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Revealing the effect of LiOH on forming a SEI using a Co magnetic "probe"†

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The solid-electrolyte-interphase (SEI) plays a critical role in lithium-ion batteries (LIBs) because of its important influence on electrochemical performance, such as cycle stability, coulombic efficiency, *etc.* Although LiOH has been recognized as a key component of the SEI, its influence on the SEI and electrochemical performance has not been well clarified due to the difficulty in precisely controlling the LiOH content and characterize the detailed interface reactions. Here, a gradual change of LiOH content is realized by different reduction schemes among $Co(OH)_2$, CoOOH and CoO. With reduced Co nanoparticles as magnetic "probes", SEI characterization is achieved by *operando* magnetometry. By combining comprehensive characterization and theoretical calculations, it is verified that LiOH leads to a composition transformation from lithium ethylene di-carbonate (LEDC) to lithium ethylene mono-carbonate (LEMC) in the SEI and ultimately results in capacity decay. This work unfolds the detailed SEI reaction scenario involving LiOH, provides new insights into the influence of SEI composition, and has value for the co-development between the electrode materials and electrolyte.

Introduction

Lithium-ion batteries (LIBs) have greatly facilitated the development of portable electronic devices, and more recently, enabled the realization of electric vehicles.[1–4] Because of its important role in cycle stability, coulombic efficiency *etc.*, the solid-electrolyte-interphase (SEI) has attracted extensive attention.[5,6] The SEI consists of multiple components, and the influence of each individual component has been a central topic in SEI studies. It has been verified that the main components of the SEI include LiF, Li_2CO_3, Li_2O, LiOH and some organic compounds.[7,8] These components have different roles in the SEI. For example, LiF can act as an effective passivation layer to prevent further electrolyte decomposition,[9] while Li_2CO_3 mainly acts as an ionic conductor to transport lithium ions, thus facilitating charge transfer.[10–12] Although extensive investigations have been performed,[13] many questions remain open owing to the complexity and instability of SEI components.

The influence of LiOH, a key component in the SEI, on the SEI has been widely considered.[14–22] In previous research, LiOH in the SEI was generally believed to come from water contamination.[15,17] While others found that LiOH can naturally form during the SEI formation.[14,16] Recently, some viewpoints about the influence of LiOH on the SEI were proposed.[21–23] Hu *et al.* found that the conversion of LiOH to Li_2O and LiH may exist in the SEI,[23] which can provide extra storage capacity. However Wang *et al.*[22] and Xie *et al.*[21] believed that LiOH can influence the SEI components and result in interface instability, because LiOH can lead to LEMC production, instead of the LEDC as commonly thought.[24,25]

Despite these efforts and the proposed reaction mechanism, the detailed influence of LiOH on the SEI has not been studied specifically, and the change of electrochemical performance from this influence has not been explained. The challenge on this topic lies in the difficulty of meticulously controlling the LiOH content in the SEI, so the changes of the SEI and electrochemical performance under LiOH influence are too weak to monitor. Interestingly, the transition metal hydroxide reduction process will produce LiOH[26–28] and the conversion reactions and SEI formation voltages do not overlap. This provides the opportunity of controlling the content of LiOH when the SEI is formed in a low voltage range. Moreover, transition metal

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nanoparticles can significantly promote the SEI formation,[29–31] which further facilitates SEI characterization. Technically, *operando* magnetometry is highly sensitive to magnetic changes caused by the SEI,[32,33] which provides a new and intuitive characterization technique for studying the influence of LiOH on the SEI.

In this work, the control of different LiOH content levels was achieved through the reduction reactions with $Co(OH)_2$, CoOOH and CoO, as shown below.

$$Co(OH)_2 + 2Li^+ + 2e^- \rightarrow Co^0 + 2LiOH \quad (1)$$

$$CoOOH + 3Li^+ + 3e^- \rightarrow Co^0 + 1LiOH + Li_2O \quad (2)$$

$$CoO + 2Li^+ + 2e^- \rightarrow Co^0 + 0LiOH + Li_2O \quad (3)$$

Other than the control of the LiOH content, the product Co^0 can be used as a "probe" to detect the magnetic change by *operando* magnetometry. Fig. 1 shows the diagram of this experimental design. Combined with X-ray absorption spectroscopy (XAS) and other characterization techniques, our results show that although LiOH provides some additional capacity, it can result in component variation from LEDC to LEMC in the SEI, along with the formation of some Li_2CO_3 aggregates. These reaction effects directly result in SEI instability, eventually leading to capacity decay. We further verified that the LiOH influence is mainly related to EC decomposition by adjusting electrolyte composition. These findings are important for understanding the effects of various components in the SEI and the synergistic development between electrodes and electrolyte materials.[34,35]

Results and discussion

$Co(OH)_2$, CoOOH and CoO were selected as research objects because the obtained Co nanoparticles can catalyze SEI formation and LiOH presents different concentrations (Fig. 1b), and both of them are produced in the reduction process.[29,30] Three materials were designed with the same morphology to ensure that morphology would not lead to differences in electrochemical performance. Pure nano-disk-like $Co(OH)_2$ particles (β-$Co(OH)_2$) were prepared using a simple wet chemical precipitation method, while CoO and CoOOH were obtained by thermal decomposition and oxidation reactions from $Co(OH)_2$, respectively (Fig. S1 ESI†). As shown in Fig. S2a,† XRD patterns of the three materials clearly reveal that all characteristic peaks are in perfect agreement with the standard card (JCPDS card no. 74-1057, 73-1213, and 75-0418) without any impurities. Magnetic hysteresis curves in Fig. S1b† confirm that all materials show paramagnetic behavior. The high-resolution Co 2p spectrum (Fig. S2c and d†) shows the Co valence states of $Co(OH)_2$, CoOOH and CoO, respectively. In Fig. S2c and e,†

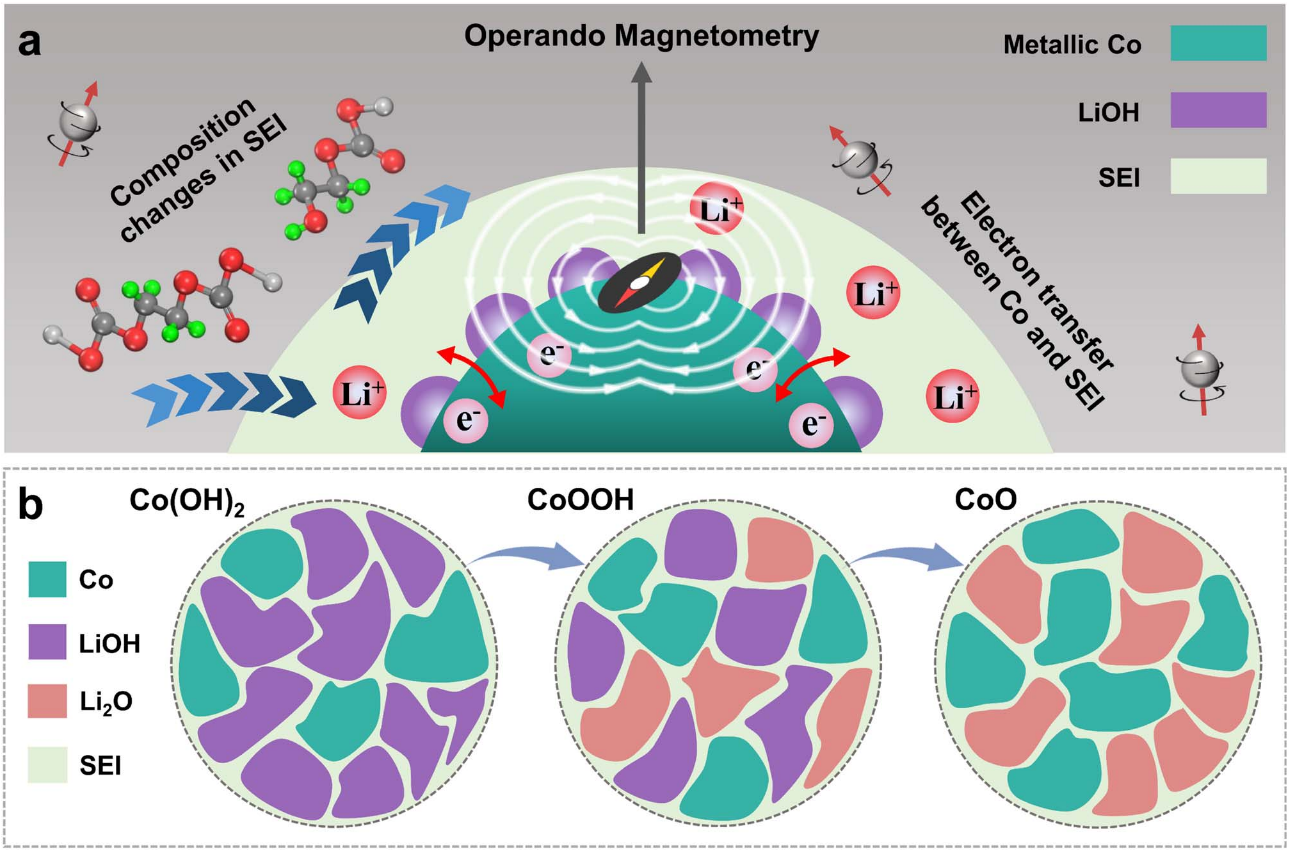

Fig. 1 Diagram of experimental design. (a) Diagram of a Co magnetic "probe". (b) Diagram of the LiOH content of $Co(OH)_2$, CoOOH and CoO (reduced product).

satellite peaks center at 785.9 eV and 802.7 eV, and two peaks located at 780.2 eV and 795.9 eV correspond to Co^{2+}. The characteristic peaks of Co^{3+} are located at 779.8 and 781.2 eV,[36] as seen in Fig. S2d.† The Co–OH content difference of the three materials can be proved in the high-resolution O 1s spectrum of Fig. S3a–c†. The ratio of Co–OH and Co–O bonds shows the materials change from $Co(OH)_2$ to CoO.[37] The Co–OH bond in CoO can be attributed to unavoidable surface water contamination.[38] As shown in Fig. S2f–h,† although CoOOH and CoO experience structural changes during oxidation and annealing reactions, they maintain nano-disk-like morphology with a size of about 5 μm. Fig. S4a–i† show the high-resolution TEM (HRTEM) images of the three materials, and all of them show nano-disk-like morphology with high crystallinity. EDS mapping images (Fig. S5a–c†) provide clear evidence of the high homogeneity of Co and O elements in the three materials.

The electrochemical cycling performance of $Co(OH)_2$, CoOOH and CoO was investigated with Li metal as the anode. In Fig. 2a, the initial capacity of $Co(OH)_2$ and CoOOH reaches 2001.9 and 2183.5 mA h g^{-1} under 100 mA g^{-1}, which are far beyond their theoretical capacity based on conversion reactions (577 and 856 mA h g^{-1}, respectively). According to previous studies, this kind of extra capacity in transition metal compounds may be related to space charge[39] and hydride formation reaction.[23,27] However, these two aspects are not sufficient to support such a high capacity. And what is strange is that the capacities of $Co(OH)_2$ and CoOOH drop dramatically to 1179.8 and 1326.2 mA h g^{-1} over the next ten cycles, while CoO does not exhibit this phenomenon. As shown in Fig. 1a, CoO LIBs yield an initial capacity of 1129.4 mA h g^{-1} under 100 mA g^{-1}, but demonstrate a capacity increase in the subsequent ten cycles to 1399.6 mA h g^{-1}. This difference in electrochemical performance can be seen more clearly in Fig. 2b. Capacity increases can be attributed to surface layer activation or morphological changes,[40] while capacity decay during the initial cycles is believed to be related to SEI instability.[41–43] As shown in Fig. 2c, the capacity decay of $Co(OH)_2$ and CoOOH mostly comes from the voltage range from about 0.8 to 0.01 V, which is the main range of SEI formation. Note that voltage plateau changes of the three materials here can be attributed to amorphous transformation and particle crushing.[44] These results indicate that the capacity decay of $Co(OH)_2$ and CoOOH may be related to SEI instability. Actually, in transition metal hydroxide materials, this inevitable capacity decay in the initial cycles is very widespread (Table S1†),[26–28,45–47] and the intrinsic reason should be related to the reduction product LiOH. We conducted electrochemical impedance spectroscopy (EIS) on $Co(OH)_2$, CoOOH and CoO (initial and discharged to 0.01 V), as shown in Fig. S6† and 2d. It can be seen that initial impedances of the three materials are small and close to each other (Fig. S6†). However, after discharging to 0.01 V, all of them show obvious SEI characteristics,[48] and clear semicircle curves appear in a high frequency range (Fig. 2d). And the SEI impedance decreases with the decrease of LiOH content, which agrees with their different cycle performance. Obviously, SEI difference leads to these different impedance results. All of these electrochemical characterization results indicate that the SEI instability directly causes capacity decay during the initial cycles, and can be attributed to the influence of LiOH.

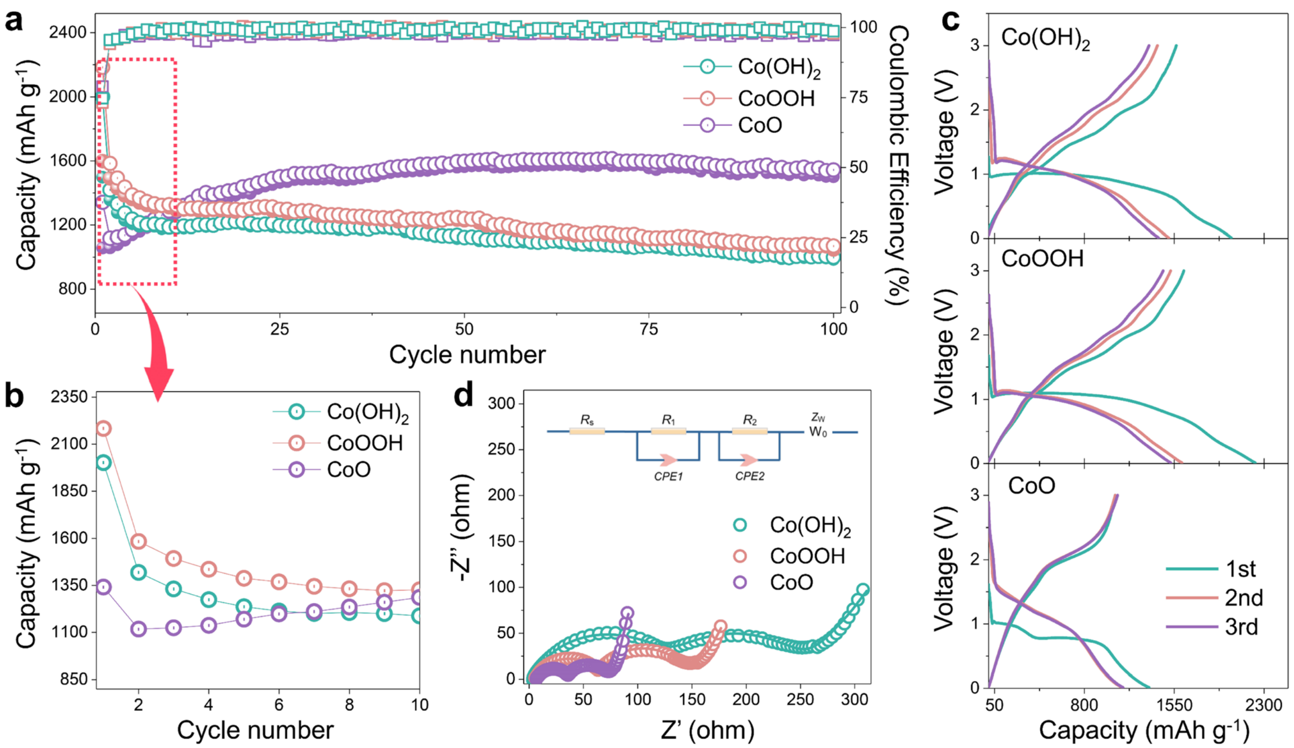

Fig. 2 Electrochemical characterization of the three materials. (a) Cycling performance of $Co(OH)_2$, CoOOH and CoO half cells at a current density of 100 mA g^{-1}. (b) The initial ten cycles of the three materials. (c) Galvanostatic charge–discharge curves of $Co(OH)_2$, CoOOH and CoO at a current density of 100 mA g^{-1}. (d) The Nyquist curves of the three products after discharged to 0.01 V.

TEM was carried out to analyze the SEI difference between $Co(OH)_2$, CoOOH and CoO. TEM images are exhibited in Fig. 3a–c, corresponding to the SEI of $Co(OH)_2$, CoOOH, and CoO (discharged to 0.01 V), respectively. TEM images show that the SEIs of $Co(OH)_2$, CoOOH and CoO are significantly different. The SEIs of $Co(OH)_2$ and CoOOH are very uneven. For $Co(OH)_2$, the SEI thickness varies from 10.3 to 19.1 nm, and for CoOOH from 16.7 to 23.7 nm. However, the SEI of CoO is well maintained at 13.2 nm. Moreover, we found some agglomerating inorganic substances in the SEI of $Co(OH)_2$ and CoOOH (Fig. S7a and b†). In sharp contrast, the SEI of CoO maintains a good amorphous state and no agglomerated particles can be found (Fig. S7c†). SEM tests showed similar results. As shown in Fig. S8,† the SEI formed on the surface of $Co(OH)_2$ and CoOOH electrodes is thick, while the SEI on the CoO electrode surface is very thin. This contrast indicates that compared to CoO, the SEIs of $Co(OH)_2$ and CoOOH are unstable. Fig. S9† shows the uniform distribution of Co and LiOH (or Li_2O) nanoparticles after the discharging process. Interestingly, LiOH, Co and Li_2O can be found on $Co(OH)_2$ and CoOOH electrode surfaces (Fig. 3d–f). Co and LiOH come from the conversion reaction, while Li_2O should come from the lithiation reaction of LiOH ($LiOH + Li^+ + e^- \rightarrow Li_2O + LiH$).[23] These TEM results agree well with previous reports,[23,27,45] in which similar results were verified by nuclear magnetic resonance (NMR), TEM, and theoretical calculation, indicating that LiOH lithiation indeed exists. To sum up, TEM results indicate that although the LiOH lithiation reaction can bring some extra capacity, it can also lead to SEI instability.

In order to analyze the LiOH influence on SEI components, we performed XPS characterization on $Co(OH)_2$, CoOOH and CoO (discharge to 0.01 V), with high-resolution C 1s, O 1s, F 1s and Li 1s XPS spectrum analysis, respectively. The XPS analysis results of F 1s and Li 1s spectrum are overall consistent among the three materials (Fig. S10a–f†), while the XPS analysis results of C 1s and O 1s spectra have obvious difference. As seen in Fig. 3g, the components observed at about 290, 288.5, 286.4, 285, and 284.4 eV can be attributed to CO_3, O=C–O, C–O, C–H and C–C bonds, respectively.[49–51] With the decrease of LiOH content (from $Co(OH)_2$ to CoOOH and CoO), the relative content of C–O and O=C–O in the XPS C 2p spectrum gradually increases, while CO_3 gradually reduces. This phenomenon is also reflected in the O 1s spectrum. With the decrease of LiOH, the relative content of C=O increases. Due to the higher main peak of Li_2CO_3 or $ROCO_2Li$, the difference of C=O is not as obvious as that in high-resolution C 1s. Note that the Li_2O bond in the CoO O 1s spectrum should come from the conversion reaction of CoO.[52,53] The SEI of CoO is thinner, allowing XPS to detect the electrode material. In contrast to one O=C–O functional group in each LEMC, LEDC has a longer chain structure, with two such functional groups in each molecule (Fig. S11†). Combined with such structural difference and our characterization results, the composition change from LEDC to LEMC in the SEI under LiOH influence can be confirmed, which is

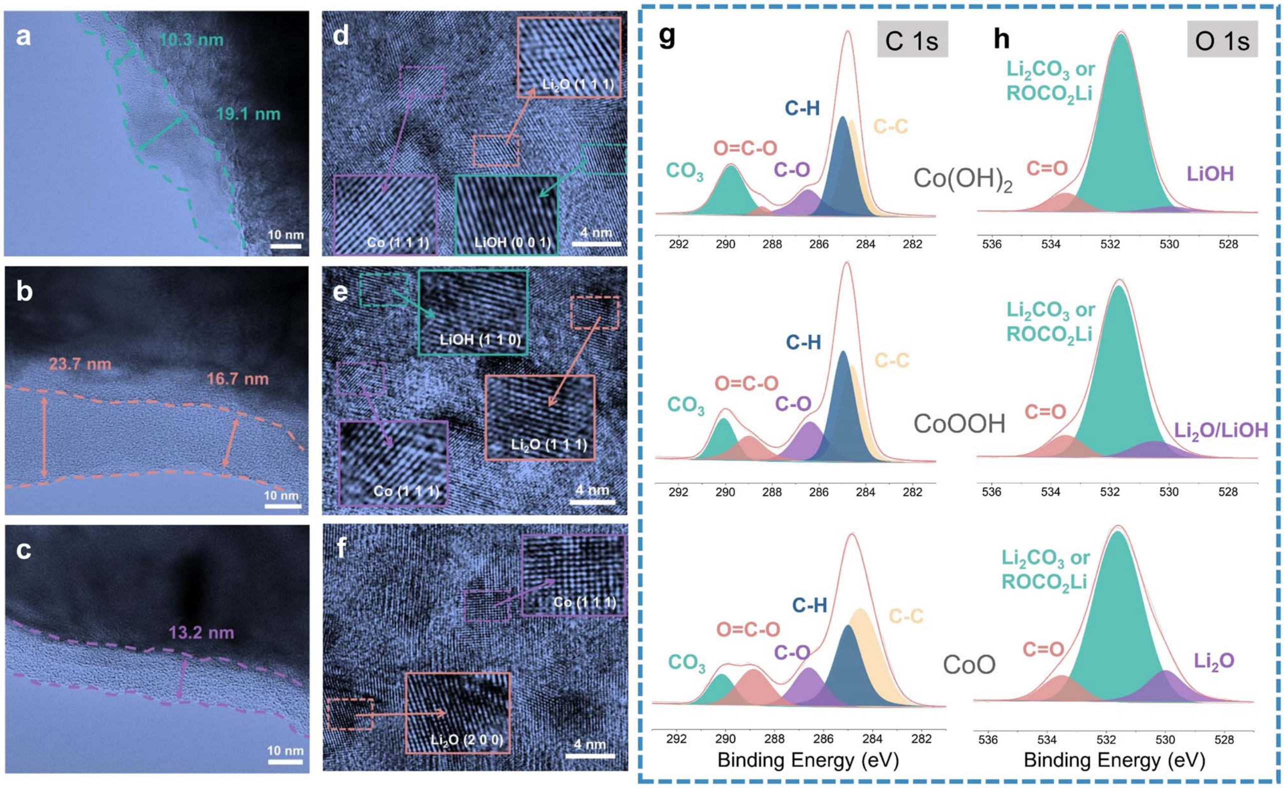

Fig. 3 TEM and XPS characterization of the three materials. TEM images of (a) $Co(OH)_2$, (b) CoOOH and (c) CoO electrodes (discharged to 0.01 V). HRTEM images of (d) $Co(OH)_2$, (e) CoOOH and (f) CoO electrodes (discharged to 0.01 V). XPS high-resolution (g) C 1s and (h) O 1s spectra for the three materials (discharged to 0.01 V).

consistent with the theoretical speculations of Wang *et al.*[22] and Xie *et al.*[21] Considering the change of CO_3 content in high-resolution C 1s spectrum analysis, the inorganic substances gathered in the SEI can be attributed to Li_2CO_3. In addition, the XPS etching technique shows that with the increase of etching depth, the C═O bonds in $Co(OH)_2$ and CoOOH disappear along with the appearance of Li_2O/LiOH peaks (Fig. S12a and b†). In contrast, the Li_2O peak appears when CoO is etched at only 5 nm, and it has little change with the increase of etching depth (Fig. S12c†). These results were similar to TEM and SEM results, indicating a thinner thickness of the CoO SEI.

During the discharging process, Co^0 nanoparticles can generate in all three materials, which can promote SEI formation.[29,30,32,33] There is electron exchange between Co and the SEI during SEI formation and decomposition.[32,33] This makes Co nanoparticles suitable magnetic "probes" to indirectly detect the SEI differences among the three materials (Fig. 1a).[32,33] Considering this effect and the sensitivity of *operando* magnetometry to this process,[54–56] cyclic voltammetry (CV) along with *operando* magnetometry in real time was carried out for $Co(OH)_2$, CoOOH and CoO (Fig. S13a–f†). As shown in Fig. 4a–c, we selected the magnetic response of the second cycle to better compare the magnetization change. Note that magnetic background has been removed, and magnetic signals of other components during the cycle can be ignored (ESI, Section S4†). Therefore, magnetization was calculated per gram of Co. The real-time magnetization response has multiple peaks and valleys at different voltages, which can be indexed as V_1 to V_5.

Due to the different structures and reaction kinetics, reaction potentials (V_1 to V_5) of the three materials have a little difference. *Ex situ* M–H measurements accompanied by a Langevin fit were carried out to analyze the reaction degree of the three materials.[57] Electrons filled in Co^0 nanoparticles based on space charge can be released in an *ex situ* environment,[32,33,39,57,58] so the magnetization of Co^0 can be fully reflected. As we can see in Fig. 4d–f, all of them show superparamagnetism and can be fitted by the Langevin equation[59] (ESI, Section S5†). The fitting results (Fig. 4d–f) show that the magnetization of $Co(OH)_2$, CoOOH and CoO reaches 135.2, 128.7 and 118.75 emu g_{Co}^{-1}, respectively. The saturation magnetization almost reaches the general magnetization of Co^0 nanoparticles,[60,61] indicating that the conversion reaction has overall completed. In addition, *ex situ* MH measurement and Langevin fitting were performed on the three materials with different cycle numbers to analyze the comminution situation of the materials. As shown in Fig. S14,† particle sizes of all three materials did not change dramatically during the first ten cycles, and the Co particle size basically remained at about 3 nm. This result excludes the possibility that the difference of capacity decay is caused by a different particle comminution situation.

The magnetic response can be divided into two ranges, the conversion reaction range (before V_1 and after V_5) and the

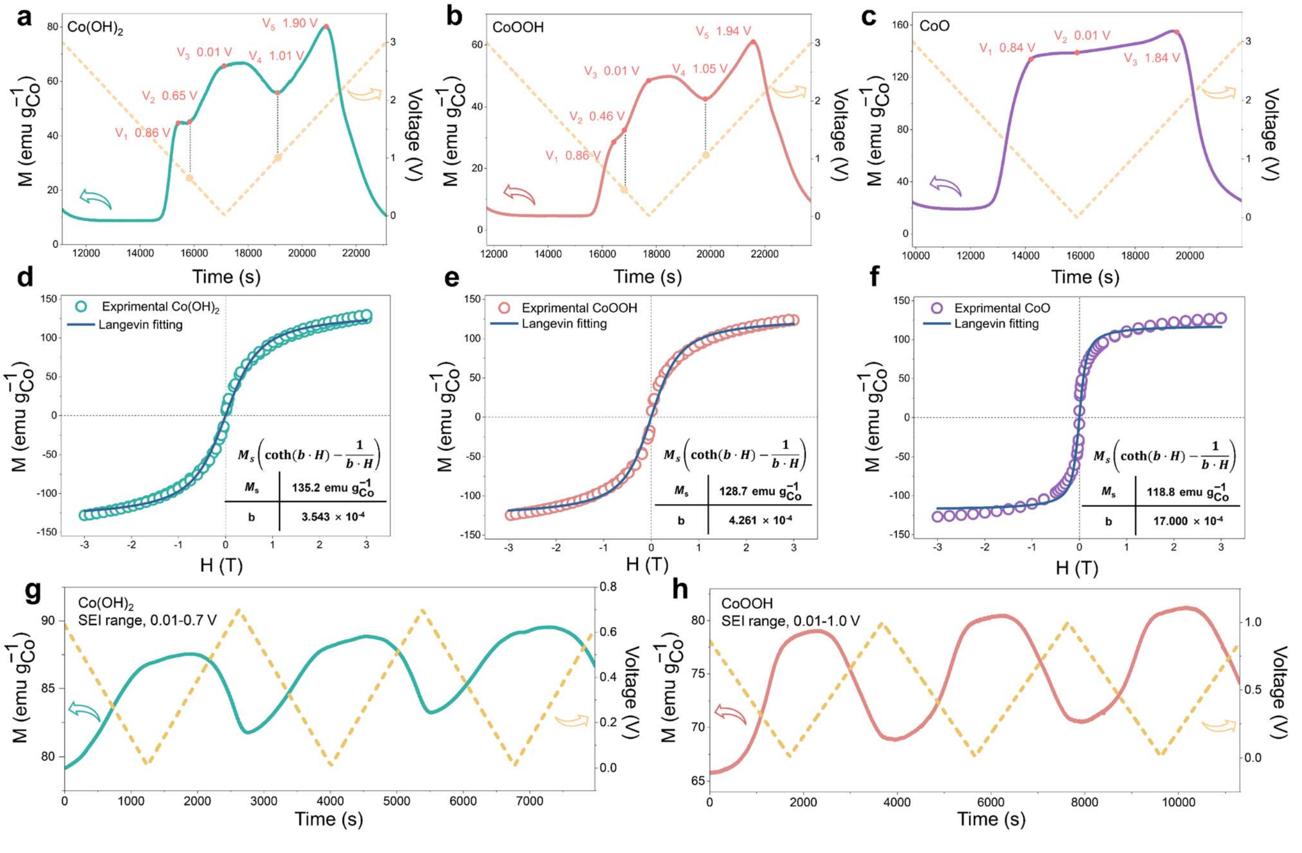

Fig. 4 Magnetometry of the three materials. *Operando* magnetometry (second cycle) curves of (a) $Co(OH)_2$, (b) CoOOH and (c) CoO. *Ex situ* M–H curves of (d) $Co(OH)_2$, (e) CoOOH and (f) CoO (discharge to 0.01 V), accompanied by a Langevin fit. *Operando* magnetometry (SEI range) curves of (g) $Co(OH)_2$ and (h) CoOOH.

interfacial reaction range (V_1–V_5),[40] the latter is the focus of our research. From the magnetic response of interfacial reaction, it can be clearly found that compared to CoO, the magnetizations of $Co(OH)_2$ and CoOOH have a totally different variation tendency in a low voltage range (from about 0.8 to 0.01 V), and the magnetization increases and decreases reversibly between V_2 and V_4. However, the magnetization of CoO has no obvious change in the range of V_1 to V_3. In order to determine the reaction mechanism of the low voltage range, CV measurement and *operando* magnetometry were conducted. As shown in Fig. S15, S16†, 3g and h, the results of $Co(OH)_2$ and CoOOH in the range from V_4 to V_5 show space charge characteristics, and the trend of magnetization is consistent with voltage. While the range from V_3 to V_4 shows SEI characteristics, the trend of magnetization is opposite to voltage (Fig. 3g and h).[32,33,39] These results verify the contribution of space charge in extra capacity. More importantly, these results indicate that the different magnetic response trends of $Co(OH)_2$ and CoOOH are related to SEI changes influenced by LiOH. In combination with the theory perspectives of Co promoting SEI formation,[29,30] it can be safely inferred that the SEI has a more drastic reaction process under the influence of LiOH, resulting in more electron transfer between Co and the SEI (ESI, Section S6†). This drastic reaction should be related to the transition from LEDC to LEMC mentioned above. Due to this transition, the SEI becomes unstable, which makes continuous electrode and electrolyte contact and incessant SEI formation. As a result, the initial capacity of $Co(OH)_2$ and CoOOH is unusually high and decline rapidly in subsequent cycles.[41–43]

Besides, we noticed that the *operando* magnetization of $Co(OH)_2$ and CoOOH at 0.01 V is much lower than that of CoO, which may be due to the influence of space charge caused by the complex interface. It was proposed that further lithiation reaction would occur at the interface between Co nanoparticles and LiOH, to form Co_xH_y in the discharging process.[27] Also, previous research has shown that adsorption of H ions on the Co surface can cause orbital reconstruction, thus leading to magnetic changes.[62] Considering the possibility of these two influences, the magnetization of Co adsorption of H and Co_xH_y formation were calculated theoretically, respectively (ESI, Section S7.1†). The calculated results show that both reactions can inevitably lead to Co magnetization reduction, and Co magnetization decreases along with the increase of H atoms, which is consistent with our characterization results. This indicates that the overall low magnetization of $Co(OH)_2$ and CoOOH is attributed to the influence of space charge and/or H atom adsorption. Obviously, results of magnetometry and theoretical calculation indicate that Co_xH_y formation is also an important origin of extra capacity. We found that the oxidation potential (V_5) of CoOOH was very close to that of $Co(OH)_2$ (V_5). The reaction potential of oxidation to Co^{3+} should be significantly different from that of oxidation to Co^{2+}. The difference of 0.04 V here is obviously unreasonable. Based on this, Co K-edge XAS spectra were recorded to analyze the oxidation process of CoOOH. As shown in Fig. S17,† only Co^{2+} can be found in the electrode material (fully charged to 3 V). This indicates that the electrochemically driven oxidation process cannot oxidize Co^0 to Co^{3+}, which is similar to the oxidation process of Fe.[39,58,63] This result debunks many previous studies on the Co^{3+} material mechanism.[64–67]

It has been verified that SEI instability dominates the rapid capacity decay in the initial cycles. In order to further analyze the composition change in the SEI, soft XAS spectra analysis with a total electron yield (TEY) model was carried out. The three materials were discharged to 0.01 V and charged back to 1.7 V, respectively.[68,69] Note that the conversion reaction of LiOH cannot be triggered in this voltage range, so the spectral contrast here is mostly attributed to the SEI reactions. In Fig. 5a–c, the features of O K-edge soft XAS spectra located at 532.4 eV and 533.7 eV correspond to LiOH and Li_2CO_3, respectively.[70,71] The data (Fig. 5a–c) show clearly that Li_2CO_3 forms in the SEI of the three materials at the discharge state. In the SEI of $Co(OH)_2$ and CoOOH, the content of LiOH demonstrates an obvious increase during the charging process to 1.7 V. While the content of LiOH in the SEI of CoO is almost unchanged. This indicates that LiOH is actively involved in the SEI related reaction. SEI becomes unstable under LiOH influence during the charging process, and partial decomposition or dissolution occurs, leading to a thinner SEI. As a result, XAS results showed more signals of LiOH, which is on the electrode material surface. Note that the LiOH in CoO stems from surface water contamination, which is consistent with the XPS results (Fig. S3c†). The comparison of Li_2CO_3 content among the three materials can be found in Fig. S18.† The Li_2CO_3 level of $Co(OH)_2$ and CoOOH samples is higher than CoO at both 0.01 V and 1.7 V. In C K-edge soft XAS spectra (Fig. 5d–f), the 288.6 eV feature originates from the C–H, while the feature at 290.4 eV originates from the C=O functional group.[70,71] The intensity contrast between the peaks of C–H and C=O changes significantly among the samples, and the intensity of the C=O peak, relative to the C–H peak, gradually increases from $Co(OH)_2$ and CoOOH to CoO. This can be attributed to the influence of LiOH, under which LEDC transformed into LEMC.[22] These results are consistent with the XPS results discussed above. SEI differences among the three materials can also be reflected in Co L-edge soft XAS spectra. As shown in Fig. S19,† signals of Co^0 in $Co(OH)_2$ and CoOOH are negligible, but detectable in CoO. XAS has a limited probe depth of the electron yield, which indicates that the SEIs of $Co(OH)_2$ and CoOOH are thicker than that of CoO, which is related to the continuous generation of the SEI under the influence of LiOH. When the monitoring depth was increased, Co particles were successfully detected in all three materials (Fig. S20†). Based on all soft XAS characterization results and theory in related studies,[21] a transformation path from LEDC to LEMC under the influence of LiOH can be proposed, which can be formulated as:

$$\text{LEDC} + \text{LiOH} \rightarrow \text{LEMC} + Li_2CO_3 \quad (4)$$

Gibbs free energy calculation was used to determine the possibility of this reaction path. Theoretical calculation (ESI, Section S7.2†) was carried out in the presence and absence of Co, respectively. Theoretical results show that ΔG of this reaction is -0.56 eV. When the reaction is performed on the Co

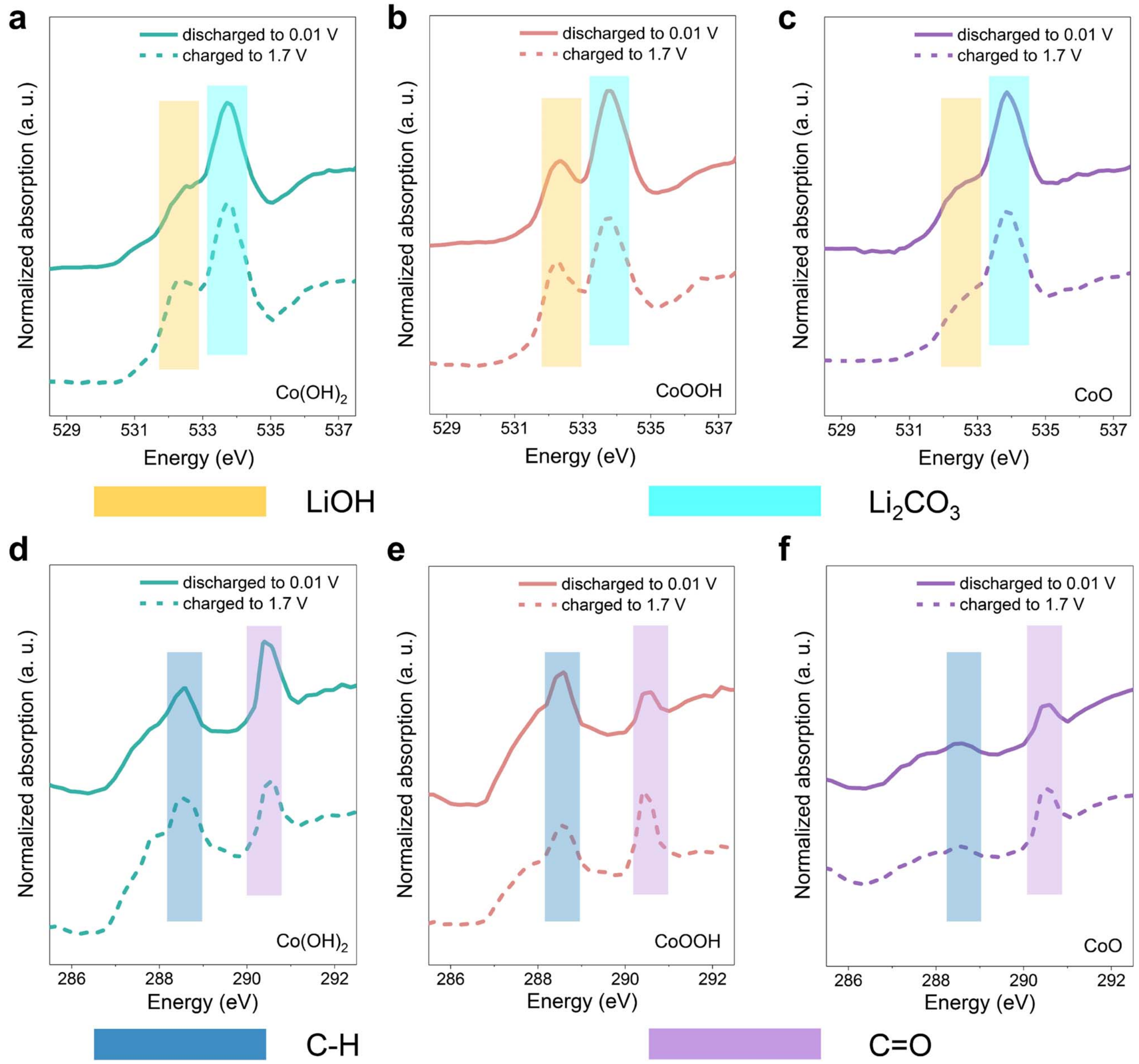

Fig. 5 Soft XAS characterization (TEY model) of the three materials, probe depth is about 5–10 nm. O K-edge soft XAS spectra of (a) Co(OH)$_2$, (b) CoOOH and (c) CoO. C K-edge soft XAS spectra of (d) Co(OH)$_2$, (e) CoOOH and (f) CoO.

surface, ΔG is -1.48 eV (Fig. 6a). This suggests that this reaction can take place spontaneously, which is similar to the results of Xie *et al.*[21] However, it is worth noting that water cannot directly react with LEDC, and it is LiOH that converted from water that directly reacts with LEDC. This reaction is easier to take place after adsorption on the Co surface, which indicates that Co plays an obvious catalytic role. This is consistent with the results of *operando* magnetometry. As shown in Fig. 4a and b magnetization of Co(OH)$_2$ and CoOOH shows a significant change between V_2 and V_4, which can be attributed to the electron exchange between the SEI and Co during Co the catalysis process.[29,30]

To further unfold the detailed reaction procedure, the electrolyte composition was adjusted to analyze the reaction path of the transformation from LEDC to LEMC. Considering that EC is the most reactive component in the electrolyte, which will form LEDC through the reaction path: EC + 2e$^-$ + 2Li$^+$ → LEDC + C_2H_4,[7,72,73] we replaced the EC component in the electrolyte with more chemically inert FEC.[22,74,75] As we can see in Fig. S21,† the initial capacity decay of Co(OH)$_2$ and CoOOH is significantly improved through this electrolyte adjustment. At the same time, the electrolyte adjustment inevitably leads to a different degree of capacity decline among all three materials. This suggests that the influence of LiOH is directly related to EC decomposition. The composition adjustment of the electrolyte reduces LEDC formation and brings about more LiF,[76,77] which isolates the contact between LiOH and the SEI, thus inhibiting the influence of

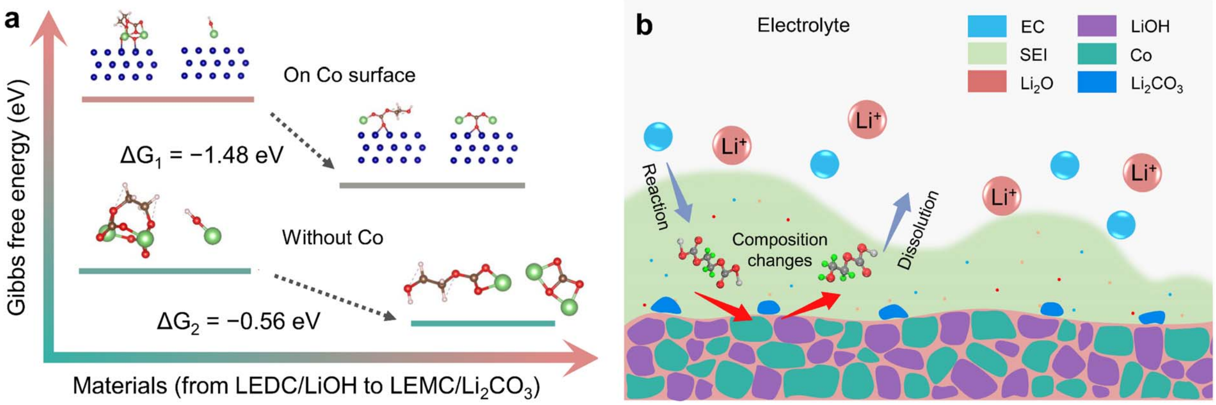

Fig. 6 Diagram of theoretical calculation and SEI composition changes. (a) Theoretical calculation of the transformation from LEDC to LEMC, the calculation was carried out in the absence of Co and on the surface of Co particles, respectively. (b) Schematic diagram of the mechanism of SEI composition change.

LiOH. Obviously, the cycle performance of transition metal hydroxides can be improved by adjusting the composition of the electrolyte. Note that LiOH is the main impurity caused by water contamination in typical electrode materials,[15,17,21,23] and adjusting electrolyte composition, especially stabilizing EC decomposition, can be a promising strategy to suppress the influence of water on cycle performance. Considering the uncertainty of the transformation path from LEDC to LEMC under water influence,[78] these results provide significant experimental evidence for this issue.

Based on the above discussion, a complete mechanism diagram of the influence of LiOH on the SEI was presented as follows:[22,24,25]

$$\mathrm{EC} + 2e^- + 2\mathrm{Li}^+ \rightarrow \mathrm{LEDC} + \mathrm{CH_2{=}CH_2} \quad (5)$$

$$\mathrm{LEDC} + \mathrm{LiOH} \rightarrow \mathrm{LEMC} + \mathrm{Li_2CO_3} \quad (6)$$

$$\mathrm{LEMC} + \mathrm{DMC} \rightarrow \mathrm{LMC} + \mathrm{EC} + \mathrm{CH_3OH} \quad (7)$$

Three equations give the complex variation of SEI composition. In the process of discharging to low voltage, the SEI begins to form (eqn (5)) along with further lithiation of LiOH and Co_xH_y formation. These reactions occur almost simultaneously, along with space charge, resulting in unusually high capacity. With the formation of the SEI, LiOH nanoparticles at the interface between the SEI and electrode material gradually affect the components of the SEI (eqn (6) and (7)), resulting in SEI fragmentation and uneven distribution (Fig. 6b). This process may be related to the side reaction of LEMC (eqn (7)) and its high solubility in the electrolyte.[18] SEI instability results in continuous contact between the electrolyte and electrode material, continuously generating a thicker SEI and bringing unusually high capacity. Li_2CO_3 gradually accumulates in the SEI and forms obvious particles during this process. As a result, the rapid capacity decay of $Co(OH)_2$ and CoOOH in the initial cycles is due to SEI instability from LiOH. As the cycle progresses, this kind of LiOH effect stabilizes after about ten cycles, and some extra capacity is retained.

Conclusions

In summary, using Co as a magnetic "probe", the effect of LiOH on the SEI was systematically analyzed by *operando* magnetometry, and the relationship between the effects and electrochemical performance was clarified for the first time. We found that LiOH can lead to the transformation of SEI components from LEDC to LEMC, during which part of the Li_2CO_3 will accumulate in the SEI. These effects lead to an inevitable capacity decay in the first few cycles. Adjusting the electrolyte composition can effectively eliminate this detrimental reaction, which is found to be directly related to the EC component in the electrolyte. In addition, it is proved that origins of extra capacity of $Co(OH)_2$ and CoOOH are space charge storage, hydride formation reaction and continuous SEI formation/dissolution. This work is of vital significance for promoting the understanding of the SEI and the synergistic effect of electrode materials and electrolyte. Practically, the findings are also valuable for the development of electrode materials, which often involve the LiOH formation from humid air exposure.

Data availability

The datasets supporting this article have been uploaded as part of the ESI.†

Author contributions

H. H, Q.-H. Li and Q. Li designed this study. Z. Zhao and F. Zhang wrote the manuscript and carried out most of the experiments with the exception at the following. Z. Zhuo and W. Yang carried out XAS experiments. F. Zou, W. Song and Y. Zhao carried out theoretical analysis. W. Ye performed experiments with TEM. X. Xu and X. Sang performed experiments with magnetometry. Y. Pan supervised DFT calculation. K. Wang, and C. Lin supervised XRD and STEM experiments. H. Li contributed to editing of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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