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Elucidate the formation and consumption mechanism of lithium oxides in lithium-oxygen batteries by combining the transfer-reaction model and the DFT calculation

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ABSTRACT

Lithium-oxygen (Li-O₂) batteries are considered one of the most promising energy storage devices for the next generation due to their high theoretical energy density. However, its poor cycle efficiency and discharge performance hinder the large-scale application. Understanding the complicative positive electrode reaction of Li-O₂ batteries can help overcome these difficulties. This work establishes a transfer-reaction model to simulate the multi-step reactions during the discharge of Li-O₂ batteries. It is found that the internal diffusion of oxygen causes local deposition of Li₂O₂ at the interface, leading to deterioration of diffusion and the end of discharge. The intermediate product LiO₂ accumulates uniformly through the electrode, while the generated singlet oxygen exhibits a characteristic of less at the interface and more inside. By using DFT to calculate the reaction rate constant, the model is proved to achieve the connection between macro and micro levels well. This work hopes to inspire future multi-scale research into Li-O₂ batteries and contribute to the realization of high-performance metal-air battery design as soon as possible.

1. Introduction

With the growing demand for energy storages devices, the lithiumoxygen (Li-O₂) batteries has become a research hotspot in recent years on account of their rather high theoretical energy density (~3500 Wh/ kg)[1,2].Although great progress has been made, many challenges such as poor charge and discharge ability[3], complicated multi-step[4] and side reactions[5] and degenerating cycle performances[6] still hinders the large scale commercialization of Li-O₂ batteries. One of the main reasons for the poor discharge ability can be attributed to the formation of the discharge product Li_2O_2 . Li_2O_2 is non-conductive and difficult to dissolve in the electrolyte, so it often accumulates in the pores of the electrode, especially in the oxygen enrichment, which directly leads to the increasing difficulty of electron transference and oxygen diffusion during the discharge process[7,8]. Thus, a detailed description of the battery reaction process is necessary to overcome the above challenges. An amount of modeling work has already been carried out to study the discharge behavior under various working conditions. The difference of battery component structure, especially the open ratio of the positive electrode, directly affects the transference of oxygen, thereby changing the discharge performance of the battery[9]. Considering the effect of the electrolytes, it is elucidated that moderate electrolyte concentrations and a certain component with different solvent molecules have a positive contribution to the discharge capacity of the batteries. Surprisingly, some side reactions when carbon dioxide[10] and water[11] molecules exist would alleviate the electrode surface passivation to some extent, thus leading to better discharge ability. Heterogeneous pore network model (PNM) has also been constructed to study the transport characteristics in the actual porous structure and demonstrate the effects of the internal connection structure of the electrode pores[12].

The above work has provided great help for us to understand the

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working principle of lithium oxygen batteries and can also serve as an important reference for experiments. However, many of them only consider a simplified reaction model with one-step reaction to generate Li₂O₂, which may not be consistent with the actual situation and detailed enough to offer a thorough understanding for the formation process of Li₂O₂[13,14]. Recently, investigators have found two different reaction paths for Li₂O₂ formation during the discharge process, which is called surface pathway and solution pathway respectively. The surface pathway tends to form the thin film shaped $Li_2O_2[15,16]$, while the solution pathway tends to form the toroidal $Li_2O_2[17,18]$. The dissolution of LiO₂ plays a critical role in undergoing which pathway to react[15,17]. Moreover, in the solution mechanism, the self-disproportionation reaction of LiO₂ produces singlet oxygen with extremely high chemical activity, which will seriously deteriorate the performance of Li-O₂ batteries [19-21]. Therefore, it is urgent to understand the multi-step battery reactions, especially the two pathways to generate Li₂O₂, which greatly dominate the discharge process of the battery. At present, the impact of multi-step reactions and their important features are seldom considered.

This work provides a comprehensively detailed battery model by considering both surface and solution pathways and examining the concentration changes of LiO_2 , a critical intermediate of the reaction. We also study the distribution of singlet oxygen to learn how it accumulates. We use the DFT theoretical calculation method to get the rate constant of the discharge reactions and compare the constant with the assumed one in the model. This work provides a new paradigm for studying Li-O_2 batteries and other types of batteries by combining transfer-reaction model with DFT calculation, realizing the connection between two levels of methods, and offers a rigorous theoretical reference for related experiments.

2. Method

2.1. Reaction equation

The dominant reactions on the anode and cathode during discharge in non-aqueous Li- O_2 batteries can be described as follows:

Anode
$$Li \rightarrow Li^+ + e^-$$
 (1)

Cathode
$$O_2 + 2Li^+ + 2e^- \rightarrow Li_2O_2$$
 (2)

The discharge process involves the oxidation of lithium at the anode and the reduction of oxygen to form Li_2O_2 at the cathode. The formation of Li_2O_2 during discharge is believed to occur through different pathways, due to the various morphologies of Li_2O_2 observed in experiments [22,23]. Specifically, LiO_2 acts as an intermediate when oxygen diffuses to the cathode interface.

$$O_2 + Li^+ + e^- \rightarrow LiO_2 \tag{3}$$

Next, the LiO_2 formed on the electrode will undergo two distinct pathways to generate Li_2O_2 , namely the solution pathway and the surface pathway. These can be described as follows[14–17,24,25]:

$$\text{LiO}_2 \rightarrow \phi \text{LiO}_{2(\text{sol})} + (1 - \phi) \text{LiO}_{2(\text{suf})}$$
(4)

 ϕ is the dissolution coefficient, which represents the proportion of the dissolved part.

The solution pathway commences with the dissolution of LiO_2 in the electrolyte. Subsequently, the dissolved LiO_2 undergoes complete separation into Li^+ and O_2 . This separation initiates a self-disproportionation reaction that results in the formation of toroidal Li_2O_2 particles.

$$2\text{LiO}_{2(\text{sol})} \rightarrow \text{Li}_2\text{O}_{2,\text{particle}} + \text{O}_2^* \tag{5}$$

It should be noted that the generated oxygen comprises two types, ground-state triplet oxygen and highly reactive singlet oxygen.

$$O_2^* \rightarrow \chi^1 O_2 + (1 - \chi)^3 O_2$$
 (6)

Different from the solution pathway, the LiO_2 absorbed on the electrode surface converts to film-like Li_2O_2 through the surface pathway, a single electron transfer reaction.

$$LiO_{2(suf)} + Li^{+} + e^{-} \rightarrow Li_{2}O_{2,film}$$
(7)

The two pathways reactions are shown in the Fig. 1a. The formation of Li_2O_2 through two distinct pathways leads to different deposition morphologies and ultimately affects the discharge performance of $Li-O_2$ batteries. The solution pathway is found to be beneficial to battery discharge due to the formation of toroidal particles, which can effectively alleviate electrode surface passivation[13,26]. Conversely, the surface pathway is found to be detrimental, as it results in rapid surface passivation and subsequent discharge termination due to an increase in film-like Li_2O_2 thickness[14,15,17]. Electrolytes with a low Gutman acceptor number (AN) or donor number (DN) prefer the surface pathway, while the solution pathway is favored for those with high Gutman numbers[27,28], thus in this model, DME with 1 M LiPF₆ is adopted to enhance solution pathway.

2.2. Transport equation

A two-dimensional mathematical model, as depicted in Fig. 1b, has been developed to investigate the mechanism of a non-aqueous Li-O_2 battery during discharge. This model incorporates the description of mass, current, species transport, and reaction kinetics within the electrode. The computational domain comprises a thin lithium metal anode, a separator, and a porous carbon cathode.

The transports of Li, O_2 , and LiO_2 in the electrolyte are considered. Li_2O_2 deposits once it is formed due to its low solubility in the electrolyte, so its transfer is not considered. Material balance equations for species in the solution phase can be expressed as follows:

$$\frac{\partial(\varepsilon c_i)}{\partial t} = -\nabla \cdot N_i + r_i \tag{8}$$

where ε is the porosity of the electrode, c_i is the bulk concentration of species *i*, N_i is the molar flux of species *i* in the porous solution averaged over the electrode, and r_i is the volumetric generation rate of species *i* from the electrode material to electrolyte within the porous electrode.

Neglecting the convection term, the diffusion fluxes equations for mass transfers of Li^+ , O_2 , and LiO_2 in the cell can be defined as:

$$N_{\text{Li}^{+}} = -D_{\text{Li}^{+}}^{eff} \nabla c_{\text{Li}^{+}} + \frac{i_{l}t_{+}}{F}$$

$$N_{\text{O}_{2}} = -D_{\text{O}_{2}}^{eff} \nabla c_{\text{O}_{2}}$$

$$N_{\text{LiO}_{2}} = -D_{\text{LiO}_{2}}^{eff} \nabla c_{\text{LiO}_{2}}$$
(9)

where $D_{\text{Li}^+}^{eff}$, $D_{\text{O}_2}^{eff}$ and $D_{\text{LiO}_2}^{eff}$ are the effective diffusion coefficients of Li⁺, O₂ and LiO₂ in the electrode, respectively. t_+ is the transference number of Li⁺, *F* is Faraday's constant, and i_l is the current density in the electrolyte which can be expressed as:

$$i_{l} = -\kappa^{eff} \nabla \phi_{l} - \frac{2RT\kappa^{eff}}{F} (t_{+} - 1) \left(1 + \frac{\partial \ln f}{\partial \ln c_{\mathrm{Li}^{+}}} \right) \nabla \ln c_{\mathrm{Li}^{+}}$$
(10)

where κ^{eff} is the effective ionic conductivity, ϕ_l is the ionic potential, T is the temperature, R is the universal gas constant, and f is the activity coefficient of LiPF₆ salt. The current density in the electrode is presented by Ohm's law:

$$i_s = -\sigma^{eff} \nabla \phi_s \tag{11}$$

where σ^{eff} is the effective electronic conductivity of the electrode and ϕ_s is the electronic potential. The effective parameters $D_{Li^+}^{eff}$, $D_{O_2}^{eff}$, $D_{LiO_2}^{eff}$, κ^{eff}



Fig. 1. (a) The discharge reactions through two pathways. (b) Schematic computation domain of a Li-O₂ battery during discharge.

and $\sigma^{e\!f\!f} {\rm can}$ be corrected based on porosity effect by Bruggeman correlation.

$$D_{\mathrm{Li}^{+}}^{eff} = \varepsilon^{1.5} D_{\mathrm{Li}^{+}}$$

$$D_{\mathrm{O}_{2}}^{eff} = \varepsilon^{1.5} N_{\mathrm{O}_{2}}$$

$$\kappa^{eff} = \varepsilon^{1.5} \kappa$$

$$\sigma^{eff} = (1 - \varepsilon)^{1.5} \sigma$$
(12)

where D_{Li^+} , D_{O_2} , κ and σ are the diffusion coefficient of the Li⁺ and O₂ in electrolyte and the conductivity of electrolyte and electron in the cathode, respectively.

2.3. Conservation equation

The charge conservation in the porous cathode is given as follows:

$$\nabla i_l + \nabla i_s = 0 \tag{13}$$

The charge transport between the solution electrolyte and solid electrode is linked with the electrochemical reactions at the interface:

$$\nabla i_l = a j_c \tag{14}$$

where *a* is the active specific area of the porous cathode and j_c is the local reaction current density generated by electrochemical reaction. The source term r_i in Eq. (8) is given by:

$$r_i = \sum_m -\frac{as_{i,m}}{nF} j_{c,m} + r_d \tag{15}$$

where $s_{i,m}$ is the stoichiometric coefficient of species *i*, and *n* is the number of transferred electrons in the electrochemical reaction *m*. The r_d denotes the source term from the disproportionation reaction (Eq. (5)).

2.4. Rate expressions

The reaction on lithium anode is described by the Bulter-Volmer equation as:

$$j_a = i_{a,0} \left\{ \exp\left[\frac{(1-\beta)nF}{RT}\eta_a\right] - \exp\left(\frac{-\beta nF}{RT}\eta_a\right) \right\}$$
(16)

where $i_{a,0}$ is the exchange current density, η_a is overpotential for reaction at anode and relates with E_a^0 , the equilibrium voltage of reaction (Eq. (1)), β is the symmetry factor equal to 0.5:

$$\eta_a = \phi_s - \phi_l - E_a^0 \tag{17}$$

For the LiO_2 formed by Eq. (3), the following modified Butler-Volmer equation is applied because the electrochemical reaction relies on the concentrations of the reactants:

$$j_{c_1} = k_{a_1} c_{\text{Li}+} c_{O_2} \exp\left(\frac{\beta F \eta_{c_1}}{RT}\right) - k_{c_1} c_{\text{LiO}_2} \exp\left(-\frac{(1-\beta)F \eta_{c_1}}{RT}\right)$$
(18)

Likewise, the formation of the film-like Li_2O_2 through Eq. (7) can be described as:

$$j_{c_2} = k_{a_2} c_{\text{Li}+} + c_{\text{LiO}_2} \exp\left(\frac{\beta F \eta_{c_2}}{RT}\right) - k_{c_2} c_{\text{Li}_2\text{O}_2} \exp\left(-\frac{(1-\beta)F \eta_{c_2}}{RT}\right)$$
(19)

where k_a and k_c in Eq. (18) and Eq. (19) denote the anodic and cathodic reaction kinetic constants in each electrochemical reaction, respectively. The overpotentials η_{c_1} and η_{c_2} are defined as:

$$\eta_{c1} = \phi_s - \phi_l - E_{c_1}^0 - \Delta \phi_{film} \eta_{c2} = \phi_s - \phi_l - E_{c_2}^0 - \Delta \phi_{film}$$
(20)

where $E_{c_1}^0$ and $E_{c_2}^0$ are the equilibrium voltages of Eq. (3) and (7), respectively. $\Delta \phi_{film}$ is the voltage drop across the film-like Li₂O₂ deposition, which can be estimated as:

$$\Delta \phi_{film} = j_c R_{film} \varepsilon_{\text{Li}_2 \text{O}_2(suf)} \tag{21}$$

where j_c equals the sum of j_{c_1} and j_{c_2} , R_{film} denotes the electrical resistance across the film-like Li₂O₂, and $\varepsilon_{\text{Li}_2O_2(suf)}$ is the volume fraction of the filmlike Li₂O₂. It should be noted that we consider the increase in electrical resistance caused by surface pathway here, while solution pathway does not increase electrical resistance. This is consistent with previous experimental findings that surface reactions cause electrode surface polarization, which is not conducive to battery discharge, while solution reactions are the opposite.

During the electrochemical reaction, the deposition of Li_2O_2 leads to a change in porosity, which results in a decrease in the surface area of the electrode/electrolyte interface. Thus, the effective specific surface area *a* of electrode in Eq. (14) is corrected by a geometric relation:

$$a = a_0 \left[1 - \left(\frac{\varepsilon_{\text{Li}_2 \text{O}_2}}{\varepsilon_0} \right)^p \right]$$
(22)

where $\varepsilon_{\text{Li}_2\text{O}_2}$ equals the sum of $\varepsilon_{\text{Li}_2\text{O}_2(suf)}$ and $\varepsilon_{\text{Li}_2\text{O}_2(toro)}$, $\varepsilon_{\text{Li}_2\text{O}_2(toro)}$ is the volume fraction of the toroidal Li₂O₂. *p* is a fitting parameter indicating the effect of Li₂O₂ morphology on the specific surface area of the electrode.

The disproportionation of LiO_2 reaction is not an electron transfer reaction, so that the rate of the chemical reaction is determined using standard kinetic models:

$$r_d = k_f c_{\rm LiO_2}^2 - k_r c_{\rm O_2} c_{\rm Li_2O_2}$$
(23)

where k_f and k_r are the discharge and charge rate constants of Eq. (5), respectively, and are described as follows[29]:

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$$k_{f} = k_{c_{2}} \frac{1}{\tau_{1}} \frac{1}{k_{1}} \exp\left(\frac{\alpha_{c}F}{RT}\phi_{s}\right)$$

$$k_{r} = k_{a_{2}} \frac{1}{\tau_{2}} \frac{1}{k_{2}} \exp\left(\frac{\alpha_{c}F}{RT}\phi_{s}\right)$$
(24)

Safari et al.[29] provide the rate constants k_1 and k_2 . The characteristic time constants τ_1 and τ_2 are associated with the desorption and adsorption of LiO₂ between the electrode surface and electrolyte. The values of τ_1 and τ_2 vary with the solubility and dissolution rate of LiO₂ in the electrolyte, respectively. Furthermore, the current density impacts the disproportionation reaction rate through an exponential term that involves the discharge potential.

The changes of the volume fractions of film like and toroidal Li_2O_2 in the cathode are given as follows:

$$\frac{\partial \varepsilon_{\text{Li}_2\text{O}_2(surf)}}{\partial t} = aj_{c,2} \frac{M_{\text{Li}_2\text{O}_2}}{F\rho_{\text{Li}_2\text{O}_2}}$$

$$\frac{\partial \varepsilon_{\text{Li}_2\text{O}_2(toro)}}{\partial t} = ar_d \frac{M_{\text{Li}_2\text{O}_2}}{\rho_{\text{Li}_2\text{O}_2}}$$
(25)

where $M_{\text{Li}_2\text{O}_2}$ and $\rho_{\text{Li}_2\text{O}_2}$ are the molecular weight and density of Li_2O_2 . The cathode porosity ε is given by:

$$\varepsilon = \varepsilon_0 - \varepsilon_{\text{Li}_2\text{O}_2} \tag{26}$$

2.5. Boundary conditions

The boundaries of the computational domain of the $Li-O_2$ cell, as depicted in Fig. 1b, are illustrated as follows:

Boundary (1) represents the anode/separator interface, boundary (2) and (3) represents the symmetric boundaries, boundary (4) represents the separator/cathode interface, boundary (5) represents the cathode/ baffle interface, and boundary (6) represents the cathode/air interface.

For solid-phase current, it changes with the open ratio at the cathode/air interface.

$$i_{s,2346} = 0$$
, $i_{s,5} = i_{app} / (1 - OR)$ (27)

where i_{app} is the applied current density, and *OR* denotes cathode opening ratio, the fraction of empty surface (boundary (6)), and when it comes to 100%, the cathode is fully open.

For liquid-phase current, it is equal to the discharge current at the anode/separator interface, and the separator/cathode interface.

$$i_{l,14} = i_{app}, \ i_{l,2356} = 0$$
 (28)

For lithium-ion transfer, it follows Faraday's law at the anode/ separator interface.

$$N_{\rm Li^+,1} = i_{app}/F, \ N_{\rm Li^+,2356} = 0$$
 (29)

Oxygen diffuses inward from the cathode/air interface.

$$N_{O_2,12345} = 0, \ c_{O_2,6} = c_{O_2}^0$$
 (30)

Where $c_{O_2}^0$ is the initial O₂ solubility in the electrolyte.

 ${\rm LiO}_2$ only diffuses inside the cathode with a diffusion amount of 0 at the boundary.

$$N_{\rm LiO_2\,123456} = 0 \tag{31}$$

It should be noted that the dimensionless distances on the x-axis and y-axis represent $L/(L_{sep} + L_{pos})$ and $H/H_{electrode}$, respectively.

2.6. Assumptions

Following several reasonable assumptions have been utilized in this mathematical model.

1. The $Li-O_2$ cell operates under isothermal conditions at room temperature, which is 298.15 K, thus the thermal effect is disregarded

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[30].

2. O₂ dissolves in the electrolyte at saturation concentration[24].

3. Convection and evaporation of the electrolyte is ignored[31,32].

4. The pores in the cathode are filled with liquid phase electrolyte, and the influence of pore connections is disregarded[30].

5. The $\rm Li_2O_2$ is the main final reaction product and other side products are not considered [4].

2.7. Numerical conditions

The mathematical equations, which are subject to the boundary conditions, are discretized using the finite element method and solved using the MUMPS method within the COMSOL 6.0a solver. To simulate the discharge process of the Li-O₂ battery over time until the terminal conditions are reached, a transient calculation is employed. Refined grids are adopted to ensure calculating accuracy.

2.8. Density functional theory calculation

The density functional theory (DFT) calculation is performed on the Vienna ab initio simulation package (VASP)[33], adopting the generalized gradient approximation (GGA) for the projector-augmented wave (PAW) potential for the interaction between electron and ion and the exchange-correlation function proposed by Perdew, Burke, and Ernzerhof (PBE)[34,35]. The cutoff energy during structural optimization is set as 500 eV, while the force and energy convergence are 0.02 eV/Å and 10^{-5} eV. A vacuum layer of 15 Å and DFT-D3 correction method[46] is employed to eliminate the influence of periodic structures and interaction between the adsorbate and substrate, and the implicit solvent model [47] is used to describe the effect of the electrolyte. In this work, the static dielectric constant of DME is set to 7.3. A 5 × 5 × 1 Monkhorst-Pack k-point grid is adopted to sample the Brillouin zone.

3. Results and discussion

3.1. Model validation

To verify the accuracy of the model, Fig. 2 compares the differences between the simulated discharge voltage and specific capacity and the values measured experimentally[31] when *OR* equals 100%. The



Fig. 2. The comparison between simulation and experiment results[31] (Copyright 2013, Elsevier) of discharge voltage and capacity at distinct current densities $(0.5 \text{ A m}^{-2}, 1.0 \text{ A m}^{-2}, 2.0 \text{ A m}^{-2})$ when OR equals 100%. The simulation temperature is set at 298.15 K.

simulated data is found to match well with the experimental data. It can be observed that the voltage slowly decreases with discharge time, forming a relatively obvious voltage plateau. Taking a current density of 0.5 Am^{-2} as an example, the simulated voltage plateau is 2.75 V, while the experimental voltage plateau is 2.76 V. However, at the end of discharge, there will be a significant voltage polarization. The simulated voltage inflection point is 2.65 V, while the experimental inflection point is 2.68 V. When reaching the inflection point, the battery discharge voltage rapidly decreases and then discharge ends soon. The high consistency between simulated and experimental values in two important characteristics of battery discharge, platform voltage and turning point voltage[36], proves the rationality and reliability of the model establishment. Therefore, we continue to discuss the operating mechanism of Li-O₂ batteries, and the influence of open-cell structure based on this validated model.

3.2. Species transfer in batteries

The transfer of oxygen in the cathode plays a dominant role in the battery operation, directly affecting the discharge capacity of the battery. Fig. 3a shows the concentration distribution of oxygen at different discharge stages of the battery with a current density of 0.5 A m⁻² when OR equals 100%. It can be observed that the concentration distribution of oxygen is relatively uniform in the initial stage of discharge. At 25% discharge capacity, the concentration span of oxygen through the entire cathode only decreases from 3.5 to 1.7 mol m⁻³. Oxygen is sufficient for

the discharge reaction, thus forming the voltage platform for discharge in Fig. 2. But as the discharge proceeds, the concentration gradient of oxygen gradually increases. At the end of the discharge (100% discharge capacity), oxygen is mainly concentrated at the interface between the cathode and air, and rapidly exhausts near the interface (dimensionless distance of 0.9). This phenomenon is caused by the continuous deposition of Li₂O₂ from the analysis in the following text. Thus, the discharge reaction inside the cathode cannot be maintained, leading to the discharge turning point in Fig. 2, where the voltage rapidly decreases and the discharge terminates. Fig. 3b compares the concentration distribution of oxygen at the same discharge stage under two different current densities. At 25% discharge capacity, the oxygen concentration at 0.5 A m⁻² current density decreased from 3.5 at the interface to 1.7 mol m^{-3} at the depth of the cathode, while the oxygen concentration at $1\,A\,m^{-2}$ current density decreased from 3.5 to $0.75\,mol\,m^{-3}$ Therefore, as the current density increases, the oxygen consumption rates inside the cathode turns larger. However, at the end of discharge, the oxygen concentration distribution under the two current densities is consistent. Therefore, the higher the current density, the earlier the oxygen concentration distribution reaches the state of discharge termination. The significant decrease in discharge time leads to the phenomenon in Fig. 2 where the discharge capacity of the battery rapidly drops with the increase of current density.

During the discharge process, the main product of the reaction, Li₂O₂, gradually deposits in the cathode pores, hindering the transfer of oxygen. Fig. 3c shows the deposition of Li₂O₂ at different discharge



Fig. 3. (a) The concentration distribution of oxygen across the cathode at different discharge stage at the current density of 0.5 A m^{-1} . (b) The comparison between concentration distribution of oxygen at two current densities of $0.5 \text{ an} 1.0 \text{ A m}^{-1}$. (c) The volume fraction of Li₂O₂ across the cathode at different discharge stage at the current density of 0.5 A m^{-1} . (d) The porosity across the cathode at different discharge stage at the current density of 0.5 A m^{-1} . The simulation temperature is set at 298.15 K.

stages. At 25% discharge capacity, Li₂O₂ is uniformly generated in the cathode, with a volume fraction of about 0.1. At 50% and 75% capacity, the difference of Li₂O₂ volume fraction through the entire cathode is also less than 0.1. However, at the end of discharge, the difference between the Li₂O₂ volume fraction at the interface and that at the depth of the cathode reaches 0.4. This phenomenon turns out that in the early stage of discharge, the amount of Li2O2 generated in various parts of the cathode is roughly the same. The uniform deposition of Li₂O₂ is related to the abundant oxygen across the cathode in initial status, which can effectively maintain the discharge reaction. At the end of discharge, Li₂O₂ generated at the interface dominates, while the amount of Li₂O₂ generated internally is very small. This is because the deposition of Li₂O₂ at the interface hinders the inward diffusion of oxygen, leading to the much lower rate of internal discharge reaction than that at the interface. Fig. 3d shows that at 100% discharge capacity, the porosity at the interface decreases to 0.1, and most of the pores have been occupied by the generated Li₂O₂ (the volume fraction of Li₂O₂ at the interface has reached 0.65), which makes it extremely difficult for oxygen to transfer in the pores, resulting in an internal oxygen consumption greater than the supply. The internal oxygen concentration gradually decreases, thus leading to a small amount of internal reaction, and the main location of the discharge reaction occurs at the interface.

To conclude, the deposition of Li_2O_2 makes it increasingly difficult for oxygen to transfer inward, and the discharge reaction occurs mainly at the interface. Uneven reaction occurrence leads to premature decline in battery capacity even though the internal pores of the electrode are not completely occupied.

Based on the fully open structure, the working conditions of batteries under different open ratios are studied. As shown in Fig. 4, the discharge capacity increases along with the open ratio. When the open ratio reaches 75%, the discharge capacity reaches 1160 mAh g^{-1} , which is very close to the 1240 mAh g^{-1} at full aperture. When the open ratio is small, from to 12.5–50%, the discharge specific capacity shows a good proportional relationship with the open ratio, which is consistent with the experimental results of Jiang et al.[37].

Fig. 5 shows the distribution of oxygen concentration and Li_2O_2 volume fraction across the cathode at a current density of 0.5 mAh g⁻¹ when OR equals 25%, while Fig. 6 shows the ones when OR equals 75%. As shown in Fig. 5a, when the open ratio equals 25%, at 25% capacity, the oxygen concentration distribution is concentrated at the cathode opening, and there is a clear dead zone in the rib which is not in contact



Fig. 4. The discharge voltage and specific capacity of the battery with 100%, 75%, 50%, 25%, 12.5% open ratio cathode at a current density of 0.5 A m⁻². The simulation temperature is set at 298.15 K.

with oxygen. The oxygen concentration is at a low value (about 0.52 mol m^{-3}) in the dead zone, and the discharge reaction mainly occurs at the interface opening zone. Li₂O₂ deposits a large amount at the opening, which blocks the channel and exacerbate the difficulty of oxygen transfer. At the same time, due to the reduction of the discharge area of the cathode, the local discharge reaction near the opening zone will increase to maintain the required current density, and the corresponding oxygen consumption rate is larger, resulting in the oxygen concentration distribution reaching the terminal state shown in Fig. 3a earlier. The premature termination of the discharge leads to a significant decrease of the specific capacity of the battery. However, when the open ratio equals 75%, there is no obvious dead zone for oxygen transfer in the initial stage, and the deposition of Li2O2 at the interface is not limited to the opening, as shown in Fig. 6h. The volume fraction of Li₂O₂ near the rib (boundary (5)) reaches 0.40, which is slightly smaller than 0.55 at the opening (boundary (6)). This means that the working state of the battery is close to fully open cell, so the discharge capacity of the battery only decreases a little as shown in Fig. 4. Due to the impossibility of using fully open cell in practical applications[37], optimizing the open structure to approach fully-open performance is feasible.

3.3. Research on multi-step reaction products

The intermediate product of the reaction, LiO₂, will participate in the subsequent two reaction mechanisms, namely the solution mechanism and the surface mechanism. However, the products of each mechanism are not identical, and the solution mechanism is not a charge transfer reaction[38], so the ratio of the two pathways directly affects the discharge of the battery [23,39]. The concentration changes of LiO₂ during discharge have rarely been reported. Therefore, as shown in Fig. 7a, we study the concentration distribution of LiO₂ at different discharge stages. The LiO2 concentration gradient is very small through the entire cathode, such as at 25% discharge capacity, LiO2 concentration maintains at around 3.9 mol m^{-3} both at the interface and inside the cathode, while at 75% discharge capacity, the ${\rm LiO}_2$ concentration gradient increases relatively, with a concentration of 5.8 mol m^{-3} at the interface and 5.5 mol m^{-3} inside the cathode. At the end of discharge, the LiO₂ concentration is approximately uniform throughout the cathode, around 9 mol m^{-3} . In fact, the concentration of LiO₂ increases with discharge time across the electrode, and from 25% to 50% capacity, the increase is about 0.7 mol m^{-3} , but from 75% to 100% capacity, the increase reaches 3.5 mol m⁻³. The extent of LiO₂ concentration increase varies at different stages. Considering that the battery is in constant current discharge, the discharge time experienced by both is equal. This difference can be attributed to that the amount of LiO₂ generated through discharge reaction (Eq. (3)) is more than the sum of the amount consumed through discharge reaction (Eq. (7)) and disproportionation reaction (Eq.(5)), and thus LiO₂ accumulates during discharge spatially. Moreover, the equilibrium potential of discharge reaction (Eq.(3)) (3 V) is higher than that of discharge reaction (Eq.(7)) (2.86 V). As the discharge progresses, the electrode voltage gradually decreases and the overpotential increases, and reaction (Eq.(3)) accelerates more than reaction (Eq.(7)), so the LiO2 accumulation rate becomes larger compared with the initial discharge stage. As shown in Fig. 3c, the amount of Li2O2 generated on the entire cathode is not the same, but the amount of LiO₂ is almost uniform in space. The reason for this phenomenon we deduced is that each discharge reaction involves oxygen participation, indicating that more discharge reactions occur at interfaces with higher oxygen concentrations and less occur at internal electrodes with lower oxygen concentrations. Consequently, the accumulation of LiO_2 after experiencing discharge reactions (Eq.(3)) and (Eq. (7)) is roughly equivalent across the cathode, which explains why LiO₂ can accumulate spatially with a relatively small concentration gradient.

The solution mechanism of LiO_2 dissolved in electrolyte occurs and have been reported to generate singlet oxygen with extremely high chemical activity[40], which is harmful to battery operation. The



Fig. 5. The concentration distribution of O_2 across the cathode at different discharge stage, (a) 25% discharge capacity, (b) 50% discharge capacity, (c) 75% discharge capacity, (d) 100% discharge capacity at a current density of 0.5 A m⁻² under 25% open ratio. The volume fraction of Li₂O₂ across the cathode at different discharge stage, (e) 25% discharge capacity, (f) 50% discharge capacity, (g) 75% discharge capacity, (h) 100% discharge capacity at a current density of 0.5 A m⁻² under 25% open ratio. The simulation temperature is set at 298.15 K.



Fig. 6. The concentration distribution of O_2 across the cathode at different discharge stage, (a) 25% discharge capacity, (b) 50% discharge capacity, (c) 75% discharge capacity, (d) 100% discharge capacity at a current density of 0.5 A m⁻² under 75% open ratio. The volume fraction of Li₂O₂ across the cathode at different discharge stage, (e) 25% discharge capacity, (f) 50% discharge capacity, (g) 75% discharge capacity, (h) 100% discharge capacity at a current density of 0.5 A m⁻² under 75% open ratio. The simulation temperature is set at 298.15 K.

generation ratio of singlet oxygen and triplet oxygen has been calculated by Li et al.[41] through DFT calculations, and the generation ratio of the two products is 0.237 and 0.763, respectively. Fig. 7b shows the accumulation amount of oxygen generated by the reaction at different discharge stages. It should be noted that both the singlet oxygen and triplet oxygen can be consumed and accumulated in a certain proportion [40]. At 25% capacity, the concentration of oxygen near the boundary (4) is 0.22 mol m⁻³, while at 75% capacity, the concentration inside increases to 0.42 mol m⁻³. However, the amount of accumulation near the interface in both stages is less than 0.1 mol m⁻³. The difference in oxygen accumulation amount between the interface and the internal electrode can be speculated to the fact that the oxygen consumption rate of the discharge reaction at the interface is larger than that inside the electrode. The accumulation amount of the oxygen generated increases spatially until discharge reaching around 95% capacity. The oxygen accumulation amount at 95% capacity is lower than that at 25% capacity, and at the end of discharge, the oxygen accumulated throughout the cathode exhausts. This phenomenon is because the external oxygen transfers smoothly at the initial discharge stage, and the oxygen on the cathode is abundant for the reactions. However, at the end of discharge, as shown in Fig. 3a, we have deduced that the oxygen transfer is more difficult and the oxygen on the cathode is deficient to react, so the



Fig. 7. (a) The concentration distribution of LiO_2 across the cathode at different discharge stages. (b) The concentration distribution of O_2 generated through solution pathway across the cathode at different discharge stages. (c) The volume fraction of Li_2O_2 generated through two mechanisms at the cathode/air interface at a current density of 0.5 A m⁻². (d) The volume fraction of Li_2O_2 generated through two mechanisms at the cathode/air interface at a current density of 1.0 A m⁻². The simulation temperature is set at 298.15 K.



Fig. 8. The concentration distribution of LiO_2 across the cathode at different discharge stage, (a) 25% discharge capacity, (b) 50% discharge capacity, (c) 75% discharge capacity, (d) 100% discharge capacity at a current density of 0.5 A m⁻² under 25% open ratio. The concentration distribution of LiO_2 across the cathode at different discharge stage, (e) 25% discharge capacity, (f) 50% discharge capacity, (g) 75% discharge capacity, (h) 100% discharge capacity at a current density of 0.5 A m⁻² under 75% open ratio. The simulation temperature is set at 298.15 K.

discharge reaction directly consumes the previous accumulated oxygen.

To investigate the proportion of surface and solution mechanisms, the composition of Li_2O_2 generated at the interface under a current density of 0.5 A m⁻² is shown in Fig. 7c. At the terminal of discharge, the volume fraction of Li_2O_2 generated through the surface mechanism is 0.55, accounting for 82% of the total volume fraction, while the volume fraction of Li_2O_2 generated through the solution mechanism is 0.12, accounting for 18% of the total. The significant difference in proportion between the two pathways indicates that the surface mechanism plays a dominant role during battery operation. When the current density increases from 0.5 to 1 A m⁻², as shown in Fig. 7d, the volume fraction of Li_2O_2 generated through the solution mechanism only accounts for 8.3% of the total volume fraction, which is due to the increase in current density directly deteriorating the dissolution of LiO_2 in the electrolyte, then inhibiting the progress of the solution mechanism. This phenomenon has also been observed by previous experiments[29].

The influence of two-dimensional porous structure on the concentration distribution of LiO₂ and the accumulation of generated singlet oxygen which is proportional to the total generated oxygen is shown in Fig. 8 and Fig. 9. Regardless of whether the open ratio is 75% or 25%, the concentration gradient of LiO₂ is very small. At 100% capacity, the maximum concentration difference of LiO₂ between the two electrode structures is only 0.16 (Fig. 8d) and 0.01 (Fig. 8h) mol m⁻³. This is consistent with the previous analysis, as the difference in open ratio only changes oxygen transfer in different cathode locations and hardly affects the uniform accumulation of LiO2 across the electrode. However, the open ratio has a direct impact on the accumulation of singlet oxygen generated. With a 25% open ratio, the maximum singlet oxygen generated concentration at 10% capacity is 0.06 mol m^{-3} (Fig. 9a), then gradually decreasing. With a 75% open ratio, the maximum oxygen concentration is 0.08 mol m^{-3} (Fig. 9g), which is reached at 75% capacity and decreases afterwards(oxygen concentration at 90% capacity in Fig. 9h is less than that at 25% capacity in Fig. 9e). This is because the accumulation of singlet oxygen depends on whether oxygen at a certain location is sufficient for the discharge reaction, otherwise, it will directly consume the generated oxygen, so when the opening ratio is small, the generated oxygen is consumed in advance, and the amount of oxygen accumulation decrease earlier.

3.4. Rate constant validation

To connect the transfer-reaction model with the microscopic mechanism, we conduct DFT calculations on surface mechanism reactions which play a dominant role, and the Gibbs free energy changes of each part are shown in Fig. 10. The Gibbs free energy for each step is calculated as follows[42,43]:

$$\Delta G = \Delta E + \Delta Z P E - T \Delta S \tag{32}$$

 ΔE is the change in the electronic energy. ΔZPE is the difference in zero-point energies. ΔS is the change in entropy. As we conclude in the previous section, the generated LiO₂ is roughly equivalent to the consumed LiO₂, Eq.(3) largely determines the subsequent generation of Li₂O₂, directly affecting the discharge performance, so we take it as the research object. By using the Marcus theory [44], we can quantify the



Fig. 10. The Gibbs free energy variation diagram of the LiO_2 and Li_2O_2 generation from surface mechanism reaction.



Fig. 9. The concentration distribution of singlet O_2 generated across the cathode at different discharge stage, (a) 10% discharge capacity, (b) 25% discharge capacity, (c) 50% discharge capacity, (d) 75% discharge capacity at a current density of 0.5 A m⁻² under 25% open ratio. The concentration distribution of singlet O_2 generated across the cathode at different discharge stage, (e) 25% discharge capacity, (f) 50% discharge capacity, (g) 75% discharge capacity, (h) 90% discharge capacity at a current density of 0.5 A m⁻² under 75% open ratio. The simulation temperature is set at 298.15 K.

kinetic parameter of the reaction (Eq.(3)). The reaction rate constant can be derived from the following equation :

$$r = Z \exp\left(-\frac{\Delta G_{\rm D}^*}{k_{\rm B}T}\right) \tag{33}$$

where *Z* is the frequency factor of the reaction and is estimated to be 10^2 M⁻¹ s⁻¹, as Eq.(3) is a heterogeneous reaction. k_B is the Boltzmann constant. ΔG_D^* is determined by both the intrinsic reaction and external field effects and can be calculated as follows[45]:

$$\Delta G_{\rm D}^* = \frac{1}{4\lambda} \left(\Delta G^0 + \lambda \right) \tag{34}$$

where ΔG^0 is the standard free energy change of the charge transfer reaction and λ is the reorganization energy considering the solvation effects. The reorganization energy can be calculated as proposed by Houchins et al. [45]:

$$\lambda = \frac{\Delta_{\rm e}^2}{8\pi\varepsilon_0} \left(\frac{1}{D_{\rm OD}} - \frac{1}{D_{\rm SD}} \right) \left(\frac{1}{a_{\rm D}} + \frac{1}{a_{\rm A}} - \frac{2}{r} \right)$$
(35)

where Δ_e is the total transferred charge in the reaction, D_{OD} is the optical dielectric constant and D_{SD} is the static dielectric constant. a_D and a_A are the radius of the two spheres, the electron donor lithium atom and the electron acceptor oxygen molecule. r is the separation between the donor and acceptor and is set to be 3.5 Å[45].

Due to the gradual increase of overpotential in the discharge reaction, the average rate constant of LiO₂ generation from surface mechanism in the transfer-reaction model is calculated by Eq.(18) to be 2.125 $\times 10^{-7}$ M⁻¹ s⁻¹, while the reaction rate constant calculated by the reorganization energy model is 2.811 $\times 10^{-7}$ M⁻¹ s⁻¹. The calculation results of both are equal in magnitude, proving the accuracy of the reorganization energy model[45]. The consistency of the calculation results indicates that the model conforms to the reaction mechanism and can effectively achieve the connection between micro and macro levels. In addition, based on the step diagram of Gibbs free energy[48–51], our calculated equilibrium voltage is 2.53 V. It is worth mentioning that as this is an adsorption reaction, the equilibrium voltage of the reaction is different from that of the elemental reaction (2.86 V).

4. Conclusion

We construct a transfer-reaction model to describe the discharge process of Li-O₂ batteries. We find that the transfer of oxygen deteriorates with the increasing resistance of internal diffusion during the discharge reaction, which is caused by the local generation of Li₂O₂ at the interface. Besides, the retention of oxygen at the interface also intensifies the local deposition of Li₂O₂, leading to the end of the discharge. For the intermediate product of the reaction, LiO_2 , we find that it is relatively uniform in space, because the generation and consumption of LiO₂ in the discharge reaction are roughly equal in space. We investigate the singlet oxygen and triplet oxygen generated by the solution mechanism, and their concentration distribution through the electrode shows a higher concentration at the interface than inside. This is because the oxygen generated at the interface is quickly consumed by the discharge reaction, but there is a larger accumulation of oxygen inside due to the lower reaction rate. By establishing two-dimensional structures with different pore ratios, we find that a smaller open ratio leads to an increase in oxygen transfer resistance and the battery advances to the later stage of the discharge with a lower discharge capacity. Because the surface mechanism is the only discharge reaction, so the conclusion drawn from our work should be to reduce the rapid deposition rate of Li₂O₂ on the surface and inside of porous electrodes through other methods, prolong the time of surface mechanism occurrence, and thereby increase the discharge capacity of Li-O₂ batteries. We also use the Marcus theory to calculate the rate constant of LiO2 generation reaction and find that the result calculated by the reorganization energy model is very close to the assumed values in our simulation, which proves that the transfer-reaction model achieves a good connection between macroscopic and microscopic levels. We hope that this work can contribute to designing appropriate cathode structures and conducting the multi-scale research on the working mechanism of Li-O₂ batteries, hoping to enlighten subsequent research towards achieving highly rechargeable nonaqueous metal-air batteries earlier.

CRediT authorship contribution statement

Jiadong Wu: Writing – original draft, Validation, Software, Methodology, Formal analysis, Data curation. Cheng Lian: Writing – review & editing, Supervision, Resources, Investigation, Funding acquisition. Jia-Hui Li: Writing – review & editing, Validation, Supervision, Software, Methodology, Formal analysis. Honglai Liu: Writing – review & editing, Supervision, Resources, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.cattod.2024.114700.

References

- J. Lu, L. Li, J.B. Park, Y.K. Sun, F. Wu, K. Amine, Aprotic and aqueous Li-O₂ batteries, Chem. Rev. 114 (2014) 5611–5640, https://doi.org/10.1021/ cr400573b.
- [2] A.C. Luntz, B.D. McCloskey, Nonaqueous Li-air batteries: a status report, Chem. Rev. 114 (2014) 11721–11750, https://doi.org/10.1021/cr500054y.
- [3] H. Kim, W.J. Kwak, H.G. Jung, Y.K. Sun, Limited effects of a redox mediator in lithium-oxygen batteries: indecomposable by-products, J. Mater. Chem. A 8 (2020) 5622–5628, https://doi.org/10.1039/c9ta13612f.
- [4] Y. Wang, L. Hao, M. Bai, Modeling the multi-step discharge and charge reaction mechanisms of non-aqueous Li-O₂ batteries, Appl. Energy 317 (2022) 119189, https://doi.org/10.1016/j.apenergy.2022.119189.
- [5] M. Balaish, J.W. Jung, I.D. Kim, Y. Ein-Eli, A critical review on functionalization of air-cathodes for nonaqueous Li-O₂ batteries, Adv. Funct. Mater. 30 (2020) 1808303, https://doi.org/10.1002/adfm.201808303.
- [6] S. Zhao, L. Zhang, G. Zhang, H. Sun, J. Yang, S. Lu, Failure analysis of pouch-type Li-O₂ batteries with superior energy density, J. Energy Chem. 45 (2020) 74–82, https://doi.org/10.1016/j.jechem.2019.09.029.
- [7] M. Augustin, P.E. Vullum, F. Vullum-Bruer, A.M. Svensson, Inside the electrode: Looking at cycling products in Li-O₂ batteries, J. Power Sources 414 (2019) 130–140, https://doi.org/10.1016/j.jpowsour.2018.12.088.
- [8] A. Dutta, K. Ito, Y. Kubo, Establishing the criteria and strategies to achieve high power during discharge of a Li-air battery, J. Mater. Chem. A 7 (2019) 23199–23207, https://doi.org/10.1039/c9ta07427a.
- [9] Y. Wang, L. Hao, Effects of cathode structure on the discharge performance of nonaqueous Li-O₂ batteries, Electrochim. Acta 425 (2022) 140703, https://doi.org/ 10.1016/j.electacta.2022.140703.
- [10] Y. Wang, L. Hao, M. Bai, A modeling study of the cycling behavior of non-aqueous Li-O₂ batteries, J. Electrochem. Soc. 168 (2021) 020524, https://doi.org/10.1149/ 1945-7111/abe16e.

- J. Wu et al.
- [11] Y. Wang, L. Hao, M. Bai, Modeling the influence of water on the performance of non-aqueous Li-O₂ batteries, Appl. Energy 330 (2023) 120356, https://doi.org/ 10.1016/j.apenergy.2022.120356.
- [12] A. Torayev, A. Rucci, P. Magusin, A. Demortiere, V. De Andrade, C.P. Grey, C. Merlet, A.A. Franco, Stochasticity of pores Interconnectivity in Li-O₂ batteries and its impact on the variations in electrochemical performance, J. Phys. Chem. Lett. 9 (2018) 791–797, https://doi.org/10.1021/acs.jpclett.7b03315.
- [13] Y.X. Ren, T.S. Zhao, P. Tan, Z.H. Wei, X.L. Zhou, Modeling of an aprotic Li-O₂ battery incorporating multiple-step reactions, Appl. Energy 187 (2017) 706–716, https://doi.org/10.1016/j.apenergy.2016.11.108.
- [14] Z. Lyu, L. Yang, Y. Luan, X.R. Wang, L. Wang, Z. Hu, J. Lu, S. Xiao, F. Zhang, X. Wang, F. Huo, W. Huang, Z. Hu, W. Chen, Effect of oxygen adsorbability on the control of Li₂O₂ growth in Li-O₂ batteries: implications for cathode catalyst design, Nano Energy 36 (2017) 68–75, https://doi.org/10.1016/j.nanoen.2017.04.022.
- [15] N.B. Aetukuri, B.D. McCloskey, J.M. Garcia, L.E. Krupp, V. Viswanathan, A. C. Luntz, Solvating additives drive solution-mediated electrochemistry and enhance toroid growth in non-aqueous Li-O₂ batteries, Nat. Chem. 7 (2015) 50–56, https://doi.org/10.1038/nchem.2132.
- [16] D. Aurbach, B.D. McCloskey, L.F. Nazar, P.G. Bruce, Advances in understanding mechanisms underpinning lithium-air batteries, Nat. Energy 1 (2016) 1–11, https://doi.org/10.1038/nenergy.2016.128.
- [17] Z. Lyu, Y. Zhou, W. Dai, X. Cui, M. Lai, L. Wang, F. Huo, W. Huang, Z. Hu, W. Chen, Recent advances in understanding of the mechanism and control of Li₂O₂ formation in aprotic Li-O₂ batteries, Chem. Soc. Rev. 46 (2017), https://doi.org/ 10.1039/c7cs90095c, 6073-6073.
- [18] S. Basak, S. Baaij, S. Ganapathy, C. George, H. Tempel, H. Kungl, E.M. Kelder, H. W. Zandbergen, M. Wagemaker, R.-A. Eichel, Accessing lithium-oxygen battery discharge products in their native environments via transmission electron microscopy grid electrode, ACS Appl. Energy Mater. 3 (2020) 9509–9515, https://doi.org/10.1021/acsaem.0c01803.
- [19] D. Cordoba, H.B. Rodriguez, E.J. Calvo, Operando fluorescence detection of singlet oxygen inside high-performance Li-O₂ batteries, J. Phys. Chem. C. 127 (2023) 78–84, https://doi.org/10.1021/acs.jpcc.2c06821.
- [20] Z. Jiang, Y. Huang, Z. Zhu, S. Gao, Q. Lv, F. Li, Quenching singlet oxygen via intersystem crossing for a stable Li-O₂ battery, PNAS 119 (2022) e2202835119, https://doi.org/10.1073/pnas.2202835119.
- [21] J.W. Mullinax, C.W. Bauschlicher, J.W. Lawson, Modeling singlet oxygen-induced degradation pathways including environmental effects of 1,2-Dimethoxyethane in Li-O₂ batteries through density functional theory, J. Phys. Chem. A 126 (2022) 7997–8006, https://doi.org/10.1021/acs.jpca.2c06386.
- [22] L. Johnson, C. Li, Z. Liu, Y. Chen, S.A. Freunberger, P.C. Ashok, B.B. Praveen, K. Dholakia, J.-M. Tarascon, P.G. Bruce, The role of LiO₂ solubility in O₂ reduction in aprotic solvents and its consequences for Li-O₂ batteries, Nat. Chem. 6 (2014) 1091–1099, https://doi.org/10.1038/NCHEM.2101.
- [23] A. Khetan, A. Luntz, V. Viswanathan, Trade-offs in capacity and rechargeability in nonaqueous Li-O₂ batteries: solution-driven growth versus nucleophilic stability, J. Phys. Chem. Lett. 6 (2015) 1254–1259, https://doi.org/10.1021/acs. jpclett.5b00324.
- [24] D. Gruebl, B. Bergner, D. Schroeder, J. Janek, W.G. Bessler, Multistep reaction mechanisms in nonaqueous lithium-oxygen batteries with redox mediator: a model-based study, J. Phys. Chem. C. 120 (2016) 24623–24636, https://doi.org/ 10.1021/acs.jpcc.6b07886.
- [25] B.D. Adams, C. Radtke, R. Black, M.L. Trudeau, K. Zaghib, L.F. Nazar, Current density dependence of peroxide formation in the Li-O₂ battery and its effect on charge, Energy Environ. Sci. 6 (2013) 1772–1778, https://doi.org/10.1039/ c3ee40697k.
- [26] Z.H. Cui, X.X. Guo, H. Li, Equilibrium voltage and overpotential variation of nonaqueous Li-O₂ batteries using the galvanostatic intermittent titration technique, Energy Environ. Sci. 8 (2015) 182–187, https://doi.org/10.1039/ c4ee01777c.
- [27] J.B. Haskins, H.H. Pham, A. Khetan, V. Viswanathan, J.W. Lawson, Lithium peroxide growth in Li-O₂ chemical disproportionation and electrochemical mechanisms: a potential-dependent Ab initio study with implicit solvation, J. Phys. Chem. C. 125 (2021) 436–445, https://doi.org/10.1021/acs.jpcc.0c08610.
- [28] T.K. Zakharchenko, A.V. Sergeev, A. D. Bashkirov, P. Neklyudova, A. Cervellino, D. M. Itkis, L.V. Yashina, Homogeneous nucleation of Li₂O₂ under Li-O₂ battery discharge, Nanoscale 12 (2020) 4591–4601, https://doi.org/10.1039/ c9nr08493b.
- [29] M. Safari, B.D. Adams, L.F. Nazar, Kinetics of oxygen reduction in aprotic Li-O₂ cells: a model-based study, J. Phys. Chem. Lett. 5 (2014) 3486–3491, https://doi.org/10.1021/jz5018202.

- [30] Y. Wang, L. Hao, M. Bai, Modeling studies of the discharge performance of Li-O₂ batteries with different cathode open structures, J. Electrochem. Soc. 168 (2021) 070517, https://doi.org/10.1149/1945-7111/ac1032.
- [31] U. Sahapatsombut, H. Cheng, K. Scott, Modelling of operation of a lithium-air battery with ambient air and oxygen-selective membrane, J. Power Sources 249 (2014) 418–430, https://doi.org/10.1016/j.jpowsour.2013.10.128.
- [32] A. Torayev, A. Rucci, P.C.M.M. Magusin, A. Demortière, V. De Andrade, C.P. Grey, C. Merlet, A.A. Franco, Stochasticity of pores interconnectivity in Li-O₂ batteries and its impact on the variations in electrochemical performance, J. Phys. Chem. Lett. 9 (2018) 791–797, https://doi.org/10.1021/acs.jpclett.7b03315.
- [33] G. Kresse, J. Furthmuller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Phys. Rev. B Condens Matter 54 (1996) 11169–11186, https://doi.org/10.1103/PhysRevB.54.11169.
- [34] J. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. 77 (1996) 3865–3868, https://doi.org/10.1103/ PhysRevLett.78.1396.
- [35] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmentedwave method, Phys. Rev. B 59 (1999) 1758–1775, https://doi.org/10.1103/ PhysRevB.59.1758.
- [36] A. Torayev, A. Rucci, P.C.M.M. Magusin, A. Demortiere, V. De Andrade, C.P. Grey, C. Merlet, A.A. Franco, Stochasticity of pores interconnectivity in Li-O₂ batteries and its impact on the variations in electrochemical performance, J. Phys. Chem. Lett. 9 (2018) 791–797, https://doi.org/10.1021/acs.jpclett.7b03315.
- [37] J. Jiang, H. Deng, X. Li, S. Tong, P. He, H. Zhou, Research on effective oxygen window influencing the capacity of Li-O₂ batteries, ACS Appl. Mater. Interfaces 8 (2016) 10375–10382, https://doi.org/10.1021/acsami.6b02586.
- [38] C.O. Laoire, S. Mukerjee, K.M. Abraham, E.J. Plichta, M.A. Hendrickson, Elucidating the mechanism of oxygen reduction for lithium-air battery applications, J. Phys. Chem. C. 113 (2009) 20127–20134, https://doi.org/ 10.1021/jp908090s.
- [39] Y. Zhang, X. Zhang, J. Wang, W.C. McKee, Y. Xu, Z. Peng, Potential-dependent generation of O₂ and LiO₂ and their critical roles in O₂ reduction to Li₂O₂ in aprotic Li-O₂ batteries, J. Phys. Chem. C. 120 (2016) 3690–3698, https://doi.org/ 10.1021/acs.jpcc.5b12338.
- [40] Y.K. Petit, E. Mourad, C. Prehal, C. Leypold, A. Windischbacher, D. Mijailovic, C. Slugovc, S.M. Borisov, E. Zojer, S. Brutti, O. Fontaine, S.A. Freunberger, Mechanism of mediated alkali peroxide oxidation and triplet versus singlet oxygen formation, Nat. Chem. 13 (2021) 465–471, https://doi.org/10.1038/s41557-021-00643-z.
- [41] J.H. Li, J. Wu, Y.X. Yu, Singlet oxygen vs. triplet oxygen: functions of 2D-MoO₃ catalysts in conquering catastrophic parasitic-reactions in lithium- and sodium-oxygen batteries, J. Mater. Chem. A 9 (2021) 10186–10198, https://doi.org/10.1039/d1ta00699a.
- [42] J. Rossmeisl, Z.W. Qu, H. Zhu, G.J. Kroes, J.K. Norskov, Electrolysis of water on oxide surfaces, J. Electroanal. Chem. 607 (2007) 83–89, https://doi.org/10.1016/ j.jelechem.2006.11.008.
- [43] A. Valdes, Z.W. Qu, G.J. Kroes, J. Rossmeisl, J.K. Norskov, Oxidation and photooxidation of water on TiO₂ surface, J. Phys. Chem. C. 112 (2008) 9872–9879, https://doi.org/10.1021/jp711929d.
- [44] R.A. Marcus, Electron transfer reactions in chemistry. Theory and experiment, Pure Appl. Chem. 69 (1997) 13–29, https://doi.org/10.1351/pac199769010013.
- [45] G. Houchins, V. Pande, V. Viswanathan, Mechanism for singlet oxygen production in Li-ion and metal-air batteries, Acs. Energy Lett. 5 (2020) 1893–1899, https:// doi.org/10.1021/acsenergylett.0c00595.
- [46] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, J. Chem. Phys. 132 (2010) 154104, https://doi.org/10.1063/ 1.3382344.
- [47] B. Roux, T. Simonson, Implicit solvent models, Biophys. Chem. 78 (1999) 1–20, https://doi.org/10.1016/s0301-4622(98)00226-9.
- [48] J.H. Li, J. Wu, Y.X. Yu, Theoretical exploration of single-layer Tl₂O as a catalyst in lithium-oxygen battery cathodes, J. Phys. Chem. C. 124 (17) (2020) 9089–9098, https://doi.org/10.1021/acs.jpcc.9b09665, 112.
- [49] J.H. Li, Y.X. Yu, How do oxygen vacancies influence the catalytic performance of two-dimensional Nb₂O₅ in lithium- and sodium-oxygen batteries? Chemsuschem 14 (24) (2021) 5488–5498, https://doi.org/10.1002/cssc.202101691.
- [50] Y.X. Yu, Effect of defects and solvents on silicene cathode of nonaqueous lithiumoxygen batteries: a theoretical investigation, J. Phys. Chem. C. 123 (1) (2019) 205–213, https://doi.org/10.1021/acs.jpcc.8b10367.
- [51] J.H. Li, Y.X. Yu, Enhanced catalytic performance of pillared δ-MnO₂ with enlarged layer spaces for lithium- and sodium-oxygen batteries: a theoretical investigation, Nanoscale 13 (48) (2021) 20637–20648, https://doi.org/10.1039/d1nr07407e.