Renewable energy technologies for environmental, social, and economic sustainability offer enormous potential for meeting future demands for clean energy and efficient utilization. The performance of current electrical energy storage systems falls short of market requirements for deep penetration in transportation, industrial, and residential sectors of economy. The major challenge in realizing this potential is to break through existing technology barriers and stimulate innovative ideas for new advanced energy storage systems. Lithium ion batteries (LIBs) are considered the systems of choice for many mobile and stationary applications, because of their high energy and high power performance characteristics. LIBs enabled the revolution of portable electronic devices and reinvigorated a quest for batteries to power hybrid-electric and electric vehicles. However, existing battery technologies still face cost and performance challenges, including barriers in specific energy, energy density, service life, and charge efficiency at high rates.

The performance of batteries is limited by the fundamental behavior of the materials used in the cell, including electrode active materials, additives, and other supporting components. Although often perceived as a simple electrochemical device, batteries are inherently complex and dynamic systems. Their successful operation relies heavily on a series of interrelated mechanisms, some involving instability of the components induced by charge-discharge cycles and formation/reaction of metastable phases. The ability to achieve long-term stability requires careful elucidation of the underlying physical and chemical processes. Thus, it is essential to develop and use advanced, especially in situ and non-invasive, characterization tools and methodologies to study these processes in a wide variety of temporal and spatial resolutions.

Existing state-of-the-art characterization techniques have reached a high level of maturity. Rapid progress in spectroscopic, microscopic, and scattering methods has already led to new and fascinating insights into the nature of chemical and interfacial processes in energy storage devices. In situ, non-invasive characterization techniques are considered a great challenge, yet a vital approach, to achieve better understanding of the mechanisms of the underlying processes relevant to energy storage in the operating environments and conditions. In this special issue, we present a few articles that describe some recent notable accomplishments made in this area.

The application of in situ X-ray spectroscopy and imaging is discussed by Shearing et al. Particularly the X-ray absorption spectroscopy (XAS) and X-ray tomography are considered as powerful techniques to study electrode materials used in batteries. The advantages of element-specific, short timeframe for data collection, small sample size, short range order probing, and penetrative nature of X-rays through crystal structure make such techniques attractive for in situ characterization of electrode materials in an electrochemical cell. In the case of transition metal oxide cathode materials, the near edge structure information can tell the valence changes of the metal redox centers so one can identify their role in the energy band and crystal structural correlation, which is useful for material engineering. Computed tomography (CT) and focused ion beam (FIB) are discussed in the context of high spatial, and in some cases with temporal, resolution applications to study electrode components used in battery cells and their microstructural changes upon degradation.

The in situ analytical electron microscopic techniques described by Meng et al. are capable of probing nanoscale electrochemical phenomena in a model all-solid-state SnO2 | Li0.17V0.69S0.10O4 | LiCoO2 micro-battery. Analytical transmission electron microscopy (TEM) that combines imaging, diffraction, and spectroscopy/spectrometry is a powerful tool to observe in situ structural changes at the electrode/electrolyte interface during cell operation. The special procedures used for fabricating the micro-battery and in situ observation of Li and transition metal distribution in the battery are presented and discussed. The authors show the progression of reactions in the cell with information derived from high spatial resolution imaging and chemical analysis.

In situ scanning probe microscopy for studies of electrode/electrolyte interface with high spatial resolution, is presented by Inaba et al. Highly oriented pyrolytic graphite (HOPG) is used as a model electrode for the illustration. The decomposition of electrolyte to form the solid electrolyte interphase (SEI) on HOPG is discussed and images are used to show how the morphology of the SEI layer formation is correlated with underpinning electrochemical process. Graphite composite, thin film Sn, and spinel electrodes are further used in the illustration to show surface/interfacial morphological changes and their impacts on electrode performance.

Dupré et al. provide a review of NMR techniques for studying electrode/electrolyte interfacial behavior and failure mechanism with aging in LIBs. Particularly interesting is the understanding of the mechanism of surface layer formation on positive electrode materials and its effect on electrode performance. The authors explain how 6Li NMR signals can be integrated and associated with intercalated Li⁺ versus Li-containing species in the SEI layer to study the nature of the SEI layer formation on the positive electrode in different environments. Similarly, the 19F and 31P NMR signals are utilized to distinguish chemical origins of the electrolyte decomposition products in the SEI layer. The integrated NMR peak intensity can also provide quantitative temporal resolution on the degradation processes on the electrode surface. In combination with other complementary techniques such as X-ray photoelectron spectroscopy (XPS) and optical spectroscopy useful information on the interfacial property changes can be gathered and analyzed to provide a comprehensive understanding of the electrode surface degradation process.

The utility of 7Li NMR in the in situ study of electrode materials used in LIBs is further illustrated by Trease et al. The authors explain how the quadrupolar interaction of the

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7Li resonances can yield information on the local structure around a given nucleus in an electrochemical reaction and give three examples on anode materials' \textit{in situ} studies. 7Li NMR is used to probe the Li intercalation in the graphitic layers and the staging phenomena. Dendrite formation on metallic Li and Li interaction with Si are also illustrated and discussed.

In summary, we are delighted to present these inspiring studies to illustrate the state-of-the-art of some notable \textit{in situ} characterizations for LIB research. With such ability to probe and monitor the dynamic composition and structural changes associated with charge and mass transport, the detailed mechanism of the system operation and functionality of its components can now be better understood. These new exciting characterization capabilities will impact many scientific areas in electrical energy storage R&D and other related fields related to interfacial science.

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