

Abstract

Lithium-ion batteries play a crucial role in the decarbonization of various sectors, especially transportation and housing, that traditionally rely on fossil fuels. The exponential growth of the lithium-ion batteries market has led the battery industry to face sustainability challenges, from mining to recycling. Indeed, lithium-ion batteries performance gradually decreases over time as they are used. When the capacity drops below 80%, lithium-ion batteries are considered no longer suitable for electric vehicle applications. However, after the first life, lithium-ion batteries can still be used in other applications, referred to as "second life", thereby reducing waste and the energy consumption associated with manufacturing new batteries.

In this context, accurately estimating the internal states of lithium-ion batteries during their operation is essential to ensure safety and maintain optimal performance throughout their first life. Furthermore, precise state estimation is equally critical to ensure that lithium-ion batteries can operate safely, efficiently, and reliably in second-life applications after their initial use.

Mechanics plays a significant role in lithium-ion batteries. The interaction between lithium ions and the microstructure of electrodes causes the deformation of the battery during operation. As a result, the battery swells during charge and shrinks during discharge. Furthermore, the intercalation of lithium ions within the microstructure of electrodes causes stress and crack propagation, which is one of the main causes of the degradation of battery performance throughout its life, i.e. capacity decay and impedance rise. Despite mechanical degradation, mechanics is useful in lithium-ion batteries because mechanical measurements can be used for the estimation of the degradation mechanisms and to improve battery aging prognostics.

The main objectives of this work are: (a) To experimentally measure the battery response to different user-defined current rates, and investigate the variation in the battery response with aging. (b) To understand the correlation between the electrochemical and mechanical phenomena occurring within the battery, and exploiting this correlation, to demonstrate how the battery deformation response provides the same information as the voltage response. (c) To study fracture propagation into electrode microstructure, and provide electrode design guidelines limiting fracture. (d) To develop a diagnostics procedure based on mechanical deformation measurements, which allows the quantification of the degradation mechanisms (loss of lithium inventory and loss of active material) regardless of the current rates. (e) To develop a physics-based model for battery aging prognostics, overcoming the limits of the models existing in the literature, and including the modeling of the evolution of the mechanical behavior of the battery throughout aging.

Batteries with different chemistries (LCO-graphite, LFP-graphite, and NMC111-graphite) and formats (prismatic and pouch) are tested. In particular, the mechanical response in terms of thickness change, voltage, and surface temperature responses are recorded during the characterization test, performed at different current rates, both during charge and discharge. Aging tests are carried out on LCO-graphite battery samples, steadily charging and discharging the battery with a fixed C-rate, and performing periodic reference performance tests to evaluate the variation in capacity, internal resistance, mechanical (reversible deformation during a single charge/discharge cycle, and irreversible deformation), thermal and electrical response throughout aging. Interestingly, a perfectly linear relation between the capacity loss of the battery and the irreversible deformation of the battery is observed.

The developed diagnostics procedure is based on tracking how the peaks positions in the differential expansion curve (second derivative of battery deformation with respect to capacity) change during aging. This procedure is applied to the aging test performed on the LCO-graphite battery, demonstrating that the diagnostics results obtained with deformation measurements at high current rates are consistent with those obtained with traditional voltage-based measurements, carried out at low currents.

From a modeling point of view, a physics-based model called POLIDEMO is developed to predict the evolution of battery performance during aging. POLIDEMO is a multi-physics and multi-scale model that includes the modeling of the electrochemical and mechanical phenomena occurring within the battery during operation, as well as the main degradation mechanisms, such as crack propagation due to mechanical fatigue, growth of the solid electrolyte interface and irreversible swelling. Mechanics in POLIDEMO is modeled

following a multi-scale approach. The input of the mechanical sub-model is the lithium flux on the electrode microstructure, computed through the macroscopic electrochemical battery sub-model. From the lithium flux, the lithium concentration gradient within the electrode is computed, resulting in stress distribution and, thus, fracture propagation. Stress intensity factor is computed for two purposes: (a) giving design guidelines to limit fracture of electrode microstructure, and (b) modeling the battery degradation based on the interplay between mechanical damage and side reactions. At the macro-scale, the battery deformation is computed based on the deformation of electrode microstructure due to lithium intercalation. Irreversible swelling resulting from the electrochemical side reactions is also computed. POLIDEMO is validated against the experimental measurements performed on LCO-graphite battery, and using the degradation indicators identified through the differential mechanical measurements.

In the near future, the developed diagnostics methodology will be applied to other aging data sets performed on batteries with different chemistries and formats. Furthermore, a general law combining the degradation indicators will be defined for the estimation of the state of health of the battery, which is still missing in the literature. Furthermore, POLIDEMO will be released in open access, aiming to provide a tool for academic and industrial communities that can enhance the understanding of aging mechanisms and facilitate the development of improved strategies for battery management and optimization.