Co-Sintering Study of Na$_{0.67}$[Ni$_{0.1}$Fe$_{0.1}$Mn$_{0.8}$]O$_2$ and NaSICON Electrolyte–Paving the way to High Energy Density All-Solid-State Batteries

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Sodium is a promising candidate for stationary storage applications, especially when the demand for lithium-ion batteries increases due to electromobility applications. Even though its energy density is lower, Na-ion technology is estimated to lead to a cost reduction of 30% compared to Li-ion technology. To improve safety as well as energy density, Na-based all-solid-state-batteries featuring solid electrolytes such as beta-alumina and sodium superionic conductors and cathode materials such as Na$_3$V$_2$(PO$_4$)$_3$ and Na$_x$CoO$_2$ have been developed over the past years. However, the biggest challenge are mixed cathodes with highly conductive interfaces, especially when co-sintering the materials. For example, a promising sodium superionic conductor type Na$_3$Zr$_2$Si$_2$PO$_{12}$ electrolyte sinters at 1,250°C, whereas the corresponding Na$_3$V$_2$PO$_{12}$ cathode decomposes at temperatures higher than 900°C, posing a bottleneck. Thus in this paper, we synthesized Na$_{0.62}$[Ni$_{0.1}$Fe$_{0.1}$Mn$_{0.8}$]O$_2$ as cathode material for all-solid-state sodium-ion batteries via a relatively cheap and easy solution-assisted solid state reaction processing route. The thermal investigations of the pure cathode material found no degradation up to 1,260°C, making it a perfect match for Na$_3$Zr$_2$Si$_2$PO$_{12}$ electrolyte. In our aim to produce a co-sintered mixed cathode, electron microscopy investigation showed a highly dense microstructure and the elemental mapping performed via energy dispersive X-ray spectroscopy and secondary ion mass spectrometry confirm that Na$_3$Zr$_2$Si$_2$PO$_{12}$ and Na$_{0.62}$[Ni$_{0.1}$Fe$_{0.1}$Mn$_{0.8}$]O$_2$ do not react during sintering. However, the active cathode material forms a sodium rich and a sodium deficient phase which needs further investigation to understand the origin and its impact on the electrochemical performance.

Keywords: sodium, NASICON, solid electrolyte, solid-state-batteries, composite cathode
INTRODUCTION

In recent decades, lithium-ion batteries (LIB) have seen a significant increase in their technological advancement and economical importance (Zubi et al., 2018; Zeng et al., 2019; Avicenne, 2020). Their application in portable devices such as e.g., phones, household tools, and electric vehicles requires high performance as well as a high degree of safety. One approach to increase safety and energy density is by replacing the liquid with a more mechanically stable, heat and voltage resistant solid electrolyte (McKissock et al., 2008; Finsterbusch et al., 2018). These so-called solid-state batteries (SSB) are at the initial stages of development which means more and more research is being carried out to develop cheaper and safer battery technology. Additionally, the environmental friendliness of LIB is also a concern due to the mining of raw materials and the carbon footprint involved in their production. While energy storage is not a general solution without de-carbonization of electricity generation, long cycle stability and the pursuit of finding environmentally friendly alternatives to lithium are significantly important (Larcher and Tarascon, 2015; Peters et al., 2016). Among alternatives, sodium is a promising candidate as it is 1,000 times more abundant than lithium in the Earth’s crust, and this does not include seawater sodium. A high abundance leads to low material cost, e.g., Na₂CO₃ is approx. 60 times cheaper than Li₂CO₃ and the gap is widening with increasing demand for LIBs (Peters et al., 2019). In terms of performance, sodium is three times heavier than lithium (23 g mol⁻¹ compared with 6.9 g mol⁻¹), and 0.3 V less electropositive, which means that gravimetric and volumetric penalties (~15%) are unavoidable. This makes sodium batteries ideal for applications where energy density is not the highest ranking performance indicator, e.g., in stationary storage applications (Yabuuchi et al., 2014). Especially, since early estimations for Na-ion technology forecast a cost reduction of 30% as compared to Li-ion technology (Larcher and Tarascon, 2015).

To combine both approaches, Na-SSBs featuring solid electrolytes such as beta-alumina and NaSICON (Ma and Tietz, 2020) and cathode materials such as Na₃V₂(PO₄)₃ (Gopalakrishnan and Rangan, 1992) and Na₂CoO₂ (Doeff et al., 1995) have been developed over the past years. The biggest challenge for SSB technology however is to fabricate a mechanically, electrochemically, and chemically stable electrode-electrolyte interface. Most of the available electrode and electrolyte materials have different sintering temperatures and different thermal expansion coefficients. This causes delamination of interfaces when cathode and electrolyte are co-sintered. For example, a promising NaSICON type Na₃Zr₂Si₂PO₁₂ electrolyte sinter at 1,250°C, whereas the corresponding NaSICON type Na₃V₂PO₁₂ cathode decomposes at temperatures higher than 900°C, posing a bottleneck (Lalère et al., 2014; Lan et al., 2019). Furthermore, research has gone into improving the contact between electrolyte and electrode, e.g., through laminating by applying a soft interlayer of polymers (Gao et al., 2018) or ionic liquids (Liu et al., 2016; Zhang et al., 2017). Although somewhat successful, the materials challenges associated with the interfaces in these systems still remains the major hurdle for achieving high-temperature stability and high voltage all-solid-state batteries with polymer or liquids. Ultimately, co-sintering remains the best option to fabricate a fully inorganic ASSB without the necessity for liquid or gel type additive in any form. The following characteristics are needed to obtain good inorganic cells (Inoishi et al., 2017):

1) Electrolyte and cathode should have similar sintering temperatures (if not the same),
2) Have similar thermal expansion coefficient to avoid cracking and
3) Be chemically stable.

An inherent problem of these systems, however, is the volume expansion and contraction of the active cathode material as Na ions are intercalated and de-intercalated during charging- and discharging-cycles (Zhang et al., 2017). The rigid electrode/electrolyte interface cannot sustain the constant volume change that leads to crack formation and increased polarization, which eventually degrades the cell capacity (Ma et al., 2019). One way to overcome this issue is by using a cathode material that has a negligible volume change during cycling. One such material has recently been reported by Choi et al. i.e., Na₆[Ni₀.₁Fe₀.₁Mn₀.₈]O₂ and it has a volume change of only 3.3% during cycling (Choi et al., 2020).

Mn-based materials are low cost and simple to manufacture (Yabuuchi et al., 2014). Various MnO₂ based materials were investigated in detail for liquid based cells, e.g., by the Minakshi group (Minakshi and Ralph, 2013). The crystal structures and a Na-ion insertion/extraction-ability of sodiated manganese oxide (Na₁₋ₓMnO₂) were earlier reported by Parent et al., (Parant et al., 1971). Among them, P’2-NaₓMnO₂ is stable even at temperatures as high as 1,000–1,200°C (Stoyanova et al., 2010), which is similar to that of NASICON solid electrolyte. This material has an initial discharge capacities of ~200 mA h g⁻¹ in the voltage range of 1.5–4.4 V (Kumakura et al., 2016) when cycled at ~2.7 V (Choi et al., 2020). However, this material suffers strong volume changes during desodiation process and this structural instability leads to a gradual capacity fading (Choi et al., 2018; Choi et al., 2019). Choi et al. (Choi et al., 2020) recently reported that by doping Mn with Ni and Fe in P’2-NaₓMnO₂, volume change is reduced to only ~3.3% when cycled between fully sodiated and desodiated states. The composition of fully sodiated and desodiated state is P’2-Na₀.₉[NaₓFe₀.₁Mn₀.₈]O₂ and OP4-Na₀.₀₇[NaₓFe₀.₁Mn₀.₈]O₂ and their structure is shown in Figure 1. We opted for P’2-Na₀.₆₇[NaₓFe₀.₁Mn₀.₈]O₂ (NNFM) due to its high thermal and cycling stability and the high discharge capacity of 220 mA h g⁻¹ reported in literature (Choi et al., 2020).

Among solid electrolytes, we chose a NASICON type composition Na₃Zr₂Si₂F₆O₁₂ (NZSiP) that has a conductivity of 5 mS cm⁻¹ at room temperature (Ma et al., 2019). The sintering temperature of NZSiP is between 1,200 and 1,300°C, which matches the thermal stability window of NNFM. Therefore, we attempted to co-sinter the NNFM and NZSiP. In this study, we have investigated the thermal and
chemical stability of NNFM as cathode and NZSiP as electrolyte material to fabricate a mixed cathode for potential use in all-solid-state battery.

MATERIALS AND METHODS

**Na₃.4Zr₂Si₂.4P₀.6O₁₂ Synthesis**

NZSiP was synthesized using the solution-assisted solid-state-reaction (SA-SSR) (Ma et al., 2016). Stoichiometric amounts of NaNO₃ (Merck, ACS), ZrO(NO₃)₂·xH₂O (Sigma-Aldrich, techn. grade), Tetraethyl orthosilicate (Merck, ≥ 99%) and NH₄H₂PO₄ (Merck, ACS) were dissolved in deionized water at room temperature. The solution with formed precipitates was dried at 70°C and calcined at 800 °C for 4 h with a heating and cooling rate of 5 K/min in air. The calcined powder was finally ball milled with a mixture of 3 and 5 mm zirconia balls (50:50 by weight) in ethanol for approx. 72 h or until a median particle size of 1–2 μm was reached.

**Na₀.6₇[Ni₀.₁Fe₀.₁Mn₀.₈]O₂ Synthesis**

Na₀.6₇[Ni₀.₁Fe₀.₁Mn₀.₈]O₂ was synthesized via a SA-SSR route (Ma et al., 2016). Stoichiometric amounts of Ni(NO₃)₂·6 H₂O (VWR, ACS), Fe(NO₃)₂·9 H₂O (VWR, ACS), Mn(NO₃)₂·4 H₂O (Merck, EMSURE), and NaNO₃ (Merck, ACS), with a 10% excess of Na to compensate for sodium loss, were dissolved in deionized water at room temperature. The solution was dried while stirring on a hotplate at 100°C. As described by Choi et al., (Choi et al., 2020), the formed powder was calcined at 500°C to remove the nitrates. Afterward, the powder was ground with mortar and pestle before calcining again at 800°C. Finally, the powder was uniaxially pressed into pellets with 13 mm diameter at 100 MPa for 2 min and further sintered at 1,200°C for 10 h or 1,260 °C for 6 h in air.

The calcined powders of NZSiP and NNFM were mixed in a weight-ratio of 1 to 1 and ball milled together with a mixture of 3 and 5 mm ZrO₂ balls (50:50 by weight) in ethanol for 24 h. The resulting material was uniaxially pressed into pellets of 13 mm diameter with 100 MPa and sintered at 1,200°C for 10 h or
and subsequent sintering at 1,260 °C. The terminal faces were ground and with addition of 2 ml HF were filled to 50 ml. Of each sample two measurements were conducted with 1/100 and 1/10 dilution. The behavior of the powder on heating in artificial air (mixture N2/O2 of 80/20) was investigated by DTA/TG-MS (Netzsch, STA449 F1 Jupiter, and QMS 403C Aëolos). The crystal structure of Na0.67[Ni0.1Fe0.1Mn0.8]O2 was confirmed by X-ray diffraction (XRD, Bruker D4 ENDEAVOR diffractometer with Cu Kα-radiation).

Shrinkage behavior during sintering was investigated with dilatometry (402C Netzsch, Germany) on specimens prepared from powder precursors by uniaxial pressing at 100 MPa into round pellets of 8 mm diameter. Thermal expansion coefficient was investigated by push-rotdilatometer 402C from Netzsch, Germany, calibrated with a sapphire single crystal. NNFM and NZSiP specimens were prepared from powder precursors by uniaxial pressing at 150 MPa into a rectangular shape (40 mm × 5 mm × 3–5 mm) and subsequent sintering at 1,260°C. The terminal faces were then cut and polished to a sample length of 25 mm and then measured.

The co-sintered composite was further investigated with SEM and EDX (Carl Zeiss NTS GmbH, Zeiss Ultra 55 and Zeiss Supra 50 VP3). TOF-SIMS analysis were performed by using TOF-SIMS V system (ION-TOF GmbH, Münster, Germany). The measurements were done in a dual beam setting (Iltgen et al., 2017) in non-interlaced mode (Dellen et al., 2016). For the materials erosion, a 1 keV oxygen ion beam was rasterized over an area of 300 μm2 × 300 μm2. For generation of analyzed secondary ions, a focused 25 keV Bi3 ion beam was used and the Bi ion gun was operated in the high current bunch mode. The analyzed area was 50 μm2 × 50 μm2 and centered within the sputter crater to avoid crater edge effects. Between the sputtering and analysis pulses, a low energy (20 eV) electron flood gun was used to compensate for sample charging during the sputter processes. The data analysis was carried out by using Software package SurfaceLab 6 (ION-TOF GmbH).

RESULTS AND DISCUSSION

Chemical Composition
The compositions determined by ICP-OES of NNFM after heat treatment at 500, 800, and 1,200°C are shown in Table 1. It confirms a minimal loss of ~1 mol% Na after calcining at 800°C, considering an experimental error of ± 3%. A higher 10 mol% Na loss is observed after sintering at 1,200°C and is due to the evaporation of sodium oxide and in agreement with (Choi et al., 2020). This is the reason why an excess of Na was used to synthesis the NNFM to achieve a final composition with stoichiometry close to Na0.67 [Ni0.10Fe0.10Mn0.80]O2. Furthermore, for NZSiP, the elemental analysis confirmed a composition of Na3.43[Si2.51(18)P0.59(3)]O12 even after 1,260°C for 6 h.

Thermal Stability
To study the thermal stability of NNFM/NZSiP co-sintered samples, we first performed DTA/TG-MS analysis of a NNFM powder pre-calcined at 500°C as shown in Figure 2A. A gradual weight loss of around 3% up to 550°C is observed due to the removal of absorbed moisture and CO2. A sharp weight loss is subsequently observed around 600°C which corresponds to a decomposition of sodium nitrate (Gordon and Campbell, 1955; Yuvraj et al., 2003). From 800°C onwards, no further weight loss is observed which verifies the thermal stability of NNFM up to 1,200°C. For this reason, NNFM was calcined at 800°C to prepare a precursor material which can be subsequently used for co-sintering with the NZSiP. The calcined NNFM was then mixed with calcined NZSiP in a 50/50 ratio (w/w) and DTA/TG-MS analysis of the mixture was done. Figure 2B shows again a

![Figure 3](image-url)
gradual weight loss up to around 600°C due to removal of moisture and CO₂. Around 800°C we can observe another minor weight loss which could be due to oxidation of still leftover nitrates and a mass loss of just over 1% can be observed around 1,200°C. The high temperature mass loss is minor weight loss which could be due to oxidation of still leftover nitrates and a mass loss of just over 1% can be observed around 1,200°C. The high temperature mass loss is reversible, as we can see from the cooling curve. Therefore, this is most likely from oxygen removal in the oxide phase, which reinserts during cooling. However, measurements were performed in air, so oxygen removal from the sample could not be measured. Overall, DTA/TG-MS indicates no decomposition or reaction of the two materials.

The shrinkage behavior of an NZSiP and NNFM composite is shown in Figure 3. An overall shrinkage of more than 35% confirms a very good co-sinterability of these two materials.

**Coefficient of Thermal Expansion**

To further investigate the co-sinterability, the thermal expansion curve of the NNFM/NZSiP composite was measured on pre-sintered samples as shown in Figure 4. The hysteresis in the cooling and heating curves of the two samples indicate the influence of micro-cracks, which has already been described elsewhere (Naqash et al., 2018). The linear coefficients of thermal expansion CTE of NNFM and NZSiP were calculated using Eq. 1. The thermal expansion curve was linear only in the temperature range (ΔT) of 200–900°C therefore only the change of length (ΔL) during this temperature range was used. Here L₀ is the original length.

\[
\text{CTE} = \frac{\Delta L}{\Delta T \cdot L_0} \tag{1}
\]

NNFM has a CTE of around 16·10⁻⁶ K⁻¹ which is about 2.5 times the CTE of NZSiP. We observed minimal cracking between the NNFM and NZSiP grains in the microstructure of the NNFM/NZSiP composite (see microstructure section Figure 5). This is surprising since the CTE values are independent of crystal orientation. If the crystal anisotropy is considered, an even stronger CTE mismatch and therefore very high residual stresses in the composite could be expected (Mücke et al., 2021). Still, this difference in the CTE appears to be within an acceptable range that the mismatch can be tolerated.

**Crystal Structure**

The crystallographic investigations via XRD reveal that NNFM is only partially adapting a P'2-type Na0.67[Ni0.1Fe0.1Mn0.8]O2 crystal structure after calcination at 800°C (Figure 6B). A minor side phase can be observed showing a peak at 16.6° 2θ, which is unidentified due to its very low intensity. After sintering at 1,200°C, NNFM is fully crystallized and adapts a pure P'2 phase, as expected from (Choi et al., 2020). Furthermore, our investigation also reveals that pure NNFM is stable even up to 1,260°C and forms the desired phase (Figure 6C), which, to our knowledge, has not been reported so far.

After confirming the thermal stability of NNFM, the phase stability of NZSiP/NNFM composite was investigated and is shown in Figure 6. The green pellets of mixed cathode with 50:50 wt. ratio of NZSiP and NNFM were sintered at 1,200°C, shrank by 20% laterally and resulted in highly dense composite with approx. 98% of relative density. This is assuming a perfect 50:50 mixture by weight and theoretical densities of 3.27 and 4.11 g/cm³ for NZSiP and NNFM, respectively. The XRD of the polished cross-section of this pellet in Figure 6 shows the NZSiP and the NNFM phases are fully crystallized after co-sintering at 1,200°C for 10 h in air. However, secondary phases also seem to be forming. The unidentified reflections can be matched with spinel phase (Ni, Fe, Mn)₂O₄ (space group 227: Fd-3m; ICSD: 085807) and with Na₂ZrSiO₅ [space group 14: P21/c; (Wilson and Glasser, 1987)]. While the formation of the spinel phase could explain the appearance of a low sodium NNFM phase (described in Interdiffusion and Side Phases), neither EDX nor SIMS can detect another phase formation. Therefore, it is more likely, that NZSiP partially crystallizes in the P21/c space group when co-sintered together with NNFM. Further investigation is necessary to understand what this means for the electrochemical performance. Such secondary phases might have a detrimental effect, if they impede the ionic or electronic conductivity or cannot be re-sodiated. After sintering the composite at 1,260°C for 6 h in air, the specimen was deformed, which could be due to a partial melting of either NNFM, NZSiP or a combination of glass-forming elements that do not generate x-ray reflections. This phenomenon is in agreement with the findings of computational studies by Miara et al. for lithium battery materials, where they used lithium potential to predicted the cathode-electrolyte stability (Richards et al., 2016). They observed that generally the electrolyte materials that are predicted to be stable at the cathode voltage show low reaction energies as they come entirely from the mixing of cathode and electrolyte compositions and do not involve redox activity. The same can be translated to increased reactivity and mobility of charge carriers in the NNFM/NZSiP composite at the interface at
extreme sintering temperatures. Therefore, we proceeded with our investigation on co-sintered material processed at slightly reduced temperature of 1,200°C.

Microstructure
The microstructure of NNFM/NZSiP composites after sintering at 1,200°C for 10 h in the air is investigated via SEM and shown in Figure 5, where a high densification is evident. The two phases NNFM and NZSiP in the composite are clearly distinguishable with a brightness difference in the backscattered scanning electron images (Figure 5B). The NZSiP appears slightly brighter compared to the NNFM since it has a higher mean atomic number ($Z_{\text{NZSiP}} = 20.3$ and $Z_{\text{NNFM}} = 17.8$). The presence of only a few cracks—which seemingly propagate more through grains rather than along grain boundaries as highlighted by the arrows—and few voids are also visible indicating a relatively good contact between the grains of two phases. The overall microstructure gives an impression that NNFM and NZSiP phases have a good adhesion. The cracks are formed during the cooling step of the sintering process that generates high stresses at the intergranular interface due to the high anisotropic nature of these compounds. The formation of cracks is minimized by a slow cooling rate of 5 K/min and it can also be further reduced.

Interdiffusion and Side Phases
To investigate intergranular diffusion of cations between NNFM and NZSiP or a reaction at their interface, elemental mapping was performed on the polished cross section of NNFM/NZSiP sintered composite using the EDX and TOF SIMS and the results are shown in Figures 7, 8. The major cations of NZSiP are Zr and Si and that of NNFM are Mn, Ni and Fe. In the elemental mapping, a distinct difference between Zr-Si (b-c) and Mn-Ni-Fe (d-f) shows no evidence of intergranular elemental diffusion. Both grains have sharp phase boundaries indicating the likelihood of any reaction is low even though XRD indicates unidentified phases. Both EDX and SIMS show that NASICON phase is uniform throughout the analyzed area. However, the areas where NNFM is expected, Na elemental maps show two distinct regions of higher and lower transition metals concentration, as evident in Figures 7A,D–F. These two regions also correlate to varying Na signal as indicated by arrows in EDX mapping Figure 7A and SIMS mapping.
**FIGURE 7** | Elemental analysis of NNFM/NaSICON co-sintered specimen using EDX. Arrows highlighting Na rich (blue) and Na poor (red) NNFM regions.

**FIGURE 8** | SIMS analysis results of co-sintered NNFM/NZSiP specimen. Arrows highlighting Na rich (blue) and Na poor (red) NNFM regions.
Figure 8A. In EDX images, two distinct phases of NNFM are seen i.e., a Na-containing and non-Na-containing phase. However, in SIMS, which is a more sensitive analysis technique, it is seen as both NNFM phases have Na but of different content. Although stable when sintered individually, apparently the pre-calcined powder crystallizes into a sodium rich NNFM phase and a sodium deficient NNFM when sintered with NaSICON. This is in agreement with XRD findings (Figure 6) where an additional phase formation was observed. The lack of sodium could also be partially attributed to its evaporation upon prolonged exposure to high temperatures, which is 10 h at 1,200°C in these samples. Further investigations are however required to fully understand and prevent this phenomenon. Since no diffusion of any other element is observed aside from sodium content, both EDX and SIMS confirm the stability of NZSiP and NNFM. Any reaction of NZSiP and NNFM would have led to intergranular elemental diffusion of elements. This is clearly seen by sharp intergranular boundaries and no concentration gradient when Zr and Mn maps of EDX and SIMS are overlaid in Figure 9.

CONCLUSION

We successfully synthesized a pure NNFM as cathode material for all solid state sodium-ion batteries via a relatively cheap and easy processing route SA-SSR. Contrary to conventional sol-gel synthesis, which uses chelating agents such as citric acid and sucrose, we were able to produce phase pure P’2-type Na0.62[Ni0.10Fe0.10Mn0.80]O2 without the need of burning off carbonaceous material and emitting extra CO2, making this a cheap and industrially scalable method for active materials production for Na-SSBs. The thermal investigations of NNFM found no degradation up to 1,260°C. However, co-sintering NNFM with solid electrolyte NZSiP at 1,260°C led to partial melting, showing similar trends as their Li-counterparts where the active-material/solid-electrolyte mixtures are less stable than the individual components. When sintered at a slightly reduced sintering temperature of 1,200°C for 10 h, the composite cathode shrank by almost 35% in volume. No significant intergranular cracks were observed, which shows that the measured CTE of NNFM, which is 2.5 times that of NZSiP, is within an acceptable range. The elemental mapping performed via EDX and SIMS confirm that NZSiP and NNFM do not react during sintering, however, NNFM forms a sodium rich and a sodium deficient phase. Further investigation is required to understand this phenomenon and its impact on the electrochemical behaviour of the cathode, which will be investigated in the future. In conclusion, NNFM appears to be a promising candidate for fabricating mixed cathodes for all-solid-state sodium-ion battery as it can be co-sintered together with most promising NASICON type NZSiP.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

GD and SN designed the experiments, synthesized the materials and are main authors of the manuscript. SN and UB gave excess to and performed SIMS measurements and analysis. MF, OG and DF edited the manuscript and gave valuable advice. All authors approved the submitted version.

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REFERENCES

Avicenne (2020). "The Rechargeable Battery Market 2019-2030". 28th (2020) ed. Paris: Avicenne Energy).

Choi, J. U., Jo, J. H., Park, Y. J., Lee, K. S., and Myung, S. T. (2020). Mn-Rich P2'-Na0.67[Ni0.2Fe0.8Mn0.2]O2 as High-Energy-Density and Long-Life Cathode Material for Sodium-Ion Batteries. Adv. Energ. Mater. 10 (27), 1–10. doi:10.1002/aenm.202001346

Choi, J. U., Park, Y. J., Jo, J. H., Kuo, L.-Y., Kagahachi, P., and Myung, S.-T. (2018). Unraveling the Role of Earth-Abundant Fe in the Suppression of Jahn-Teller Distortion of P2'-Type Na2S3Mn2O6: Experimental and Theoretical Studies. ACS Appl. Mater. Inter. 10, 40978–40984. doi:10.1021/acsami.8b16522

Choi, J. U., Yoon, C. S., Zhang, Q., Kagahachi, P., Jung, Y. H., Lee, K.-S., et al. (2019). Understanding on the Structural and Electrochemical Performance of Orthorhombic Sodium Manganese Oxides. J. Mater. Chem. A. 7, 202–211. doi:10.1039/c8ta08796b

Dellen, C., Gehre, H.-G., Möller, S., Tsai, C.-L., Breuer, U., Uhlenbruck, S., et al. (2016). Time-of-flight Secondary Ion Mass Spectroscopy Study of Lithium Intercalation Process in LiCoO2 Thin Film. J. Power Sourc. 321, 241–247. doi:10.1016/j.jpowsour.2016.04.084

Doeff, M. M., Visco, S. J., Yanping, M., Peng, M., Lei, D., and De Jonghe, L. C. (2010). Room-Temperature Demonstration of a Sodium Superionic Conductor with Grain Conductivity in Excess of 0.01 S cm–1 and its Primary Applications in Symmetric Battery Cells. J. Mater. Chem. A. 7, 7766–7776. doi:10.1039/c9ta00448

Mckissock, B., Lonselle, P., and Vogel, E. (2008). Guidelines on Lithium-Ion Battery Use in Space Applications. Cleveland, Ohio: Glenn Research Center.

Minakshi, M., and Ralph, D. (2013). A Novel Sodium-Ion Rechargeable Battery. ECS Trans. 45, 95–102. doi:10.1149/04529.0905ecst

Mücke, R., Finsterbusch, M., Kagahachi, P., Fattakhova-Rohlfing, D., and Guillon, O. (2021). Modelling Electro-Chemical Induced Stresses in All-Solid-State Batteries: Anisotropy Effects in Cathodes and Cell Design Optimisation. J. Power Sourc. 489, 1–9. doi:10.1016/j.jpowsour.2020.229430

Naqash, S., Gerhards, M.-T., Tietz, F., and Guillon, O. (2018). Coefficients of Thermal Expansion of Al- and Y-Substituted NaSICON Solid Solution Na3+x2AlXyZr2-x2Si2PO12. Batteries 4, 03390. doi:10.1139/batteries4033903

Parant, J.-P., Olazcuaga, R., Devalette, M., Fouassier, C., and Hagemüller, P. (1971). Sur quelques nouvelles phases de forme Na3MnO2 (x < 1). J. Solid State. Chem. 3, 1–11. doi:10.1016/0022-4596(71)90001-6

Peters, J., Buchholz, D., Passerini, S., and Weil, M. (2016). Life Cycle Assessment of Sodium-Ion Batteries. Energy Environ. Sci. 9, 1744–1751. doi:10.1039/c6ee00640j

Peters, J. F., Peña Cruz, A., and Weil, M. (2019). Exploring the Economic Potential of Sodium-Ion Batteries. Batteries 5 (1), 1–15. doi:10.3390/batteries5010010

Richards, W. D., Miara, L. J., Wang, Y., Kim, J. C., and Ceder, G. (2016). Interface Stability in Solid-State Batteries. Chem. Mater. 28, 266–273. doi:10.1021/acs. chemmater.5b04082

Stoyanova, R., Carlier, D., Sendova-Vassileva, M., Yoncheva, M., Zhecheva, E., Ntihantova, D., et al. (2010). Stabilization of Over-stoichiometric Mn4+ in Layered Na2/3MnO2. J. Solid State. Chem. 183, 1372–1379. doi:10.1016/j.jssc.2010.04.024

Wilson, G. and Glasser, F. P. (1987). Powder Diffraction, Vol. 2 (3). Cambridge: Cambridge University Press, 176–179. doi:10.1117/12.941148

Yabuuchi, N., Kubota, K., Dahbi, M., and Komaba, S. (2013). A Novel Sodium-Ion Rechargeable Battery. Chem. Rev. 114, 11636–11682. doi:10.1021/cr500192f

Yuvanar, S., Fan-Yuan, L., Tsong-Huei, C., and Chui-Tih, Y. (2003). Thermal Decomposition of Metal Nitrates in Air and Hydrogen Environments. J. Phys. Chem. B. 107, 1044–1047. doi:10.1021/jp026961c

Zeng, X., Li, M., Abd El-Hady, D., Alshitari, W., Al-Bogami, A. S., Lu, J., et al. (2014). Ultralong Cycle Life. Adv. Mater. Inter. 27, 22329–22339. doi:10.1002/asia.8b60705

Zuber, G., Dufo-López, R., Carvalho, M., and Pasaoglu, G. (2018). The Lithium-Ion Battery: State of the Art and Future Perspectives. Renew. Sustain. Energ. Rev. 89, 292–308. doi:10.1016/j.rser.2018.03.002

Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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