Development of high-throughput methods for sodium-ion battery cathodes

Tham Adhikari, Alex Hebert, Michel Adamič, Jacqueline Yao, Karlie Potts, and Eric McCalla*

Department of Chemistry, McGill University, Montreal, H3A 0B8, Canada

* Corresponding author: eric.mccalla@mcgill.ca

Abstract

Combinatorial synthesis of Li-ion batteries has proven extremely powerful in screening complex compositional spaces for next-generation materials. To date, no Na-ion counterpart exists wherein Na-ion cathodes can be synthesized in such a way to be comparable to that obtained in bulk synthesis. Herein, we develop a synthesis route wherein hundreds of mg-scale powder samples can be made in a total time of 3 days. We focus on materials in the Na-Fe-Mn-O pseudo-ternary system of high immediate interest. Using a sol-gel method, developed herein, yields both phase-pure combinatorial samples of $Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$ and $NaFe_{1/2}Mn_{1/2}O_2$, consistent with previous reports on bulk samples of interest commercially. By contrast, the synthesis route used for Li-ion cathodes (namely co-precipitations) does not yield phase pure materials, suggesting that the sol-gel method is more effective in mixing the Na, Fe and Mn than co-precipitation. This has important consequences for all attempts to make these materials, even in bulk. Finally, we demonstrate that these mg-scale powder samples can be tested electrochemically in a combinatorial cell. The resulting cyclic voltammograms are in excellent agreement with those found on bulk samples in the literature. This demonstrates that the methodology developed here will be effective in characterizing the hundreds of samples needed to understand the complex ternary systems of interest, and that such results will scale-up well to the g and kg-scale.

Keywords: Combinatorial synthesis, X-ray diffraction, Na-ion cathode, layered oxides, high-throughput electrochemistry

Introduction

Over the past two decades, there has been a dramatic increase in the amount of energy storage required due to the current push toward the widespread use of electric vehicles and the effort to develop storage systems capable of supporting a large amount of intermittent renewable energies on the grid.[1] Since their commercialization 1990, lithium-ion (Li-ion) batteries have achieved great success in portable electronics and are now beginning to make electric and hybrid vehicles attainable.[2] The high demand of Li-ion batteries raises concerns on its sustainability, primarily due to the limited supply and uneven geographical distribution of lithium. As such, rechargeable batteries consisting of cost-effective and naturally abundant electrode materials are becoming an appealing choice for next-generation energy storage systems. Given sodium's high natural abundance, sodium-ion (Na-ion) batteries are considered to be a promising alternative to replace Li-ion batteries in portable electronics. [3] However, as the performance of Na-ion batteries is not yet comparable to that of Li-ion technology, a large effort is underway to improve them. In particular, the cathode performance continues to be a limitation of this technology and continues to prompt significant research efforts in the discovery if better Na-ion cathodes. Of the classes of materials of interest for Na-ion cathodes, layered oxides have received a great deal of attention.[4] In particular, $Na_{2/3}MO_2$ (M=Fe, Mn, Ni…) in the P2 structure represent a promising material with high reversibility. In 2012, Yabuuchi *et al*. reported the solid state synthesis of P2-type $Na_{0.66}Fe_{0.5}Mn_{0.5}O_2$ that delivered 190 $mAhg^{-1}$ and demonstrated 79% capacity retention after 30 cycles.[5] Since then, there has been minimal effort to synthesize other materials in the Na-Fe-Mn-O system, with no systematic study having been performed in this important pseudo-ternary system. This is likely due to the high number of samples that would be required to characterize the entire system and the fact that no combinatorial synthesis methods have been developed for Na-ion cathodes.

Recently, a methodology was developed for the combinatorial synthesis of Li-ion cathode materials. This enabled the extensive exploration of ternary and quaternary systems of interest for Li-ion cathodes.[6-11] This method involved using a solution-dispensing robot to mix varying volumes of metal nitrates followed by a precipitator such as ammonium hydroxide. The result, after heating to high temperatures, were approximately 2 mg powder samples demonstrating the same phases as obtained in g and kg scale syntheses. One particular challenge in the combinatorial synthesis of Li-ion cathodes was the loss of lithium experienced during high temperature annealing and this had to be minimized to obtain phases relevant to bulk syntheses.[9] This methodology was used to map the entire Li-Ni-Mn-Co oxide pseudo-quaternary system, with over a thousand different samples prepared and characterized with X-ray diffraction (XRD).[8] While this study mapped the structural evolution across the phase space, it was unable to develop structure-performance relationships, as no comprehensive electrochemical characterization was performed.[12] To date, most high-throughput electrochemical studies of cathode materials have been limited to thin film cathodes[11,13-16] and electrode formulations.[17-19] Recently, a methodology was developed for high-throughput electrochemical testing of powder cathode materials wherein 64 cyclic voltammograms can be collected simultaneously at a modest rate of 0.1 Vh^{-1}.[20] The strength of this methodology was demonstrated by the electrochemical mapping of the entire Li-Mn-Ni-O system, to complement its structural mapping performed in 2013.[21] The specific capacities measured with this cell have a standard deviation of about 7.5 % and is a result of how the electrodes are prepared. As such, this variability in capacity will not differ in a Na-ion cell.

However, severe overpotentials may occur if Na metal is used instead of Li metal as the couter/reference electrode, it is therefore important here to confirm that Na-ion cathodes can cycle effectively in the combinatorial cell yielding peak potentials comparable to that seen with bulk samples and specific capacities with comparable standard deviations as those obtained in the Li-ion combinatorial cells.

Herein, we develop a high-throughput method for the synthesis of Na-Fe-Mn-O mixed oxide materials heavily studied as Na-ion cathodes (this is similar to that done for Li-ion cathodes).[8,9] The particular challenges that need to be overcome here are Na loss during synthesis and poor mixing of the Na, Mn and Fe prior to high temperature sintering. Furthermore, the cell used in ref. [20] will be tested here with two Na-Fe-Mn-O materials made by the newly developed sol-gel combinatorial synthesis in order to ensure that Na-ion cathodes can be cycled effectively in high-throughput. Both of these contributions are absolutely essential to ensure that the combinatorial approach will prove effective in both understanding the structural phase diagrams and screening battery performance.

Experimental

Synthetic Method

Two synthesis routes were thoroughly tested. First, a co-precipitation method was used to make combinatorial samples (here, combinatorial samples are powders on the order of 2-5 mg each) of both $Na_{0.66}Fe_{0.5}Mn_{0.5}O_2$ and $NaFe_{0.5}Mn_{0.5}O_2$. In this method, stoichiometric amounts of sodium, iron and manganese nitrate precursors (~2M) were dispensed with the solution-dispensing robot (Opentrons OT-2). Excess amounts of precipitator (either ammonium hydroxide or ammonium bicarbonate) were then added to each sample. 10% excess sodium was used to avoid sodium loss (these amounts are consistent with that typically used in bulk syntheses).[22] The samples were preheated at 60°C to dry the samples, then heated in box furnace (various temperatures and times were tested). The second synthesis method tested was to use the sol-gel approach to first make a Na, Fe and Mn citrate gel. As in the co-precipitation method, stoichiometric amounts of nitrate precursors were first dispensed with the solution dispensing robot. Citric acid (2M, 2:1 ratio of citric acid to metal cations) was then dispensed to each of the samples. This synthesis was performed in a 96-well plate using an OT-2 robot as shown in Figure 1. Samples were heated at 60°C overnight to form the gel. The resulting gels were crushed into powders and transferred to an alumina plate for high-temperature heating, as shown in Figure 1d. The samples were pre-heated at 400°C for 2h to decompose the nitrates and remaining citric acid. Finally, the samples were heated to high temperature (various temperatures between 750 and 950°C for times ranging from 3 to 12h). The heating was again performed in a box furnace in air (though use of a tube furnace under flowing oxygen was also tested). Sol-gel samples were also prepared on the g-scale (bulk samples) to ensure the feasibility of scale-up from the combinatorial scale. The bulk samples were synthesized using a sol-gel synthesis where nitrate precursors and citric acid were heated at 100°C with constant stirring for 20 minutes, pressed into pellets and then annealed at 850°C for 12h.

Characterization

The morphologies of the materials were determined using a scanning electron microscope (Hitachi SU-8020). Powder X-ray diffraction (PXRD) patterns of the as–prepared samples were collected using a Bruker D8 Discover X-ray diffractometer with a Cu source in the scattering angle range from 10-90° with step size 0.02°. Lebail fits were performed to extract lattice parameters using the software Rietica. The elemental composition of the samples was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 8300, PerkinElmer).

Electrochemical tests were performed in the combinatorial cell. The electrolyte used was 1M sodium perchlorate in propylene carbonate with 2% fluoroethylene carbonate, glassy fiber filters were used as the separator and sodium metal as the anode. Electrochemical characterization was performed by performing cyclic voltammograms (CV) between 1.5-4.3 V vs. Na/Na^+ on a Neware battery tester. The combinatorial electrochemical data was collected using an in-house assembled potentiostat described elsewhere[23]. Two cells were assembled, each with a checkerboard pattern such that half the cells contained $NaFe_{0.5}Mn_{0.5}O_2$ and the other half contained $Na_{0.66}Fe_{0.5}Mn_{0.5}O_2$. The first cell was cycled repeatedly using a scan rate of 0.1 V h^{-1}. The second cell was cycled with the following sequence of sweep rates: 0.05, 0.1, 0.2, 0.4, 1.4, 2.8 and 5.6 V h^{-1}. This sequence was used to test the rate performance of the electrodes. The combinatorial electrochemical cell was based on a design developed by the Dahn lab[23] and recently adapted for use with Li-ion cathode powders in the McCalla lab as described in detail in Ref. [20]. The primary objective of using the combinatorial electrochemistry here is to demonstrate that good cycling performance can be obtained for Na cathodes in high-throughput and that the cell-to-cell variation in capacity of about 15 mAh/g achieved in the Li cells could also be achieved for Na combinatorial cells thereby ensuring useful screening of potential cathodes. No significant changes to the method developed in Ref. [20] was required here, except for the use of Na metal as the anode and the Na containing electrolyte used. The two materials synthesized in this work (namely $Na_{0.66}Fe_{0.5}Mn_{0.5}O_2$ and $NaFe_{0.5}Mn_{0.5}O_2$) were arranged in a checkerboard fashion on the 8x8 test plate in order to verify that no contamination between neighboring cells takes place.

Results and Discussions

Material Characterization

X-ray diffraction patterns of both combinatorial and bulk samples of P2-$Na_{0.66}Fe_{0.5}Mn_{0.5}O_2$ synthesized by co-precipitation and sol-gel method are shown in Figure 2a. This shows that all peaks index well to the P2 structure (red vertical lines), though the co-precipitation sample on the combinatorial scale shows an extra peak at about 41° that we attribute to $NaFeO_2$ or a $NaFeO_2$-like phase. The fact that the combinatorial co-precipitation sample shows an impurity phase not seen in previous studies[5] reveals poor mixing of Na, Fe and Mn in the precursor phase (after the co-precipitation). It should be noted that this impurity phase appeared in all of the combinatorial syntheses attempted by co-precipitation (we varied all the parameters that were of import in the Li-ion counterparts: temperature, time, atmosphere, precipitator used). The bulk co-precipitation sample in Figure 1a shows no contamination phase, but it must be emphasized that a mixing step was added after the co-precipitation (ball mill or mortar and pestle). Only combinatorial samples made by the sol-gel method demonstrated a phase-pure product that is consistent to that published in the literature for these compositions.[4,5] Figure S1a similarly shows that this was the case for the second key composition in the Na-Fe-Mn-O system: $NaFe_{1/2}Mn_{1/2}O_2$, only the sol-gel method yields phase pure combinatorial samples.

Furthermore, Figure 2b shows the diffraction patterns for the sol-gel samples in different synthetic temperatures and heated for various times. All samples sintered for 3h and 6 h show a tiny amount of the $NaFeO_2$-like phase, while the samples heated for 12 h are single phase. It shows hexagonal symmetry with P63/mmc space group which is isostructural with P2-type Na_xCoO_2. The XRD data were fit using the Lebail method and the resulting fits are shown in Figure 3. Clearly, the highest quality fits are obtained for the sol-gel samples. This again shows that the materials produced using the co-precipitation method are not consistent with those obtained in the literature using the solid-state synthesis route. [24] The lattice parameters are summarized in Table 1 and demonstrate that the combinatorial P2-$Na_{0.66}Fe_{0.5}Mn_{0.5}O_2$ samples can be indexed to the P63/mmc space group with lattice parameters in excellent agreement with those previously published. Lattice parameters were also extracted for the O3-$NaFe_{0.5}Mn_{0.5}O_2$ from Figure S1a. Table 1 shows that the lattice parameters detailed here differ slightly from those published previously by Yabuuchi *et al.*[5] but this can be attributed to the fact that the material in the Yabuuchi paper was not phase pure as the authors point out. This again points out the importance of performing the thorough combinatorial studies proposed herein as many compositions are required to map out the single-phase regions in these complex phase diagrams.

It is now critical to ensure that sodium loss during synthesis is not dramatically changing the compositions of the materials. This can be disastrous: in the case of Li-ion cathodes Li loss could only be mitigated by heating no higher than 800 °C in flowing oxygen. We similarly need to establish whether or not sodium loss limits the synthesis conditions that can be used for the small mg-scale samples. In particular, 12 h at 850 °C gave phase pure samples, this is potentially the ideal synthesis conditions. Table 2 shows the ICP results for the combinatorial materials made by the sol-gel method. All the samples were dispensed with 10% excess Na. Interestingly, there is no more than 10% Na loss for all samples heated at 850 ºC in air, even for 12 h. This remarkably low level of sodium loss from mg-scale samples indicates that this synthesis route does in fact yield the desired compositions as well as the desired phases as confirmed by the XRD data. At 950 °C, however, the sodium loss becomes more important after 12 h, *i.e.* the heating time that yielded phase-pure materials. We therefore identify 850 °C for 12h as the optimal conditions for combinatorial synthesis of Na-Fe-Mn-O materials as these conditions yield phase-pure materials at all compositions having been studied to date in this system. It will also be interesting to perform the combinatorial studies at lower temperatures to see how the phase diagram evolves with sintering temperature.

The final issue with respect to synthesis that must be addressed is whether these materials are stable in air. For this purpose, the series of O3-$NaFe_{0.5}Mn_{0.5}O_2$ co-precipitation samples shown in Figure S1b were stored in air under ambient conditions. No change whatsoever are seen in the XRD patterns over the course of 6 weeks. Samples in the Na-Fe-Mn-O system therefore appear to be stable, certainly over the lifetime of the combinatorial experiments.

Characterization of Battery Performance

One important factor ensuring that electrochemical measurements scale-up well is that the material obtained here using the combinatorial synthesis method must have a comparable morphology to that obtained by bulk methods (this is why high-throughput studies on thin film electrodes do not show the same performance obtained in the bulk, *e.g*. ref. [14]. Thus, prior to electrochemical tests, SEM images of the combinatorial samples were taken as shown in Figures 3d and 4. For all samples, the primary particles have flake like structure and shows few hundred nanometers particle size. In addition, the particles are agglomerated to form secondary particles on the order of 10 μm or more diameter. This is important: all commercialized electrode materials have such a morphology with large secondary particles in order to minimize the surface area contact between the electrode and the electrolyte where parasitic reactions occur. The sol-gel method therefore yields a morphology comparable to that of commercialized Li-ion cathode materials and this is considered ideal.

Electrochemical tests here were performed on the P2-$Na_{0.66}Fe_{0.5}Mn_{0.5}O_2$ and O3-$NaFe_{0.5}Mn_{0.5}O_2$ samples synthesized by the sol-gel method at 850 °C in air. A combinatorial cell with the two materials arranged in a checkerboard fashion was cycled for 7 full cycles between 1.5 and 4.3 V at 0.1 Vh^{-1} (after initial discharge to 1.5 V) and the results for the first cycle are shown in Figure 5 while the data obtained for all cycles are shown in Figure S3. The * in Figure 5 marks a small peak that is present in P2-$Na_{0.66}Fe_{0.5}Mn_{0.5}O_2$ and absent in O3-$NaFe_{0.5}Mn_{0.5}O_2$. The presence/absence of this peaks tracks through the entire checkerboard showing that contamination between neighboring pads did not occur. These CVs show redox peaks at the same potentials as those reported in the literature for P2- $Na_{0.66}Fe_{0.5}Mn_{0.5}O_2$ as summarized in Table 3. Table 4 and Figure 6a,c summarize both the average specific capacities and average voltages for both materials in this checkerboard cell. The standard deviations in both average voltage and capacity are comparable to those obtained in the Li-ion cathode tests using this same cell as reported in ref. [20]. The standard deviation for capacity in the P2 material is only about 7.6 % which is nearly identical to the 7.57 % previously obtained for $LiCoO_2$ in this same cell. This demonstrates that the combinatorial electrochemical approach demonstrated here will be as effective in screening Na-ion cathodes as it is for Li-ion counterparts.

Table 4 also compares the discharge capacities to those obtained from the literature. In the case of P2-$Na_{0.66}Fe_{0.5}Mn_{0.5}O_2$ the capacity obtained here on first discharge is slightly lower than that found in the literature but the fade with cycling is less severe such that after 7 cycles the two match perfectly (137.4 and 138 $mAhg^{-1}$). It should be noted that this capacity fade is common for this material and consistent with that reported previously (e.g. ref. [26]) demonstrating that the combinatorial cell gives comparable cycling performance to that found using traditional coin cells. The fact that the combinatorial samples show both voltages and capacities in good agreement with those of bulk samples implies that the combinatorial method will be effective in screening for first cycle energy density (the product of voltage and capacity) one of the most critical parameters in developing competitive next-generation batteries and that the results will scale-up well to large-scale syntheses used industrially. By contrast to the P2 materials, the capacities obtained here for O3-$NaFe_{0.5}Mn_{0.5}O_2$ are higher than those from the literature (140.3 vs 121 $mAhg^{-1}$ for the first cycle), and the capacity fade with cycling reported here is also less severe (91% capacity retention vs. 88% in ref. [5]). This can be attributed to the fact that the material from the literature (ref. [5]) was obtained at a lower temperature of 700 °C and showed a contaminant phase. This therefore demonstrates that the O3 materials obtained at higher temperatures may in fact be closer in performance to the P2 phases than previously reported in ref. [5]. On-going work is currently underway to screen the entire Na-Fe-Mn-O pseudo-ternary system and tracking the electrochemical performance across the O3 to P2 transition is proving of particular interest.

A second checkerboard cell was assembled and cycled between 1.5 and 4.3 V at various sweep rates. It was first discharged to 1.5 V at 0.1 Vh^{-1}. Then full cycles were performed in the following sequence: 0.05, 0.1, 0.2, 0.4, 1.4, 2.8 and 5.6 Vh^{-1}. The resulting average capacities and average voltages for each material is plotted in Figure 6c,d. It should be first noted that the drop-off in capacities here with cycling rate is severe and considerably more severe than typically seen in coin cells (e.g. refs. [5] and [26]). The increase in the difference between the average charge and discharge voltages with rate seen in Figure 6d is also indicative of poor rate performance. We attribute this very poor rate performance to the fact that only a very limited amount of mixing is possible between the active material and carbon black in making the combinatorial electrodes. This combinatorial method is therefore only appropriate at slower rates where capacities and voltages are comparable to those found in coin cells at similar rates. This rate test was therefore performed primarily to verify that 0.1 Vh^{-1} is sufficiently slow to ensure accurate screening of the active material's performance rather than being limited by the quality of the electrode mixing. For the O3 material, both 0.05 Vh^{-1} and 0.1 Vh^{-1} give very similar average capacities and average voltages as can be seen in Figure 6b,d indicating that 0.1 Vh^{-1} is in fact sufficiently slow to ensure the full capacities are obtained. For the P2 material, the comparison takes a little more care. Although the cycle at 0.05 Vh^{-1} shows a higher capacity than at 0.1 Vh^{-1}, it is in fact very close to the first cycle capacitites seen in Figure 6a at 0.1 Vh^{-1}. Therefore, the rate test in Figure 6b shows both the impact of the rate and also the poor cycling performance of the P2 material. Comparing the first cycle capacities at both 0.05 and 0.1 Vh^{-1} show excellent agreement, confirming that 0.1 Vh-1 is a sufficiently slow sweep rate to ensure that the combinatorial screening will scale-up well to experiments performed on bulk materials with well mixed electrodes.

Conclusion

A combinatorial sol-gel synthesis route was developed for the synthesis of highly stable Na-Fe-Mn-O oxide cathode materials for sodium-ion batteries. The crystal structure, elemental composition, morphology and electrochemistry of the combinatorial samples made in the mg-scale were all in excellent quantitative agreement with those reported for bulk samples in the literature. The combinatorial samples made by the sol-gel method showed single phases at both compositions reported in the literature under the conditions we now deem optimal for the combinatorial synthesis (850 °C for 12 h). Importantly, sodium loss was quite limited under these conditions and does not therefore pose any impediment to study the entire Na-Fe-Mn-O system. It is of note that sintering temperatures and times are both larger for the synthesis of Na-ion cathodes here as compared to Li-ion cathodes. This implies that much of the challenge encountered here in the synthesis may be a result of slower Na diffusion as compared to Li during high temperature synthesis. The high-throughput combinatorial electrochemistry previously developed for Li-ion cathodes was also shown to be effective in screening Na-ion cathodes. This first successful attempt to develop a combinatorial synthesis route for Na-ion cathodes now paves the way for a complete structural and electrochemical study of the pseudo-ternary system and many other important systems in the development of Na-ion batteries.

Acknowledgements

This work was funded by the Natural Sciences and Engineering Research Council of Canada under the auspices of a Discovery grant as well as an FRQNT new researcher grant. This research was also supported by funding from the McGill Sustainability Systems Initiative through the Innovation Fund.

Supporting Information

The supplemental text includes Figures S1-S4.

References

(1) You, Y.; Manthiram, A. Progress in High-Voltage Cathode Materials for Rechargeable Sodium-Ion Batteries. *Adv. Energy Mater.* **2018**, 8 (2), 1701785.

(2) Hwang, J.-Y.; Myung, S.-T.; Sun, Y.-K. Sodium-Ion Batteries: Present and Future. *Chem. Soc. Rev.* **2017**, 46, 3529–3614.

(3) Zhou, Y.-N.; Wang, P.-F.; Niu, Y.-B.; Li, Q.; Yu, X.; Yin, Y.-X.; Xu, S.; Guo, Y.-G. A P2/P3 Composite Layered Cathode for High-Performance Na-Ion Full Batteries. *Nano Energy* **2019**, 55, 143–150.

(4) Xu, J.; Chou, S.; Wang, J.; Liu, H.; Dou, S. Layered P2-Na0. 66Fe0. 5Mn0. 5O2 Cathode Material for Rechargeable Sodium-Ion Batteries. *Chem. Electro. Chem.* **2014**, 1 (2), 371–374.

(5) Yabuuchi, N.; Kajiyama, M.; Iwatate, J.; Nishikawa, H.; Hitomi, S.; Okuyama, R.; Usui, R.; Yamada, Y.; Komaba, S. P2-Type Na x [Fe 1/2 Mn 1/2] O 2 Made from Earth-Abundant Elements for Rechargeable Na Batteries. *Nat. Mater.* **2012**, 11 (6), 512.

(6) Yanase, I.; Ohtaki, T.; Watanabe, M. Application of combinatorial process to LiCo1-xMnxO2(0<X<0.2) powder synthesis. *Solid State Ionics* **2002** 151, 189–96.

(7) Fujimoto, K.; Takada, K.; Sasaki, T.; Watanabe, M. Combinatorial approach for powder preparation of pseudo-ternarysystem LiO0.5–X–TiO2 (X: FeO1.5, CrO1.5 and NiO). *Appl. Surf. Sci.* **2004,** 223, 49–53.

(8) Brown, C. R.; McCalla, E.; Watson, C.; Dahn, J. R. Combinatorial Study of the Li–Ni–Mn–Co Oxide Pseudoquaternary System for Use in Li–Ion Battery Materials Research. *ACS Comb. Sci.* **2015**, 17 (6), 381–391.

(9) McCalla, E.; Carey, G. H.; Dahn, J. R. Lithium Loss Mechanisms during Synthesis of Layered LixNi2−xO2 for Lithium Ion Batteries. *Solid State Ionics* **2012**, 219, 11–19.

(10) McCalla, E.; Rowe, A. W.; Camardese, J.; Dahn, J. R. The Role of Metal Site Vacancies in Promoting Li–Mn–Ni–O Layered Solid Solutions. *Chem. Mater.* **2013**, 25 (13), 2716–2721.

(11) Carey, G. H.; Dahn, J. R. Combinatorial Synthesis of Mixed Transition Metal Oxides for Lithium-Ion Batteries. *ACS Comb. Sci.* **2011**, 13 (2), 186–189.

(12) McCalla, E. Consequences of Combinatorial Studies of Positive Electrodes for Li-Ion Batteries. *Springer Science & Business Media*, **2014**.

(13) Fleischauer, M. D.; Dahn, J. R. Combinatorial Investigations of the Si-Al-Mn System for Li-Ion Battery Applications. *J. Electrochem. Soc.* **2004**, 151 (8), A1216–A1221.

(14) Fleischauer, M. D.; Topple, J. M.; Dahn, J. R. Combinatorial Investigations of Si-M (M= Cr+ Ni, Fe, Mn) Thin Film Negative Electrode Materials. *Electrochem. Solid-State Lett.* **2005**, 8 (2), A137–A140.

(15) West, W.C.; Whitacre, J.F.; White, V.; Ratnakumar, B.V. Fabrication and testing of all solid-state microscale lithium batteries for microspacecraft applications. *J. Micromech. Microeng.* **2001**, 12, 58–62.

(16) Warren, C.J.; Robert, C.; Haushalter, C.; Matsiev, L. Method for creating and testing a combinatorial array employing individually addressable electrodes. *U.S. Patent No.* 6,187,164, **2001**.

(17) Roberts, M. R.; Spong, A. D.; Vitins, G.; Owen, J. R. High Throughput Screening of the Effect of Carbon Coating in LiFePO4 Electrodes. *J. Electrochem. Soc.* **2007**, 154 (10), A921–A928.

(18) Roberts, M. R.; Vitins, G.; Owen, J. R. High-Throughput Studies of Li1− XMgx/2FePO4 and LiFe1− YMgyPO4 and the Effect of Carbon Coating. *J. Power Sources* **2008**, 179 (2), 754–762.

(19) Spong, A. D.; Vitins, G.; Guerin, S.; Hayden, B. E.; Russell, A. E.; Owen, J. R. Combinatorial Arrays and Parallel Screening for Positive Electrode Discovery. *J. Power Sources* **2003**, 119–121, 778–783.

(20) Potts, K. P.; Grignon, E.; McCalla, E. Accelerated Screening of High Energy Li-Ion Battery Cathodes. *ACS Applied Energy Materials* **2019**, 2, 8388-8393.

(21) McCalla, E.; Rowe, A. W.; Shunmugasundaram, R.; Dahn, J. R. Structural Study of the Li–Mn–Ni Oxide Pseudoternary System of Interest for Positive Electrodes of Li-Ion Batteries. *Chem. Mater.* **2013**, 25 (6), 989–999.

(22) Yoshida, J.; Guerin, E.; Arnault, M.; Constantin, C.; de Boisse, B. M.; Carlier, D.; Guignard, M.; Delmas, C. New P2-Na0. 70Mn0. 60Ni0. 30Co0. 10O2 Layered Oxide as Electrode Material for Na-Ion Batteries. *J. Electrochem. Soc.* **2014**, 161 (14), A1987–A1991.

(23) Fleischauer, M. D.; Hatchard, T. D.; Rockwell, G. P.; Topple, J. M.; Trussler, S.; Jericho, S. K.; Jericho, M. H.; Dahn, J. R. Design and Testing of a 64-Channel Combinatorial Electrochemical Cell. *J. Electrochem. Soc.* **2003**, 150 (11), A1465–A1469.

(24) Chen, J.; Zhong, S.; Zhang, X.; Liu, J.; Shi, S.; Hu, Y.; Wu, L. High Performance of Hexagonal Plates P2-Na2/3Fe1/2Mn1/2O2 Cathode Material Synthesized by an Improved Solid-State Method. *Mater. Lett.* **2017**, 202, 21–24.

(25) Yuan, D.; Hu, X.; Qian, J.; Pei, F.; Wu, F.; Mao, R.; Ai, X.; Yang, H.; Cao, Y. P2-Type Na0. 67Mn0. 65Fe0. 2Ni0. 15O2 Cathode Material with High-Capacity for Sodium-Ion Battery. *Electrochim. Acta* **2014**, 116, 300–305.

(26) Bai, Y.; Zhao, L.; Wu, C.; Li, H.; Li, Y.; Wu, F. Enhanced Sodium Ion Storage Behavior of P2-Type Na2/3Fe1/2Mn1/2O2 Synthesized via a Chelating Agent Assisted Route. *ACS Appl. Mater. Interfaces* **2016**, 8, 2857-2865.

Tables:

Table 1: Lattice parameters obtained in this study compared to those previously published in the literature.[4,5]

Sample type	Target phase	T (°C)	*a* (Å)	*c* (Å)
Bulk	$Na_{0.66}Fe_{0.5}Mn_{0.5}O_2$	850	2.9213(1)	11.2713(3)
Combinatorial	$Na_{0.66}Fe_{0.5}Mn_{0.5}O_2$	850	2.9139(1)	11.2732(3)
Xu *et al.*	$Na_{0.66}Fe_{0.5}Mn_{0.5}O_2$	850	2.9154	11.2599(3)
Combinatorial	$NaFe_{0.5}Mn_{0.5}O_2$	850	2.9121(1)	16.9212(3)
Combinatorial	$NaFe_{0.5}Mn_{0.5}O_2$	950	2.9132(1)	16.8841(3)
*Yabuuchi *et al.*	$NaFe_{0.5}Mn_{0.5}O_2$	700	2.959	16.522

* XRD pattern showed a minority contaminant phase.

Table 2: ICP results for the combinatorial (2-3 mg) samples produced by the sol-gel method. In all cases, the target composition was $Na_{0.66}Fe_{0.5}Mn_{0.5}O_2$ and 10% excess sodium was dispensed.

Sintering conditions	Fe	Mn	Na
850°C,3h	0.50	0.50	0.68
850°C,6h	0.50	0.50	0.69
850°C,12h	0.50	0.50	0.66
950°C,3h	0.50	0.50	0.70
950°C,6h	0.49	0.51	0.61
950°C,12h	0.50	0.50	0.56

Table 3: Peak positions based on the cyclic voltammograms shown in Figure 5 compared to those obtained from ref. [25]. The voltage is *vs*. Na/Na$^+$ and peak labels are shown in Figure S4. Yuan *et al.* refers to Ref. [25]

Peak	Voltage (V) (this study)	Voltage (V) (Yuan *et al.*)
A	1.98	2.01
b	2.49	2.52
c	3.32	3.32
d	4.17	4.18

Table 4: Comparison of the average electrochemical property values obtained with the combinatorial cell to those found in the literature. Refs. [26] and [5] were used to obtain the literature values for $Na_{0.66}Fe_{0.5}Mn_{0.5}O_2$ and $NaFe_{0.5}Mn_{0.5}O_2$, respectively. Both of those literature results involve cycling between 1.5 and 4.3 V at a rate of 12 or 13 mA g^{-1}, which proves to be quite comparable to the combinatorial CVs performed with the same voltage window at a sweep rate of 0.1 V h-1. RSD refers to root standard deviation.

	discharge capacity (mAh g^{-1})			average discharge voltage (V)	
material	Combinatorial	RSD	Literature	Combinatorial	RSD
$Na_{0.66}Fe_{0.5}Mn_{0.5}O_2$					
cycle 1	162.7	12.4	179	2.67	0.02
cycle 7	137.4	10.4	138	2.47	0.03
$NaFe_{0.5}Mn_{0.5}O_2$					
cycle 1	140.3	14.1	121	2.68	0.02
cycle 7	127.6	14.0	106	2.53	0.03

Figure captions:

Figure 1. Illustrations of the various steps in the sol-gel synthesis of Na-Fe-Mn-O materials. (a) The dispensing of the nitrate precursors using the solution-dispensing robot, (b) the mixed nitrate precursors with citric acid, (c) the product after gel formation, and (d) the crushed gel sample on alumina plate prior to high temperature heating.

Figure 2. X-ray powder diffraction patterns of P2-$Na_{0.66}Fe_{0.5}Mn_{0.5}O_2$ made using various synthesis routes (a), and the combinatorial sol-gel samples made with various heating conditions (b). The vertical red lines indicate the positions of the P2 phase peaks according to ref. [5]. The contaminant peak attributed to an $NaFeO_2$-like phase is labeled in both panels.

Figure 3. Results of the Lebail fits performed on the P2-$Na_{0.66}Fe_{0.5}Mn_{0.5}O_2$ material obtained from either (a) bulk co-precipitation, (b) combinatorial co-precipitation, (c) bulk sol-gel and (d) combinatorial sol-gel. Black points are experimental data while the red curves are calculated and the blue curves are the difference. The inset shows an SEM image of the sol-gel combinatorial sample.

Figure 4. Representative scanning electron microscopy images for sol-gel combinatorial samples of P2-$Na_{0.66}Fe_{0.5}Mn_{0.5}O_2$ synthesized at 850°C for 3h (a), 6h (b) and 12h (c); and at 950°C for 3h (d), 6h (e), and 12h (f).

Figure 5. Cyclic voltammograms obtained for 32 P2-$Na_{0.66}Fe_{0.5}Mn_{0.5}O_2$ combinatorial samples shown with white backgrounds, and 32 O3--$NaFe_{0.5}Mn_{0.5}O_2$ samples are shown on gray backgrounds. All 64 cells were cycled simultaneously at a sweep rate of 0.1 Vh^{-1}. The * mark a small redox peak that is systematically present in only the P2 samples showing no evidence of contamination.

Figure 6. Summary of the electrochemical properties extracted from both combinatorial electrochemical cells. (a,c) are obtained for the cell cycled repeatedly at 0.1 Vh^{-1} while (b,d) show the results of the rate tests. (a,b) show the average specific capacities, and (c,d) show the average voltages. In all cases, filled symbols are obtained during discharge while open symbols represent charging.

Figures:

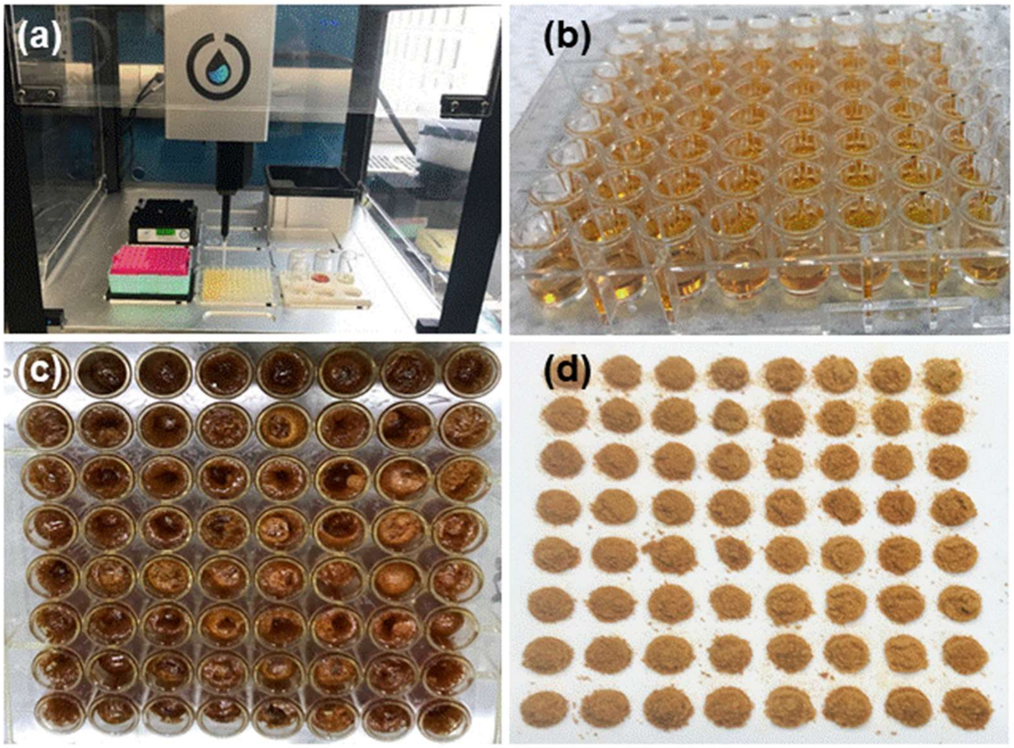

Figure 1.

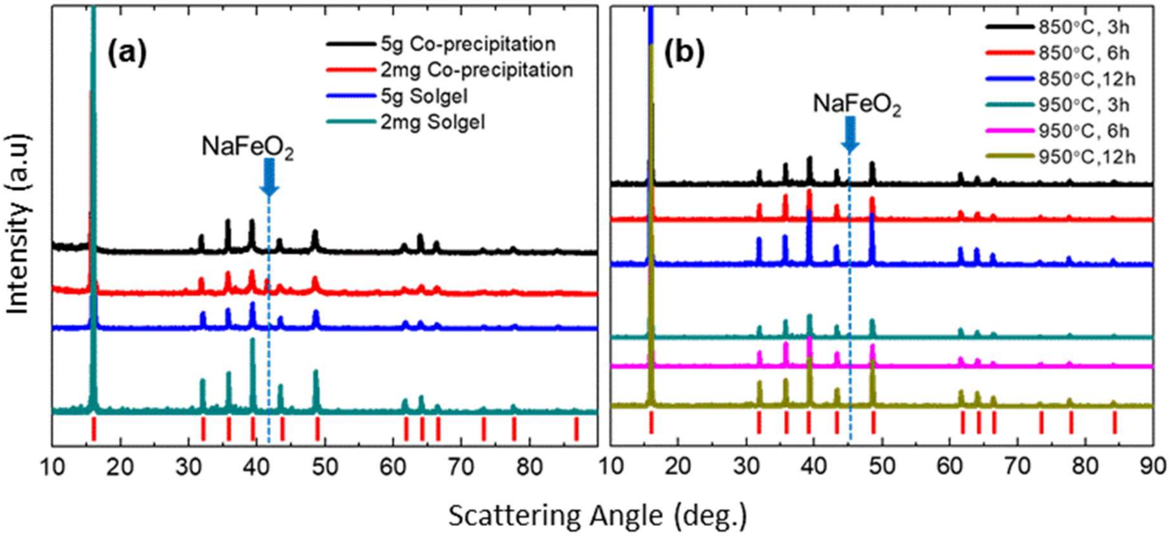
(a)
5g Co-precipitation
2mg Co-precipitation
5g Solgel
2mg Solgel
NaFeO$_2$
(b)
850°C, 3h
850°C, 6h
850°C,12h
950°C, 3h
950°C, 6h
950°C,12h
NaFeO$_2$
Intensity (a.u)
10
20
30
40
50
60
70
80
10
20
30
40
50
60
70
80
90
Scattering Angle (deg.)

Figure 2.

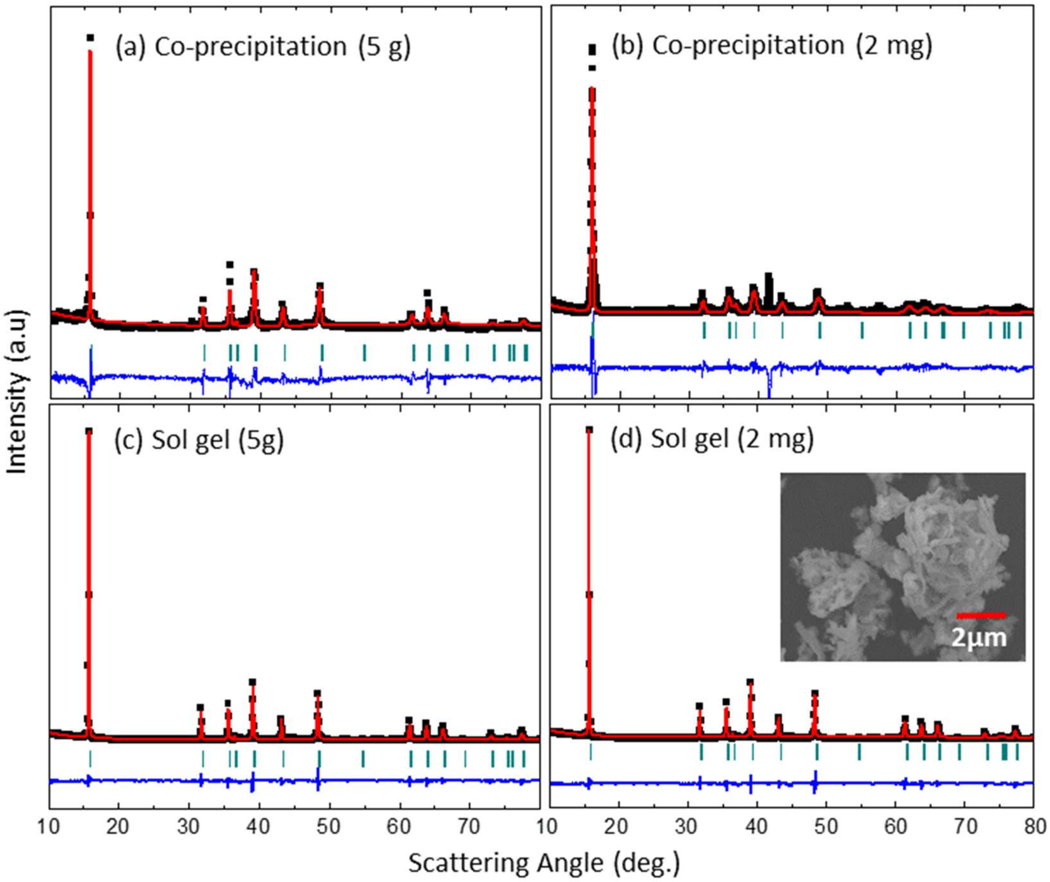
(a) Co-precipitation (5 g)
(b) Co-precipitation (2 mg)
(c) Sol gel (5g)
(d) Sol gel (2 mg)
2μm
Intensity (a.u)
Scattering Angle (deg.)
10
20
30
40
50
60
70
10
20
30
40
50
60
70
80

Figure 3.

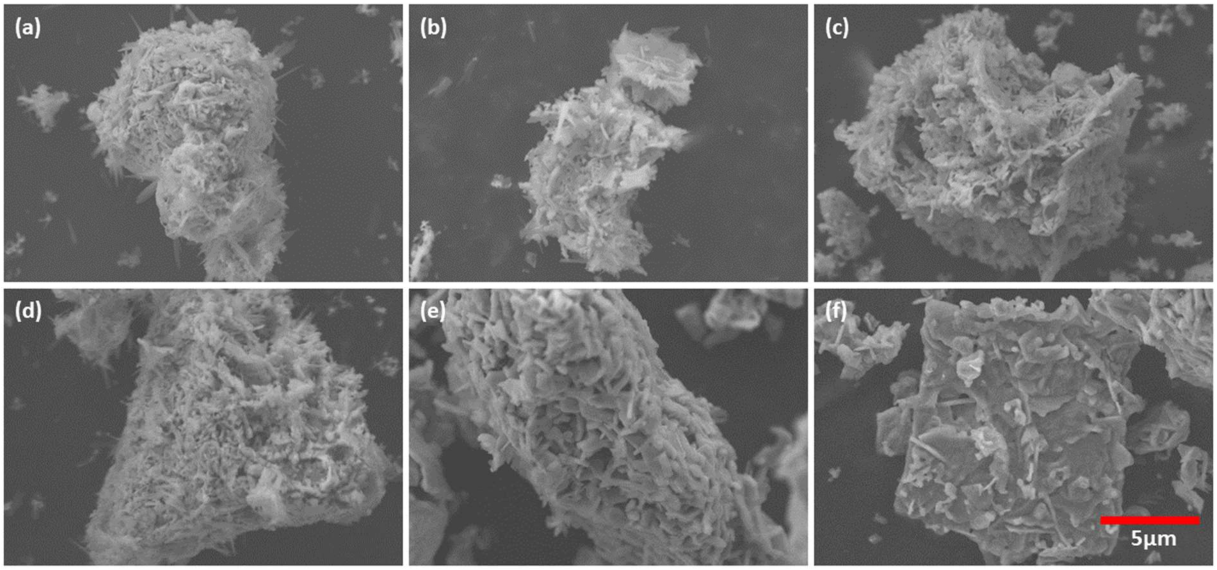

Figure 4.

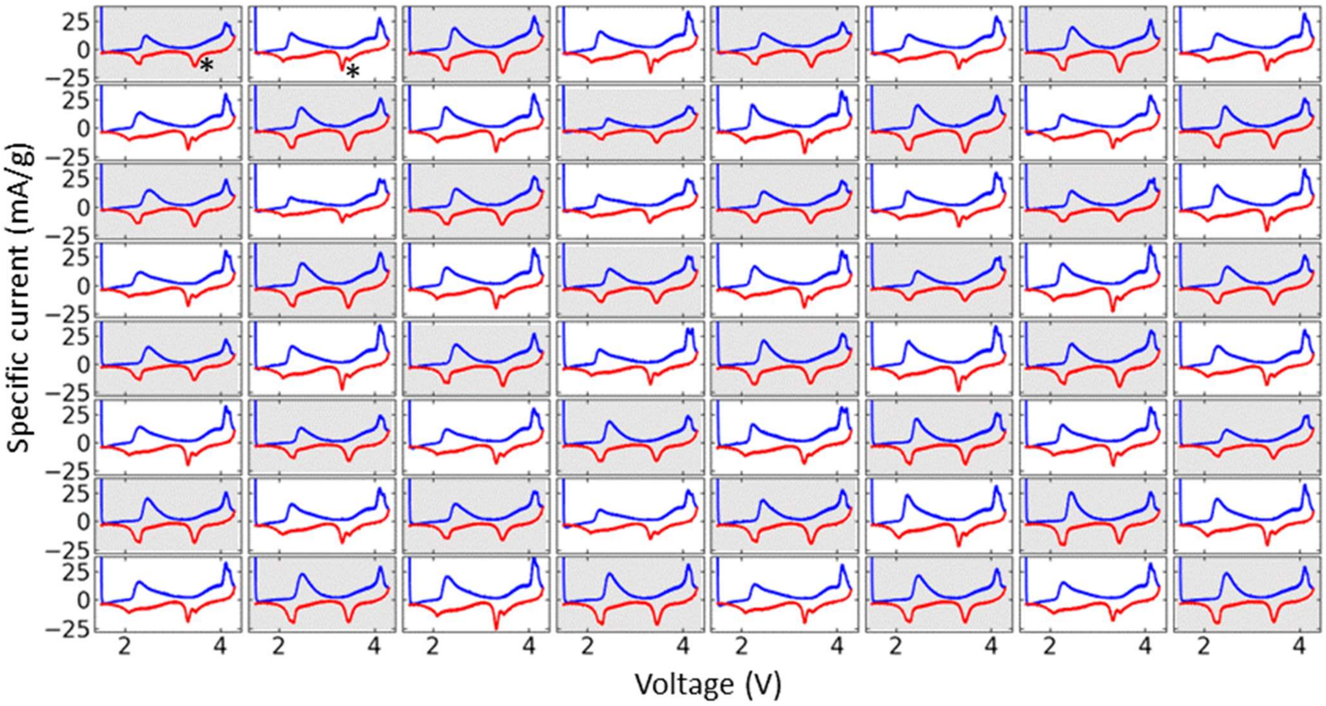

Figure 5.

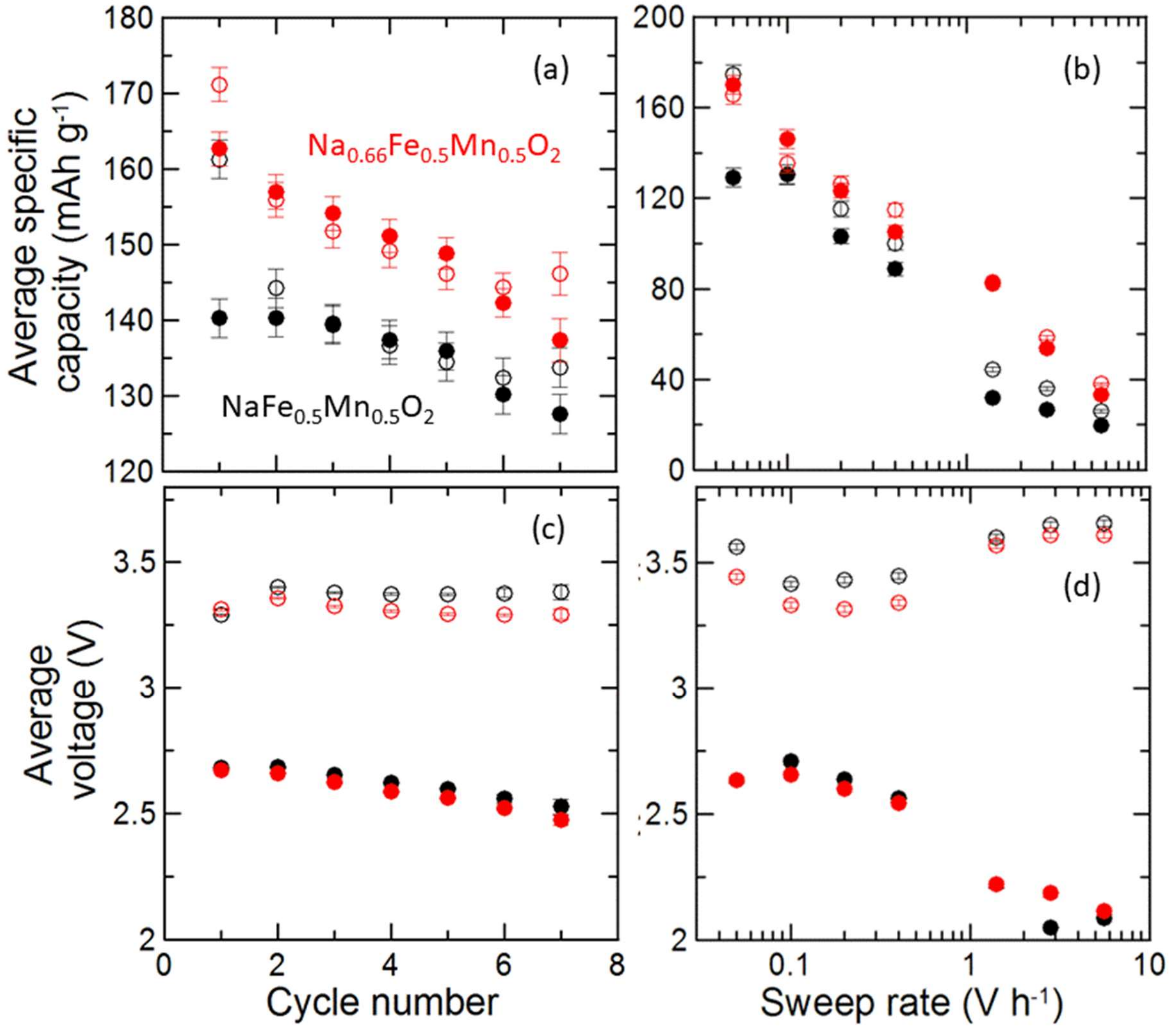
(a)
(b)
(c)
(d)
Na$_{0.66}$Fe$_{0.5}$Mn$_{0.5}$O$_2$
NaFe$_{0.5}$Mn$_{0.5}$O$_2$
Average specific capacity (mAh g^{-1})
Average voltage (V)
Cycle number
Sweep rate (V h^{-1})
120
130
140
150
160
170
180
0
40
80
120
160
200
2
2.5
3
3.5
0
2
4
6
8
0.1
1
10

Figure 6.

Table of Contents Graphic: