Calendar, cycling, and fast charging aging in Li-ion batteries

Insights into battery degradation through electrochemical-thermal modelling

Lithium-ion batteries are the most widely adopted technology for energy storage applications due to their high energy density and operational efficiency. However, over time, they are subject to various degradation mechanisms that negatively impact their performance and compromise their safety. This work focuses on analysing these degradation mechanisms with the objective of improving the understanding of the processes responsible for performance decline during battery operation. A combined approach, based on both experimental investigations and numerical modeling, was adopted to achieve a more comprehensive description of the phenomena. The modeling activity is based on the extension of the well-known Doyle-Fuller-Newman model (P2D model), leading to the development of a more detailed three-dimensional model, referred to as the P4D model, capable of reproducing the complex geometry of cylindrical jellyroll structures.

Experimental activities were conducted on 21700 LG cylindrical lithium-ion cells under different operating conditions. Two main types of aging studies were performed: cycling aging tests, which involved repeated charging and discharging cycles at defined temperatures, C-rates, and state-of-charge windows, and calendar aging tests, where the cells were stored under controlled temperature and at defined state-of-charge conditions for extended periods. The data collected during these tests were used for the calibration and validation of the developed model. Electrochemical characterization techniques, such as electrochemical impedance spectroscopy and differential capacity analysis, were employed to monitor the evolution of internal resistance, capacity fade, and other key parameters indicative of degradation mechanisms.

The P2D model was extended by replacing the one-dimensional geometry that represent the electrodes and separator thicknesses with a three-dimensional representation that captures the jellyroll structure of cylindrical cells. This approach allows for a more accurate simulation of the distribution of lithium ions, electrical potential, and reaction rates across the electrode surfaces, taking into account the inhomogeneity effects introduced by the cylindrical geometry. Specific degradation mechanisms such as loss of active material, growth of the solid electrolyte interphase, and lithium plating, were mathematically formulated and incorporated into the model equations to simulate their effects over time under different operating conditions.

Finally, the model was further refined by coupling the electrochemical equations with electromagnetic formulations. In particular, Maxwell-Ampère's law was introduced into the model to capture the inductive phenomena observed in commercial cylindrical cells.

The P4D model was validated against experimental data collected during aging and impedance spectroscopy tests. Simulation results demonstrated the ability of the model to replicate observed capacity fade, resistance increase, and impedance behaviour across different frequencies and operating conditions. The high-frequency impedance spectra obtained from simulations matched

experimental data, providing a more complete description of the dynamic response of lithium-ion batteries during impedance spectroscopy.

Analysis of the simulation outputs enabled the identification of dominant degradation mechanisms under specific aging protocols and provided quantification of their contribution to overall performance loss.