The stability of P2-layered sodium transition metal oxides in ambient atmospheres

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Air-stability is one of the most important considerations for the practical application of electrode materials in energy-harvesting/storage devices, ranging from solar cells to rechargeable batteries. The promising P2-layered sodium transition metal oxides (P2-NaxTmO2) often suffer from structural/chemical transformations when contacted with moist air. However, these elaborate transitions and the evaluation rules towards air-stable P2-NaxTmO2 have not yet been clearly elucidated. Herein, taking P2-Na0.67MnO2 and P2-Na0.67Ni0.33Mn0.67O2 as key examples, we unveil the comprehensive structural/chemical degradation mechanisms of P2-NaxTmO2 in different ambient atmospheres by using various microscopic/spectroscopic characterizations and first-principle calculations. The extent of bulk structural/chemical transformation of P2-NaTmO2 is determined by the amount of extracted Na+, which is mainly compensated by Na+/H+ exchange. By expanding our study to a series of Mn-based oxides, we reveal that the air-stability of P2-NaTmO2 is highly related to their oxidation features in the first charge process and further propose a practical evaluating rule associated with redox couples for air-stable Na,TmO2 cathodes.
Practical application is always the ultimate goal for state-of-the-art technologies and devices, such as perovskite solar cells, thin-film transistors, and electrochemical batteries. Air-stability is undeniably one of the key issues that researchers should consider, because any air-instable compounds must be prepared, stored and assembled in dry or even inert atmospheres, leading to an increase in expense and can even jeopardize whether they are successfully commercialized.

Sodium ion batteries (SIBs) promise the potential for large-scale grid storage, due to the high abundance and wide distribution of Na sources as compared to their lithium counterparts. Among various sodium storage cathodes, layered sodium transition metal oxides (NaₓTmO₂) have gained significant attention owing to their great variety of compositions, ease of scalable preparation and high reversible specific capacity. In the past forty years, the NaₓTmO₂ family has been greatly enriched not only thanks to the tremendous efforts toward superior cathodes with higher energy density and more stable superstructures, but has also benefited from the development of electrolytes and characterization techniques. Nonetheless, NaₓTmO₂ electrodes are still haunted by three major challenges, i.e. irreversible phase transitions during cycling, insufficient electrochemical performances and air/moisture instability.

The undesired structural transformations in charge/discharge processes, such as P2-O2 in Na₀.₆₇MnO₂, P2-P2’ in Na₀.₆₅MnO₂ and O3-P3 in Na₀.₆₅₂MnO₂, can be suppressed or delayed by element substitution, thus resulting in improved cycling stability and rate capability. The contact between air-instable NaₓTmO₂ and moisture-air usually produces cracks, electrical insulation species, and hydration phases, which result in a shorter lifetime and poorer rate capability of the exposed layered oxides. Therefore, air-stability is considered an important factor to evaluate a qualified NaₓTmO₂ electrode.

Recently, Manthiram’s group reported that O₃-Na₀.₆₇MnO₂, which reacts with H₂O and CO₂, generating NaOH, Na₂CO₃, Na₂CO₃·H₂O and NiO on the particle surfaces and leading to declined electrochemical performances. However, these degradation (Ni loss) reactions have not yet been extensively observed in Ni-poor/Ni-free NaₓMnO₂ materials, whether exposed to air or immersed in water. Unlike degradation, H₂O insertion is widely encountered in P2-NaₓTmO₂ electrodes and can be easily distinguished by X-ray diffraction (XRD), because the intercalation of H₂O expands the interlayer distance of the Na⁺ layers from ~5 to ~7 Å and even up to ~9 Å.

Kubota et al. proposed the Na⁺/H⁺ exchange mechanisms in O3-type NaₓMeO₂ oxides and Rojo’s group further identified the presence of H⁺ in the Na⁺ layers using a neutron powder diffraction technique. In addition, in the presence of H₂O, CO₂ was believed to get inserted into the transition metal layers of P2-Na₂/₃Fe₀.₃Mn₀.₃O₂. These works provide valuable insights into the structural evolutions of NaₓTmO₂ upon air-exposure. However, rational connections between these intertwined reactions, especially as to why and when the water molecules insert into the Na⁺ layers, and which factor determines the extent of the structural transformation have not been thoroughly studied yet.

Fundamental understanding of structural/chemical evolutions in moisture is not only critical for the employment of NaₓTmO₂ as electrodes in both organic and aqueous SIBs, but also provides guidance to the fabrication and application of layered transition metal oxides in other battery systems, such as the favorable Ni-rich cathodes for lithium ion batteries. For layered sodium-based oxides, it is widely recognized that the air-instability in P2-type oxides is much more severe than that in O3-type NaₓMnO₂. Herein, based on the P2-Na₀.₆₀MnO₂ and P2-Na₀.₆₇Na₀.₃₃Mn₀.₆₇O₂ oxides, we unearth the underlying science that triggers the hydration of P2-NaₓTmO₂ and outline the structural and chemical evolution mechanisms of P₂-NaₓTmO₂ oxides upon air exposure.

Importantly, the surface-sensitive time-of-flight secondary ion mass spectroscopy (TOF-SIMS) results reveal that the CO₂ cannot insert into the layered structure. Our results indicate that Na⁺/H⁺ exchange, rather than O₂ oxidation, dominates the compensation of extracted Na⁺ and the hydration is closely related to the contents of remaining Na⁺ ions in the structure. The critical sodium content is therefore proposed to evaluate whether H₂O is able to intercalate into the sodium layers. In addition, the study of a series of P₂-NaₓTmO₂ oxides indicates that the air-stability is closely associated with the voltage features of the charge process in the first cycle, and a practical principle related to the redox couple in the 1st cycle is thus proposed to evaluate the air-stability of NaₓTmO₂. These new insights into the degradation mechanisms upon air-exposure will facilitate the development of practical layered Li/Na/K transition metal oxides.

Results
Features of hydration phases. To investigate the air-stable mechanisms, the structures and characterizations of hydration phases should be clarified first. The Na₀.₆₇MnO₂ sample attained by solid-state reaction exhibits a typical P2 structure (space group: P6₃/mmc) with a layer spacing of ~5.5 Å (Fig. 1), according to the powder X-ray diffraction (XRD) patterns in Supplementary Fig. 1a. The commonly reported hydration impurity phase in the NaₓTmO₂ is bixenite, whose structure is very similar to that of P₂-Na₀.₆₇MnO₂, except the presence of extra water molecules in the sodium layers and a broader interlayer distance.
of ~7.1 Å. With further H2O insertion, the buserite phase with layer spacing of ~9.1 Å can be identified (Fig. 1 and Supplementary Fig. 1a). In addition to the difference in the interlayer spacing, the birnessite and buserite phases possess a different pattern of Na+ and H2O arrangements in the sodium layers. For birnessite ([Na0.30(H2O)0.43]MnO2), according to the Rietveld refinement results44 (Supplementary Table 1 and Fig. 1b) and the neutron powder diffraction patterns (NPD)45, the O ion of inserted H2O molecule locates at the same site of Na+; while for the highly hydrated buserite ([Na0.24(H2O)2]MnO2), the Na+ ions are sandwiched by the inserted H2O molecules46,47, as illustrated schematically in Fig. 1. Since buserite is seldom encountered in the moisture-exposed Na3TiO2, the hydration phase discussed below is referred to birnessite phase unless otherwise specified. It should be further pointed out that the Na+ content in hydrated Na0.67TiO2 sample is <0.67 due to the Na+ loss upon air-exposure, as shown in the following sections. XRD, NPD and 23Na-magic-angle-spinning nuclear magnetic resonance spectroscopy (MAS NMR, Supplementary Figs. 1–3 and Note 1) are three powerful techniques to identify the hydration impurities (birnessite) in Na3TiO2 oxides, by characterizing the structural transitions, i.e. increased interlayer spacings. Fourier-transform infrared spectroscopy (FTIR) and 23Na{1H} rotational-echo double-resonance (REDOR)48 can be used to detect the existence of water molecules and protons in the Na3TiO2 compounds, respectively (Supplementary Fig. 4 and Notes 1, and 2).

The structural transitions of the moisture-exposed P2-Na0.67TiO2. To investigate the structural changes of P2-Na0.67TiO2 during the air-exposure, Na0.67TiO2 and Na0.67Ni0.33Mn0.67O2 were selected as model compounds for air-rollable and air-stable electrodes, respectively27, to be exposed in different atmospheres of dry CO2, relative humidity (RH) 18% (without CO2), RH 15% and RH 93% for 3 days (“Methods” part). As shown in the XRD patterns (Fig. 2a, b) and inductively coupled plasma-atomic emission spectrometry (ICP-AES) results (Supplementary Table 2), the targeted materials were successfully prepared. It can be observed that all XRD peaks of Na0.67MnO2 remain unchanged when placed in the dry CO2 atmosphere (Fig. 2a), revealing that water is an inevitable component to destabilize Na0.67TiO2. At the atmospheres of RH 18% and RH 15% + CO2, the hydration peaks (labeled with z) emerge and their intensities increase with the presence of CO2. With further increase in the relative humidity (RH 93% + CO2), all of the XRD peaks can be indexed to the hydration phase and NaHCO3 labeled with V), indicating that the Na0.67MnO2 is totally hydrated and partial Na+ diffuses out from the sodium layers. For Na0.67Ni0.33Mn0.67O2, no obvious hydration peaks can be identified in all of the exposed samples (Fig. 2b), suggesting Na0.67Ni0.33Mn0.67O2 is more stable than Na0.67MnO2 in moist atmosphere. To quantify the hydration extent of the exposed samples, Rietveld refinements on the XRD patterns were conducted with a two-phase model and the results are shown in Fig. 2c. The mass ratios of hydrated phases in the exposed Na0.67MnO2 samples are 0%, 42%, 58%, and 100% at the atmosphere of dry CO2, RH 18%, RH 15% + CO2, and RH 93% + CO2, respectively, revealing that P2-Na0.67MnO2 components are more vulnerable to H2O with both the existence of CO2 and the increment of relative humidity. Figure 2d–i depicts the morphological change of Na0.67MnO2 and Na0.67Ni0.33Mn0.67O2 powder after the exposure to the atmosphere of RH 93% + CO2 for 3 days. Scanning electron microscopy (SEM) images in Fig. 2d, g show that the surface of as-prepared Na0.67MnO2 and Na0.67Ni0.33Mn0.67O2 particles are clean and smooth. After exposure, severe delamination damages and a massive of intragranular cracks can be observed in hydrated Na0.67MnO2 sample (Fig. 2e), as a result of the significant volume expansion of ~30% during the hydration process. Besides structural changes, NaHCO3 particles are found on the surface of hydrated Na0.67MnO2, as shown in the energy dispersive X-ray spectroscopy (EDS) elemental mapping results (Fig. 2f). Moreover, the crystals with very regular morphologies can be observed in the exposed-Na0.67MnO2 powder (Supplementary Fig. 5a, b), which should be unambiguously identified to NaHCO3 according to the FTIR (Supplementary Fig. 4a) and EDS mapping results in Supplementary Fig. 5c. The formation of sodium salt is also observed in the air-exposed electrodes. As shown in Supplementary Fig. 6, sodium bicarbonate particles with nanoflakes morphology appear at the surface of the active materials. For exposed-Na0.67Ni0.33Mn0.67O2 sample, as shown in Fig. 2h, a rough surface is formed and there is no evidence of crack and layer glide, indicating that the morphological change of Na0.67Ni0.33Mn0.67O2 during exposure is more moderate than the Na0.67MnO2 sample (Fig. 2e). However, the EDS mapping results in Fig. 2i reveal that the NaHCO3 particles are formed on the surface of exposed-Na0.67Ni0.33Mn0.67O2, indicating the Na+ loss in the Na0.67MnO2 compound during exposure.

**The role of CO2.** The presence of CO2 makes a big difference in the structural transformations of P2-Na3TiO2 upon moisture-exposure (Fig. 2c). To characterize the functionality of CO2, we applied the TOF-SIMS to ascertain whether CO2 intercalates into the bulk of the P2-Na3TiO2 during hydration. In order to eliminate the influence of the surficial sodium bicarbonate species (Fig. 2f and Supplementary Fig. 4), we adopted a scavenging process (see details in the Methods section). The FTIR spectra in Fig. 3a reveal that NaHCO3 in the hydrated Na0.67MnO2 sample is successfully removed. TOF-SIMS depth profiles acquired on the scavenged powder show that the H2O (OH−) and Mn ions (MnO2− and MnO2−) appear at both surface and bulk of the powder (Fig. 3b), in good agreement with our refinement results (Supplementary Table 1). The signal intensity of C2H5OH− in the bulk (~165 a.u., Supplementary Fig. 9 and Note 4) is only 2.5% compared to that of the prevailed OH− (65k a.u.). Considering that the water content in hydrated Na0.67MnO2 is ~0.45 mol per chemical formula unit (Supplementary Table 1), it is therefore reasonable to conclude that the C atoms in the bulk of the hydrated samples are negligible. Furthermore, the cross-sectional TOF-SIMS chemical mapping images of the tested secondary particles (Fig. 3c) show that the intensity of C-related species (e.g. C3H7O−, NaC2O−, C−) is much lower than OH− and Mn-based ions and the remaining carbonate trace is mainly distributed on the surface rather than the bulk of the particles. This fact coincides well with the depth profile results in Fig. 3b and Supplementary Fig. 9. Therefore, the function of CO2 is to increase the acidity at the particle’s surface.
and accelerate the Na⁺ loss rather than insert into the bulk of the Naₐ₋ₓTmO₂ phases.

The critical sodium contents (nₐ) for hydration. Although Na₀.₆₇Ni₀.₃₃Mn₀.₆₇O₂ has been reported to be one of the most air-stable P₂-NaₓTmO₂ oxides, the chemical change is observed in the EDS mapping as demonstrated in Fig. 2i. Furthermore, as shown in Fig. 4a, with longer exposure time, the intensity of the NaHCO₃ diffraction peaks increases while the (002) diffraction peak shifts to lower 2θ (Supplementary Fig. 10). It is worth noting that the intensity of ²³Na{¹H} REDOR signal for the exposed Na₀.₆₇Ni₀.₃₃Mn₀.₆₇O₂ sample decreases with ¹H irradiation as a function of the spin-echo time, as compared to that without ¹H irradiation. This result confirms that H⁺ ions are in close proximity to the sodium atoms in the structure of the exposed Na₀.₆₇Ni₀.₃₃Mn₀.₆₇O₂ sample. Thus, it is more likely that the H ions replace those lost Na⁺, indicative of the Na⁺/H⁺ exchange mechanism. Moreover, given that the exposed electrodes usually exhibit improved open circuit potential, another charge compensation mechanism, i.e. the oxidation of transition metal ions by O₂ has been also proposed. To validate which mechanism dominates the Na⁺ loss process, X-ray absorption spectroscopy (XAS) was carried out. According to the previous results, during the first charge process of Na₀.₆₇Ni₀.₃₃Mn₀.₆₇O₂ electrode within 2.0–4.4 V (vs. Na⁺/Na), Mn⁴⁺ ions remain stable and the oxidation/reduction of Ni ions compensates the electrochemical extraction/insertion of Na⁺. As shown in Supplementary Fig. 13a, both position and shape of the Ni K-edge remain unchanged, indicating that the valence state of Ni ions in the exposed Na₀.₆₇Ni₀.₃₃Mn₀.₆₇O₂ is nearly the same as in the pristine sample. The valence state of Mn ions in pristine and hydrated Na₀.₆₇MnO₂ samples has been also investigated by XAS. The pre-edge peak and main edge of Mn K-edge XAS
Fig. 3 TOF-SIMS results of the hydrated Na0.67MnO2 sample. a The comparison of FTIR spectra of the hydrated Na0.67MnO2 and hydrated Na0.67MnO2 after the scavenging process, indicating that after scavenging, most of the sodium (bi)carbonate impurities was removed. b TOP-SIMS spectra of OH–, MnO2–, MnO–, and C2HO– secondary ion fragments over 500 s Cs+ sputtering along the depth profile of the sample after scavenging processes. c TOF-SIMS chemical mapping of the hydrated Na0.67MnO2 after the scavenging process, showing the distribution of OH–, MnO2–, MnO–, C2HO–, NaC2O2–, and C– secondary ions.

Fig. 4 The structural and chemical evolution mechanisms upon air-exposure. a The XRD evolutions of Na0.67Ni0.33Mn0.67O2 powder exposed at RH 93% + CO2 atmosphere for different times (MgO was used as internal indicator). b 23Na{1H} REDOR-dephased 23Na MAS NMR spectra (MAS rate: 25 kHz) and c The XRD patterns of exposed NaxNi0.33Mn0.67O2 electrodes with various Na+ content x. d The FTIR spectra of Na0.67MnO2 samples with various hydration degrees. e The structure model of single layer Na+ loss structure for calculating hydration energies. f The calculated hydration energies for Na0.67MnO2 at various sodium contents x.
correspond to $1s \rightarrow 3d$ and $1s \rightarrow 4p$ transitions, respectively. However, the structural changes during hydration (Supplementary Fig. 13b) severely complicate the chemical shift of the main edge such that it becomes difficult to determine the valence state of Mn ions. Thus the pre-edge region could provide more reliable valent-state information[50]. As can be seen from Supplementary Fig. 13b, the splitting and intensity of pre-edge peaks of Mn ions are similar for all of the pristine, partially hydrated and totally hydrated samples, indicating that the changes of the valence state of Mn ions are negligible during hydration. The XAS results suggest that Na$^{+}$/H$^+$ exchange might be the main reaction that compensates for the extracted Na$^+$ in the moisture-exposed Na$_0$Tm$_0$O$_2$. To confirm this conclusion, we stored the Na$_0$Tm$_0$O$_2$ sample in three different atmospheres for 3 days, e.g. O$_2$, RH 93% + CO$_2$ with the presence of O$_2$, and RH 93% + CO$_2$ without O$_2$. The XRD patterns in Fig. 2a and Supplementary Fig. 13c suggest that O$_2$ makes smaller difference than both CO$_2$ and water to the structural changes of Na$_0$Tm$_0$O$_2$.

To gain deeper insight into the structural/chemical transformation mechanisms of P2-Na$_x$TmO$_2$ materials upon air-exposure, a series of Na$_0$Ni$_{0.33}$Mn$_{0.67}$O$_2$ electrodes with different Na$^+$ contents were prepared by extracting Na$^+$ electrochemically, and then exposed at RH 93% + CO$_2$ atmosphere for 3 days. As shown in Fig. 4c, the hydration phase is absent at Na$_0$Ni$_{0.33}$Mn$_{0.67}$O$_2$ electrodes within sodium contents of 0.67 ≤ $x$ ≤ 0.44. In $x$ = 0.38, the diffraction peaks of the hydration phase appear and its intensity increases with the further decrease of Na$^+$ contents. This result implies that hydration highly depend on the Na$^+$ contents. Specifically, if the sodium content $x$ is lower than a critical sodium content $n_c$ (0.38–0.44 for Na$_0$Ni$_{0.33}$Mn$_{0.67}$O$_2$ electrode), P2-Na$_x$TmO$_2$ materials are vulnerable for hydration and vice versa. The correlation between hydration degree and sodium contents $x$ is also observed in Na$_0$Mn$_{0.67}$O$_2$ compounds. As representatively shown in Fig. 4d, the intensity of NaHCO$_3$ absorption peaks are positively associated with the hydration degrees of Na$_0$Ni$_{0.33}$Mn$_{0.67}$O$_2$ sample.

The density function theory (DFT) calculation was carried out to further understand the critical sodium content $n_c$. As shown in Fig. 4e and Supplementary Fig. 13d, two different sodium extraction models of single layer and double layer were considered, which correspond to the staging and random sodium extraction mechanisms, respectively[15]. The energy difference between P2-Na$_x$TmO$_2$ with and without water molecules is defined as hydration energy. DFT calculation results in Fig. 4f show that when $x > 0.52$, the hydration energy of Na$_0$Mn$_{0.67}$O$_2$ is higher than 0 eV, suggesting that water molecules cannot get inserted into the material. When the sodium content is lower than 0.52, the hydration energy is lower than 0 eV, thus the hydrated structure is more stable than the un-hydrated structure. The foregoing energy analysis provides a chemical basis for understanding the sodium-content-dependent property in the hydration of Na$_0$Mn$_{0.67}$O$_2$ samples.

In the atmosphere without CO$_2$:  
\[ x \cdot H_2O + Na_{0.67}^+ Tm_{0.33}^{2+} = Na_{0.67}^+ Tm_{0.33}^{2+} + x \cdot NaOH \]  
In the atmosphere with scarce CO$_2$:  
\[ x \cdot CO_2 + x \cdot H_2O + 2 \cdot Na_{0.67}^+ Tm_{0.33}^{2+} = 2 \cdot Na_{0.67}^+ Tm_{0.33}^{2+} + x \cdot Na_2CO_3 \]  
In the atmosphere with abundant CO$_2$:  
\[ x \cdot CO_2 + x \cdot H_2O + Na_{0.67}^+ Tm_{0.33}^{2+} = Na_{0.67}^+ Tm_{0.33}^{2+} + x \cdot NaHCO_3 \]  

The influence of structural changes on the electrochemical performances of P2-Na$_x$TmO$_2$.

In this section, we carefully investigate the influences of the above structural and chemical changes on the electrochemical performances of Na$_0$Tm$_0$O$_2$ and Na$_0$Ni$_{0.33}$Mn$_{0.67}$O$_2$ electrodes. As shown in Fig. 5a, the pristine Na$_0$Tm$_0$O$_2$ shows a high initial discharge capacity of 176 mAh g$^{-1}$ at the current density of 12 mA g$^{-1}$ within 2.0–4.4 V. After 50 cycles, 66% of the initial capacity was retained, which coincides well with the previous results[10,23]. For the hydrated Na$_0$Tm$_0$O$_2$ electrode, the reversible capacity is negligible at the initial cycles. In the 9th cycle, although the discharge capacity increased to ~150 mA h g$^{-1}$, abnormal electrochemistry, such as long charging plateaus, large voltage hysteresis and low coulombic efficiency are also observed. These deviant electrochemical performances indicate that the large amount of H$_2$O in the hydrated electrode has a pernicious influence on the organic-electrolyte based batteries.

The electrochemical performances of pristine Na$_0$Ni$_{0.33}$Mn$_{0.67}$O$_2$, Na$_0$Ni$_{0.33}$Mn$_{0.67}$O$_2$ exposed in RH 93% + CO$_2$ for 3 days (denoted as exposed-Na$_0$Ni$_{0.33}$Mn$_{0.67}$O$_2$), and Na$_0$Ni$_{0.33}$Mn$_{0.67}$O$_2$ immersed in water for 20 days (denoted as immersed-Na$_0$Ni$_{0.33}$Mn$_{0.67}$O$_2$) are presented in Fig. 5c–f. As shown in Fig. 5c, the pristine Na$_0$Ni$_{0.33}$Mn$_{0.67}$O$_2$ exhibited much lower coulombic efficiency than the pristine Na$_0$Ni$_{0.33}$Mn$_{0.67}$O$_2$ samples have very similar initial charge-discharge curves, suggesting that their structure and redox center are nearly identical[8]. However, the initial charge capacities of the exposed-Na$_0$Ni$_{0.33}$Mn$_{0.67}$O$_2$ (70 mA h g$^{-1}$) and immersed-Na$_0$Ni$_{0.33}$Mn$_{0.67}$O$_2$ (77 mA h g$^{-1}$) are lower than that of the pristine Na$_0$Ni$_{0.33}$Mn$_{0.67}$O$_2$ (85 mA h g$^{-1}$), further confirming the loss of Na$^+$ ions during the exposure and immersing processes. Fig. 5d compares the cycling stability of the three electrodes. It can be observed that the exposed-Na$_0$Ni$_{0.33}$Mn$_{0.67}$O$_2$ exhibits much lower coulombic efficiency than the pristine Na$_0$Ni$_{0.33}$Mn$_{0.67}$O$_2$ due to the influence of the sodium bicarbonate on the surface of exposed-Na$_0$Ni$_{0.33}$Mn$_{0.67}$O$_2$ particles. At the voltage range of 2.0–4.0 V, the pristine Na$_0$Ni$_{0.33}$Mn$_{0.67}$O$_2$ material shows no evidence of capacity degradation after 100 cycles. In contrast, the immersed-Na$_0$Ni$_{0.33}$Mn$_{0.67}$O$_2$ and exposed-Na$_0$Ni$_{0.33}$Mn$_{0.67}$O$_2$ samples decay fast in capacity, and retain low discharge capacity of 56 and 53 mA h g$^{-1}$, corresponding to the capacity retention of 74% and 70%, respectively. To get more insight
Na0.67Ni0.33Mn0.67O2 samples immersed in water for 20 days and exposed in RH 93%. The inset shows the charge-discharge curve at the 2nd cycle. d and 100th cycles with frequency varied from 100 kHz to 10 mHz.

The electrochemical performances of air-exposed Na0.67MnO2 and Na0.67Ni0.33Mn0.67O2. a The cycling performance of pristine Na0.67MnO2; the inset shows the charge-discharge curve at the 2nd cycle. b The charge-discharge curves and cycling stability of totally hydrated Na0.67MnO2 sample. c-f The electrochemical performances within the voltage range of 2.0–4.4 V of three Na0.67Ni0.33Mn0.67O2 samples (pristine Na0.67Ni0.33Mn0.67O2, Na0.67Ni0.33Mn0.67O2 samples immersed in water for 20 days and exposed in RH 93% + CO2 for 3 days). e The initial charge-discharge curves at 12 mA g⁻¹. d The cycling stability of the three samples at 120 mA g⁻¹ (after two formation cycles at 12 mA g⁻¹). e The comparison of the impedance responses at the 1st and 100th cycles with frequency varied from 100 kHz to 10 mHz. f The rate capability of three samples at the voltage range of 2.0–4.0 V.

The structural transformation of hydrated phases upon calculation in air. We have concluded that the sodium extraction (mainly compensated by Na⁺/H⁺ exchange) and H₂O insertion are two continuous similar transition processes during the exposure of P2-NaxTmO₂ samples, which usually impair their intrinsic electrochemical performances. The following questions need to be clarified: (i) whether or not these exposed samples can be recovered to their original structure and how, and (ii) what is the stoichiometry of hydrated phases (birnessite)? Therefore, in this section, the structural transitions of hydrated samples at the temperature range of 25–130 °C were investigated by in situ variable-temperature XRD technique. As shown in Fig. 6, five different stages can be observed in the in situ variable-temperature XRD pattern of the hydrated Na₀.₆₇MnO₂. The mass loss at stage a (25–130 °C) is ≈15.1%, which includes decomposition of NaHCO₃ and extraction of water. At this stage, the hydration structure is well maintained. From stage a to stage b, the hydrated phase is most probably transformed into a protonated phase (Supplementary Fig. 15 and Note 5) by two-phase reaction mechanisms at ~130 °C. The crystallinity of the Na₀.₆₇-x,MnO₂ phase at stage c (217–297 °C) is much lower than stage b, which might be resulted from the loss of protons. In addition, the sodium carbonate begins to decompose and results in the mass loss in stage c. With further increase in temperature, the crystallinity of Na₀.₆₇-x,MnO₂ increases, as shown in stage d. It should be pointed out that the decomposition temperature of Na₂CO₃ is lower than 800 °C due to the small sizes of the Na₂CO₃ particles (Fig. 2 and Supplementary Fig. 5) and the catalytic effect of transition metal oxides on reducing the energy requirement of Na₂CO₃ decomposition. When the temperature is higher than 483 °C, the (100) and (103) peaks (at ~35° and ~43°, respectively) of the P2 phase emerge gradually, indicating the P2-Na₀.₆₇MnO₂ phase gradually recovers at stage c. However, the mass loss of 0.45% during 130–217 °C corresponds to x = 0.61 in Na₀.₆₇-x,HₓMnO₂, exceeding the amount of lost Na⁺ ions (x + z = 0.39, Supplementary Table 4), suggesting that the decomposition of Na₂CO₃ begins at stage b (130–217 °C). In conclusion, with the increase of temperature, the hydrated Na₀.₆₇MnO₂ sample undergoes dehydration and NaHCO₃ decomposition (70–130 °C), deprotonation (130–217 °C), Na₂CO₃ decomposition (>130 °C) and the recrystallization of P2 phase (>483 °C) process. In our recent work, we demonstrate that Na₀.₆₇Zn₀.₁Mn₀.₆₇O₂ is a promising Na-ion battery cathode with outstanding cycling stability and better air-stability than Na₀.₆₇MnO₂. Therefore, we also performed the in situ variable-temperature XRD of totally hydrated Na₀.₆₇Zn₀.₁Mn₀.₇O₂ powder. Obviously, the structural transformation of the hydrated Na₀.₆₇Zn₀.₁Mn₀.₇O₂ in Supplementary Fig. 16 is different from that of the hydrated Na₀.₆₇MnO₂. From the hydration phase

Fig. 5 Electrochemical performances of air-exposed Na₀.₆₇MnO₂ and Na₀.₆₇Ni₀.₃₃Mn₀.₆₇O₂. a The cycling performance of pristine Na₀.₆₇MnO₂; the inset shows the charge-discharge curve at the 2nd cycle. b The charge-discharge curves and cycling stability of totally hydrated Na₀.₆₇MnO₂ sample. c-f The electrochemical performances within the voltage range of 2.0–4.0 V of three Na₀.₆₇Ni₀.₃₃Mn₀.₆₇O₂ samples (pristine Na₀.₆₇Ni₀.₃₃Mn₀.₆₇O₂, Na₀.₆₇Ni₀.₃₃Mn₀.₆₇O₂ samples immersed in water for 20 days and exposed in RH 93% + CO₂ for 3 days). e The initial charge-discharge curves at 12 mA g⁻¹. d The cycling stability of the three samples at 120 mA g⁻¹ (after two formation cycles at 12 mA g⁻¹). e The comparison of the impedance responses at the 1st and 100th cycles with frequency varied from 100 kHz to 10 mHz. f The rate capability of three samples at the voltage range of 2.0–4.0 V.
the left. Hydrated and P2 phases are labeled with “□” and “●”, respectively. (stage a) to the protonated phase (stage b), the combined mechanism of two-phase and solid-solution reactions can be recognized. Moreover, the temperature range of deprotonation of the hydrated Na0.67Zn1/9Mn2/3O2 sample is elusive and the temperature of the recrystallization of P2-type Na0.67Zn0.1 Mn0.9O2 phase (376 °C) is lower than that of Na0.67MnO2 (483 °C). The above results indicate that if the Na0.67TmO2 samples undergo sodium-loss and further hydration processes upon air-exposure, high-temperature annealing can be used to recover their original structures (the results of verification test are shown in Supplementary Fig. 17 and Note 6). Although the comprehensive structural/chemical evolution mechanisms during annealing are highly dependent on the stoichiometry of the exposed materials.

| Temperature (°C) | Mass Percentage (%) |
|-----------------|---------------------|
| 25–130          | Low                 |
| 150–220         | Low                 |
| 220–297         | High                |
| 297–483         | Low                 |
| 570             | Low                 |

The temperature ranges from 25 to 570 °C. The TGA curves are shown at the right. The temperature ranges from 25 to 570 °C. The TGA curves are shown at the right. Hydrated and P2 phases are labeled with “□” and “●”, respectively. The comprehensive structural/chemical evolution mechanisms upon air-exposure. Based on our analysis above, we summarize the structural and chemical transitions of the P2-Na0.67MnO2 components upon air exposure in Fig. 7a. At the initial stage, because of the low formation energy of layered Na0.67TmO2 oxides, the sodium ions are lost from the bulk and form amorphous Na2CO3/NaHCO3 layer on the surface of particles or even Na2CO3/NaHCO3 crystals with charge-compensation mechanism of Na+/-H+ exchange. The formation energy increases with the extraction of Na+ ions and finally the P2-Na0.67TmO2 oxides are stable at the sodium content of 0.67-x-z in a specific environment. If the remaining sodium content 0.67-x-z is lower than the critical sodium content n, the water molecules go into the sodium layers and form the hydration phases. Considering the full decomposition of generated sodium salts and the recrystallization of the degraded structures, once the Na0.67TmO2 is protonated or hydrated, high-temperature calcination is needed to recover the hydrated forms back to the original structure. In addition to the above structural transitions, the outer layer of Na0.67TmO2 particles decomposes into transition-metal oxides/hydroxides when exposed to air or immersed in water. As shown in Supplementary Fig. 20, after exposing Na0.67Cu0.33Mn0.67O2 at RH 93% + CO2 for 6 days, the Cu2O and NaHCO3 impurities can be observed in the XRD pattern, indicating that degradation is more or less an inevitable process at the surface of exposed Na0.67TmO2 compounds. Manthiram’s group also reported that the Ni-rich layered sodium oxide transforms into NiO and Na2CO3 in the surface26. In brief, the structural and chemical transitions coexist, rather than a single protonation/Tm-oxidation, hydration, and degradation mechanism.

Evaluating the air-stability of Na0.67TmO2 electrodes. The choice and evaluation of air-stable Na0.67TmO2 electrodes have attracted enormous attention. It has been widely accepted that the Ni/Mn superlattice prevents the intercalation of H2O since P2-Na0.67Ni0.33Mn0.67O2 was found to be resistant to hydration in moist air27. However, our results demonstrate that Na0.67Ni0.33Mn0.67O2 is not as stable in moist air as it was expected, while other reported air-stable electrodes, such as Na0.78Cu0.27Zn0.06Mn0.67O2,28 Na0.67Ni0.22Cu0.11Ti0.11Mn0.56O2,29 Na0.79Cu0.29Fe0.19Mn2/3O230 do not have superlattice ordering in Tm layers. Therefore, the crucial factors, as well as the evaluation principles related to the air-stability of Na0.67TmO2 electrodes, have yet to be re-explored.

Therefore, we compared the air-stability of five layered oxides with different Mn valence-state and redox potential, e.g. Na0.67MnO2, Na0.67Al1/9Mn9/9O2, Na0.67Cu0.1Mn0.9O2, Na0.67Zn0.1Mn0.9O2, and Na0.67Ni0.33Mn0.66O2, at the atmosphere of dry CO2, RH 18%, RH 15% + CO2, and RH 93% + CO2. The XRD patterns and ICP-AES results of these pristine oxides are presented in Supplementary Fig. 21 and Table 5, respectively. In addition, the XRD patterns and the corresponding quantification of the hydration extents of the exposed samples are shown in Supplementary Fig. 22. According to the refinement results in Supplementary Fig. 22e, it is confirmed once again that more structural and chemical changes of Na0.67TmO2 occur with the increase of relative humidity and the presence of CO2. Moreover, it can be clearly observed.
that the air-stability of these investigated layered oxides follows the order of Na$_{0.67}$Ni$_{0.33}$Mn$_{0.67}$O$_2$ > Na$_{0.67}$Zn$_{0.17}$Co$_{0.33}$Mn$_{0.5}$O$_2$ > Na$_{0.67}$Mn$_2$O$_3$. As shown in Supplementary Fig. 24, although the valence state of Mn ions or the redox potential of the initial charge process (Supplementary Fig. 23). To confirm this hypothesis, several electrodes were prepared and exposed to the atmosphere of RH 93% + CO$_2$. As shown in Supplementary Fig. 24, although the valence state of Mn ions in Na$_{0.67}$Co$_{0.33}$Mn$_{0.67}$O$_2$ exhibits the main voltage plateaus.

**Discussion**

In summary, a comprehensive investigation of the structural and chemical transformations of P2-Na$_{0.67}$Mn$_2$O$_3$ in different ambient atmospheres has been carried out. Using advanced technique characterizations and systematic investigation, we clarified and rationalized these intertwined reaction processes and their determining factors. For example, the critical roles of relative humidity and CO$_2$ in the air-stability of P2-Na$_{0.67}$Mn$_2$O$_3$, the extraction of Na$^+$ ions from Na$_{0.67}$Ni$_{0.33}$Mn$_{0.67}$O$_2$ when exposed to moist air or emerged in water, the influence of
moisture-exposure on the electrochemical performances of Na$_x$TmO$_2$, the precise quantification of water contents in hydrated phases, and the significance of crystallinity on the air-stability of Na$_x$TmO$_2$, etc. Furthermore, based on the detailed mechanisms, including the Na extraction at the initial stage of moisture-exposure, the dominate Na$^+/H^+$ exchange charge-compensation mechanism, and the critical sodium content ($n_\text{i}$), we proposed a general and in-depth picture on the chemical/structural evolutions of P2-Na$_2$TmO$_2$ during moisture-exposure. In addition, by extending the study to a variety of layered sodium-based oxides (Na$_{0.6}$/M$_2$Mn$_1$O$_3$, with M = Ni, Zn, Fe, Al, Co, Li, Mg, Cu, etc.) we have also demonstrated that the redox potential properties in the first charge process could be used as an empirical rule for evaluating the air-stability of Na$_x$TmO$_2$ electrodes. Our results provide significant new clues for the design, synthesis, storage, and application of layered sodium cathodes, as well as other alkali-metal transition metal oxides.

Methods

Preparation of layered materials. The pristine Na$_x$TmO$_2$ cathodes have been synthesized by high-temperature solid-state reactions. Stoichiometric amounts of raw materials, e.g. MnO$_x$ (99.95%, Aladdin), ZnO (99.90%, Aladdin), NiO (99.99%, Aladdin), A$_3$O$_5$ (99.99%, Aladdin), TiO$_x$ (99.9%, Aladdin), CuO (99.9%, Aladdin), Li$_2$CO$_3$ (99.99%, Aladdin), and Na$_2$CO$_3$ (99.99%, Aladdin) were ball-milled with acetone solvent for 3.5 h at 500 rpm. Then dried at 120 °C overnight, pressed into pellets and heated at 900 °C for 15 h in air. After slowly cooled to 150 °C in the furnace, the pellets were transferred to an Ar-filled glove box immediately, ground and kept the final products in the Ar-filled glove box.

Hydration tests. The saturated salt solutions could produce stable relative humidity in a closed system at a certain temperature. To study the effect of different ambient atmospheres on the structural and chemical stability of Na$_x$TmO$_2$, the prepared Na$_x$TmO$_2$ powders are put in a centrifuge tube and then aged on an air tight container under different storage conditions at the constant temperature of 40 °C. They are dry CO$_2$, controlled humidity of RH 18% (without CO$_2$), RH 15% with CO$_2$, RH 9% with CO$_2$, dry CO$_2$, controlled humidity of RH 18% (with CO$_2$), RH 15% with CO$_2$, RH 9% with CO$_2$, dry CO$_2$, controlled humidity of RH 18% (without CO$_2$) atmosphere. To maintain the humidity conditions of dry CO$_2$, RH 15% with CO$_2$, RH 9% with CO$_2$, dry CO$_2$, controlled humidity of RH 18% (with CO$_2$), RH 15% with CO$_2$, RH 9% with CO$_2$, dry CO$_2$, controlled humidity of RH 18% (without CO$_2$) atmosphere, water saturation is achieved by placing the saturated NaOH solution at the bottom of the container and then dried with CaCl$_2$. The accurate RH is determined by a hygrometer, whose accuracy is ±1%. The elemental compositions of pristine and exposed samples were confirmed by inductive coupled plasma atomic emission spectrometry (ICP-AES) analysis (IRIS Intrepid II XSP, Thermo Electron). Before ICP-AES and Time-of-flight secondary ion mass spectroscopy (TOF-SIMS) testing, we applied a scavenging process to remove the Na$_x$CO$_3$/NaHCO$_3$ products in the Ar atmosphere on the structural and chemical stability of Na$_x$TmO$_2$, the dominate Na$^+/H^+$ moisture-exposure, the dominate Na$^+/H^+$ exchange charge-compensation mechanism, and the critical sodium content ($n_\text{i}$) were applied to confirm the presence of H$^+$ in the exposed materials. Geometry-independent information about the $^{23}$Na$^+/H^+$ dipole couplings can be conveniently obtained from the plot of signal attenuation (1-scale) versus the dipolar evolution time ($\tau_{\text{sep}}$). In all MAS NMR measurements, the variable temperature (VT) gas temperature was set to 315 K. The in situ XRD experiments were performed in air and on a BrukerD8 Discover diffractometer equipped with a Cu Ka radiation. Infrared spectra were recorded on a Nicolet 570 FT-IR (Thermo Fisher Scientific Inc., Madison, USA) spectrometer. X-ray absorption spectroscopy (XAS) data were acquired in the transmission mode at the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF) at room temperature, and the incident beam was monochromatized by a Si (111) double-crystal monochromator. TOF-SIMS were performed on a TOF-SIMS instrument (ION TOF GmbH). The depth profiling and high-resolution mapping were conducted at the high current mode and burst alignment mode, respectively, with a pulsed Bi$^{+}$ ion beam (30 keV). The sputtering was conducted by a 500 eV Cs$^+$ ion beam with the area of 100 μm × 100 μm, and the analyzed areas for depth profiling and high-resolution mapping are typically 100 μm × 100 μm and 50 μm × 50 μm with the pixel of 128 × 128.

Electrochemical tests. The electrodes are composed of 80 wt% of active materials, 10 wt% of polyvinylidene fluoride (PVDF) and 10 wt% acetylene carbon black. The mass loading of active materials is 2.5–3 mg cm$^{-2}$. The cleaned aluminum foil was used as current collector. The electrochemical performances were tested in 2052 coin cells which assembled in an Ar-filled glove box, using 1 M NaPF$_6$ in Propylene carbonate (PC, 98 vol%) and Fluoroethylene carbonate (FEC, 2 vol%) as the electrolyte, Whatman glass fiber filter as the separator, and sodium metal as the counter electrode. The galvanostatic charge-discharge processes were conducted on multichannel battery tester (Neware, CT-4008-SV16mA-164). The electrochemical impedance spectroscopy (EIS) was conducted by a four-channel multifunctional electrochemical workstation (Versa STAT MC. America), at the cell voltage of 4.0 V and with the frequency range of 100 kHz to 0.01 Hz.

DFT calculation. The DFT calculations were performed on VASP (Vienna ab initio Simulation Package) and the exchange-correlation interactions of electron were described with spin-polarized generalized gradient approximation (GGA) and parameterized by PBE formula. The projector-augmented wave approach and GGA + U method were used to evaluate the electron-ion interactions and the localization of the electron densities of the TM ions, respectively. The U value of Mn was set to 3.9 eV and the wave functions were expanded by plane wave with a kinetic energy cut-off of 520 eV. The Monkhorst-Pack scheme was used for the integration in the irreducible Brillouin zone with a k-point mesh resolution of 2×2×2 Å$^{-1}$. The lattice parameters and atomic coordinates were fully relaxed, and the final forces on all atoms were <0.01 eV Å$^{-1}$. For the DFT calculations, a $3 \times 3 \times 1$ supercell, which contains 12 Na, 36 O, and 18 Mn has been adopted. Sodium contents of x = 0.667, 0.556, 0.500, 0.444, and 0.389 in Na$_x$MnO$_2$ correspond to 12, 10, 9, 8 and 7 Na ions in the supercell, and the number of different structures for each Na contents is C$_{12}^1$, C$_{12}^2$, C$_{12}^3$, C$_{12}^4$, and C$_{12}^5$, respectively. Therefore, 1574 kinds of structures should be considered based on the enumeration method. Such computation load is however too heavy to be carried out and 9 of them have been considered. Specifically, we considered two different sodium extraction models for the five different Na contents. The number of calculated structures for x = 0.667, 0.556, 0.500, 0.444 and 0.389 in Na$_x$MnO$_2$ are 1, 2, 2, 2, 2, respectively, as shown in Fig. 4f (page 11 in the manuscript). Moreover, the residual Na sites were chosen randomly and then one water molecule was put into an empty Na site also randomly.

All data availability

All important data that support the findings of this study are presented in the manuscript and supplementary information file. Source data are available from the corresponding author on request.

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Author contributions

W.Z., J.Liu, and Y.Y. conceived the project. Y.Y. supervised the project. W.Z., J.Q., J.Liu, M.W., Y.L., R.F., and Y.Y. designed the experiments. W.Z. and J.Q. performed the materials synthesis and electrochemical testing. W.Z., J.Q., X.L., H.H., H.L., C.L., and J.Li, performed the characterizations. F.R. completed the computational calculations. W.Z., J.Q., X.L., F.R., G.F.O., H.D., J.Liu, Y.L., R.F, and Y.Y., analyzed the data and proposed the mechanisms. W.Z., J.Liu, R.F., and Y.Y., wrote the initial paper. All authors discussed the results and commented on the paper.

Competing interests

The authors declare no competing interests.

Additional information

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