From Atoms to Cells: Multiscale Modelling of $LiNi_xMn_yCo_zO_2$ (NMC) Cathodes for Li–ion Batteries

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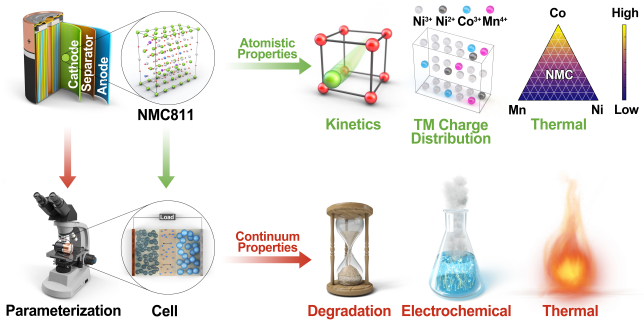
Abstract

First–generation cathodes for commercial lithium–ion batteries are based on layered transition-metal oxides. Research on ternary compounds, such as $LiCoO_2$, evolved into mixed–metal systems, notably $Li(Ni,Mn,Co)O_2$ (NMC), which allows significant tuning of the physical properties. Despite widespread application in commercial devices, the fundamental understanding of NMC is incomplete. Here, we review the latest insights from multiscale modelling, bridging between the redox phenomena that occur at an atomistic level to the transport of ions and electrons across an operating device. We discuss changes in the electronic and vibrational structure through the NMC compositional space and how these link to continuum models of electrochemical charge/discharge cycling. Finally, we outline the remaining challenges for predictive models of high–performance batteries, including capturing the relevant device bottlenecks and chemical degradation processes, such as oxygen evolution.



Lithium–ion batteries (LIBs) were developed by Whittingham in the 1970s[1,2] but did not become a promising technology until 1979, when Goodenough and Mizushima successfully demonstrated $LiCoO_2$ as a cathode and Yoshino developed a carbon-based anode instead of reactive lithium.[3] These were successfully commercialized by Sony in 1991 and have since become instrumental in portable electronics, electric vehicles, and grid storage applications.[4–10] However, to fully electrify the transport and energy sectors, further advancements in LIBs are required to achieve higher energy densities, better longevity, and lower cost, from sustainable materials. The performance of a battery is highly dependent on the choice of cathode material and the transition metals they are composed of.[11–14]

$LiCoO_2$ offered a number of attractive features, including ease of synthesis, reversible lithium insertion, high specific energy density, and high thermal stability.[15–17] However, its application was limited due to capacity fade and the cost/geopolitical issues of cobalt mining, which made large scale energy storage solutions impractical.[18,19] Other oxide materials, such as $LiNiO_2$ and $Li_xMn_2O_4$ were considered, each with their own challenges, such as the longevity and safety of $LiNiO_2$[20] and $Li_xMn_2O_4$ showing irreversible structural changes, due to strong Jahn–Teller effects and low capacity.[21] Partial replacement of Co in $LiCoO_2$ with Ni and Mn was considered, resulting in the layered oxide $LiNi_xMn_yCo_zO_2$, where $x+y+z=1$, commonly termed NMC, with subsequent numbers relating to the ratio of the transition metals.[9,22–24] These NMC materials were able to achieve a more balanced performance, preserving favourable voltage characteristics, reaching a higher capacity ($200\,\mathrm{mAh\,g^{-1}}$), and addressing cost and abundance issues.[25–27] NMC also demonstrates improved electrochemical performance, enhanced rate capability,[17,28] and better cycle life/thermal stability.[29,30]

The tuning of the transition metal compositions of NMC has been a focus of research, in an effort to optimise desirable battery properties including capacity, cyclic rate, electrochemical stability, and lifetime, whilst also reducing cost.[31] Many NMC compositions are already in use, with commercial applications shifting from NMC111 to higher Ni compositions, including NMC811 ($LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$).[32] Current investigations are now focused towards further reducing the Co content and optimising Ni–rich compositions, such as NMC811, to improve the performance of current and future generation batteries for long–range electric vehicles[33] and for use in all–solid–state LIBs.[24,25,27,34–36]

Despite the improved properties of Ni–rich NMC, these materials still exhibit rapid voltage and capacity fading, as well as poor structural and thermal stability,[17,37,38] leading to severe degradation.[31,39–43] Degradation can occur through a range of physical and chemical processes, resulting in loss of lithium inventory (LLI), loss of active material (LAM), and/or impedance increase.[44] Attempts have been made to circumvent these degradation processes using approaches including surface coating, doping with ions, and electrolyte modification;[11,45] however, current experimental probes are limited in the detail they can provide. Additional challenges lie in improving safety and prolonging the life of batteries, requiring optimal thermal and operational management. These are areas where computational modelling can provide insight and direction.

Atomistic techniques, including Density Functional Theory (DFT) and Molecular Dynamics (MD), and continuum techniques, including the Doyle–Fuller–Newman (DFN) model and its simplification, the single particle model (SPM),[46,47] broadly describe battery modelling techniques from the atomic to cell level.[48] DFT is well suited for investigating electronic structure, whereas MD, either *ab initio* or classical, can be used to provide vital information

on system dynamics. These atomistic models can provide insights into material properties, but can be limited by scale. Continuum modelling, a larger scale computational technique, is better placed to provide cell level properties. The DFN model assumes the electrodes are comprised of a homogeneous matrix of spherical particles and is able to predict the dynamics and internal states of a battery, for example, Li concentration within active materials. The SPM is a further simplification that considers one representative particle.

Combining atomistic and continuum model predictions within a multiscale modelling framework can provide a more detailed understanding of the charge and mass transport processes, resulting in more accurate predictions of battery behaviour.[49–51] DFT has increasing been utilised in parameterisation of larger scale techniques, such as classical MD.[50,52–56] One popular approach has been to use DFT calculations of migration mechanisms and activation barriers of Li-ions, in conjunction with classical MD studies of Li-ion diffusion, to gain a more complete analysis of the dynamic properties.[57,58] In a similar vein, DFT calculations of activation energies for different events to construct the basis for kinetic Monte Carlo (kMC) simulations.[59] kMC is a natural technique to include different time scale dynamic events. For example, Röder et al. used a combination of the continuum scale pseudo two-dimensional (P2D) model and a heterogeneous surface film growth model based on kMC to obtain electrochemical information, including open circuit potential (OCP), C-rate tests, and potential during film formation.[60] These predictions were in good agreement with the equivalent experimental measurements.

In this perspective, drawing from our experience as part of the multiscale modelling project of the Faraday Institution in the United Kingdom, we highlight the importance of modelling NMC cathode materials across length and time scales. We also provide an outlook to current and future challenges faced in the modelling of multicomponent cathode materials for electrochemical energy storage.

Electrons: Oxidation State Competition

The practical use of Ni–rich NMC materials in LIBs faces various challenges, including structural degradation and capacity fading. The redox reactions and consequent reversible capacity of NMC are primarily influenced by the cation ordering and spin interaction of active elements in the transition metal layers.[11,31,40,61,62] Different compositions and charge distributions result in the appearance of various valence states, e.g. Ni^{2+}, Ni^{3+}, Ni^{4+}, Co^{3+}, Co^{4+}, Mn^{4+}.[62] The coexistence and interactions of these multivalent transition metal charges and spins make it difficult to determine unique ground states for NMCs.[62] Understanding the range of transition metal oxidation states, and the roles they play in degradation processes, is therefore crucial for improving these promising cathode materials.

Ni is a key redox active element in NMC. Experimentally, Ni in NMC811 is present as a mixture of Ni^{2+} (with ground–state electronic configuration of $t_{2g}{}^6e_g{}^2$) and Ni^{3+} ($t_{2g}{}^6e_g{}^1$) oxidation states, with an average value close to 3+.[63–65] During charging–discharging cycling, Ni^{2+} can migrate from the Ni plane to the Li plane, creating Li/Ni disorder.[31,39,40] This leads to a structural transformation (layered to defective spinel/disordered rock–salt transition) and blocks the Li^+ migration channels.[40] Structural transformation is thought to be the origin of cracking and subsequent performance degradation upon lithium extraction.[37,64,66] The

dissolution of NMC, resulting in capacity attenuation, can occur due to metal disproportionation.[67] Ni disproportionation in pristine NMC811 has not been reported experimentally; however, simulations have predicted $2Ni^{3+} \rightarrow Ni^{2+} + Ni^{4+}$ disproportionation in $LiNiO_2$.[68] Charge disproportionation is observed in other cathode materials, such as pristine $LiMn_2O_4$, where $2Mn^{3+} \rightarrow Mn^{2+} + Mn^{4+}$ disproportionation is considered to be the main cause of Mn dissolution. Understanding active metal disproportionation is essential as it poses a threat of poisoning the anode[69,70] and forming inorganic layers in solid electrolyte interphase (SEI) layers,[71] which, in turn, lead to capacity fade.

The complex ordering and multivalent nature of transition metals poses significant challenges for modelling. Previous theoretical investigations have studied the influence of oxidation states on various properties of NMC materials.[25,72–76] These studies, employing various DFT functionals, have calculated Jahn–Teller distortion effects, atomic magnetic moments, and densities of states to assign metal oxidation states on the transition metal atoms. There are discrepancies observed in the literature, depending on choice of method and functional used to calculate these properties.

Sun and Zhao[25] reported that Ni^{2+} is predominant over Ni^{3+} in NMC333, NMC442, and NMC532, whereas with the increase of Ni content, the occupation of Ni^{3+} steadily increases at the cost of Ni^{2+}, as shown in Figure 1(a). In NMC811, the fraction of Ni^{3+} is reported as 58 %, whereas there is no presence of Ni^{4+} in the pristine structure.[25] In contrast, Susai et al.[76] observed fractions of Ni^{2+}, Ni^{3+}, and Ni^{4+} at around 27.1 %, 62.5 %, and 10.4 %, respectively, as shown in Figure 1(b). Dixit et al.[73] have also reported the presence of Ni^{4+} ($\approx$ 10 %) along with Ni^{2+} ($\approx$ 23 %) and Ni^{3+} ($\approx$ 66 %), which is in closer agreement with the findings of Susai et al.. The fraction of Ni^{4+} has shown to be influenced by the lithiation state, with Ni^{4+} concentration increasing rapidly in Ni–rich NMC materials as a function of Li content. However, the distribution of Ni oxidation states is not greatly influenced by doping, Figure 1(b) .[73,76] Sun and Zhao[25] also reported on the existence of Co^{2+} ions along with Co^{3+} ions in pristine NMCs, an observation which was opposed by Dixit et al..[73] Based on magnetic moments and projected density of states calculations, Dixit et al. proposed that Co remains as Co^{3+} in different pristine NMCs.[73] Mn^{4+} remains in close proximity to Ni^{2+}, influencing the super–exchange interactions among transition metals.[77] The aforementioned discrepancies between methods could be associated to the different choice of functional, where Dixit et al.[73] have employed a pure DFT approach. It could be also associated to the use of different sets of effective "+U" on-site Coulomb interaction parameters for transition metals. e.g. the employed parameters vary as U_{eff} = 6.7, 4.2, and 4.91 eV,[25] and 5.96, 5.10 and 5.00 eV[76] for Ni, Mn, and Co, respectively.

As mentioned earlier, specific transition metal oxidation states have been implicated in degradation processes in NMC materials. With the mixed valence states of Ni^{2+}/Ni^{3+}, Ni^{3+} has the priority to exchange with Li, and changes to a Ni^{2+} state with a spin–flip, to form strong linear Ni^{2+}–O_2— Ni^{2+}/Mn^{4+} super–exchange networks.[77,78] This acts as the driving force in tuning Ni/Li disorder. The presence of Ni^{4+} promotes electrolyte decomposition, forming side-products that adversely affect Li^+ transport at the electrode—electrolyte interface; thermal instability and oxygen evolution.[79] Therefore, proper elucidation of TM oxidation states in NMCs is required for their fruitful applications in LIBs. Although computationally demanding, to get better insight into the electronic properties of NMCs, the use of electronic structure approaches that can deal with the high levels of electron correlation

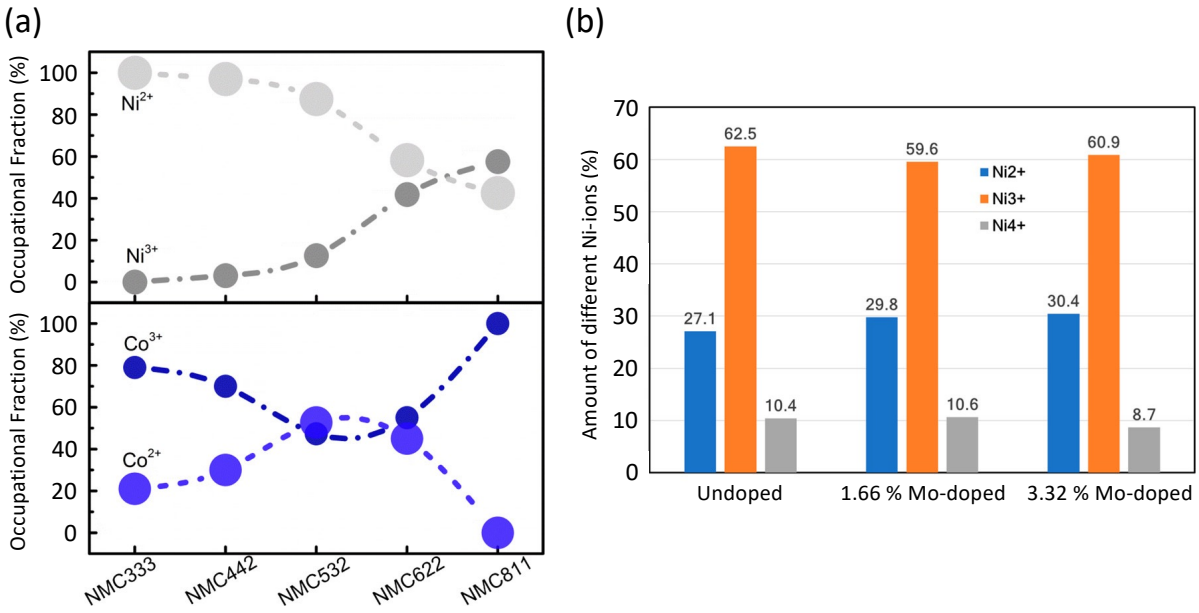


Figure 1: (a) Occupation fraction of Ni^{2+}/Ni^{3+} and Co^{2+}/Co^{3+} in the five NMC compositions. Reprinted with permission from Ref. 25. Copyright 2017 American Chemical Society. (b) Distribution of Ni-ions in different oxidation states Ni^{2+}, Ni^{3+}, and Ni^{4+} for undoped and Mo-doped NMC811 materials. Adapted from Ref. 76 (2019, American Chemical Society).

and strong competition between oxidation states is necessary. Beyond DFT, the application of techniques such as dynamical mean field theory may yield important insights into complex transition metal oxide electrodes.

Ions: Modelling of Diffusion

Understanding ion diffusion is crucial for the development of batteries with high power density, especially in solid electrodes, which presents slow ion diffusion compared to electrolytes. Ionic diffusion can often be considered as a sequence of "hops" made by ions moving between distinct crystallographic sites.[80] The rate of diffusion can be understood through the diffusion coefficient, D.

Wei et al. used DFT to investigate the hopping mechanisms in a range of NMC compositions and lithiation states.[81] The authors found that Li is more likely to diffuse via oxygen dumbbell hopping (ODH) at the early stage of charging (delithiation). When more than $\frac{1}{3}$ of Li is removed, tetrahedral site hopping (TSH) becomes more dominant. For both ODH and TSH, Li surrounded by Ni are more likely to diffuse. Wei et al. also calculated diffusion coefficients for the same NMC compositions and found them to be several orders of magnitude larger than the experimental measurements.[81] Comparably, Cui et al. used DFT to calculate the diffusion coefficients of NMC532 and NMC622. When compared to diffusion measured experimentally, the calculated DFT values were orders of magnitude larger than the experimental measurements.[82] More recently, Zhu et al. also observed this disparity in the magnitude of the diffusion coefficients for NMC442, NMC532, NMC622, and NMC71515.[83]

There have been several additional DFT studies on Li-ion migration in the pure bulk NMC-based materials using *ab initio* MD and nudged elastic band (NEB) techniques, most of which overestimate the diffusion rate in these materials, compared to experimental measurements of the real material.[84–88] DFT is well suited to investigating electronic properties and local hopping mechanisms.[87] However, when it comes to long–range diffusion, DFT is limited by time- and length- scales. Features which affect diffusion rates, such as grain boundaries and defects,[89] cannot be easily incorporated into the models. Classical MD is therefore better suited for calculating long–range diffusion, allowing simulations over longer time- and length-scales, and incorporating micro-structural features not easily included at the DFT scale.

In classical MD, the chemical interactions are described using interatomic potentials.[90–93] There are many forms of interatomic potentials, with the ability to describe heteropolar solids, such as NMC. A widely used interatomic potential for investigating diffusion properties is the Coulomb–Buckingham potential.[94] The Coulomb–Buckingham potential is derived from the Born model,[95,96] where the potential energy of the system is expressed as:

$$E(r_{ij}) = \sum_{ij} \frac{Q_i Q_j}{4\pi\varepsilon_0 r_{ij}} + \sum_{ij} A\ exp(\frac{-r_{ij}}{\rho}) - C r_{ij}^{-6} \tag{1}$$

Here, i and j are ions of charge Q_i and Q_j at a distance of r_{ij}, and ε_0 is the permittivity of free space. In the second term, A, ρ, and C are the parameters associated with the Buckingham potential. A describes long–ranged point charge electrostatic interactions, ρ is an exponentially decaying repulsive interaction, that attempts to describe interatomic repulsion at short ion–ion separations, and C describes dispersion.

Core–shell models, such as the widely used adiabatic shell model,[97] can be used with the interatomic potential to introduce polarisability into classical MD simulations.[98–102] This is done by separating the atom into two objects (the core and the shell) and tethering them together through a spring. The atomic mass is divided between the core and shell, commonly with 10 % of the atomic mass assigned to the shell.[103,104] Standard rigid ion models are not able to capture Jahn-Teller effects, which are known to be a pronounced feature in metal oxide materials, such as NMC.[21,25,72–76,105] By separating the core and shell into separate objects, through introducing a core–shell model, some aspect of the Jahn-Teller symmetry lowering can be described. However, a full treatment requires a description of angular overlap terms that require further parameterisation[106]

One classical MD study on NMC, reported for NMC111, employed core–shell Buckingham potentials.[107] Lee and Park investigated the defect energies in fully lithiated NMC111, finding the formation of defects to be unfavourable with high energies. They found the most favourable defect formation as the Li–Ni anti–site defect (0.84 eV). The authors also attempted to analyse the Li^+ diffusion dynamics; however, with no Li vacancies present, hopping events would be infrequent and isolated. Therefore, migration was not observed within the 1 ns timeframe.

To highlight the importance of capturing the complexities of layered oxide materials, such as mixed metal charges, we used Lee and Park's potentials with different NMC compositions and states of lithiation. The charge placed on the Ni was adapted in accordance with the oxidation state in the composition as, to the best of our knowledge, no interatomic potentials exist in literature for Ni^{3+}. We found that the potentials proposed for fully lithiated

NMC111 are not transferable. Indeed, a catastrophic structural collapse is observed upon removing Li (Figure 2). Classical models based on fixed–charge modelling are incapable of describing dynamic redox processes and the associated Jahn Teller instabilities. Different NMC compositions and lithiation states results in mixed transition metal oxidation states and charge disproportion, as discussed previously. Representing this complexity with classical interatomic potential models is challenging.[108–110]

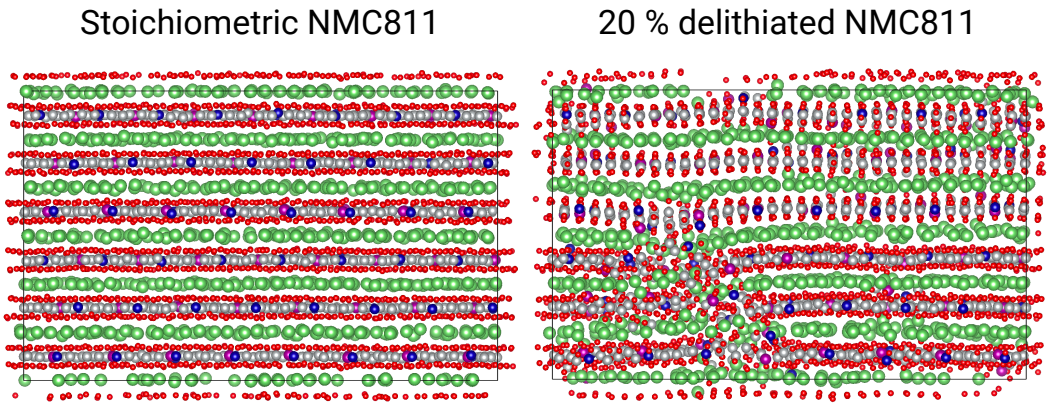


Figure 2: Structure images for fully lithiated and 20 % delithiated NMC811 after an initial equilibration MD simulation using the interatomic potentials from Lee and Park.[107]

The development of interatomic potentials, which requires model parameterisation with respect to a set of target observables, is a difficult task for these systems. For layered structures, variations of the Buckingham potential form have been developed, some using rigid–ion models,[111–114] and others using core–shell models,[99–102,107,111,115] with a mixture of formal and partial charges. We made attempts to apply the fitting routines from established codes, including the General Utility Lattice Program (GULP),[116] Atomicrex,[53] dftfit,[54] and potfit.[55] Each code possesses unique functionality, however, none were able to produce robust potentials, capable of adequately describing the atomic interactions, for NMC or $LiNiO_2$. A software, POtential Parameter Optimisation for Force–Fields (PopOff),[52] has been specifically developed within the Faraday Institution for fitting different permutations of the Buckingham potential. Its modular design allows flexible fitting of both rigid–ion and core–shell models, as well as formal and partial charges. Here, we discuss important aspects of fitting cathode potentials using this code.

In systems such as NMC and $LiNiO_2$, the longer–range Coulombic terms are much larger than the short–range interactions. In these cases, the atom charges need to be scaled down (partial charges) to restore the influence of the short–range interactions. A scaling factor of 60 % formal charge is commonly used,[117] however, partial charges are system dependent. Figure 3 (a) shows χ^2 (fit error) for a fitted Buckingham potential for $LiNiO_2$ reducing with the charge scaling factor, until approximately 60 % of the formal charge, where it starts to plateau. This is in broad agreement with literature, with a slightly improved fit at ∼50 % formal charge.

Fitting rigid–ion potentials for $LiNiO_2$ with partial charges resulted in a fit error of $\chi^2 = 1.67$. By introducing a core–shell potential on the oxygen, with Li and Ni remaining rigid–

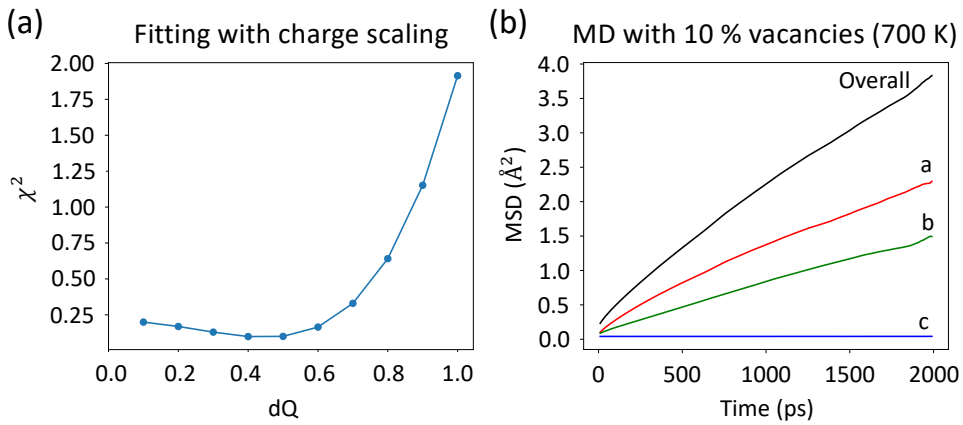


Figure 3: (a) Plot of the fit error, χ^2, of $LiNiO_2$ as a function of the charge scaling factor, dQ, and (b) Plot of the mean squared displacement of Li in $LiNiO_2$ with 10 % Li vacancies at 700 K. As this is a layered material, it is expected that no movement will occur in the c direction, only in a and b.

ion, χ^2 was reduced to 0.37. This presents evidence that a core–shell potential is required to more accurately reproduce the forces and physics of the system. In the case of the oxygen core–shell potential, the fitting process resulted in a spring constant of 15.443 eV·Å^{-2}, with a charge of -1.48 e on the shell and 0.520 e on the core. Here, the best fit (lowest χ^2) was a core–shell model on the oxygen in a partial charged system. The resulting potential was used with a 10 % delithiated $LiNiO_2$ supercell at 700 K to conduct MD studies on the diffusion within the material. The mean squared displacement, Figure 3 (b), represents small movements of Li, however, the resulting self–diffusion coefficient, 6.664×10^{-8} cm^2 s^{-1}, is within the measured range.[118,119] These results indicate that including a core–shell model for the oxygen and using partial charges are necessary to include in interatomic potential models, to get a more accurate representation of these systems.

The results presented here for comparing core–shell, rigid–ion, and formal/partial charges highlight the careful consideration needed when fitting potential models for heteropolar solids, such as NMC. Fitting parameters also need to be tailored to the type of study being conducted. For example, if interatomic potentials are fit only to structural properties, they cannot be expected to describe the redox behaviour of a cathode. If electronic features such as dielectric constant are included, then redox chemistry should be better represented. Other features such as charge equilibrium and ligand field effects should also be considered. Fitting to every material property is not feasible, however, fitting to a broad range of the most relevant properties to the study is needed.

Tools are currently in development to make fitting interatomic potentials more accessible, including more advanced statistical sampling that can train more robust models with less data.[52,53,55,120] In particular, machine learning (ML) has emerged as a powerful approach for developing interatomic potentials.[56] One example is the development of accurate Li–Si potentials. Building on prior Si potentials,[121–123] Artrith et al. and Onat et al. both developed neural network models for Li in amorphous Si anodes.[124,125] These works helped underline the possibilities of ML potentials especially for battery materials modelling.[56]

More generally, deep learning MD or "on-the-fly" ML is an emerging alternative for studying dynamic properties of materials beyond the limits of traditional simulations. Houchins and Viswanathan developed ML potentials for NMC and used a neural network model, trained on DFT calculations with a prediction accuracy of 3.7 meV/atom and 0.13 eV/Å for energy and force, respectively.[126] Wang et al. also used ML interatomic potentials and MD coupled with on-the-fly ML tensor potentials.[127] The calculation efficiency was reported to increase by 7 orders of magnitude compared to *ab initio* MD, significantly reducing the uncertainty in calculated migration energies and improving agreement experiment. With all the proposed benefits of ML potentials, certain limitations should also be noted such as the treatment of long-range electrostatics that are critical for ionic solids. However, ongoing developments include the description of electrostatics model parameters, such as partial charges, local dipoles, and polarisability.[128,129]

Phonons: Thermal Transport

Crystals are often considered as consisting of atoms held in static positions through stiff chemical bonds. In reality, atoms are constantly vibrating around their average crystallographic positions in even the hardest of crystals. Lattice dynamics, based on the calculation of the interatomic force constants in a crystal, is a powerful tool to model thermal effects, from heat capacity to thermal expansion. Recently, the description of anharmonic effects including vibrational lifetimes and thermal conductivity has become accessible for multicomponent solids.

There have been a number of studies on the thermal properties of NMC. Yang et al. reported the harmonic phonon dispersion for the $LiMO_2$ (M = Ni, Co, Mn) endpoints in the NMC oxide system.[105] These results reveal that the Jahn–Teller effect is more pronounced in the crystalline $LiMnO_2$, with three distinct bond lengths for the transition metal-O bonds. The authors found that the medium and low frequency modes are mainly due to motion of Li and transition metals, while the high frequency modes (> 14 THz) are vibrations involving the transition metal and O atoms. The phonons also provide information of a group, theoretical analysis within the group assigns the irreducible representations of the acoustic and optic branches. Of these, some modes are infra–red (IR) active or Raman active, which is comparable with experimental IR/Raman spectra, with differences likely due to the volume expansion at finite temperature.[130] For NMC alloy systems, Sun and Zhao showed that the longitudinal acoustic mode frequency increases from NMC333 to NMC811 (Figure 4), due to the weaker electron screening.[25]

Both the electrochemical and thermal properties of NMC depend on its composition. An increase in Ni content results in an increase in specific discharge capacity and total residual lithium content. However, the corresponding capacity retention and safety characteristics gradually decreased, as shown in Figure 5a.[17] Increasing Ni/Mn content leads to lattice thermal conductivity suppression.[105] Thermal conductivity decays exponentially with increasing temperature, due to enhanced phonon scattering, resulting from the larger thermal population of phonon modes. Figure 5 b shows that, at room temperature, NMC811 has the lowest predicted thermal conductivity of $9.3\,\mathrm{W\,m^{-1}\,K^{-1}}$, while NMC622 and NMC111 are higher at 13.3 and $17.9\,\mathrm{W\,m^{-1}\,K^{-1}}$, respectively. In most devices, the thermal conductivity

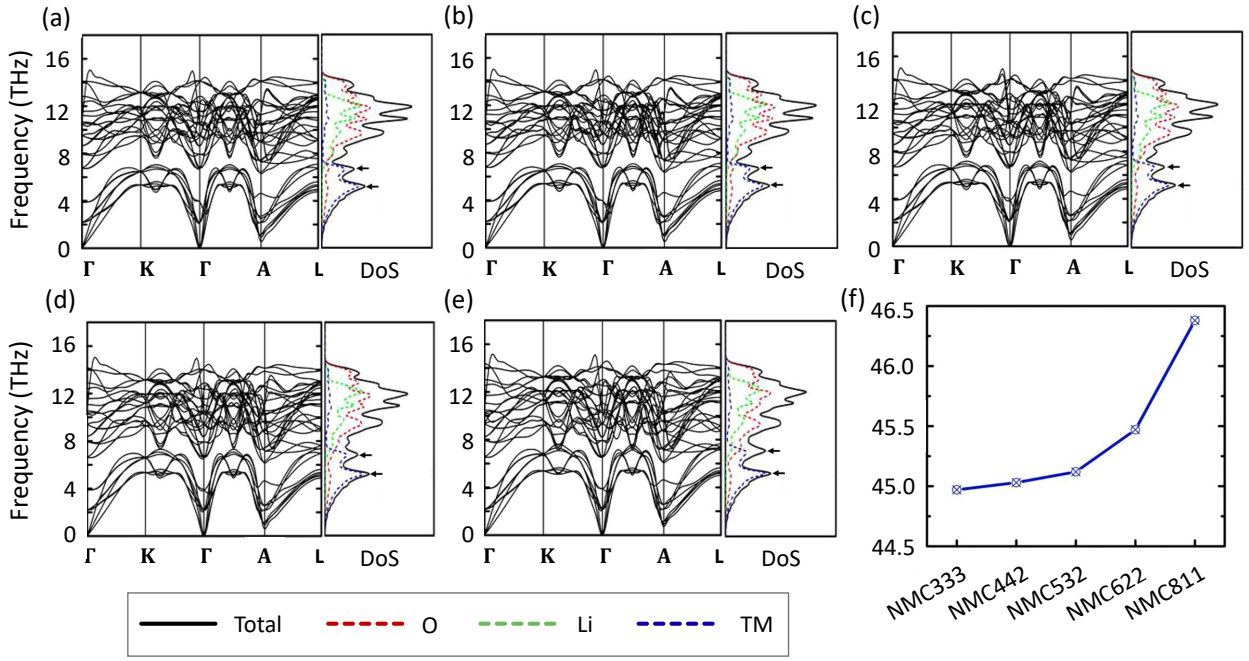


Figure 4: (a-e) Phonon dispersion and density of states (DoS) of NMC333, NMC442, NMC532, NMC622, and NMC811, respectively. Above the acoustic branch (0–6 THz) lies a dense optic phonon branch that reflects the structural complexity of these mixed-metal oxides. (f) Longitudinal acoustic frequency in the five NMC compounds around the Γ point of the Brillouin zone. Adapted from Ref. 25 (2017, American Chemical Society).

is much lower than these theoretical upper limits.[131,132] Both charging (delithiation) and having smaller grain sizes in polycrystalline cathode materials softens the lattice, leading to smaller phonon velocities and stronger phonon scattering.[133,134] These studies show the accessibility of tuning cathode material properties systematically by optimizing the ratio of the transition metals in NMC alloys, overcoming some of the challenges in battery cathode design.

Cells: Operation and Degradation

Atomistic modelling is ideal for investigating bulk and localised behaviour, however, these predictions do not provide macroscopic information on material behaviour at the cell level. Here, continuum models are well suited to provide further detail and insights. These are governed by mathematical expressions that relate concentrations and potentials (partial differential equations). Values describing different properties, such as diffusion coefficients and equilibrium potentials, are required as inputs or parameters, which can be obtained from experiments or using the atomistic simulation techniques discussed earlier.

One example of a continuum level model is the DFN model, this requires over 25 parameters, with the exact number being dependent on how the equations are expressed.[135] These parameters are related to the physical, chemical and electrochemical properties of the cell, incorporating the ionic and electron transport properties of individual electrodes and

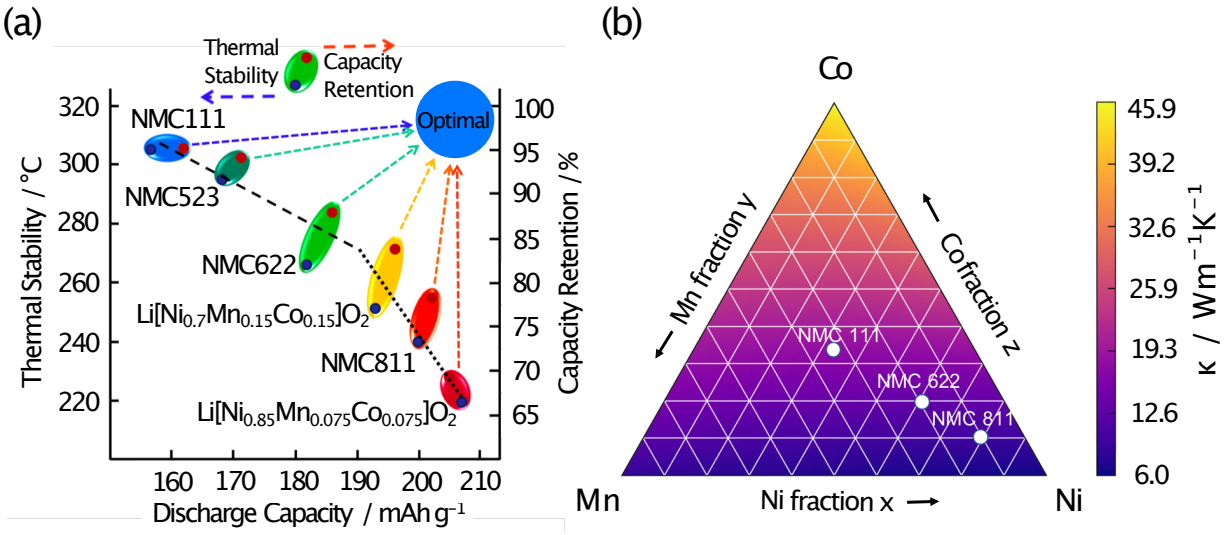


Figure 5: (a) Relation between discharge capacity, and thermal stability and capacity retention of NMC batteries. Adapted from Ref. 17 (2013, Elsevier). (b) Ternary map of the thermal conductivity map κ of the NMC system with consideration of mass variation at the cation site. Adapted from Ref. 105 (2020, American Chemical Society).

the electrolyte. Parameter estimation can be used to simplify the process, where only voltage and current measurements of the battery are used to elucidate the specific parameters, removing the need for a cell teardown, i.e. dismantling the cell to extract the components for extensive characterisation.[136] Care must be taken due to the large number of parameters that have to be fitted, and the potential for over fitting. Computational expense can preclude the use of this model in battery management systems and often simple equivalent circuit models are favoured instead.[137] The DFN model has been used extensively in battery material development, as it provides more detailed physical insights compared to other model classes.[138]

Recent interest in Ni–rich cathodes has seen the DFN model used extensively to understand the use of graded electrodes (containing multiple electrode particle sizes), to deconvolute capacity and power fade predictions, and to investigate the efficacy of tab and electrode designs for fast charging.[139–141] This research has been dependent on parameter sets for NMC materials being reported, however, these values may not reliably describe the properties of Ni–rich NMC, because studies often use parameters determined for cathodes with lower/unknown Ni content. For example, Richardson et al. modelled an NMC material, using the properties of $LiNi_{0.4}Co_{0.6}O_2$, directly measured by Ecker et al..[139,142] Kindermann et al. measured the geometry of an NMC –with unknown stoichiometry– electrode, extracted from a Samsung cell.[140] Electrode diffusivity and reaction rates were estimated and not evaluated directly, while the equilibrium potential was represented by that of an NMC111 material reported elsewhere.[143]

Several NMC batteries with low nickel content have been experimentally parameterised.[142,144,145] Ecker et al. reporting of the physical and chemical properties of a commercial cell also offered a comparison of different techniques used to evaluate the electrode diffusivity.[142] Schmalstieg

et al. investigated an NMC111 battery, mapping the exchange current density, its activation energy, and electrode diffusivity as a function of lithiation, by defining the stoichiometries of each electrode.[144] Liebig et al. studied the electrochemical behaviour of a large format NMC cell, extending the model predictions to include thermal behaviour.[145] These papers outline the cell properties required for simulations and the methods used to determine them. Thermal properties at the atomistic scale can be connected to performance and inform material selection for application. For example, $LiCoO_2$ has a significant entropy change compared to other cathode materials, including NMC. Analysis for NMC indicates a small amount of reversible heat generation, therefore thermal management of NMC-based batteries is more effective.[146] Parameterisation is essential for modelling NMC cathode materials. Simulations act as a powerful tool to investigate the properties of NMC and optimise design without the need to conduct resource–intensive experiments, but the reliability of predictions is dependent on the quality of data used to construct the model.[147]

Although the methodologies developed in these works can be applied to other materials, for modellers investigating Ni–rich NMC materials these properties provide limited utility, as they do not accurately describe their behaviour.[148] This is attributed to the presence of different thermodynamic phases compared to NMC811, which affects the dependency of the material physical and electrochemical properties on the state of lithiation.[17] For example, the H2 $\rightarrow$ H3 phase transition above 4.1 V has not been reported in NMC materials with Ni content below 80 %.[149]

More recently, cells with NMC811 chemistries have been parameterised; Chen et al. elucidated the parameters for a commercial 21700 cylindrical cell containing NMC811 vs Graphite-SiO_x, and validated and tuning these values for cell discharge.[150] Sturm et al. reported a full electrochemical–parameterisation of a DFN model, to study lithium plating during fast charging of a NMC811/SiC cell.[141,151]

Traditionally, the sourcing of parameters required an extensive literature search and/or knowledge of prominent authors in the field, to collate a collection of parameters which represented the component parts in a cell. It should be noted that this often relied of various sources, with no complete data-set from a single cell parameterisation and validation experiment. Recently, the development of databases and software that collate parameter values for battery components have streamlined this process and proved essential for modelling applications.[152,153] Wang created a database that details over 100 parameterisations of batteries and the individual components and techniques that have been used to determine them.[154] Additionally, Python Battery Mathematical Modelling (PyBaMM), a software package explicitly developed for continuum modelling, caters for multiple model definitions (e.g. DFN, SPM, and SPMe (SPM with electrolyte)) and allows the construction of virtual batteries from various component chemistries.[155] These include parameters for the commercial NMC811 electrode mentioned above,[150] which have been utilised in multiple investigations.[152,153] PyBaMM is a powerful tool for in modelling NMC behaviour, amongst other materials and cell chemistries. It provides researchers with parameter sets and robust code to simulate the electrochemical and thermal behaviour in relatively few lines of code (Figure 6).

Validation of model predictions requires experimental data, from charge-discharge voltage curves at different current densities and long-term cycling experiments. Providing open data sets of parameter values and raw experimental validation data files improves accessibility and transparency of these models. There are several instances where data sets have been made

available; Chen et al. have made available data on the discharge and subsequent relaxation of the NMC811–based cylindrical cell that was used in the validation of the parameter set in Ref. 156.[150] Devie et al. have provided data sets on the degradation of 18650 cylindrical cells, based on NMC, NCA, and LFP chemistries.This ongoing study examines the influence of operating conditions on the ageing of cells (Ref. 158).[157]

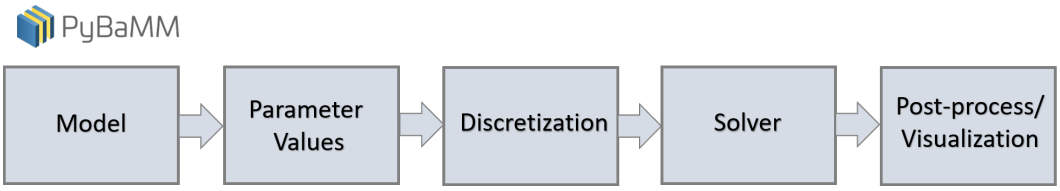


Figure 6: The PyBaMM workflow has been designed to use a pipeline approach to define, discretize, and solve using electrochemical models. Adapted from Ref. 155 (2021, Ubiquity Press).

It is important to be aware of the nuances in reported parameter values which arise from the different test set-ups and methodologies, and the collation of values from various sources, some assumed or fitted, often used to populate the full parameter table. The thermal and electrochemical behaviours of battery materials have been widely described, being able to use these to accurately predict cell degradation has proven more difficult. Partially due to these difficulties in accurate parameter measurements during the cell cycling, and hence the limited full parameter and validation data-sets from a single cell source. Edge et al. provide a detailed guide to understanding degradation modes, their mechanisms and the resulting effects, to design experiments and develop cell life-time models.[159] There are two key degradation modes for the NMC positive electrode material which directly affect impedance, power, and capacity: loss of lithium inventory and loss of active material.[160,160] Repeated cycling causes volume changes, resulting in particle cracking,[161] and leading to loss of contact between the particles and current collector.[160] The cathode electrolyte interphase (CEI) layer, which forms in the cracks, triggers side reactions with the electrolyte, leading to passivation layer formation and consumption of lithium ions (LLI) and hence impedance increase.[160] Operating at high voltages ($\geq$3.7 V) also promotes CEI formation, as well as other detrimental surface processes, such as gas evolution (O_2, CO_2, and CO).[162] NMC811 has a higher susceptibility towards oxygen evolution, due to its higher nickel content.[163] Long term cycling and operating at high voltages and temperatures also causes dissolution of transition metals,[164] and NMC811 has a higher susceptibility to this due to the reactivity of highly oxidised nickel cations with the electrolyte.[165] Accurate prediction of cell behaviour requires monitoring of these processes and deciphering of the interplay between processes. Knowledge of the changes in the physical, chemical and electrochemical parameters are needed for validation of these models. Examples of NMC degradation models include SPM[166,167] and DFN.[168]

Oxygen evolution can be modelled as the oxidation of electrolytes at the positive electrode introducing a simple, kinetically limited Tafel equation[166,168] in the DFN/SPM model. Jana et al. proposed that the capacity fade is a linear function of the oxidation current density, which the authors used in the Tafel equation to model the electrolyte oxidation at the NMC111-type positive electrode.[167] However, theoretical understanding and available

models for the source of the oxygen evolution and its effect on the capacity fade are not well developed. Recently, Ghosh et al. have proposed a physics–based shrinking core model for the degradation of NMC811 electrodes that undergo a structural reorganisation involving oxygen loss and the formation of a disordered (spinel or rock-salt structure) passivation layer.[169] The model considers O-release from the bulk–passivation layer interface and the rate of reaction is controlled by either O-diffusion through the passivation layer or the reaction kinetics at the interface. Li–entrapment and growth of the passivation layer cause capacity fade. Two limiting cases, *'diffusion dominated'* and *'reaction dominated'*, manifest with a variation in the relative rates of O-diffusion and O-release, and the thickness of the passivation layer.

Transition metal dissolution at the positive electrode is modelled using a first order chemical reaction, limited by the concentration of H^+ ions in the electrolyte.[170] H^+ ions are generated from $LiPF_6$ salt dissociation in the electrolyte and solvent oxidation at the positive electrode. While $LiPF_6$ dissociation in the presence of H_2O is modelled using a chemical reaction rate, solvent oxidation is modelled using irreversible Butler–Volmer kinetics.[170] Lin et al. provide detailed DFN model equations for transition metal dissolution at the lithium manganese oxide type positive electrode, coupled with SEI layer formation at the negative electrode. Transition metal deposition on the negative electrode is also included in the model.[168] The growth of the CEI can be modelled in a similar way to any of the SEI layer growth models.

Key degradation processes that take place at the positive electrode material and their effects have been discussed and fundamental characterisation techniques that aide tracking and monitoring of these processes have been introduced. In order to use models to estimate aging mechanisms during normal or even fast charging, accurate determination of the parameters that describe the physical, chemical, and electrochemical properties of the cell is key. Electrochemical techniques are fast and practical diagnostic tools used in *in situ* characterization of battery performance, providing information on capacity, resistance, and coulombic efficiency. The reliability of models to predict a cell's behaviour is highly dependent on the type of cell, and requires accurate experimental parameter and validation data, preferably from a single source cell.

Summary and Outlook

We have reviewed recent progress in the modelling of NMC electrodes from the atomic to the cell scale. Looking at each length scale, a number of challenges can be identified. For electronic structure studies, proper elucidation of the oxidation states of mixed transition metals in NMC materials during battery cycling is important. Layered oxides with high Ni content have three critical challenges: cyclic degradation, thermal instability, and air instability, all of which are related to the reactivity of Ni^{3+} or Ni^{4+} in contact with the liquid organic electrolyte or ambient air.[43] The presence of multiple transition metals with mixed oxidation states also impacts the thermodynamic stability of NMC materials, which remain difficult to describe in traditional phonon descriptions of crystal vibrations and associated free energy contributions.

For molecular dynamics studies, one bottleneck is the lack of interatomic potentials with

the ability to accurately describe essential properties of electrodes, such as the redox chemistry associated with battery cycling. To achieve this, fitting potentials to better training data and more sophisticated functional forms is needed. Progress has also been made in using machine learning to develop more flexible potentials. Deringer et al. recently published a progress update, showing how machine learning is improving interatomic potentials by "learning" from electronic structure data, giving better accuracy in approximating material properties;[56] however, a challenge there is in the transfer from simple elemental solids to multicomponent oxides.

Inaccuracies in continuum models manifest due to the lack of complete parameter sets and differences in experimental design. Realistic models for cell lifetime and operation require a comprehensive understanding of degradation processes. To obtain representative data, greater physical and chemical characterisation is needed, particularly from in-situ studies. The use of multiple diagnostic tools can produce a rich data for greater accuracy in parameterisation and validation of models, leading towards the design of more realistic models for life time prediction. It should also be noted that literature information may not be representative of the active material in the cell being modelled and mistakes can easily be propagated.[48] The construction of a parameter database could prevent the reproduction of errors, however equally important is an understanding of the experimental techniques used in parameter extraction and the model assumptions. Ideally, the theory underpinning the experimental parameter extraction needs to be consistent with that of the model to make truly robust predictions.

Life-time prediction from continuum models do not necessarily need the precise degradation mechanism, as LAM or LLL can be reproduced through many different negative or positive electrode lithium loss mechanisms. However greater understanding of the physics of the processes is required for truly accurate and predictive models. These can be used, for example, to identify key conditions for extending cell life-time and performance. Degradation experiments and fundamental molecular scale studies (including DFT), to understand the mechanisms, are essential for the development of whole–cell degradation models.[155]

Connecting continuum and atomistic model predictions can provide a more detailed understanding of the charge and mass transport processes, resulting in more powerful predictions of battery behaviour. Attempts to join length scales have previously been attempted, however, there is no simple solution due to the difference in mathematical principles used in each model.[171] Continuum models comprise of partial differential equations (PDEs), while atomistic models often use discrete models.[172] This difference in mathematical principles leads to different calculable properties. For example, in atomistic modelling, charge transport is related to self–diffusion within the crystal, whereas charge transport in continuum modelling relates to macroscopic diffusion in the electrode, often being experimentally determined. Solutions to overcome this mismatch in calculable properties are of great interest and one of the biggest challenges in obtaining consistent, multiscale models of NMC in particular and battery technologies in general.

Biographies

Lucy M. Morgan: Lucy received her PhD in Chemistry from the University of Kent before taking a role as a postdoctoral research associate at the University of Bath. Her research has focused on scientific code development and the molecular dynamics modelling of of NMC cathode materials and argyrodite solid electrolytes.

Mazharul M. Islam: After obtaining his PhD in Theoretical Chemistry from the University of Hannover, Mazharul has worked as a research associate/fellow at the University of South Australia, CNRS in Paris, the University of Bonn, and the University of Bath. He is currently a research associate at the University of Cardiff.

Hui Yang: Hui graduated with an Erasmus Mundus Masters in Theoretical Chemistry and Computational Modelling (TCCM) from KU Leuven (Belgium). She was awarded her PhD in Physics from University College London (UK) and is currently a postdoctoral researcher at the Imperial College London (UK), working on thermal transport in batteries.

Kieran O'Regan: Kieran is a PhD student at the University of Birmingham and the Faraday Institution. His research involves the parameterisation of different battery chemistries, focusing on commercial cells. His research has led to the spin-out company About:Energy, that provides tailored battery testing and modelling services to industry.

Anisha N. Patel: Anisha received her PhD from the University of Warwick in electrochemistry studying graphite. She completed a fellowship at the University of Paris Diderot, followed by a postdoc at Ulm University, and is currently a research electrochemist and facility manager focusing on failure in Li ion and solid state batteries.

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Emma Kendrick: Emma is Professor of Energy Materials at the University of Birmingham and has worked in industry and academia extensively on energy materials and devices. Her research focuses on the translation of novel functional materials into applications, with battery technology being a key theme. Emma holds over 100 publications and 21 patents.

Monica Marinescu: Monica is a Senior Lecturer in the Department of Mechanical Engineering at Imperial College. She creates a variety of models, electrochemical and reduced order, and bespoke experiments to identify the mechanisms limiting the performance of batteries and supercapacitors, and inform the design of better cells and packs.

Gregory J. Offer: Gregory is Professor in Electrochemical Engineering, Imperial College London. His research is at the interface between the science and engineering of electrochemical devices and focuses on understanding the limits of operation, degradation mechanisms and failure modes of batteries, supercapacitors and fuel cells.

Benjamin J. Morgan: Benjamin is a Royal Society University Research Fellow at the University of Bath. His research uses atomic-scale modelling to understand energy materials, with a focus on understanding structure–composition–property relationships in lithium-ion battery materials.

M. Saiful Islam: Saiful is Professor of Materials Modelling at Oxford University after a period at the University of Bath. Raised in London, Saiful obtained his PhD from UCL, then a fellowship at Eastman Kodak, New York. He received the 2020 ACS Award for Energy

Chemistry and presented the 2016 BBC Royal Institution Christmas Lectures.

Jacqueline Edge: After completing her Ph.D. in Hydrogen Storage at UCL, Jacqueline ran the Energy Storage Research Network in the Energy Futures Lab at Imperial College London. She currently works in the Mechanical Engineering Department as a Project Leader for the Faraday Institution, managing the Multiscale Modelling of Li-ion Batteries project.

Aron Walsh: Aron is Professor of Materials Design at Imperial College London. He leads a team of researchers working on the development and application of computational tools to model energy conversion and transport in materials at the atomic scale.

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Quotes

- Understanding active metal disproportionation is essential as it poses a threat of poisoning the anode
- If interatomic potentials are fit only to structural properties, they cannot be expected to describe the redox behaviour of a cathode
- Both the electrochemical and thermal properties of NMC depend on its composition
- Fitting potentials to better training data and more sophisticated functional forms is needed
- Realistic models for cell lifetime and operation require a comprehensive understanding of degradation processes