

Bridging multi-scale characterization technologies and digital modelling to evaluate lithium battery lifetime

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Abstract

The safety, durability and power density of lithium-ion batteries (LIBs) are currently inadequate to satisfy the continuous growth in demand due to the proliferation of renewable energy sources and the emerging markets of grid-scale battery applications. Rapid progress has been made from material engineering to system design combining

experimental and simulation modeling to enhance LIB performance. Limited by the spatial and temporal resolution, state-of-the-art advanced characterization techniques fail to fully reveal the coupled degradation mechanisms in LIBs at different scales (from coin cells to packs). Computational approaches can digitize the multi-scale electrochemical/mechanical/thermal process in LIBs contributing to their fundamental investigation. Strengthening the interaction and iteration between characterization and modelling improves understanding of reaction mechanisms, and in turn that design and management of LIBs. In this perspective, the typical examples of bridging the multi-scale characterization techniques and modelling are discussed, and future prospectives evaluated. The critical parameters extracted from multi-scale characterization can serve as digital input for modelling. Furthermore, advanced computational techniques including cloud computing, big data, machine learning can also aid progress in developing understanding and control of the whole battery life cycle, which enables the development of digital twin models corresponding to physical objects. It is anticipated that this work will provide a roadmap for further research that can enable the next-generation of high-energy-density LIBs.

1. Introduction

With increasing environmental issues, achieving carbon-neutral society has become a global consensus. Ambitious targets to cut carbon emissions, encourage clean energy techniques and realize carbon-neutral growth have been put forward by countries all over the world, e.g. China aims to cut CO₂ emissions net-zero by 2060^{1, 2}. A promising means to reduce the dependence of our societies on fossil fuels is the development of advanced energy materials^{3, 4}. Lithium-ion batteries (LIBs) show great potential as high performance energy storage devices for consumer electronics, electrified transportation and grid-level energy storage systems because of their inherent advantages, such as high energy density, high working voltage, low self-discharge rate, and long cycle stability, over other traditional battery systems (e.g. lead acid battery, nickel-metal hydride battery)⁵⁻⁷. Despite impressive progress in LIB technologies since the first invention of commercial LIBs in 1992⁸, further expansion and large-scale application of LIBs are currently hindered by limited fast charging ability, relatively low energy density, safety concerns under thermal/mechanical/electrical abuse conditions, capacity decay and cycle stability⁸⁻¹¹.

Achieving higher energy density has been a priority in recent LIB research to realize longer driving mileage for EV application and longer usage time for portable electronic devices, where high capacity cathode and anode materials have been developed. High voltage cathode material (e.g. high voltage LiCoO₂, Ni-rich and Li-rich layered oxide) elevate the working voltage and offer higher specific capacity to deliver high energy density^{12, 13}. However, several challenges have to be solved before the realization and large-scale commercialization of high-voltage cathode materials including the

instability of organic electrolyte (electrolyte decomposition and interface formation)¹⁴, structural rearrangement and distortion (irreversible crystal structure change at deeply delithiated states)¹⁵, transition metal dissolution and shuttling effects^{16, 17}, stress accumulation and crack formation^{18, 19}, which lead to low coulombic efficiency and fast capacity decay. While for the high capacity anode materials such as silicon and lithium metal, the cycle stability is the biggest challenge, as the electrolyte tends to reduce on the anode surface to form a solid electrolyte interface (SEI) owing to the limited electrochemical window and high reducing activity^{20, 21}. Meanwhile, a large volume change during cycling not only triggers crack formation/propagation and eventually pulverization of anode particles, but also reveals fresh reductive surface for SEI formation, all leading to severe capacity degradation²²⁻²⁴.

Revealing the reaction and degradation mechanisms in LIBs can provide in-depth understanding of electrochemistry/thermal/mechanical process and inspire new strategies to improve LIB performance. Multi-scale characterization and battery monitoring techniques have been developed to investigate the complex reaction process in LIBs, including electronic /crystal structural properties, morphologic characterizations, interfacial-sensitive componential analysis, etc. Unfortunately, some of the reaction mechanisms in LIBs still remains uncertain because of the limited time-spatial-elemental resolution of current characterization approaches. With the development of computational techniques, multi-scale simulation theory and methods have been developed to understand underpinning mechanisms beyond experimental characterization. For example, first-principle computations have been widely used to investigate the atomic structure and electronic structure, equilibrium voltage, ion mobility and diffusion mechanism, etc. The practical reaction process and material properties of LIBs can be abstracted as parameter and simulated in equations, which is independent of limitation of experimental characterizations. Meanwhile, battery management, which ensures the optimized operation of LIBs with high safety, also calls for precise modelling. Strengthening the interaction and iteration between characterization and modellings will undoubtedly provide deeper understanding of reaction mechanism, design and management for LIBs.

In this work, we try to bridge multi-scale experimental characterization and computational simulation for better understanding, design and management of LIBs. New frameworks including “Physical Space”, “Cloud Space” and “Digital Space” will be created to evaluate the overall lifespan of lithium batteries, which cover the multi-scale design and manufacturing process regarding material synthesis, characterization, electrochemical performance, and safety. The key parameters affecting the multi-scale LIB performance and the degradation mechanism will be summarized. All the experimental characterizations and raw data produced during the practical operation of LIBs will be collected, which is defined as the “Physical Space”. The experimental

investigation can be digitized or parameterized and then used as input for multi-scale modelling. “Cloud Space” is created to store and deal with tremendous data collected from characterizations or monitoring in-real time operation of LIBs, as well as carrying out the calculation results. With the rapid development of advanced computational technology especially the data-driven techniques such as Cloud, machine learning, etc., “Digital Space” is created where the continuous iteration between physical space and cloud space happens based on data-driven artificial intelligence. The comprehensive understanding of the cross-scale degradation phenomenon, and the data-driven intelligent full-life battery management will benefit the future development of battery technologies in a diversity of applications.

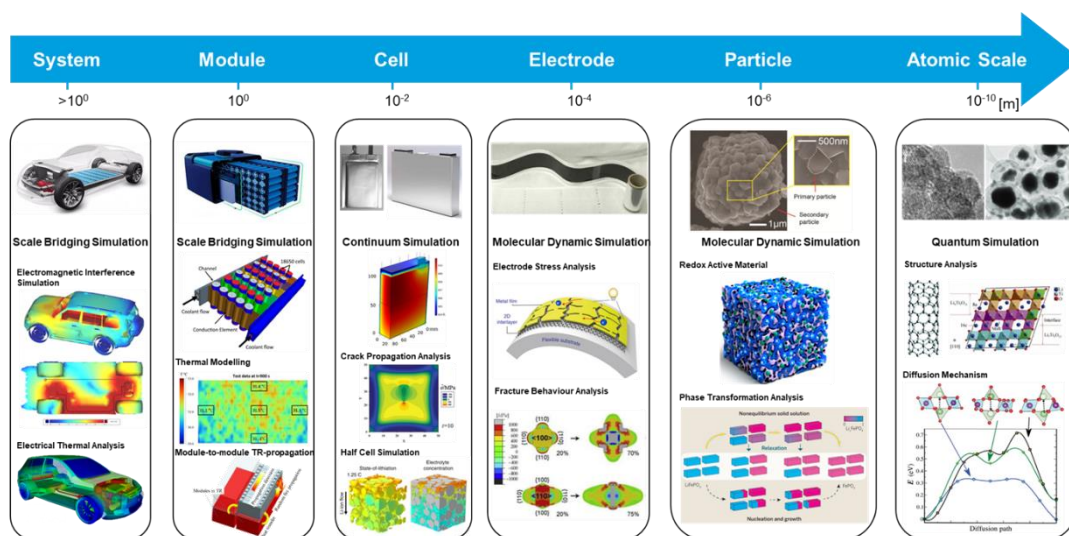


Figure 1. Multi-scale processing and simulation from system design to material properties.

2. Multi-scale battery design: from system control to material property

Promoting LIB performance, including high energy/power density, and cycle stability under thermal and mechanical abuse conditions¹⁰, relies on the in-depth understanding of the lithium batteries and rational multi-scale design from intrinsic material properties to application (e.g. EV, mobile electric devices). In this section, key parameters that affect LIB performance, as well as critical challenges retarding the improvement at different scales, will be summarized.

System control. The stable energy/power output, reliability and controllability of the lithium-ion battery system under different abuse operating conditions still remains challenging despite great improvement during past decades. The practical application of lithium batteries in various electrical power system not only rely on the battery performance but also the battery monitoring and control. Thousands of lithium batteries (cells) can make up the array of a battery module. The battery management system (BMS) ensures the stable and reliable operation of the whole module. It is challenging but imperative to monitor the single cell state to prevent safety issues such as thermal

runaway and predict the longevity of the whole system based on the single cell performance. Sensors have been employed to monitor the operation statuses of batteries and provide data for BMS control. While current BMS systems rely on vehicle-mounted smart computers, it is challenging to deal with the massive data produced during battery operation. With the rapid development of computational technology as well as information and communication technology, it is now promising to introduce cloud server and cloud BMS for the precise control of battery systems.

Electrode. Ideal electrodes provide sufficient ionic and electronic conducting paths to ensure fast rate performance, and robust mechanical stability to resist volume change²⁵. The electrode microstructure and morphology have great influence on the rate performance, for example an aligned electrode structure with less tortuosity will contribute to fast ionic diffusion^{26, 27}, while sacrificing volumetric energy density. The chemical composition of the electrode is also important, such as highly conductive carbon to accelerate electron transfer²⁸, or highly adhesive binders to provide mechanical support^{29, 30}. To increase the mass energy density, the none-active material including current collector, binder, conductive carbon should be rationally reduced.

Particle scale. The physical/chemical properties (including morphology characteristics, specific surface, particle size, crystallinity, etc.) of the electrode particle have significant influence on reaction and charge transfer on the electrode surface, determining the cycling stability and rate performance. Surface impurities and the exposure of high valance state transition metals with high catalytic activity aggravate the interfacial decomposition of electrolyte on the cathode surface^{31, 32}. The random crystallographic orientation of the primary cathode particles lead to significant anisotropic volume change, resulting in potential crack formation and severe electrolyte decomposition^{33, 34}, which will be mitigated in a single-crystal cathode^{35, 36}. Lithium de-solvation can take place on the electrode surface before lithium ions intercalate into the electrode host, where the local solvation structure and interaction toward electrode surface can greatly influence the rate performance^{37, 38}. While on the anode surface, the electrolyte can be reduced to form solid electrolyte interface (SEI) preventing further electrolyte decomposition^{20, 39, 40}.

Atomic scale. Considerable efforts have been devoted to optimizing the electrochemical performance of the electrode material. The intrinsic crystal structure of the lithium ion host and the atomic local interaction determines the capacity of the cathode and anode materials^{13, 41}. To increase the specific energy density, the equilibrium voltage of lithium ion intercalation is expected to be increased as much as possible within the stable electrochemical window of the electrolyte^{42, 43}. The increased lithium concentration within the lithium-host materials will trigger structural evolution such as phase change leading to the evolution of equilibrium voltage. reflected in the voltage profiles^{44, 45}. The typical characteristics of the voltage profile can help to analyse structural evolution

and also serves as data for battery diagnostics. The elevated power density of lithium batteries relies on the ionic mobility within the electrode materials which is called the rate capability⁴⁶. The ionic mobility is determined by the energy barrier to insertion/extraction of the lithium ions into/from the lithium-host structure of the electrode material^{47, 48}. Better understanding of the ion migration pathway will help to enhance the power density performance. Safe and stable operation under different current and temperature conditions is greatly valued. The enhancement of cycle stability depends on the intrinsic thermal stability of electrode materials, the structural tolerance for reversible lithium de/insertion, and interfacial stability to resist electrolyte decomposition^{49, 50}. Combination of atomic experimental characterization and computational investigation with high throughput and accuracy is essential to develop high performance energy materials and discover the in-depth reaction mechanisms.

To meet the ever-increasing energy density and safety demand of lithium batteries, a comprehensive and in-depth understanding from atomic physical/chemical properties, multi-scale characterization of reaction and degradation mechanism, to macro scale system designs should be integrated with experimental and computational exploration.

3. Degradation mechanism and characterization

Failure of lithium batteries not only limit the energy storage capability and power output but also trigger hazardous problems including fire and explosions owing to thermal-runaway^{10, 51}. The battery management system (BMS) is designed to real-time monitor the battery performance, estimate battery module state, diagnose safety and fault, predict lifespan, and manage thermal conditions^{3, 52}. The timely and precise control from lithium battery pack to single cell relies on the in-depth understanding of battery degradation mechanisms. Real-time data (voltage, current, EIS, temperature, pressure, deformation, etc.) generated from an operational battery serve as input for the control/simulation/estimation equations in BMS, which help to maximize battery safety, reliability, and longevity. The complex and coupled nature of the component and multi-physic/chemical interactions require the combination of multi-scale/dimensional characterization.

3.1. Multiscale degradation

The most distinct external characters of battery degradation are power fade, capacity fade and safety concerns. To get better insights into degradation, the factors affecting battery life and relating degradation process are discussed in detail, as shown in **Fig. 2**. Herein, three main degradation mode: loss of active lithium ion, the electrode degradation and the loss of electrolyte will be discussed from the perspectives of different length-scales.

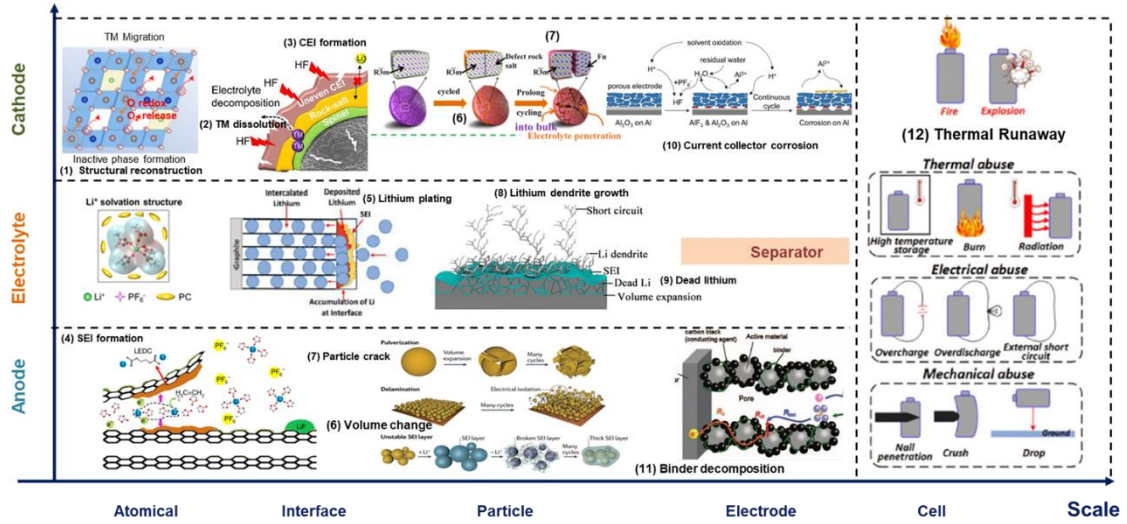


Figure 2. Multi-scale degradation mechanisms.

Loss of active lithium ion. Lithium ion batteries utilise reversible lithium ion de-/intercalation in electrode materials^{8, 37}. The active lithium ions are defined as lithium ions transferred from cathode to anode during the discharge process in a full cell, which determines the practical capacity during each cycle. The loss of active lithium ion can occur due the following processes:

(i) *Diffusion controlled lithium ions trapping within electrodes.* During the lithiation process, at particle scale, lithium ions will intercalate into the electrode leading to a one-way lithium ion diffusion gradient toward the electrode core (or towards the current collector at electrode scale). The lithiation process will stop at a pre-cutoff potential when the inward lithium ion diffusion rate becomes too slow to maintain the operating current density. While in the de-lithiation process, the diffusion of lithium ions can be two-way (being extracted at the electrolyte/electrode surface or diffuse reversely toward the electrode core or current collector). Without enough time or driving force to fully extract lithium ions from the electrode, a portion of lithium ions will be trapped within electrodes, which will accumulate gradually in the following cycles and finally lead to capacity fade⁵³.

(ii) *Formation and thickening process of decomposition layer on electrolyte interface.* Solvent and interface-forming additives in the electrolyte will react on the electrode surface when the voltage exceeds the corresponding HUMO/LUMO window^{54, 55}. Lithium ions will be consumed in the SEI/CEI to form ion-conductive and electron-insulative compounds such as LiF, LEDC, Li₂CO₃ etc., which can be aggravated by surface defects, high operating voltage and temperature⁵⁶. Unfortunately, SEI/CEI will crack and reform if they cannot withstand large volume change of the electrode during cycling, resulting in more consumption of active lithium ions^{22, 57}.

(iii) *Lithium plating on the anode surface and lithium dendrite formation.* Metallic

lithium will deposit on the anode surface if the lithium ions are unable to intercalate owing to the overcharge of full-cell, or sluggish ion intercalation dynamics under high current load or low temperature⁵⁸⁻⁶⁰. During overcharge processes (high state of charge, high SOC), the potential of the lithiated anode surface is low, and underpotential deposition of lithium ion occurs when the potential continues to drop down below 0 V (vs. Li/Li⁺)⁶¹⁻⁶³. While under high current load, lithium ions aggregate on the anode surface. The sluggish interfacial ionic intercalation speed, de-solvation procedure and limited lithium diffusion within the electrode retard lithium intercalation, leading to metallic lithium formation on the anode surface^{64, 65}. Low operating temperature will further slowdown intercalation and aggravate lithium plating⁶⁶⁻⁶⁸. Owing to the formation of metallic lithium, the electrolyte will decompose consuming extra active lithium ions. “Dead lithium” will form when the metallic lithium falls off from the anode surface⁶⁹⁻⁷¹. Even worse, the growth of metallic lithium dendrites may pierce the porous separator and reach the cathode leading to internal short circuit accompanied by thermal runaway (electrolyte fire, battery explosion)^{10, 60, 72}.

Electrode degradation. In conventional lithium batteries, the electrode is composed of active electrode material, conductive carbon, binder and current collector⁸. Similarly to the definitions of active lithium ions, the active electrode material can be defined as lithium ion hosts with available sites for lithium intercalation. The loss of active electrode material is one of the most important causes of electrode degradation. Meanwhile, as a minority component in electrodes, the electrochemical stability of binders and conductive carbon have great influence on battery performance^{29, 73, 74}. Current collectors also face corrosion issues during cycling.

(i) *Loss of active electrode particles.* During the repeated lithiation/de-lithiation process, the electrode material can undergo significant volume change, (e.g. silicon 300 %, S 180 %, Sn 160 %) ⁷⁵⁻⁷⁷. For the anode particles, the mechanical stress will damage the bulk electrode material, leading to particle cracks such as graphite exfoliation⁷⁸⁻⁸⁰, silicon/Sn pulverization^{57, 81, 82}. Besides the mechanical cracks in transition metal oxide cathodes⁸³⁻⁸⁵, transition metals (Mn, Ni, Co, Fe) will escape the cathode host and dissolve into electrolyte (known as transition metal dissolution)⁸⁶⁻⁸⁸, which often happens at elevated temperature, high states of charge (SOC) and HF etching⁸⁸⁻⁹⁰. The dissolution of the transition metal not only trigger the phase change of the cathode leading to active particle loss but also will deposit on the anode surface to introduce SEI formation or even dendrite growth^{87, 91, 92}.

(ii) *Binder fade.* Ideal binders are expected to provide robust adhesive force to maintain electrode integrity during cycling. However, the conventional Polyvinylidene Fluoride (PVDF) binder is reported to possess insufficient adhesion and will swell in organic electrolytes leading to contact loss between active material particles and conductive carbon or between particles and current collector⁹³⁻⁹⁵. Meanwhile, binders will

decompose at elevated temperature and under high voltage, all leading to severe capacity decay^{96, 97}.

(iii) *Current collector fade*. Active cathode and anode material is coated on aluminum and copper foil current collector respectively to deliver the electrons from electrode to the external circuit⁸. Trace HF contamination in the electrolyte and any over-discharge process will accelerate copper corrosion⁹⁸. Once the copper dissolves in the electrolyte, it can re-deposit on the anode surface to trigger dendrite growth and short-circuit relating issues⁹⁸. Any deposited metallic copper on the SEI can block lithium pathways and impede lithium mobility. While for the aluminum current collector on the cathode side, the dissolved Al^{3+} ions (reported to happen at high potentials) might deposit on the cathode surface to inhibit lithium ion intercalation⁹⁹. Furthermore, they might also migrate and deposit on the anode surface to trigger similar problems as copper corrosion¹⁰⁰. The continuous corrosion of current collector will lead to contact loss between active materials and current collector, resulting in resistance increase and capacity decay^{101, 102}.

Loss of electrolyte. Conventional electrolytes for LIBs contains lithium salt, organic solvent and various additives¹⁰³. The electrochemical window evaluates the stable operating voltage range of the electrolyte toward different electrode materials. The lithium salt is reported to react with trace H_2O in the electrolyte to form HF ($\text{LiF} + \text{H}_2\text{O} \rightarrow 2\text{HF} + \text{LiF} + \text{POF}_3$)¹⁰⁴. HF will further attack the electrode material and the current collector leading electrode degradation. The organic solvent will be reduced on the anode surface during the battery formation process, for example, ethylene carbonate (EC) is reported to be single-electron reduced to form lithium alkylcarbonates¹⁰⁴. While on the cathode side, the high valent state of transition metal and high operating potential will also aggravate electrolyte decomposition on the cathode surface to form a CEI¹⁰⁵. Ideal SEI/CEI will form a lithium conductive but electron insulative interface to prevent further electrolyte decomposition. However, the SEI/CEI is not always robust enough to sustain the huge volume change of the electrodes during cycling, and fresh anode or cathode surface will be exposed to the electrolyte. Continuous growth of such interface will not only consume the electrolyte and lithium ions but also give rise to interfacial resistance^{106, 107}.

Cell failure under abuse operating condition. Batteries are frequently operated in abuse conditions: (1) Electrical abuse including over-charge/over-discharge, external short-circuit, fast charge/discharge, etc.; (2) Mechanical abuse including unexpected deformation, stress, destructive penetration, etc.; (3) Thermal abuse including un-even thermal distribution, localized hotspots, wide range operating temperature, etc. Such abuse conditions will aggravate degradation processes. Taking the elevated operating temperature for example, atomic process such as transition metal dissolution, interfacial reactions such as electrolyte decomposition, non-uniform lithium diffusion and

distribution at electrode scale will be accelerated.

In summary, the degradation of lithium batteries always involves coupled electrochemical/mechanical/thermal multi-scale process, further deteriorating under various abuse operating conditions. Many efforts have been devoted to investigate specific degradation reaction, however there are still undiscovered failure mechanisms, especially under practical and dynamic operating conditions.

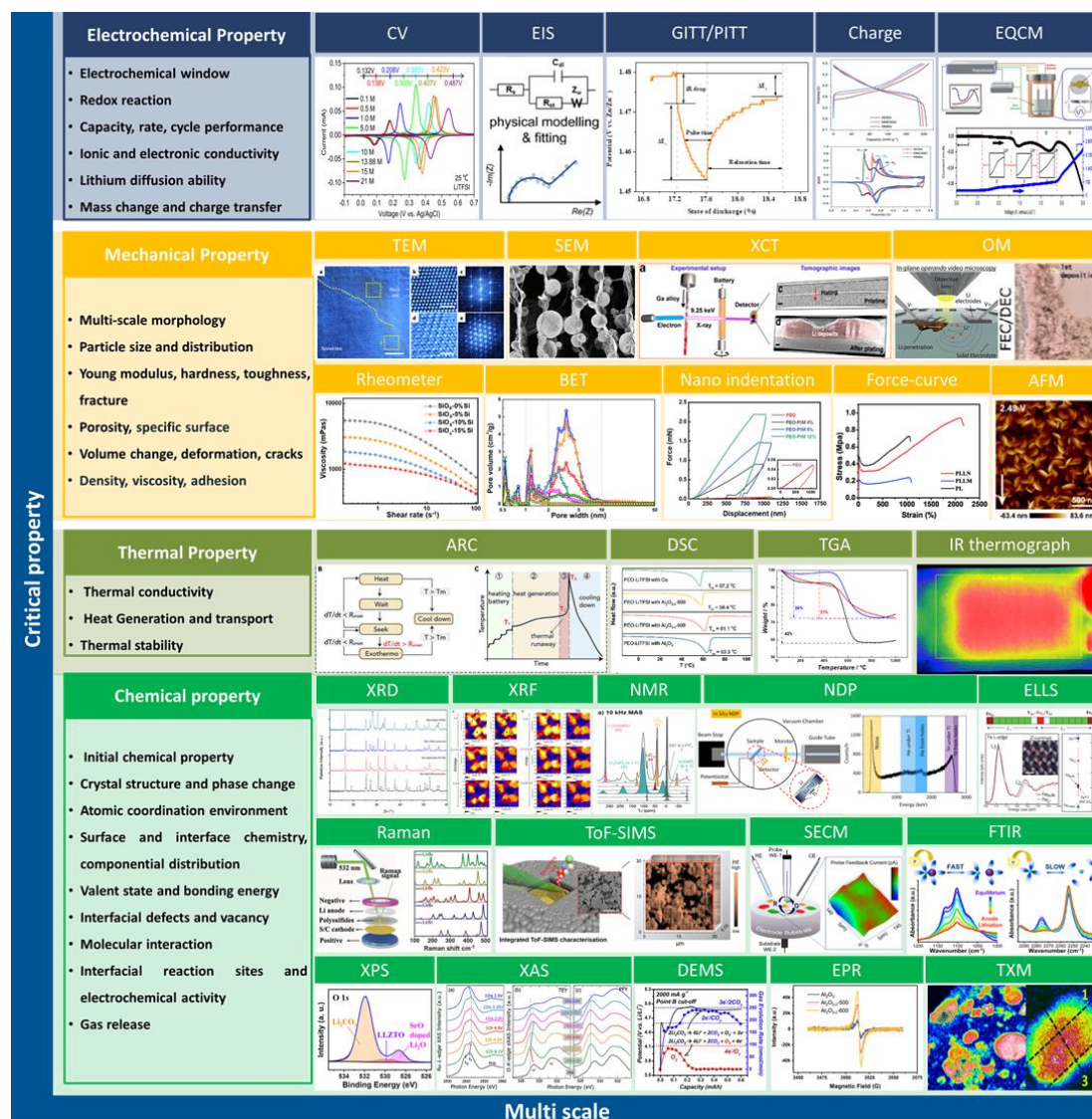


Figure 3. Critical properties evaluated by multi scale/dimension characterizations. (I think this needs a more detailed caption)

3.2. Multi-scale/dimension characterization

3.2.1 Critical properties and characterization

In-depth understanding of the reaction and degradation mechanisms is essential for

optimizing high-performance electrode materials as well as the practical application of large-scale energy-storage systems. With the fast development of advanced electrochemical analysis and material characterization techniques, the overall electrochemical performance, atomic structure and chemical compositional information can be acquired more precisely. Meanwhile, the combination of electrochemical control/analysis with material characterization techniques make it possible investigate the degradation mechanisms in real-time and *in-situ/operando*. **Figure 3** summarizes the critical properties and the corresponding multi-scale characterization options. More attention will now be paid on how they are involved in investigating the multi-scale reaction mechanism in LIBs.

Electroanalytical methods and electrochemical properties. Traditional electroanalytical methods including cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), galvanostatic intermittent titration technique (GITT), potentiostatic intermittent titration technique (PITT) and galvanostatic charge/discharge are frequently utilized to research the electrochemical process of LIBs. ***Constant current/voltage control methods.*** The basic galvanostatic charge/discharge measurement are utilized to measure the capacity and rate performance of lithium batteries. The voltage curve represents characteristic redox reaction or phase change in the lithium battery, for example, the voltage plateau reflects the phase change between FePO_4 and $\text{Li}_{1-x}\text{FePO}_4$ ^{38, 108}. Besides, the lithium diffusion behavior on the electrode interface and within the electrode can be measured based on derived constant current control methods. For example, the GITT combines the constant current discharge/charge and relaxation to calculate the lithium diffusion coefficients in equilibrium processes¹⁰⁹⁻¹¹¹, the galvanostatic pulse method can be employed to investigate the non-equilibrium interfacial lithium diffusion in LFP¹⁰⁸.

Cyclic voltammetry (CV) method. In typical CV scanning, the current density is recorded while the potential range is scanned at a certain sweep rate. Redox reactions in LIBs can be revealed by the CV peaks. Accordingly, the electrochemical stability (or also called electrochemical window) of various components in LIBs (electrolyte, electrode material, binder, etc.) can be determined. Atomic reactions such as SEI formation^{39, 112}, lithium intercalation/de-intercalation and structural/elemental change within electrode material^{38, 39, 113} can be investigated. Meanwhile, the diffusion and the capacitance behavior in the capacity performance can be identified by varying CV scan speed based on Henrick and Conway's equation^{114, 115}.

Electrochemical impedance spectroscopy (EIS). EIS has been frequently used to detect the interfacial process and reaction dynamics in lithium batteries. During EIS measurements, a small sinusoidal potential or current are applied across a range of frequencies, whilst the amplitude and phase shift of the output current or voltage are recorded, respectively, and the battery impedance spectrum is consequently obtained¹¹⁶.

All the reaction process is converted into impedance spectrum in EIS testing, which includes the internal resistance, charge transfer resistance and Warburg impedance. As the EIS brings negligible change to the battery state, it is regarded as a powerful tool to investigate the dynamic process that brings resistance increase, discussed in **Section 3.1**. Besides, the EIS can be also employed to calculate the lithium ion conductivity (e.g. ionic conductivity, transference number in solid electrolyte research)¹¹⁷ and the lithium ion diffusion coefficient¹¹⁶, etc.

Morphologic/Mechanical properties and characterization. The generalized mechanical properties include the multi-scale morphology (nano-scale morphology and particle size, particle distribution and porosity in electrodes), mechanical parameters (Young modulus, hardness, toughness), and dynamic mechanical evolution (volume change and particle deformation, crack formation and fracture in particle and electrodes).

Trans-dimensional morphology characterization. High-resolution electron microscopy techniques including Scanning Electron Microscopy (SEM), Focussed ion beam microscopy (FIB) and Transmission Electron Microscopy (TEM), enable *ex-situ* atomic/nano-scale morphologic and structural imaging. While *in-situ* observation by such high energy electron-based microscopy techniques damage the unstable component (such as SEI), cryo-FIB/SEM and cryo-TEM have recently been introduced to observe the electron-beam sensitive samples including lithium dendrites and the SEI¹¹⁸⁻¹²⁰. Due to the strict working environment of such techniques (high vacuum, no liquid, limited space, etc.), such measurements may still miss information related to the practical operation of real batteries.

While the electron-based microscopy often reveals the 2D microscopic imaging or the surface characteristics, X-ray based techniques particularly X-ray computed tomography (XCT) help to reveal the bulk structure and 3D imaging information by quantificationally and visually reconstructing the spatial distribution of the various electrode components due to the attenuation of the incident beam¹²¹⁻¹²³. Based on different modes including absorption, diffraction, fluorescence and phase-contrast, successful applications of XCT in lithium battery research involve the lithium dendrite observation^{124, 125}, electrode deformation, volume change and crack formation of electrode particle^{126, 127}, formation of reaction interface^{128, 129}, crack formation and propagation in the solid electrolyte¹³⁰, etc., which can range from nanometer-particles to pouch cells or cylindrical cells with centimeter scale. However, XCT is limited in distinguishing different carbonaceous components in lithium batteries especially binder and conductive agents, which may need contrast-enhancing agents such as carbon coated Fe nanoparticles¹³¹.

Optical microscopy offers characterization scales from micrometer to centimeter and

has been widely used in lithium battery research¹³², such as observing the volume change of the electrode during cycling¹³³, lithium dendrite growth^{134, 135}, the stress evolution and the color change after reaction (e.g. polysulfide formation in lithium battery¹³⁶). Besides conventional imaging optical microscopes, infrared thermography, fluorescence microscopy and optical fibers have been introduced in lithium battery research. Infrared thermography can measure the temperature distribution with high spatial resolution as a non-destructive and contactless tool for thermal analysis of lithium pouch cells or pack¹³⁷⁻¹³⁹. Fluorescence microscopy detects the fluorescence signal during cycling so that the molecular population heterogeneities and complex kinetics^{140, 141}. Optical fibers can be implanted into batteries to collect and transfer light information, which have been employed to investigate the temperature distribution, gas release and stress accumulation^{142, 143}.

Mechanical properties measurement. Lithium de-/intercalation will introduce extra mechanical stress within the electrode particles. The repeatedly huge volume change of the electrode particles might cause cracking, fracture and even pulverization leading to fast degradation^{69, 84, 126}. The measurement of mechanical parameters including stress and strain, Young modulus, hardness, fracture toughness are also important. Atomic force microscopy (AFM) can not only observe the nano-scale morphology evolution¹⁴⁴⁻¹⁴⁶ but also measure the nano-mechanical properties. The force-distance curve reflects the interaction force between AFM probes and sample surface which can reveal the nano-scale mechanical properties in LIBs, e.g. the Young's modulus of SEI on anode surface⁵⁹ and the modulus/contact stiffness evolution of electrode material during cycling^{147, 148}, etc.. Nano-indentation also called as depth-sensing indentation can be applied to measure the nano-scale mechanical properties, including the force-curve, elastic and plastic properties, viscoelasticity and creep properties. For example, the hardness of lithium metal and strain rate under different loads can be measured¹⁴⁹, along with measuring the hardness of the solid polymer electrolyte to evaluate the lithium dendrite resistance ability¹¹⁷. In the practical application of lithium batteries in electrical vehicles or portable electronic devices, different mechanical loading (tensile stress, indentation, shear stress) will be applied. The mechanical stability of the electrodes and cells significantly affect the long-term and safely battery operation, which can be measured by macroscopical tensile testing. For example, in the research of binders for LIBs, peel testing has been frequently conducted to evaluate the adhesion force within binder, electrode particles and current collector^{150, 151}. Indentation and tensile stress has been applied to pouch cells to monitor the crash condition and evaluate the mechanical integrity and safety performance¹⁵²⁻¹⁵⁴.

Thermal properties and characterization. In conventional lithium ion batteries, the heat can be generated in reversible and irreversible way. Electrochemical intercalation produces reversible heat, while side reaction and joule effect produces irreversible heat.

With the continuous undesirable heat generation, thermal runaway will be triggered as a severe safety problem (fire and explosion) for LIBs¹⁰. Thermal runaway will be aggravated under some abuse operating condition including electrical abuse (e.g. short-circuit, overcharge, extreme charge/discharge), thermal abuse (e.g. high temperature heating), and mechanical abuse (e.g. stabbing, extreme deformation)^{155, 156}. It is important to have deep understanding of the heat generation and heat transport at different scales. The intrinsic thermal stability of the different components (electrode particles, electrolyte, separator, binder, conductive carbon, etc.) in LIBs can be measured by a thermal gravimetric analyzer (TGA)¹⁵⁷⁻¹⁶⁰. Differential scanning calorimetry (DSC) can also be applied to investigate the reaction heat and rate (e.g. heat evolution from precursor to final cathode¹⁶¹), crystallinity (e.g. solid polymer electrolyte¹¹⁷) by measuring the heat flow. For the cell level, accelerating rate calorimetry (ARC) has been used for thermal runaway research^{162, 163}. For example, Ouyang's group has employed ARC to investigate the thermal issues of different pouch cells and battery modules^{164, 165}. Typical temperature points can be identified and ascribed to the representative thermal reaction process during heating. Li's group has employed ARC to explore the thermal stability of solid electrolytes with metallic lithium¹⁶⁶. NASICON-type electrolyte such as LAGP can be reduced by lithium metal and release heat. The elevating temperature will further activate the release of oxygen and lead to thermal runaway.

Initial chemical properties and interfacial chemistry. The complex chemical composition and chemical reactions of lithium batteries challenge the in-depth understanding of reaction and degradation mechanisms. Besides, the multiphase (liquid, solid and gas) interfaces of electrode and electrolyte, between electrode particles, further increase the difficulty in revealing instantaneous reaction process.

Atomic/nanoscale chemical characterizations. X-Ray Diffraction (XRD) can be employed to investigate the atomic structure, structural evolution, and phase change in LIBs^{121, 167}. X-ray absorption spectroscopy (XAS) focusses on the local electronic structure and element chemical state^{121, 168}. Electron energy loss spectroscopy (EELS) analysis the atomic-scale electron state in energy materials, including the elemental valence and concentration distribution, e.g. the chemical composition distribution of the cathode from surface to bulk¹⁶⁹. Nuclear magnetic resonance (NMR) captures the localized atomic structure and environment, e.g. recognizing the lithium diffusion path by analyzing ⁷Li spectra¹⁷⁰. Neutron related characterization including neutron depth profiling (NDP), neutron diffraction (ND) and neutron reflectometry (NR), are sensitive to light elements such as H and Li. Thus, the phase change triggered by lithium ion de-/intercalation can be analyzed^{41, 171, 172}.

Interfacial chemistry characterizations. The electrode-electrolyte interface has been a critical concern in lithium batteries with complex interfacial behavior including ion de-

/intercalation, electrolyte decomposition and formation of intermediate interface, reaction product nucleation and dissolution^{103, 112}, etc. Advanced interfacial characterizations have been developed to investigate the interfacial reaction on the electrode/electrolyte interface. In Fourier transform infrared spectroscopy (FTIR), the molecular structure of the samples can be identified with different infrared light absorption ability¹⁷³. Thus, the electrolyte decomposition and reaction product (e.g. SEI, CEI)¹⁷⁴⁻¹⁷⁶ as well as interaction within polymer can be detected^{151, 177}. Raman spectroscopy can also provide molecular information within energy materials by detecting the energy shift of the scattered light after interacting with molecular vibrations¹⁷⁸. With other signal enhancing techniques such as surface-enhanced and tip enhanced methods, the dynamic reaction on the ultrathin electrode surface can be observed¹⁷⁷⁻¹⁸⁰. X-ray photo electron spectroscopy (XPS) can observe the element chemical shift by detecting the electron or the valence electron release of the sample atom after X-ray radiation⁴¹. XPS is widely used to qualitatively or semi-quantitatively identify the valent state and the chemical composition of the electrode materials^{39, 179}. Time-of-flight secondary ion mass spectrometer (TOF-SIMS) is another useful surface-sensitive tool which can use the ion beam to remove outermost sample surface and map the element distribution^{180, 181}. Compared with SEM/EDS, TOF-SIMS can provide more accurate information of lithium ions. Scanning electrochemical probe microscopy (SEPM) employ the probes to interact with the sample surface to collect electrochemical information of the electrode materials, which includes the various scanning electrochemical microscopy (SECM), scanning probe microscopy (SPM) such as AFM, scanning tunneling microscopy (STM) and electrochemical strain microscopy (ESM)^{182, 183}, etc. The SEPM help us to quantify the redox activity, ionic fluxes and electron transfer for better understanding of the interfacial chemistry^{184, 185}. In conventional lithium batteries, gas generates when electrolyte decompose or cathode structural reconstruction to release detrimental gas such as CO₂, C₂H₄, H₂ or O₂^{104, 186, 187}. And in newly developed metal-gas batteries, gas participates in the reaction to deliver energy output such as Li-O₂ battery, zinc-air battery^{145, 188}, etc. While the above characterizations mainly focus on the solid or liquid phase, differential electrochemical mass spectrometry (DEMS) probes the gas release and evolution during cycling^{189, 190}.

Table 1. Multi-scale modeling-assisted characterization techniques and key extracted features.

	Characterizations	Key features extracted	scale	Typical examples	Relevant model
Imaging techniques	Tomographic analysis				
	Time-of-flight secondary ion mass spectrometry(TOF-SIMS)	High resolution elemental distribution; Chemical elemental valent state and distribution, 2D and 3D morphology	Atomic and particle scale	Elemental distribution and three-dimensional (3D) visualization of interfacial reaction product in LiPON based solid thin film battery.	Density functional theory (DFT) calculations, ab initio MD simulations ¹⁹¹
	X-ray computed tomography(XCT)	Morphologic characterizations including electrode structure evolution, porosity, tortuosity	Particle and electrode scale	Pore-scale characteristics measurement and simulation of electrolyte flow within electrodes' pores	Lattice Boltzmann method (LBM), finite volume method (FVM) ¹⁹²
	Scanning electron microscope (SEM)	Morphology and structure features, interfacial elemental distribution	Particle and electrode scale	Mechanical interactions regulate the kinetics of lithiation and morphological evolution of the silicon nanowires.	Finite element modelling based on a theory of coupled diffusion and large elastic-plastic deformation ¹⁹³
	Transmission Electron Microscope (TEM) and Electron Energy Loss Spectroscopy (EELS)	Sub/ultra-microscopic structure, crystal lattice parameters, atomic elemental distribution	Atomic scale	Phase evolution and lithium diffusion during cycling in electrodes	Density functional theory (DFT), ab initio molecular dynamics (AIMD)

					simulations ¹⁹⁴
	scanning electrochemical microscopy(SECM)	Interfacial redox activity and electrochemical reaction current distribution	Particle scale	SEI formation on the lithium metal anode and simulation of secondary current density distribution	Finite element simulation ¹⁹⁵
	Atomic Force Microscopy (AFM)	Interfacial morphology, nano-mechanics, nano electro/magnetic properties	Atomic scale	Determination of Lithium Diffusion Coefficients in single particle LiCoO ₂	Three-dimensional diffusion simulations based on Fick's first law ¹⁹⁶
	Optical microscope	Macroscopical morphology	Particle and electrode scale	Lithium dendrite growth within the solid electrolyte	3D finite element model ¹³⁵
	Neutron Radiography/Tomography, Neutron Depth Profiling (NDP)	Chemical distribution especially light element such as Li and Na, crystal lattice parameters	Atomic scale	In-situ monitoring the lithium spatial distribution of lithium metal anodes	Molecular dynamics (MD) calculations based on density functional theory (DFT) ¹⁹⁷
	Nuclear magnetic resonance (NMR)/Magnetic Resonance Imaging (MRI)	NMR-active nuclei chemical shift	Atomic scale	Lithium ion transmission in solid electrolyte	Large-scale molecular dynamics (MD) simulations ¹⁹⁸
Non-imaging techniques	Electrochemical analysis				
	Cyclic Voltammetry and linear sweep	Redox peak, current intensity	Electrode	Lithium ion de-solvation process on	Single particle model based on

	voltammetry		scale	the electrode surface	Fick's diffusion law ³⁸
	Electrochemical impedance spectroscopy (EIS)	Interfacial resistance, charge transfer resistance, intrinsic resistance	electrode, cell, module scale	The influence of SEI growth rate, thermal and current condition on the battery independence response.	Mathematical and multi-physics based modeling ¹⁹⁹
	Surface chemical analysis				
	X-ray photoelectron microscopy (XPS)	Chemical shift and binding energy; Chemical composition of reaction product; Valent state distribution and evolution of transition metal in cathode material	Atomic scale	Coating LiF layer on SiOx anode to prevent electrolyte decomposition	DFT, ab initio simulation ²⁰⁰
	Raman spectrum	Molecular vibrational level, chemical component, Raman peak shifts and shape changes	Atomic scale	Lithium ion intercalation mechanism in anode material	First-principles calculations ²⁰¹
	Fourier transform infrared spectroscopy(FTIR)	Vibration and rotational frequency of chemical bond or functional groups	Atomic scale	Solvent structure in electrolyte	Molecular dynamics simulations ²⁰²
	Themo-mechanical analysis				
	TGA, DSC and ARC	Weight change during thermal heating, typical reaction temperature,	Particle, electrode	Thermal abuse resistance in battery	Physical model ²⁰³

		thermal energy flow, typical state transition temperature, heat generation	and cell scale	packs; Thermal stability of electrode material	
	Structure and chemical analysis				
	Differential Electrochemical Mass Spectrometer (DEMS)	Gas release and evolution	Atomic scale	Gas release during cathode structure evolution in high voltage LCO cathode	First-principle methods ¹⁸⁶
	X-ray diffraction (XRD)	Crystal structure lattice parameters	Atomic scale	Phase evolution of cathode after lithium ion intercalation	DFT ²⁰⁴

3.2.2 Integrating characterizations with modeling

Multi-scale characterization provides abundant information to understand the physical/chemical properties and reaction/degradation mechanism in lithium batteries. However, some of them are still not accessible owing to the limitation of the characterization methods. Furthermore some experimental research is time-consuming and high cost. Computational methods have made tremendous advances during the past decades, which can provide support for experimental characterization. **Table 1** summarizes representative characterization techniques and relating extracted key features, and shows typical examples on how they combine with modeling methods.

For the electrochemical analysis, the CV is a commonly used electrochemical analysis techniques that can obtain redox peak and current intensity during the electrochemical reaction. Feng Pan's group has developed a single-particle testing method and relating modeling to investigate the electrolyte/electrode interfacial behavior³⁸. Single particle electrodes have been developed by distributing LiFePO₄ nano-particles in the conductive network of carbon nanotubes, leading to a depolarization effect and sharp CV peak. By modifying the Butler–Volmer equation, Nernst equation and Arrhenius equation into a novel single particle model, the extracted CV information can be employed to determine the pre-exponential factor and reveal the different de-/solvation process in aqueous and organic electrolytes. For the structural and chemical analysis, taking XRD and XPS for example. XRD extracts the crystal structure lattice parameters which can reveal the structural evolution during cycling. Density-functional theory (DFT) as an atomistic simulation has been successfully introduced to cooperate with XRD to analyse crystal structure during lithium de-/intercalation^{179, 204}. Amy C. Marschillok's group integrated DFT calculations and in-situ XRD to reveal the structural transformation in Li_{1.1}V₃O₈ during cycling²⁰⁵. Stable phase during lithium ion intercalation can be clearly identified combining the XRD and DFT results. And the preferential orientation can be explained where the [100] orientations dominated a tetragonal cubic structure. XPS extracts the chemical shift and bonding energy of the nano-scale sample interface, which can be employed to distinguish the reaction product after electrolyte decomposition and SEI formation. Kang Xu' group applied XPS to investigate the interfacial chemical composition on Ni-rich cathodes after the decomposition of basalt ether electrolytes. The XPS identification of the reaction product further guided the molecular dynamic calculation on the reaction mechanism of FSI⁻ and TFSI⁻²⁰⁶. For the imaging techniques, experimental characterization coupled with computational techniques can further reveal morphologic information. For example, the XCT extracts the three-dimensional morphologic and structural features including electrode structure, porosity and

tortuosity. Matthew T. McDowell's group employed XCT to visualize the chemo-mechanical degradation of a solid-state electrolyte¹³⁰. The formation and propagation of the cracks in the $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$ (LAGP) can be monitored. Finite element analysis (FEA) are used to simulate the evolution of stresses due to the formation of interfaces between LAGP and lithium metal based on the XCT observation.

Experimental characterizations collect abundant information which can serve as fundamental condition or hypothesis for modeling research, contributing for improved imaging of morphologic, structural, or componential characters in lithium batteries. Computational methods have great advantages in dealing with the digital information, so the key features extracted from multi-scale characterization, as shown in **Table 1**, can be digitally processed and used in multi-scale modeling.

4. Multi-scale model application

Limited by the spatial-temporal resolution of existing characterization methods, some of the reaction and degradation mechanism remain either empirical or unknown. Benefiting from the rapid development of computational techniques, multi-scale advanced modeling and simulation provide more theoretical evidence, explanation and prediction for battery design from material to practical engineering products. In this section, we will discuss the parameter-oriented multi-scale models and their linked methods for lithium battery research. **Figure 4** shows the multi-scale modelling from the material and particle level, composite electrode level to cell and pack layer level.

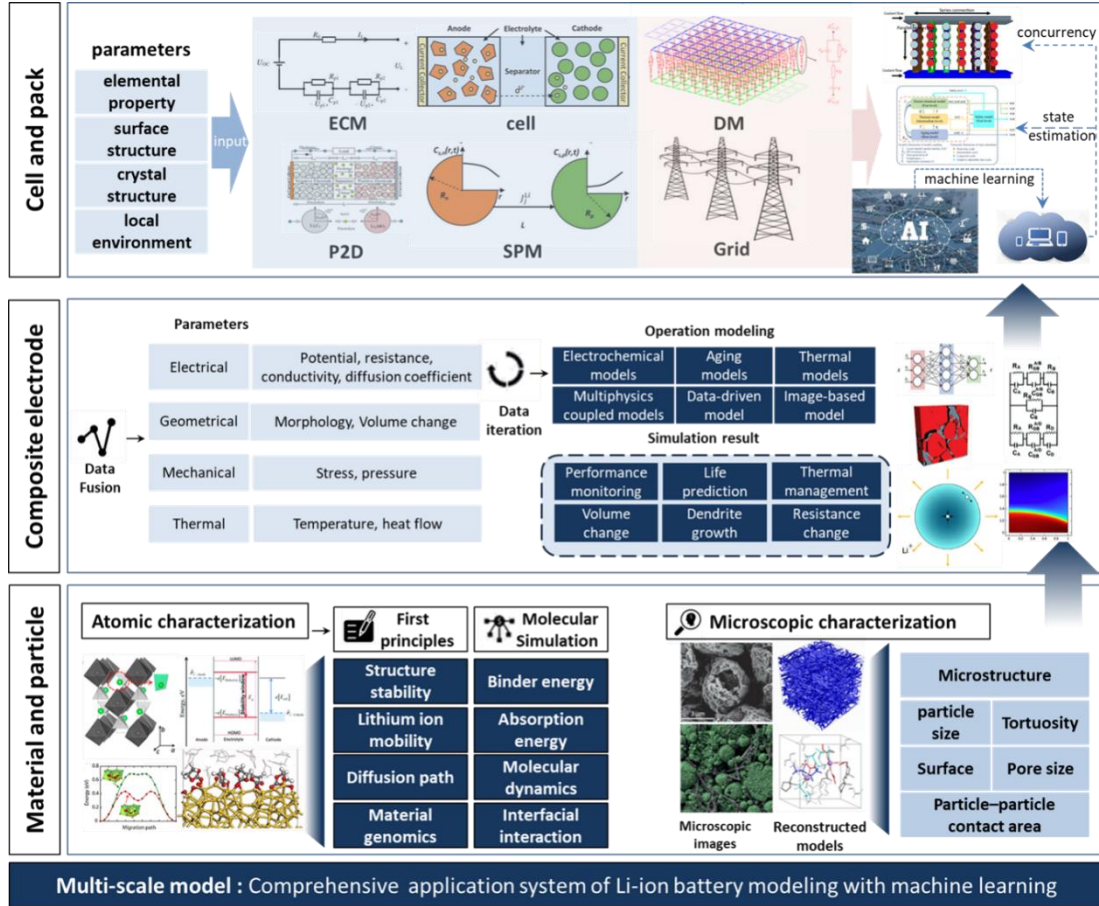


Figure 4. Multi-scale parameters in LIBs and corresponding multi-scale model. (again I think a more detailed caption is needed here)

4.1. Atomic and material level

Structural evolution, lithium ion storage and diffusion. Atomistic models such as density functional theory (DFT), molecular dynamics and their derived methods provide quantitative information at the atomic/nano scale about lithium ion storage and diffusion, interfacial stability and reaction⁴⁷. The energy density of lithium batteries is determined by the maximum specific capacity delivered by the electrode material and the working voltage. The capacity is directly related to the lithium ion storage sites within the electrode material structure, and the structure stability after lithium ion de-intercalation. While the equilibrium cell voltage affect the energy output²⁰⁷. For example, the conventional cathode material LiCoO_2 (LCO) has been widely used in commercial lithium-ion batteries. Before high-voltage LCO came out, it was reported that only half of the lithium ions in fully-lithiated LCO could de-intercalate due to the structure instability of LCO under high states-of-charge^{208, 209}. First principles computations can be employed to explore the structure stability of LCO with various engineering strategies like doping or coating^{210, 211}. The structural stability also influences the thermal and electrochemical stability. Oxygen release is found in some

oxide-based cathode materials such as Li-rich material under a high charge state. Xiaodong Chen's group conducted DFT calculations to confirm that the Mg_2TiO_4 coating can effectively suppress the oxygen release in $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$, because the Mg and Ti stabilize the surface oxygen by enhancing the energy barrier of oxygen evolution reaction²¹². While the lithium ion de-/intercalation in the electrode material change the voltage between cathode and anode, the voltage curve profiles record the voltage evolution during cycling which can reveal the structure evolution in return. Maria L. Sushko's group conducted ab initio simulations based on density functional theory to simulate the voltage profiles after the introduction of oxygen vacancies in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ (LNMO) cathodes, where oxygen deficiency is proven to promote the formation of disordered Ni/Mn configurations²¹³. The improvement of the rate performance demands the fast diffusion of lithium ions both within the material and on the electrode/electrolyte interface. The lithium ion diffusion within the solid materials is reported to be the rate-determining step as the lithium ion transport through the electrolyte is much faster. The ab initio molecular dynamics (AIMD) can help to investigate the ion-diffusion paths and kinetics. For example, Swapan K. Pati's group combined DFT and AIMD to predict the possible lithium migration path in 2D boron sheets²¹⁴ where Li^+ transfer from one 'H' site to another through the top of boron atom.

Interfacial chemistry. In conventional lithium batteries, the electrolyte transfers lithium ions between cathode and anode. The organic electrolyte tends to decompose either on the reductive anode surface or on the oxidized cathode surface limited by the HOMO/LUMO energy level^{103, 106}. Molecular dynamics is widely used to evaluate the stability of electrolyte and investigate the interaction on the electrode/electrolyte interface²¹⁵⁻²¹⁷. The electrolyte decomposition and the relating reaction interface on the anode surface (SEI) and the cathode surface (CEI) can be also investigated by atomic calculation. Kang Xu's group combined quantum chemistry (QC) calculations and molecular dynamics simulations to monitor the decomposition behavior of lithium salt (LiFSI) and solvent (Tetramethylene sulfone) on the graphite and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) surface²¹⁸. Stable SEI and CEI can form on the electrode surface to enable long term operation of a high-voltage (4.85 V) LNMO/graphite full cell. The de-/solvation process on the electrolyte/electrode surface can be also simulated by ab initio theoretical investigations under DFT. Jiaxin Zheng and Feng Pan's group calculated the $\text{H}_2\text{O}/\text{EC}$ absorption at LiFeO_4 and FePO_4 surfaces to demonstrate that the Janus solid-liquid interface enabled fast Lithium ion de-solvation process to enable high rate performance²¹⁹. With the ability to investigate the structure stability, lithium ion mobility and interfacial interaction at atomic scale, atomic calculations have recently been combined with machine-learning and other data-driven methods to explore new energy materials with high performance. Material genomics is an arisen paradigm for

energy material research. Crystal structures as well as their connection and interaction with local environment can be simulated to investigate the structural electrochemistry with high-throughput^{220, 221}.

4.2. Particle and electrode level

Lithium ion diffusion and stress distribution. Different particle and electrode scale models have been developed in the past decades. In 1975, Newman pioneered the development of porous electrode theory²²², and Doyle later used it to describe electrochemical models for Li-ion cells²²³. Fick's law of diffusion is used for capturing the active material concentration²²⁴, Ohm's law for electrical potential distributions²²⁵, and the Nernst and Butler-Volmer equations for capturing thermodynamics and reaction rate³⁸. Most physics-based battery modelling techniques today derived are based on these early developed fundamental methods. Mesoscale simulations including electrical equivalent circuit models, electrochemical models, aging models, thermal models, multiphysics-coupled models, mathematical modeling, etc. have been developed to investigate the lithium diffusion behavior, thermal diffusion, mechanical stress and structure destruction, and aging mechanism at particle and electrode level.

Lithium diffusion within the electrode and the mechanical structure integrity during cycling are two important properties at the particle and electrode level. At the particle level, lithium de-/intercalation within the active materials will introduce internal stress leading to particle cracks^{33, 226}. Ann Marie Sastry's group developed a stress-diffusion coupling model to investigate the intercalation-induced stresses during the discharge process in LiMn_2O_4 ²²⁷. Simulations of ellipsoidal particles revealed that larger particle size and higher current density will introduce higher intercalation-induced stress, which could be potentially reduced by large aspect ratios. The accumulated stress will change the localized environment. Jun Xu's group constructed an axisymmetric finite element computational model to simulate the mechanical stress between two contact Si-C core-cell particles²²⁸. The contact behavior would cause a high nonuniform stress gradient which influence the Li^+ diffusion.

On the particle surface, solvated lithium ions should de-solvate the solvent molecular before intercalate into the electrode particles, which will significantly influence the rate performances. Single particle models can simulate the de-/solvation process in lithium batteries^{38, 229}. The solvated structure between lithium ions and solvents, the lithium salt concentration in the electrolyte, the current density and operating temperature can affect the de-solvation process, changing the electrochemical window, the interface reaction constants, and the activation energy. Another interfacial behavior on the particle surface is the electrolyte decomposition. The electrolyte will decompose because of limited electrochemical window or the interfacial electrocatalytic sites on particles¹⁰³. Such

decomposition will trigger the formation of SEI/CEI, increase the interfacial resistance to retard the interfacial de-/solvation of lithium and bring extra stress ions on particle surface. Jinhan Chen's group established a mathematical model to simulate the stress of heterogeneous SEI on a spherical electrode surface²³⁰. When the battery is fully charged, the peak tensile stress within the SEI will generate at the interface between the active material and the inorganic layer. Consequently, a functional gradient heterogeneous SEI is therefore suggested to improve the performance of lithium batteries.

Structural recognition and reconstruction in electrode level. Composite electrodes comprise active materials, conductive carbon, polymer binder and current collectors. The lithium diffusion ability and mechanical stability are two critical properties for the composite electrode. The lithium diffusion can be affected by electrode structure (such as particle distribution, porosity, tortuosity, conductive carbon and binder, etc.), interfacial properties of the electrode particles (such as the electrolyte decomposition, reaction interface and relating interfacial resistance), and the electrolyte composition (concentration, etc.)²³¹. The three-dimensional microstructural characteristics of composite electrodes have significant influence on the electrochemical and mechanical properties of LIBs, which demands for quantitative microscopic imaging and predictive modeling. As mentioned before, many microscopic imaging techniques including X-ray CT, FIB-SEMS, TOF-SIMS, synchrotron-based techniques have been employed to investigate the morphologic characteristics in LIBs, which can be assisted by material modeling based on the tomographic reconstruction data to reveal the true microstructure. After the recognition of micro-structures, the geometric information can be applied in multiscale models to reveal the lithium diffusion and degradation mechanism. For example, David A. Shapiro and co-workers employed soft X-ray tomography assisted by computed spectro-tomography to reveal the dynamic 3D morphology and oxidation states distribution of transition-metal cations in LFP with high resolution of 11 nm²³². Cross-sectional strain distribution within single particles can be measured and reconstructed with high resolution. Besides morphological modelling, the stress accumulation within the electrodes can be also simulated. Ying Shirley Meng and co-workers employed Coherent X-ray diffraction imaging (CXDI) in Bragg geometry to in-situ study the spatial and temporal strain evolution of a single LNMO cathode nanoparticle²³³. Based on the morphologic evolution, the lithium diffusion in the electrodes can be also investigated. Zhongwei Chen and co-workers applied nano-scale X-ray computed tomography to obtain structure information such as porosity and specific surface area in LFP electrodes²³⁴. The electrode microstructure reconstructed by nano-XCT data was incorporated in the micro-scale modelling to simulate the intercalation flux. Then, the intercalation flux was employed to the macroscale

simulation as more precise state variables such as electric potentials and species concentrations. Consequently, the distribution of lithium concentration inside the electrode microstructure and the macroscale level discharge/charge behavior under different current density and various SOC can be simulated.

Stress evolution in particles and distribution in electrodes. Mechanical stability evaluates the ability to retain structure integrity as well as normal function and survive internal (particle volume change, formation of reaction interface, growth of lithium dendrite, etc.) and external stress (extrusion, strike, vibration, indentation, etc.)^{69, 82, 84, 85}. The volume change during the lithium ion de-/intercalation process within the electrode particles can cause contact loss between the electrode particles and the conductive network, triggering performance decay^{82, 231}. The particle morphology significantly affects the stress distribution owing to the anisotropic mechanical properties. It is common that some modelling works idealize the geometry of electrode particle to be simple shapes such as spheres or thin films with isotropic mechanical properties such as Young's modulus. In this way, the deformation and stress distribution can be simulated in a single particle²³⁵⁻²³⁷. The accumulation of the deformation and stress of the particles then trigger the mechanical degradation at the electrode scale. Maenghyo Cho and co-workers demonstrated a multi-scale model to reveal the electrochemical and mechanical response of an amorphous silicon thin film during cycling²³⁸. The atomic stress-dependent energy barrier for the lithium ion migration and the molar excess Gibbs free energy were calculated by DFT, which were further involved in the continuum simulation at microscale to investigate the nonlinear lithium diffusion behavior. A cell-scale model coupled by diffusion and large deformation was then developed to determine the non-equilibrium cell potential as a function of the surface lithium concentration using Butler-Volmer kinetics. Consequently, the cross-scale lithium diffusion and stress evolution within Silicon anodes could be simulated. While many efforts have been paid to the electrode particles, binder as a minority component in electrodes can also affect the mechanical response. Seungjun Lee's group developed a chemo-mechanical model to investigate how the multiple binder connections affect the lithium concentration distribution and the stress levels in the model single particle systems during lithiation²³⁹. Excessive compressive stress will be generated on the electrode/polymer interface with more binder connections to cause the lithium deficiency and particle disintegration.

4.3. Cell and pack level

Under the practical operation of lithium batteries at cell and pack level, safety considerations including thermal and mechanical behavior share the equal importance of the electrochemical performance. Jwo Pan's group developed a series of models to

simulate the mechanical abuse situation in lithium battery module. For example, a macroscopic homogenized foam material model can simulate the tensile behavior of the battery module²⁴⁰. The simulation results can precisely simulate the stress-strain curve of lithium-ion battery module under tensile, constrained compression and punch indentation condition with high goodness toward experimental data. Finite element simulations build the geometrical models based on the practical morphological characters. Multi-physical interaction (thermal, electrochemical, mechanical condition) can be coupled to simulate the battery performance under operating condition. Xia Yong and co-workers developed a 3D finite element model to simulate the dynamic deformation process of pouch cell under impact loading²⁴¹, which can reveal the battery deformation information for all component parts benefiting for the prediction of battery internal failure.

The thermal heat generated within the lithium batteries can be caused by reaction heat (decomposition of materials, etc.) and thermal efficiency during discharge-charge process, which can be simulated by a thermal model and electrochemical model respectively. Xingjiang Liu and co-workers developed a thermal and electrochemical coupled model to simulate the thermal behavior of LFP/C cell²⁴². They demonstrated that the melt-down temperature of the separator significantly influenced the thermal runaway behavior. Andreas Jossen's group modified the large-scale electro-thermal model for pouch cells²⁴³. They succeeded in simulating the cell temperature distribution under different polarization conditions. Heat generation will be accelerate under high current density, Michael Fowler and co-workers developed a high-fidelity 3D multi-layer physics-based lithium-ion battery model²⁴⁴. The heat generation on the current collector and the tabs could be also simulated. The heat generation close to the tabs are triggered by the active material and current collector. Most importantly, they showed that the temperature gradient across the thickness of a multi-layer cell is negligible. Short-circuits can be triggered under mechanical, electrical and thermal abuse conditions, which will in-return aggravate the thermal runaway and chain reaction leading to fast capacity decay and hazard like fire and explosion¹⁵⁶. Thermal resistance models²⁴⁵, mathematical model^{246, 247}, thermal-electrical models⁶² are employed to simulate the heat generation and propagation, temperature distribution and final thermal runaway in pouch cells and packs.

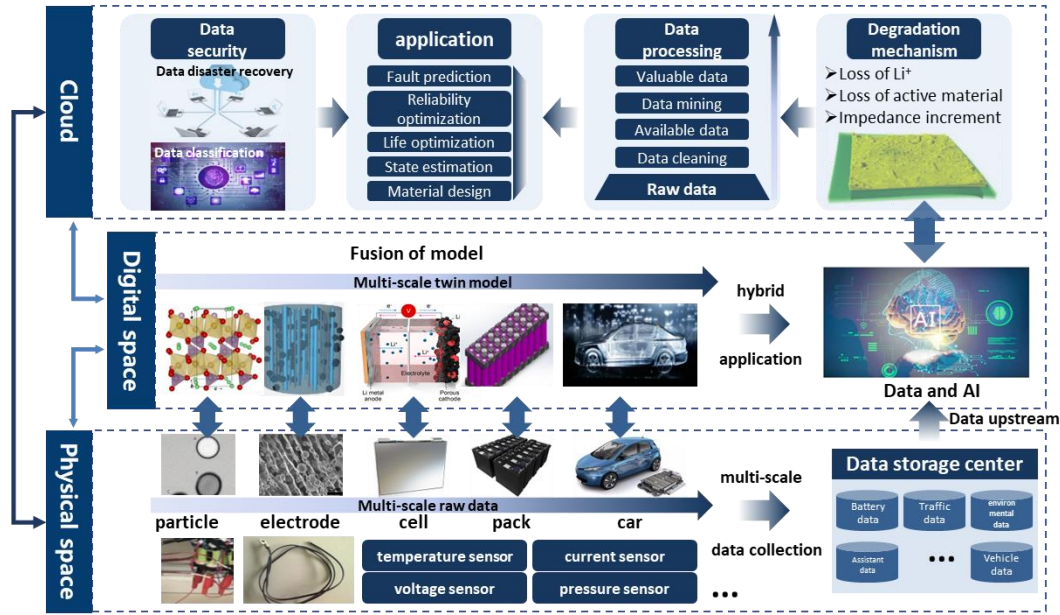


Figure 5. CHAINS: physical characterization, multi-scale modelling, cloud control and digital twins for in-depth understanding of lithium battery degradation mechanism, state monitoring and battery control.

5. Outlook

Digital space based on the physical characterizations, multi-scale modelling and cloud control technology.

Recently, a *CHAIN* (Cyber Hierarchy And Interactional Network) framework has been demonstrated to enable digital solution for battery full-lifespan management regarding the material synthesis, characterization, electrochemical performance and safety. In this work, a seed CHAIN framework toward the multi-scale characterization technologies and digital modelling is demonstrated. Intelligent algorithms and machine learning techniques are driving LIBs design research toward the big data era. These data-based computational technology requires sufficient data collection, data processing to ensure accurate output. Multi-scale modellings abstracts the electrochemical/mechanical/thermal properties and process in LIBs into parameterized models which can be conveniently involved in data-driven computational technology. Conventional characterizations extract different information from material properties to reaction process in LIBs. Among the various characterizations, the output of electrochemical analysis methods (e.g. CV and EIS) is often data-based which can be directly used in some modelling studies. Some imaging techniques such as SEM monitor the morphologic characters which need to be digitalized before serving as input in modellings. **Figure 5** shows the demonstrated framework that applying cloud control techniques based on “physical space” to create “digital twins space” for in-depth

understanding of lithium battery degradation mechanism, state monitoring and battery control. The following perspectives are proposed to develop the demonstrated seed CHAIN framework.

Multi-scale characterization/monitoring and “Physical space”. All the information acquired from different characterizations and monitoring (from the material, particle to EVs, from battery data to operating condition) create the “physical space”. Following perspectives are addressed in experimental data collection:

(1) *Characterizations combination.* Different characterization methods have been developed to extract the key features affecting LIB performance and reveal the degradation mechanisms, which may need further improvement in their time-spatial-componential resolution. Regarding the cross-scale and multidimensional characteristics of reactions in LIBs, combining the various characterizations to detect different signal simultaneously is necessary for better understanding of LIB chemistry. For example, *in-situ* AFM has the capability to measure nanoscale morphology evolution and mechanical properties, but lacks chemical analysis. Spectroscopy-based interfacial techniques including Raman, FTIR, Fluorescence, etc. can be combined with AFM to provide chemical information.

(2) *Non-destructive characterizations.* While many *in-situ* characterizations employ the *in-situ* cell as substitution for real batteries, more advanced non-destructive and *operando* characterization that are widely used in industry or medical examination can be introduced to the battery research, such as ultrasonic scanning^{248, 249}, photoacoustic imaging²⁵⁰, thermal imaging²⁵¹, electromagnetic/magnetically dependent techniques, etc..

(3) *Collecting battery status by sensors.* Sensors have been developed to monitor the practical operating condition of lithium ion batteries. Electrical (voltage, current, EIS, etc.), mechanical (deformation, stress, etc.), thermal (temperature, heat, etc.) signals can be obtained to inform control via the BMS. The widely used commercial sensors are mostly external and delayed which cannot reflect the real-time complicated reaction within batteries. Embedded sensors with multifunction should be rationally designed to provide more information during the battery operation.

Data digitalization, multi-scale modelling and “Cloud space”. With the massive data produced and collected in physical space, “Cloud Space” is created to store and deal with the tremendous data collected from characterization or monitoring in-real time operation of LIBs, as well as carrying out the multi-scale modelling.

(1) *Internet of things.* While the vehicle-mounted BMS platforms have limited calculation ability, the large operating data of lithium batteries cannot be dealt with.

With the development of Internet of Things (IoT) technologies, all the data collected from sensors can be uploaded to the cloud server. After been processed and simulated in Cloud space, commands will be sent back to BMS for better control of battery operation.

(2) *Date digitalization and processing.* All the experimental characterizations and raw data produced during the practical operation of LIBs will be uploaded in cloud servers. While some experimental characterizations provide the non-digital information, key features extracted will be converted/digitalized before they could be involved in multi-scale modelling. For example, converting the true microstructure into statistically equivalent microstructures in 2D or 3D digital space²⁵ which can be further used in numerical modelling. More mathematical theories and methodologies can be introduced to topologize or digitalize the real material interaction. For example, Feng Pan's group introduced graph theory into the identification of crystal structures²⁵². By converting the real bond length and bond angle into topological relationship, they succeeded in automatic deduplication for big materials database. After the data collection, specific methodology for data cleaning, parameter extraction, fusion and clustering will be carried out to obtain a sorted database.

(3) *Multi-scale modelling.* The processed data will be classified and stored in the modelling data space which will then distributed to selected modelling. While the reaction process always involves multi-physical/chemical steps, coupled modelling (cross-scale/dimension) should be further developed to investigate the electrochemical/mechanical/thermal process in LIBs. More data-driven and machine learning modelling will be employed in the cloud simulation²⁵³. All the modelling can be operated in the cloud space (including super computers, servers) with high efficiency and accuracy. The delivered simulation results include: (I) providing in-depth understanding for multi-scale degradation mechanism; (II) discovering novel energy material with better performance; (III) optimizing the operating condition for maximum use of existed LIBs; (IV) monitoring the operation of LIBs, diagnosing safety danger, and predicting lifespan.

Digital twins and “Digital space”. With the rapid development of advanced computational technology especially the data-driven techniques such as Cloud, machine learning, etc., “Digital Space” is created where the continuous iteration between physical space and cloud space happens based on data-driven artificial intelligence and enable the ability to real-time prediction, optimization, monitoring, controlling of application terminals in LIBs.

Artificial intelligence and Machine learning. The massive data produced in “Physical space” and “Cloud space” challenge traditional data management methods. Machine

learning will be fused with close-loop optimisers to evaluate the overall lifespan of lithium batteries. The extracted data from physical space will also serve as correction or reference for the output of cloud modelling to modify the multi-scale cloud-based modelling and control, where the data-driven modelling will keep improving when trained with such data iteration. .

Real time control of LIBs performance. Low latency cyber-physical systems will be created to enable real-time adaptive control of LIBs based on the precise monitoring from the on-board sensor measurement and the high-throughput multi-scale simulation.

Guide for material synthesis and mechanism research. Compared with the traditional time-consuming material synthesis and characterizations, more computational technologies will be involved in digital twins to enable the autonomous computer-assisted characterizations and material synthesis. There have been some successful applications of “Artificial Chemist”, where smart systems based on machine learning can be employed to discover and optimize chemicals²⁵⁴, autonomously carry out characterizations with high-precision²⁵⁵.

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