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Chemical speed dating: the impact of 52 dopants in Na-Mn-O cathodes

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Abstract:

Na-Mn-O cathodes are very promising for sodium-ion batteries but suffer major setbacks related to long-term cycling and stability in air. With our high-throughput approach, a systematic investigation of 52 different dopants from across the periodic table into Na_{0.66}MnO₂ is performed. The chemical composition of $Na_{0.66}Mn_{0.9}M_{0.1}O_{2+\delta}$ (M: dopant) is utilized to unravel the impact of dopants on the layered structure and investigate how different dopants influence the battery performance and air/moisture stability. A broad range of doping was possible with 20 different dopants fully integrating into the Na-Mn-O structures, including several previously unstudied dopants (Si, Sc, Ga, Rb, Rh, Cs, Re, and Tl). This yields high interest novel cathodes including the Rb-doped sample with a high specific capacity of 200 mAh g⁻¹, as well as Mo and Nb-doped samples with excellent capacity retentions of 98 % and 100 % respectively after 10 cycles compared to 92 % in the undoped Na_{0.66}MnO₂. Air/moisture stability of the cathode material is systematically studied, and a number of compositions show ultra-high stability in air. This systematic approach provides a rapid overview of the benefits of individual dopants, and also provides an excellent opportunity to elucidate trends across the periodic table. Significantly, we find that the presence of reversible anionic redox (absent in the undoped samples) correlates remarkably well to the bond valence sum of the dopants, implying that dopants can serve to tune the polarity of M-O bonds and encourage anionic redox behavior. Such "speed dating" reveals fundamental chemical insights and guides further design.

1. Introduction

The secondary battery is one of the most important energy storage technologies due to its high energy density, fast response rate, and versatile application scenarios.^{1–3} Particularly, the lithiumion battery is in high demand with outstanding electrochemical performance. However, long-term reliance on this technology is far from assured with limited mineral resources of lithium, the environmental/geopolitical problems from the usage of cobalt and nickel, and the sustainability challenge with recycling spent batteries.^{4–7} Such anxieties about the future of the lithium-ion battery leads researchers toward the potentially more sustainable and cost-effective sodium-ion battery, which has a similar operating mechanism and comparable electrochemical properties.

There have been a number of attempts to develop cathode materials appropriate for sodium-ion batteries. These include layered oxides^{2,8} compared to lithium-ion cathodes like LiCoO₂, tunnel-structure materials⁹, and polyanionic compounds.^{10,11} Among different materials, layered oxides are one of the most prominent candidates due to their facile manufacture, high energy density, large specific capacity, and excellent Na⁺ conductivity. Delmas et al. demonstrated two principal types of layered oxides: P (Na in prismatic sites) and O (Na in octahedral sites). In the Delmas notation, a number is used to indicate the minimum number of sodium layers that must be considered before the structure repeats itself.¹² The commonly reported structures are P2, P3, and O3. In particular, the P2-type structure shown in Figure 1 often demonstrates the best electrochemical properties with fast Na⁺ diffusion and good capacity retention. However, there are only three well-reported elements Mn¹³, Co¹⁴, and V¹⁵ that can form P2 materials without dopants being added. Owing to disadvantages from the toxicity and limited resources of Co and low working voltage of V, Mn is the most promising candidate for P2 material. Meanwhile, Mn-based materials have several merits, such as cheap cost, low toxicity, high reversible capacity, and tunable properties by doping.^{16,17}

For Na_{0.66}MnO₂ (NMO) materials, the sintering temperature is crucial.¹⁸ At temperatures below 620 °C, the P2 phase is formed. While at temperatures above 620 °C, the P2 structure will transform into distorted orthorhombic structure, noted as the P'2 structure. Kumakura et al. reported P2-Na_{0.6}Mn_{0.9} $\square_{0.1}$ O₂ material (P2-NMO) and found 0.1 vacancies (\square) in the MnO₆ layer were introduced during cooling.¹⁹ However, cyclability was compromised by the local distortion caused by the Mn vacancies. Pure P'2-Na_{0.64}MnO₂ was reported by quenching from 1050 °C with

co-operative Jahn-Tell distortion (CJTD) triggered by Mn^{III} (t_{2g}^3 - e_g^1) ions. However, since the P'2 material shows multiple sub-phase transformations and Na⁺/vacancy distortions, it has been believed that the Jahn-Teller distortion (JTD) leads to irreversible transition and degradation of the layered structure.^{19,20} Even though Na_xMnO₂ materials have been investigated for decades, Recently, Kulka et al. demonstrates the synergic effect in P2 and P'2 structure, where the appropriate composite of both P2 and P'2 can achieve long-term cycling.²¹ Moreover, there are a number of studies showing that the P2-NMO material can be stabilized at 850 °C or above by doping. Previously tested dopants include Li^{22,23}, Mg ²⁴⁻²⁶, Fe²⁷⁻²⁹, Co^{30,31}, Ni³²⁻³⁴, Zn^{35,36}, Al³⁷, Cu^{38} , and their combinations^{39–42}. Doping has been proven as an effective approach to modify the structure, enhance the electrochemical property and cyclability, and increase air/moisture stability. For example, Kwon studied $Na_{0.7}[Mn_{1-x}Li_x]O_{2+y}$, and found that when x = 0.07, the charge/discharge curve was smoothed, and negligible capacity decay was observed with 150 mAh g⁻¹ after 120 cycles when cycled from 3.0 to 3.8 V vs Na/Na⁺.⁴³ Mg-doped material Na_{0.66}Mg_{0.28}Mn_{0.72}O₂ is reported with large reversible capacity of 220 mAh g⁻¹ with a smooth CV curve.²⁶ However, only this very limited list of dopants has been studied and there is no clear trend or fundamental understanding as to why one dopant outperforms the others, or even a clear picture as to which dopant is best. Furthermore, new high-entropy materials such as $NaNi_{0.12}Cu_{0.12}Mg_{0.12}Fe_{0.15}Co_{0.15}Mn_{0.1}Ti_{0.1}Sn_{0.1}Sb_{0.04}O_2$ are now being studied⁴⁴, though without a clear understanding of the role of each dopant in these outstandingly complex compositions it is very difficult to glean any benefit from the high-entropy aspect. The recent work from Zhao et al. revealed the pattern between the chemical compositions and structures by means of extensive data mining. This work allows the prediction of whether P2 or O3 layered oxide crystal structures will form using the concept of cation potential.⁴⁵ Therefore, such data-driven research is most effective when it leads to a simple parameter as a predictor for future design. The current research has as objective to establish such relationships for the battery performance of the materials, not only the structure taken.

Another important aspect of research into layered oxides for Na cathodes is the extent to which anionic redox can be accessed reversibly in order to enhance capacity. The extent of anionic redox is highly affected by doping. According to Zheng et al., the Cu-doped material Na_{0.67} Mn_{0.72}Cu_{0.28}O₂ displays oxygen redox activity with low voltage hysteresis, which is encouraged by Cu-O bonding directed to the O-2*p* orbital.⁴⁶ Furthermore, Mg/Cu-codoping into P2-

Na_{0.67}Mn_{0.75}Ni_{0.25}O₂ demonstrates that the oxygen redox reversibility is enhanced through modifying the metal-oxygen bond energy with the presence of peroxo-like $O_2^{2^2}$ species at 4.2 V charged stage.⁴⁷ Two dominant theories have been used to explain the activity of anionic redox.^{48–50} One is through transition metal-driven reduction coupling mechanism, where the oxygen symmetry rearrangement of the MO₆ octahedra can stabilize the peroxo-like $O_2^{2^2}$ species, allowing for electron transfer. The other theory assumes that anionic redox is triggered by the presence of alkali metal ions, as a result of the reduced overlap between the O 2*p* orbitals and alkaline *s* orbital. In both theories, the degree of ionic-covalent nature of the M-O bond evidently plays an important role of anionic redox activity by altering the electron density available for redox reactions in the vicinity of the oxygen ions. Thus, this leads to the reasonable assumption that doping, or a substitution of the metal of that M-O bond would alter the anionic redox activity as the nature of the bond is changed.

Moreover, the structural stability of the layered oxides when exposed to air/moisture is a crucial practical consideration. This issue is particularly important considering that cathode materials may be manufactured from one country and shipped overseas for assembly. Some Mn-based oxides are extremely unstable in humid air, posing a great challenge in maintaining the structural integrity during the manufacturing process. Zuo et al. reported that the change of the XRD patterns can be observed only under air condition (RH 18 %) after exposure to air for Na_{0.67}MnO₂ material.⁵¹ For Mn-based materials, Nazar et al.⁵² found that Mn³⁺ can be oxidized into Mn⁴⁺ in the presence of the oxidizer O₂ in humid air to maintain charge neutrality while structural deformation happens. This process can increase the first charge hysteresis and degrade the battery performance.⁵² Therefore, an approach to transforming Mn³⁺ into Mn⁴⁺ by substituting low-valence dopant in the pristine material can increase air stability. However, owing to the lack of rational design for air-stable materials, there are only a few air-stable compositions reported such as Na_{0.66}Ni_{0.33}Mn_{0.67}O₂⁵¹ and Na(Fe_{0.32}Ni_{1/3}Mn_{1/3}Al_{0.01})O₂⁵³.

In a previous study⁵⁴, we used high-throughput methods developed in ref.⁵⁵ to systematically screen the Na-Fe-Mn-O pseudo-ternary system. This system showed a large P2 solid-solution region with a rich variety of both performance and air-stability as the Fe and Na content varies. For example, we found that 10% doping of Fe into the Na-Mn-O materials was sufficient to

dramatically change the cyclic voltammograms such that the numerous phase transformations rampant in the Na-Mn-O materials were suppressed. The material with low Fe content also showed the best air stability as determined by X-ray photoelectron spectroscopy (XPS). Herein, we applied the high throughput screening illustrated in Figure 1 to make Na_{0.66}Mn_{0.9}M_{0.1}O_{2+δ} (M: dopant) materials with 52 different dopants in order to further understand what dopants can play a similar (or even improved) role to Fe. The target phases in this study are therefore any layered oxides that are electrochemically active, including P2, P'2, and P3. We aim to both discover the impact of dopants on the phase compositions and also on the battery performance. Through this systematic approach we establish the relationships between the dopants and resulting structure, electrochemical properties, and air stability. We further correlate trends to common chemical properties such as electronegativity and bond valence. New insights provided herein will serve as effective guidelines toward rational design of novel materials.



Figure 1: The scheme of the workflow to realize fast chemical "speed dating" and the two main active materials investigated in this study, the layered structure, and the tunnel structure. It should be noted that the P'2 structure appears identical to the P2 structure on the scale shown here, however, the MO_6 octahedra are slightly distorted.

2. Experimental Section

2.1 Material Preparation

A sol-gel method was applied for the high-throughput synthesis to achieve combinatorial Na_{0.66}Mn_{0.9}M_{0.1}O₂ materials, as described in detail in refs.⁵⁴⁻⁵⁶. NaNO₃ and Mn(NO₃)₂ (Sigma-Aldrich) solutions (2.4 M) were prepared as precursors and dispensed into an 8×8 well plate with the molar ratio of 0.66:0.90 according to the stoichiometry. Aqueous solutions (1M) of various dopants listed in Table S1 were prepared into 1M solution and added to the above precursor solutions at a rate of 1:9 to manganese. Since the choice of precursor might influence the final products, the nitrate salts were preferably selected as the dopant solution for sol-gel synthesis and the full list of precursors is given in Table S2. Citric acid (3 M), as a chelating agent with an equal molar fraction to the metal cations, was pipetted subsequently to stabilize the oxidation states of transition metal ions. The gelation process was then carried out at 65 °C for 2 days to create homogeneous precursor gels via strong carboxylic group bonding. To prevent cross-contamination, the obtained 8×8 set of gels were pulverized and transferred onto an alumina plate mounted with an 8×8 aluminum smokestack by separating samples into independent combustion chambers. The samples were preheated at 400 °C for 2 hr to combust the citric acid and nitrates (heating rate: 2 °C min⁻¹). After removing the smokestack, the samples were then calcined at 850 °C for 12 hr in ambient air (heating rate: 5 °C min⁻¹), followed by 5 °C min⁻¹ cooling rate. The lowest temperature at the position of a sample in the Muffle furnace was measured to be 843 °C, which assures even heat distribution across all samples considering the good thermal conductivity of the alumina substrate. The P'2 and P2 Na_{0.66}MnO₂₊₈ samples were synthesized by the above method but followed by quenching at 650 °C and 500 °C, respectively. The samples were transferred directly from the furnace onto a copper foil placed on a steel slab within 10 sec of opening the furnace door. Through the above high-throughput method, 51 different doped samples (5 mg each) and undoped P2 and P'2 NMO layered oxides were synthesized. 4 batches of samples (a total of 256 samples) were synthesized to demonstrate the reproducibility and feasibility.

2.2 X-ray diffraction

The obtained samples were characterized all via high-throughput powder X-ray diffraction (XRD) measurement⁵⁶. Equipped with a Panalytical Empyrean diffractometer with a Mo target, the high-

throughput XRD was carried out in transmission mode (60 kV, 40 mA). To develop fast but highquality XRD patterns for Mo K α radiation ($\lambda = 0.70926$ Å for K α_1), a scatting angle range of 4– 30° was investigated, which corresponds to 10-70° for Cu radiation. The major peak intensity with over 3000 counts was obtained for each sample within 10-min scan, which can be adopted for further Rietveld refinements. A 3D-printed sample holder was designed to keep samples on a clear mylar foil without cross-contamination in order to realize a high-throughput and automated detection. The resulting XRD patterns have had Mo K α_2 stripped and converted to Cu-K α_1 angles for ease of comparison to the literature that typically uses Cu-radiation XRD. The identification and refinement of all XRD patterns were conducted using Panalytical's HighScore Plus software. Multiple phase Rietveld refinement was performed on all XRD patterns using the CIF files selected by the automated phase identification performed in batch mode, shown in Table S1.

2.3 *Electrochemistry*

To investigate the electrochemical performance, combinatorial cells were utilized using 8×8 sample materials as the cathode, as described in refs.^{54,55,57}. 64 parallel channels were devised into a printed circuit board (PCB, Optima Tech) with 64 gold pads coated in aluminum foil. The cathodes were composed of 2 mg of active materials combined with 20 wt% carbon black, followed by drop-casted onto the contact pads via N-methyl-2-pyrrolidone (NMP) with 20 wt% polyvinylidene fluoride (PVDF). NMP was then vaporized overnight at 80 °C, to yield an active material loading of 20 mg/cm². In an Ar-filled glove box, the assembly of the combinatorial cell was performed with 1M sodium perchlorate in propylene carbonate (PC) with 2 wt% fluoroethylene carbonate (FEC) as the electrolyte. Sodium metal foil was used as the anode, along with a GF/D glass microfibre prefilter as a separator. On a lab-built high-throughput electrochemical system⁵⁶, cyclic voltammetry (CV) was carried out with the voltage between 1.5 and 4.3 V versus Na/Na⁺ at different scan rates (2750 Keithley). The electrochemical properties such as specific capacities and average voltages were extracted from the processed data for multiple cycles and scan rates. The CVs were also converted to voltage profiles by integrating *Idt* to obtain the capacity as a function of voltage. The excellent reproducibility was investigated and reported with RSD of 7% on specific capacities.⁵⁵ Two protocols were used, one to investigate capacity retention and the other to determine the rate performance. The capacity retention was

tested at a constant scan rate of 0.1 V/h CV for 10 cycles. The rate performance was carried out at different rates sequentially: 0.1, 0.2, 0.4, 1.0, and 2.0 V h^{-1} with 2 cycles at each rate.

2.4 Accelerated aging

Following the above work on single-dopant samples, several dopants that effectively stabilize the P2 phase and/or improved electrochemical performance were then selected for a co-doping study aimed at determining stability in air. The compositions were Na_{0.66}Mn_{0.9}M_{0.05}M'_{0.05}O₂ where M and M' were limited to: Li, Mg, Al, Si, Fe, Co, Ni, Cu, Ga, and Rb. The resulting array of co-doped samples was synthesized with the above-described method and stored for various periods of time in different atmospheres to test stability. First, they were stored for 2 weeks in dry air (RH < 10 %), then ambient air for 1 week (RH = 45 %), finally, humid air for 1 week (RH > 90 %). The different humidity level environments were obtained using a vapor source and a desiccant (DreriteTM) in an enclosed system and monitored by a humidity meter. The temperature was maintained within 23 ± 1 °C. X-ray diffraction was performed after each storage step. The XRD patterns were fit and analyzed as described above.

3. Results and Discussion

3.1 Structure analysis

A few representative XRD patterns are shown in Figure 2 along with the fits obtained after automated phase identification and Rietveld refinement of the XRD results. Four distinct electrochemically active phases (P2, P'2, P3, and the tunnel structure) are observed, revealing that dopants have a significant influence on the phase stability. Three different undoped NMO materials are obtained, with the obtained phase depending on both composition and temperature profile as described in the introduction. Based on the literature, we expect to form P'2 - NMO above 620 °C and P2-NMO below 620 °C by intaking oxygen to form vacancies on the transition metal layers. Herein, pure P'2 and P2 are achieved by quenching from 650 °C and 500 °C, respectively, as shown in Figure 2b at the same starting stoichiometry of Na_{0.66}MnO₂. However, a binary sample with P2 and P'2 phases was obtained for the sample slowly cooled down from 850 °C (i.e., the synthesis conditions used for all doped samples herein). The XRD patterns with some dopants are simple to analyze, Li and Si, for instance, stabilize the pure P2 and pure P'2 phases, respectively. Rb-doped sample, however, resulted in a similar XRD pattern as slow-cooling NMO

(mixture of P2 and P'2), which makes it difficult to confirm that Rb integrated into both (Table S1 shows changes in lattice parameters in both phases with Rb substitution suggesting it at least partially dopes both phases). In other cases, such as Mo, the fraction of P2 present drops dramatically with the P'2 phase becoming dominant. This demonstrates that the introduction of dopants can modify structural compositions dramatically, as changing formation energies of the two phases allows for the preferences of one phase conversion over the other.



Figure 2: Representative XRD patterns for different doped and undoped samples fit in 4 active material phases: P2, P'2, P3, and tunnel structure. 3 different undoped samples, Mn-P2/P'2, Mn-P'2, and Mn-P2 are obtained by slow cooling from 850 °C, quenching from 650 °C, and quenching from 500 °C, respectively.

Quantitative analysis of the phase compositions is based on the Rietveld refinement results and are summarized in Figure 3 and shown in detail in Table S1. In Table S1, we report the percent doped as being the fraction of dopant that is estimated to be in the NMO phases (either P2, P'2, tunnel, or P3) by accounting for the amount of dopant in the other phases identified in HighScore.

Ultimately, Figure 3 and Table S1 show that 20 different dopants fully dope into the NMO structures. Interestingly, of these 20 effective dopants Si, Sc, Ga, Rb, Rh, Cs, Re, and Tl have not been reported previously. Accessing such breadth of available chemistry illustrates the power of a systematic high-throughput approach. It should also be recognized when considering dopants with large ionic radii such as K, Rb, Cs that the dopants may in fact substitute into the Na sites which has 33% vacancies in the target compositions. For example, P2-Na_{0.612}K_{0.056}MnO₂ was successfully synthesized and reported by Wang et al.⁵⁸ with 240 mAh/g, implying that such 1s dopants doping into the sodium layer can be an attractive design strategy, and this will be discussed further below in regard to the electrochemical results. It is also important to recognize that among the inactive phases shown in Table S1, a number of these phases may form solid solution, making it impossible to determine the fraction of dopant introduced into the layered structures. For example, Mn₂O₃ is the most common phase, and many dopants can form binary oxides with manganese as illustrated in Table S1, such as Ca, V, Sr, Y, Pd, Te, Ba, W, Ir and La. This makes the level of dopant impossible to identify in such samples given that the dopant concentration in the Mn₂O₃ phase cannot be identified. Similarly, Mn solubility into a dopant-containing 'other' phase may result in an overestimation of dopant in this phase and thus leading to calculated dopant levels being underestimated or even negative in Table S1. Even considering an underestimation of doping, the XRD analysis clearly demonstrate a high degree of doping into the NMO phases of interest for Na-ion batteries as discussed above and the impact of the dopants will be further discussed in the electrochemistry section.



Figure 3: Relative phase compositions of the 4 electrochemically active phases (P2, P'2, P3, and tunnel structure) and other phases, distributed over the periodic table for M in $Na_{0.66}Mn_{0.9}M_{0.1}O_{2+\delta}$ materials.

In Figure 3, the fractions of the layered P2 and P'2 phases are illustrated in red and yellow, respectively, and are the dominant phases throughout much of the periodic table in this study. These two dominant phases are the focus of this study and generally grouped in hexagonal (P2) and orthorhombic (P'2) crystal structures respectively. The shape of the first high-intensity peak at around 16° can indicate the relative ratio of these two phases as the P'2 peak appears at a slightly lower angle than the P2 peak as shown in Figure S1 shows at a slightly higher angle. Specifically, P'2 shows a slightly larger lattice parameter c than that of P2. Specific to the goodness-of-fit (*GoF*) values, excellent fits are obtained for GoF values less than 3 when XRD patterns have low backgrounds as is the case here.⁵⁹ The range of *GoF* values for scans with P'2 and P2 phases only are from 1.15 to 2.68 and by visual inspection these all correspond to high quality fits where the residuals at every peak are within 10% of the peak height. There are some meaningful trends over the periodic table related to the presence of these two phases. First, the slow-cooled NMO material

in Figure 3 was obtained with 66% P2 and 34% P'2, while the nominal composition of Na_{0.66}MnO₂ implies 66% Mn³⁺ and 33% Mn⁴⁺. The XRD results here show that a number of dopants (Li, Mg, Fe, Co, Ni, Zn, and Ga) produce pure P2 materials, again with only 10 % substitution of Mn. All of these substituents are subvalent to Mn⁴⁺ such that their integration is expected to result in some Mn³⁺ being oxidized to Mn⁴⁺ thereby reducing the Jahn Teller distortion effect. Moreover, the ionic sizes of these dopants are all close enough to form solid solutions in the MnO₆ slab. However, Al doping resulted in 91 % P2 structure, indicating that it is not as effective in suppressing the transformation to P'2 as say Ga (100 % P2) which takes the same oxidation state (3+), and its ionic size is very close to that of Mn⁴⁺ (0.535 vs. 0.53 Å in 6-fold coordination). Thus, the nature of the dopants plays a critical role in stabilizing the P2 structure concerning providing Jahn-Teller active Mn ions and also being the right size to fit the space.

On the other hand, a single P'2 structure is only obtained with Si doping. This is certainly in part due to the fact that Si^{4+} doping results in reduction of Mn^{4+} back to Mn^{3+} , thereby increasing the J-T effect, but there are other supervalent dopants that do not purely stabilize the P'2 phase. Boron in this study also shows a dominant P'2 structure at 93%, shown in Figure 2b, despite taking the 3+ state. Boron doping into NMO material was recently reported by Vaalma et al. who demonstrated that at 900 °C B-doped NMO could be achieved but this resulted in 4 different phases being present ⁶⁰. We also found that Mo, W can lead to more P'2 structure. Again, there is more to the role of the dopants in stabilizing phases other than can be simply understand from their oxidation states.

Besides P2 and P'2 phases, P3 and tunnel structure $Na_{0.44}MnO_2$ were also found by doping as shown by Figure 3. The Rh-doped material results in a pure P3 structure as shown in Figure 2. This P3 structure shows a larger *c* lattice parameter compared to the P2 structure, after converting *c* to the same scale as P2 (i.e. to a unit cell with the same number of layers), obtaining 11.26(4) Å compared 11.05(3) Å for slowly-cooled NMO, indicating larger interstitial distance allowing for Na⁺ diffusion. P3 structures can also be potential cathode materials with reported excellent capacity retention: 78 % after 500 cycles⁶¹. From our previous report⁵⁴, we found that the P3 material can accommodate more Na content than that of P2, which can potentially solve the Na deficiency issue for P-type cathode materials. Further work examining Rh-doped materials with higher Na content may therefore be warranted. The tunnel structure (shown in Figure 1) was mainly found in Ti, V and Bi-doped samples. Compared to undoped Na_{0.44}MnO₂, the Ti-doped sample shows a larger lattice volume, where the lattice parameters show an increase as follows: : *a* from 9.064(9) (undoped) to 9.127(1) Å, for *b* from 26.22(3) to 26.32(4) Å, for *c* from 2.814(4) to 2.838(4) Å. A similar trend was also reported by Doeff et al.⁶². Such volume enlargement can potentially increase the Na⁺ diffusion channel, this will be revisited below.

3.2 Electrochemical analysis

High-throughput electrochemical cyclic voltammetry (CV) was performed on all 10 % doped samples, as shown in Figures 4 (as CVs) and 5 (as voltage curves calculated from the CVs). The electrochemical properties are extracted and summarized in Figures 6 and S2-S4. In the CV curves, the difference dopants demonstrate dramatic differences in the charge/discharge curves. Effectively, the CV curves can be well-correlated to the structure as discussed above. Li, Mg, Al, Fe, Co, Ni, Zn, Cu, and Ga-doped samples show very smooth CV curves for the P2 structure, where the main redox Mn³⁺/Mn⁴⁺ peaks located at 2.3 V and 2.1 V. In contrast, the Rh-doped P3 sample shows smooth and broad redox Mn³⁺/Mn⁴⁺ peaks at 3.0 V and 2.1 V, a characteristic shape of a P3 structure consistent with our previous study.⁵⁴ However, P3 materials typically undergo P3-O3/O3' structural change, which can result in sluggish Na⁺ transport at higher voltages.⁶³⁻⁶⁶ This is consistent with the fact that the P3 structure has a considerably larger voltage difference (polarization) than the P2 structure as shown in Figure 6b.



Figure 4: The first cycle of the combinatorial cell with 52 different doped $Na_{0.66}Mn_{0.9}M_{0.1}O_{2+\delta}$ samples and the tunnel-structure $Na_{0.44}MnO_2$ samples. The P2-NMO sample is highlighted in light pink. The outline indicates the pure phase: yellow-P2, red-P'2, green-P3, and blue-tunnel structure. The cyclic voltammetry is performed between 1.5 V to 4.3 V vs Na/Na⁺ at the scan rate of 0.1 V h^{-1} .

In contrast to the P2 structure, the P'2 structure can produce multiple peaks in the CVs as shown in Figure 4, which has been consistently associated with multiple phase transitions taking place during electrochemical cycling.^{19,67} During the Na⁺ insertion and extraction, Na⁺/vacancy ordering forms, leading to different diffusion energy paths on the different sites and resulting in multiple peaks. Si and Al-doped samples shown in Figure 4 demonstrate that the main oxidation peaks of the P'2 material shift up to a higher voltage as compared to P2 materials. Simultaneously, the difference between charge/discharge peak voltage is increased, indicating higher polarization for the P'2 phase, also confirmed in Figure 6b. Kumakura et al. demonstrated that 7 sub-phases of P'2-NMO can be identified by operando XRD.¹⁹ Even though several sub-phases were found, the P'2 material still showed comparable cyclability to P2, which indicates such phase transitions can still be highly reversible. Similarly, we also found that P'2 materials (Si and Mo-doped) in this study exhibit decent capacity retentions after 10 cycles of about 91 and 98 %, as compared to 89 % for pure P2 phases (Co, Ni, and Zn-doped). For the average discharge voltage, B, Si, and Modoped samples (P'2 domain) show higher voltages than undoped NMO. Due to the distortion of the MnO₆ octahedra, the cooperative Jahn-Teller effect caused by doping alters the crystal structure, which in turn adjusts the local chemical environment of Mn and the electrochemical potential of the cathode materials.



Figure 5: The first charge, discharge and second charge of the combinatorial cell with 52 different doped $Na_{0.66}Mn_{0.9}M_{0.1}O_{2+\delta}$ samples and the tunnel-structure $Na_{0.44}MnO_2$ sample. The voltage

curves here were obtained by processing the CVs shown in Figure 4. The outline indicates the pure phase materials: yellow-P2, red-P'2, green-P3, and blue-tunnel structure. Due to sodium-deficiency in the pristine materials, it is possible to reinsert more sodium into the cathode than was removed during the charge; this appears as negative capacities in the voltage curves here.

Regarding the tunnel structure, the Ti-doped sample shows the highest discharge voltage and the lowest voltage difference (shown in Figure 6b), which adds a new strategy to modify the average voltage by introducing the tunnel structure. Figure 5 shows the Ti-doped sample has the lowest hysteresis compared to the layered structure. Enhancements to the electrochemical performance of this material is assumed to be due to the increased lattice parameters allowing for higher degree of Na⁺ diffusion, to be discussed below with regards to diffusion constants. The practical capacity of the tunnel structure Na_{0.44}MnO₂ was reported as 121 mAh g⁻¹,^{68,69} while the Ti-doped material herein shows an initial discharge capacity of 120 mAh/g and 99 % retention after 10 cycles. Compared to the CV for the tunnel-structure Na_{0.44}MnO₂ shown in Figure 4, the Ti-doped sample exhibits fewer phase transition peaks, which means the Ti-doped composite material can be a promising cathode material featuring smooth charge/discharge curves, high voltage, and low hysteresis.



Figure 6: Electrochemical properties for the 52 different doped Na_{0.66}Mn_{0.9}M_{0.1}O_{2+ δ} samples extracted from the combinatorial cell. (a) Specific capacities on the first charge in yellow, the first discharge in deep blue, and the tenth discharge in cyan. 10-cycle retention is calculated and plotted in purple as the secondary y-axis. (b) Average voltage of the second change in turquoise, the second discharge in gray. The voltage difference is calculated by the subtraction of the charge and discharge average voltages, as shown in yellow as the secondary y-axis.

Despite the successes outlined above, some doping elements show negative effects on the cathode performance. Often, as is the case for Te, Pt, and Sn, this correlates to a lower fraction of the layered phases (Figure 3). This demonstrates that the inactive phases can potentially restrain the battery performance, shown in Figure 6, where the poorly performing samples with extra inactive phases show depressed capacities and larger voltage differences as a result of higher electrode polarization. To reduce these inactive phases, strategies including changing the precursor material and modifying the synthesis temperature are required.

Figure 5 shows the voltage profiles of the first charge and discharge, and the second charge. Several electrochemical properties can be investigated by this plot. Firstly, the overlapping of the first and second charge curve could imply the air stability and irreversible phase transformation on the first charge.⁵² Ni, Fe, Li, Cu, and Ga-doped samples show better overlapping, which indicates that the as-prepared samples at OCV show a very similar Na⁺ diffusion profile. From our previous study and Duffort et al.,⁵² the first charge curve can show less overlapping due to the intake of CO₂ and moisture or Na₂CO₃ deposit on the particle surface, which could hinder the Na⁺ and electron conductivity. Moreover, such an air-stable feature has practical significance, inspiring us to conduct the air-stability test, discussed in the section below.

Secondly, hysteresis of the charge/discharge curve can indicate the polarization of the charge/discharge processes. In Figure 5, the materials with primarily the P'2 phase (such as Si, B-doped samples) show a larger hysteresis at the high voltage plateau, compared to P2 materials (e.g. Ni-doped). This is because fewer phase transition processes are found in P2. However, the undoped P2-NMO and Rh-doped P3 show a large hysteresis, which can imply lower conductivity of the material.

Moreover, the voltage profile can also be an indicator of the electrolyte-cathode interphase stability as shown in previous studies.^{54,70} The charge endpoint slippage effect can demonstrate the irreversible electrolyte consumption by oxidation at high voltage operation. Mg, Al, Co, Ni-doped samples exhibit minor slippage effects. Particularly, the Mg-doped sample shows the least electrolyte oxidation, which implies Mg doping can sustain interphase stability at high voltage.

Given the benefits seen for a number of dopants, it is important to determine the role of morphology on improving battery performance. Figure S9 shows SEM images obtained for 9 highly performing materials including the undoped. There is no systematic change in morphology with all samples showing porous agglomerates of platelets that are on the order of 1 μ m in size. The Rb-doped sample however shows larger platelets such that a longer diffusion path may be needed in this sample. Otherwise, there is no clear change in morphology with the dopants studied here.

3.3 Rate Performance

After analysis of initial CV, the rate performance is investigated by performing cycles at different scan rates, with representative CVs shown in Figure 7. As the scan rate increases, not only do peak currents increase but the redox peaks are also separated by increasing overpotentials, as shown in Figures 7a-f. The capacities at different scan rates are calculated and summarized in Figures 7g and 8a. The peak current under the different scan rates is subsequently obtained and plotted in Figure 7h.

In a CV, the faradaic current is influenced by the gradient concentration of the Na⁺, which may be limited by diffusion. By changing the scan rate, such diffusion control will behave differently. In Figures 7a-c, P2 materials maintain the smooth CV curve. Notably, the Fe-doped sample shows the lowest increased specific current at the endpoint of charge, indicating better rate performance with lower overpotential. While the Fe-doped sample has a lower specific capacity than the Ni-doped, it surpasses the Ni-doped in performance at 2.0 V h⁻¹ as seen in Figure 7g. When more P'2 is present than in the undoped sample (34 %), the multiple peaks are still visible but they are less sinuous at higher scan rates as shown in Figures 7d-f. Although it seems counterintuitive, the multiple peaks do not interfere with the rate performance. There is a long-held belief that the multiple subphase transition and Na⁺/vacancy ordering will have a negative impact the rate performance. Our systematic study, however, shows that rate performance is comparable with or without these transitions. For example, P'2 Si-doped sample with multiple phase transitions has a

rate performance of 80 % (1 V h^{-1} capacity/0.1 V h^{-1} capacity), compared to 81 % for P2 Fe-doped sample.



Figure 7: (a-f) The CV rate test results for the Ga, Fe, Ni, B, and Rb-doped and undoped samples at the sequential scan rates of 0.1, 0.2, 0.4, 1.0, and 2.0 V h⁻¹ with half cycle number started with discharge and followed by charge capacities. (g) Specific capacities extracted from the CV rate test. (h) The linear regression of the peak current and square root of scan rate. The Randles-Sevcik equation shown in (h) demonstrates the linear relationship between the peak current (i_p) and square root of scan rate (v), which is used to calculate the Na⁺ diffusion coefficient (D).

The Randles-Sevcik (R-S) diffusion coefficient is calculated using the R-S equation shown in Figure 7h. The correlation factors demonstrate that these layered structures obey the R-S eq., where the redox peak current is proportional to the square root of the scan rate. In the R-S eq., *n* is the number of electron transferred in the redox Mn^{3+}/Mn^{4+} , *A* is the electrode area (cm²), *C* is the concentration of the electrolyte (mol cm⁻³), and *v* is the scan rate (V s⁻¹). It is worth noting that the calculated diffusion coefficient *D* is the overall Na⁺ diffusion within the battery. The R-S diffusion coefficient can therefore be utilized here to compare the Na⁺ conductivities of different cathode materials tested in our high-throughput study. It should be noted that diffusion constant extracted in this manner become an estimate in cases where multiple phases are present as the diffusion constant of each phase will contribute differently depending on a number of factors such as particle

size, and spatial distribution of phases. Nonetheless, samples that show a high diffusion constant despite having multiple phases present must have excellent diffusion through at least one of the phases.



Figure 8: The rate performance properties extracted from the CV rate test. (a) Specific discharge capacities extracted at different scan rate of 0.1, 0.2, 0.4, 1.0 V h⁻¹. The rate performance is calculated from the ratio of the discharge capacities (extracted from CVs) between the rate of 1.0 V h⁻¹ and 0.1 V h⁻¹. (b) Randles-Sevcik diffusion coefficients are extracted from the rate test. The red dashed line shows 10^{-8} cm² s⁻¹ as the threshold obtained here for the diffusion coefficient.

In Figure 8b, it seems there is a diffusion constant threshold of about 10^{-8} cm² s⁻¹, which is probably due to an innate Na⁺ diffusion mechanism. This is in good agreement with results from ref.⁷¹ who obtained values in the range of 4.4 - 8.6×10^{-8} cm² s⁻¹ for P2-Na_{0.67}Mn_xCo_{1-x}O₂ materials. The threshold shows that there may be an intrinsic limitation to how far we can design high-rate-performance NMO-based materials. This limiting effect can also be seen in Figure 8a, where the capacity ratio of about 80 % between 1 V h⁻¹ and 0.1 V h⁻¹ is systematically obtained for the majority of layered structures. From the Pearson correlation chart in Figure S6, we also found there is a correlation between certain parameters as shown in scatter plots in Figure 86 and 9d. Of highest interest specific capacities correlate well to diffusion coefficients (Figure 9d). It can be concluded that diffusion of Na⁺ is a bottleneck in the layered structures, and that the inactive phases found in Tables S1 not only decrease the capacity of the battery, but also hinder Na⁺ diffusion through the composite electrodes.

It is also worth noting that the Rh-doped P3 material shows a lower rate performance and diffusion coefficient compared to the P2 structure (e.g. Ni-doped). As we discussed above, Figures 4 and 6b show that the P3 material has a larger voltage difference and broader redox peak, which is consistent with the lower diffusion coefficient. The tunnel structure, however, shows better rate performance with 90 % capacity retained at 1 V h⁻¹ compared to 0.1 V h⁻¹ for Ti-doped NMO. Even though multiple peaks and Na⁺ diffusion steps are shown in Figure 4, such an excellent rate performance can be a fascinating foundation to design novel materials.



Figure 9: Chemical property trends over the periodic table in Na_{0.66}Mn_{0.9}M_{0.1}O₂₊₈. (a) The heat map of the calculated bond valence mismatch of MO₆ octahedra. (b) The heat map of the extracted discharge capacities from 4.0 - 4.3 V. (c) The scheme of MO₆ octahedra and the calculation of the bond valence theory, where v_{ij} is the individual bond valence contribution for the i-j bond, R_{ij} is the bond length between the ith and jth ions, R_o is a tabulated parameter of ideal bond lengths, and *b* is an empirical constant. (d) The plot of diffusion coefficients *vs*. first specific discharge capacities. (e) The trend between the electronegativities of the dopants and the first average discharge voltage.

3.4 Accelerated aging

As mentioned above, air stability is an important metric of the cathode material for practical Naion battery applications. Hence, we utilize an accelerated aging protocol to investigate air stability.

XRD patterns were collected from materials at four stages: fresh prepared; 2 weeks in dry air (RH < 10 %); 1 week in ambient air (RH = 45 %); and 1 week in humid air (RH > 90 %). The results are summarized in Figure 10. All pristine co-doped samples shown in Figure 10d are made up of the P2 and P'2 phases only. The representative XRD patterns in Figures 10 a,b show dramatically different behavior when exposed to various air and moisture environments. The undoped-P2 phase degrades rapidly by intaking water even under dry air with less than 10 % RH, showing the instability of undoped P2 as it can easily transform into the birnessite phase (Na_{0.23}MnO₂·0.7H₂O), shown in Figure 10c. During the transformation, water molecules are incorporated into the layered structure. Interestingly, hydrated birnessite phase shows a very sharp (002) peak. The interslab distance (proportional to the c axis) rises from 5.6 Å in the P2/P'2 structures to 7.1 Å in birnessite, which explains why the (002) peak appears at a much lower angle. The sharp birnessite peaks indicate that this hydrate phase has excellent crystallinity implying high conversion rates from the original layered structures within particles. Such finding is consistent with the report from Zhang et al.⁷² The Li/Co-codoped sample, however, shows a very high resistance against air and moisture (Figure 10b), indicating that such doping can greatly hinder the kinetics of the transformation. Zuo et al. reported that this transformation may accompany the oxidation of the transition metal.⁵¹ Therefore, low oxidation-state dopants can prevent the transformation process by increasing the Mn⁴⁺ content over Mn³⁺ by charge balancing. This explanation agrees well with the trend we found in Figure 10 d-e, where monovalent Li shows the best stability; the bivalent Mg and Cu show mild stability; and the tetravalent Si shows the worse stability. Besides the chemical valence, there are also synergistic effects from the co-doping, especially for trivalent dopants. The single-doped Al and Fe samples show only 66 % and 78 % of the P2 phase remaining after exposure to humid air, but the air stability improved after co-doping, such as with Ni, Co, and Ga. Therefore, the combinatorial map offered in Figure 10 can be a very useful guideline for the designing of airstable materials, overcoming the major roadblock to commercialization of these materials.



Figure 10: The accelerated aging investigation. (a,b) XRD patterns and fitting for the undoped P2-NMO and Na_{0.66}Mn_{0.9}Li_{0.05}Co_{0.05}O₂ at different storage conditions, and shown on a larger scale in Figure S8. (c) The schematic diagram based on ref. ⁵¹ of the mechanism of water insertion into the layered structure resulting in an increase in the interslab distance and thereby shifting the (002) peak to lower angles in the XRD patterns. Layered structures P2 and P'2 composition ratios under different storage scenarios (i.e. 100 % represents any combination of P2 and P'2 phases only): fresh (d), after 2 weeks in dry air (e), after 1 week in regular air (f) and after 1 more week in humid air (g). Note: d-g are measurements on a single set of samples, the storage is performed sequentially.

3.5 Trends across all dopants

Exploratory data analysis was conducted with visual statistic approaches such as Pearson correlation and the heat-map periodic table to investigate the trend for material designing, illustrated in Figure 9, S2. Therefore, we can understand if any strong or mild correlation exists amongst various variables including the chemical nature of the dopants, structures, and electrochemical properties. As mentioned above, Figure 9d demonstrates that Na⁺ diffusion acts as a bottleneck limiting the amount of Na that can be cycled. Only when the diffusion constant reaches the threshold of 10^{-8} cm² s⁻¹ is it possible to obtain specific capacities above 160 mAh g⁻¹. This is a noticeable finding that further modifications meant to improve other properties in the layered oxides must not be at the expense of the diffusion constant. Moreover, with the help of the

Pearson chart, we found there is a mild positive correlation between the electronegativity of the dopants and the average voltage. When a more electronegative dopant is incorporated into the material, the voltage is subsequentially raised, as a result of the inductive effect to lift the electrochemical potential higher than the Na/Na⁺ (0 V). Such trend can also be observed from the literatures, where the voltage increases with the electronegativity, such as for 3d metals from Ti to Cu: Ti $(0.7-1.2 \text{ V})^{73,74}$, V $(1.5-1.8 \text{ V})^{75,76}$, Mn $(2.2-2.7 \text{ V})^{17}$, Fe $(3.2-3.4 \text{ V})^{77}$, Co $(2.7-3.7 \text{ V})^{78}$, Ni $(3.5-4.0 \text{ V})^{79}$, and Cu $(3.7-4.1 \text{ V})^{80}$. Additionally, the voltage decay is one of the significant issues to maintain the energy of the battery. In this study, we observed the voltage retention is inverse proportional to the discharge voltage, where the low-voltage materials however gain voltage after 10 cycles, as demonstrated in Figure S7a. Such aspect of voltage retention is also an interesting strategy to design the material to sustain the energy density during extended cycling.

Finally, Figure 4 shows some dopants have a distinct pair of reversible redox peaks at 4.1 V (discharge) and 4.2 V (charge). The undoped materials do not show any peak here indicating that this is not manganese redox. In the doped materials, we observed these peaks in both samples where the dopant is electrochemically active (e.g., Cu and Ni), and also in a high number of dopants that are electrochemically inactive (e.g., K, Rb, Cs, Zr, Cd, and Tl). In the case of inactive dopants, the extra peak at 4.1/4.2 V can only be attributed to reversible oxygen redox as electrolyte oxidation can be ruled out since it is primarily irreversible and continues to oxidize during the down sweep of voltage which does not occur here. For the redox active species, we still speculate that the peaks at 4.1/4.2 V are at least partially due to anionic redox, but there may also be cationic contribution from the dopants. Interestingly, in ref. ¹⁹ undoped Na_{0.6}Mn_{0.9 \square 0.1}O₂ materials (both P2 and P'2 phases) show an oxidation peak near 4.1 V but no corresponding discharge peak until below 3.5 V. Although this is likely oxygen redox, it is poorly reversible; clearly the dopants discussed here result in highly reversible oxygen redox, as opposed to what has been seen in $Na_{0.6}Mn_{0.9}\square_{0.1}O_2$ materials that rely on the transition metal vacancies only to induce oxygen redox. The anionic redox process is deemed to be a capacity booster to the cathode material and a way to dramatically increase the energy density.⁴⁸ The high number of inactive dopants that induce anionic redox here provides us with a unique opportunity to determine what property in these dopants enables the anionic redox. Therefore, we quantify the high voltage capacity in Figure 9b by calculating the discharge capacity from 4.0 to 4.3 V. The capacity ranges from 0 to 20 mAh/g, a seemingly small amount, but it should be noted that this is for 10 % substitution only, such that

materials with a greater percentage of these dopants will result in considerably higher anionic capacity. Figure 9b shows a remarkable pattern across the periodic table with a number of inactive dopants in the left section of the table showing activity, but also another set of elements near the end of the transition metals (e.g., Tl, In, Cd, Ga).

The trend of anionic redox across the periodic table is so systematic that it warrants deeper understanding. The first parameter we consider that could be related to induction of anionic redox is the electronegativity of the elements, shown in Figure S5. It could be expected that a low electronegativity would allow oxygens to pull more electrons to themselves and thereby have them not lying so deep in the band structure (this can be viewed as increasing the ionic character of the Mn-O bonds via the inductive effect⁸¹). There are certainly similarities between Figure 9b and S4, particularly with the left side of the table showing high activities (red in both cases). However, the electronegativity does not show the trend near the end of the transition metals (e.g. In, Tl have relatively high electronegativities). We speculate that the limitation of the electronegativity here is that it does not take into account the oxidation states and the ionic-covalent nature of the M-O bond, and as such it only explains part of the trend. We therefore explore the bond valence sum approach. Figure 9c shows the bond valance mismatch (BVM)⁸² for each dopant when introduced at a Mn site into the P2 structure (though the trend is unaffected if the P'2 structure is used instead as the local structure is very similar). The trend in BVM in Figure 9c is incredibly well related to that of the anionic activity in 9b with ions with extremely high valence values (high negative mismatch values) with values below approximately -1.4 (value for Sn which shows the smallest anionic peak) correlating with induced anionic activity. In fact, the only elements that break the pattern are: (i) Pb, Bi and Te, (that all show low anionic activity, but they also show either the tunnel or 'other' phases in figure 4), (ii) the Zr sample with ZrO₂ as a secondary phase (as reported by Yu et al., this exhibits anionic redox activity by Zr^{4+} forming a coating and doping by regulation of electronic state of O 2p energy level⁸³), and (iii) Ni, Cu that show more anionic activity than expected but are both known to show cationic redox. We therefore propose that bond valence mismatch may be an excellent predictor of whether or not a dopant may induce oxygen redox in its vicinity in the NMO layered structures. It should be noted that elements like K, Rb and Cs may in fact have such a large mismatch that they occupy Na sites, but nonetheless their mismatch on the Na site is also very large (-2.3 to -6.2). A highly negative value in Figure 9a implies that the dopant is too big for the site in the lattice, which again implies the electron(s) occupy the space

near the neighbouring oxygens more so than when smaller dopants are utilized. The fact that the bond valence approach is a calculation for given ions (rather than atoms as is the case for electronegativity) clearly gives a better predictor of anionic redox activity.

4. Conclusions

Further to previous research, this high-throughput doping study on Na_{0.66}Mn_{0.9}M_{0.1}O_{2+ δ} was performed with 52 different M elements, followed by comprehensive and informative exploratory data analysis. The structure information and electrochemical properties of 4 active phases, P2, P'2, P3, and tunnel structure, have been identified and investigated, with the help with high-throughput XRD and electrochemical tests. The results confirm a strong correlation between the structure and battery performance. This broad-view doping study of Na-Mn-O materials provides the framework for rational design guidelines for this family of materials, highlighting how combinatorial studies are imperative. The dopants, Li, Mg, Fe, Co, Ni, Zn, and Ga, show beneficial impact on stabilizing the P2 structure and suppress phase transformations during electrochemical cycling as indicated by the smoothed CV curve. The dopants, Si, B, Mo, and W, however, preserve the co-operative Jahn-Teller distortion for Mn^{III} (t_{2g}³-eg¹), which leads to the P'2 phase and multiple peaks observed on CV.

Even though the conventional view concerning P'2 materials is that multiple sub-phase transitions lead to degradation of the battery, we still found the promising dopants such as Si, B, and Mo can stabilize the distorted structure with comparable electrochemical properties. Mo-doped sample delivers 168 mAh g⁻¹ first discharge capacity with 98 % retention after 10 cycles. Moreover, the serendipity in this work demonstrated a number of previously unstudied (or understudied) dopants such as Ga, B, Si, Rb, Mo, In, Re, Cs, Tl, and Tb lead to promising novel battery materials.

Beyond simply uncovering promising new materials, exploratory data analysis was utilized to explore correlations over the periodic table. For the capacity booster, the anionic redox triggered by various dopants were identified and investigated, which exhibits the similar trend with calculated bond-valence mismatch for the octahedral MO₆. Considering that the air/moisture instability of Mn-containing Na cathodes is a crucial roadblock to commercialization, accelerated aging tests provide an invaluable guideline for designing stable materials. The co-doping study demonstrates that as little as 5 % Li-codoped samples, Na_{0.66}Mn_{0.9}Li_{0.05}Co_{0.05}O₂, for example, substantially improve the air stability to over 99 % structure retention, compared to 0 % in the

undoped P2 NMO in a one-month aging regimen. We have demonstrated that a small content of subvalent dopants such as Li, Mg, and Cu are sufficient to dramatically enhance the air stability.

In sum, through the high-throughput method and data-driven exploration, this study successfully provided many novel insights towards higher energy density, fast charging, and more-air-stable cathode materials in sodium-ion batteries. These new understandings among the chemical compositions, crystal structures, air/moisture stability, and electrochemical properties can lead to new methodologies of rational material design and development.

Supplemental Information

Supporting information associated with this paper is available online. Figures S1-S9; Tables S1-S2.

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TOC graphic:

