



Electronic Structure Engineering of Cathode Materials: Mechanisms and Perspectives

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Abstract

The electronic structure of a cathode material sets its redox chemistry, energy density, transport kinetics and structural stability, yet it is rarely discussed in conjunction with the structural design strategies that are used to improve performance. This perspective links electronic energy levels to the electrochemical properties of cathode materials. We first describe how transition-metal 3d and O 2p states, orbital hybridization, charge distribution and interfacial energy-level alignment control capacity, voltage, rate capability and cycling stability. We then re-examine four common strategies, namely elemental doping, defect engineering, composite-structure design and surface modification, in terms of what each does to the electronic states: dopant-induced orbital reconstruction, defect-related states, interfacial charge redistribution, band alignment and surface electronic modulation. These changes act on redox activity, on ion and electron transport and on interfacial stability. We close by arguing that the evolution of the electronic structure during cycling,

and the deliberate engineering of energy levels, should guide the design of high-energy-density, durable cathodes.

Keywords: electronic structure, cathode materials, energy-level engineering, layered oxides, elemental doping.

1 Introduction

Transition-metal (TM) layered oxides are leading cathode candidates for high-energy-density power batteries because of their high theoretical capacities [1–3]. Ni-rich compositions such as $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (NCM811) deliver high capacity through $\text{Ni}^{2+}/\text{Ni}^{3+}/\text{Ni}^{4+}$ redox while using less of the costly elements [4]. As the Ni content rises, however, both the electronic structure and the crystal structure become less stable, and $\text{Li}^+/\text{Ni}^{2+}$ cation mixing, surface reconstruction and interfacial side reactions follow [5, 6]. High-voltage and Li-rich cathodes have been developed to push the operating voltage and capacity further by using additional high-potential redox processes. Manipulating the local electronic structure of electrode materials, for example through dual-ion doping that shifts the TM 3d–O 2p band positions, has provided new routes to tune these electrochemical synergies [7]. In Li-rich layered oxides, O 2p orbitals take part in anionic



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redox alongside the conventional TM cationic redox and supply extra capacity [8], but the same process brings lattice-oxygen release, voltage decay and poorer long-term cycling stability [9].

Cathode development therefore faces a trade-off. Deeper TM redox, anionic redox and a higher operating voltage all raise capacity and energy density. Pushed too far, the accompanying changes in electronic structure destabilize the electronic states of the material and lead to structural degradation and interfacial instability. During high-voltage cycling, for example, the shift of the cathode Fermi level can promote electrolyte oxidation and decomposition and leave an unstable cathode electrolyte interphase (CEI) [10], and unstable hybridization between TM 3*d* and O 2*p* orbitals can cause oxygen release and irreversible lattice reconstruction [11]. Elemental doping, defect engineering, composite-structure design and surface modification are all used to counter these problems. They have mostly been developed by empirical optimization, and their mechanisms are usually explained through crystal-structure evolution, ion diffusion or interfacial stabilization, without a common description in terms of electronic structure. Looking at these strategies from the standpoint of electronic energy levels helps to clarify what each of them actually does.

The next section relates the electronic-structure features of cathode materials to capacity, voltage, rate capability and cycling stability. Section 3 then re-examines the four strategies above from this standpoint, and Section 4 gives our view of where electronic-structure engineering of cathodes should go next.

2 Electronic Structure and Electrochemical Properties of Cathode Materials

The electronic structure of a cathode determines which redox processes are accessible, how charge is transferred, and whether the structure survives repeated lithium extraction and insertion (Figure 1). Crystal structure and composition are the usual starting points for discussing performance. The electronic energy landscape is more fundamental: the relative positions of the TM 3*d* states, the O 2*p* states and the Fermi level fix the redox activity, the electronic conductivity and the interfacial reactivity of the material.

2.1 Electronic Structure and Capacity

The reversible capacity is set by the number of electrons exchanged in the redox reaction during lithium extraction and insertion:

$$Q = \frac{nF}{3.6M} \quad (1)$$

where Q is the theoretical specific capacity (mAh g^{-1}), n is the number of electrons transferred per formula unit, F is the Faraday constant ($96\,485 \text{ C mol}^{-1}$) and M is the molar mass of the formula unit (g mol^{-1}).

In conventional cathodes the capacity comes from oxidation and reduction of the TM ions. In layered oxides such as LiCoO_2 and $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ it is tied to the TM 3*d* states: on charging, electrons are removed from occupied TM states and Co^{3+} is oxidized to Co^{4+} , or $\text{Ni}^{2+}/\text{Ni}^{3+}$ to Ni^{4+} [12, 13].

TM redox is limited by the number of electronic states available. Li-rich layered oxides add oxygen redox on top of it [14]: during deep delithiation the O 2*p* states contribute to charge compensation, so more electrons can be exchanged reversibly than TM redox alone allows.

In electronic terms, the overlap and relative energy of the TM 3*d* and O 2*p* states decide whether these extra redox states can be reached. A suitable configuration activates more reversible redox centers and raises the specific capacity. Too much oxygen redox destabilizes the lattice oxygen and leads to irreversible oxygen release, so the gain in capacity has to be weighed against the stability of the electronic structure (Figure 1).

2.2 Electronic Structure and Voltage

The open-circuit voltage of a cell is the difference between the electrochemical potentials of the anode and the cathode:

$$V_{\text{oc}} = \frac{\mu_{\text{A}} - \mu_{\text{C}}}{e} = \frac{\Delta E}{e} \quad (2)$$

where μ_{A} and μ_{C} are the electrochemical potentials (Fermi levels) of the anode and cathode, e is the elementary charge, and ΔE is the energy difference between the electronic states involved in the redox reaction (Figure 1).

A lower cathode Fermi level means a stronger tendency to accept electrons, a higher redox potential and a higher operating voltage. The energies of the TM 3*d* and O 2*p* states are therefore what determine the

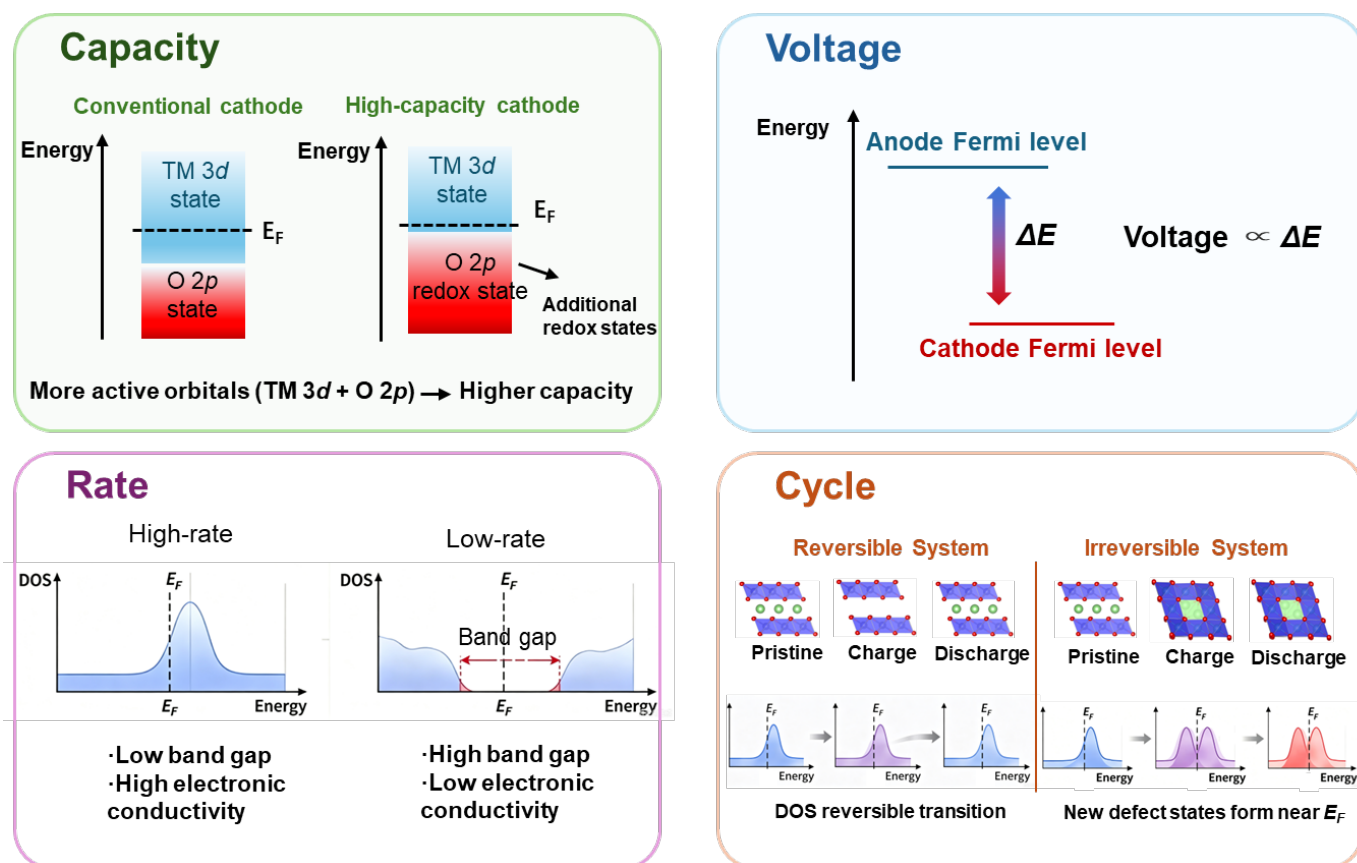


Figure 1. Electronic structure as a bridge between cathode materials and electrochemical performance. DOS: density of states.

voltage [13]. In LiFePO_4 , for example, the strongly covalent P-O bonds of the PO_4^{3-} polyanion exert an inductive effect: they weaken the Fe-O covalency, lower the energy of the Fe 3d redox states, and so raise the $\text{Fe}^{2+}/\text{Fe}^{3+}$ potential [15]. Spectroscopic and computational studies have further shown that the occupied Fe 3d and O 2p states undergo a non-rigid reshuffling during (de)lithiation, keeping the redox-active states pinned near the Fermi level and thereby stabilizing the oxygen framework through the charge and discharge process [16]. In layered oxides the same end is reached by adjusting TM-O orbital hybridization, which shifts the electronic energy levels and tunes the operating voltage [17].

Raising the voltage is thus a matter of regulating electronic energies. Aligning the redox-active states appropriately gives access to high voltage without giving up structural stability.

2.3 Electronic Structure and Rate Capability

Rate capability depends on how fast Li ions diffuse and electrons move. Fast charge transfer needs enough electronic states near the Fermi level for electrons to migrate.

Materials with continuous states and a high density of states (DOS) near the Fermi level generally conduct electrons well and show fast redox kinetics. Materials with a wide band gap and few states near the Fermi level conduct poorly and have low rate performance. LiFePO_4 is the familiar case: structurally very stable, but a poor electronic conductor because of its insulating electronic structure. Carbon coating improves its rate capability by tuning the electronic structure of the surface layer, opening additional electronic pathways and lowering the barrier to charge transport [18].

High-rate performance therefore calls for control of the band structure and of the states near the Fermi level. In practice the rate capability is also limited by lithium-ion diffusion in the lattice and along grain boundaries, so electronic-structure engineering has to raise electron mobility while keeping the lithium diffusion pathways open [19]. Surface engineering strategies, such as introducing electronically conductive Co nanoshells onto Ni-rich particles, have demonstrated that simultaneously enhancing electron transport and Li^+ diffusion kinetics is achievable through targeted interfacial

modification [20].

2.4 Electronic Structure and Cycling Stability

Long-term cycling stability depends on whether the electronic structure evolves reversibly as lithium is repeatedly extracted and inserted. Ideally the electronic states and the redox processes are the same after each cycle.

At high voltage, large changes in electronic structure can cause irreversible structural reconstruction and interfacial degradation. In high-nickel layered oxides, unstable Ni 3*d* and O 2*p* states lead to oxygen release, surface phase transformation and TM migration, which increase the impedance and reduce the capacity. The electronic interaction between cathode and electrolyte also controls how the CEI forms and how stable it is. When the cathode Fermi level falls below the highest occupied molecular orbital of the electrolyte components, electrons are transferred from the electrolyte to the cathode; the electrolyte is thereby oxidized, and unstable interfacial products accumulate.

Surface modification strategies — ranging from bulk co-substitution combined with stabilizing surface coatings [21] to electronically passivating protective layers on the active-material surface [22] — can suppress continuous interfacial electron transfer to the electrolyte, stabilize the CEI and extend cycle life. Cycling stability thus depends on the reversibility of the electronic energy landscape as well as on structural integrity.

These four relationships are the basis on which the strategies of the next section are examined.

3 Electronic Structure Engineering of Cathode Materials

3.1 Dopant-Induced Electronic Structure Regulation

Elemental doping is among the most widely used ways to improve cathode performance [26–28]. Its benefits are usually attributed to lattice stabilization, suppressed cation mixing, a changed interlayer spacing or inhibited phase transitions. These structural changes are coupled to the electronic structure of the host. A dopant brings new atomic orbitals and alters the local chemical environment, and so reconstructs the electronic states of the host. The resulting changes in orbital energy, hybridization, charge distribution and local bonding in turn change the TM valence states, orbital occupancy, spin states and crystal structure.

Doping can be read as a sequence: electronic-state reconstruction, orbital hybridization, local-bonding regulation, charge redistribution, and finally structural stabilization.

Mo doping of NCM811 is a representative case. Mo usually enters the TM layer as a high-valence cation such as Mo⁶⁺. The DOS in Figure 2(a-c) shows that Mo changes the electronic structure of the host considerably [23]: Mo-derived states appear alongside the original Ni 3*d* and O 2*p* states, and the Ni-related states are redistributed. The dopant is more than a structural stabilizer, because its orbitals take part directly in reshaping the distribution of electronic states.

The reconstructed electronic structure also redistributes charge and changes the valence of neighboring TM ions. A high-valence dopant such as Mo⁶⁺ on a lower-valence TM site requires charge compensation, which is taken up by the surrounding Ni ions. In Mo-doped NCM811 the relative populations of Ni²⁺ and Ni³⁺ change with Mo content, which shows that the dopant alters the local redox environment of Ni. This valence change is a consequence of the electronic reconstruction and not a separate chemical effect. A dopant can thus regulate the redox-active TM states even when it takes no direct part in the main charge-compensation process.

Doping also changes the spatial distribution and occupancy of the TM *d* electrons. As Figure 2(d-f) shows, a change in the local chemical environment of a TM center alters the shape of its *d* orbitals and their interaction with neighboring ligands [24]. The strength and direction of *d-p* overlap depend strongly on the local coordination geometry and bond lengths, so a dopant near a TM center changes where the electronic states sit in space as well as in energy, and with them the local bonding of the host.

This orbital picture connects electronic structure with structural distortion. When a TM ion has an electronically degenerate configuration, a change in orbital occupancy can drive local symmetry breaking and lattice distortion. Conversely, changing the ligand environment by doping can lift the degeneracy without a large geometric distortion. Fluorine substitution is an example. In Mn³⁺-containing disordered rock-salt cathodes, replacing O²⁻ with F⁻ changes the Mn-ligand hybridization and breaks the electronic symmetry around Mn. The two *e_g* orbitals are then no longer equivalent, and the driving force for Jahn-Teller distortion is reduced (Figure 2(g-i)) [25].

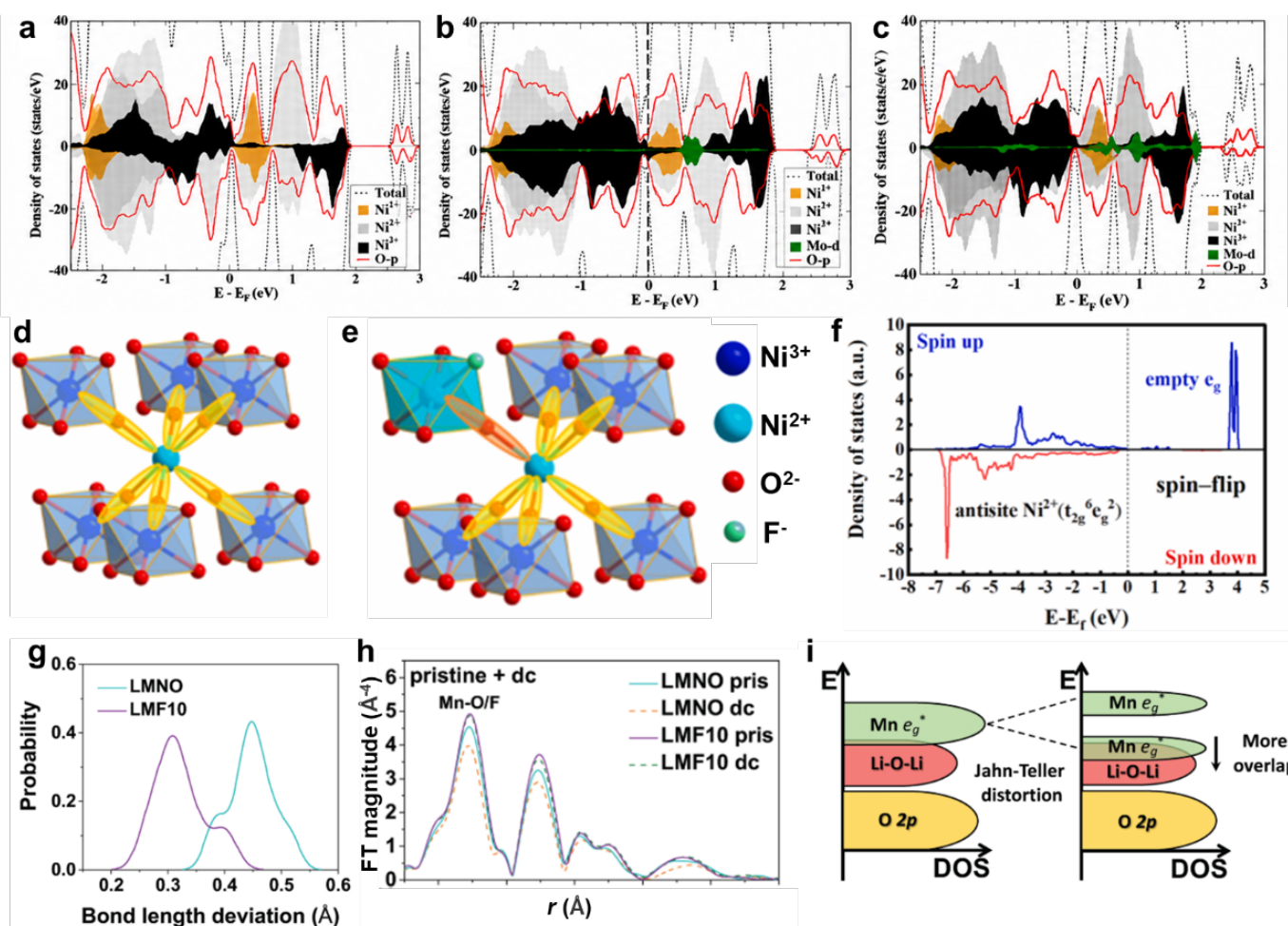


Figure 2. Electronic structure and local structural evolution induced by elemental doping. (a-c) DOS showing the redistribution of TM and O 2p states and dopant-derived electronic states [23]. Copyright 2019, American Chemical Society. (d, e) Spatial distributions of TM *d* orbitals and their hybridization with neighboring ligand orbitals. (f) Spin-resolved DOS illustrating the evolution of TM electronic configurations [24]. Copyright 2024, Elsevier. (g) Bond-length deviation distributions before and after doping. (h) Experimental and calculated local coordination structures associated with Mn-O/F bonding. (i) Schematic illustration of dopant-induced *e_g* orbital splitting and modified Mn-O orbital overlap [25]. Copyright 2019, Wiley.

The bond-length distributions (Figure 2(g)) and the extended X-ray absorption fine structure (EXAFS) results (Figure 2(h)) show the structural consequence directly. The calculated Mn-O/F bond-length deviation peaks near 0.45 Å in the non-fluorinated sample (LMNO) and near 0.30 Å in the fluorinated sample (LMF10), a decrease of about 33% that indicates weaker Jahn-Teller distortion. The EXAFS data further show that the reduced distortion in LMF10 is retained more reversibly over charge and discharge, whereas LMNO is left with a larger residual distortion after cycling.

The smaller distortion is tied to the orbital energy levels. As sketched in Figure 2(i), Jahn-Teller distortion splits the originally degenerate Mn *e_g* states into a lower and a higher level. The lower, occupied level moves toward

the Li-O-Li-related states and increases the overlap between Mn and O states. Fluorination changes the local Mn-ligand hybridization and the orbital energy distribution, and this affects the redox pathway and the electrochemical stability: the share of TM redox relative to oxygen redox increases, and oxygen loss is suppressed.

The examples in Figure 2 show that doping acts on several levels at once. Electronically, dopants add or redistribute states and change orbital occupancy and spin state. In terms of bonding, the altered hybridization changes the strength and geometry of the metal-ligand interaction. Structurally, bond lengths, local distortion and structural evolution change in response. Electrochemically, these changes decide how accessible and reversible the redox

reactions are, how stable the oxygen is, and how the material cycles.

3.2 Defect-Induced Electronic Structure Regulation

Defect engineering is a second route to regulating electrochemical behavior, acting through both electronic-structure reconstruction and ionic-transport modification [5, 29, 30]. Vacancies, antisite defects and stacking faults reconstruct the local electronic states without necessarily changing the overall composition [31, 32], while extended defects such as twin boundaries can simultaneously alter electron pathways and open faster ion-diffusion channels [33, 34]. In electronic terms, defects break local symmetry, alter orbital hybridization, create defect-related states and redistribute charge, and in this way change the redox activity and transport properties of the cathode.

Cation vacancies matter particularly in layered TM oxides, because removing a TM ion removes its coordination environment and perturbs the neighboring oxygen and TM sites. An example is the P2-type layered sodium cathode $\text{Na}_x\text{Ca}_{0.06}\text{Ni}_{0.22}\square_{0.11}\text{Mn}_{0.67}\text{O}_2$, into which TM vacancies ($\square$) are introduced deliberately. The vacancies create local Na-O- $\square$ and $\square$ -O- $\square$ configurations and leave some oxygen atoms without their usual TM coordination [35].

This has a direct electronic consequence. In the pristine TM-O framework, O 2p orbitals hybridize strongly with TM *d* states. Where a neighboring TM is missing the hybridization is weaker, and relatively non-bonding O 2p states form. These lie closer to the Fermi level and are oxidized more readily during deep desodiation. The PDOS calculations in Figure 3(a) follow the Ni 3*d*, Mn 3*d* and O 2*p* states as the Na content falls [35]. At high Na content the states around the Fermi level are mainly Ni 3*d*, so the initial charge compensation comes from Ni redox. As more Na is extracted, O 2*p* states contribute increasingly to the states above the Fermi level, which indicates stronger oxygen redox. The differential charge densities point the same way: early in charge, electron depletion is concentrated on Ni, consistent with Ni oxidation, while at deeper desodiation it becomes pronounced on the oxygen atoms next to TM vacancies. The vacancy therefore does more than add an “active site”; it changes which electronic states are energetically accessible for redox.

Oxygen vacancies remove an anion from the TM-O framework and affect both the electronic and the

structural properties of oxide cathodes strongly. Removing an O²⁻ ion breaks several TM-O bonds and leaves an under-coordinated TM environment. The electrons associated with the missing oxygen are redistributed over neighboring TM sites, and defect-related states can appear in the band gap or near the band edges. Oxygen vacancies can therefore narrow the effective band gap and improve electronic conductivity (Figure 3(b)) [36].

Oxygen vacancies also show the two-sided nature of defect engineering. A moderate concentration introduces useful electronic states and improves transport, but too much oxygen loss destabilizes the host. The vacancies cause local relaxation and leave TM ions under-coordinated, and these ions can migrate into neighboring Li layers and promote cation disorder and phase transformation. In spinel and layered oxide cathodes, excessive oxygen deficiency has been linked to TM disorder, lattice distortion and even transformation toward rock-salt-like structures. Operando studies have further shown that oxygen vacancies in Li-rich layered composite cathodes evolve dynamically during cycling, redistributing spatially and driving local structural transformations that feed back into the electronic state distribution; controlling this dynamic evolution is therefore as important as setting the initial vacancy concentration [38].

Defects need not involve missing atoms. Stacking faults also reconstruct the electronic structure, by changing the local coordination and the interlayer atomic arrangement. This is clearest in Li_2MnO_3 -based Li-rich layered oxides, where stacking faults arise from changes in the stacking sequence of the LiMn_2 layers. Different stacking configurations give different local Li-O-Li environments and hence different oxygen electronic states.

Comparing the calculated electronic structures of fault-free and faulted Li_2MnO_3 models connects the local defect to the energy levels. The faulted structures have smaller band gaps than the fault-free one, which means that a stacking fault reconstructs the local electronic environment and makes oxygen-derived states more accessible for redox, in addition to changing the layer geometry. Specifically, the fault lengthens the Li-O bonds and reduces the Li-O-Li bond angle (Figure 3(c)) [37]. Both changes weaken the interaction between oxygen and its neighboring cations and raise the energy of the unhybridized O 2*p* states. Higher-energy O 2*p* electrons are easier to remove, so oxygen is oxidized more readily on

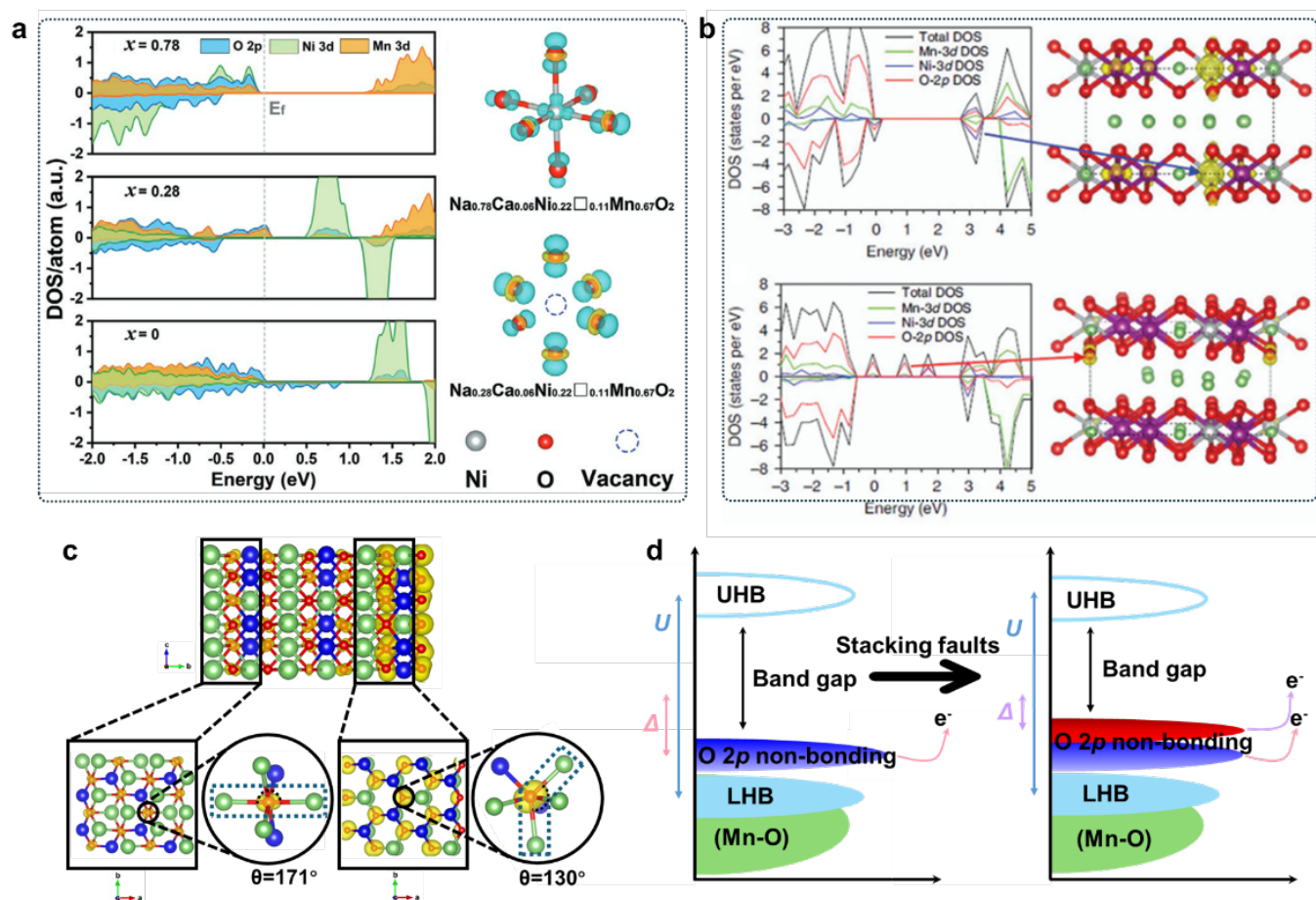


Figure 3. Defect-induced electronic structure reconstruction and its influence on local coordination and redox behavior. (a) Projected density of states (PDOS) and charge-density distributions of TM-vacancy-containing layered oxide cathodes [35]. Copyright 2021, Wiley. (b) DOS and corresponding atomic configurations for oxygen-vacancy-containing cathodes [36]. Copyright 2020, Royal Society of Chemistry. (c) Structural models and local coordination environments associated with stacking faults. (d) Schematic electronic structures illustrating the evolution of O 2p non-bonding states, lower Hubbard band (LHB), and upper Hubbard band (UHB) induced by stacking faults [37]. Copyright 2023, Wiley.

charging (Figure 3(d)) [37]. The greater oxygen redox activity caused by stacking faults is thus an energy-level effect that originates in local structural reconstruction, and it is more specific than a general increase in disorder.

The aim of defect engineering is accordingly to build a local electronic environment in which the desired redox states are accessible and unwanted structural reconstruction is suppressed, whatever the type or concentration of defect used to get there. Defects act as localized regulators of electronic structure that link atomic-scale disorder to macroscopic electrochemical behavior.

3.3 Composite-Structure-Induced Electronic Structure Regulation

Composite-structure design regulates electronic structure by introducing interfaces between chemically or structurally different phases [41, 42].

The synthesis of Li-rich layered composites such as $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}]\text{O}_2$, in which Li_2MnO_3 and LiMO_2 structural units are combined within a single particle, established the material basis on which such interfacial design strategies operate [43]. A dopant mainly changes the electronic environment around itself, and a defect reconstructs states through a local structural perturbation. A composite creates an extended interfacial region in which two different electronic environments coexist and interact. The charge redistribution, orbital hybridization and energy-level reconstruction at the interface can change the redox behavior and charge transport of the cathode substantially.

The nanoscale composite of Li_2MnO_3 and LiTMO_2 in Li-rich layered oxide cathodes is a representative case. The two components have similar layered structures but different electronic structures and redox characteristics. Li_2MnO_3 contains relatively

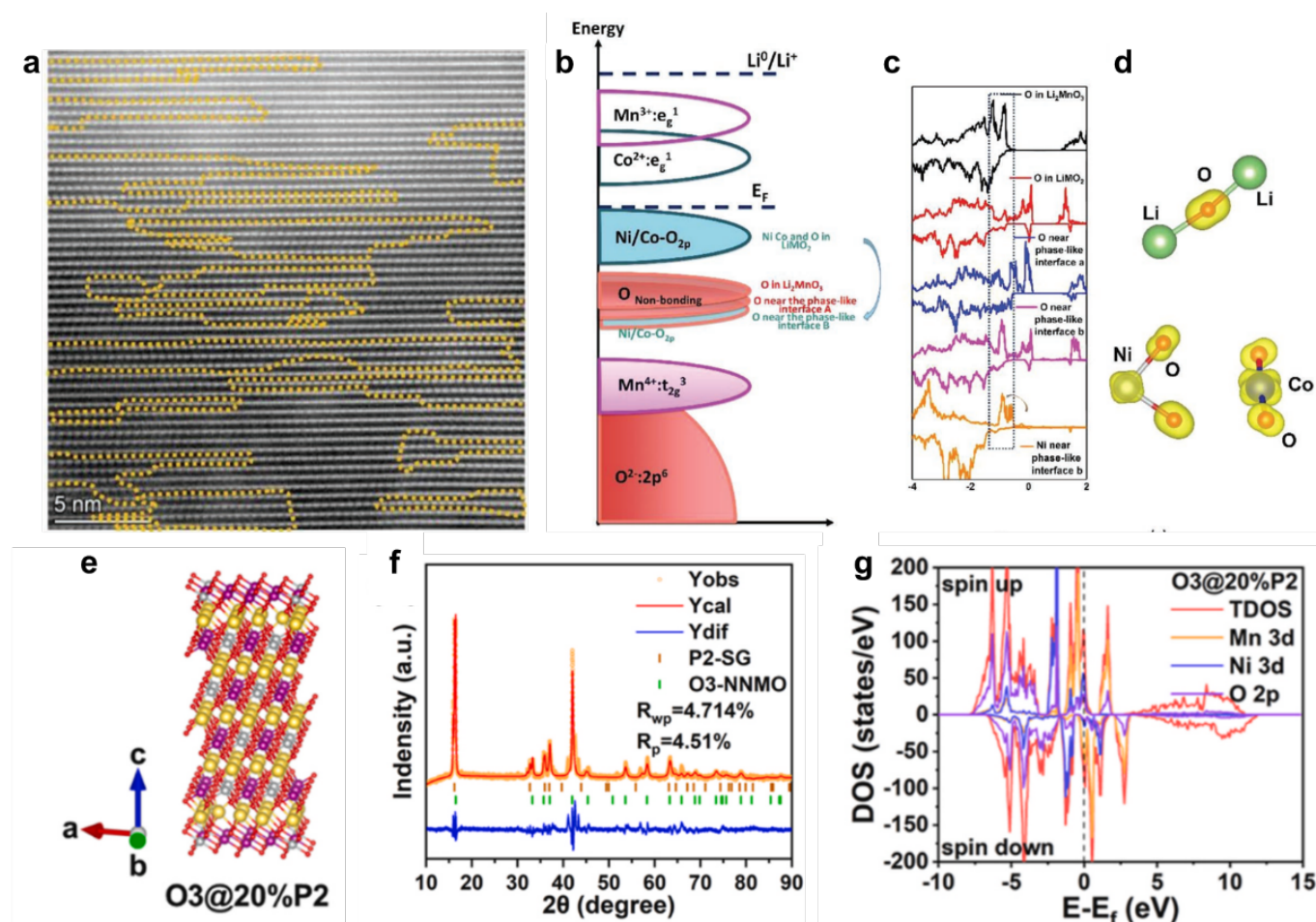


Figure 4. Interface-induced electronic structure regulation in composite cathode materials. (a) Atomic-scale scanning transmission electron microscopy image of the $\text{Li}_2\text{MnO}_3/\text{LiTMO}_2$ composite. (b) Schematic electronic structures of the local environments formed when the Li_2MnO_3 and LiTMO_2 structures are dispersed in one another. (c) O PDOS in different local environments and PDOS of Ni near the interface. (d) Partial charge density around O in the Li_2MnO_3 structure in the slightly lower energy range [39]. Copyright 2023, Wiley. (e) Structural model of the $\text{O3@20\%P2}$ heterostructure. (f) X-ray diffraction pattern and Rietveld refinement of the $\text{O3@20\%P2}$ heterostructure. (g) DOS of the $\text{O3@20\%P2}$ heterostructure [40]. Copyright 2025, Elsevier.

non-bonding O 2p states that can take part in oxygen redox at high potential, whereas LiTMO_2 contains strongly hybridized TM 3d-O 2p states associated mainly with TM redox. When the two are dispersed and intergrown at the nanoscale, many “phase-like interfaces” form, with local coordination environments that occur in neither bulk component (Figure 4(a-c)) [39]. In the bulk Li_2MnO_3 regions the oxygen-derived states near the Fermi level are mostly non-bonding O 2p. Near a phase-like interface the local environment of O, Ni and Co is reconstructed, and O 2p and TM 3d states overlap further. In particular, the Ni e_g states shift to lower energy and overlap with O 2p states to form relatively low-energy Ni-O bonds. Partial charge-density calculations show substantial σ - or π -type overlap between Ni/Co and oxygen atoms near the interface (Figure 4(d)). Whether Li-rich layered oxides are solid solutions or two-phase

composites is still debated, and the answer affects how interfacial electronic states in composite cathodes should be interpreted. Combined experimental and computational work is needed here.

The interface, then, is an electronically reconstructed region with its own local states and not merely a physical boundary between two phases. Because the coordination environment is altered and orbitals from both components interact, the interfacial states can differ markedly from those of either bulk.

The same idea applies to heterostructured layered sodium cathodes, for example the O3@P2 composite in which a P2-type phase is coherently integrated with an O3-type phase. Structural models and diffraction analysis show that the lattice parameters of the two phases are more closely matched in the composite, which reduces the mismatch and allows a coherent

interface to form (Figures 4(e) and 4(f)) [40].

The O3/P2 interface also changes the electronic states of the composite. The calculated DOS of O3@20%P2 has more states near the Fermi level than either individual phase, which suggests a higher electronic conductivity (Figure 4(g)). The heterointerface can thus offer an electronically favorable path for charge transfer and contribute to the faster reaction kinetics of the composite. This electronic effect is coupled to ionic transport. The P2 phase has relatively open prismatic Na^+ diffusion pathways and the O3 phase is a high-Na-content reservoir, so the combination brings different transport and storage characteristics into a single particle. The optimized O3@20%P2 material shows a higher average Na^+ diffusion coefficient than either the O3 or the P2 component, together with lower polarization and faster kinetics.

Maximizing the amount of a second phase is therefore not the point of composite design. What matters is the electronic coupling across the interface: energy alignment, orbital compatibility, interfacial charge transfer and the degree of hybridization between the two phases should be considered together with lattice matching and ion transport. Seen this way, a composite is a means of building new interfacial electronic states, and it links nanoscale architecture to macroscopic electrochemical performance.

3.4 Surface Modification-Induced Electronic Structure Regulation

The cathode surface is where the active material meets the electrolyte, and its electronic structure governs interfacial charge transfer, electrolyte decomposition, ion transport and structural degradation. In high-voltage cathodes in particular, Li^+ extraction keeps changing the surface electronic states and makes the TM-O framework more oxidizing, while the high cathode potential drives electrolyte oxidation and CEI formation. A surface layer is often described as a physical barrier between cathode and electrolyte. It does more than that: it reconstructs the surface electronic structure and the interfacial energy-level landscape, and so regulates both the electrochemical reactions and the stability of the interface.

One effect of surface modification is to reconstruct the electronic structure of the near-surface region. Figure 5(a-c) gives an example for a Li-rich oxide (OLO) coated with the fast ion conductor $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{LiBr}$ (LBB) [44]. Figure 5(a) compares the Li^+ migration barriers near the surface before

and after coating. The barrier is about 0.61 eV in the pristine oxide and 0.43 eV after the LBB coating is applied; within the coating itself it is 0.32 eV. The coating therefore both modifies the near-surface electronic structure and provides an easier diffusion path for Li^+ . The PDOS in Figures 5(b) and 5(c) shows the electronic origin of this effect. The coated material has much more overlap between TM 3d and O 2p states around the Fermi level than the pristine oxide, and the original band gap is partly filled by TM states, giving a more metallic electronic structure and additional paths for electron transport.

Band alignment is a more direct way to judge the electronic compatibility of a coating and a cathode. In vanadium-phosphate-coated Li-rich layered oxides (LLO), $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP) and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (NVP) were chosen as coatings because they have open frameworks for Li^+ transport and electronic states that can overlap with those of the LLO substrate [45]. The calculated LLO/LVP interface has a straddling band alignment and the LLO/NVP interface a staggered one (Figure 5(d)). The conduction band minimum (CBM) of LVP lies about 1.2 eV above that of LLO and its valence band maximum (VBM) about 0.5 eV below. For NVP, the CBM is about 3.2 eV and the VBM about 0.8 eV higher than those of LLO. The energy levels measured on the coated materials (Figure 5(e)) show, however, that the electronic structure of the heterointerface cannot be predicted by superimposing the isolated components. LVP-LLO has a lower ionization potential than pristine LLO (6.20 versus 7.38 eV) and an upward-shifted VBM, and the CBM of NVP-LLO is also shifted. Interfacial bonding and charge redistribution have evidently reconstructed the original states. The coating thereby forms an electronic bridge between the cathode and the surface layer: the band alignment sets the direction and extent of interfacial charge transfer, and the reconstructed states influence surface redox reactions and electron transport.

Figures 5(f) and 5(g) illustrate how the composition and structure of the CEI affect the reactions between a Ni-rich oxide cathode and a graphite anode [46]. In the baseline electrolyte, a poorly passivating CEI forms on the Ni-rich oxide, accompanied by a thick anode electrolyte interphase (AEI), TM crossover and Li-dendrite-related degradation. With the LiBOB-containing electrolyte the CEI is more robust and B/O-rich and the AEI is thinner, which suppresses TM crossover and improves passivation. CEI formation is closely tied to the electronic and chemical

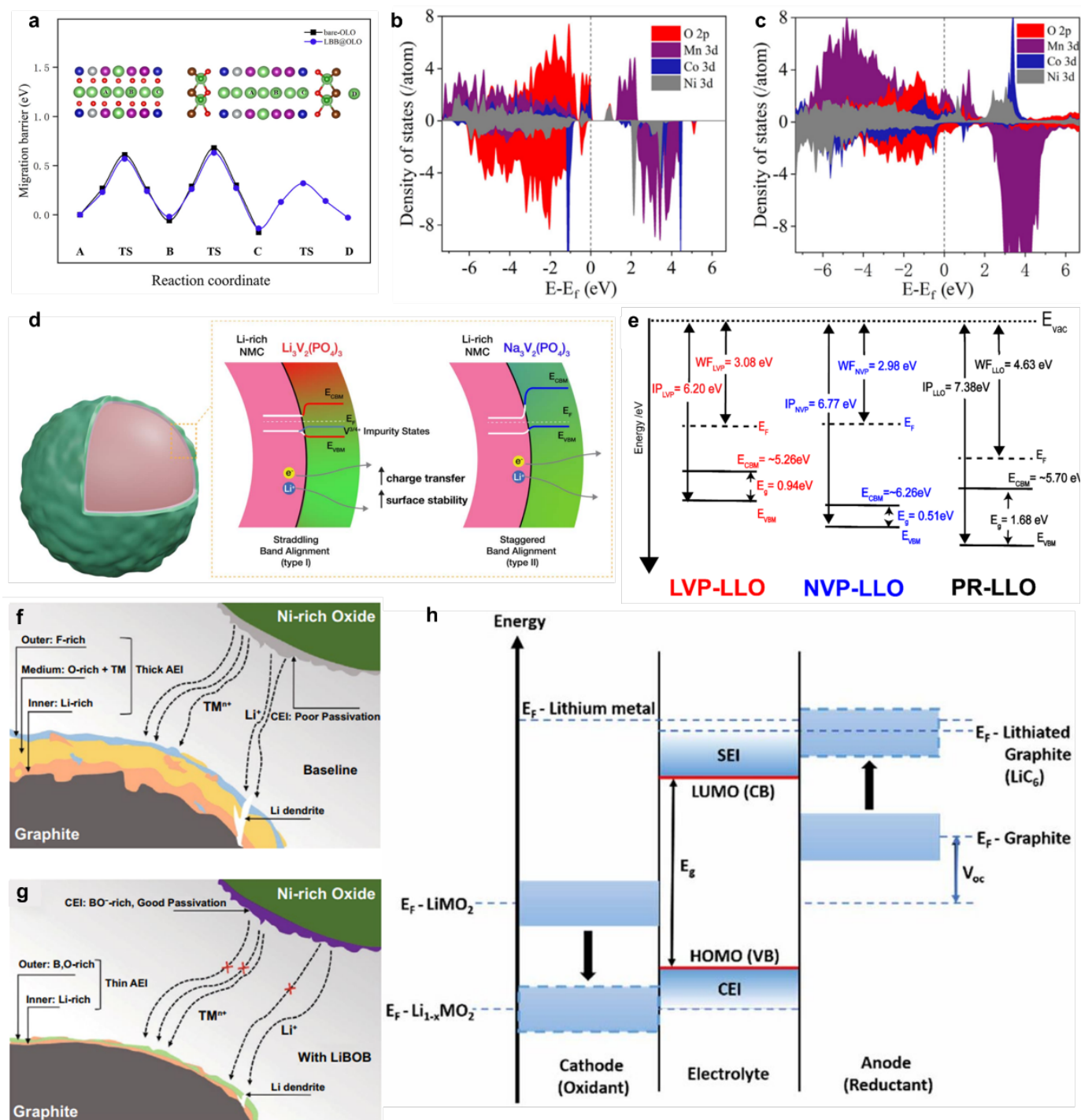


Figure 5. Surface modification-induced regulation of electronic structure, interfacial transport, and electrode-electrolyte reactions. (a) Calculated Li⁺ migration energy profiles along the surface diffusion pathway for pristine 0.5Li₂MnO₃·0.5LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ (OLO) and Li₂O-B₂O₃-LiBr (LBB)-coated OLO (LBB@OLO). (b, c) PDOS of the pristine and surface-modified cathodes [44]. Copyright 2024, Elsevier. (d) Schematic illustration of the interfacial band alignment and charge-transfer processes between Li-rich layered oxide (LLO) and Li₃V₂(PO₄)₃ (LVP) or Na₃V₂(PO₄)₃ (NVP) surface coatings. (e) Experimentally determined energy-level diagrams of LVP-coated LLO (LVP-LLO), NVP-coated LLO (NVP-LLO) and pristine LLO (PR-LLO) [45]. Copyright 2022, Royal Society of Chemistry. (f, g) Schematic illustration of the interaction between the CEI and the anode electrolyte interphase (AEI) caused by TM crossover with (f) the baseline electrolyte and (g) the LiBOB-containing electrolyte [46]. Copyright 2022, Springer Nature. (h) Schematic energy-level diagram of the cathode/electrolyte/anode system [47]. Copyright 2021, IOP Publishing.

state of the cathode surface. A poorly passivating CEI cannot block interfacial electron transfer and allows the electrolyte to keep decomposing. The products then modify the cathode surface further, promote TM dissolution, and affect the interphase on the anode. The cathode surface and the CEI are best treated as one dynamically coupled electronic interface. This coupling matters most at high voltage: once the cathode potential exceeds the practical oxidation stability of the electrolyte, a robust CEI is needed to stop continuous side reactions. Surface modification can therefore improve cycling stability indirectly, by setting the initial surface electronic structure and through it the composition and stability of the CEI.

Figure 5(h) gives a system-level energy-level picture that connects cathode surface modification with CEI formation, illustrating how the relative positions of the cathode Fermi level, electrolyte frontier states and interphase barriers together govern interfacial stability [47]. The cathode, electrolyte and anode have different electronic energy levels, and the CEI and the solid electrolyte interphase (SEI) add interfacial barriers. During charging the cathode Fermi level moves down as Li^+ is extracted, and the position of the electrolyte frontier states determines whether electron transfer and electrolyte oxidation are thermodynamically possible. A surface layer is effective, then, when it keeps the cathode Fermi level and the electrolyte frontier states apart electronically while still letting Li^+ through.

4 Conclusions and Perspectives

Doping, defect engineering, composite-structure design and surface modification are usually treated as separate strategies. From the standpoint taken here they are different ways of reconstructing electronic states, through orbital regulation, defect-induced states, interfacial charge redistribution, band alignment and surface electronic modulation, and these changes control redox reactions, ion and electron transport and electrode-electrolyte interactions. The electrochemical behavior of a cathode follows from the coupled evolution of electronic structure, atomic structure, ion transport and interfacial chemistry, and no single structural parameter can fully account for this behavior. Electronic energy levels can serve as a common descriptor for comparing different cathode-engineering strategies. The same reasoning carries over to other alkali-ion cathodes such as sodium-ion layered oxides: the relationships among TM $3d/\text{O } 2p$ orbitals, Fermi-level position and

electrochemical behavior are analogous, although the energy-level values differ between Li-based and Na-based materials.

Several problems remain. Most studies deal with static electronic structures, whereas a working cathode changes continuously in composition, valence state, lattice structure and interface during charge and discharge. Future work should follow the electronic energy levels as they evolve from bulk to surface and interface under realistic operating conditions. The goal of electronic-structure regulation should also be a balance among redox activity, transport kinetics and interfacial stability, and not maximum electronic activity for its own sake. Combining computation, operando characterization and data-driven materials design may eventually give quantitative relationships between structural descriptors, electronic energy levels and electrochemical performance. Precise control of the electronic energy landscape would then offer a general route to improving capacity, voltage, rate capability and cycling stability together.

Data Availability Statement

No new data were generated or analyzed in support of this perspective.

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Conflicts of Interest

The authors declare no conflicts of interest.

AI Use Statement

The authors declare that no generative AI was used in the preparation of this manuscript.

Ethical Approval and Consent to Participate

Not applicable.

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