



Cite this: *EES Batteries*, 2025, **1**, 744

## Electronic modulation strategies for enhanced cathode catalysis in lithium–oxygen batteries: challenges, advancements, and future perspectives

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Lithium–oxygen ( $\text{Li}–\text{O}_2$ ) batteries have emerged as a promising rechargeable energy storage technology, offering exceptionally high theoretical energy density, which makes them attractive for applications in electric vehicles, renewable energy storage, and portable devices. Despite their potential, the practical application of  $\text{Li}–\text{O}_2$  batteries is significantly hindered by challenges such as high overpotential, low discharge capacity, poor rate capability, and unstable cycle life. These issues primarily arise from the insulating nature of the discharge product ( $\text{Li}_2\text{O}_2$ ) and the sluggish electrochemical kinetics of the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). Addressing these challenges requires the development of efficient and stable cathode catalysts. Recent advancements in cathode catalyst design have provided valuable insights into the structure–performance relationship, especially regarding how electronic modulation can enhance catalytic efficiency. This review systematically examines the challenges, recent advancements, and future perspectives of cathode catalyst design for  $\text{Li}–\text{O}_2$  batteries. Particular emphasis is placed on understanding how the electronic properties of catalysts influence battery performance and exploring innovative strategies, such as external-field-assisted catalysis, to optimize catalytic activity. Furthermore, the review discusses future research directions, including precise molecular and atomic-level modulation of catalyst electronic structures, advanced *in situ* characterization techniques, and the synergistic optimization of electrode/electrolyte interfaces, aiming to provide theoretical guidance for developing high-performance  $\text{Li}–\text{O}_2$  batteries.

Received 28th March 2025,  
Accepted 4th May 2025

DOI: 10.1039/d5eb00060b  
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### Broader context

Lithium–oxygen ( $\text{Li}–\text{O}_2$ ) batteries, with their remarkably high theoretical energy density, are at the forefront of next-generation energy storage technologies. As the demand for sustainable energy solutions grows, particularly for electric vehicles and grid-scale storage,  $\text{Li}–\text{O}_2$  batteries offer a promising alternative to conventional lithium-ion systems. However, their practical application remains hampered by fundamental challenges, including high overpotential, poor cycle stability, and low efficiency due to the insulating nature of lithium peroxide ( $\text{Li}_2\text{O}_2$ ) and sluggish oxygen redox reactions. Recent progress in catalyst development, particularly through electronic modulation strategies, has opened new avenues for enhancing catalytic activity, stability, and overall battery performance. This review provides a comprehensive analysis of these advancements, offering insights that could pave the way for more efficient, durable, and scalable  $\text{Li}–\text{O}_2$  battery systems. By addressing the key challenges and identifying future research directions, this work contributes to the broader effort of making high-energy-density batteries viable for real-world applications.

### 1. Introduction

Lithium–oxygen ( $\text{Li}–\text{O}_2$ ) batteries have garnered significant attention as a next-generation energy storage technology due to their exceptionally high theoretical energy density (up to  $3500 \text{ W h kg}^{-1}$ ). This remarkable energy density positions them as transformative solutions for electric vehicles, grid-scale energy storage systems, and portable electronics.<sup>1</sup> Compared to conventional lithium-ion batteries (LIBs),<sup>2–4</sup>  $\text{Li}–\text{O}_2$  batteries offer a promising pathway towards sustainable and efficient energy storage. However, the practical deploy-

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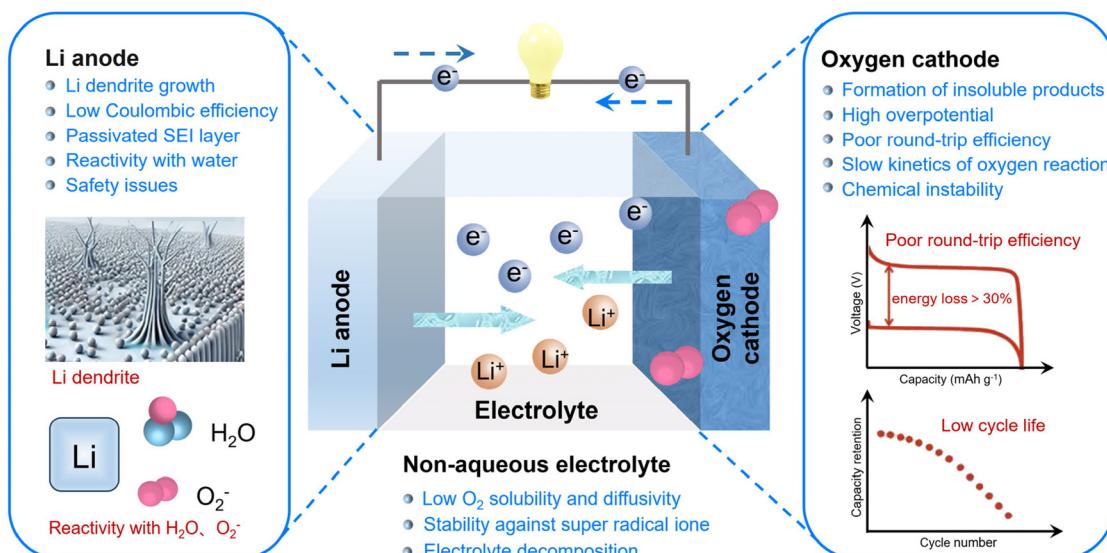


Fig. 1 Major challenges for the rechargeable Li–O<sub>2</sub> battery.

ment of Li–O<sub>2</sub> batteries faces several critical challenges that hinder their large-scale application. These challenges primarily stem from the complex electrochemical processes at the cathode, where the formation of insulating lithium peroxide (Li<sub>2</sub>O<sub>2</sub>) during discharge and its sluggish decomposition during charging result in high overpotential and limited cycle life.<sup>5–10</sup>

Despite the impressive theoretical energy density of Li–O<sub>2</sub> batteries, their practical application is significantly constrained by the intricate interplay of multi-scale electrochemical processes (Fig. 1). At the cathode interface, the wide band gap and insulating nature of the discharge product Li<sub>2</sub>O<sub>2</sub> pose substantial obstacles to electron and ion transport during both charge and discharge cycles, leading to interface passivation.<sup>11,12</sup> Consequently, the kinetics of the ORR and OER in Li–O<sub>2</sub> batteries are relatively slow, leading to increased charge/discharge polarization and a decline in energy

efficiency (<65%). Existing cathode materials struggle to maintain high activity over long cycles. Additionally, high costs and limited material availability, particularly the reliance on noble metal catalysts<sup>13–15</sup> and scarce carbon materials,<sup>13,16–18</sup> hinder large-scale application. During dynamic cycling, the disproportionation of Li<sub>2</sub>O<sub>2</sub> and the generation of singlet oxygen (<sup>1</sup>O<sub>2</sub>) can cause electrolyte decomposition, forming byproducts such as Li<sub>2</sub>CO<sub>3</sub> and carboxylic acids in ether-based electrolytes.<sup>19,20</sup> This process leads to cathode pore blockage and interfacial failure. At charging voltages exceeding 3.4 V, the electrochemical decomposition of LiO<sub>2</sub> or Li<sub>2</sub>O<sub>2</sub> further generates <sup>1</sup>O<sub>2</sub>, and the auto-oxidation of superoxide species and O<sub>2</sub> has been identified as a common mechanism of electrolyte degradation. Solid-state electrolytes have garnered considerable attention due to their enhanced chemical stability; however, they continue to face challenges related to poor ionic conductivity. A critical issue concerning the lithium anode is the



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undesirable morphological evolution during repeated lithium plating and stripping.<sup>21,22</sup> In particular, at higher current densities, lithium metal surfaces can develop mossy (dense, porous microstructures) and dendritic (sharp, outward-protruding) growth. Dendritic growth can lead to electrical short circuits in the battery, posing severe safety risks if the lithium dendrites penetrate the separator and contact the O<sub>2</sub> electrode. Additionally, the formation of mossy structures results in low coulombic efficiency due to the continuous formation of new solid electrolyte interphase (SEI) layers on the increased lithium surface area.<sup>23</sup> Moreover, the emergence of electrically isolated lithium structures renders portions of the lithium metal electrochemically inactive. These challenges fundamentally stem from the suboptimal regulation of electrode/electrolyte interfacial reaction pathways.

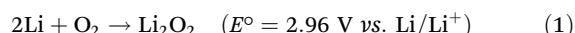
In recent years, with advancements in materials science and electrochemical theory, significant breakthroughs have been made in the design and optimization of Li–O<sub>2</sub> batteries.<sup>5,42–45</sup> Notably, substantial progress has also been achieved in the field of cathode catalysis (Fig. 2). The rational design and precise control of catalysts with excellent reaction kinetics, reversibility, and high ORR/OER activity are crucial for advancing the practical application of Li–O<sub>2</sub> batteries. Breakthroughs in density functional theory (DFT) calculations and *in situ* characterization techniques have enabled researchers to progressively elucidate the structure–activity relationship between catalyst electronic properties and ORR/OER kinetics.<sup>46,47</sup> This provides critical theoretical support for advancing Li–O<sub>2</sub> battery technology and its practical applications. This review begins by examining the fundamental charge–discharge mechanisms of Li–O<sub>2</sub> batteries and the critical role of cathode catalysts. It discusses the charge transfer mechanisms at the electrolyte–Li<sub>2</sub>O<sub>2</sub>–cathode interface and integrates recent advancements in cathode catalyst design, with a particular focus on the influence of catalyst electronic properties on catalytic activity (Fig. 3). A systematic analysis is provided on various tuning strategies, including d-band center modulation in metals, optimization of p-band non-metallic sites, occupancy of e<sub>g</sub> orbitals, orbital hybridization, exposed

crystal facet engineering, and external-field-assisted innovations, all of which contribute to enhancing catalytic performance. Finally, the current state of cathode catalyst design for Li–O<sub>2</sub> batteries is discussed, along with perspectives on future research. This review provides theoretical insights and guidance for the design and further optimization of advanced cathode catalysts.

## 2. Mechanism and charge transport path of Li–O<sub>2</sub> battery

### 2.1 Mechanism for Li–O<sub>2</sub> battery electrochemistry

The fundamental working mechanism of Li–O<sub>2</sub> batteries relies on the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER),<sup>54,55</sup> which alternately occur during discharge and charge cycles to enable energy storage and release (eqn (1)).



The discharge process of Li–O<sub>2</sub> batteries relies on the ORR at the cathode, wherein oxygen molecules are reduced to solid lithium peroxide (Li<sub>2</sub>O<sub>2</sub>) through a series of multi-step electron transfers (Fig. 4).<sup>56</sup> The specific reaction begins with the adsorption of O<sub>2</sub> molecules onto the cathode surface, followed by the acceptance of an electron, forming superoxide ions (O<sub>2</sub><sup>–</sup>) (eqn (2)). The kinetics of this step are significantly influenced by the oxygen concentration in the electrolyte and the surface activity of the catalyst. O<sub>2</sub><sup>–</sup> ions then combine with Li<sup>+</sup> from the anode to form an intermediate product, LiO<sub>2</sub>. The stability of LiO<sub>2</sub> is contingent upon the donor number (DN) of the electrolyte solvent<sup>57,58</sup> and the adsorption strength ( $\Delta E_{\text{ads}}$ ) of the cathode catalyst. In low-DN solvents (e.g., TEGDME), the solvation of Li<sup>+</sup> in the electrolyte is weak, leading to a tendency for LiO<sub>2</sub> to undergo secondary electrochemical reduction or disproportionation reactions at the electrode surface (eqn (3)–(5)). Conversely, in high-DN solvents (e.g., DMSO), facilitate the effective solvation of Li<sup>+</sup>, enabling LiO<sub>2</sub> to dissolve into the



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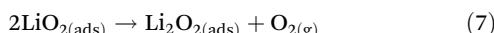
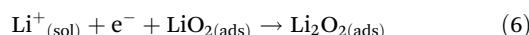
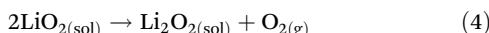
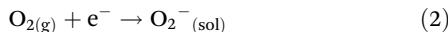


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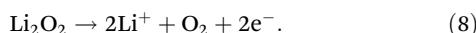
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electrolyte and undergo disproportionation reactions, resulting in the formation of toroidal  $\text{Li}_2\text{O}_2$  particles (eqn (6) and (7)).

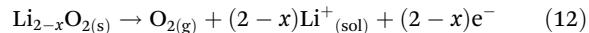
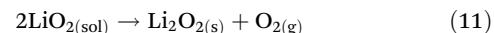
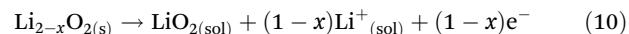
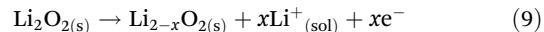


During the charging process, the decomposition of  $\text{Li}_2\text{O}_2$  plays a critical role in energy storage (Fig. 5). This process involves the OER, whose sluggish kinetics lead to a high overpotential (typically  $>1$  V), which is a fundamental issue limiting the efficiency of the battery.<sup>55,59</sup> The mechanism of OER is complex, and the reaction pathway, as well as the presence of intermediates, remains a subject of ongoing debate. Peng *et al.* used *in situ* surface-enhanced Raman spectroscopy (SERS) to monitor the charging process and found that the oxidation of  $\text{Li}_2\text{O}_2$  did not exhibit characteristic peaks for the  $\text{LiO}_2$  intermediate (such as the O–O vibrational peak at  $1130\text{ cm}^{-1}$ ).<sup>60</sup> They proposed that  $\text{Li}_2\text{O}_2$  decomposes through a direct two-electron transfer pathway:



Further studies indicate that, similar to the discharge mechanism, oxidation pathway of  $\text{Li}_2\text{O}_2$  during the charging process is influenced by the DN of the electrolyte solvent. During charging,  $\text{Li}_2\text{O}_2$  first undergoes a delithiation reaction to form the  $\text{Li}_{2-x}\text{O}_2$  intermediate (eqn (9)). In high-DN solvents,  $\text{Li}_{2-x}\text{O}_2$  dissolves into  $\text{LiO}_{2(\text{sol})}$  and subsequently undergoes disproportionation to generate  $\text{O}_2$  (eqn (10) and (11)). In contrast, in low-DN solvents, the  $\text{Li}_{2-x}\text{O}_2$  intermediate under-

goes further oxidation *via* a solid-state mechanism to release  $\text{O}_2$  (eqn (12)).



## 2.2 Reaction interfaces and electron transport pathways in charging and discharging processes

In  $\text{Li}-\text{O}_2$  batteries, the electrolyte–catalyst interface is the core region where charge transport and ORR/OER occur, involving the adsorption, transport, dissociation of reactants, as well as the nucleation and decomposition of  $\text{Li}_2\text{O}_2$ .<sup>61,62</sup> The wide band gap characteristic of the  $\text{Li}_2\text{O}_2$  discharge product leads to an extremely low intrinsic conductivity ( $\sigma_{\text{ea}} = 2.2 \times 10^{-13}\text{ S cm}^{-1}$ ), and as discharge proceeds, both electron and ion transport become increasingly restricted.<sup>63,64</sup> Significant efforts have been made to study the active reaction interfaces and transport limitations during the charging and discharging processes of  $\text{Li}-\text{O}_2$  batteries.<sup>63,65–67</sup>

Wang *et al.* conducted staged discharge experiments in tetraglyme electrolyte using isotope labeling, sequentially introducing  $^{16}\text{O}_2$  and  $^{18}\text{O}_2$ .<sup>48</sup> Analysis using scanning electron microscopy (SEM) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) revealed that the ring-shaped  $\text{Li}_2\text{O}_2$  product exhibits a layered distribution, with  $\text{Li}_2^{18}\text{O}_2$  enriched on the outer surface (electrolyte interface) and  $\text{Li}_2^{16}\text{O}_2$  concentrated in the inner layer (electrode interface) (Fig. 6a). This finding supports the hypothesis that  $\text{Li}_2\text{O}_2$  preferentially grows at the  $\text{Li}_2\text{O}_2$ –electrolyte interface. By reversing the isotope introduction sequence (introducing  $^{18}\text{O}_2$  first, followed by  $^{16}\text{O}_2$ ), the  $\text{Li}_2\text{O}_2$  enrichment order was correspondingly reversed, further



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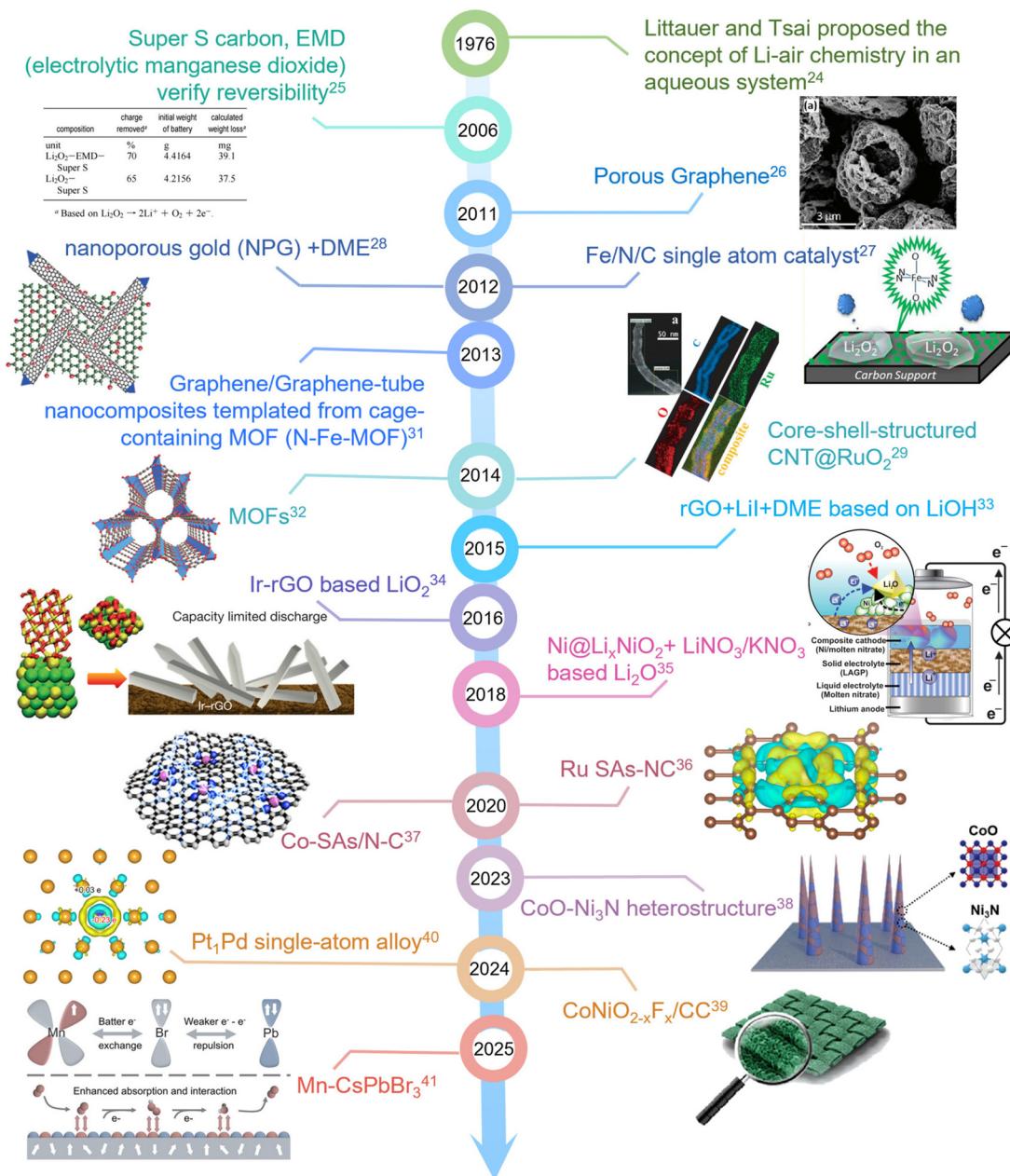
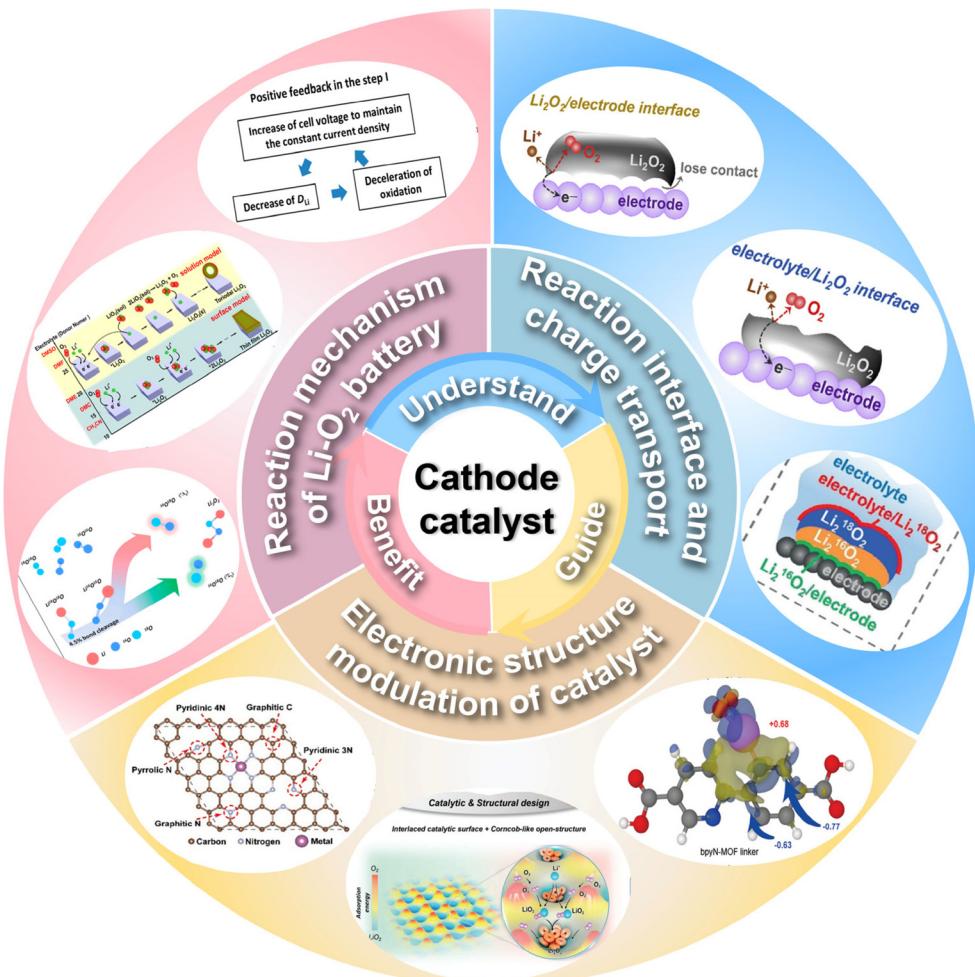


Fig. 2 Timeline of the development of Li–O<sub>2</sub> battery cathode catalysts.<sup>24–41</sup>

validating the correlation between oxygen evolution sequence and isotope distribution within Li<sub>2</sub>O<sub>2</sub> particles. Wang *et al.* employed an Au electrode | Li<sub>2</sub>O<sub>2</sub> thin film | Li<sup>+</sup>/DMSO electrolyte system to *in situ* SERS. By discharging at a high current density (100  $\mu$ A cm<sup>-2</sup>), an ultrathin Li<sub>2</sub>O<sub>2</sub> film was formed on the Au surface *via* a surface growth mechanism. Initially, the battery was pre-discharged in a <sup>18</sup>O<sub>2</sub> atmosphere, forming a Li<sub>2</sub><sup>18</sup>O<sub>2</sub> film. Subsequently, switching to <sup>16</sup>O<sub>2</sub> for discharge, as shown in Fig. 6b, SERS observations revealed that Li<sub>2</sub><sup>16</sup>O<sub>2</sub> formed from <sup>16</sup>O<sub>2</sub> gradually replaced Li<sub>2</sub><sup>18</sup>O<sub>2</sub> at the Au electrode interface, indicating that the ORR occurred at the buried Au|Li<sub>2</sub>O<sub>2</sub> interface.<sup>65</sup> In this scenario, O<sub>2</sub> and Li<sup>+</sup> can penetrate

the previously deposited Li<sub>2</sub>O<sub>2</sub> film, likely through grain boundaries or defect channels, reaching the underlying gold electrode surface. The transport-limiting mechanism suggests that electron transport is the primary limiting factor responsible for the sudden failure of the battery during discharge.<sup>65</sup> The extremely low electronic conductivity of Li<sub>2</sub>O<sub>2</sub> ( $\sigma_{ea} = 2.2 \times 10^{-13}$  S cm<sup>-1</sup>) prevents efficient electron transport to the reaction interface, leading to a sharp voltage drop. Although the ionic conductivity of the Li<sub>2</sub>O<sub>2</sub> film is relatively low ( $\sigma_{io} = 3.1 \times 10^{-12}$  S cm<sup>-1</sup>), experimental results indicate that Li<sup>+</sup> and O<sub>2</sub> can slowly diffuse to the interface through defect channels in the film, suggesting that ion transport is not the primary limit-





**Fig. 3** A schematic illustration outlining the key topics discussed in this work, including a comprehensive analysis of the reaction mechanisms in  $\text{Li}-\text{O}_2$  batteries,<sup>48,49</sup> the understanding of reaction interfaces and charge transfer mechanisms,<sup>20,50,51</sup> and the investigation of the electronic states of cathode catalysts.<sup>39,52,53</sup>

ing factor. Therefore, increasing the porosity and amorphous nature of  $\text{Li}_2\text{O}_2$  can enhance defect density, facilitate  $\text{Li}^+/\text{O}_2$  transport, and mitigate electron transport limitations.

During the charging process, the charge transport pathway at the electrolyte–catalyst interface is significantly influenced by the charging rate and overpotential.<sup>69,70</sup> At low rates and low overpotentials, the solid-solution decomposition and solvent-mediated steps during charging initiate at the  $\text{Li}_2\text{O}_2$ –electrolyte interface. Wang *et al.* revealed the oxygen release behavior of  $\text{Li}_2\text{O}_2$  particles through isotopic tracing experiments.<sup>48</sup> As shown in Fig. 6c, for micron-sized particles with the outer layer of  $\text{Li}_2^{18}\text{O}_2$  (in contact with the electrolyte) and the inner layer of  $\text{Li}_2^{16}\text{O}_2$  (in contact with the electrode), OEMS monitoring during charging reveals that  $^{18}\text{O}_2$  is released first (accounting for the first quarter of the total charge capacity), followed by  $^{16}\text{O}_2$  becoming dominant. This indicates that oxygen loss originates at the  $\text{Li}_2\text{O}_2$ /electrolyte interface rather than the  $\text{Li}_2\text{O}_2$ /electrode interface. A comparison between the pure carbon electrode (VC) and the ruthenium/carbon catalyst

electrode (Ru/VC) reveals that both electrodes follow the same oxygen release sequence. However, the Ru/VC electrode exhibits a reduction in charging overpotential by approximately 500 mV. This difference is attributed to the Ru catalyst, which stabilizes lithium-deficient phases on the  $\text{Li}_2\text{O}_2$  surface (*e.g.*,  $\text{Li}_{2-x}\text{O}_2\text{-Ru}$ ) through interfacial chemical adsorption, maintaining contact, facilitating charge transfer, and enhancing reaction kinetics. If  $\text{O}_2$  primarily evolves at the  $\text{Li}_2\text{O}_2$ -electrolyte interface, electrons and ions must penetrate  $\text{Li}_2\text{O}_2$  during charging, despite  $\text{Li}_2\text{O}_2$  being a well-known wide-bandgap insulator. In fact, numerous studies have demonstrated that  $\text{Li}^+$  vacancies and hole polarons are the primary charge carriers in  $\text{Li}_2\text{O}_2$ .<sup>67,70,71</sup> Perfectly ordered  $\text{Li}_2\text{O}_2$  is a wide-bandgap insulator, with an HSE-calculated bandgap of 4.2 eV. However, under non-stoichiometric conditions or in the presence of defect states (*e.g.*, lithium vacancies), polaron conduction pathways can be activated. In  $\text{Li}_2\text{O}_2$ , hole polarons exhibit an in-plane migration barrier of only 68 meV, significantly lower than the interlayer hopping barrier.<sup>72</sup> This suggests that controlling

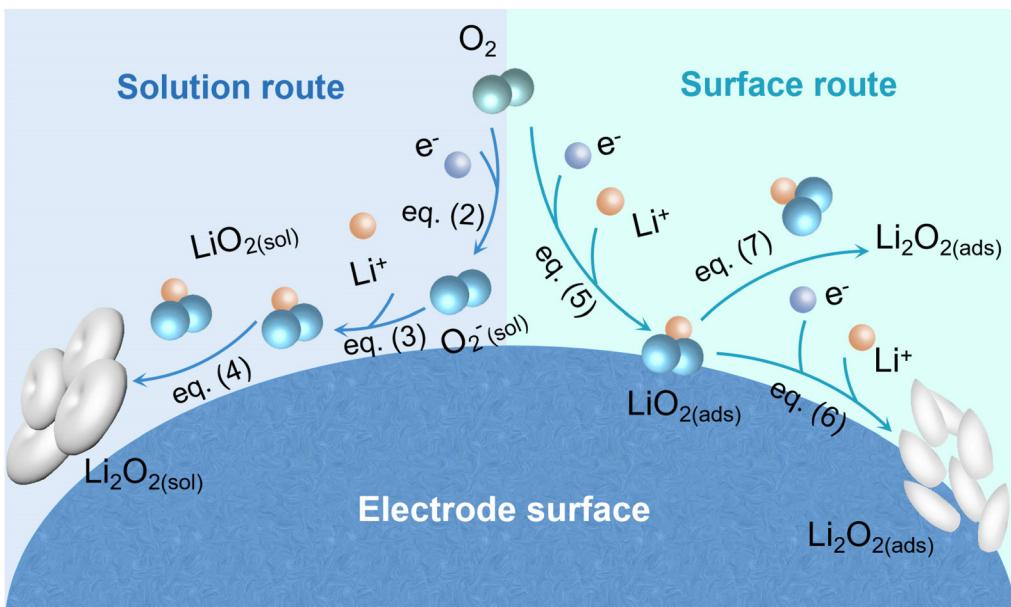


Fig. 4 Oxygen reduction mechanistic pathways in nonaqueous  $\text{Li}-\text{O}_2$  batteries.

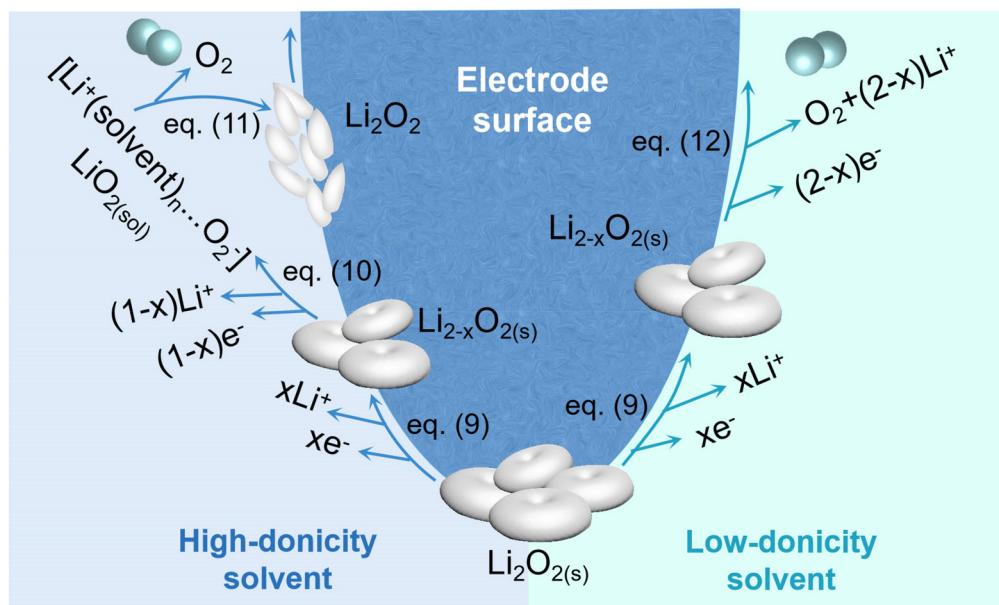
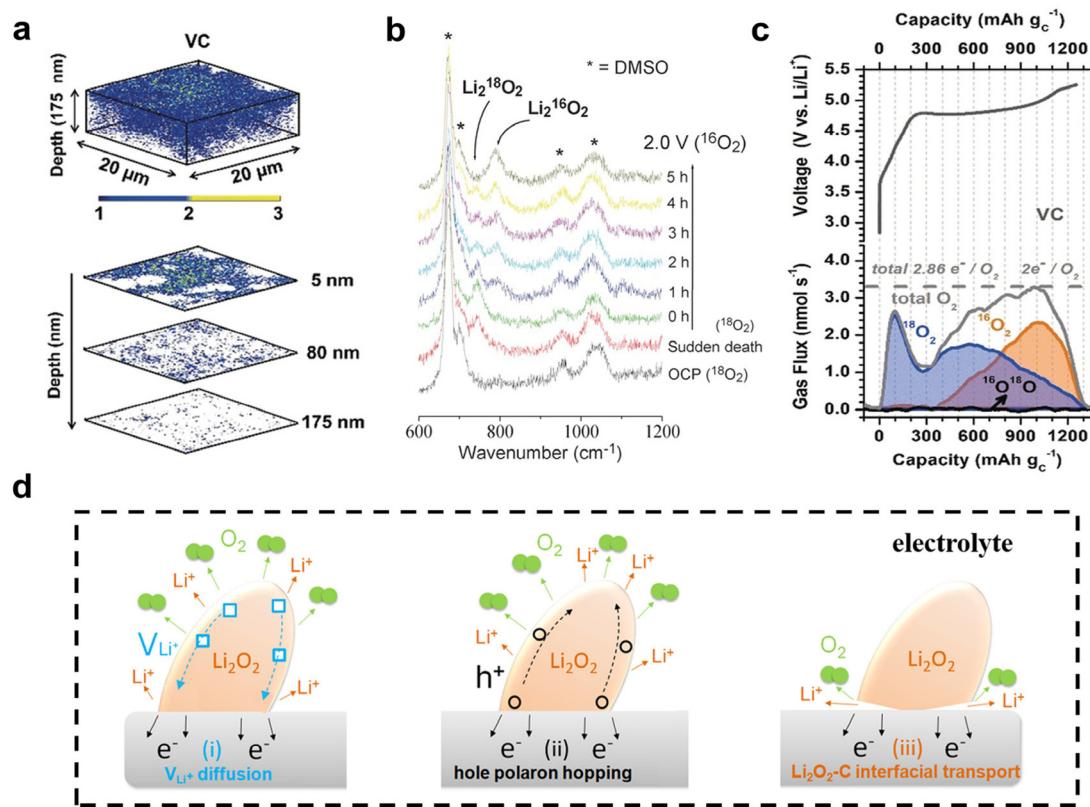


Fig. 5 Oxygen evolution mechanistic pathways in nonaqueous  $\text{Li}-\text{O}_2$  batteries.

crystal orientation can optimize charge transport efficiency, providing valuable insights for electrode material design, such as tuning exposed crystal facets. Ball milling introduces grain boundaries and dislocation defects, increasing the overall conductivity of  $\text{Li}_2\text{O}_2$  by approximately two orders of magnitude, from  $3.4 \times 10^{-13} \text{ S cm}^{-1}$  to  $1.1 \times 10^{-10} \text{ S cm}^{-1}$  at room temperature. Additionally, it generates a high-mobility  $\text{Li}^+$  “spin reservoir”, significantly enhancing ionic transport kinetics.<sup>73</sup> Amorphous  $\text{Li}_2\text{O}_2$  exhibits unique transport properties due to its disordered structure. Its ionic conductivity ( $2 \times 10^{-7} \text{ S}$

$\text{cm}^{-1}$ ) is 12 orders of magnitude higher than that of its crystalline counterpart, effectively mitigating lithium-ion transport limitations during charge-discharge cycles in  $\text{Li}-\text{O}_2$  batteries.<sup>69</sup> By optimizing electrode design (e.g., incorporating a porous structure), the synergy between the high ionic conductivity of the amorphous phase and rapid  $\text{O}_2$  diffusion channels can alleviate electron transport bottlenecks and extend the activity of the reaction interface. Koffi *et al.* proposed that transition metals and their oxides can act as reaction promoters by chemically converting  $\text{Li}_2\text{O}_2$  into lithium metal oxides, which



**Fig. 6** (a) 3D distribution of <sup>18</sup>O in discharge products reconstructed from ToF-SIMS depth profiling, with three selected depth layers.<sup>48</sup> (b) *In situ* SERS collected at open circuit potential (OCP, black) and at the end of discharge under a <sup>18</sup>O<sub>2</sub> atmosphere (red), followed by spectra recorded during discharge in a <sup>16</sup>O<sub>2</sub> atmosphere at 2.0 V vs. Li/Li<sup>+</sup> over 0–5 hours.<sup>65</sup> (c) Charging curves of a Li–O<sub>2</sub> battery using a VC electrode, along with OEMS analysis of oxygen evolution.<sup>48</sup> (d) Schematic illustration of charge transfer during Li<sub>2</sub>O<sub>2</sub> decomposition in the charging process. Decomposition occurs at the Li<sub>2</sub>O<sub>2</sub>–electrolyte interface, where charge transfer is mediated by (i) Li<sup>+</sup> vacancy diffusion and (ii) hole polaron hopping; (iii) reactions take place at the Li<sub>2</sub>O<sub>2</sub>–cathode interface.<sup>68</sup>

subsequently facilitate oxygen release *via* an electrochemical delithiation process.<sup>74</sup>

In summary, defect engineering, including grain boundary modulation, amorphization, and nanostructuring of Li<sub>2</sub>O<sub>2</sub>, can alleviate charge transport limitations during the charge–discharge cycles of Li–O<sub>2</sub> batteries.<sup>75–77</sup> At low charging rates, the decomposition of Li<sub>2</sub>O<sub>2</sub> can be sustained through bulk and surface Li<sup>+</sup> vacancy diffusion (Fig. 6d(i)) as well as hole polaron migration (Fig. 6d(ii)). However, when the transport rate fails to keep up with the charging current, at high charging rates or high potentials, the formation of a thick Li<sub>2</sub>O<sub>2</sub> film impedes charge transport, shifting the reaction site to the Li<sub>2</sub>O<sub>2</sub>–cathode interface (Fig. 6d(iii)).<sup>68</sup> Nevertheless, the stepwise decomposition at the interface can cause the structural collapse of Li<sub>2</sub>O<sub>2</sub> particles from the base, leading to void formation. Detached Li<sub>2</sub>O<sub>2</sub> loses electrical contact, preventing its participation in subsequent reactions and accelerating capacity degradation.<sup>78</sup> Therefore, enhancing the adhesion between Li<sub>2</sub>O<sub>2</sub> and the cathode or designing hierarchical porous electrodes, where micropores trap reaction products and nanopores limit particle detachment, can mitigate electrochemical detachment and improve cycling performance. Notably, although the formation of a dense Li<sub>2</sub>O<sub>2</sub> film restricts bulk

transport, it helps maintain local electrical contact, highlighting the need for morphology control to balance transport properties and interfacial stability. Highly active solid-state catalysts (*e.g.*, Ru) enhance charge transport by forming metal oxide interfaces and stabilize Li<sub>2</sub>O<sub>2</sub> intermediates through direct solid–solid interactions, thereby lowering the lithium extraction energy barrier and reducing overpotential.<sup>79</sup> On one hand, the coupling interaction between the electrode surface and Li<sub>2</sub>O<sub>2</sub> can regulate the interfacial delithiation process. On the other hand, this necessitates that the substrate material exhibits strong resistance to Li<sub>2</sub>O<sub>2</sub> oxidation. The oxidation tendency or multivalent capability of the catalyst determines its ability to stabilize Li<sub>2</sub>O<sub>2</sub> intermediates, thereby influencing OER activity.<sup>74</sup> The position of the catalyst's d-band center directly influences the adsorption strength and decomposition pathway of Li<sub>2</sub>O<sub>2</sub>. Interfacial hybridization can create delocalized electronic channels, leading to charge redistribution. Qian *et al.* designed a nickel-based catalyst encapsulated in carbon nanotubes (CNTs), denoted as Ni/Ni<sub>3</sub>C-CNT.<sup>66</sup> The electron delocalization of the inner Ni/Ni<sub>3</sub>C material induces interfacial charge interactions, redistributing the electron density and surface electrostatic potential of the outer carbon shell. This modulation of surface adsorption states governs the kine-

tics of  $\text{Li}-\text{O}_2$  chemistry. The  $\text{Ni}/\text{Ni}_3\text{C}-\text{CNT}$  catalyst exhibits moderate adsorption strength toward superoxide intermediates, effectively lowering the reaction energy barrier and achieving remarkable rate performance.

### 2.3 Rational design of cathode catalysts

In  $\text{Li}-\text{O}_2$  batteries, the precise tuning of the cathode catalyst's electronic structure directly determines catalytic activity and reaction kinetics.<sup>80,81</sup> The position of the d-band center in transition metal catalysts significantly influences the reaction energy barrier by modulating the adsorption free energy of reaction intermediates (e.g.,  $\text{O}_2^-$ ,  $\text{LiO}_2$ ,  $\text{Li}_2\text{O}_2$ ). Guo *et al.* employed a high-entropy strategy to design a series of alloy catalysts with widely distributed d-band centers.<sup>116</sup> Their study revealed that catalytic activity follows a volcano-shaped curve as a function of adsorption strength, adhering to the Sabatier principle of heterogeneous catalysis. It was demonstrated that an excessively high d-band center leads to overly strong interactions between the catalyst and intermediate species, resulting in slow desorption kinetics and an increased reaction energy barrier. Conversely, an extremely low d-band center provides insufficient binding strength, causing product loss and surface passivation. As a demonstration of the trade-off between adsorption and desorption strength, HEA-PtIr exhibited the highest catalytic activity in  $\text{Li}-\text{O}_2$  batteries, displaying an optimal adsorption capability. Additionally, a high surface electron density enhances the accessibility of active sites, facilitating oxygen molecule adsorption and dissociation. Intrinsic defects in catalysts, such as non-metal and metal vacancies, can introduce unsaturated coordination sites, enhance electronic conductivity, and lower reaction energy barriers. Heteroatom doping can modulate local electron density through orbital hybridization. For example,  $\text{Co}_3\text{O}_4$  with a higher concentration of surface oxygen vacancies promotes the formation of  $\text{Li}_2\text{O}_2$  morphologies that are more easily decomposable during charging, thereby enhancing battery reversibility and cycling stability.<sup>82</sup> A cation vacancy-rich composite,  $\text{VCo}-\text{CoSe}_2@\text{MXene}$ , exhibited enhanced covalency upon Co vacancy introduction, facilitating electron transfer from  $\text{Ti}_3\text{C}_2$  MXene to  $\text{CoSe}_2$  and optimizing the electronic structure of interfacial Co sites.<sup>83</sup> Notably, the secondary Co site adjacent to the Co vacancy served as an active center for the oxygen reduction reaction, leading to a low overpotential (0.35 V) and excellent cycling stability (250 cycles at 500  $\text{mA g}^{-1}$ ) in  $\text{Li}-\text{O}_2$  batteries. Heteroatoms, such as metal dopants, also serve as an effective strategy for modulating local electron density. Loading various metal elements onto  $\text{Co}_3\text{O}_4$  hollow spheres to substitute  $\text{Co}^{3+}$  centers in the octahedral structure establishes electron transfer pathways that stabilize  $\text{Co}^{3+}$  centers during charge-discharge cycles.<sup>84</sup> This strategy maximizes the number of available active sites, facilitates oxygen adsorption and  $\text{Li}_2\text{O}_2$  nucleation, and spatially separates active  $\text{Co}^{3+}$  centers, directing the growth of well-dispersed  $\text{Li}_2\text{O}_2$  nanosheets.

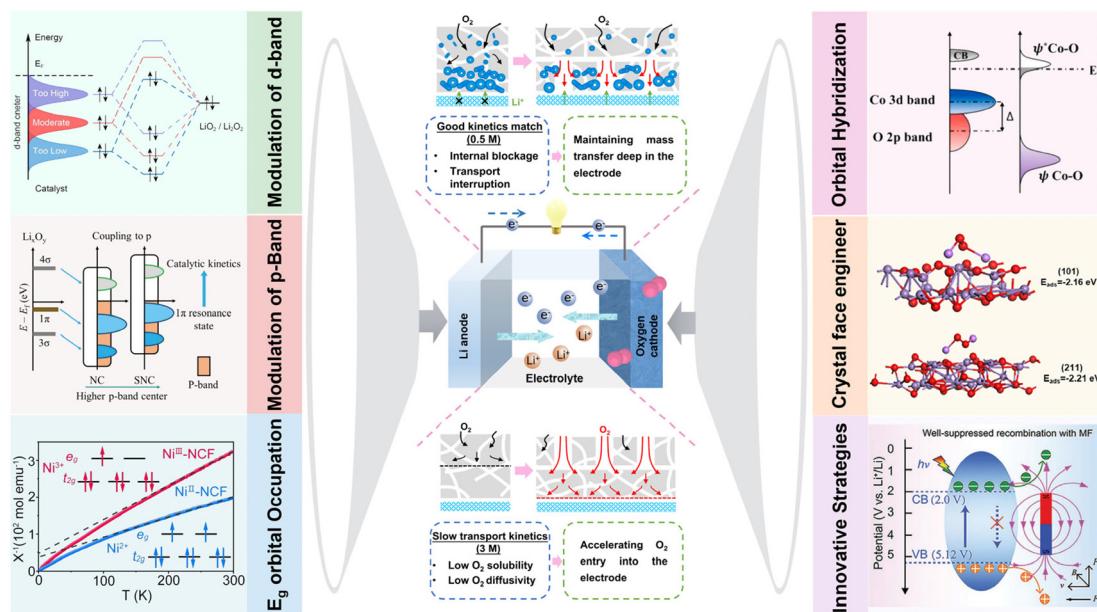
The design of the air cathode directly influences charge transfer efficiency at the electrolyte/catalyst interface, thereby determining overall battery performance.<sup>85,86</sup> First, the air

cathode must exhibit high electrical conductivity. The deposition of  $\text{Li}_2\text{O}_2$  can lead to electrode surface passivation. At low overpotentials, electrons must transfer from the insoluble  $\text{Li}_2\text{O}_2$  to the cathode surface, necessitating a cathode material with high electronic conductivity. Studies have shown that integrating catalysts with conductive materials (e.g., carbon nanotubes,<sup>87</sup> graphene<sup>88</sup>) can significantly enhance cathode conductivity and improve charge-discharge performance. Catalytic activity is a key performance metric for the air cathode. The cathode catalyst must effectively catalyze the ORR and OER reactions to reduce overpotential and enhance battery energy efficiency.<sup>89,90</sup> The electronic structure of the catalyst, particularly the electron density of the metal d-band, surface electron density, and adsorption capacity for intermediates, directly influences catalytic performance. Proper tuning of the d-band center can optimize the catalyst's adsorption energy for reaction intermediates, thereby enhancing catalytic activity. Additionally, defects and doped sites on the catalyst surface can increase the number of active sites, further facilitating electrochemical reactions.<sup>91</sup> Furthermore, the air cathode must exhibit high chemical stability. During long-term battery operation, the formation and decomposition of  $\text{Li}_2\text{O}_2$  is a recurring process, requiring the catalyst to maintain structural and functional stability. Side reactions, such as the formation of  $\text{LiOH}$  and  $\text{Li}_2\text{CO}_3$ , may block cathode pores, hindering long-term battery performance. Therefore, air cathode materials should possess strong corrosion resistance and durability to suppress side reactions and ensure the long-term stability of catalytic active sites. Structurally, the air cathode should have a high porosity to provide sufficient space for oxygen adsorption and  $\text{Li}_2\text{O}_2$  deposition.<sup>92</sup> Studies have shown that mesoporous and microporous structures facilitate efficient  $\text{Li}_2\text{O}_2$  storage and gas diffusion, thereby improving discharge capacity and rate performance.

## 3. Modulating cathode catalyst electronic properties

In  $\text{Li}-\text{O}_2$  batteries, the electronic structure of the cathode catalyst plays a decisive role in the adsorption/desorption behavior of reaction intermediate, charge transfer efficiency, as well as the reaction pathways, energy barriers, and overall performance of the ORR and OER.<sup>93-95</sup> In recent years, with advancements in DFT calculations and *in situ* characterization techniques, researchers have gradually unveiled the structure-activity relationships between catalyst electronic properties and catalytic activity. This has led to the development of a multiscale design approach guided by electronic regulation. Therefore, this paper systematically reviews the current primary strategies for optimizing electronic structures, including the modulation of the metal d-band center, optimization of non-metallic p-orbital sites,  $e_g$  orbital occupancy, orbital hybridization, facet-directed exposure, and innovative strategies assisted by external fields. It also explores their role and potential in enhancing the electrochemical performance of Li-





**Fig. 7** This work discusses strategies for modulating the electronic properties of catalysts, including modulation the metal d-band center,<sup>116</sup> non-metallic p-orbital sites,<sup>117</sup>  $E_g$  orbital occupation,<sup>106</sup> orbital hybridization,<sup>118</sup> optimization of exposed crystal facets,<sup>119</sup> and innovative approaches assisted by external fields.<sup>120</sup>

$O_2$  batteries (Fig. 7). Table 1 provides a summary of key parameters for several representative cathode catalysts in  $Li-O_2$  batteries reported over the past three years, including categories, electrolytes used, overpotential, discharge capacity, and cycle life, for readers to gain a comprehensive understanding. This review aims to deepen the understanding of catalytic mechanisms and provide theoretical and practical guidance for the rational design of high performance cathode catalysts.<sup>52,66,83,84,96-115</sup>

### 3.1 Modulation of the d-band center

Research on the regulation of catalyst electronic structures, particularly d-band center optimization, has been continuously emerging, providing a solid theoretical foundation and experimental evidence for improving the performance of  $Li-O_2$  batteries across various material systems and design strategies.<sup>121-125</sup> Guo *et al.* systematically investigated the effect of d-band center position on the adsorption strength of oxygen intermediates by designing a series of alloy catalysts with a broad distribution of d-band centers (a wide range of adsorption strengths) through a high-entropy strategy.<sup>116</sup> The binding energies of  $LiO_2/Li_2O_2$  with five different alloys exhibit corresponding energy conversion efficiencies, as shown in Fig. 8a and b. As the d-band center decreases in the order of HEA > PtIr > HEAPtIr > HEAIr > HEAPt, it confirms that the relationship between oxygen binding energy on the catalyst and energy conversion efficiency is not linear but follows a volcano-type trend. The peak performance is observed for HEAPtIr (d-band center = -2.64 eV), which exhibits the lowest overpotential of 0.38 V and an energy conversion efficiency exceeding 80%. The projected and integrated crystal orbital

Hamilton population (pCOHP and iCOHP) values further quantitatively evaluate the interaction between O1 and O2 bonds (Fig. 8c). From HEAPt to HEAPtIr, as the binding energy increases, a greater number of antibonding states become occupied, indicating that HEAPtIr further weakens the interaction between O1 and O2 compared to HEAIr and HEAPt. Notably, the -iCOHP values of HEA and PtIr are close to zero, indicating minimal interaction between oxygen atoms. This weak interaction makes the decomposition of  $LiO_2$  (or  $Li_2O_2$ ) more challenging, ultimately affecting the kinetics of the charging process. Fig. 8d and e summarize the relationship between the d-band center of cathode catalysts and catalytic activity in  $LiO_2$  batteries. An excessively high d-band center results in overly strong interactions with oxygen species, leading to slow desorption kinetics, which hinders subsequent reactions and deactivates active sites. Conversely, an excessively low d-band center provides insufficient binding strength, leading to product loss and sluggish charge transfer, which is detrimental to rate performance and stability. An optimal d-band center ensures appropriate adsorption strength with oxygen species, balancing adsorption and desorption, thereby achieving the ideal point in the Sabatier relationship. In the study of high-entropy perovskite oxide ( $LaSr(5TM)O_3$ ), five transition metal elements (TM = Cr, Mn, Fe, Co, Ni) occupy the B-site metal lattice.<sup>81</sup> As shown in Fig. 8f, the compressive strain in  $LaSr(5TM)O_3$  effectively modulates the occupancy state of the 3d orbitals at active cobalt sites ( $Co^{2+} \rightarrow Co^{3+}$ ). Consequently, the d-band center of Co shifts from -2.08 eV to -1.37 eV (Fig. 8g and h), enhancing the adsorption capability of  $LiO_2$  intermediates at cobalt sites. Additionally, the high electron-withdrawing capability of Cr sites ensures sufficient

**Table 1** Summary of recent progress in different cathodic catalysts and the corresponding electrochemical performance for Li–O<sub>2</sub> batteries

Cathode catalyst	Electrolyte	Overpotential (V)/ [current (mA g <sup>-1</sup> )]	Capacity (mA h g <sup>-1</sup> )/ [current (mA g <sup>-1</sup> )]	Cycles [current (mA g <sup>-1</sup> )]/ limited capacity (mA h g <sup>-1</sup> )	P.Y	Ref.
MnCr <sub>0.5</sub> Co <sub>1.5</sub> O <sub>4</sub>	1 M LiTFSI/TEGDME	0.67/100	16 388/100	329/(200/1000)	2024	94
WCoFe@Ni	1 M LiTFSI/DMSO	1.24/200	5800/200	>400/(500/1000)	2023	95
Mo <sub>3</sub> P@MO	—	1.05/100	4720/500	500/(500/500)	2022	96
Ni-NG SAC	1 M LiTFSI/TEGDME	—/200	24 248/200	>500/(300/1000)	2024	97
Ti <sub>0.87</sub> O <sub>2</sub> /MXene	—	0.69/200	13 596/100	407/(1000/600)	2024	81
SPC-2	1 M LiTFSI/TEGDME	1.04/200	20 287/200	226/(200/600)	2022	98
CeO <sub>2</sub> – $\delta$	1 M LiTFSI/DMSO	1.09/250	—	>35/(250/10 000)	2023	99
GMS-sheets	1 M LiTFSI + LiNO <sub>3</sub> /TEGDME	0.82	>6200 mA h g <sup>-1</sup> /0.4 mA cm <sup>-2</sup>	260/(0.4 mA cm <sup>-2</sup> )/4 mA h cm <sup>-2</sup>	2023	100
bpyN-MOF	1 M LiTFSI/TEGDME	0.487/200	17 275/100	270/(2000/1000)	2024	51
NiCo <sub>2</sub> O <sub>4</sub> @CeO <sub>2</sub>	1 M LiTFSI/TEGDME	1.07/500	5586/500	400/(500/500)	2022	101
GMS-CP	0.5 M LiTFSI/TEGDME	—	6727/100	307/(0.1 mA cm <sup>-2</sup> )/0.25 mA h cm <sup>-2</sup> )	2023	102
Ir <sub>1</sub> /Co <sub>3</sub> O <sub>4</sub>	—	0.305/200	16 861/200	180/(200/500)	2023	82
UIO-66-NH <sub>2</sub>	—	0.87/100	12 261/100	169/(200/1000)	2023	103
NiIII-NCF	1 M LiTFSI/TEGDME	0.92/500	16 800/500	>200/(500/1000)	2022	104
PtAu	1 M LiTFSI/TEGDME	0.36/100	5049/100	220/(500/1000)	2022	105
Ce <sub>1</sub> /CoO	1 M LiTFSI/TEGDME	0.46/250	37 462/250	136/(250/1000)	2024	106
FeCo-N <sub>4</sub> /HCS	1 M LiTFSI/TEGDME	0.64/200	1637/200	275/(200/1000)	2023	102
Ru <sub>0.8</sub> Pd <sub>0.2</sub> /Fe-CNCs	1 M LiTFSI/TEGDME	0.84/100	31 211/100	300/(200/1000)	2023	107
Ni/Ni <sub>3</sub> C-CNT	1 M LiTFSI/25% EMIM-BF <sub>4</sub> + 75% DMSO	0.43/200	21 612/0.5 mA cm <sup>-2</sup>	170/(0.5 mA cm <sup>-2</sup> )/0.5 mA h cm <sup>-2</sup> )	2022	65
NiRu-HTP	—	0.76/200	18 280/500	>200/(500/1000)	2022	108
Na-Pb-MOF	—	0.52/100	6247/100	140/(100/1000)	2023	109
TA-ZIF@Ru-280	1 M LiTFSI/TEGDME	—	7000/200	300/(200/500)	2023	110
NiCO <sub>2</sub> O <sub>4</sub> /MnO <sub>2</sub>	1 M LiTFSI/TEGDME	0.73/0.5 mA cm <sup>-2</sup>	7000/0.2 mA cm <sup>-2</sup>	800/(0.2 mA cm <sup>-2</sup> )/0.5 mA h cm <sup>-2</sup> )	2024	111
Pd <sub>3</sub> Pd	1 M LiTFSI/TEGDME	0.45/100	7746/—	175/(500/1000)	2023	112

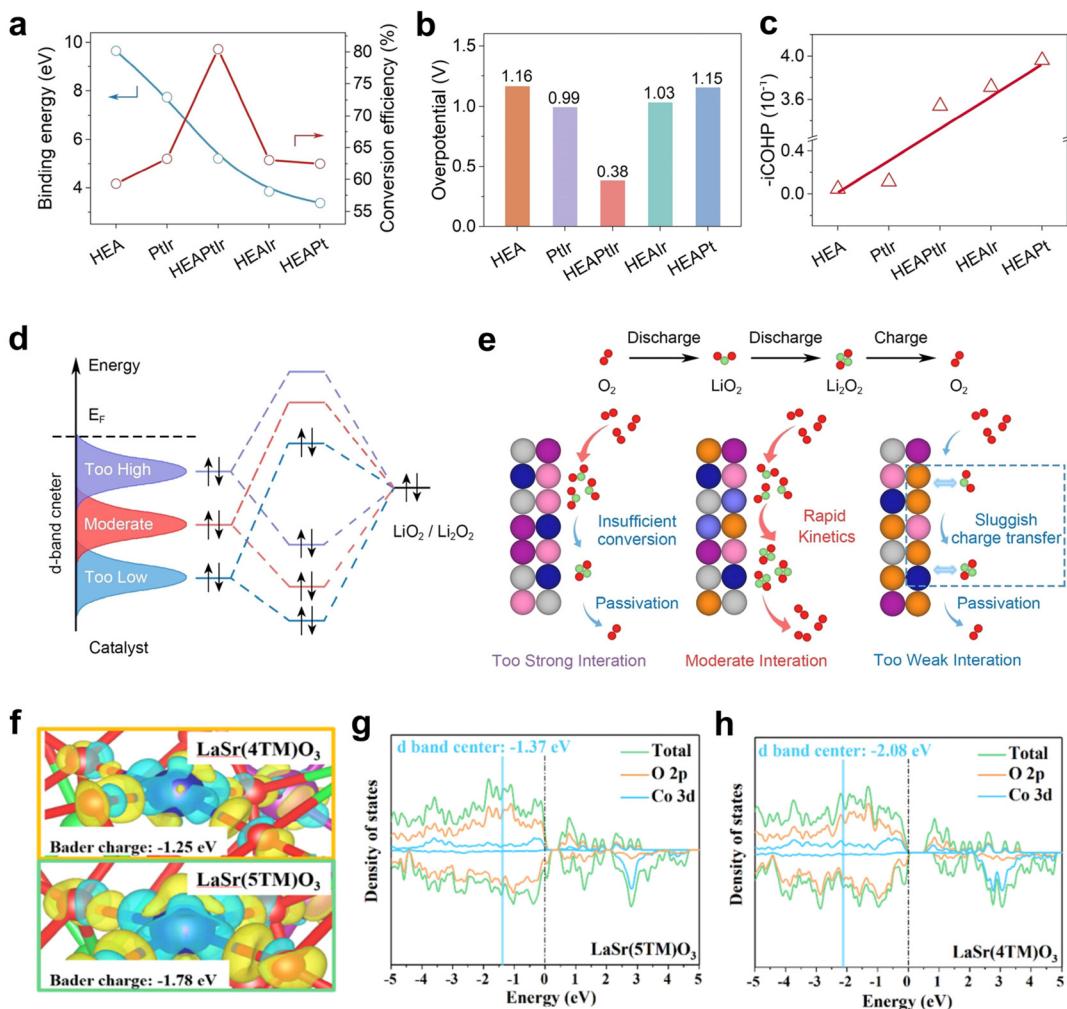
electron exchange, further strengthening the adsorption of LiO<sub>2</sub>. The charge–discharge overpotential is reduced to 0.79 V, extending the cycle life to 226 cycles.

By employing a heteroatomic doping strategy, such as Ni-doped RuO<sub>2</sub> catalysts (Ni-RuO<sub>2</sub>), electron redistribution effectively lowers the d-band center of RuO<sub>2</sub>, thereby weakening the adsorption strength of oxygen intermediates.<sup>126</sup> The Ni-RuO<sub>2</sub> catalyst exhibits a low overpotential of 0.79 V and an extended cycle life exceeding 791 cycles. Additionally, non-metal doping effectively induces electron delocalization, leading to changes in the d-band center at metal sites. As illustrated in Fig. 9a, moderate N doping in Ni<sub>5</sub>P<sub>4</sub> (N-Ni<sub>5</sub>P<sub>4</sub>/5N-Ni<sub>5</sub>P<sub>4</sub>) induces a downward shift in the d-band center, whereas higher doping levels (10N/15N-Ni<sub>5</sub>P<sub>4</sub>) lead to an upward shift. This suggests that appropriate doping can optimize the adsorption/desorption equilibrium of oxygen intermediates during the redox cycle. As the d-band center shifts downward, the antibonding states induced by O 2p–Ni 3d coupling move further away from the Fermi level, weakening the interaction between intermediates and the catalyst surface. Meanwhile, the significant contribution of P 2p orbitals to the TDOS near the Fermi level (Fig. 9b) ensures that the system retains high conductivity after oxygen intermediate adsorption, facilitating the growth of discharge products. Theoretical calculations indicate that a downward shift in the d-band center enhances antibonding orbital electron occupancy (Fig. 9c), thereby reducing the dissociation energy barrier of oxygen species, providing a key descriptor for catalyst design.<sup>127</sup> A novel bimetallic conductive metal–organic

framework (MOF) catalyst, NiRu-HTP, significantly enhances the oxygen reduction/evolution reaction (ORR/OER) kinetics in Li–O<sub>2</sub> batteries by synergistically tuning the d-band center and interfacial orbital hybridization.<sup>111</sup> As shown in Fig. 9d and e, the d-band centers of Ni-HTP and NiRu-HTP are –1.82 eV and –1.43 eV, respectively. The upward shift of the d-band center in NiRu-HTP enhances its interaction with O<sub>2</sub> molecules. DFT calculations indicate that at the Ni–N<sub>4</sub> site, the d<sub>xz</sub> and d<sub>yz</sub> orbitals of Ni overlap with the  $\pi$  orbitals of O<sub>2</sub>, forming (d<sub>xz</sub>/d<sub>yz</sub>– $\pi$ )\* orbitals (Fig. 9f). At the Ru–N<sub>4</sub> site, the d<sub>z<sup>2</sup></sub> and d<sub>xz</sub> orbitals of Ru couple with the  $\sigma$  and  $\pi$  orbitals of O<sub>2</sub>, forming (d<sub>z<sup>2</sup></sub>– $\sigma$ )\* and (d<sub>xz</sub>– $\pi$ )\* orbitals, respectively (Fig. 9g). In NiRu-HTP, the (d<sub>z<sup>2</sup></sub>– $\sigma$ )\* and (d<sub>xz</sub>– $\pi$ )\* orbitals exhibit lower electron occupancy and higher energy levels, indicating enhanced adsorption of O<sub>2</sub>. As shown in Fig. 9h and i, differential charge density maps further confirm that O<sub>2</sub> adsorption energy on NiRu-HTP (–1.47 eV) is significantly higher than that on Ni-HTP (0.28 eV). Additionally, NiRu-HTP transfers more electrons to O<sub>2</sub> (0.47 e<sup>–</sup> compared to 0.22 e<sup>–</sup>), indicating more effective O<sub>2</sub> activation. By tuning the d-band center to regulate the oxygen reduction and evolution reaction pathways, the NiRu-HTP cathode significantly reduces charge–discharge polarization to 0.76 V and maintains stable performance over 200 cycles without significant degradation.

Through heterointerface engineering,<sup>103,129,130</sup> as demonstrated in the Co<sub>3</sub>O<sub>4</sub>@NiFe<sub>2</sub>O<sub>4</sub> composite catalyst (Fig. 9j and k), the introduction of a heterogeneous interface can modulate the occupancy state of d orbitals at active metal sites *via* elec-





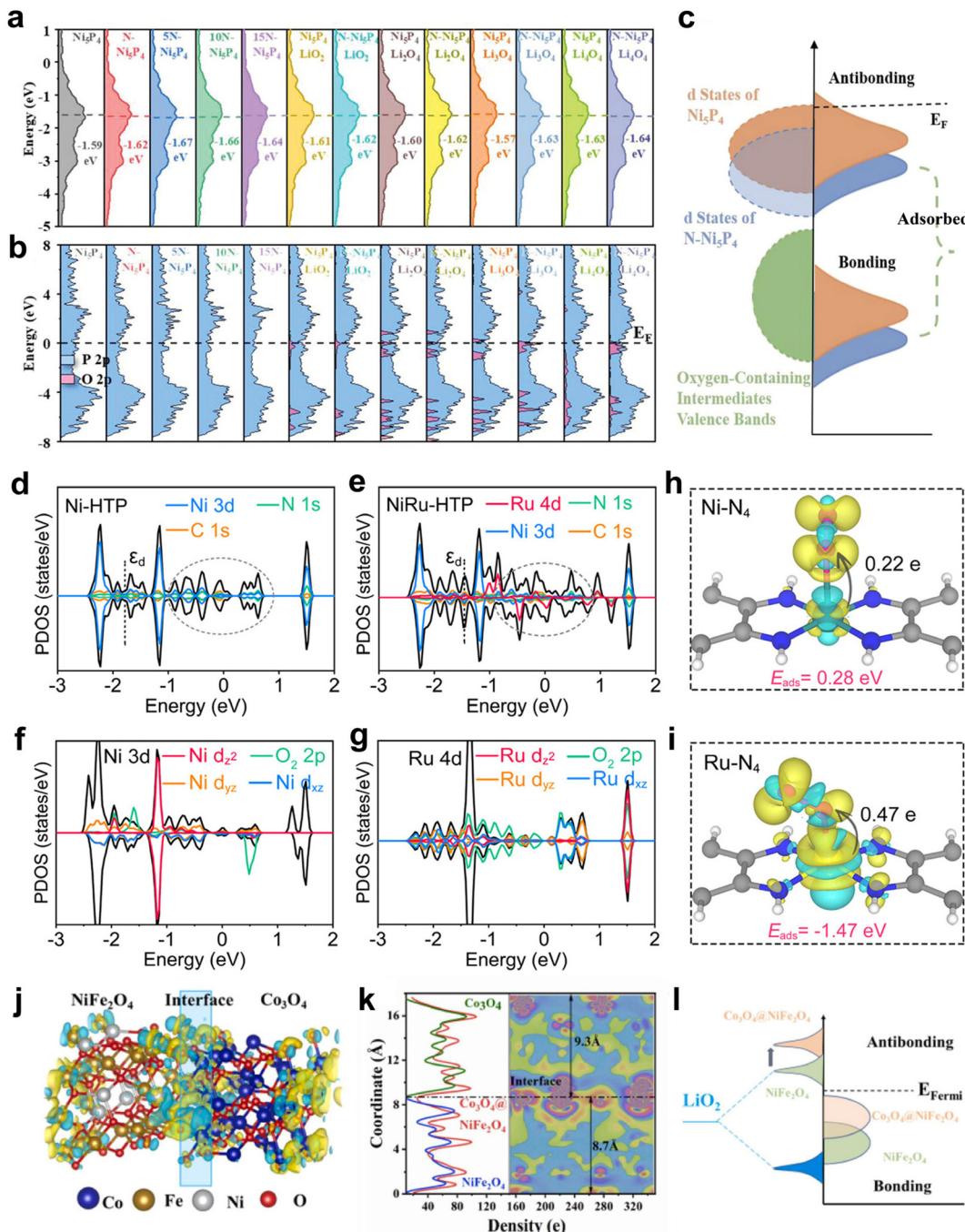
tron redistribution, leading to an upward shift of the d-band center.<sup>128</sup> This enhances oxygen intermediate adsorption and reaction kinetics (Fig. 9l). Additionally, high-entropy alloy (HEA) heterostructures (HEA@Pt) optimize the d-band center position of catalysts through the synergistic effects of multiple metal components and interfacial electron redistribution.<sup>131</sup> Single-atom catalysts also exhibit significant advantages in d-band center modulation.<sup>53,84,132,133</sup> A single-atom Ir catalyst (Ir@CeO<sub>2</sub>) supported on the (111) facet of CeO<sub>2</sub> leverages the electronic buffering effect of CeO<sub>2</sub>, which shifts the d-band center of Ir sites closer to the Fermi level.<sup>133</sup> This enhances Lewis acidity and effectively optimizes the adsorption of LiO<sub>2</sub> intermediates.

In recent years, significant progress has been made in optimizing the reaction kinetics of Li–O<sub>2</sub> batteries by tuning the d-band center of catalysts.<sup>111,116,134,135</sup> Studies have shown that the position of the d-band center directly determines the

adsorption strength of oxygen intermediates (LiO<sub>2</sub>, Li<sub>2</sub>O<sub>2</sub>), thereby influencing the energy barriers and cycling stability of the ORR/OER. Strategies such as high-entropy alloy design, heteroatomic doping, interface engineering, and single-atom catalysis achieve precise modulation of the d-band center at active sites through electronic structure rearrangement (e.g., orbital hybridization, charge transfer, and strain effects). These approaches enable a balance between the adsorption and dissociation kinetics of oxygen intermediates, significantly reducing charge–discharge polarization and extending cycle life, thereby elucidating the complexity and feasibility of d-band center regulation.<sup>66,136,137</sup>

### 3.2 Modulation of p-band non-metallic center

Research on optimizing p-band non-metallic sites primarily focuses on modifying non-metallic sites, such as nitrogen doping,<sup>138,139</sup> phosphorization,<sup>100,117</sup> sulfidation,<sup>113</sup> and non-



**Fig. 9** (a) d orbitals PDOS of  $\text{Ni}_5\text{P}_4$  with different levels of N doping and after adsorption of oxygen-containing intermediates. (b) P 2p and O 2p orbital distributions before and after adsorption of oxygen-containing intermediates on  $\text{Ni}_5\text{P}_4$  and  $\text{N}-\text{Ni}_5\text{P}_4$ . (c) Schematic diagram of bonding interactions between the valence band of surface adsorbates and the metal d-band.<sup>127</sup> TDOS and PDOS of Ni 3d and O 2p orbitals in (d)  $\text{NiN}_4-\text{O}_2$  within Ni-HTP and (e)  $\text{Ru N}_4-\text{O}_2$  within NiRu-HTP. PDOS distribution of (f) Ni 3d orbitals and (g) O 2p orbitals corresponding to (d) and (e). Differential charge density of (h) Ni-HTP and (i) NiRu-HTP after  $\text{O}_2$  adsorption, where cyan and yellow regions indicate charge depletion and accumulation, respectively.<sup>111</sup> (j) Differential charge density map of  $\text{Co}_3\text{O}_4@\text{NiFe}_2\text{O}_4$ . (k) Planar-averaged charge density difference (CDD) distribution on the surfaces of  $\text{Co}_3\text{O}_4$ ,  $\text{NiFe}_2\text{O}_4$ , and  $\text{Co}_3\text{O}_4@\text{NiFe}_2\text{O}_4$  (right); numerical values on the left indicate specific surface charge densities of each material. (l) Schematic diagram of valence band interactions between adsorbed  $\text{LiO}_2$  and the Ni 3d orbitals on  $\text{NiFe}_2\text{O}_4$  and  $\text{Co}_3\text{O}_4@\text{NiFe}_2\text{O}_4$  surfaces.<sup>128</sup>

metal vacancy introduction,<sup>113,140</sup> to enhance the electronic structure and reaction kinetics of catalysts. For instance, non-metal doping reconstructs the electronic structure of carbon-based catalysts. Surface phosphorization of sawdust-derived

carbon catalysts (Fig. 10a) effectively mitigates the corrosion between carbon materials and the electrolyte/products.<sup>100</sup> As shown in Fig. 10b, the SPC cathode features an open and orderly microchannel structure, providing efficient mass trans-

fer pathways,  $\text{Li}_2\text{O}_2$  storage space, and a highly active three-phase interface during the charge–discharge process in  $\text{Li}-\text{O}_2$  batteries. As illustrated in Fig. 10c–e, the doped P atoms preferentially substitute one N atom in pyrrolic-N sites, forming graphitized P–N active sites that act as reaction kinetics promoters. Compared to untreated carbon electrodes, SPC electrodes accelerate reaction kinetics through high  $\text{O}_2/\text{LiO}_2$  adsorption energies ( $\text{O}_2$ :  $-1.15$  eV,  $\text{LiO}_2$ :  $-2.03$  eV) and enhanced conductivity. Even under long-term cycling in the presence of highly oxidative discharge products ( $\text{Li}_{2-x}\text{O}_2$ ), SPC effectively suppresses byproduct formation and corrosion of sawdust-derived carbon catalysts. Further studies reveal that introducing sulfur anions into nitrogen–carbon catalysts (SNC) forms N–S pairs, effectively tuning the p-band center of pyridinic nitrogen groups. This accelerates the formation and decomposition of  $\text{Li}_{1-3}\text{O}_2$  intermediates, reducing the battery overpotential to  $0.35$  V.<sup>117</sup>

Oxygen vacancies, as key regulators of catalyst electronic structures, exhibit significant interfacial reaction optimization effects in  $\text{Li}-\text{O}_2$  batteries. Studies indicate that precisely controlling the concentration of oxygen vacancies can effectively direct the nucleation and decomposition pathways of  $\text{Li}_2\text{O}_2$ .<sup>3,82,142,143</sup> In cobalt oxide-based studies,  $\text{Co}_3\text{O}_4$  nanoboxes with varying surface oxygen vacancy concentrations were synthesized as cathode materials for  $\text{Li}-\text{O}_2$  batteries by controlling catalyst particle size.<sup>82</sup> Fig. 10f a<sub>1–3</sub> and b<sub>1–3</sub> depict the electrode surfaces of the samples in their initial state, after full discharge, and after charging, respectively. After discharge, small-sized S- $\text{Co}_3\text{O}_4$ , due to its high specific surface area and abundant oxygen vacancies, induces the uniform deposition of  $\text{Li}_2\text{O}_2$  in a thin-film morphology with smaller and evenly distributed particles. In contrast, large-sized B- $\text{Co}_3\text{O}_4$ , with insufficient oxygen vacancies, results in the aggregation of  $\text{Li}_2\text{O}_2$  into micron-sized clusters ( $\sim 4$   $\mu\text{m}$ ). The surface of S- $\text{Co}_3\text{O}_4$  contains more oxygen vacancies, providing additional nucleation sites for  $\text{Li}_2\text{O}_2$ . This facilitates the formation of highly dispersed and smaller-sized  $\text{Li}_2\text{O}_2$ , ensuring better contact with the catalyst surface. During subsequent charging, the efficient transport of  $\text{Li}^+$  and electrons at the interface facilitates the rapid decomposition of  $\text{Li}_2\text{O}_2$ , enhancing the battery's reversibility and cycling stability. However,  $\text{Li}_2\text{O}_2$  catalyzed by B- $\text{Co}_3\text{O}_4$  continues to migrate and aggregate on the catalyst surface, forming larger particles that reduce decomposition efficiency during charging. As cycling progresses,  $\text{Li}_2\text{O}_2$  continuously accumulates (Fig. 10g). This provides valuable insights into the structural design of cathode catalysts and the regulation of  $\text{Li}_2\text{O}_2$  morphology in  $\text{Li}-\text{O}_2$  batteries. The hollow catalyst TA-ZIF@Ru-280, synthesized via chemical etching, significantly enhances electron transport capability and reaction kinetics by optimizing active sites and oxygen vacancy distribution.<sup>113</sup> Similarly,  $\text{CuS}_{1-x}$  nanoflowers, designed and synthesized based on a defect engineering strategy, serve as cathode catalysts for  $\text{Li}-\text{O}_2$  batteries, effectively optimizing reaction kinetics.<sup>141</sup> Sulfur vacancies induce changes in the valence state distribution of Cu and trigger charge redistribution (Fig. 10h). This shifts the Fermi level of  $\text{CuS}_{1-x}$  toward the

conduction band, significantly enhancing its electronic conductivity (Fig. 10i). Additionally, sulfur vacancies create electron-deficient regions, providing unsaturated Cu active sites that facilitate stable  $\text{LiO}_2$  adsorption. This promotes the formation of highly conductive  $\text{LiO}_2$  intermediates *via* surface pathways, thereby lowering the decomposition energy barrier of  $\text{Li}_2\text{O}_2$  (Fig. 10j). This modification not only enhances the electronic conductivity of the catalyst but also strengthens charge transfer at Cu active sites, improving the adsorption stability of intermediate species.

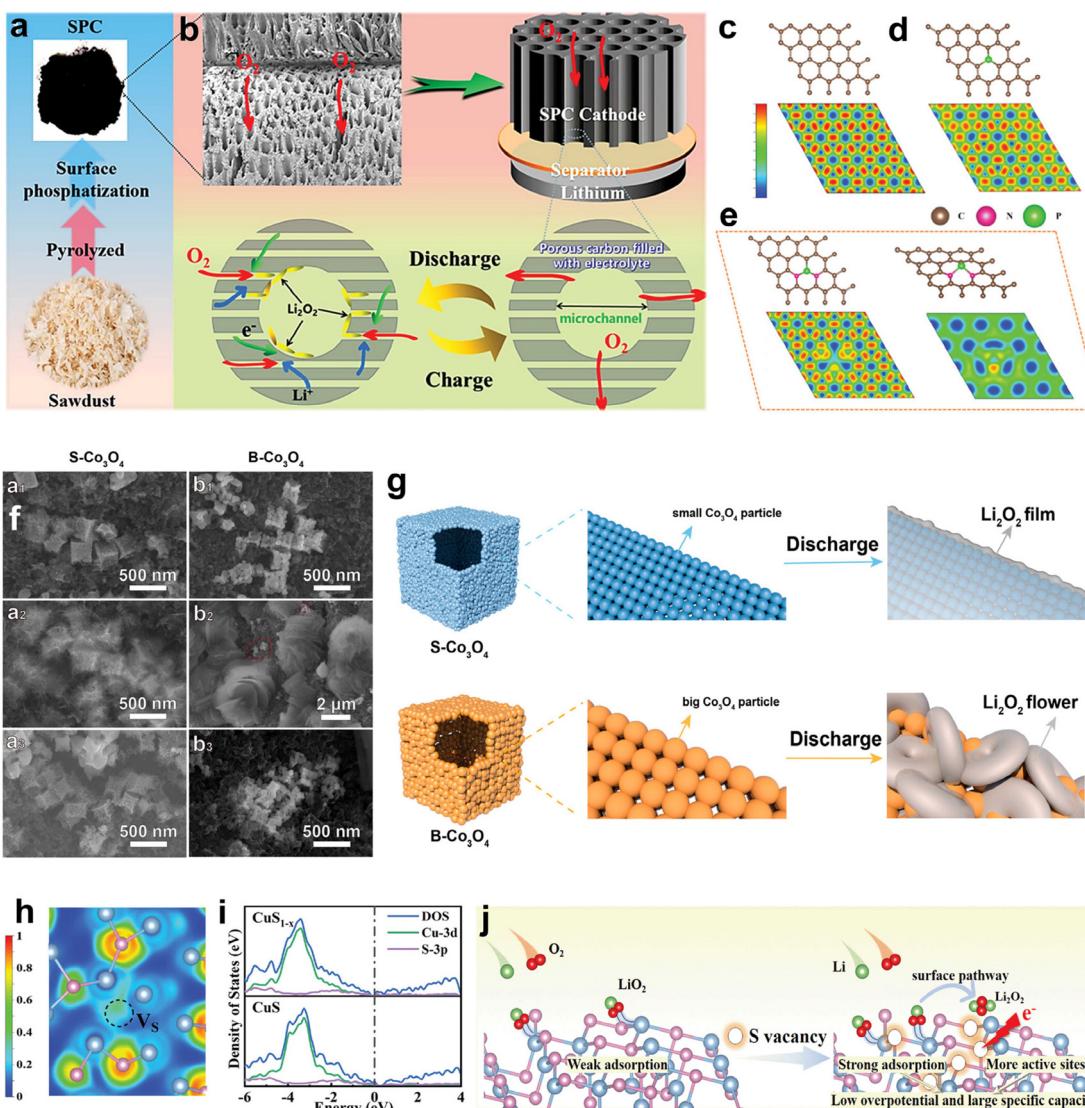
### 3.3 $e_g$ orbital occupation

The occupancy of the  $e_g$  orbitals serves as a key descriptor for the electronic structure of transition metal ion d-orbitals, directly influencing the adsorption–desorption equilibrium between catalyst surfaces and reaction intermediates.<sup>106,144,145</sup> According to molecular orbital theory, tuning the  $e_g$  orbital occupancy modulates the filling degree of antibonding orbitals ( $\sigma$  and  $\pi$ ), thereby adjusting the adsorption energy of intermediates such as  $^*\text{O}_2^-$ ,  $^*\text{LiO}_2$ , and  $^*\text{Li}_2\text{O}_2$ . The design of an ideal catalyst requires precise regulation of electron distribution within an optimal  $e_g$  orbital occupancy range to balance adsorption and desorption, ultimately achieving high-performance ORR and OER activities.

The introduction of highly electronegative metal elements (*e.g.*, Mo or Au) effectively modulates the  $e_g$  orbital occupancy of neighboring metal atoms. For example, in the PtAu alloy, the highly electronegative Au captures more  $e_g$  electrons from Pt, resulting in Pt atoms in PtAu having fewer  $e_g$  electrons compared to those in PtRu.<sup>107</sup> As shown in Fig. 11a, the Pt 4f peak of PtAu exhibits a noticeable blue shift relative to that of PtRu. PDOS calculations reveal that the number of  $e_g$  electrons on the Pt 5d orbitals in PtAu is 2.84, lower than the 2.96 in PtRu (Fig. 11b). The reduced  $e_g$  occupancy of Pt in the PtAu alloy leads to an upward shift of the Pt d-band, significantly decreasing antibonding electrons and thereby enhancing the adsorption strength between  $\text{LiO}_2$  and PtAu. Consequently, during the decomposition of  $\text{Li}_2\text{O}_2$ , PtAu exhibits a lower energy barrier (0.842 eV) compared to PtRu (1.01 eV) (Fig. 11c). Specifically, in the oxygen reduction reaction ORR process, the PtRu catalyst exhibits weak affinity toward  $\text{LiO}_2$ , leading to the formation of ring-shaped  $\text{Li}_2\text{O}_2$  *via* a solution-growth model. The insufficient  $\text{Li}_2\text{O}_2$ /cathode interface results in sluggish OER kinetics and undesired side reactions. In contrast, the strong interaction between  $\text{LiO}_2$  and the PtAu cathode facilitates the deposition of  $\text{Li}_2\text{O}_2$  nanosheets on the PtAu electrode surface *via* a surface-growth model. Benefiting from the superior contact interface between  $\text{Li}_2\text{O}_2$  nanosheets and the PtAu electrode, PtAu demonstrates a lower OER energy barrier and outstanding catalytic activity. Consequently,  $\text{Li}-\text{O}_2$  batteries based on the PtAu cathode exhibit a low charge overpotential of 0.36 V and excellent cycling stability over 220 cycles (with a capacity limit of 1000 mA  $\text{h g}^{-1}$ ), ranking among the best-performing noble metal-based cathodes reported to date.

Spin-state modulation alters the electron distribution of transition metal ions, thereby influencing the occupancy of

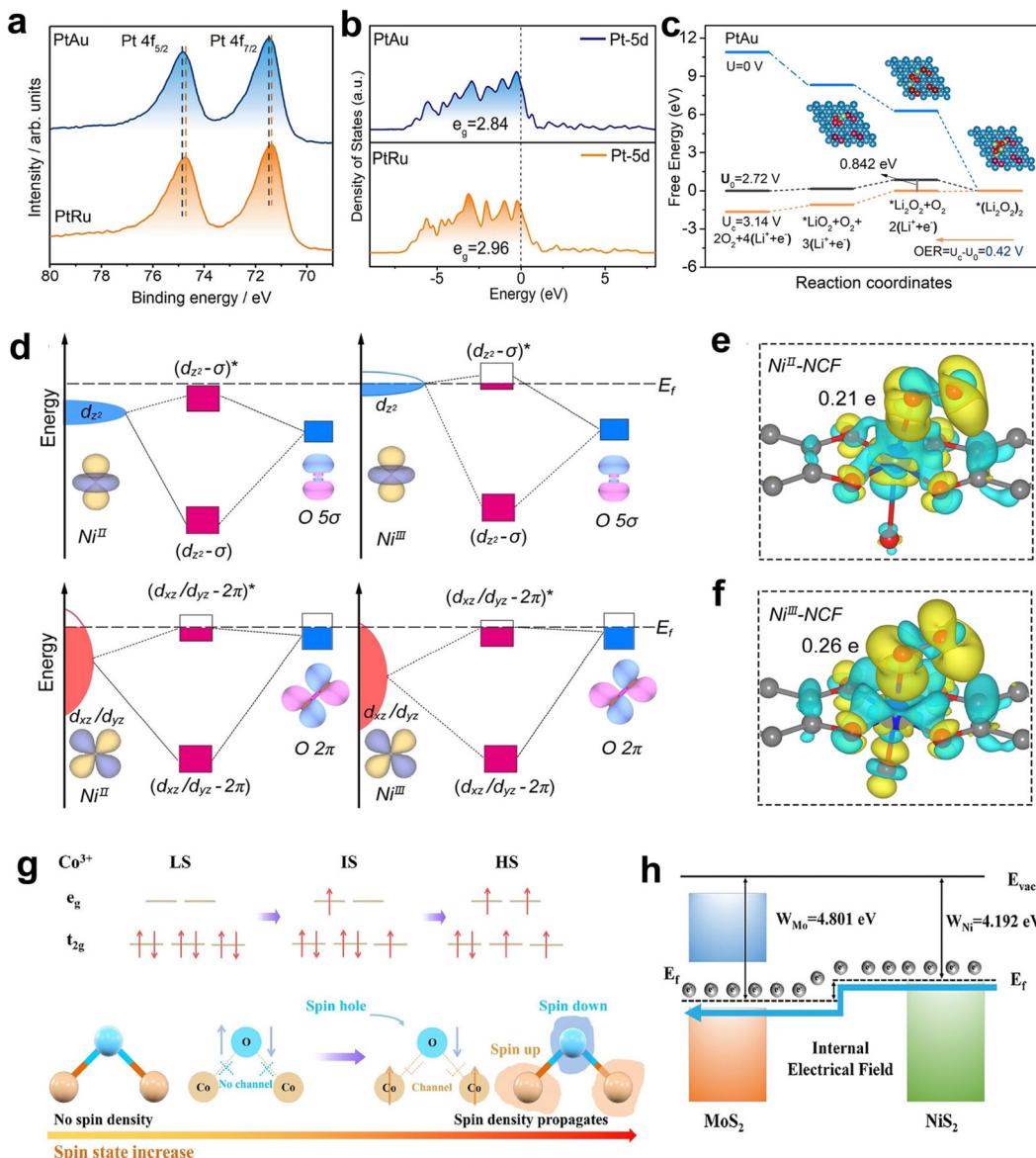




**Fig. 10** (a) Schematic illustration of SPC catalyst synthesis. (b) Schematic diagram of a Li–O<sub>2</sub> battery using an SPC cathode. The SPC cathode features an open and orderly arranged microchannel structure, facilitating Li<sup>+</sup> transport and oxygen diffusion. (c) Electronic structure of carbon and ELF. ELF of graphitized (d) P–C sites and (e) P–N sites.<sup>100</sup> (f) Ex situ SEM images of (a<sub>1</sub>–a<sub>3</sub>) S–Co<sub>3</sub>O<sub>4</sub> and (b<sub>1</sub>–b<sub>3</sub>) B–Co<sub>3</sub>O<sub>4</sub> cathodes at different stages: (a<sub>1</sub> and b<sub>1</sub>) initial state; (a<sub>2</sub> and b<sub>2</sub>) fully discharged state; (a<sub>3</sub> and b<sub>3</sub>) fully charged state. (g) Schematic illustration of the Li<sub>2</sub>O<sub>2</sub> formation mechanism on S–Co<sub>3</sub>O<sub>4</sub> and B–Co<sub>3</sub>O<sub>4</sub> surfaces.<sup>82</sup> (h) ELF of CuS<sub>1-x</sub>. (i) TDOS of CuS and CuS<sub>1-x</sub>. (j) Schematic illustration of the mechanism by which CuS<sub>1-x</sub> catalyst enables high-performance catalysis.<sup>141</sup>

the e<sub>g</sub> orbitals.<sup>147–149</sup> In two-dimensional MOFs, oxidative treatment of NiII-NCF nanowire arrays adjusts the spin state of some Ni<sup>2+</sup> metal centers (t<sub>2g</sub><sup>6</sup>e<sub>g</sub><sup>2</sup>) to a higher valence state, Ni<sup>3+</sup> (t<sub>2g</sub><sup>6</sup>e<sub>g</sub><sup>1</sup>), leading to a significant increase in e<sub>g</sub> orbital occupancy.<sup>106</sup> As illustrated in Fig. 11d, the orbital hybridization between Ni and O<sub>2</sub> is analyzed. Compared to the antibonding orbitals (d<sub>z<sup>2</sup></sub>–σ)\* and (d<sub>xz</sub>/d<sub>yz</sub>–2π)\* in NiII-NCF, the (d<sub>z<sup>2</sup></sub>–σ)\* orbital in NiIII-NCF exhibits a higher energy level with lower electron occupancy, which favors oxygen adsorption and enhances the Ni<sup>3+</sup>–O<sub>2</sub> interaction. Bader charge analysis reveals that NiIII-NCF (Fig. 11f) transfers more electrons (0.26 e<sup>–</sup>) to O<sub>2</sub> compared to NiII-NCF (0.21 e<sup>–</sup>) (Fig. 11e), thereby enabling stronger O<sub>2</sub> activation and an increased electron

transfer rate. The high affinity of Ni<sup>3+</sup> sites toward the Li<sub>2</sub>O<sub>2</sub> intermediate facilitates the formation of nanosheet-like Li<sub>2</sub>O<sub>2</sub> within the voids between NiIII-NCF nanowires. As a result, Li–O<sub>2</sub> batteries based on the NiIII-NCF cathode exhibit a remarkably high specific capacity of 16 800 mA h g<sup>–1</sup> and stable cycling performance exceeding 200 cycles. Similarly, in ZnCo<sub>2</sub>O<sub>4</sub> spinel structures, high-temperature calcination induces a transition of cobalt ions from a low-spin state (t<sub>2g</sub><sup>6</sup>e<sub>g</sub><sup>0</sup>) to a high-spin state (t<sub>2g</sub><sup>4</sup>e<sub>g</sub><sup>2</sup>), significantly increasing the delocalization of e<sub>g</sub> orbital electrons (Fig. 11g). This enhancement facilitates spin-selective charge transfer during the ORR/OER process and accelerates reaction kinetics through the formation of spin channels.<sup>144</sup>



**Fig. 11** (a) XPS spectra of the Pt 4f region for PtAu and PtRu cathodes. (b) PDOS of the Pt 5d orbitals in PtRu and PtAu. (c) Free energy profiles of the PtAu cathode under different potentials. The inset illustrates the optimized crystal structures of PtAu with specific adsorbates at the corresponding reaction steps.<sup>107</sup> (d) Schematic representation of the interaction between adsorbed O<sub>2</sub> and the d<sub>2z</sub> and d<sub>xy/yz</sub> orbitals of the Ni site in NiII-NCF and NiIII-NCF. Differential charge density distribution for O<sub>2</sub> adsorption on (e) NiII-NCF and (f) NiIII-NCF.<sup>106</sup> (g) Schematic diagram illustrating different spin states of Co<sup>3+</sup> and the formation of the Co–O–Co spin channel with increasing Co<sup>3+</sup> spin state.<sup>144</sup> (h) Work functions of MoS<sub>2</sub> and NiS<sub>2</sub>, along with a schematic depiction of the formation of an internal electric field.<sup>146</sup>

Heterostructures regulate the electronic distribution of catalysts through interfacial effects, serving as another critical strategy for optimizing e<sub>g</sub> orbital occupancy. In Ni/Mn-MOF, Mn doping further enhances the e<sub>g</sub> orbital occupancy of Ni, significantly improving electronic coupling between Ni and redox intermediates.<sup>145</sup> As a result, this battery achieves an exceptionally high specific capacity of 28 464 mA h g<sup>-1</sup> at 100 mA g<sup>-1</sup> while maintaining long-term cycling stability over 524 cycles. A hierarchical NiS<sub>2</sub>-MoS<sub>2</sub> heterostructure nanorod, synthesized via hydrothermal and chemical vapor deposition methods, features abundant defects and a mesoporous structure.

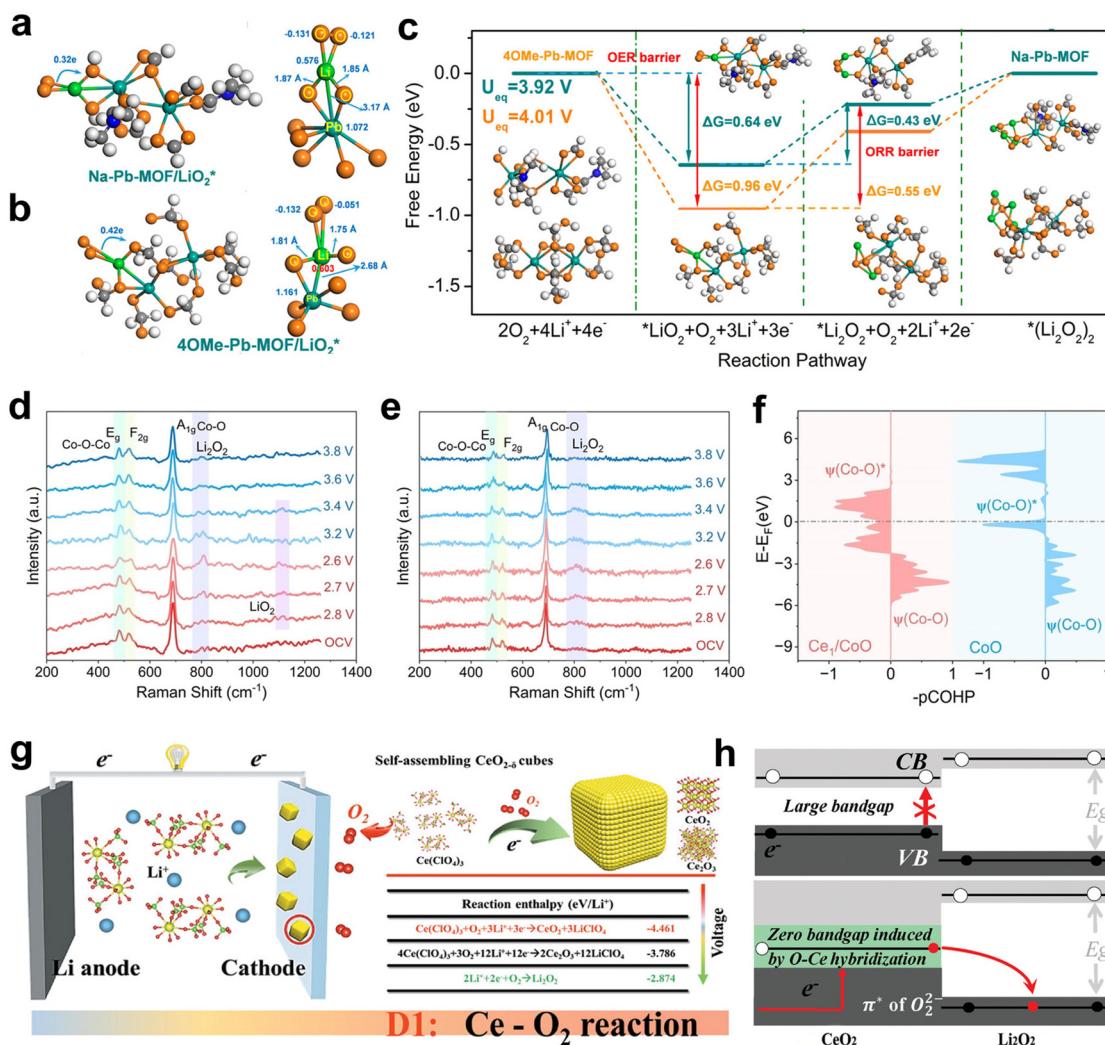
ture.<sup>146</sup> The work function difference between NiS<sub>2</sub> (4.192 eV) and MoS<sub>2</sub> (4.801 eV) induces charge transfer from NiS<sub>2</sub> to MoS<sub>2</sub>, leading to the formation of an internal electric field (Fig. 11h). This internal field optimizes the e<sub>g</sub> orbital occupancy of Mo atoms, as electrons are partially captured by highly electronegative Ni atoms, thereby reducing antibonding orbital occupancy. Consequently, the system achieves a balanced adsorption strength for oxygen intermediates (LiO<sub>2</sub>, Li<sub>2</sub>O<sub>2</sub>). The Li–O<sub>2</sub> battery based on the NiS<sub>2</sub>-MoS<sub>2</sub> cathode exhibits a coulombic efficiency of 99.65% and maintains stable performance even after 450 cycles at 1000 mA g<sup>-1</sup>.

### 3.4 Orbital hybridization

In recent years, catalyst design based on orbital hybridization strategies has achieved breakthrough progress in the field of Li–O<sub>2</sub> batteries.<sup>118,150,151</sup> In the spinel-structured MnCr<sub>0.5</sub>Co<sub>1.5</sub>O<sub>4</sub>, the introduction of Cr<sup>3+</sup> at octahedral sites extends the Co<sup>3+</sup>–O bond length and reduces lattice symmetry, leading to enhanced Co–O bond covalency.<sup>96</sup> This increased metal–oxygen covalency accelerates charge transfer in oxygen-related reactions, thereby promoting the reversible deposition and decomposition of Li–O<sub>2</sub> battery discharge product. Orbital hybridization can also be effectively tuned by modifying the coordination environment of metal centers.<sup>112,134,152</sup> In the single crystalline naphthalene lead MOF (Na–Pb-MOF), which features seven-coordinated PbO<sub>7</sub> nodes, the Pb–O bond length (2.88 Å) is longer than that in the six-coordinated PbO<sub>6</sub> nodes of the tetramethoxy lead MOF (4OMe–Pb-MOF) (2.37 Å).<sup>112</sup>

This elongation weakens the coupling between Pb 5d and O 2p orbitals, optimizing orbital interactions and improving the adsorption properties of intermediates such as LiO<sub>2</sub> (Fig. 12a and b). Consequently, this enhancement lowers the activation energy for both LiO<sub>2</sub> reduction to Li<sub>2</sub>O<sub>2</sub> and LiO<sub>2</sub> oxidation to O<sub>2</sub> (Fig. 12c), significantly reducing the overall battery overpotential (0.52 V) and enabling stable cycling performance over 140 cycles.

Rare-earth elements play a unique role in band hybridization due to their inner-shell orbitals and the strong localization of 4f electrons.<sup>101,108,153,154</sup> In the Ce single-atom-anchored CoO system (Ce<sub>1</sub>/CoO), Ce 4f and Co 3d orbitals undergo hybridization mediated by oxygen bridges, forming a dynamic electron reservoir that flexibly regulates the adsorption–desorption equilibrium of reaction intermediates.<sup>108</sup> As illustrated in Fig. 12d, *in situ* SERS reveals reversible changes



**Fig. 12** (a) Bader charge analysis of LiO<sub>2</sub> adsorption on Na–Pb-MOF and (b) 4OMe–Pb-MOF. (c) Gibbs free energy curves of Na–Pb-MOF and 4OMe–Pb-MOF. The inset illustrates the optimized crystal structures of adsorbates at different reaction steps.<sup>112</sup> (d) Surface-enhanced *in situ* SERS of Ce<sub>1</sub>/CoO and (e) CoO cathodes. (f) Crystal orbital Hamilton population (COHP) analysis of the Co–O bond in Ce<sub>1</sub>/CoO and CoO.<sup>108</sup> (g) DFT calculations and schematic representation of CeO<sub>2</sub>/Ce<sub>2</sub>O<sub>3</sub>/Li<sub>2</sub>O<sub>2</sub> formation during discharge. (h) Schematic representation of charge transfer from CeO<sub>2</sub> to the O<sub>2</sub><sup>2-</sup>–π\* energy level in Li<sub>2</sub>O<sub>2</sub>.<sup>101</sup>



in the Raman signals of the  $\text{Ce}_1/\text{CoO}$  cathode during charge–discharge cycles. The characteristic O–Co–O bending ( $E_g$ ) and Co–O stretching ( $A_{1g}$ ) vibrations gradually weaken, suggesting increased surface disorder and distortion of the  $\text{CoO}_6$  octahedral structure, thereby maintaining a highly active state. This indicates that  $\text{Ce}_1/\text{CoO}$  facilitates self-regulating catalysis throughout the  $\text{Li}-\text{O}_2$  battery cycling process. In contrast, after a single charge–discharge cycle, the  $E_g/A_{1g}$  Raman peak intensities of  $\text{CoO}$  fail to return to their initial state, suggesting potential surface reconstruction or loss of active sites (Fig. 12e). As shown in Fig. 12f, compared to  $\text{CoO}$  ( $\text{ICOHP} = -0.66$  eV), the  $\text{Ce}_1/\text{CoO}$  system exhibits a richer bonding state between Co and coordinated oxygen atoms ( $\text{ICOHP} = -0.70$  eV). This indicates an increased number of Co–O bonding orbitals and their enhanced occupancy below the  $E_F$ , ensuring the stability of Co–O bonds under redox conditions. Benefiting from the enhanced orbital coupling, the  $\text{Ce}_1/\text{CoO}$  cathode delivers an ultra-high discharge capacity of  $37\,462$  mA h g<sup>-1</sup> at a current density of  $250$  mA g<sup>-1</sup>, representing a 125% and 750% increase compared to  $\text{CoO}$  ( $16\,629$  mA h g<sup>-1</sup>) and  $\text{CeO}_2$  ( $4408$  mA h g<sup>-1</sup>) cathodes, respectively (Fig. 12g). An *in situ* electrochemical strategy was employed to synthesize a metastable  $\text{CeO}_{2-\delta}$  catalyst, where the cerium–oxygen reaction ( $\text{Ce}^{3+} + \text{O}_2 + \text{e}^- \rightarrow \text{CeO}_{2-\delta}$ ) occurs between  $\text{Ce}^{3+}$  in the electrolyte and  $\text{O}_2$ , forming oxygen vacancy-rich  $\text{CeO}_{2-\delta}$  nanocubes with high-energy (311) crystal facets (Fig. 12g).<sup>101</sup> By optimizing the O–Ce hybridized electronic structure, an electronic transport bridge was established between lattice oxygen and neighboring cerium atoms, creating a direct charge transfer channel from the Ce-4f orbitals in  $\text{CeO}_2$  to the  $\text{O}_2^{2-}-\pi^*$  orbitals in  $\text{Li}_2\text{O}_2$  (Fig. 12h). This facilitated  $\text{Li}-\text{O}_2$  reactions, leading to the formation of submicron  $\text{Li}_2\text{O}_2$  shell layers, thereby unlocking the capacity limitations of  $\text{Li}-\text{O}_2$  batteries. As a result, the discharge capacity increased significantly to  $32\,015$  mA h g<sup>-1</sup> at  $250$  mA g<sup>-1</sup>, far surpassing that of conventional  $\text{CeO}_2$  based cathodes ( $5703$  mA h g<sup>-1</sup>).

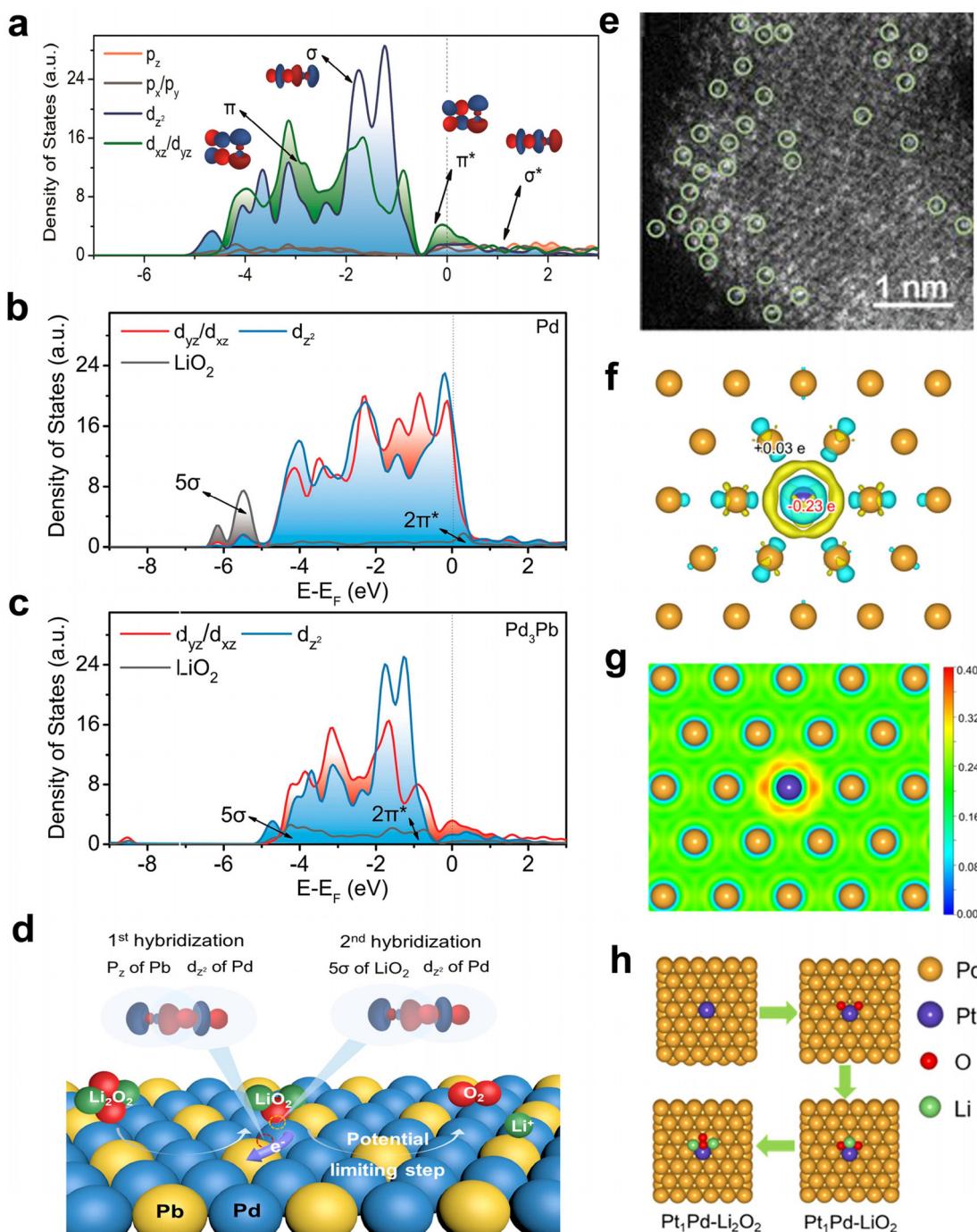
The study of intermetallic compounds<sup>115</sup> and single-atom alloy<sup>40,155</sup> catalysts has introduced innovative pathways in orbital hybridization strategies.  $\text{Pd}_3\text{Pb}$  nanocubes synthesized *via* a wet-chemistry method exhibit an ordered intermetallic structure, where Pd single atoms are uniformly dispersed within a Pb matrix, forming stable Pd–Pb covalent bonds.<sup>112</sup> Intra-molecular hybridization between the Pd 4d orbitals and Pb 6p orbitals lowers the d-band energy level of Pd (Fig. 13a), leading to an increase in the oxidation state of Pd. As shown in Fig. 13b and c, the influence of intra-molecular d–p hybridization results in a reduced overlap between the bonding and anti-bonding states of the Pd  $4d_{z^2}-5\sigma$  and  $4d_{xy}/d_{yz}-2\pi^*$  orbitals upon  $\text{LiO}_2$  adsorption. This weakens the orbital interaction with  $\text{LiO}_2$ . By leveraging both intra-molecular p–d orbital hybridization (direct coupling between Pd 4d and Pb 6p orbitals within  $\text{Pd}_3\text{Pb}$ ) and inter-molecular orbital hybridization (interaction between Pd 4d and  $\text{LiO}_2$   $5\sigma/2\pi^*$  orbitals), a cascade electron regulation system is established, effectively optimizing the electronic structure of the catalyst (Fig. 13d). This cascade-oriented orbital hybridization in  $\text{Pd}_3\text{Pb}$  enables

an ultra-low OER overpotential of  $0.45$  V in  $\text{Li}-\text{O}_2$  batteries, achieving outstanding cycling stability over 175 cycles at a fixed capacity of  $1000$  mA h g<sup>-1</sup>. A  $\text{Pt}_1\text{Pd}$  single-atom alloy catalyst was synthesized *via* a one-step wet-chemistry method. As shown in Fig. 13e, Pt atoms are uniformly dispersed within ultrathin Pd hexagonal nanosheets, occupying Pd lattice sites in a single-atom form and forming stable Pt–Pd covalent bonds.<sup>40</sup> The ELF (Fig. 13f) and Bader charge analysis (Fig. 13g) reveal that Pt single-atom sites exhibit electron enrichment ( $-0.23e$ ), while Pd sites experience electron depletion ( $+0.03e$ ), resulting in a strong electronic localization effect. This electronic redistribution facilitates the activation of the  $\text{O}_2/\text{Li}_2\text{O}_2$  redox couple, effectively lowering the energy barriers for the ORR and OER. As illustrated in Fig. 13h,  $\text{O}_2$  preferentially adsorbs at Pt sites, promoting the two-step reduction process of  $\text{LiO}_2 \rightarrow \text{Li}_2\text{O}_2$  while suppressing the formation of byproducts such as  $\text{Li}_2\text{CO}_3$ . These findings provide an important theoretical framework for the design of highly efficient  $\text{Li}-\text{O}_2$  battery cathode catalysts based on orbital engineering. By precisely tuning metal–oxygen bonding characteristics,<sup>101,108,151,156</sup> local electronic structures at active sites,<sup>96,150,157</sup> and orbital coupling strength,<sup>40,112</sup> this strategy offers a pathway to overcoming limitations in reaction pathway control and stability that challenge conventional catalysts.

### 3.5 Crystal face engineering design

Regulating the deposition pathway of discharge products through rational catalyst design has been widely employed to control the morphology and structure of  $\text{Li}_2\text{O}_2$ . Given that the ORR/OER reactions occur at the surface of oxygen catalysts, cathode catalyst facet engineering is considered an effective approach to enhance catalytic activity and modulate the deposition/decomposition pathway of discharge products by exposing specific crystal facets.<sup>99,158–160</sup> Studies have shown that two-dimensional  $\text{Mn}_3\text{O}_4$  nanosheets supported on graphene preferentially expose the (101) facet. The adsorption energy of  $\text{Li}_2\text{O}_2$  on the  $\text{Mn}_3\text{O}_4$  (101) facet ( $-2.16$  eV) is significantly lower than that on the (211) facet ( $-5.67$  eV), indicating that the (101) facet facilitates the desorption of  $\text{Li}_2\text{O}_2$  and reduces the decomposition energy barrier.<sup>119</sup> By exposing the (101) facet and introducing oxygen vacancies,  $\text{Mn}_3\text{O}_4$  NS/G effectively reduces the adsorption energy of  $\text{Li}_2\text{O}_2$ , lowers the charge overpotential to  $0.86$  V, and achieves an ultrahigh specific capacity of  $35\,583$  mA h g<sup>-1</sup> at  $200$  mA g<sup>-1</sup>. Similarly, two-dimensional layered structures with chemical bonding, such as stacked Ag–Te tetrahedral layers, predominantly expose the Ag-terminated (200) crystal facet.<sup>161</sup> The (200) facet exhibits adsorption energies of  $0.487$  eV and  $0.963$  eV for  $\text{LiO}_2$  and  $\text{Li}_2\text{O}_2$ , respectively, indicating physical adsorption. This facilitates the efficient formation of  $\text{Li}_2\text{O}_2$  *via* a two-electron pathway, as supported by the  $\Delta G-U$  phase diagram, which reveals a voltage window of  $2.27$ – $2.31$  V (Fig. 14a–c). In contrast, the (102) facet exhibits stronger adsorption (weaker chemical adsorption), which suppresses  $\text{Li}_2\text{O}_2$  conversion. The narrow-bandgap telluride  $\text{Ag}_2\text{Te}$  successfully mitigates the facet-dependent catalytic anisotropy, with both the 2D stacked surface (200) plane and the side-

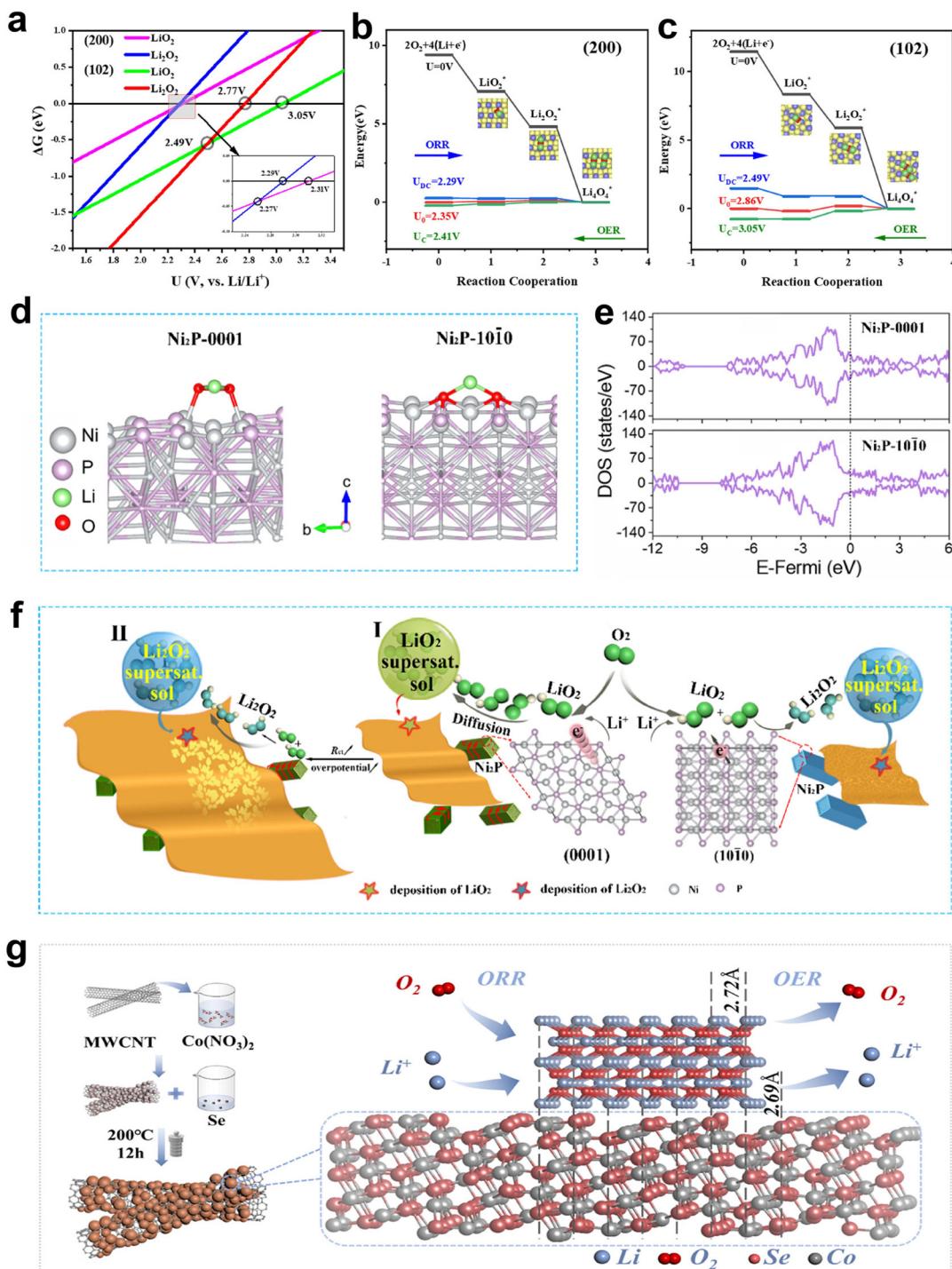




**Fig. 13** (a) DOS of Pd  $d_{z^2}$ ,  $d_{xz/yz}$  orbitals and Pb  $p_x, p_y, p_z$  orbitals after intra-molecular p-d orbital hybridization in  $\text{Pd}_3\text{Pb}$ . (b) DOS of Pd 4d  $d_{yz/d_{xz}}$  orbitals in Pd. (c) DOS of Pd 4d  $d_{yz/d_{xz}}$  orbitals in  $\text{Pd}_3\text{Pb}$  with adsorbed  $\text{LiO}_2$ . (d) Schematic representation of cascade orbital-oriented hybridization from intra-molecular Pb-Pd p-d hybridization in  $\text{Pd}_3\text{Pb}$  to inter-molecular orbital hybridization between  $\text{Pd}_3\text{Pb}$  ( $\text{Pd}$   $d_{xz/yz}$  and  $d_{z^2}$ ) and  $\text{LiO}_2$  ( $2\pi^*$  and  $5\sigma$ ), using the  $d_{z^2}$  orbital along the z-axis as an example.<sup>115</sup> (e) AC-HAADF-STEM image of the  $\text{Pt}_1\text{Pd}$  alloy (single-atom Pt marked with green circles). (f) ELF values of  $\text{Pt}_1\text{Pd}$ . (g) Charge density difference distribution (regions of electron enrichment and depletion) in  $\text{Pt}_1\text{Pd}$ . (h) Schematic representation of the discharge pathway of a  $\text{Li}-\text{O}_2$  battery on the  $\text{Pt}_1\text{Pd}$  surface.<sup>40</sup>

plane exhibiting exceptional catalytic activity. As a result,  $\text{Li}-\text{O}_2$  batteries based on the  $\text{Ag}_2\text{Te}$  cathode demonstrate an ultra-long cycling lifespan of over 300 cycles at a high current density of  $500 \text{ mA g}^{-1}$ , with a fixed capacity of  $1000 \text{ mA h g}^{-1}$ .

Crystal facet engineering, as an important strategy to regulate the deposition pathways of discharge products and enhance catalytic performance in  $\text{Li}-\text{O}_2$  batteries, demonstrates significant application potential.<sup>162-164</sup> By precisely



**Fig. 14** (a) Reaction phase diagram of the Ag<sub>2</sub>Te cathode on the (200) and (102) crystal facets. (b) Gibbs free energy diagram of the Ag<sub>2</sub>Te(200) and (c) (102) crystal facet during the ORR/OER process.<sup>161</sup> (d) Comparison of adsorption energies of the LiO<sub>2</sub> intermediate on Ni<sub>2</sub>P(0001) and (1010) crystal facets. (e) DOS analysis of Ni<sub>2</sub>P(0001) and (1010) crystal facets. (f) Schematic representation of the nucleation and growth mechanisms of discharge products on Ni<sub>2</sub>P(0001) and (1010) crystal facets.<sup>160</sup> (g) Synthesis pathway of Co<sub>0.85</sub>Se@CNT and schematic illustration of the lattice matching between the Co<sub>0.85</sub>Se(101) crystal facet and the Li<sub>2</sub>O<sub>2</sub>(100) crystal facet.<sup>165</sup>

controlling the exposed orientation of catalyst facets and their surface electronic structures, it is possible not only to modulate the adsorption behavior of intermediates such as LiO<sub>2</sub> and Li<sub>2</sub>O<sub>2</sub> but also to induce the formation of discharge products

with specific morphologies, thereby alleviating electrode passivation. Moreover, integrating oxygen vacancy introduction, lattice matching effects, and porous structure design can further optimize the distribution of active sites, reduce polariza-

ation, and improve cycling stability. This approach provides both theoretical insights and practical pathways for the development of highly efficient and stable cathode materials for Li<sub>2</sub>O<sub>2</sub> batteries.

Crystal-facet-controlled Ni<sub>2</sub>P nanorods were synthesized on Ni foam *via* a hydrothermal-phosphorization strategy, effectively regulating the nucleation, growth, and morphology of LiO<sub>2</sub> and Li<sub>2</sub>O<sub>2</sub>.<sup>160</sup> DFT calculations reveal that the adsorption energies of LiO<sub>2</sub> on the Ni<sub>2</sub>P(0001) and (1010) facets are -0.42 eV and -1.87 eV, respectively (Fig. 14d). Compared to the (1010) facet, the (0001) facet exhibits a higher DOS near the Fermi level, indicating a stronger electron transport capability for the Ni<sub>2</sub>P-0001 cathode (Fig. 14e). As illustrated in Fig. 14f, Ni<sub>2</sub>P-0001, which preferentially exposes the (0001) facet, induces the formation of large-sized Li<sub>2</sub>O<sub>2</sub> sheet-like and porous nanostructures due to its weak LiO<sub>2</sub> adsorption energy and high electron transport rate. This mitigates the passivation effect caused by insulating discharge products. Therefore, the deposition behavior and morphology of discharge products can be effectively tuned by controlling the preferentially exposed facets of the Ni<sub>2</sub>P catalyst.

The lattice matching effect is also an important strategy for regulating facet exposure properties. As illustrated in Fig. 14g, the grain-refined Co<sub>0.85</sub>Se@CNT catalyst exhibits a (101) facet with a lattice spacing of 2.69 Å, which is highly matched with the (100) facet of Li<sub>2</sub>O<sub>2</sub> (2.72 Å).<sup>165</sup> This strong lattice matching serves as a template for the epitaxial growth of Li<sub>2</sub>O<sub>2</sub>, promoting its oriented formation while suppressing the generation of side products. As a result, Li-O<sub>2</sub> batteries based on the Co<sub>0.85</sub>Se@CNT cathode demonstrate exceptional cycling stability of over 2400 hours at a current density of 100 mA g<sup>-1</sup>.

## 4. Innovative strategies in enhancing catalytic performance

External field-assisted strategies offer innovative approaches to overcoming the intrinsic activity limitations of cathode catalysts in Li-O<sub>2</sub> batteries. By introducing energy inputs such as light,<sup>166-168</sup> electricity,<sup>169</sup> magnetism,<sup>41,120</sup> or heat,<sup>75</sup> it is possible to dynamically regulate the local electronic structure at the catalyst interface, carrier distribution, and reaction kinetics. These modulations significantly enhance the activity and stability of both the ORR and OER. Unlike conventional chemical modifications, external fields enable real-time and directional control of the catalytic process through non-contact intervention. This approach has shown particular advantages in addressing key challenges such as high overpotentials and poor cycling stability. In recent years, the emergence of novel strategies, including photo-electrochemical synergistic catalysis, magnetothermal-induced lattice vibrations, and piezoelectric field-enhanced charge separation, has not only deepened the understanding of multiphysics coupling mechanisms but also accelerated the transition of Li-O<sub>2</sub> batteries from passive energy storage systems to intelligent, responsive platforms.

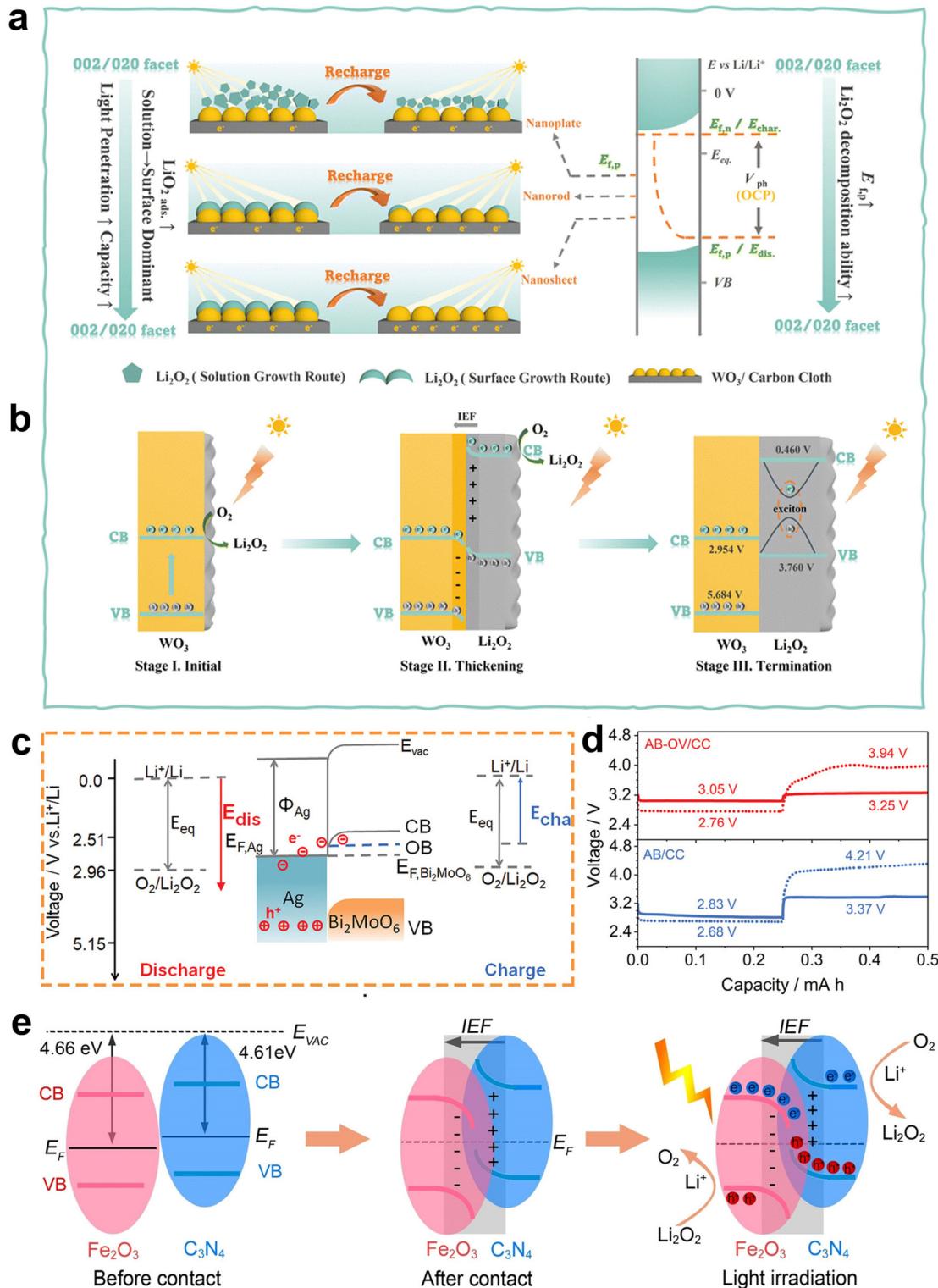
Photo-assisted strategies have emerged as an innovative approach to addressing Li-O<sub>2</sub> battery challenges, as they can

enhance the kinetics of redox reactions through the synergistic effect of photo-generated electron-hole pairs.<sup>170-174</sup> A study on facet-controlled WO<sub>3</sub> photoanodes revealed that by increasing the proportion of exposed (002)/(020) crystal facets in the WO<sub>3</sub> photoelectrode, a controllable transition from the solution-growth mode to the surface-growth mode of Li<sub>2</sub>O<sub>2</sub> formation can be achieved (Fig. 15a).<sup>175</sup> Furthermore, the Li<sub>2</sub>O<sub>2</sub> layer deposited during the discharge process can form a Z-type heterojunction with WO<sub>3</sub>. This photo-assisted discharge process occurs in three stages, as shown in Fig. 15b: (I) initial stage: the photo-generated electrons from WO<sub>3</sub> are consumed to reduce O<sub>2</sub>, forming a thin Li<sub>2</sub>O<sub>2</sub> film on the electrode surface; (II) thickening stage: the Li<sub>2</sub>O<sub>2</sub> layer formed interacts with WO<sub>3</sub> to create a Z-type heterojunction, which promotes exciton dissociation and generates free electrons, further accumulating discharge products; (III) termination stage: as Li<sub>2</sub>O<sub>2</sub> continues to accumulate, its enhanced exciton binding energy inhibits carrier separation, ultimately leading to the termination of the discharge process. Ultimately, the WO<sub>3</sub> photoanode, dominated by the (002) facet, achieves an extremely low overpotential of 0.07 V and maintains high cycling stability for over 200 hours.

Interface engineering and heterojunction construction have further enriched the electronic modulation strategies for photocatalysts. A composite cathode containing oxygen vacancies, Ag/Bi<sub>2</sub>MoO<sub>6</sub> (denoted as AB-OV/CC), demonstrates enhanced full-spectrum light absorption from ultraviolet to visible regions through the synergistic effects of Ag's localized surface plasmon resonance (LSPR) and the oxygen vacancies in Bi<sub>2</sub>MoO<sub>6</sub>.<sup>176</sup> The LSPR-generated hot electrons from Ag are injected into the oxygen vacancies band of Bi<sub>2</sub>MoO<sub>6</sub>, rather than its conduction band, enabling efficient charge separation (Fig. 15c). The accelerated oxygen reaction kinetics lead to the formation of amorphous Li<sub>2</sub>O<sub>2</sub>, resulting in an elevated discharge plateau voltage of 3.05 V. During charging, photoexcited holes rapidly decompose the amorphous Li<sub>2</sub>O<sub>2</sub>, lowering the charge plateau voltage to 3.25 V. This enables a high initial round-trip efficiency of 93.8% (Fig. 15d). An S-type heterojunction photoelectrode based on Fe<sub>2</sub>O<sub>3</sub>/C<sub>3</sub>N<sub>4</sub> was constructed, in which interfacial Fe-N bonds (bond length: 2.42 Å) and an internal electric field (IEF) synergistically promote directional separation of photo-generated charge carriers.<sup>177</sup> This structure establishes a unique electron transport pathway with spatially separated redox centers, where photoelectrons are concentrated on C<sub>3</sub>N<sub>4</sub> and photogenerated holes on Fe<sub>2</sub>O<sub>3</sub>. During discharge, electrons in the conduction band of C<sub>3</sub>N<sub>4</sub> reduce O<sub>2</sub> to form LiO<sub>2</sub> intermediates, which further convert into Li<sub>2</sub>O<sub>2</sub>, while holes in the valence band of Fe<sub>2</sub>O<sub>3</sub> participate in the oxidation reaction. During charging, holes in Fe<sub>2</sub>O<sub>3</sub> oxidize Li<sub>2</sub>O<sub>2</sub> to O<sub>2</sub>, while electrons in C<sub>3</sub>N<sub>4</sub> reduce Li<sup>+</sup> to metallic lithium (Fig. 15e). This design achieves a high discharge voltage of 3.13 V and a low charge voltage of 3.19 V, resulting in a round-trip efficiency approaching 98%.

Photocatalytic technologies also offer new perspectives for dynamically regulating discharge products in Li-O<sub>2</sub> batteries.

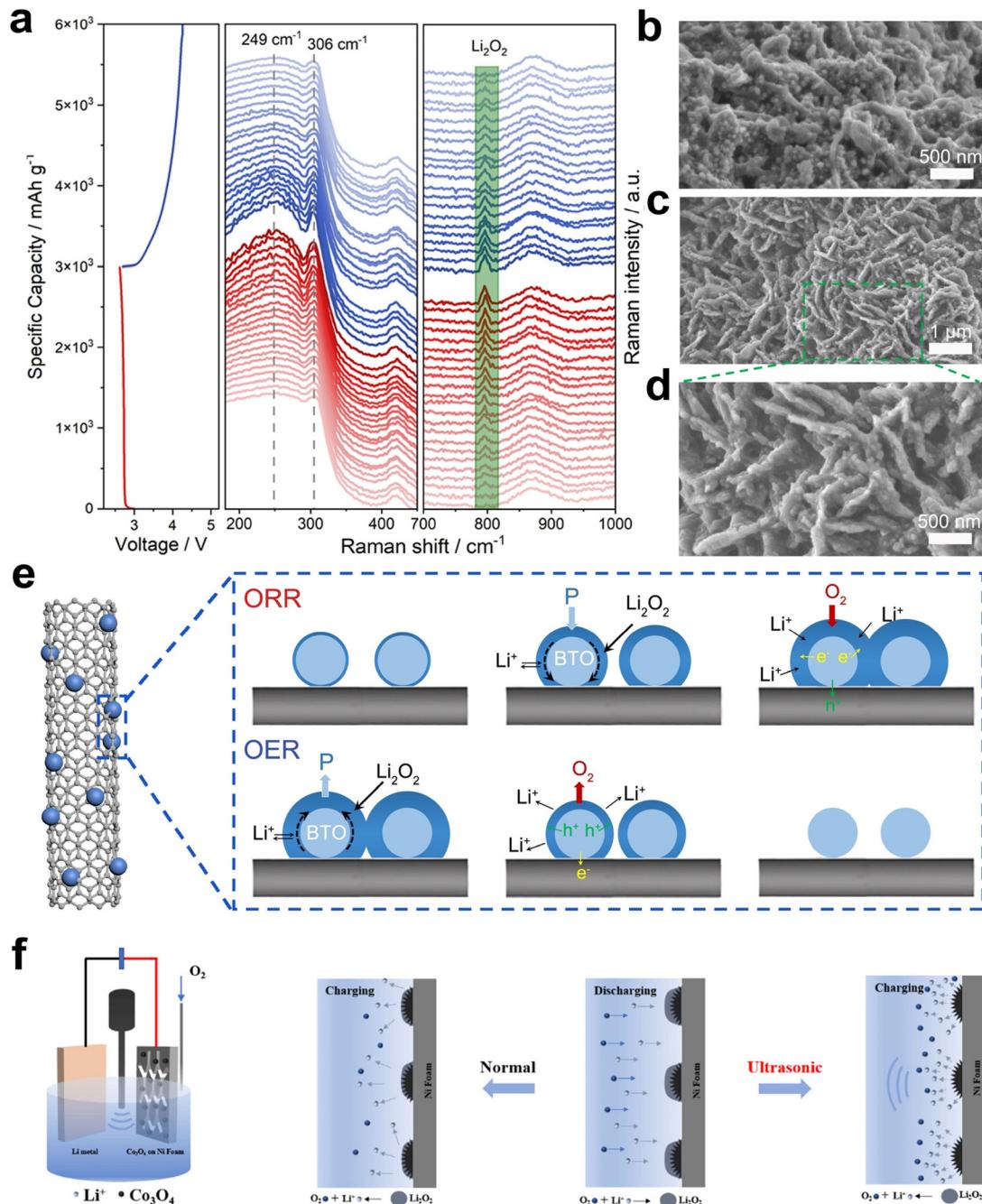




**Fig. 15** (a) Facet-controlled  $\text{Li}_2\text{O}_2$  growth pathways and the photocatalytic activity of  $\text{WO}_3$  in photo-assisted  $\text{Li}-\text{O}_2$  batteries. (b) Proposed mechanism of the photo-assisted discharge process, consisting of three distinct stages.<sup>175</sup> (c) Reaction mechanism of the AB-OV/CC photo-cathode in photo-assisted  $\text{Li}-\text{O}_2$  batteries. (d) Discharge/charge profiles of AB-OV/CC and AB/CC photo-cathodes at a current density of 50 mA g<sup>-1</sup> under illuminated (solid lines) and dark (dashed lines) conditions.<sup>176</sup> (e) Schematic illustration of directional charge transfer induced by the internal electric field at the  $\text{Fe}_2\text{O}_3/\text{C}_3\text{N}_4$  interface.<sup>177</sup>

By employing a cathode composed of light-responsive gold nanoparticles exhibiting SPR, combined with reduced graphene oxide (Au/rGO), recent studies have revealed the critical role of matching ORR kinetics with lithium-ion transport rates in determining battery performance.<sup>178</sup> Under light irradiation, this system significantly alleviates the phenomenon of “sudden battery death” caused by  $\text{Li}^+$  concentration polarization, introducing a novel concept of dynamic control.

Furthermore, a porphyrin-based MOF incorporating  $(\text{Fe}_2\text{Ni})\text{O}(\text{COO})_6$  clusters has been used as a photo-cathode to substantially enhance the performance of photo-assisted  $\text{Li}-\text{O}_2$  batteries.<sup>179</sup> The coupling between Ni 3d and Fe 3d orbitals strengthens ligand-to-metal cluster charge transfer (LMCT), thereby promoting the separation of excitons into free charge carriers. This process effectively suppresses recombination of photo-generated electron-hole pairs and activates the gene-



**Fig. 16** (a) *In situ* electrochemical Raman spectra collected on the BTO-CNT cathode at a current density of  $300 \text{ mA g}^{-1}$ . (b) SEM image of the BTO-CNT cathode at a discharge depth of  $1500 \text{ mA h g}^{-1}$  and a current density of  $300 \text{ mA g}^{-1}$ . (c and d) Low- and high-magnification SEM images of the BTO-CNT cathode at a discharge depth of  $3000 \text{ mA h g}^{-1}$  under a current density of  $300 \text{ mA g}^{-1}$ . (e) Schematic illustration of  $\text{Li}_2\text{O}_2$  formation and decomposition on the BTO surface.<sup>169</sup> (f) Schematic diagram of the ultrasonic charging mechanism on the electrode surface.<sup>180</sup>



ration of  $O_2^-$ , rather than  $^1O_2$ . Under light irradiation of  $100\text{ mW cm}^{-2}$ , the FeNi-TCPP-based photo-assisted  $\text{Li}-\text{O}_2$  battery achieves a remarkably low overall overpotential of 0.28 V and a round-trip efficiency of 92%.

In addition to photo-assisted catalysis,<sup>174,181-183</sup> researchers have explored a broader range of external field-assisted strategies.<sup>120,180</sup> One such innovative approach utilizes a stress field, with  $\text{BaTiO}_3$  (BTO) piezoelectric material as the core.<sup>169</sup> As shown in Fig. 16a, Raman scattering peaks at  $249\text{ cm}^{-1}$  and  $306\text{ cm}^{-1}$  correspond to the symmetric and asymmetric crystal structures of BTO. During discharge,  $\text{Li}_2\text{O}_2$  products rapidly accumulate on the surface of BTO (Fig. 16b-d), and the Raman scattering peaks at  $249\text{ cm}^{-1}$  and  $306\text{ cm}^{-1}$  are significantly enhanced, indicating increased lattice distortion of BTO. This is attributed to the intrinsic stress generated by the continuous accumulation of  $\text{Li}_2\text{O}_2$ , which causes  $\text{Ti}^{4+}$  ions to shift along specific crystal axes toward the  $\text{O}^{2-}$  direction. Consequently, the  $\text{O}^{2-}$  ions undergo electronic polarization displacement, generating a spontaneous polarization electric field that drives carrier separation and transport. This allows for the continuous separation and accumulation of electrons and holes, while the conduction and valence bands are tilted to favor enhanced ORR and OER kinetics (Fig. 16e). This coupling strategy between intrinsic stress and electric field at the surface effectively accelerates the interfacial transport rate of  $\text{Li}^+$  and improves the redox reaction kinetics in  $\text{Li}-\text{O}_2$  batteries. The study on  $\text{Co}_3\text{O}_4$  grown on nickel foam as a cathode explores the impact of acoustic fields on the performance of  $\text{Li}-\text{O}_2$  batteries.<sup>180</sup> Ultrasonic charging plays a positive role in enhancing

mass transfer processes, suppressing concentration polarization, promoting the rapid decomposition of  $\text{Li}_2\text{O}_2$ , and increasing the exposure of active sites (Fig. 16f). Ultrasonic energy, which can be converted into mechanical and thermal energy, aids in the decomposition of  $\text{Li}_2\text{O}_2$ , exposing more active sites and enhancing the rate of the OER. Experimental results demonstrate that under ultrasonic charging conditions with a duty cycle of 5 : 5 and a power of 675 W, the overpotential is reduced by 25.9%, and the battery's cycle life is extended from the typical 67 cycles to 321 cycles.

Magnetic field-assisted strategies have shown promising potential among multi-field coupling technologies due to the unique Lorentz force effect, which can suppress the rapid recombination of photoexcited electrons and holes. A three-dimensional porous  $\text{NiO}$  nanosheet on nickel foam ( $\text{NiO}/\text{FNi}$ ) was employed as a photoelectrode.<sup>120</sup> As a p-type semiconductor,  $\text{NiO}/\text{FNi}$  generates photoinduced electrons and holes under illumination. As illustrated in Fig. 17a, electrons in the conduction band (CB, 2.04 V vs.  $\text{Li}^+/\text{Li}$ ) facilitate the ORR, while holes in the valence band (VB, 5.16 V vs.  $\text{Li}^+/\text{Li}$ ) accelerate the oxidation of  $\text{Li}_2\text{O}_2$  during the OER, thereby reducing both discharge and charge overpotentials. When an external magnetic field (5 mT) is applied, the Lorentz force acts in opposite directions on the photoexcited electrons and holes, effectively suppressing their recombination (Fig. 17b). Serving as an integrated bifunctional photo-cathode,  $\text{NiO}/\text{FNi}$  combines magnetic effects with photoelectric conversion capabilities, enabling effective regulation of internal electrochemical properties, charge and lithium-ion transport, and redox reac-

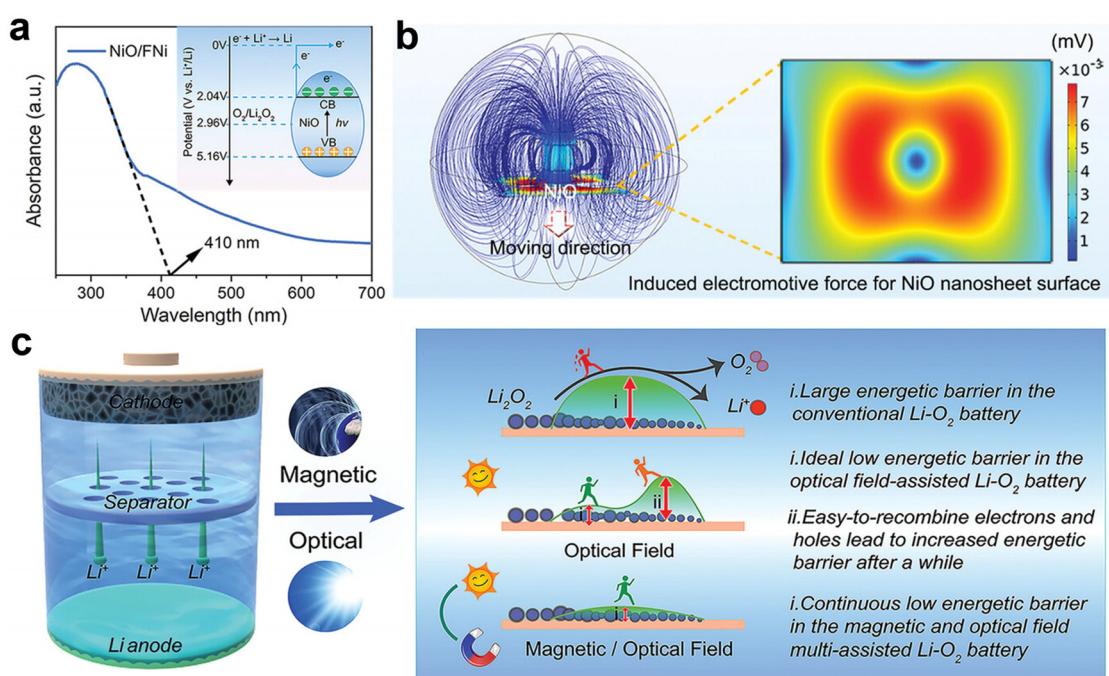


Fig. 17 (a) UV-vis absorption spectrum of  $\text{NiO}/\text{FNi}$ . Inset: energy band diagram of  $\text{NiO}/\text{FNi}$ . (b) Schematic illustration of the induced electromotive force (EMF) in  $\text{NiO}$  under relative motion within a magnetic field, along with a COMSOL simulation of the surface EMF distribution on  $\text{NiO}$  under magnetic assistance. (c) Schematic diagram of the working mechanism of a  $\text{Li}-\text{O}_2$  battery under combined light and magnetic field assistance.<sup>120</sup>



tion kinetics within the battery (Fig. 17c). The device operates stably at an ultra-low charging voltage of 2.73 V and achieves a high energy efficiency of 96.7% along with excellent cycling stability.

Field-assisted strategies, by dynamically modulating reaction kinetics and interfacial behaviors in batteries, hold theoretical promise for overcoming the intrinsic performance limitations of conventional catalysts.<sup>184,185</sup> However, their practical implementation still faces multiple challenges, including device integration, energy efficiency, cost control, and engineering scalability. At present, the coupling of external fields with electrochemical systems is not yet suitable for large-scale fabrication or industrial deployment. For instance, magnetic field-assisted strategies often require embedding permanent magnets or electromagnetic coils within the battery, which not only increases the device's volume and weight but may also induce variations in reaction site selectivity due to magnetic field gradients within porous electrodes. This necessitates complex magnetic shielding or gradient field designs for effective control. In the case of light-field strategies, the introduction of transparent windows (e.g., quartz or flexible polymers) into the battery casing can compromise system sealing, increasing the risk of electrolyte leakage and ambient gas permeation. Moreover, the uneven distribution and attenuation of light within porous structures can result in non-uniform activation of catalytic sites, limiting the overall reaction efficiency. Traditional photocatalysts are also prone to activity loss under prolonged illumination due to lattice oxygen depletion induced by photogenerated holes. More critically, the application of external fields typically requires additional energy inputs, such as light sources or electromagnetic devices, leading to relatively high power consumption and poor overall energy conversion efficiency.<sup>186,187</sup> Therefore, key directions for future research include the design of highly responsive materials, the development of energy recovery mechanisms, and the use of green energy sources to power the external fields, all aimed at improving system efficiency and promoting practical viability.

## 5. Conclusion and future perspectives

In recent years, significant progress has been made in the design and performance optimization of cathode catalysts for Li–O<sub>2</sub> batteries, laying a critical foundation for enhancing energy efficiency, cycling stability, and practical application potential. This review begins with an overview of the basic reaction mechanisms in Li–O<sub>2</sub> batteries, systematically summarizing the key role of cathode catalyst electronic properties in modulating the ORR and OER kinetics, as well as the corresponding structure–activity relationships based on current core research findings and innovative strategies. Through breakthroughs in DFT calculations and *in situ* characterization techniques, research has revealed the intrinsic relationships between catalyst electronic structures, such as the metal

d-band center, non-metallic p-orbital sites, e<sub>g</sub> orbital occupancy, orbital hybridization, optimization of exposed facets, and external field-assisted strategies. These insights progressively highlight the close connection between catalyst electronic structure and reaction activity, providing important theoretical support for the advancement of Li–O<sub>2</sub> battery technology and the rational design of efficient cathode catalysts. Notably, innovative strategies, including external field-assisted technologies such as light, sound, electricity, and magnetism, offer new dimensions for improving catalytic efficiency, achieving performance breakthroughs beyond traditional thermodynamic limitations.

Despite the remarkable progress in the design of cathode catalysts for Li–O<sub>2</sub> batteries, several critical areas still require further investigation to advance the practical application of this technology.

Future research should focus on the precise modulation of catalyst electronic structures at the molecular and atomic levels, with the goal of establishing quantitative structure–activity models that correlate adsorption free energy, electron transfer numbers, and catalytic activity. Such models will provide a fundamental basis for enhancing the kinetics of the ORR and OER and guide the rational design of high-performance cathode catalysts. Electronic structure optimization should not be limited to the modification of individual materials; instead, future efforts can explore the integration of different catalytic components. Designing composite materials or heterointerfaces to leverage synergistic effects between components can further improve catalytic performance. For example, metal–carbon composite materials can significantly enhance electrical conductivity and reaction kinetics. Moreover, emerging strategies such as external field-assisted catalysis and solid-state battery systems have shown great potential for improving both catalytic efficiency and long-term stability.

Although correlations between the electronic states of cathode catalysts and their catalytic activity can be established, such structure–activity relationships do not fully capture the actual reaction mechanisms. Under operating conditions, the nanoscale structures and coordination environments of active sites often undergo dynamic changes, diminishing the relevance of performance relationships derived solely from the catalyst's initial state. Therefore, the integration of advanced *in situ* characterization techniques is essential. For example, *in situ* X-ray absorption fine structure (XAFS) spectroscopy can identify the true active sites on electrode surfaces; *in situ* SERS enables the investigation of interfacial reactions and the capture of reaction intermediates during charge–discharge cycles; *in situ* UV-vis absorption spectroscopy allows monitoring of <sup>1</sup>O<sub>2</sub> dynamics and associated parasitic reactions. Additionally, TOF-SIMS provides precise compositional and three-dimensional spatial analysis of discharge products. Moreover, the development of theoretical modeling methods under realistic working conditions, such as molecular dynamics simulations, enables real-time tracking of the evolution of catalyst surfaces, active sites, and intermediates



during reactions. These approaches help unravel reaction mechanisms and the dynamic nature of active sites. By integrating theoretical simulations with experimental studies, a deeper understanding of the formation and decomposition kinetics of  $\text{Li}_2\text{O}_2$  can be achieved, offering a solid theoretical foundation for the design of next generation high efficiency catalysts.

The optimization of cathode, electrolyte, and anode interfaces must be pursued in a coordinated manner, encompassing the development of stable solid–liquid interfaces, enhancement of ionic conductivity, and improvement of interfacial durability and resistance to contamination. For example, electrolytes with low donor numbers tend to form thin  $\text{Li}_2\text{O}_2$  films, making them suitable for applications requiring high stability, whereas high donor number electrolytes promote the formation of  $\text{Li}_2\text{O}_2$  toroids, which are beneficial for achieving high discharge capacities. Therefore, it is essential to develop electrolytes that simultaneously offer high solubility and high diffusion coefficients. Catalyst degradation induced by reactive oxygen species, such as  $\text{O}_2^-$  and  ${}^1\text{O}_2$ , along with the accumulation of side products ( $\text{Li}_2\text{CO}_3$  and  $\text{LiOH}$ ), can significantly reduce charging efficiency and increase energy loss. Designing catalysts capable of converting  ${}^1\text{O}_2$  into its less reactive triplet state ( ${}^3\text{O}_2$ ) is key to suppressing these undesirable side reactions. The lithium metal anode, due to its high reactivity, readily reacts with electrolytes and oxygen, leading to dendrite formation and increased risk of short circuits. Strategies such as constructing artificial solid electrolyte interphase (ASEI) layers, introducing lithium host materials, and optimizing lithium stripping/plating mechanisms have proven effective in improving the cycling stability and safety of the anode.

## Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request. All relevant data generated or analyzed during this study have been properly cited and referenced within the manuscript. Any additional data or materials can be made accessible to interested researchers, in accordance with the data sharing policies of EES Batteries.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work was supported by the Science and Technology Development Fund (FDCT) of Macao S.A.R (0033/2023/ITP1, 0022/2023/RIB1, 046/2019/AFJ and 0070/2023/AFJ), the Multi-Year Research Grants (file no. MYRG2022-00223-IAPME and MYRG-GRG2024-00166-IAPME) from the Research Services and Knowledge Transfer Office at the University of Macau.

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