial battery cycling and protects the electrode from corrosion and the electrolyte from reduction [16,17]. However, in the long term, SEI's thickness and shape continues to grow and penetrates the porous structure of the negative electrode. It leads to (i) loss of effective surface of the electrode (ii) increased resistance against Li ions penetration and (iii) loss of cycleable lithium [18–20]. Note that the electrolyte materials define the SEI shape and properties [21]. Studies show that the high temperatures enhance the aging associated with SEI formation [22–24] and low temperatures lead to Li plating due to the lower rate of lithium diffusion which reduces the cycleable lithium [25]. Another aging factor in the negative electrode can be the mechanical or electrical contact loss between the anode active materials and connecting parts due to the cycling [26]. Most of the aging models in the material and electrode level focus on the aging in the negative electrode/electrolyte interface as they believe that side reactions, and as a result SEI formation, are more likely in the negative electrode due to its potential [27,28].

Aging in the positive electrode happens slightly differently than in the negative electrode. The SEI formation in the positive electrode is dependent on the material used in the electrode but it cannot be detected easily [29]. Experiments show that the impedance rise due to the cycling in the negative electrode is higher than the positive electrode [30]. This indicates that the main SEI formation takes place on the negative electrode surface. Although the first stage of aging in the Li-ion cell is the SEI formation and cycleable Li loss in the negative electrode, the second stage in the battery cell aging is the loss of active materials in the positive electrode. This causes the cathode to be more intercalated at the end of each discharge [24]. The cathode active material loss can be the result of structural disordering, phase transitions and metal dissolution [31]. The positive electrode aging is not limited to the active materials loss; it also can be caused by the inactive components degradation as binder decomposition, corrosion of the current collector and oxidation of the conductive agents [32]. Literature in the positive electrode aging mainly focus on the experimentally oriented studies and do not present mathematical modeling of the aging in the cathode. Fig. 3 summarizes the aging causes in the positive and negative electrodes.

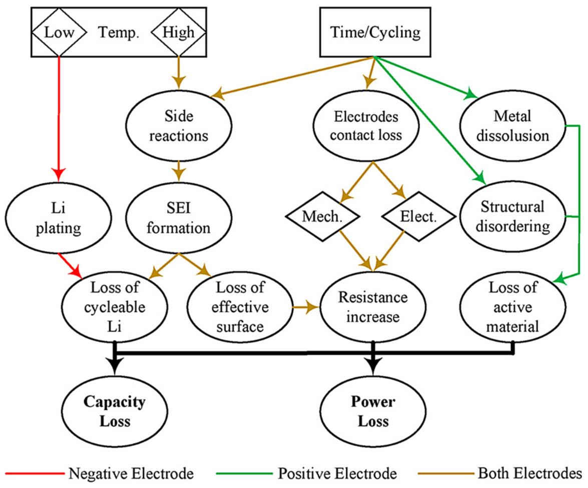

Fig. 3. Main aging factors in the negative and positive electrodes.

2.1. Pseudo-2D models

These models are based on the porous electrode models by Doyle and expand them by including diffusion in the electrolytes and electrode as well as Butler-Volmer kinetics. These non-linear set of partial differential equations are one of the most used physics-based models. Equations include the conservation of charge in the electrode or solid phase (1) and electrolyte (2) as well as the conservation of species (Li) in the solid (3) and electrolyte (4). The dynamic performance is represented by the Butler-Volmer kinetics (5).

Conservation of charge in the solid phase:

$$\begin{aligned} &\frac{\partial}{\partial x}\left(\sigma^{eff}\frac{\partial}{\partial x}\phi_s\right) = j^{Li} \\ &\text{BC: } -\sigma_-^{eff}\frac{\partial}{\partial x}\phi_s|_{x=0} = \sigma_+^{eff}\frac{\partial}{\partial x}\phi_s|_{x=L} = \frac{I}{A} \end{aligned} \tag{1}$$

Conservation of charge in the electrolyte:

$$\begin{aligned} &\frac{\partial}{\partial x}\left(\kappa^{eff}\frac{\partial}{\partial x}\phi_e\right) + \frac{\partial}{\partial x}\left(\kappa_D^{eff}\frac{\partial}{\partial x}\ln c_e\right) = -j^{Li} \\ &\text{BCs:} \frac{\partial}{\partial x}\phi_s|_{x=L_-} = \frac{\partial}{\partial x}\phi_s|_{x=L_+ + L_{sep}} = 0 \\ &\frac{\partial}{\partial x}\phi_e|_{x=0} = \frac{\partial}{\partial x}\phi_e|_{x=L} = 0 \end{aligned} \tag{2}$$

Conservation of species in the solid phase: