Guidelines for Air-Stable Lithium/Sodium Layered Oxide Cathodes

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ABSTRACT: The rational design of intercalation materials plays an indispensable role in continuously improving the performance of rechargeable batteries. The capability of some very promising layered oxide materials for positive electrodes (cathodes), such as sodium layered oxides and Ni-rich lithium layered oxides, are limited by several key challenges. Air stability is one of the issues that should be tackled appropriately. In this Perspective, we present the reaction mechanisms of layered oxides when exposed to moist atmospheres, the critical factors that affect the air stability of layered oxides, and the practical strategies toward air-stable electrodes. Based on the above understandings, we highlighted several pivotal research directions for further investigations of air stability of layered oxides. We expect that continued exploration in understanding the air stability of layered oxides will help to advance the design and lower the expense of cost-effective and high-energy cathodes for Li- and Na-ion battery technologies.
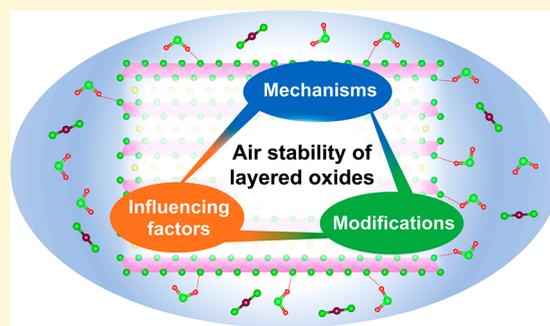
Lithium-ion batteries (LIBs) have been developed as the dominant energy storage technology to power most of our portable electronic devices and electric vehicles, because of their high energy density and long cycle life.[1−5] As complementary to LIBs, sodium-ion batteries (NIBs) have been proved to be ideal candidates for large-scale energy storage. NIBs share similar cell configuration and working mechanisms with LIBs, have the merit of abundant Na sources, and hold the possibility to utilize low-cost transition-metal element (Mn and Fe)-based layered oxide cathodes.[6]

As the global demand for renewable, green, and carbon-neutral energy increases, it is necessary to explore and develop more reliable and sustainable layered oxides for both LIBs and NIBs.[7−9] The lithium and sodium transition-metal layered oxides ($LiTMO_2$ and Na_xTMO_2, also termed as layered oxide cathodes) are the most successfully commercialized cathodes for LIBs and hold great promise for NIBs, respectively. They are built up by ordered stacking of alternate transition-metal layers (TMO_2) and alkali-metal (Li^+, Na^+) layers. Based on the local environments of alkali-metal ions (octahedral or prismatic sites) and the stacking models (ABCABC or ABAB) of TMO_2 layers, the layered oxides can be classified into several structural types, i.e., O2-, P2-, O3-, and P3-types, among others.[10] The commercially available $LiCoO_2$ and $LiNi_xCo_yMn_{1-x-y}O_2$ are O3-type materials. Meanwhile, different structural types of P2, O3, and P3-types can be obtained for Na_xTMO_2 by modulating the stoichiometry ratio of Na-TM atoms and preparation methods.[11] By exchanging Na^+ with Li^+, the P2-type Na_xTMO_2

can be transformed to O2-type $LiTMO_2$.[12] These layered oxides exhibit diverse electrochemical and chemical properties due to structural and chemical differences. For example, the P2-type sodium layered oxides usually exhibit better electrochemical reversibility and fewer phase transformations during charge−discharge processes than their O3-type counterparts. The two-dimensional structure of layered oxide cathodes makes them the natural hosts for the alkali-metal ions of Li^+,[13] Na^+,[14] and K^+,[15] as well as other ions or small molecules, such as pyridine,[16] H^+,[17,18] and H_2O.[17,19−21] When exposed to moist atmospheres, layered oxide materials might react with the compounds that are adsorbed on their surface and thereby deteriorate their structure and electrochemical performance. Accordingly, the air-sensitive layered oxides should be well-protected from the moist atmospheres to maintain their structure and stoichiometry, rendering a higher manufacturing and preservation cost.

The air stability of layered oxides attracted some attention in the early 2000s.[20,22] However, because the first generation's commercialized cathodes for LIBs are relatively stable in ambient atmospheres, the importance of the air stability of

layered oxides in rechargeable batteries has not been fully recognized until Ni-rich $LiTMO_2$ and NIBs were put on the commercialization schedule. Hitherto, one major concern of the layered oxides is related to the capability of being preserved and operated at ambient atmospheres, which determines their feasibility in cost-effective battery systems. Although the reaction mechanisms between water and some of the layered oxides have been reported, a comprehensive understanding of the air stability of layered oxides has not yet been reached. Therefore, this Perspective intends to emphasize the fundamental and practical aspects of the air stability of layered oxides. First, we shed light on the reaction mechanisms of layered oxides, especially the structural and stoichiometric changes in moisture. Subsequently, we provide a short overview of the critical factors that affect the stability of layered oxides in moist air. Finally, we disclose and conclude the major challenges and practical strategies for improving the air stability of layered oxides.

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The air-stable electrode materials should be first clarified before deciphering the air stability issues of layered oxides.

The chemical reactions between electrode active materials and moisture are greatly influenced by the exposure time and the gas components in the ambient atmospheres, especially the concentrations of $H_2O_{(g)}$ (relative humidity) and $CO_{2(g)}$. Taking P2-type $Na_{0.67}Ni_{0.33}Mn_{0.67}O_2$ as an example, 4.7% of the Na ions are extracted from the bulk after being exposed in the 18% relative humidity (RH) atmosphere (without CO_2) for 3 days, while 15.1% of the Na ions were extracted under the 93% RH + CO_2 atmospheres at the same exposure time.[17] These results indicate that the air stability of electrode active materials is highly dependent on the atmospheric conditions, which should be particularly identified when evaluating the air stability of electrode active material.

For an electrode material to be defined as air-stable after being exposed to a specific atmosphere for a given time, its structure, stoichiometry, and electrochemical performance should be well-maintained, with respect to the pristine material. As shown in Figure 1, the chemical composition of the material should remain relatively stable during exposure, e.g., the change of Li (Na) content should be lower than 5%. Regarding the structural characteristics, the exposed material should own the same crystalline phase, same symmetry, and rather similar lattice parameters, i.e., new phases should not arise. Finally, the tiny structural and stoichiometric changes, including the appearance of reaction products (i.e., Na_2CO_3 and Li_2CO_3) on the exposed material, should exert little influence on its electrochemical characteristics, such as redox behaviors, specific and volumetric capacities, cycling stability, and rate capability.

The reaction pathways of $Na_{0.67}TMO_2$ upon air exposure are summarized in Figure 2a.[17] $Na_{0.67}TMO_2$ remains stable when exposed in dry atmospheres, such as CO_2, N_2, and O_2. However, when it is exposed to moist atmospheres, Na ions are extracted from the bulk of ex-$Na_{0.67}TMO_2$ (where the prefix "ex-" indicates the exposed material) with the charge-compensation mechanisms of Na^+-H^+ exchange and/or TM oxidation and form $NaOH/Na_2CO_3/NaHCO_3$ compounds. In a specific environment with constant relative humidity and stable concentrations of the various gases, the Na^+ content of ex-$Na_{0.67}TMO_2$ has a tendency to approach the constant value of $0.67-x-z$ upon increasing exposure time (Figure 2a). However, if $0.67-x-z$ is lower than the critical sodium content (n_c), water

Structure
No change of:
Crystalline phase;
Symmetry;
Lattice parameters

Stoichiometry
Minor compositional changes

$Na_xTMO_2 \longrightarrow Na_{x-y}TMO_2$
$y/x < 0.05$

$LiTMO_2 \longrightarrow Li_{1-z}TMO_2$
$z < 0.05$

Air-stable Layered Oxides
in a given atmosphere for a given time

Electrochemical Performances
No change of:
Voltage profiles;
Specific/volumetric capacity;
Rate capability;
Cycling stability
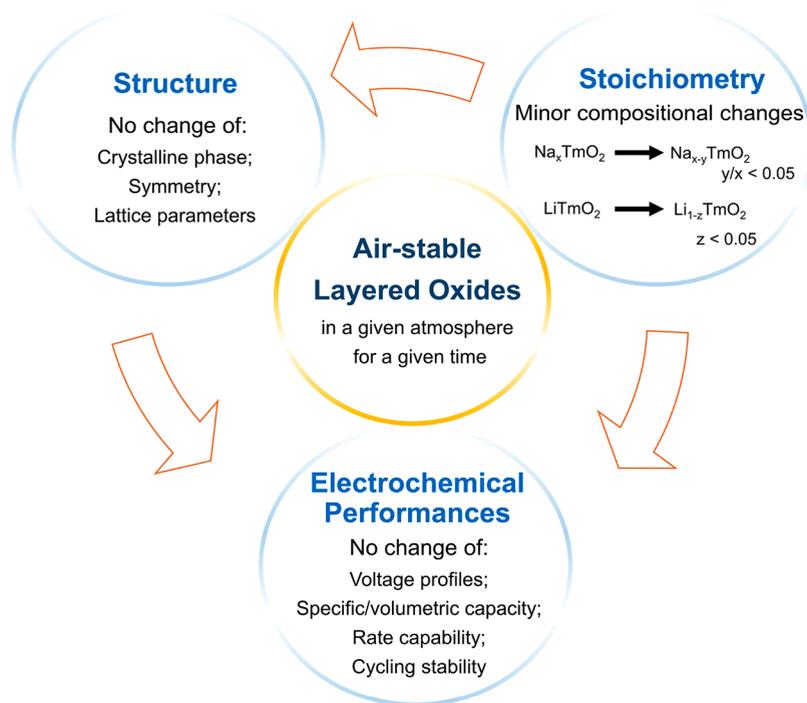
**Figure 1. Requirements for air-stable electrode active materials.**
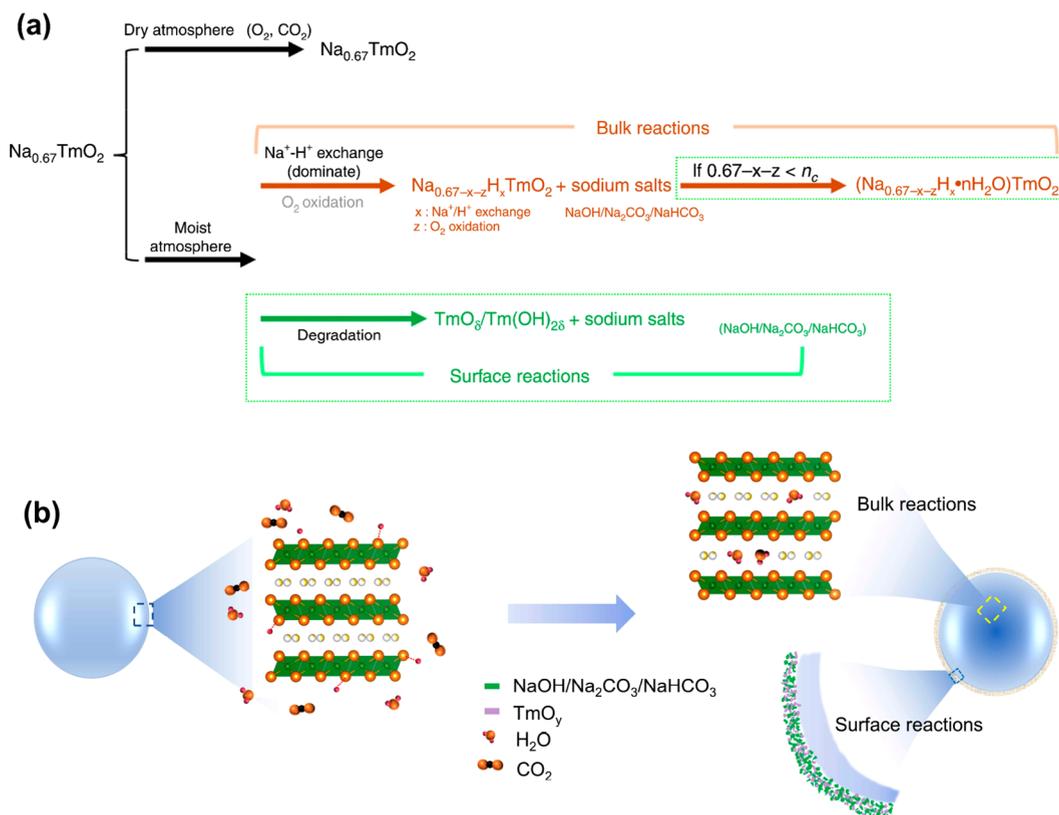
Figure 2. Chemical and structural evolutions of ex-Na_xTmO_2: (a) reaction pathways and (b) schematic illustration of chemical and structural evolution mechanisms of Na_xTmO_2 when exposed in moist atmospheres. [Panel (a) was reproduced with permission from ref 17. Copyright 2020, Nature Publishing Group.]

molecules insert into the sodium layers of $Na_{0.67-x-z}TMO_2$ and form the hydration phase (Figure 2b).

The chemical reactions of Na_xTMO_2 and $LiTMO_2$ in a moist atmosphere that are dependent on the CO_2 content are as follows:[17]

(Only the $Na^+(Li)^+$-H^+ exchange mechanism is considered here.)

$$zH_2O + Na_x(Li)TMO_2 = Na_{x-z}(Li_{1-zx})H_zTMO_2$$
$$+ zNa(Li)OH \qquad \text{(without } CO_2) \qquad (1)$$

$$zCO_2 + zH_2O + 2Na_x(Li)TMO_2$$
$$= 2Na_{x-z}(Li_{1-x})H_zTMO_2 + zNa_2(Li_2)CO_3$$
$$\text{(low concentration of } CO_2) \qquad (2)$$

$$zCO_2 + zH_2O + Na_x(Li)TMO_2$$
$$= Na_{x-z}(Li_{1-z})H_zTMO_2 + zNa(Li)HCO_3$$
$$\text{(high concentration of } CO_2) \qquad (3)$$
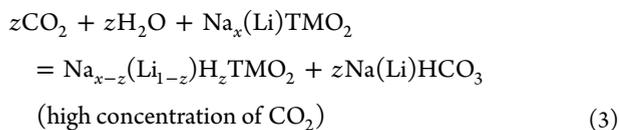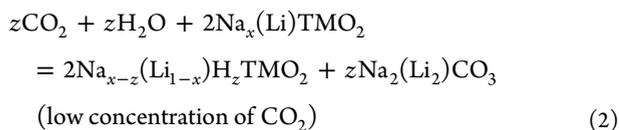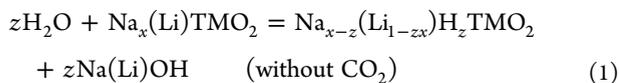
If the $Na^+(Li)^+$ content is lower than n_c, the hydration process occurs:

$$Na_{x-z}(Li_{1-x-z})H_zTMO_2 + yH_2O$$
$$= [Na_{x-z}(Li_{1-x-z})H_z(H_2O)_y]TMO_2 \qquad (4)$$
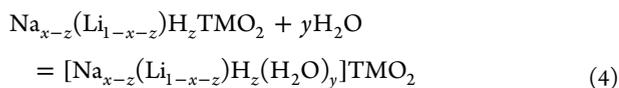
Figures 3a–c show the morphological evolutions of Na products in ex-$Na_{0.67}MnO_2$. Soon after being exposed to moist air, nanosized crystals form on the particle surface (Figure 3a).

Upon increasing exposure time, the crystals grow and gradually cover the entire particle (Figure 3b). Moreover, the extracted Na^+ might also migrate from the particle surface and recrystallize into micrometer-sized crystals (Figure 3c) through micro-solutions formed by the absorption of water molecules.

Na^+ is not homogeneously distributed in the aged compound, but is highly dependent on the sizes and depth of particles. Chou and co-workers prepared single-crystal $Na_{0.84}CoO_2$ samples with average sizes of 1 mm × 0.5 mm × 0.1 mm and aged them in an ambient environment with RH = 55% for 2.5 years.[23] The electron probe microanalysis (EPMA) results demonstrate that the Na content (x in Na_xCoO_2) increases from ∼0.3 on the surface to 0.46, 0.5, and 0.7 within the depth of 10, 20, and 30 μm, respectively.[23]

In addition, the chemical degradation mechanisms occurring on the surface of ex-$Na_{0.67}TMO_2$ particles differ from those occurring in the bulk. For example, the Cu_2O (Figure 3d), Li_2CO_3, and NiO impurities have been observed in the exposed $Na_{0.67}Cu_{0.33}Mn_{0.67}O_2$, $Na_{0.67}Li_{0.2}Mn_{0.8}O_2$, and Ni-rich ex-$Na_{0.67}TMO_2$ oxides, respectively.[17,24] On the other hand, no Mn-related oxides/hydroxides appear in ex-$Na_{0.67}MnO_2$, but MnOOH is observed after immersing the material in water for 20 days. Therefore, not all but a large number of sodium layered oxides degrade into TMOs or hydroxides upon exposure to moist atmospheres, as illustrated in Figure 2.

Similar structural and chemical reactions have been observed in $LiTMO_2$. As well as Na_xTMO_2, water is the most critical factor to destabilize $LiTMO_2$ during materials preparation, storage, and electrode preparation.[25] According to the previous references, when $LiTMO_2$ materials, such as $LiNiO_2$,[22,26] Li-rich layered oxides,[27] $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$,[25,28] Li-
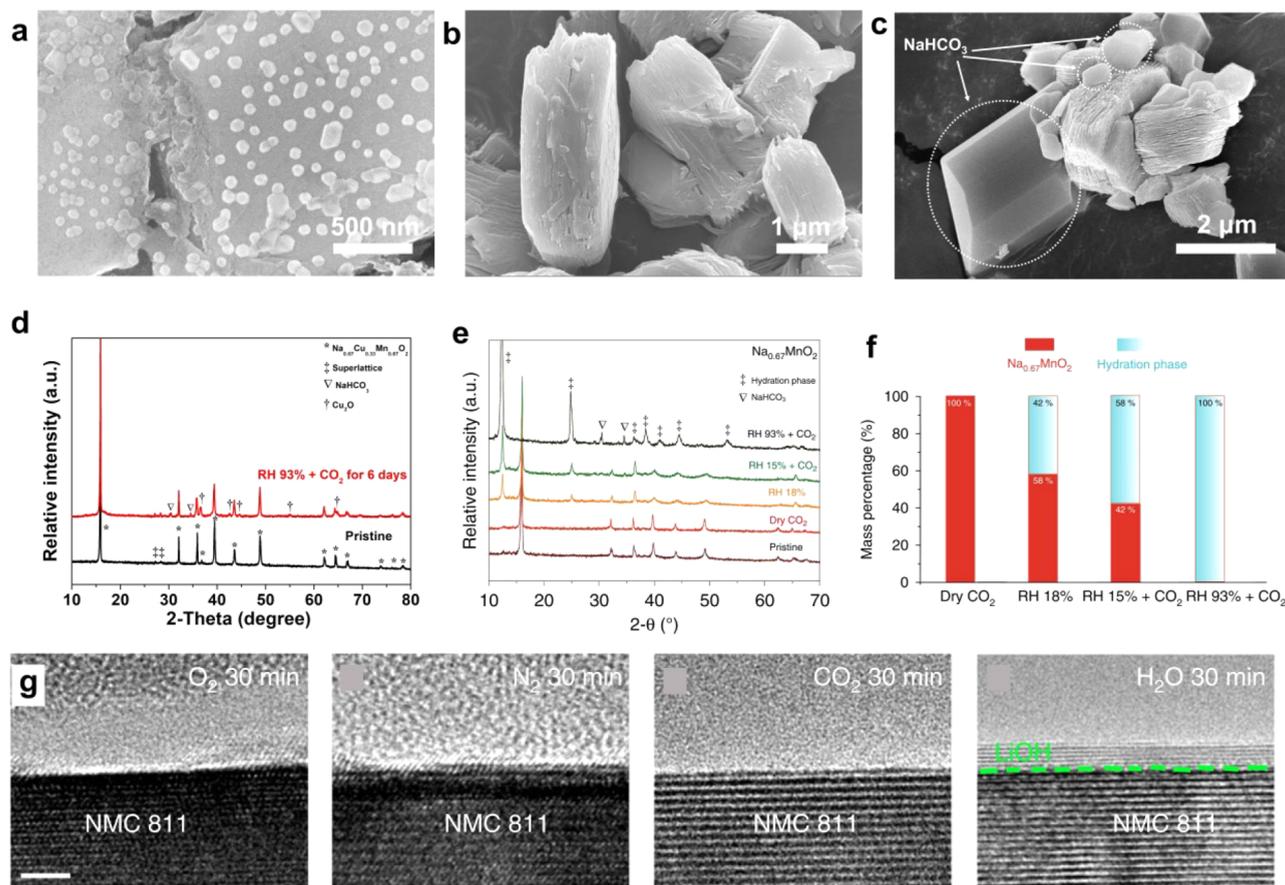
Figure 3. Reaction mechanisms of Li and Na layered oxides during air exposure. SEM images of (a) short-term and (b, c) long-term (6 days) exposed P2-type $Na_{0.67}MnO_2$ in 93% RH + CO_2. (d) XRD patterns of ex-$Na_{0.67}Cu_{0.33}Mn_{0.67}O_2$.[17] (e) XRD patterns and (f) corresponding Rietveld refinements results of P2−$Na_{0.67}MnO_2$ in different atmospheres. [Reproduced with permission from ref 17. Copyright 2020, Nature Publishing Group.] (g) Chemical evolutions of NMC811 in different atmospheres. [Reproduced with permission from ref 30. Copyright 2020, Nature Publishing Group.]

$Ni_{0.8}Mn_{0.1}Co_{0.1}O_2$,[29−31] are exposed in moist atmospheres, LiOH, Li_2CO_3, and $LiHCO_3$ form either coated on the active material particles or as separated particles. Some researchers reported that Li_2CO_3 and LiOH derive from the residual Li during the synthesis procedure. This occurs when an excess amount of Li is available, which is not integrated into the final products. Otherwise, the LiOH, Li_2CO_3, and $LiHCO_3$ species are most likely arising from the chemical reactions of the active material with water and CO_2 after synthesis since these carbonate/hydroxide compounds are unlikely to exist under the sintering temperature of 700−900 °C for a few hours. Furthermore, with the extraction of a large amount of Li ions, H_2O molecules could insert into the Li layers of lithium layered oxides and form hydrated phases,[32] similar to $Na_{0.67}TMO_2$ (eqs 1−4).

The presence of CO_2 in the atmosphere affects both the reaction products (hydroxide, carbonate, or bicarbonate) and the Na (Li) content leached from the exposed layered oxide. As shown in Figures 3e and 3f,[17] the P2-type $Na_{0.67}MnO_2$ is stable in dry, but CO_2-containing atmospheres. When exposed to 18% RH and 15% RH + CO_2 atmospheres, $NaHCO_3$ and hydration phases appear, demonstrating the extraction of Na^+ and the insertion of H_2O molecules in the active material (specifically, in the Na layer). Moreover, the degree of hydration increases with both the presence of CO_2 and the increment of RH. The above results demonstrate that water vapor destabilizes the layered

oxides and that the presence of CO_2 exacerbates the chemical reactions between the layered oxides and water. In the case of lithium layered oxides, as early as in 2004, Liu et al.[22] first found that CO_2 and H_2O react with Li^+ to form Li_2CO_3 and LiOH on the surface of $LiNiO_2$. Very recently, Zhang and co-workers exposed $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811) in N_2, O_2, CO_2, and water vapor at a gas pressure of 5 × 10^{-2} Torr and room temperature for 30 min.[30] The atomic-level in situ transmission electron microscopy (TEM) images demonstrated that NMC811 is chemically resistant to N_2, O_2, and CO_2, while LiOH is formed on the surface of NMC811 when exposed to water vapor (Figure 3g).[30]

Apart from the bulk Li (Na) extraction, surface degradation is another critical concern that thwarted the large-scale manufacturing and storage of some important Li-containing cathodes. For instance, $LiNiO_2$ decomposes to NiO and O_2 when being exposed to air.[26] After being exposed to moist atmospheres or emerging in water for several days, $LiFePO_4$ degrades into Li_3PO_4,[33] $Fe(OH)_2$/Fe_2O_3,[33,34] and $FePO_4$,[35] and result in degraded electrochemical performance. Also, lithiated Ni-rich (Ni ≥ 80%) layered oxides react with air and moisture, resulting in the formation of Ni-containing oxide, hydroxide, and carbonate species, which causes an upsurge of the charge transfer resistance.[26,29,31,36,37]

Air-exposure affects the electrochemical performance of layered oxide cathodes. As shown in Figure 4a, after being
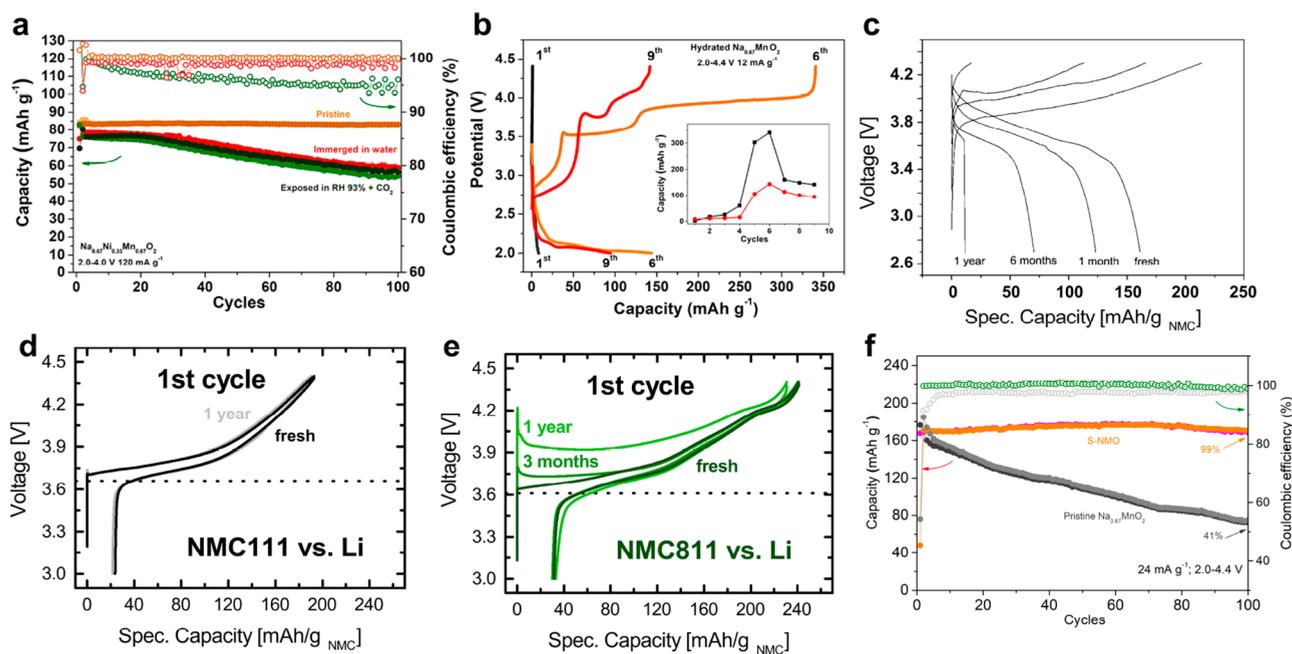
Figure 4. Electrochemical performance of ex-Na_xTMO_2 and ex-$LiTMO_2$. (a) Cycling stability of three different P2-type $Na_{0.67}Ni_{0.33}Mn_{0.67}O_2$ electrodes within 2.0−4.0 V (pristine $Na_{0.67}Ni_{0.33}Mn_{0.67}O_2$, $Na_{0.67}Ni_{0.33}Mn_{0.67}O_2$ samples that immersed in water for 20 days and exposed in 93% RH + CO_2 for 3 days).[17] (b) Charge−discharge curves of totally hydrated P2-type $Na_{0.67}MnO_2$. [Reproduced with permission from ref 17. Copyright 2020, Nature Publishing Group.] (c−e) The first charge−discharge curves of fresh and exposed samples of $LiNiO_2$ (panel (c)), NMC111 (panel (d)), and NMC811 (panel (e)).[29] [Panel (c) was reproduced with permission from ref 22. Copyright 2004, The Electrochemical Society. Panels (d) and (e) were reproduced with permission from ref 29. Copyright 2018, The Electrochemical Society.] (f) Cycling stability of pristine and air exposed P2-type $Na_{0.67}MnO_2$. [Reproduced with permission from ref 38. Copyright 2021, Nature Publishing Group.]

exposed to the moisture atmosphere of 93% RH + CO_2 for three days or immersed in water for 20 days, P2-type $Na_{0.67}Ni_{0.33}Mn_{0.67}O_2$ electrodes show lower Coulombic efficiency and faster capacity fade, compared to the pristine ones.[17] Hydrated P2-type $Na_{0.67}MnO_2$ electrodes do not operate properly exhibiting deformed charge−discharge profiles and huge polarization (Figure 4b).[17] Air-exposed $LiTMO_2$ electrodes exhibit similar phenomena. For example, their polarization grows and reversible specific capacity decreases as the exposure time of $LiNiO_2$ in air increases (Figure 4c).[22] In 2018, based on a variety of Ni-rich layered oxide $LiNi_xCo_yMn_{1−x−y}O_2$ (x = 0.7, 0.8, and 0.9), Manthiram and co-workers[31] demonstrated the formation of lithium species (LiOH, Li_2CO_3, and $LiHCO_3$) and NiO sublayer on the Ni-rich layered oxides. Al-doping could effectively limit but not suppress the side reactions. Jung et al.[29] compared the electrochemical performance and chemical reactions of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC111) and $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811) after aging in ambient air for one year. Both fresh and exposed NMC111 electrodes show similar charge−discharge profiles (Figure 4d) except for the very minor capacity disparity, because of the Li loss during exposure.[29] In contrast, ex-NMC811 electrodes exhibit much lower specific capacity and larger voltage hysteresis (Figure 4e) than fresh NMC811 electrodes. Raman and X-ray photoelectron spectroscopy (XPS) characterizations suggest that a surface layer (≤10 nm) is formed on the ex-NMC811 electrodes mostly composed of $NiCO_3$ and some hydroxide species. However, no obvious impurities appeared on the NMC111 electrode's surface, demonstrating that air stability is highly correlated with the stoichiometry of the layered oxides.[29]

Although air exposure was reported to deteriorate the electrochemical performance of many lithium and sodium layered oxide cathodes, the opposite effect has been also observed. With proper treatments after moisture exposure, P2-type Na_xMnO_2 electrodes (S-NMO in Figure 4f) exhibit a high capacity (162 mAh g$^{−1}$) and excellent cycling stability (99% of the original capacity maintained after 100 cycles at 0.2 C), greatly outperforming pristine $Na_{0.67}MnO_2$ electrodes.[38]

Besides the effect on the electrochemical performance, the formation of impurities during moisture exposure might alter the structural evolution mechanism upon Li (Na) storage and release. Chapman and coauthors[28] demonstrated that the intrinsic reaction mechanism of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) is a pure solid solution within a lithium content of 1.0−0.3. After being exposed to ambient atmosphere for 2 years, a Li_2CO_3 surface layer formed on the NCA particle, which induced electrochemical reaction heterogeneity resulting in a "two-phase behavior" during the first charge.

In conclusion, the chemical reactions between layered oxides and moist air or water are as follows. Upon exposure in moist atmospheres or $H_2O_{(l)}$, the alkali ions are extracted from the bulk of layered oxides and form the corresponding hydroxide, carbonate, and bicarbonate species. When the Li (Na) concentrations are lower than the critical Li (Na) contents, water enters into the Li (Na) layer forming hydration phases. Some layered oxides, especially those containing Ni, Cu, and Fe, decompose into TM-based oxides, hydroxides, and carbonates. Importantly, layered oxides might suffer from one or more of these degradation mechanisms, depending on their structure and stoichiometry. After exposure to moist air, most of the exposed materials exhibit worse electrochemical performance, but a few are stable and, exceptionally, e.g., Na_xTMO_2, show even better electrochemical performance.

The combination of different characterization techniques is highly needed to check the air stability of electrode active materials,[8,17,30] such as X-ray diffraction spectroscopy (XRD), TEM, scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), ^{23}Na{^{1}H} rotational-echo double-resonance (REDOR), hard/soft X-ray absorption spectroscopy (h-/s-XAS), ICP-AES, Raman, and solid-state nuclear magnetic resonance spectroscopy (ss-NMR) are highly recommended to probe the chemical and structural properties before and after air/moist exposure. The comparison of electrochemical performance via cyclic voltammetry (CV) and galvanostatic charge−discharge (CD) of electrodes made with fresh and exposed active materials also highlights the chemical and redox differences. However, the possible structural/chemical changes introduced by the electrode preparation processes[39] make the electrochemical performance comparison less reliable than the direct characterizations experiments.

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The chemical reactions of electrode materials exposed to moist air are dependent on the thermodynamic equilibrium between the chemical potentials (or energy levels) of the active materials and the absorbed species from the atmosphere. Therefore, temperature, atmospheric conditions, chemical composition, and structure of active materials are the key factors determining their stability upon exposure to moist air (see Figure 5a).

Temperature and composition of the atmosphere are external factors contributing to the degradation of the layered oxide active materials. As shown in Figure 5b, $H_2O_{(g)}$ molecules have a tendency to be absorbed on the hydrophilic surface of oxide particles exposed to moist air. The water molecules react with the active material, as described in eq 1. The extraction of Li (Na) ions is driven by the differences of both the chemical potential $(\mu_{(Li/Na)})$[17] and Li (Na) concentration between the bulk and surface layer of exposed layered oxides. Furthermore, the chemical reactions of layered oxides in moist air are also affected by the presence of CO_2 (right panel of Figure 5b), as summarized in eqs 2 and 3.

Considering the fast reaction between Li^+ (Na^+) and OH^-/CO_3^{2-}/HCO_3^-, the reaction rates of eqs 1−3) depend on the concentration of $H_2O_{(g)}$, the dissociation rates of $H_2O_{(l)}$ and H_2CO_3, the diffusion rate of Li (Na), and the electronic conductivity of the active materials. The simultaneous presence of H_2O and CO_2 accelerates the reactions since the equilibrium
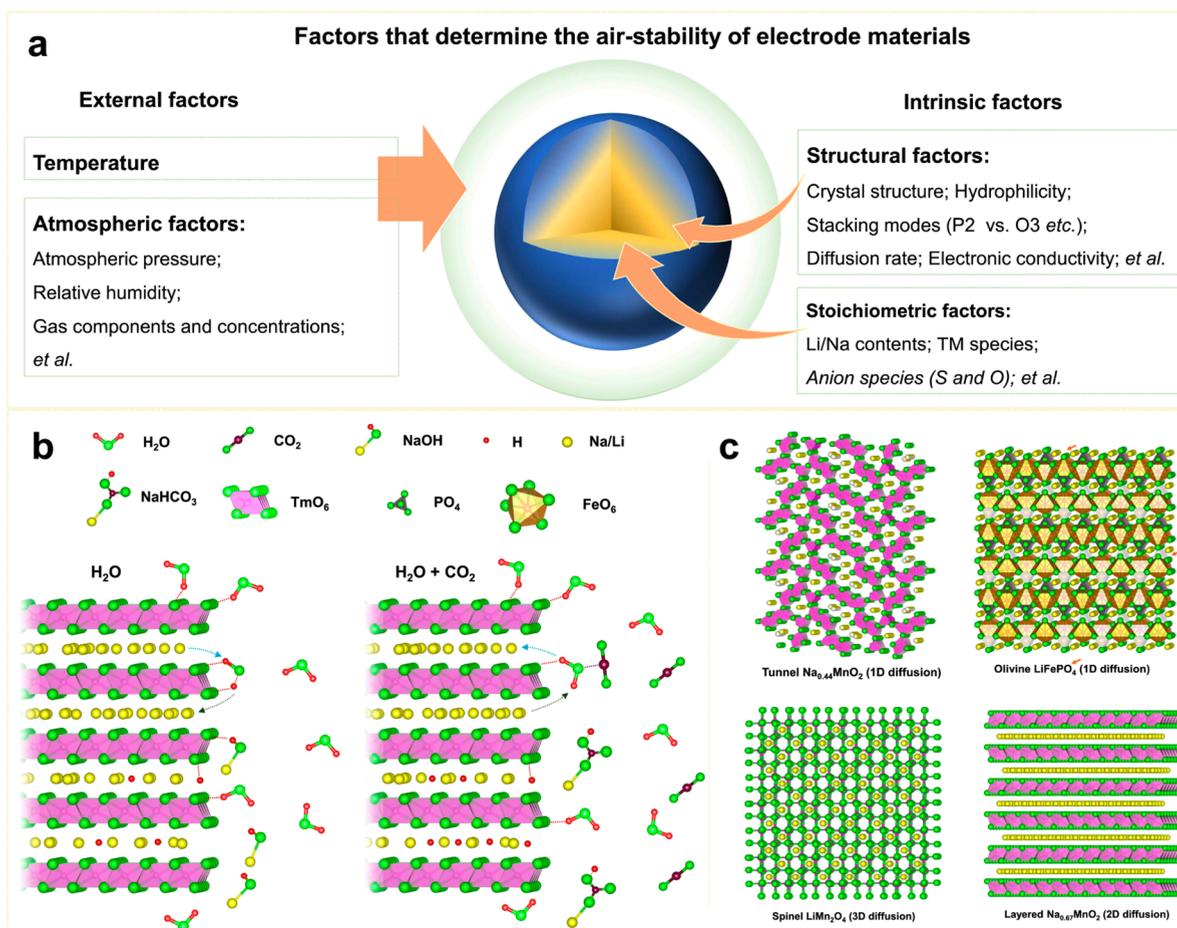

Figure 5. Influencing factors. (a) Factors that affect the air stability of electrode active materials. (b) Schematic illustrations of layered oxides in moist atmosphere without CO_2 and with the presence of CO_2. (c) Schematic illustrations of the diffusion channels of olivine $LiFePO_4$, spinel $LiMn_2O_4$, tunnel $Na_{0.44}MnO_2$, and layered $Na_{0.67}MnO_2$.

constants for the dissociation of H_2CO_3 ($K_{a1}^{\ominus} = 4.2 \times 10^{-7}$, $K_{a2}^{\ominus} = 4.7 \times 10^{-11}$) are much higher than that of water ($K_w^{\ominus} = 1.01 \times 10^{-14}$). Therefore, atmospheric pressure, RH, and $CO_{2(g)}$ are the most critical environmental factors determining the air stability of electrode materials in moist air.[17,30] Similarly, the presence of $NH_{3(g)}$, $H_2S_{(g)}$, and $HCl_{(g)}$, supporting the dissociation of water molecules, also worsen the air stability of layered oxides drastically.

Structure and stoichiometry are two critical intrinsic factors that affect the air stability of electrode active materials. Theoretically, if the differences in Li^+ (Na^+) contents as well as TM species and phase transformations are ignored, the Li^+ (Na^+) diffusion coefficients in the one-dimensional (1D) and three-dimensional (3D) diffusion channels are lower than those in 2D diffusion paths, as exemplified in Table 1. In fact, cation

Table 1. Diffusion Coefficient of Lithium and Sodium Ions in Various Electrode Active Materials

diffusion tunnel	materials	diffusion coefficient	test methods[a]	refs
1D	$LiFePO_4$	$10^{-19}-10^{-12}$ $cm^2\ s^{-1}$	EIS, CV, GITT	43, 44
	$Na_{0.44}MnO_2$	$10^{-15}-10^{-10}$ $cm^2\ s^{-1}$	GITT, EIS, PITT	45, 46
2D	Na_xMnO_2	$10^{-12}-10^{-8}$ $cm^2\ s^{-1}$	GITT	39, 47
	Na_xCoO_2	$10^{-12}-10^{-7}$ $cm^2\ s^{-1}$	EIS, PITT	48, 49
	$LiCoO_2$	$10^{-11}-10^{-7}$ $cm^2\ s^{-1}$	EIS, GITT, MSS	43, 50
3D	$Li_3V_2(PO_4)_3$	$10^{-13}-10^{-9}$ $cm^2\ s^{-1}$	EIS, GITT, PITT, CV	51, 52
	$LiMn_2O_4$	$10^{-13}-10^{-9}$ $cm^2\ s^{-1}$	Sims, GITT, PITT, EIS, CV	43, 53
	$LiNi_{0.5}Mn_{1.5}O_4$	$10^{-14}-10^{-9}$ $cm^2\ s^{-1}$	CV, EIS	54, 55
	$Na_3V_2(PO_4)_3$	$10^{-14}-10^{-10}$ $cm^2\ s^{-1}$	GITT, CV; EIS	56, 57

[a]Nomenclature: EIS, electrochemical impedance spectroscopy; CV, cyclic voltammetry; GITT, galvanostatic intermittent titration technique; PITT, potentiostatic intermittent titration technique; MSS, muon-spin spectroscopy; SIMS, secondary ion mass spectroscopy.

dislocations can easily block the diffusion in the 1D and 3D channels. As a result, although the extraction of Li^+ has been also observed in other moisture-exposed/water-emerged Li-containing electrodes, including $LiFePO_4$[33,34] and $Li_4Ti_5O_{12}$,[40] the Li^+ (Na^+) losses in olivine $LiFePO_4$ (1D), spinel $LiMn_2O_4$/$LiNi_{0.5}Mn_{1.5}O_4$ (3D), and tunnel $Na_{0.44}MnO_2$ (1D) are lower than that in layered oxides (2D, Figure 5c). With regard to Na_xTMO_2, the O3-type oxides ($x = 1$) usually have higher pristine Na contents than that of the P2-type ($x = 0.58-0.80$).[10,41] In addition, in P-type materials, Na^+ hops directly from one prismatic site to the adjacent prismatic site, while an interstitial tetrahedral site is involved for Na^+ to diffuse between two adjacent octahedral sites in O3-type structures. Therefore, the Na^+ diffusion barriers are higher in O3-type than in P2-type structures,[42] rendering O3-type structures more stable in moist air. Aside from the specific crystalline structure, electrode active materials with higher crystallinity, worse electronic conductivity, larger crystal sizes, poor hydrophilicity, and fewer structural defects show better air stability.

Beyond atmospheric and structural factors, stoichiometry, in terms of the TM species and Li^+ (Na^+) contents, also affects the air stability of layered oxides. The chemical reactions between layered oxides and the moist atmospheres are thermodynamically controlled by the formation energy of the pristine layered oxides. Specifically, the $LiTMO_2$ and Na_xTMO_2 oxides with lower electrochemical potential (μ_{Li^+}/μ_{Na^+}) have a tendency to lose their Li^+ (Na^+) in moist atmospheres and, thus, exhibit worse air stability. The electrochemical potential of the layered oxide is further affected by the redox-active TM species. For instance, as shown in Figure 6a,[17] the Na_xTMO_2 oxides based on $O^{2-/n-}$, $Cu^{2+/3+}$, and $Ni^{2+/4+}$ redox couples show better air stability, i.e., $Na_{0.67}Mg_{0.33}Mn_{0.67}O_2$, $Na_{0.67}Ni_{0.33}Mn_{0.67}O_2$, and $Na_{0.67}Cu_{0.33}Mn_{0.67}O_2$, while Na_xVO_2, $Na_{0.67}MnO_2$, Na_2RuO_3, $Na_{0.67}CoO_2$, and $Na_{0.67}Fe_{0.5}Mn_{0.5}O_2$ have poor air stability and should be stored in dry/inert atmospheres immediately once they are synthesized. Moreover, the physicochemical properties of the degradation products might also affect the air sensitivity of electrodes. For example, the low solubility of Li_2CO_3 in water might hinder the recrystallization process (Figure 3b) and result in a stable Li_2CO_3 layer on the particle surface,[58] which avoids further direct contact with moist air leading to a better stability.

To summarize, leaving aside surface degradations, the comparison of air stability of layered oxides could be schematically illustrated as Figures 6b and 6c. $LiTMO_2$ oxides usually show better air stability than their corresponding Na_xTMO_2, e.g., O3-$LiCoO_2$ is more stable than O3-$NaCoO_2$ (Figure 6b). As a result, the air stability of an O3-type Na_xTMO_2 is higher than that of the P2-type counterpart. TM species also makes a great difference in the air stability of layered oxides (Figures 6a and 6c). After being exposed in the moist atmosphere (RH = 18%) for 3 days, P2$-Na_{0.67}Ni_{0.33}Mn_{0.67}O_2$ and $Na_{0.67}Mg_{0.33}Mn_{0.67}O_2$ only lost ~5% (0.03 in 0.67) of their initial Na^+ content while P2$-Na_{0.67}MnO_2$ lost 60% (0.4 in 0.67) of its initial Na^+ content, transforming to the hydrated phase, because of the extraction of a large amount of Na^+.[17]

Designing air-stable electrode material has attracted enormous attention because it determines the complexity and cost of preparation and storage of electrode active materials. To fulfill

> To fulfill the requirements for the next generation's smart grids and electric vehicles, the application of air-stable electrodes with natural abundant resources is needed.

the requirements for the next generation's smart grids and electric vehicles, the application of air-stable electrodes with natural abundant resources is needed. In this regard, much effort is required to improve the air stability of layered oxide cathodes for Li- and Na-ion rechargeable batteries. Based on the above-summarized reaction mechanisms and discussed influencing factors, several pivotal strategies and directions are highlighted below.

As shown in Figure 7a, an eligible air-stable layered oxide should fulfill at least three requirements: (1) be thermodynamically stable/metastable; (2) offer a very limited Li^+/Na^+ loss from the bulk of particles; and (3) show no surface degradation after exposure to ambient atmospheres. Unfortunately, outstanding electrochemical performance and good air stability may not be achieved simultaneously in one electrode material. For
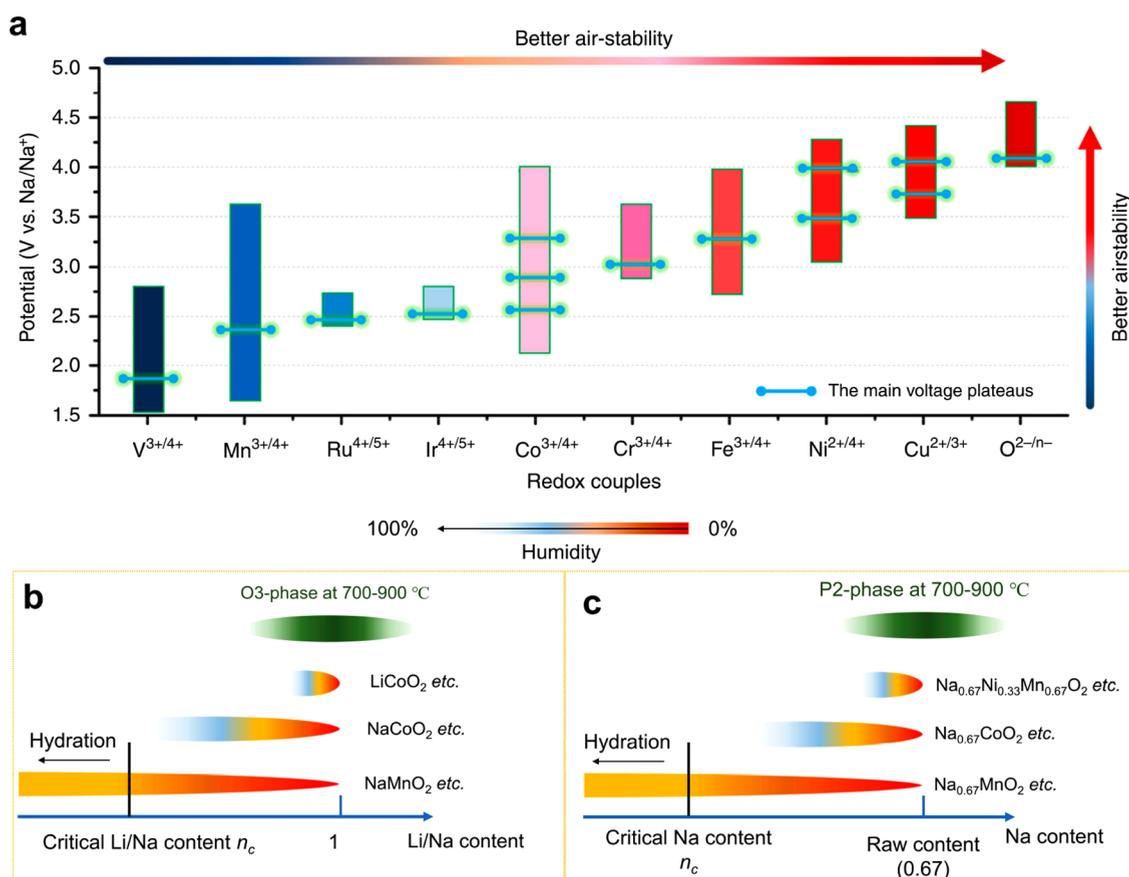
Figure 6. Comparison of air stability for different layered oxides. (a) Air stability of Na_xTmO_2 oxides based on different Tm redox couples. [Reproduced with permission from ref 17. Copyright 2020, Nature Publishing Group.] (b, c) Li^+ (Na^+) loss in exposed O3-type (panel (b)) and P2-type (panel (c)) layered oxides.

example, P2-type $Na_{0.67}Ni_{0.33}Mn_{0.67}O_2$ shows good air stability but suffers from rapid capacity decay if the upper working potential is set above 4.2 V, while P2-type $Na_{0.67}Al_{0.05}Mn_{0.95}O_2$ exhibits excellent electrochemical stability, but poor air stability.[39,59−61] Normally, air-sensitive layered oxides must be handled and stored in dry/inert atmospheres once prepared to avoid direct contact with ambient air. Upon long-term storage, poor air-stable oxides interact even with a trace amount of water in the atmosphere, leading to chemical and structural changes. Therefore, a high-temperature calcination step (above 600 °C) for a few hours is needed to remove the impurities.

Designing moisture-tolerant layered oxides would be a special strategy to alleviate the air-instability of layered oxides. Recently, a water-mediated strategy has been designed for P2−$Na_{0.67}MnO_2$, which results in the formation of a shalelike $Na_{0.21}MnO_2$ (S-NMO) with boosted electrochemical performance.[38] Besides the improved redox reversibility and structural stability during the electrochemical process, the S-NMO oxide shows excellent moisture tolerance, even being exposed to a 93% RH + CO_2 atmosphere. No hydroxide, carbonate, or bicarbonate are found in the FTIR spectra of exposed S-NMO (Figure 7b). The inserted water molecules are easily removed by heating at 160 °C in air for 2 h. Moreover, the calcination temperature could be further reduced to 120 °C under vacuum, which matches well with the drying procedure during the electrode-making process.[38] Technically, improving moisture tolerance of layered oxides is not only resulting from the elimination of the side reactions with moisture and other

species, but also the enabling of the recovery of the chemical and structural changes of the exposed layered oxides via a simple drying procedure, such as the one occurring during the electrode-making process (Figure 7c).

The absorption of H_2O on the layered oxide particle surface is a prior step for the chemical reactions to occur. Therefore, protecting the electrode material with a coating layer, such as carbon, Al_2O_3, ZrO_2, AlF_3, Li_3PO_4, tunnel $Na_{0.44}MnO_2$, olivine phosphates, and spinel phases, could partially impede the chemical and structural evolutions of layered oxides in moist air (Figure 7c). For instance, You et al. reported that a ZrO_2-coating layer can substantially improve the stability of Na-$Ni_{0.7}Mn_{0.15}Co_{0.15}O_2$ against air.[24] Blocking the water-absorption process via coating the layered oxide with a hydrophobic surface layer (Figure 7d), e.g., polyelectrolytes/surfactants of polyaniline, polypyrene, and polypyrrole, might be even more efficient to improve the stability.

Finally, since the air stability is associated with the electrochemical potential of layered oxides, it is possible to suppress the Li^+ (Na^+) loss of layered oxides in moisture by manipulating their chemical compositions, for example, increasing the contribution of high-potential redox couples of $Ni^{2+/4+}$,[60,61] $Cu^{2+/3+}$,[62−64] and oxygen redox reactions[8,59] (Figure 6a). This argument is practically supported by several air-stable sodium layered oxides, such as $Na_{0.78}Cu_{0.27}Zn_{0.06}Mn_{0.67}O_2$,[65] $Na_{0.67}Mg_{0.33}Mn_{0.67}O_2$,[17] and $Na_{2/3}Ni_{1/3−x}Cu_xMn_{2/3}O_2$.[66] The concentration-gradient structure,[67] where the concentration of moisture-sensitive elements
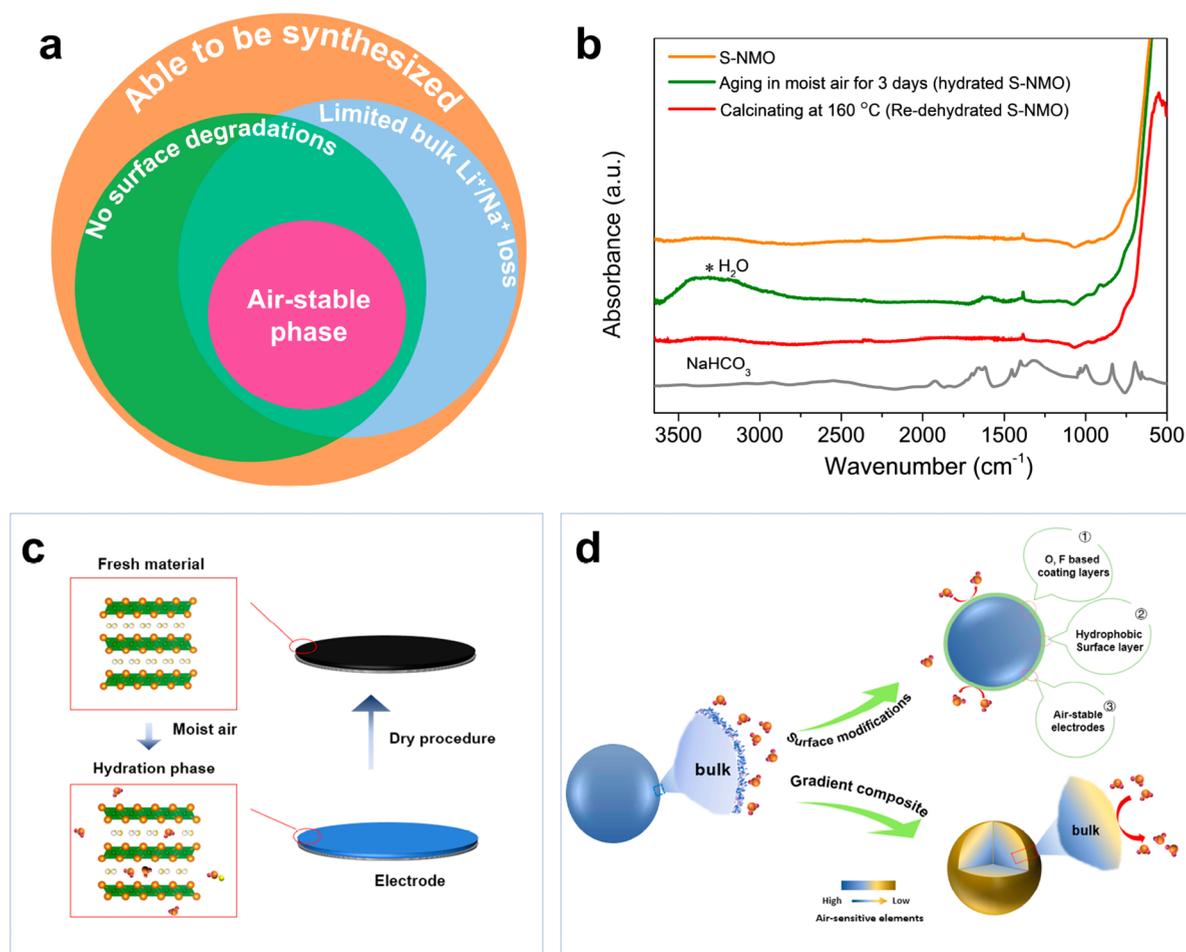
Figure 7. Designing air-stable electrode active materials. (a) Requirements for an air-stability electrode active material. (b) SEM image of S-NMO. [Reproduced with permission from ref 38. Copyright 2021, Nature Publishing Group.] (c) Schematic illustration of moisture-tolerant electrode materials. (d) Schematic illustrations of surface modification and gradient composite strategies.

decreases from the bulk to the surface of the particles, is also promising to provide improved air stability for layered oxides.

In this Perspective, we have summarized the chemical and structural reactions between layered oxide cathode materials and moist air, sorted out the factors determining the degradation, and proposed strategies toward the improvement of their air stability. Benefiting from the recent advances, a thorough understanding of the air stability of layered oxides is reached. Nevertheless, the investigation of this challenging topic is far from being completed. More efforts are urgently needed to unveil the fundamental and technological aspects.

1. Exploring Guidelines for Intrinsic Air-Stable Layered Oxides. In previous work, the initial electrochemical potential was proposed as a practical rule to evaluate the air stability of layered oxides (Figure 6a), with special regard to Li (Na) loss and hydration process.[17] Layered oxides that suffer from severe surface degradation, i.e., those containing significant amount of Ni-, Cu-, and Fe-containing oxides, are also summarized in this Perspective. Diagnosis tools for the detection of moist airborne surface contaminants on layered (Li) oxides have been developed.[17,37] However, the applicability of these empirical guidelines is limited, especially for oxides composed of several different redox couples, such as Na−Ni−Fe−Cu−Mn−O series. Since the moisture sensitivity of layered oxides is determined by the chemical potentials (or energy levels) of the active materials and absorbed species from the atmosphere, theoretical

modeling, such as thermodynamic analysis based on first-principles computation is promising to precisely predict the air stability of layered oxides. With the combination of experimental and theoretical analyses, more-detailed guidelines toward the intrinsic air-stable layered oxides will be uncovered.

2. Competition between $Li^+(Na^+)$-H^+ Exchange and TM Oxidation. As shown in Figure 2a, Li (Na) ions are extracted from the bulk of particles spontaneously when layered oxides are in contact with moist air. The charge of extracted Li (Na) ions is compensated by the insertion of H^+ and/or the oxidation of TM ions.[25,68] The ss-NMR and h-XAS characterizations[17] demonstrated that Na^+-H^+ exchange dominates the charge-compensation mechanisms in ex-$Na_{0.67}MnO_2$ and ex-$Na_{0.67}Ni_{0.33}Mn_{0.67}O_2$. However, many questions are still open, including the sequence of Na^+ (Li^+) extraction and H^+ insertion, the elements involved in the redox process, and to what extent does $Na^+(Li^+)$-H^+ exchange and TM oxidation participate in the reactions. Considering the severe structural changes during exposure and the coverage of various products on the particle surface, normal XAS and XPS might not be so reliable and other state-of-the-art characterizations are highly needed.[69−71]

3. H_2O vs H_3O^+. If the Li^+ (Na^+) content in the bulk of the particle is lower than the critical value (n_c), water molecules insert into the $Li^+(Na^+)$ layers and form hydration phases. This process prevalently occurs in aqueous batteries, aqueous supercapacitors, and ex-Na_xMnO_2 oxides. Inserted water

might exist in the layered structure as either H_2O or H_3O^+ form, strongly influencing both the local structure and the working mechanisms of layered oxides. However, convincing results have been rarely reported.

4. Identifying Balancing Li^+ (Na^+) Content of Layered Oxides in Ambient Atmospheres. When a layered oxide is exposed in a specific moist atmosphere, the remaining Li^+ (Na^+) contents have a tendency to approach a certain value, which is called the *balancing Li^+ (Na^+) content* (n_b) here. This value determines the stoichiometry of the air-stable layered oxides. If the Li^+(Na^+) content in the prepared oxides is higher than n_b, excess Li^+(Na^+) will be extracted from the bulk and form corresponding impurities. Therefore, confirming the n_b values for layered oxides in different ambient atmospheres would be helpful for designing qualified air-stable electrodes.

5. Devising new modification strategies. Normally, the structural and chemical reactions between layered oxides and moisture deteriorate the electrochemical performance of layered oxides. Nevertheless, these reactions can also regulate the structure and boost the electrochemical performance of some specific layered oxides. For example, the insertion of water expands the Li (Na) interlayer spacing in layered oxides. Based on this feature, a "water-mediated strategy" is proposed to regulate the structure of P2-type Mn-based Na_xTMO_2 oxides.[38] The modified materials show improved Na^+ mobility, near-zero-strain property, and outstanding electrochemical performance.[38] Augustyn et al. demonstrated that inserted H_2O molecules in WO_3 lead to the transition from the battery-like behavior of pristine WO_3 to the pseudocapacitive behavior of $WO_3 \cdot H_2O$.[72] Moreover, the Li^+(Na^+)-H^+ exchange can be also utilized to inject protons into the structure and regulate the electrochemical properties of layered oxides. For example, Wu and co-workers[18] demonstrated that the insertion of protons in Li-rich oxides can stabilize the anionic redox reactions during charging and improve their electrochemical performance.

In summary, layered oxide materials matching the requisites for the commercialization of the next generation's rechargeable batteries, i.e., good air stability, good thermal stability, excellent electrochemical performance, cost-effectiveness, and sustainable raw materials, are not available yet. Great efforts are still needed to achieve scientific understandings and enable technological advances on these materials.

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