Supplementary Materials for

Theory-guided experimental design in battery materials research

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Tables S1 to S3
Table S1.
Common computational methods employed in battery studies, their applications and recommendations of complementary experimental techniques for validation.

| Computational method (References) | Length scale | Time scale | Applications and recommendations of complementary experimental techniques for validation |
|-----------------------------------|--------------|------------|-------------------------------------------------------------------------------------|
| Atomistic modelling such as density functional theory (9, 50, 123) | pm – nm | fs – ps | - calculate equilibrium voltage, theoretical capacity and structural stability of battery materials.  
- can complement experimental voltage-capacity measurements using galvanostatic cycling, and current-voltage measurements using cyclic voltammetry.  
- compute energy barriers for ion diffusion in battery materials based on quantum mechanical principles.  
- can complement ion diffusion coefficient measurements using galvanostatic intermittent titration technique, and  
ionic conductivity measurements using electrochemical impedance spectroscopy.  
- calculate electronic structure of battery materials, including molecular orbitals, band structure, density of state, and charge distribution.  
- can complement electronic band structure determined using angle-resolved photoemission spectroscopy and  
inverse photoemission spectroscopy. |
| Atomistic modelling such as molecular dynamics (10) | nm | ps – ns | - simulate ion transport dynamics over time and solvation structures.  
- can complement ion distribution studies using scanning transmission X-ray microscopy.  
- model the formation, evolution and components of solid electrolyte interphases (SEIs).  
- can complement SEI structure and composition studies using liquid-phase transmission electron microscopy and ambient-pressure X-ray photoelectron spectroscopy.  
- model the electrodeposition behavior of metals and formation of dendrites under different conditions.  
- can complement scanning/transmission electron and optical microscopy studies of metal electrodeposition and dendrites. |
| Electrode/Particle-scale continuum modelling such as phase field modelling (11) | µm | µs – ms | - study phase transformations in phase separating materials such as lithium iron phosphate.  
- study dendrite formation and growth, which is a critical failure mechanism in metal batteries.  
- study active material particle cracking, which is an important degradation mechanism in metal-ion batteries.  
- can complement electron and optical micrographs of multiple phases, dendrites and active material particles. |
| Cell-scale continuum modelling such as single-particle model, pseudo-2D model and multiphase porous electrode theory (12, 13, 14, 111) | mm – cm | s – hr (can be up to days for long-term degradation studies) | - provide quantitative and explainable relationships between macroscopic inputs such as current and macroscopic outputs such as voltage, capacity, state of charge and state of health.  
- this level of modelling interfaces with battery management systems that are used to manage battery packs in practical applications such as electric vehicles.  
- can complement electrochemical characterization techniques such as galvanostatic/potentiostatic cell cycling, voltammetry and electrochemical impedance spectroscopy. |
Table S2.
Common materials characterization techniques for battery characterization and testing, and examples of complementary techniques or recommendations for experimental design.

| Analytical technique (References) | Measured signals | Experimenta  | Spatial imaging/ lateral resolution | Depth analysis/ resolution | Recommendations for experimental design, or validation of theoretical calculations |
|----------------------------------|-----------------|-------------|------------------------------------|---------------------------|----------------------------------------------------------------------------------|
| SEM/EDS (43, 50, 51)            | secondary electrons, characteristic X-rays | morphology (SEM), elemental data (EDS) | Yes, few µm (EDS) | Yes, 0.5-3 µm (EDS) | - elemental mapping data. - useful in initial visualization of particle sizes and distribution, towards development of heterogeneous and/or porous structural electrode models for theoretical prediction. |
| TEM/STEM/EDS (SAED) (51, 79) | transmitted electrons, characteristic X-rays | morphology (TEM), elemental data (EDS) | Yes, atomic resolution, to few nm (EDS) | Yes, thickness of sample | - elemental mapping data, with good lateral resolution. - crystallinity data with SAED. - useful in initial visualization of particle sizes and distribution, for development of electrode structural models. |
| cryo-TEM (50, 80)             | transmitted electrons | sample morphology | Yes, atomic resolution | Yes, thickness of sample | - study of air- and moisture-sensitive materials/interfaces possible with minimal damage from electron beam (e.g. observation of dendrite growth) - useful in generating accurate SEI structural models for theoretical prediction. |
| EDS/FIB (43, 50)             | secondary electrons/ ions | surface and cross-sectional morphology, elemental data (EDS) | Yes, few nm (EDS) | Yes, few nm | - suitable for cross-sectional observation of battery interfaces (e.g. heterogeneous SEI structures). - useful as a starting point to generate initial visualization of actual SEI structures and compositions for theoretical prediction of properties such as reaction potentials or phase transformations. |
| AFM (49)                        | atomic force between probe and sample | surface topography | Yes, atomic resolution, to few nm | No | - topographical data only, no compositional information. |
| Photoelectron spectroscopy (e.g. XPS, Auger) (43, 48, 50, 77) | electrons from near-surface atomic layers | chemical bonding information, surface and depth analysis | 10 µm – 2 mm | 10 – 30 Å surface analysis | - depth profiling possible with in situ ion-etching; suitable for depth analysis of battery interfaces, SEI composition/thickness etc. - mapping possible but generally poor lateral imaging resolution. |
| XAS/XANES (27) | X-ray absorption | chemical bonding information | No | No | - spectroscopic method for study of electronic structure in materials. - useful in conjunction with electrochemical testing for proposing new reaction mechanisms. - may be employed to validate mechanisms hypothesized by theory (need both theory and experiment to develop new mechanistic understanding). |
| Method                  | Characteristic          | Elemental Composition | Spatial Imaging/Mapping | Electrochemistry Techniques |
|------------------------|-------------------------|-----------------------|-------------------------|-----------------------------|
| XRF                    | characteristic X-rays   | Yes                   | No                      | - physical models employed in ML studies may be useful for interpretation and explaining structure-property relationships, and generalization of phenomena towards autonomous discovery of new materials. |
| XRD                    | diffracted X-rays       | Yes                   | No                      | - electrochemical kinetic studies, and derivation of reaction mechanisms. - may be coupled with in situ/ ex situ characterization (e.g. XAS, XRD, Raman spectroscopy) for mechanistic study. |
| NMR/ ssNMR Spectroscopy | chemical shift          | No                    | No                      | - useful in study of electrolyte active species or additives. - may be used in validation of predicted electrolyte species or optimization of novel electrolyte formulations. |
| UV-vis spectroscopy     | light absorption/ reflectance (electronic transitions) | No                    | No                      | - useful in studying electrolytes, or soluble species (e.g. dissolution or loss of active cathode material). |
| FTIR spectroscopy       | vibrational absorption  | No                    | No                      | - common characterization for organic conversion-type electrode materials (e.g. sulfur cathodes) |
| Raman spectroscopy      | inelastic scattering    | Yes                   | few µm, low µm resolution | - useful for study of electrolyte species or additives in solution. - spatial mapping possible, but generally low lateral imaging resolution. |
| Mass spectrometry (e.g. SIMS, TOF-SIMS) | secondary ions | chemical and molecular fragments, surface analysis | Yes, few µm, few nm | - chemical bonding data, content of impurities. - surface analysis and depth profiling. - may be used in determining SEI composition/thickness for building of computational models. |
| Galvanostatic/ potentiostatic cell cycling | current (charge), voltage | long-term cycle lifetime and rate performance Coulombic/ energy efficiencies. Energy/ power densities. | - | - |
| Voltammetry (e.g. CV, LSV) | current, voltage | mechanistic and kinetic data | - | - | - electrochemical kinetic studies, and derivation of reaction mechanisms. - may be coupled with in situ/ ex situ characterization (e.g. XAS, XRD, Raman spectroscopy) for mechanistic study. |
| Electrochemical         | AC current, voltage    | mechanistic and kinetic | - | - | - electrochemical kinetic studies. |
impedance spectroscopy (EIS) (48, 50, 127, 130)
data, charge transfer resistances, diffusion rates
- useful in studying evolution of battery interfaces or SEIs over time and after cycling (e.g. charge transfer resistances, ion diffusion coefficients).
- post-mortem characterization may be performed after cycling, EIS measurements.

Electro-chemical titration techniques (e.g. GITT, PITT) (16, 43, 60)
current, voltage
diffusion coefficients, with respect to cell voltage or state-of-charge
- -
- titration techniques allow for derivation of ion diffusion coefficients.
- complementary to DFT calculations which can be used to predict ion diffusion barriers in electrode materials, or validation of observed trends.

Abbreviations: SEM: scanning electron microscopy, EDS: energy-dispersive X-ray spectroscopy, TEM: transmission electron microscopy, SAED: selected area electron diffraction, FIB: focused ion beam, AFM: atomic force microscopy, XPS: X-ray photoelectron spectroscopy, XAS: X-ray absorption spectroscopy, XANES: X-ray absorption near edge structure, XRF: X-ray fluorescence, XRD: X-ray diffraction, NMR: nuclear magnetic resonance, ssNMR: solid-state nuclear magnetic resonance, UV-vis spectroscopy: UV-visible spectroscopy, FTIR spectroscopy: Fourier-transform infrared spectroscopy, SIMS: secondary ion mass spectrometry, TOF-SIMS: time-of-flight secondary ion mass spectrometry, CV: cyclic voltammetry, LSV: linear sweep voltammetry, GITT: galvanostatic intermittent titration technique, PITT: potentiostatic intermittent titration technique, ML: machine learning.

Table S3.
Selected examples of theory-experiment collaborative studies in battery research from contemporary literature, outlining the authors’ objectives in performing the investigation, their main findings, and potential impact of the work.

| Research objectives | Predictions from theory | Experimental findings | Validation/ correlations | Potential future impact |
|---------------------|-------------------------|-----------------------|--------------------------|------------------------|
| Identification of cathode materials for lithium-ion battery (27) | Replacing cobalt in LiCoO₂ with aluminium results Li₃AlCo₁₋ₓO₂. The material exhibits higher lithium intercalation voltage, with small enough formation enthalpy (30 meV) to form solid solutions. | Synthesized Li₃AlCo₁₋ₓO₂ sample showed higher open circuit and working voltages with reversible charge/discharge for 10 cycles. | Aluminium substitution increased cell voltage with enhancement in the equilibrium potential, which validated theory. | First-principles calculations was demonstrated as a valuable tool for identifying and evaluating candidate cathode materials. |
| Tailoring anionic redox reactions in cathodes of lithium-ion battery (27) | DFT calculations predicted the reversibility of iron and oxygen redox couples between 1.0 and 3.8 V versus Li⁺/Li, after the initial extraction of two lithium ions. Lithium-excess Li₆-O configuration, identified by DFT ensures reversibility of O⁻⁻/O²⁻ redox mechanism. | At a voltage of at ~3.5 V versus Li/Li⁺, and after the initial extraction of two lithium ions, oxidation of Fe³⁺ to Fe⁴⁺ and O²⁻ to O⁻ were observed. Oxygen evolution was also reported as the charging went beyond 3.8 V, due to oxidation of O⁻ to O²⁻. | As charging beyond 3.8 V produced oxygen evolution, with morphological changes, indicating a direct link to the theoretical predictions, hence validating it. | An improved understanding of oxygen redox can spur further development of new classes of cathode materials that can undergo simultaneous anionic/cationic redox reactions. |
| **Supressing dendritic growth through coating lithium-ion conductors on to polymeric separators for lithium metal batteries** (33) | Bader charge analysis from DFT along with simulation of polymer predicted barrier heights (i.e. activation energies) and electrodeposition stability. Furthermore, a density-driven stabilization enables suppression of dendrite growth. | Experimental validation of the lithium-ion conductor coated on polymeric separators, with lower shear modulus, showed dendrite suppression character and enhanced cycling performance. | Universal chemo-mechanical design rules can be applied for designing solid ion conduction membranes to mitigate dendrite growth. | Dendritic growth can be blocked using solid polymer electrolytes with suitably high shear modulus. May lead to further design of other “soft” polymer materials. |
| **Cation regulation approach for suppressing dendrites in lithium and zinc metal anodes** (35) | Stabilizing the electrodeposition can be achieved by negative background charge of the tethered anions. By weakening the electric field at the negative electrode, stabilization occurs. | Uniform lithium/zinc electrodeposition/plating were achieved when a layer of negatively charged collagen hydrolysate ions coated on absorbed glass mat was sandwiched between the metal anode and glass mat separator. | Interactions between positively charged lithium ions/zinc ions with negative collagen hydrolysate ions, prevented dendritic growth and ensured uniform deposition. | Unveiling cation-biomolecule interaction facilitates dendrite free uniform plating/stripping, which can be key for commercial battery design. |
| **Design and development of a micro-compartmentalized anode array for safer lithium metal batteries** (40) | Simulated electric field directions of planar Cu (P-Cu) shows a vertical pattern, whereas a unique lateral pattern was observed in case of polyimide-clad copper grid current collector (E-Cu). Further simulation of von Mises stress distributions show a ~60% stress reduction from the protruded Li dendrites in E-Cu. | After several cycles, plated lithium emerges as accumulated particles in place of the initial whisker shapes. As a result, no dendritic protrusions were formed in E-Cu. Instead, large and thick dendrites were observed in the regular case for P-Cu. | Simulation unveils underlying mechanism behind the prevention of dendrite growth. Experimental findings confirm continuous accommodation of Li metal inside micro-compartmental structures without dendrites. | This novel technique opens up new insights into the unwanted dendrite growth and can accelerate such a methodology and design for other battery anode materials. |
| **Limiting polysulfide dissolution and rapid capacity decay in lithium-sulfur batteries** (42) | Ab initio simulation predicted the strong affinity of poly(vinylpyrrolidone) as a cathode binder with Li2S and lithium polysulfides. | Usage of poly(vinylpyrrolidone) as cathode binder enhanced capacity retention with lower sulfur content in electrolyte after cycling, by preventing polysulfide dissolution. | Selection of cathode binder guided by theory ensured better electrochemical properties, with tangible benefits of higher capacity retention and Coulombic efficiency. | Correlating the binding energy of the chemical interaction between binder and cathode reaction products is a tool for the selection of unconventional binders. |
| **Addressing capacity loss due to polysulfide dissolution and to limit degradation due** | DFT calculations predicted that compared to poly-vinylidene difluoride binder, polyacrylic | Cell with polyacrylic acid showed stable performance with Coulombic efficiency close to 100%. Post- | Experimental observations validated theoretical calculations of binding interactions | Optimizing the binder-cathode interactions can be a tool for designing effective sulfur cathodes, acting |
| to volume change in sodium-sulfur battery cathodes (43) | acid (PAA) has better binding properties with sodium polysulfides. PAA also displays additional co-ordination bonding, indicating enhanced adsorption binding energies. | mortem analysis after cycling showed crack-free morphology indicating better adhesion despite volumetric expansion of the cathode. | achieved by the binders investigated. | as a tool for further exploration of alternative binders. |
|---|---|---|---|---|
| Unravelling of mechanisms by which high Na-salt concentration and pre-conditioning potentials can prevent dendrite formation, allowing for their optimization (49) | MD simulations employed to examine the effect of different salt concentrations on the interfacial nanostructure (ion number density profiles) of the C3mpyrFSI ionic liquid electrolyte at potential of zero charge. Formation of a highly aggregated Na_{x}(FSI)_{y} molten-salt-like structure was noted at inner layers close to the electrode surface. | AFM investigations showed multilayer IL interfacial nanostructure within 4.5 nm of the gold electrode. The rupture force required to break each ionic layer increases because of the strengthening of ion-ion association at 10 mol%, compared to the blank ionic liquid. Rupture force decreases as the concentration is further increased to 50 mol%. | Computational findings validated experimental observations, revealing that a molten salt-like structure at the electrode surface results in dendrite-free metal cycling at high rates. | MD simulations are a powerful tool to unravel hitherto less understood mechanisms, especially near the electrode-electrolyte interface, providing a guidance for future optimization of conditions. |
| Designing a stiff and ductile biphasic interphase on sodium metal anode (50) | DFT calculations revealed the mechanical stiffness of NaOH, whereas NaNH\textsubscript{2} showed a ductile nature. A synergistic effect was expected from the combination of both materials to promote long life stability of the Na metal anode. | High resolution TEM images showed the effectiveness of biphasic interphase on Na deposition that restricts the dendrite growth. | Stiff NaOH and ductile nature of NaNH\textsubscript{2} is predicted from DFT calculations and confirmed by experimental investigations. | This synergetic material combination can be applied for developing and designing artificial interphase for high energy rechargeable batteries. |
| Investigating the relationship between electrochemical stability in solid electrolytes and the occurrence of specific redox events (55) | DFT and MD calculations revealed the kinetically favourable indirect decomposition route of argyrodite Li\textsubscript{8}PS\textsubscript{5}Cl (LPSC) solid electrolyte (lithiation on reduction of phosphorous and delithiation on oxidation of sulfur, before decomposing into more stable products) to determine electrochemical stability window. | The (de)lithiated argyrodite phases are directly observed with X-ray diffraction (XRD) and solid-state NMR, providing direct evidence of this indirect decomposition mechanism. | Stability window was shown to be indeed due to redox events that occur during (de)lithiation, as postulated by the authors. | The findings were found to be generalizable, and can be extended to other solid-state electrolytes such as Li\textsubscript{7}La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{12} and Li\textsubscript{1.5}Al\textsubscript{0.5}Ge\textsubscript{1.5} (PO\textsubscript{4})\textsubscript{3}. |
Improving interfacial stability between the Na$_3$SbS$_4$ solid state electrolyte and Na metal anode via surface hydration (56)

| Improving interfacial stability between the Na$_3$SbS$_4$ solid state electrolyte and Na metal anode via surface hydration (56) | First-principle calculations were utilised to find probable passivating materials that are stable with Na metal. Na$_2$O and NaH are found to be promising candidates. Nudged elastic band calculations were used to investigate Na vacancy migration energies of hydrates, and identified Na$_3$SbS$_4$·8H$_2$O to possess good sodium-ion conductivity due to lower migration barriers. | Na$_3$SbS$_4$ was exposed to open atmosphere, resulting in the formation of Na$_3$SbS$_4$·8H$_2$O hydrate layer. This layer reacted with Na to form Na$_2$O and NaH as passivating materials, and was confirmed by spatially-resolved synchrotron X-ray diffraction. | Metal electrolyte interphase was characterised by non-destructive post operando synchrotron X-ray depth profiling, that gave the information of spatially resolved multi layered phase distribution, which was consistent with theoretical predictions. | Hydrates act as a potential material to stabilise interphase between solid electrolyte and metal anode. Interphase reverse design methodology can be employed to discover other possible passivating materials. |

| Reversible aluminium and magnesium ions insertion in cation-deficient anatase TiO$_2$ (60) | DFT calculations revealed that, in the presence of single and double titanium vacancies, the intercalation energy of these ions becomes more negative. Therefore, the authors introduced hydroxide and fluoride anions to engineer these vacancies. | TEM and NMR characterizations showed that number of magnesium ions intercalated directly matches the concentration of titanium vacancies, which supports their design approach. | Further testing by the galvanostatic intermittent titration technique confirmed rapid Mg ion diffusion in the vacancy engineered Ti$_{0.78}$($\square$)$_{0.22}$O$_{1.12}$F$_{0.40}$($\text{OH}^\text{−}$)$_{0.48}$ as compared to stoichiometric TiO$_2$. Similar trend was noted for Al ions. | This strategy can be applied for defect engineering as a tool to enable multivalent ion intercalation for further studies. |