Elements  
Macro  
Morphology  
Structure  
Subject  
  
The field-emission scanning electron microscopy ( FESEM ) results ( Figure S2d-f , Supporting Information ) demonstrate that the carbon encapsulated morphology can not be retained in the presence of NaOH solution due to the reaction with Mn2SiO4 .   
  
On the one hand , the mesopores can be resulted from the NaOH activation during the etching process .   
  
During the first cathodic cycle , an obvious reduction peak at around 1.4 V can be observed , but disappears in the subsequent cycles , which could be ascribed to the reduction of trace impurity possibly originated from higher oxidation state Mn ions in the electrode materials .   
  
The electrode after 100 cycles shows a much lower charge-transfer resistance than the initial value suggesting improved Li-reaction kinetics during testing in conformity with the CV results .   
  
As shown in Figure 5 a , there is no sign of additional peaks associated with other types of structure during electrochemical cycling , indicating that there is no evident appearance of a new phase .   
  
A legitimate concern could be aroused whether the water-containing anode has the negative effect on the stability of electrolyte .   
  
However , the ex situ XRD measurements indicate that the water molecules can not get out of the anode host easily , benefiting from the stable crystal structure during Li+ insertion/extraction process .   
  
Compared to the as-fabricated SMOH , the dehydrated samples show much lower capacity with the decrease of interstitial water .   
  
This could suggest that the interaction between the polymer molecule and the surface-modified MWCNTs overcame the Van der Waals interaction between the MWCNTs , which would otherwise result in separate growth of polypyrrole or the formation of aggregates .   
  
Furthermore , the presence of the MWCNTs shifted the polypyrrole oxidation peak to a higher potential , which can be attributed to the interaction between the MWCNTs and polypyrrole .   
  
The lower capacity at low current density might be due to the dissolution of deteriorated material and water decomposition at slower charge-discharge rates .   
  
On the other h , the specific discharge capacities of pure polypyrrole decreased significantly from 56.5 mA h g-1 at 50 mA g-1 to 35.4 mA h g-1 at 2000 mA g-1 .   
  
In general , it is hard to obtain nearly theoretical capacities and high-rate performances in bulk or sub-micrometer sized materials due to their low electronic conductivity and slow ion-diffusion rates .   
  
However , in the MWCNT-polypyrrole nanowires the conductive MWCNT cores offer continuous electron transport pathways , while the nano-sized polypyrrole shells simultaneously provide rapid ion and electron diffusion pathways .   
  
Comparatively , some Na0.44MnO2 rods tend to merge together after increasing the synthesis temperature to 950degC , as shown in Fig.2c .   
  
The increased surface area for the NMO-9503 sample may be caused by the well-known instability of Mn oxides above 900degC .   
  
However , the mesoscale pores have not been observed by the TEM of single Na0.44MnO2 particle shown in Fig.2d , and thus it may be caused by the stacking of adjacent particles .   
  
This partly explains the reason that the NMO-8503 and NMO-9503 samples are also able to work normally as electrode material but not in an optimized manner .   
  
Note that Na2C2O4 alone only decomposes above 500degC in open atmosphere , and its enhanced activity within the oxalate mixture may suggest the catalysis effect from the manganese oxides .   
  
The predicted band gap for the charged phase Na0.22MnO2 is 10.21eV , far larger than that of Na0.44MnO2 phase ( 2.58eV ) and Na0.66MnO2 phase ( 2.49eV ) , which indicates that the electrical conductivity of Na0.22MnO2 phase is distinctly inferior to the other two phases and thus may limit the electrode performance at the high voltage region .   
  
The cross-linking hops between these 1D channels , which have rather low activation energies , may reduce the negative influence of defects and improve rate .   
  
However the volume decreases sharply by ~10 % for the fully-desodiated structure that may result in poor rate capability .   
  
A large volume shrinkage during the last desodiation steps narrows the Na migration channels that provide the difficulty in removing all Na from NaxMn2 ( MoO4 ) 3 .   
  
During discharge , the reverse trend was observed , i.e . R2 values increased till 3.5 V and remained quite constant on further discharging down to the lower cutoff voltage ( 2.6 V ) .   
  
The discharge capacity decreased to 68 mAh g-1 after 100 cycles ; however , the efficiency gradually increased to 99 % after being 90 % initially .   
  
The behavior of the peak splitting is not clearly understood as only two different sodium sites [ Na ( 1 ) and Na ( 2 ) ] are available in the crystal structure .   
  
We speculate that each plateau may have additional energetic sites those are responsible for the spitting of the peak .   
  
Details understanding of such behavior is under progress by experimental and simulation studies .   
  
However , the capacity fade on cycling remains the issue to be solved .   
  
Peaks of Na2O2 have not been detected in the XRD pattern possibly due to a structural transformation converting the peroxide to an amorphous phase within 2h of milling .   
  
The XRD patterns of the heat treated powder obtained after thermal treatments at ~473K , shown in Fig . 2 , does not indicate any significant change in comparison to the 20h milled powders .   
  
In addition , no significant grain growth of NaMn2O4 is observed after heat treatment at ~473K ( ~10nm after 473K ) .   
  
Appearance of the Fe peak in the EDAX mainly arises from the iron contamination in the milled powder due to the SS milling media caused by frictional wear due to the impingement of the harder oxide particles with the relatively soft SS balls and the SS walls of the container .   
  
On the other h , the 1st discharge ( insertion ) capacity is only ~74mAh/g corresponding to a first cycle irreversible loss ( IR ) of ~49 % .   
  
The coulombic efficiency of the 2nd cycle though lower is also ~68 % ( IR loss ~32 % ) with a charge and discharge capacity ~110mAh/g and ~74mAh/g , respectively , which suggests that there is an extraneous side reaction occurring during the charging process .   
  
These include : possibly electrolyte decomposition occurring at the operating voltage in the presence of the NaMn2O4 electrode ; another aspect could be the generation of a solid electrolyte interphase ( SEI ) due to the electrolyte instability ; a third possibility could be the higher reactivity of the surface of the electrode due to its nanocrystalline size of the crystallites .   
  
A very drastic increase in differential capacity ( i.e . charge or current ) is observed above ~3.8V which is expected to arise probably due to electrolyte decomposition at the NaMn2O4 electrode and electrolyte interface , though the electrolyte appears to be electrochemically stable up to ~4.7V ( Fig . 5 ) in the absence of the NaMn2O4 oxide as the active phase in the electrode .   
  
Therefore , the charge capacity observed above ~3.8V during charging of the electrode is expected to be a combined effect of dealloying or de-insertion of Na ion from NaMn2O4 combined with the electrolyte decomposition reaction occurring on the surface of the electrode .   
  
In order to achieve the specific capacity closer to the theoretical value ( ~134mAh/g ) , it appears that the electrode would need to be cycled above ~4.5V which may be possible by the application of a suitable non-reactive but Na-ion conductive coating on the electrode surface which will help stabilize the surface against the extraneous electrolyte reaction occurring on the surface causing the current spike seen in Fig . 7 .   
  
However , a detailed and comprehensive ex situ/in situ XRD study is warranted to be performed for the present system in order to understand the phase formations/transformations occurring in the nanocrystalline state of NaMn2O4 at the different potentials during the insertion/de-insertion processes .   
  
This result clearly suggests that the electrolyte decomposition on the surface of the electrode during charging at ~4V increases the charge transfer resistance of the electrode due to the formation of electrolyte decomposition products on the surface of the electrode , and as result deteriorates the cycling performance of the electrode with increase in cycle numbers .   
  
It should also be noted there is no change in the internal resistance after charge at 3.6V in comparison to the uncycled electrode due to no electrolyte decomposition occurring at this charge potential .   
  
In order to protect the surface of the nanostructured NaMn2O4 synthesized by HEMM , there is a need for surface modification by applying a suitable surface coating employing a Na-ion conductive phase that will be performed in the future .   
  
In order utilize the full capacity of NaMn2O4 as well as improve the stability of the electrode , the major issue of possible electrolyte decomposition or other extraneous reactions occurring during charging ( de-insertion of Na ion ) of the electrode in the potential range above ~3.8V needs to be resolved .   
  
Second , the precursor that contains PVP and NO3- is pyrolyzed violently , and therefore burns quickly and completely when it is heated .   
  
However , when the voltage drops below 2.6V , the Mn2+ peak at 640V is enhanced significantly until the electrode is fully discharged ( 2V ) .   
  
However , the Mn2+ concentration increases rapidly once the cycling voltage drops below 2.6V .   
  
It is well known that the Mn2+ on the electrode surface is detrimental to the battery performance due to its dissolution and shuffling in the electrolyte .   
  
Our results show directly that part of the surface Mn2+ does not participate in the electrochemical reaction after extended cycles , and thus contributes to the capacity fading of the electrodes .   
  
Consistent with this work , stronger Mn2+ formation is found at the very low discharge potential .   
  
Therefore , proper surface treatment is necessary to prevent the Mn2+ evolution in both the cathode and anode at low electrochemical potentials .   
  
Based on our quantitative analysis of the sXAS results ( Figure 3 ) , the formation of Mn2+ could be suppressed if we limit the electrochemical cycling with the discharge cut-off voltage higher than 2.6V .   
  
This naturally leads to another benefit if we cycle the battery cells above 3V : the cell could become independent from an extra sodium source , typically from the anodes .   
  
Cycling in such high voltage range still retains about a half of the energy density .   
  
Although cycling with a shallow voltage range may generally improve the cycling stability and we can not rule out other factors that affects the cycling stability , especially the irreversible structural changes , we argue that the suppressed Mn2+ formation on the electrode surface at least partially contributes to the improvement of the cycling stability .   
  
Although the energy density of the NaxMnO2 electrode cycling within 4-3V is compromised ( 147Whkg-1 ) , Na-ion batteries are under scrutiny mainly due to the needs of grid-scale storage , where cost and stability is more important than energy capacity .   
  
As discussed earlier , cycling NaxMnO2 electrode above 3V naturally avoid the manufacture complication of introducing extra Na source , which will dramatically lower the cost .   
  
Furthermore , cycling above 3V does eliminate the surface Mn2+ formation and improves the cycling stability .   
  
Besides the demonstration of the suppressed Mn2+ formation by regulating the discharge cut-off voltage , revealing the Mn2+ on the surface of Na0.44MnO2 electrodes suggests that modifying and controlling the surface of the Na0.44MnO2 electrodes , e.g. , through surface coating , could be another key to optimize its electrochemical performance .   
  
With further heating to 1000 degC , as shown in the magnified image of zone 3 ( ~1 % weight loss ) , slight weight variations occurred at around 750 and 850 degC were monitored .   
  
Meanwhile , traces of unknown phases were detected in NMO850 and became less in NMO900 .   
  
The grooves on the surfaces are far less obvious than those in Figure c , which may result from the lack of morphology controlling effect of surfactant P123 to form shape-defined grooves .   
  
The voltage peaks in the oxidation process , however , exhibit values higher than those of NMO850 and were observed at 3.13 , 3.34 , and 3.54 V , respectively , indicating its more serious polarization .   
  
NMO900 , however , shows lower reversible specific capacity due to the greater greater strains strains resulting from its bigger particle size and smoother surface ( Figure d and Figure c ) .   
  
There is no evident formation of new phases or superstructures but solid-solution reaction during the Na extraction/insertion from/into the Na0.44MnO2 framework .   
  
Upon further discharging , the NMO framework kept expanding , which would cause the decrease of structure ordering , resulting in the decrease of peak intensity .   
  
Most importantly , however , no major structural changes or even structure degradation of the NMO active material could be made evident , even though NMO was stirred in water for 12 h .   
  
In fact , as it will be shown in the following , no additional current peaks for the CMC-based electrode are apparent in the CV curves which shows that H+ , if present in NMO , does not have a strong impact on the electrochemical performances .   
  
Since it occurs with both binders , this behavior is likely related to the use of the NaPF6 salt .   
  
In fact , both the shift and the increase in intensity of the peaks are not evident with the NaClO4-based electrolyte , whether using CMC or PVdF .   
  
Nevertheless , the CMC-based electrodes show weaker and broader peaks compared to the electrodes prepared with the conventional binder .   
  
As described before , a partial leakage of Na+ occurs upon the aqueous processing which may result in peak broadening and reduced intensity , due to the combination of increased disorder and lower initial Na content in the material .   
  
Furthermore , the corrosion of the aluminum current collector ( discussed later in Figure ) could also affect the performance of the cell .   
  
Once more , the data suggest that the cycling behavior is mostly affected by the sodium salt in the electrolyte and not the binder .   
  
During the initial cycles at C/10 , the Coulombic efficiency is poor in both the cells with NaClO4-based electrolyte ( e.g. , at the third cycle , the Coulombic efficiencies are 89 % and 93 % for the PVdF- and CMC-based slurries , respectively ) .   
  
The different surface degradation is known to be related to aluminum corrosion due to the increased pH value of the CMC-based slurry .   
  
In addition , Al is more degraded in the presence of the NaClO4-based electrolyte as compared to that in the NaPF6-system because of the fact that the former does not contain fluorine that can passivate the current collector .   
  
When CMC is used ( Figure a , b ) , the aluminum current collector is obviously degraded .   
  
It is clearly evident that the cycling performance of FEC-free cells is poorer , both in terms of practical capacity and capacity retention .   
  
When NaClO4 and PVdF binder are combined , the cell displays very poor capacity retention upon long-term cycling at the C/2 rate .   
  
In addition , electrodes made with both binders exhibit an impressive reversibility after the rate test as made evident from the very stable cycling when the rate is decreased back to C/2 .   
  
The exceptional performance in both half- and full-cells indicates the critical role of the CMC binder .   
  
However , it also needs to be considered that the CMC-based hard carbon electrode had to be presodiated to compensate its irreversible capacity and the Na deficiency in NMO .   
  
Therefore , future research efforts should also be dedicated to increasing the sodium content in NMO .   
  
Observed from the similar charge and discharge curves in different cycles , it is easily speculated that no apparent structural changes occur in the electrode material during cycling .   
  
Subsequently , the decreasing trend slows down to keep a capacity of 50 mA h g-1 in the 50th cycle .   
  
The smaller voltage gap ( voltage gap : 0.15 V ) between the first-cycle charge and discharge plateaus indicates the reduced polarization at a low current density with a relaxation process .   
  
The low chemical diffusion coefficient in these Na-based polyanion materials , i.e . NaFePO4 or Na2MnPO4F , could partially explain their poor electrochemical performances .   
  
The good structural reversibility and stability demonstrate that the 3-D framework structure of Na2MnPO4F is not remarkably impacted by the insertion and extraction of sodium ions during cycling .   
  
Excluding the influence of structural changes , the decay of the electrochemical capacity observed in Fig . 7 may be due to the interfacial issues of the electrodes when charged to a high voltage .   
  
By carefully comparing the charge-discharge profiles , it is shown that the extracted sodium ions above 4.0 V can not be inserted back into the electrode materials .   
  
It may be attributed to the large particle size of the CaFe2O4-type NaMn2O4 cathode ( 3-5 mm ) .   
  
As shown in Fig . 2c , there are almost no obvious performance degradations up to 200 cycles .   
  
Although the extracted Li+ during the first charge process was still residual in the battery system , it exerted little influence on the following Na+ insertion/extraction process because the Na+ concentration was 2000 times higher than that of Li+ .   
  
The Jahn-Teller distortion seriously affected the charge-discharge profiles of the LiMn2O4/Na .   
  
It is well known that the performance of a manganese-based cathode deteriorates rapidly with increasing temperatures because of the Jahn-Teller distortion and serious dissolution of Mn2+ from the electrode .   
  
A very small shoulder peak was discovered in the first charge cycle , which might originate in the complicated reactions at the surface of the fresh electrode .   
  
The weakened diffraction peaks at high-angles might be because of the blend with the conductive agent and binder of the cycled samples .   
  
Obviously , the spinel structure can not be maintained during the extraction/insertion of sodium ions .   
  
Both the charge and discharge profiles show smooth plateaus and little polarization , which is rare in manganese-based cathodes of SIBs .   
  
Although the capacity needs to be improved , the ultra-stable battery performance still encourages us for the future investigation of other post spinel cathode for SIBs .   
  
However , the CV curve of the NaMnO2 electrode was mostly symmetric with respect to the zero-current axis , which means that the faradic reactions of NaMnO2 are reversible .   
  
The evolution of oxygen at high potential may result in the excess charge capacity .   
  
After the first cycle , the charge and discharge capacity was almost equal and the reversible capacity remained unchanged at 55 mA h g-1 , giving a high coulombic efficiency at about 100 % , suggesting that there was no oxygen evolution between the voltage ranges .   
  
The decomposition of water in an aqueous electrolyte and the interaction between the aqueous electrolyte and the electrode surface may result in a relatively low coulombic efficiency .   
  
The H2 evolution at low voltage may result in this phenomenon .   
  
The full cell with Na2SO4 as the electrolyte showed very poor cyclability .   
  
It could only retain 25 % of the initial capacity after 500 cycles ( as shown in Fig . S2+ ) .   
  
The cathode material was dissolved much more seriously in the Na2SO4 electrolyte .   
  
This may result in the rapid capacity loss of the full cell that used the Na2SO4 electrolyte .   
  
The SEM images ( Fig . S4b+ ) showed that the shape was unchanged , but the surface of the NaMnO2 particle was broken indicating that the cathode was decomposed during cycling .   
  
What is more , the oxidation of the anode in its sodium-inserted state by dissolved oxygen or oxygen generated by water hydrolysis , or oxidation of the aqueous electrolyte by the charged cathode could also result in irreversible capacity loss .   
  
Whereas Na2MnP2O7 experiences a relatively big drop in discharge capacity under the same conditions .   
  
The rate capability of Na2Fe0.5Mn0.5P2O7 is dropped upon the mixing of Mn when compared with Na2FeP2O7 which is in turn associated to the inferior kinetics of Mn .   
  
Mn-based cathodes have inherently lower conductivity than Fe-based cathodes , causing relatively limited rate capability .   
  
At a slower scan rate , peak separation becomes sharper indicating a two-phase reaction .   
  
The CV data of Na2Fe0.5Mn0.5P2O7 shows broad redox peaks in the entire voltage range even at a slower rate suggesting existence of a single phase reaction .   
  
However , during the discharging process ( sodiation ) , the peaks are shifted towards small 2th values undergoing lattice expansion without the formation of any new phase ( s ) .   
  
In a partially desodiated state , exo/endothermic peaks are barely observable from differential thermal analysis ( DTA ) results indicating the absence of any phase transformation in both the materials .   
  
In general , high redox potential materials have poor thermal stability .   
  
In the first region , the initially constant and low charge transfer resistance is associated with the fast reaction rate of surface defects present in the array .   
  
In the second region , after the consumption of surface defects , the reaction propagates deeper into the bulk of the material , which leads to a lower rate and a higher Rct value .   
  
Compared with the reference samples , the frogspawn-inspired array exhibits longer range with lower Rct values in region I , suggesting its faster rate of surface reaction .   
  
As displayed in Fig . 7c and d , low coulombic efficiencies are observed at both rates during the initial few cycles .   
  
The weight loss before 150 degC is attributed to the dehydration of the precursor .   
  
No obvious weight loss could be found after 700 degC .   
  
The initial irreversible processes could be attributed to the multiatomic transition processes to relieve the structural strain for Na ion insertion-extraction and the surface reaction between the electrolyte and electrode .   
  
However , another two oxidation peaks between 3.24 and 3.60 V became stronger in the following cycles , which due to the activation process of KMn8O16 in the first cycle .   
  
After the first scan , the consequent CV curves display several pairs of symmetrical redox peaks , denoting the complex biphasic transition mechanism during charge-discharge process that had not been clearly identified .   
  
The capacity increment phenomenon is maybe caused by the slow activation process in the narrow voltage range .   
  
However , the detailed influence of incorporation of KMn8O16 still needs more investigation .   
  
For NVMPF , there was no impurity peak , which indicated that the low dose doping of Mn2+ into NVPF did not destroy the crystal structure of the material .   
  
As for the charge charge balance balance of of NVMPF NVMPF , oxygen deficiency together with the low oxidation state of Mn ( II ) in the NVMPF samples might play a role .   
  
Fig . S6+ shows the XRD patterns of the different hydrothermal times of 15 min , 25 min and 2 h , which suggest that there existed an impurity of NaF at 15 min but the pure phase of NVPF could be formed after 25 min .   
  
However , the microspheres morphology could not be kept when TEG was the only solvent .   
  
As shown in Fig . S7 , + only nanoplates could be obtained under the same synthesis conditions as used for the hierarchical NVPF hollow microspheres except for the absence of citric acid , indicating that the microspheres could not form with only TEG .   
  
The poor electrochemical performance of the NVPF samples synthesized with a hydrothermal time of 2 h might be explained by their poor crystallinity ( Fig . S6+ ) .   
  
The latter implies a high level of long-range layer stacking disorder combined with poor crystallinity , hindering an accurate structural refinement using the Rietveld method .   
  
Although no secondary phases were observed in the XRD data , one explanation could be a low-level amorphous phase .   
  
However , the spectral broadening prevents more detailed analysis .   
  
The so-formed tetrahedral Na1 sites are likely to be fixed under x > = 1.0 ( Fig . 1e ) and block the diffusion pathways , which slows down the diffusion kinetics .   
  
Na+ ion diffusion in highly sodiated NaxMn3O7 , therefore , tends to follow 1D diffusion pathways through octahedral Na2 sites , which is expected to be more sluggish than prismatic-prismatic Na+ ion diffusion at low sodiation content ( 0 < x < = 1.0 ) .   
  
The fast loss of peak current intensity upon cycling together with an increase in voltage polarization reflects the partial irreversibility of the process due to phenomena such as oxygen gas formation from the particle surface .   
  
Nevertheless , earlier works on cathode materials with oxygen-redox activity , e.g. , have shown oxygen redox activity , even though the associated anionic redox-related plateaus ( in galvanostatic data ) or current peaks ( in CV data ) are not discernible anymore .   
  
Therefore , we can not rule out oxygen redox activity in Na2.4Al0.4Mn2.6O7 after the first cycle by the absence of the high-voltage redox peaks in the CV data .   
  
The sloppy load profile of Na2.4Mn2.6Al0.4O7 compared to reported load curves for Na2Mn3O7 indicates that Al3+ ion substitution for Mn4+ ions in the TM layer alleviates the structural transitions occurring upon cycling in Na2Mn3O7 .   
  
The charge capacity above 4 V is reduced from the first cycle ( 55 mA h g-1 ) to the second cycle ( 26 mA h g-1 ) , indicating that the high-voltage redox processes are not fully reversible , most likely reflecting the irreversibility of the oxygen redox process and/or oxygen evolution reaction .   
  
By contrast , at 5C the capacity for Na2Mn3O7 was 51 % of that obtained in the first cycle at C/20 ( Fig . S15d+ ) .   
  
As the charge-discharge rate increased from C/5 to 5C , the voltage profile curves changed slightly , shortening the charge/discharge plateau at 4.0 V ( Fig . S16+ ) .   
  
Therefore , the kinetically limited process seems to be related to the high voltage oxygen redox activity , which has been described as a rate-determining step in the charge/discharge process .   
  
The relatively high Na vacancy formation energies from Na1 and Na2 indicate that the removal of these Na sites will require high charge voltages ( 4.2-5 V ) , which corresponds to the high voltage plateau in Fig . 3b and redox peaks in region C in the CV data ( Fig . 3a ) .   
  
However , the above predictions are no longer consistent with the experimental data as charging and discharging processes proceed , due to structural changes which are not considered in these calculations .   
  
This suggests that owing to the preferential hole formation excess in Al-coordinated O atoms during charging , Na2.4Al0.4Mn2.6O7 can also suffer from the formation of O-O dimers and associated O loss upon charging .   
  
Such O loss can also be supported from experiments : both cathodes display shortened high voltage plateaus during the first discharge process and subsequent charge-discharge cycles ( Fig . 4b and c ) , which indirectly indicates a decrease in the amount of redox-active O .   
  
Considering that the Mn3+O6 octahedra are Jahn-Teller active , such reduction of Mn4+ ions might have detrimental effects on the cycling stability of the studied cathodes .   
  
Other studies have also suggested the possibility of cation dopant migration to the tetrahedral site of the Na layer in layered oxides , which prevents further TM migration and stabilizes cyclability of cathodes .   
  
The shorter Al-O bond lengths and lower oxidation state of Al3+ ions distort the Na+ ion migration pathways such that these are shorter and have wider diffusion channels , which further improve Na+ ion diffusion kinetics .   
  
In addition , all such particles do not exhibit regular cubic morphologies as those prepared by the co-precipitation or single-iron source process , in which PBA is formed through the nucleation and precipitation of the dissolved hexacyanoferrate anions , while it is a solid-solid conversion for the MW-ST method .   
  
However , in practical cells , only half of these sodium ions can be cycled , because further sodium ion extraction would cause the damaging event of O2 evolution .   
  
A small amount of impurity phase exists , however , its exact composition and structure can not be identified and it is most likely to be NaxTiO2 as proposed in previous research work .   
  
Therefore , the material will not be expected to possess charge ordering as Na0.44MnO2 proposed in the early report .   
  
For aqueous sodium-ion batteries , the capacity fading at low rates observed in most of aqueous full cell systems is caused by either partial dissolution of electrode materials , or oxidation of the anode in its sodium-inserted state by dissolved oxygen or oxygen generated from overcharged cathode .   
  
Therefore , the Na0.66 [ Mn0.66Ti0.34 ] O2 half-cell exhibits a sloping voltage profile , unlike the Na0.44MnO2 where multiple plateaus were observed during Na extraction/insertion related to a series of phase transitions ( charge ordering and/or Na+/vacancy ordering ) .   
  
There is no evident appearance of a new phase formation upon Na extraction/insertion from/into Na0.66 [ Mn0.66Ti0.34 ] O2 in a wide Na content range .   
  
The XRD pattern was evaluated to determine the structure of oxidized KMnHCF , but it showed weak , noisy peaks due to the thin film of oxidized KMnHCF ( Supporting Information , Figure S6 ) .   
  
The EDXA data indicated that oxidized compound might consist of amorphous oxides or hydroxides of manganese ( i.e. , MnOx or MnOxH ) with entrapped Na ions .   
  
The small polarization of about 100 mV that is observed while discharging ( Figure 3 b ) is attributed to the small structural changes .   
  
Because higher Na content in NaxMnO2 leads to unrecoverable structural collapse , the retention of capacitance is lower for x > 0.4 .   
  
However , in prolonged operation individual graphene sheets are prone to aggregation and restacking , and hence lose their properties .   
  
Hence , we stopped the charging potential at -1.4 V , due to polarization .   
  
Most aqueous SCs operate in the voltage range below 2 V , because of the electrochemical stability of water .   
  
However , this is most severe for the case of alkaline electrolytes , which restrict the anodic potential to 0.8-1.0 V for most transition metal oxides .   
  
This high overpotential is experienced by the strong Na ion ( de ) intercalation into rGO and Na0.21MnO2 .   
  
However , a moderate IR drop of about 600 mV was observed due to 1 ) the internal resistance , 2 ) insufficient thin-film electrolyte , and 3 ) weak electrode/electrolyte interface .   
  
On the other hand , most of the carbonaceous materials showed superior specific capacitance in strongly alkaline medium , but the operating voltage was limited to 1 V .   
  
Some carbon-supported metal oxides also showed high capacitance , but exhibited very narrow potential windows .   
  
However , the Na ion can not be reinserted after long-range structural collapse , and hence the stability of Na0.21MnO2 was no longer sustained , and lower capacitance retention resulted .   
  
The discharge capacity of the Na0.44MnO2 decreased on increasing the charge/discharge rate due to the fact that the polarization increases proportionally with an increasing in applied current and insufficient time for the ions to be intercalated completely .   
  
On the other hand , the capacity retention is better at higher C rates , which is usual for aqueous electrolytes .   
  
One of the possible reasons is that at lower charge/discharge rates , enough time is available for the generation of H+ ( aq . ) from the hydrolysis of the electrolyte , which might further impose i ) H+ ( aq . ) uptake at the electrode in competition with the Na+ ( aq . ) ; and ii ) shifts of the pH value of the aqueous electrolyte towards a more acidic region , which would leading to easier hydrogen evolution .   
  
Because the anode part of the full cell is dissolved in the electrolyte and might easily diffuse through conventional separators , which would result in undesired electrochemical reactions , an ion-selective membrane has to be used .   
  
As the salt bride gives rise to an additional resistance , much slower discharge rate ( C/50 ) had to be applied .   
  
Thus , dissolved polysulfide is an excellent option as anode in aqueous-electrolyte batteries ; in this field it is rather challenging to identify suitable anode materials because of reduction potential of water .   
  
On the other hand , when the concentration difference between the polysulfide-containing vial ( 0.4 m polysulfide dissolved in 0.25 m aqueous NaNO3 ) and a vial containing only the electrolyte containing were large ( i.e. , less than 0.5 m or higher than 2 m NaNO3 concentrations were used ) , leakage of the polysulfides was observed already after 2 h , which was consisted with our previous study .   
  
Due to sluggish diffusion kinetics and large radius of sodium ions , the morphology of the materials might have a certain impact on the electrochemical performance .   
  
However , the shortened NMO-2 exhibited much higher discharge capacity than NMO-1 at high rates .   
  
Because Na0.44MnO2 is half filled by sodium , only a capacity of 30-40 mAh g-1 was provided in neutral electrolytes .   
  
Though Na0.44MnO2 has exhibited a long cycle stability in neutral electrolyte , only a very low discharge capacity of about 40 mAh g-1 was obtained for Na0.44MnO2 in previous works .   
  
It is mainly because the competitive intercalation of H+ in Na0.44MnO2 structure limits the electrochemical operation potential range for reversible sodium-ion insertion/extraction .   
  
Although Na0.44MnO2 has been developed as promising alternatives for non-aqueous and aqueous Na-ion batteries , there are many scientific and technical challenges that still hinder its large-scale application .   
  
A main issue is that Na0.44MnO2 can only deliver half of its reversible capacity during first charge .   
  
Elemental doping or substitution is a possible way to increase sodium content in Na0.44MnO2 , but the reversible capacity of the obtained products is still unsatisfactory .   
  
Besides , employing sodium rich or presodiating anodes to supply extra sodium ions for cathodes might be feasible approaches to increase available capacity of Na0.44MnO2 .   
  
According to the above discussions , Na0.44MnO2 cathode has shown promising potential for low-cost energy storage application , but it should be noted that there is a long way to go before the practical application of the Na0.44MnO2 cathode .   
  
The XRD pattern of the Na2CoSiO4/MWCNT composite material did not show any observable peak shift or broadening , which implies that the crystal lattice of the host material is unaffected by the incorporation of the carbon nanotubes .   
  
The absence of carbon peaks may be due to the relatively low content and/or the amorphous nature of the carbon additive .   
  
The staircase-type behavior of the potential during cycling suggests the presence of alternate two-phase and single-phase domains , especially in the 2.3 V-4.0 V range .   
  
Thus , because of these fluctuations , structural rearrangements of the material are inevitable .   
  
Overall , the cathode material does not show any irreversible phase change due to cycling in the voltage region studied .   
  
Although the concentration of Na/Co anti-site defects in pristine Na2CoSiO4 is insignificant , as calculated by Treacher etal . recently , we presume that the in-situ carbon coating accomplished by the solvothermal method and the incorporation of functionalized MWCNTs in this study might tend to lower the anti-site defect formation energy .   
  
Nevertheless , this formation energy should still be higher than that observed in sodium orthosilicates with Fe and Mn , since the carbon coating does not seem to deteriorate the electrode kinetics and the redox reversibility .   
  
This property of the typical sodium orthosilicate reduces the required electrochemical stability window of the electrolyte , which is crucial for the full extraction of the available sodium ions .   
  
Furthermore , the intensity of the differential capacity peaks decreases with cycle number in Na2CoSiO4 , whereas the peak height remains consistent in the case of Na2CoSiO4/MWCNT .   
  
Comparatively , the Na2CoSiO4/MWCNT cathode delivered 125 mAh g-1 with only 4 % irreversible loss of capacity on the second charging .   
  
The rate capability of both the cathodes studied are lower when compared to other SIB cathodes such as layered oxides and carbon-coated NASICON type materials [ , ] .   
  
Another interesting feature in the impedance spectra is that as the SOC increases , RS slightly decreases since the ethylene carbonate and diethyl carbonate solvent molecules are consumed during the growth of the surface film , leading to a slight increase in the Na+ ion concentration in the electrolyte .   
  
Moreover , the smaller particle size ( ~300 nm ) obtained by the solvothermal method compared to the micron-sized particles obtained by conventional methods also contributes to the sodium ion diffusion .   
  
Nonetheless , the complete and reversible sodiation of the materials is not achievable in practice because of material degradation .   
  
Thus , the substitution strategy may still result in higher practical capacities if the resulting material is stabilized upon sodiation/desodiation .   
  
The reasons for this commonly observed behavior are the sodium vacancy ordering in the sodium layers , phase transitions upon ( de- ) sodiation , and the coexistence of different phases , each comprising different sodium sites .   
  
In the extended potential window of 4.6-1.5V ( see Fig.3e ) , however , a much lower reversibility is detected .   
  
The capacity in the first charge ( 37mAh g-1 ; 0.14 eq . Na+ ) and discharge ( 133mAh g-1 ; 0.49 eq . Na+ ) steps within the 4.0-2.0V potential range are lower than those detected for N\_M .   
  
The ratio between released and uptaken charge during the first cycle ( which should not be confused with the coulombic efficiency ) of NBM , NAM and N\_M are 236 % , 180 % and 265 % , respectively , due to the sodium deficiency of the layered materials , which highlights the need for developing an appropriate pre-sodiation in order to use such materials in practical sodium-ion cells .   
  
Moreover , NBM shows the highest capacity retention after 75 cycles ( 95 % ) as compared to N\_M ( 86 % ) and NAM ( 79 % ) .   
  
However , the capacity fading increases and coulombic efficiencies decrease to about 99.2 % for all three materials .   
  
The potential profiles in a wider potential range between 4.6 and 1.5Vat 40mAg-1 ( Fig.5d ) provide evidence for a poor cyclability of all materials .   
  
Indeed , the potential profiles ( see Fig.6d ) reveal an increasing ohmic drop but do not depict a significant polarization , i.e. , strongly strongly sloping sloping potential potential profile profile , indicating that the limitation is not due to the Na+ diffusion in the active material .   
  
However , upon charge and discharge at 500mAg-1 , the material shows polarization in the consecutive 5 cycles , which is further increased at higher currents ( 1000 and 1500mAg-1 ) .   
  
Nonetheless , after such a stressing high-current test , the material does not show indications of material degradation , as proven by the almost overlapping potential profiles at 40mAg-1 recorded before and after the current-rate test .   
  
Finally , no structural degradation is evident after stressing the material at high current rates of up to 1500mAg-1 .   
  
Meanwhile , the decomposition of the organic species releases gases such as carbon dioxide , leading to abundant pore structures in the composite , which should increase surface wettability of the material .   
  
The increased capacity is benefited from the off-stoichiometric phase with more reversible sodium ions ( ~2.31 Na-ion ) .   
  
In sharp contrast , the NMP shows inferior initial capacity delivering and low current response .   
  
While for the NMP , it shows poor rate capability and become almost inactive when the C-rate goes to 2 C .   
  
In addition to the requirements of high energy/power density , stable structure during cycling and the long lifespan under high rates are also necessary for practical applications .   
  
No clear irreversible phase changes have been detected from the dQdV patterns , which further proves the highly stable structure of the material .   
  
This is probably due to some parasitic reactions , such as the decomposition of the electrolyte , especially at high voltage .   
  
No significant capacity drop was observed when the rate increased from C/100 to C/30 .   
  
When the rate increases to 1C , the capacity drops to ~60 mAh/g .   
  
Finally , it is worth noting that the experimental capacity that appears as a gradually rising potential above 4.2 V on charge , indicates that electrolyte decomposition becomes pronounced at this voltage , giving rise to the `` extra '' capacity seen on charging .   
  
In addition , the in situ cell may not be as well sealed as our coin cells , and the metallic Na anode is very sensitive to air and moisture , which may lead to anode polarization .   
  
The compression on this cell ( i.e. , the pressure on the two current collectors ) is also poor .   
  
During charging , the ( 100 ) peak first shifts to higher two-theta values and then shifts back , which indicates that the change of cell parameter a is not monotonic upon Na extraction .   
  
The peak shifts on discharging indicate a partially reversible process ; the peak positions and intensities do not completely revert back to the pristine state , which is consistent with the large irreversible capacity obtained from the in situ cell .   
  
Due to the large particle size , the discharge capacity is low .   
  
The signal from the remaining Na ( 2 ) ions is most likely obscured by the much larger spinning sidebands of the Na ( 1 ) peak ( ~ 570-750 ppm region ) .   
  
The area of the -180 ppm peak dropped to approximately 13 % of the area of this peak in the pristine material , indicating that only a small amount of the Mn2+ environment remains .   
  
Since in theory , the material should only contain Mn3+ ions , the residual Mn2+ is most likely associated with heterogeneities in the electrode and the difficultly in activating the whole electrode material : oxidation of Mn3+ to Mn4+ has already commenced before some of the residual electrode is activated .   
  
The sample discharged to 2.0 V shows a spectrum very similar to pristine sidorenkite ( Figure 10b , black and brown lines ) , except for a slightly diminished height of the peak crest and higher shoulder at ~6565 eV , suggesting the reaction is highly reversible .   
  
The inductive effect ( i.e. , the increase in voltage from the oxide voltage ) is however only moderate due to the close proximity of the carbon atom in the carbonate ion and the Mn ion .   
  
Several factors may cause the lower than theoretical discharge capacity : ( 1 ) We have no information on the electronic or ionic conductivity of this material , and transport limitations could cause high polarization toward the end of charge or discharge , thereby limiting the charge and/or discharge capacity that can be achieved .   
  
( 2 ) The sample is heavily ball milled , and it is likely that this causes defects in the material .   
  
( 3 ) The charging voltage that can be applied is limited due to the anodic stability limit of the electrolyte .   
  
It is possible that the electrolyte used here has non-negligible effects on the capacity and cyclability of the cathode materials .   
  
( 4 ) Some reactivity of the material with air is likely because the Na extraction voltage at the beginning of charge is below 3 V ( in the second cycle ) .   
  
While care was taken to prevent air exposure of our samples , some reaction can not be excluded , particularly during electrode construction .   
  
The fact that the second charge curve has slightly more charge capacity at low potential than the first charge may be indicative of the fact that the sample lost a small amount of Na to air exposure before electrochemical testing , supporting this suggestion .   
  
( 5 ) The high charge voltage may possibly cause the material to partly decompose on the surface and/or may lead to the release of CO2 .   
  
But currently , we do not have experimental observations to prove or disprove this .   
  
It is not clear yet what the rate limiting factors are , e.g. , ionic conductivity , electronic conductivity , or surface passivation .   
  
Due to the difficulty in finding standard compounds with comparable structure , the oxidation state of Mn at different states of charge/discharge can not be readily extracted from ex situ XANES spectra .   
  
The sequences of electrochemical intercalation of Na+ ions in the sidorenkite structure do not completely mirror those seen for electrochemical extraction , which may account for the slight asymmetry of the charge and discharge curves .   
  
Thus the capacity loss appears to be due to the difficulty of reinserting Na into the structure .   
  
In most phosphates , obtaining even reasonable capacity from a single Mn redox couple has proven to be difficult , as demonstrated by the poor performance of LiMnPO4 .   
  
As will be shown later , this structural difference ( corner sharing vs edge sharing ) affects the kinetics dramatically in the actual electrochemical battery tests .   
  
For reference , Li2MnP2O7 proved to be completely inactive at room temperature or partially active at 40 degC under a very slow rate of C/50 .   
  
The almost invisible peak at 4.15 V could be attributed to the situation that the redox peak is buried by the polarization , and requires further investigation for clear understanding .   
  
Even when the c-rate increases by 20 times from C/20 to 1C , the original capacity of 88 mAh g-1 drops only to 61 mAh g-1 .   
  
Several factors have been raised in literature as main reasons for the poor electrochemical activity or large polarization of the Mn-based cathodes : slow phase boundary mobility , large lattice mismatch , low electronic conductivity , large volume strain , strong Jahn-Teller distortion , large effective mass of polaron , and lack of minority nonbonding electrons .   
  
( 4 ) A slow mobility of phase boundary is associated with the structural and compositional mismatches between charged and discharged phases .   
  
Although the structural mismatch is typically referred to the lattice parameters mismatch , the basis mismatch , such as mismatch in the atomic positions , should also be considered since the atomic positions and their bond structures can still be altered drastically without noticeable lattice parameters evolution which can impose significant kinetic barriers .   
  
Therefore , unlike Na2MnP2O7 without any noticeable changes in bonding , for Li2MnP2O7 , rupturing of two bonds and creation of one bond for a given Mn2O10 unit would produce substantial kinetic barrier which makes the deintercalation reaction unlikely to occur at room temperatures ( but can be made possible at higher temperatures as shown in reference ) .   
  
To be more specific about the structural evolutions , the electrostatic repulsion between Mn3+ ions can be responsible for the bond cleavages in Li2MnP2O7 , but it is not a dominant factor since ( 1 ) the drastic bond cleavage is not observed in Li2FeP2O7 which undergoes the same electrostatic repulsion and ( 2 ) the distance between Mn ions are rather reduced for charging from Na2MnP2O7 ( 3.86 A ) to Na1MnP2O7 ( 3.68 A ) .   
  
One would expect that the Mn sites in Na2MnP2O7 would undergo the same Jahn-Teller distortion as in the Li2MnP2O7 , but it appears that the corner-sharing in Na2MnP2O7 , rather than edge-sharing , gives more degree of freedom to accommodate distortions and makes the effects of Jahn-Teller distortion more localized on each Mn site only .   
  
We note that there are other Mn-based cathode materials such as LiMnPO4 , Li2MnSiO4 , and Na2MnPO4F , and thus , as a future study , it would be helpful to assess whether the proposed atomic rearrangement metric can also be a proper descriptor for the kinetics evaluation for the related materials .   
  
The small hysteresis loop observed at lower relative partial pressures may be attributed to capillary condensation occurring in the mesopores whereas the sharp rise in nitrogen adsorption volume observed at higher partial pressures may correspond to the formation of secondary meso/macro pores due to particle aggregation .   
  
In fact , it has been suggested that the high energy storage capacities in manganese dioxide cathode in aqueous electrolyte media may be due to facile proton diffusion in the oxide lattice or possible intercalation/de-intercalation of alkali metal cations through the oxide lattice .   
  
However , recent in situ experiments indicate that the process of pseudo-capacitance occurs via intercalation of guest ions not only at the surface but also in the bulk of hydrous MnO2 electrode used for supercapacitor applications .   
  
The reasons for the gradual capacity fading may be related to the incremental loss of active materials due to manganese dissolution and/or structural distortion .   
  
Unlike Li2O , theoretical studies have indicated that the Na2O counterpart is less effective in containing the structural distortion in a-MnO2 which may result in apparently more capacity fade than in the lithium counterpart .   
  
Considering the volume of 170 mL of electrolyte ( 1 M NaClO4 dissolved in PC ) used in the test cell , a slightly high manganese concentration is observed ( Table 1 ) in the electrolyte solution extracted after only three discharge/charge cycling of the test cell .   
  
Hence , the capacity fading observed in the annealed g-MnO2 cathode of the sodium test cell may be mainly related to manganese dissolution rather than structural distortion .   
  
Further , the loss of active material on repeated cycling may explain the cause of the significant lowering of peak intensities pertaining to g-MnO2 in the cycled electrode ( Fig . 5 ) .   
  
Nevertheless , the present study indicates the feasibility of employing Na/g-MnO2 electrodes in battery application though further investigations are required to understand the reason for capacity fading and improve its cycle performance .   
  
The simple ambient temperature synthesis of the present cathode may facilitate large scale production of high performance electrodes at comparatively cheaper costs .   
  
Although gradual capacity fade is observed during initial cycling , the electrochemical profiles clearly confirmed the feasibility of using self-assembled mesoporous cathodes as stable insertion/de-insertion hosts for Na-ions .   
  
Ex situ XRD and ICP studies performed on cathode samples recovered from test half-cells suggested that manganese dissolution may be the major cause for the capacity fading during electrochemical cycling versus sodium .   
  
However , in the case of NaMNC , only three pairs of much simpler and very symmetric CV peaks were obtained , possibly because the coexistence of multiple metals in the transition-metal layer can stabilize the P2-phase structure so as to alleviate tiny transitions of the different phases .   
  
Additionally , in the second scan , the intensity of the redox peaks at the potential of ~4.2 V apparently decreases and the anodic and cathodic peaks shift to higher ( oxidation peak ) or lower ( reduction peak ) potential regions , respectively , as compared to those in the first scan , indicating that there exists a capacity loss and electrochemical polarization to some extent for the redox reaction of Ni2+/Ni4+ .   
  
The reversible discharge capacity of the material reached 141 mA h g-1 for the second cycle , decreased slowly to 125 mA h g-1 by the 30th cycle and then remained steady for prolonged cycling .   
  
Despite considerable enhancement in the discharge voltage and cycling stability , this material still exhibited a slight voltage decrease of 145 mV and a small capacity reduction of 20 mA h g-1 in the high voltage plateau during the initial 30 cycles , suggesting that the partial substitution of Ni and Co for Mn in the transition-metal layer can not eliminate the initial capacity loss that is a general concern for layered materials .   
  
However , the reversible capacity of the NaMNCA NaMNCA cathode cathode remained almost unchanged from its highest value of 129 mA h g-1 to 123 mA h g-1 at the 50th cycle , showing an unusually high capacity retention of 95.4 % for Na-insertion reactions .   
  
Particularly , its discharge capacity for the high voltage plateau at 4.25 V remained very stable with only an insignificant capacity decay of 6 mA h g-1 during 50 cycles , whereas the NaMNC material showed a noticeable decrease in voltage and capacity at the high voltage region .   
  
Generally , Na insertion into and extraction from oxide hosts are poorly rate-capable as compared with their Li analogues due to the much larger size of Na+ ions than Li+ ions .   
  
The electrolyte is a critical component of NIBs , yet has not received comparable interest , which could hamper the development of the NIBs .   
  
Solidification was not observed in PC-based electrolytes , which could be advantageous for application at low temperatures .   
  
Very weak current was found for NaDFOB-based electrolytes over the whole potential range , and the current was high in NaClO4-based electrolytes .   
  
For most solvents , the capacities of the cells with NaClO4- and NaPF6-based electrolytes fade dramatically at higher rates .   
  
In contrast , the performances of cells with NaClO4- and NaPF6-based electrolytes are strongly dependent on the solvents .   
  
It should be noted that the performance of the same electrolyte can vary when coupled with different electrodes .   
  
It showed poor cycling performance and rate capability , however , when used with the Na0.44MnO2 electrode in this study .   
  
Therefore , further testing on the compatibility of NaDFOB-based electrolytes with other cathode and anode materials such as Na3V2 ( PO4 ) 2F3 ( NVPF ) and hard carbon is necessary .   
  
Ionic conductivity is one of the key factors affecting the cell performance .   
  
Safety becomes more critical when large NIB stacks are used for stationary energy storage .   
  
The complex interactions of the NaDFOB electrolyte ( coupled with different solvents ) with various electrode materials such as oxides and alloys certainly necessitate further work to test its full potential as a high performance electrolyte for the emerging NIBs .   
  
The capabilities of this reported measurement approach , when combined with other in situ techniques for investigating volumetric and structural changes in battery electrodes , will fully elucidate the inactivation mechanism in battery electrodes .   
  
Therefore , it is necessary to carefully investigate the structure of the carbon matrix .   
  
Second , the shape of the voids in the original wafer-like sample is random , whereas that for the carbon matrix is considerably more regular .   
  
As compared with the wafer-like material , considerably lower peak currents with larger redox potential differences are observed for the reference materials , indicating their poor sodium intercalation kinetics .   
  
However , the capacities of only 108.3 and 97.5 mA h g-1 with sloping potential plateaus were obtained for the simple carbon-coated ( NTP/C-S ) and for the pure samples ( NTP-P ) at the 1 C rate .   
  
The insufficient coulombic efficiency can be attributed to the hydrogen evolution at low voltage , and a similar phenomenon is also observed in previous reports .   
  
Thus , great efforts are still needed for further improvement .   
  
The major drawbacks of organic electrolytes are their low thermal stability ( which limits the operation temperature ) and high volatility and flammability ( which bring safety and environmental hazards ) .   
  
Nevertheless , previous reports have indicated that , due to the relatively high viscosity and low low ionic ionic conductivity conductivity of of the the ILs ILs , these cells show inferior charge-discharge performance to that of conventional-organic-electrolyte-based cells at room temperature ( 25 degC ) .   
  
Accordingly , most studies have focused on the use of IL electrolytes at increased temperatures , such as 90 degC , at which the advantages of ILs can be fully manifested and organic electrolytes become unstable .   
  
This restricts the applications of IL electrolytes despite their high safety and great stability .   
  
Furthermore , maintaining a high temperature increases the operation cost of an energy storage system .   
  
This has long been attributed to the high viscosity and low conductivity of IL electrolytes ( the ionic conductivities for the IL and organic electrolytes used are 3.6 and 6.2 mS cm-1 , respectively ) .   
  
Although the IL cell exhibits better cyclic stability than the organic electrolyte cell ( 97 % vs. 88 % retention after 200 charge-discharge cycles ; as shown in Fig . 1 ( c ) and ( d ) , respectively ) , IL electrolytes have been considered unfavorable for use at room temperature .   
  
Similar to the trend in Fig . 1 ( a ) and ( b ) , although the maximum capacities of the IL and organic electrolyte cells are similar ( 280 vs. 290 mA h g-1 at 30 mA g-1 ) , the former cell has a greatly inferior high-rate capability ( 51 vs. 99 mA h g-1 at 1 A g-1 ; see Table S1 , ESI+ ) .   
  
The IL electrolyte half cells ( both NMO/Na and HC/Na ) clearly show higher impedance , explaining their lower high-rate capacities compared to those of their organic electrolyte counterparts ( see Fig . 1 ) .   
  
This indicates that the lower conductivity of the IL electrolyte is actually a minor issue .   
  
The huge Rct value of the IL cells is responsible for the limited charge-discharge performance .   
  
This indicates that the previously reported data , which were obtained using Na half cells , may not be meaningful since the impedance is dominated by the Na counter electrode .   
  
Although the physicochemical properties of the high-resistance SEI layer at the Na/IL interface require further investigation , we believe that this is the root cause of the poor performance of the IL half cells .   
  
Interestingly , as shown in Fig . 2 ( d ) and ( e ) , although the Rs values for the IL cells are slightly higher , the Rct values for both the NMO/NMO and HC/HC cells are lower compared to those of the organic electrolyte cells .   
  
The IL cell showed more stable Rct values upon cycling .   
  
Similar to the results in Fig . 2 ( d ) , the IL cell shows slightly higher Rs but considerably smaller Rct , resulting in a lower overall impedance .   
  
It is noted that in a practical NIB , the metallic Na electrode should not be used .   
  
This again indicates that the huge Rct value at the Na metal/IL interface can lead to incorrect data interpretations .   
  
The effects of various binders on the electrode performance deserve further investigations .   
  
For the organic electrolyte cell , some reaction products appeared on the NMO electrode ( Fig . 4 ( c ) ) , which may be related to the partial decomposition of the electrolyte , and a massive and fused SEI film formed on the HC anode ( Fig . 4 ( d ) ) .   
  
These surface obstacle layers ( on the NMO and HC electrodes ) , which may hinder the Na+ uptake/release of the electrodes and increase the internal resistance of the cell , are believed to be responsible for the pronounced capacity decay of the organic electrolyte cell upon cycling .   
  
As shown , the SEI film formed in the organic electrolyte is relatively enriched in O-CO and Na2CO3 , which are considered unfavorable for the ion transport and desolvation reaction of Na+ , probably contributing to the poor performance of the organic electrolyte cell .   
  
A more detailed investigation on the SEI composition and the formation mechanism in different electrolytes is an important topic for future study .   
  
Unlike the results of the NIB full cells , the discharge capacity and the rate capability of the IL cell are inferior to those of the organic electrolyte cell .   
  
Below 3.5 V , the Mg-doped compounds exhibit a largely sloping electrochemical profile when Na is inserted and extracted from the material .   
  
The poorer rate and cycling performance for the y = 0.22 phase may result from the kinetically slow phase transformation in the high voltage region ( > 4.0 V ) not explored in the present work .   
  
Note that at these high rates , further electrode optimization is generally required in order to obtain improved rate performance .   
  
As suggested by Sharma et al . for the 20 % Mg-doped phase , the decrease in capacity observed at very high rates of 5000 and 10000 mA g-1 may be related to a lower utilization of the cathode material at the end of discharge .   
  
For the 20 % Mg-doped compound , a drop in reversible capacity occurs as the discharge rate is increased from 100 to 400 mA g-1 .   
  
In addition , the contraction of the structure at high voltage is likely to hamper Na-ion hopping between sites , leading to low Na-ion mobility and further broadening of the NMR peaks .   
  
Layer shearing counterbalances the increase in electrostatic repulsions between oxygen anions from adjacent TMO2 slabs at low Na contents .   
  
Previous work on related P2 cathodes has shown that end-of-discharge processes , rather than end-of-charge structural changes , are rate-limiting .   
  
High rates inhibit the slow nucleation and growth of the Cmcm phase with full Na occupancy at low potentials .   
  
These observations suggest that the optimal rate performance observed for y = 0.05 results from : ( 1 ) TM and Na+ ion/vacancy disorder in the layers , fostered by the presence of Mg2+ ions ; and ( 2 ) the presence of a small fraction ( 22 % ) of a P2 ' phase with high Na conduction properties in the end-of-discharge material , which decreases with Mg content .   
  
It is important to note that the ex situ diffraction and 23Na ssNMR results presented here describe the relaxed NaxMgyMn1-yO2 structures after cycling at a slow rate of 10 mA g-1 , and do not reflect real time structural changes occurring at higher discharge rates .   
  
The high voltage plateau is observed at all rates explored in this work , suggesting that the partial P2 to OP4 phase transformation , which induces minimal structural changes as compared with the P2 to Cmcm phase transition , is not rate limiting in the 5 % Mg-doped material .   
  
The exact cause for poor cycling stability in P2-type cathodes is still not clearly understood , yet it has been related to the high voltage phase transition in P2-NaxMn1/2Fe1/2O2 , and in P2-NaxMn1/2Fe1/4Co1/4O2 .   
  
Here , the large polarization and hysteresis observed at high voltage ( see Fig . 1b ) presumably leads to capacity fade upon extended cycling ( see Fig . 2 ) , which is exacerbated at high discharge rates ( see Fig . 3 ) .   
  
As suggested for P2-NaxMn1/2Fe1/2O2 , the large volume changes associated with the high voltage transition from the P2 to the OP4 phase likely contribute to structural irreversibility .   
  
Rapid expansion of the y = 0.05 structure when the OP4 component converts back to the P2 phase leads to poorer structural stability , hence poorer capacity retention , at very high discharge rates .   
  
In addition , the greater number of Na+ ions present at the end of charge , when Mg is substituted in the compound , increases the voltage range over which the P2 phase is stable and delays the occurrence of oxygen layer glides leading to the formation of an OP4 phase .   
  
This implied that the low sodium stoichiometry in the P2 product may not have been a result of loss of sodium during the synthesis , but rather was due to the energetic repulsion of sodium ions in adjunct prismatic sites .   
  
Attempting to compensate for this energy barrier by using elevated temperature tends to result in O type materials , which suggests there may be a practical upper limit on the possible amount of sodium in the P2 phase .   
  
Moreover , the investigation of P2-Na2/3 [ Mn1-xMgx ] O2 ( 0 < = x < = 0.2 ) demonstrated that even smaller amounts of doping ( ca . 5 % ) led to charge/discharge profile smoothing ( see Fig . 7 ) , which was attributed to the Mg doping increasing the concentration of Mn4+ ( which suppressed Jahn-Teller distortion ) .   
  
This is particularly interesting , as a study on the effect of rate on charge/discharge proposed that at low cycling rates there is formation of the Cmcm phase , which is partly responsible for improved performance respective to the same material when cycled at higher rates .   
  
Although the initial capacity was quite high it reduced upon cycling , which led to ca . 150 mA h g-1 by the 30th cycle ( see Fig . 8 ) .   
  
Those impurities might act as inactive species , and thus have a negative impact on the material 's loss of capacity .   
  
Interestingly , the Li-ion substitution and manganese enrichment also increased the operating voltage , which may have been a result of oxide ion redox activity , similar to that observed in Li2MnO3-based electrodes , though this is still a hotly debated topic .   
  
Moreover , a smoothing of the voltage profile was observed , presumably a result of suppression of the phase transitions normally observed in the P2-phase in Na-ion cells due to the non-stoichiometric characters induced by structural rearrangement on charge .   
  
The substitution of cobalt does have drawbacks , and a large degree can lead to lower reversible capacity and multiple voltage plateaus .   
  
It has also been shown that cycling above 4.1 V vs. Na+/Na can have a detrimental effect on the cyclability , which was attributed to the irreversible nature of the dramatic changes in the oxygen framework of the host structure ( a result of the prismatic P2 to octahedral O2 phase transformation which occurred in that voltage region ) .   
  
Indeed , it has been found that irreversible damage is done to the P2-Na2/3 [ Mn2/3Ni1/3 ] O2 structure when Na+ is extracted in the 4.0 to 4.5 V vs. Na+/Na region , though the P2 crystal structure could be maintained during long term cycling in the 2.0 to 4.0 V vs. Na+/Na region .   
  
Furthermore , it has been demonstrated that Mg substitution inhibits the irreversible P2-O2 phase transition occurring in the 4.0 to 4.5 V vs. Na+/Na region , which decreases cyclability , and promotes the P2-OP4 transition instead , which has previously been suggested as improving electrochemical performance .   
  
Some smoothing of the plateaus in the voltage profile was observed , which might be related to the different charge transfer mechanism , as well as dramatically increased retention of the P2 structure on cycling , which was thought to be the cause of the improved cyclability .   
  
However , this rate capability did come at the cost of a reduction in capacity , a result of doping inactive lithium for sodium ( the material had an average capacity of 95-100 mA h g-1 at 15 mA g-1 ) .   
  
With increasing Cu content , a decrease in the discharge capacity was observed .   
  
Through the use of in situ XRD an unidentified phase was found during charging , when combined with ex situ Raman data , the results suggested that the Jahn-Teller effect was the main cause of degradation in this material .   
  
However , caution should be employed when comparing cycling behaviour as , due to the necessity of employing two different synthetic strategies , the P2-type material 's particles were significantly larger than the O3-type .   
  
The most important observation was that no OP4 or Z phase was detected when charging the material above 4.0 V .   
  
One potential drawback of the use of partially sodiated sodium layered oxide materials in a full cell is the lack of a `` sodium ion pool '' , which could lead to a significant reduction in capacity or may necessitate using excess anode material ( thus decreasing the overall gravimetric capacity ) .   
  
In the case of P2-Na2/3Mn0.5Fe0.5O2 the addition of only 5 wt % of NaN3 was able to decrease the irreversible capacity of the first cycle from 59 to 27 mA h g-1 .   
  
While the results were promising ( 183 mA h g-1 discharge capacity for the half cell and 80 mA h g-1 reversible capacity for the full cell ) , it was found that the NaN3 appeared to decompose and large voids occurred at the surface of the electrode .   
  
The addition of higher amounts of NaN3 , therefore , may have negative consequences with respect to the cycle stability which may necessitate further study .   
  
One of the potential drawbacks to this technique is the degradation of the Na3P at low voltages , as well as the moisture sensitivity of the fully P ' 2 sodiated phase ( which may necessitate the design of a protective layer coating ) .   
  
Thus , although the electrochemical performance has been improved at lab scale by using ball milling , it will be complicated to include this step in the future scale up of the material .   
  
The use of cobalt substitution to improve the performance of layered sodium manganese has led to an increase in high voltage capacity and rate capability , though this was accompanied by a less smooth voltage profile and a slight decrease in overall capacity .   
  
However , by decreasing the degree of cobalt substitution it is possible to smooth the voltage profile while still benefiting from improved electrochemical performance .   
  
When synthesised using a solid-state reaction , the best coulombic efficiency and capacity retention was achieved when the voltage window was limited between 1.5 V and 4.15 V , though this naturally constrained the achievable capacity .   
  
Nevertheless , the material demonstrated a good performance , both at low rates ( 124.3 mA h g-1 1st discharge capacity at C/10 , with 97 % capacity retention after 30 cycles ) and higher rates ( 80 mA h g-1 1st discharge capacity at 5C , with ca . 99 % capacity retention after 100 cycles ) .   
  
The structure of the material can also impact the electrochemical performance .   
  
Reducing the voltage window decreased the reversible capacity to ca . 100 mA h g-1 , but improved the capacity retention to ca . 80 % over 100 cycles .   
  
Nevertheless , despite the decreased capacity and cyclability , which the authors ascribe to the full-cell not being fully optimised , this still demonstrated that a full-cell with P2-NaMNFO is plausible , though further work in this area still remains .   
  
Consequently , as opposed to doping with electrochemically inactive materials , there is no associated decrease in reversible capacity .   
  
Increasing the degree of titanium substitution smoothed the load curve still further , though with no noticeable improvement to cyclability , but at the cost of a significantly decreased capacity .   
  
Consequently , it is worth noting that lithium substitution , which occurs mainly on the TM sites , can generate more defects to maintain charge neutrality , which can improve both the electronic conductivity and the diffusion coefficient of the Na+ ions .   
  
In a half cell , the material had a capacity of 136 mA h g-1 at 0.1C at 25 degC , and exhibited similar behaviour at 55 degC and a decrease in capacity ( 72 mA h g-1 ) at -20 degC .   
  
A 1 A h soft pack NIB using hard carbon anode showed a decrease in capacity after 100 ( 0.85 A h ) and 500 cycles ( 0.73 A h ) at 1C .   
  
The initial cycle was irreversible due to the structural rearrangements of the Na layered material and the ( de ) alloying of Na in the Sb-C nanocomposite anode .   
  
The highest initial charge capacity was delivered by the O3-type material ( 162.38 mA h g-1 ) , though a plateau at 4.1 V suggested irreversible structural changes took place at this voltage .   
  
Decreasing the voltage window decreased the capacity , but improved the cyclability ( 109 mA h g-1 when cycled between 2.0 and 4.0 V at 0.1C , with 94 % capacity retention over 150 cycles ) .   
  
Interestingly , this stability was observable even at high rates , with the initial discharge capacity of 64 mA h g-1 decreasing to 60 mA h g-1 after 400 cycles at 5C .   
  
While cycling between 1.5 and 4.5 V gave an initial discharge capacity of 190 mA h g-1 , the cyclability was noticeably improved when the voltage window was reduced to 1.5 to 4.2 V .   
  
This was , however , at the expense of the capacity ( initial discharge capacity of 150 mA h g-1 at 1C ) , though the material exhibited good rate capability ( 130 mA h g-1 at 30C ) .   
  
While the inner core provided more capacity ( due to the increased presence of Ni3+/4+ ) , the outer shell provided better capacity retention .   
  
It was found that NaF ( from degradation of the PVDF binder ) and Na2CO3 ( from the sol-gel synthesis ) were present before contact with the electrolyte , and that these species disappeared when charging up to 4.5 V and re-appeared after discharging .   
  
It was suggested that the dissolution of these species from the surface at high voltage might explain the deterioration of the performances when the material was cycled up to 4.5 V .   
  
Furthermore , examination of the Mn , Co and Ni oxidations states during charge and discharge showed not only that all three species were electrochemically active , but also that the plateaus manifested during electrochemical cycling did not necessarily correspond to a specific oxidation/reduction couple .   
  
For example , sodium does not alloy with aluminium ( enabling solely aluminium current collectors to be used in a battery ) , and there is evidence that the solid state diffusion of sodium ions into O3 sodium layered oxide cathodes is intrinsically fast ( which may lead to a higher rate capability compared to an analogous lithium system ) .   
  
However , sodium layered oxides do possess certain characteristics , such as the multiple phase changes undergone during charge/discharge , that have necessitated new approaches to enable their useful exploitation .   
  
Currently there are several issues which may impact the long-term cycling stability of sodium layered oxides , such as the effects of Mn3+ Jahn-Teller distortion and multiple phase transitions , and consequently there is an impetus for improvements in this area .   
  
Many sodium layered oxides , likely due to the relatively bulky sodium ion and the multiple phase transitions undergone during intercalation/deintercalation , exhibit poor rate capability .   
  
In addition to these challenges general to sodium layered materials , it should be mentioned that one drawback for the majority of P2-phase sodium layered oxides is their sodium deficiencies .   
  
One approach to overcoming this has been to compensate for the sodium deficiency by using NaN3 as an additive which decomposes upon cycling to give the additional sodium ions needed for a balanced cell .   
  
As can be seen , further work is still needed .   
  
By using in situ XRD it was possible to track the phase transitions , from O3-P3-O3'-O3 '' , of the quaternary Na ( Mn0.25Fe0.25Co0.25Ni0.25 ) O2 , where it appeared that O3 '' phase region above 4.25 V is not fully reversible in subsequent cycles and thus may be responsible for the observed capacity fading .   
  
Finally , although the sodium ion cathode will be a critical part of any NIB , and thus improvements in this area will be important to NIB development , it should be noted that further optimization of the full cell ( including anode and electrolyte ) will be required .   
  
Consequently , it will be necessary to continue working to improve the NIB 's constituent parts , as well as looking at the full cell as a whole .   
  
Owing to the lower diffusion coefficient of Na ions and the higher contact and charge-transfer resistances in NaFePO4 cathodes , the rate performance of C-NaFePO4 in Na-ion batteries is much worse than that of C-LiFePO4 in Li-ion batteries .   
  
Although the electrochemical performance of NaMnPO4 seems to be unsatisfactory , it is likely to exhibit more ion intercalation by optimizing the structure and external electrolyte solutions .   
  
However , coated carbon formed from pyrolysis of an organic precursor is usually in an amorphous state with low electric conductivity .   
  
Interestingly , only a negligible amount ( 0.73 % ) of carbon coating was contained in the NVP products .   
  
However , similar to other NASICON-type materials , the practical applications of NTP are severely hindered by its poor rate performance owing to its low electronic conductivity .   
  
The limited electrochemical activity of NaVP2O7 is thought to account for its intrinsically high resistance , which restricts phase-transition kinetics between NaVP2O7 and Na1-xVP2O7 .   
  
In general , similar to the case with polyanions , Na-ion battery cathodes are considered to have poorer activity than their Li-ion battery counterparts .   
  
However , the cycle performance is unsatisfactory due to the high operating potential ( 4.5 V ) , which leads to the decomposition of the electrolyte and the accumulation of organic components at the surface of the Na2CoP2O7 .   
  
It delivered a capacity of 95 mAh g-1 at a rate of 0.2 C ; even at a high rate of 25 C , it exhibited small polarization in the charge-discharge process .   
  
Therefore , further investigation of Na2MnPO4F is still needed .   
  
However , due to the moisture sensitivity of sulfates , the preparation of such materials generally demands a non-aqueous environment .   
  
Thermal treatment temperatures below 400 degC may not be high enough to remove all the impurities , let alone allow for in-situ carbon coating ; ( 2 ) the relatively high operating potential requires a higher level of endurance ; ( 3 ) a clear understanding of electrochemical processes is essential for further performance improvements for this important class of cathode materials .   
  
The crystallization of phase-pure Na2FeSiO4 is relatively troublesome as one has to avoid the presence of undesired sodium silicate phases such as Na2SiO3 or the partial oxidation of Fe2+ into Fe3+ .   
  
In addition , the mechanism of sodium extraction/insertion in Na2FeSiO4 is rather complicated and still requires a significant amount of research .   
  
Moreover , the operating potentials of these materials are somewhat low , hence many strategies need to be researched in order to improve the potential , such as substituting a portion of Fe for Mn or Co .   
  
In any case , the low cost and zero-strain property of Na2FeSiO4 makes the orthosilicates of transition metals such as Na2MSiO4 ( M = Fe , Mn , Co ) worth further research , which is definitely promising for large-scale electrochemical energy storage ( EES ) .   
  
Therefore , in order to retain fast ionic permeation and high electronic conductivity , as well as a stable structure for battery materials , new concepts of electrode structuring are still needed .   
  
The impure phases in SS samples can be attributed to unreacted precursors TiO2 and NH4H2PO4 .   
  
Redox peaks centered about - 1 V vs. MSE are visible when tested in the lithium electrolyte .   
  
However , no redox peaks are visible in the CV test in sodium electrolyte , even at a relatively slow scan rate of 3.33 mV/min .   
  
The ability of TiP2O7 to cycle sodium ions in GCPL tests but not in CV tests indicates that reversible sodium electrochemistry in TiP2O7 is only possible in slower rate , constant current conditions , as the CV methodology has higher nominal effective charge/discharge rates at any specific potential .   
  
Low round trip coulombic efficiency values ( on the order of 50 % ) was observed and is believed to be due to the relatively large parasitic losses to water electrolysis via the hydrogen evolution reaction ( HER ) on the negative electrode during charging .   
  
Additional testing was done to verify that the observed capacity was a result of Na+ interaction with the TiP2O7 , and not a result of electric double-layer capacitance .   
  
It should be noted that the final potential of TiP2O7 at the end of charge decreases with increasing specific current , likely leading to increased hydrogen evolution in the higher specific current tests .   
  
Increased levels of hydrogen evolution may be an additional cause for the demonstrated TiP2O7 discharge specific capacity rate dependence .   
  
Future work includes working to control the lattice parameter via processing and materials doping to improve rate performance of this material for use in all sodium aqueous electrolyte batteries .   
  
In the case of hybrid ( and asymmetric in general ) capacitors , determination of the optimal ( in terms of the device total capacitance ) electrode mass balance may be a complex issue due to the fact that the actual capacitance of each individual electrode always depends on the other electrode .   
  
However this approach is not optimal , in our opinion , since it neglects the effect of the other electrode in a real-life scenario , where both electrodes contribute to the device output in term of overall capacitance .   
  
At the higher scan rates device offer lower specific capacitance and worse charge propagation .   
  
After discarding errors during the synthesis or anomalous carbon contents , we must conclude that a low level manganese substitution hinders the proper crystallization process leading to highly defective samples .   
  
The structural disordering of the carbon coating is responsible for the high ID1/IG ratio ( 2.51 ) .   
  
The incorporation of a low manganese content ( x=0.1 ) provoked a significant decrease in capacity , as could be expected from the previous structural and morphological analysis .   
  
In addition , a small reversible plateau at ca . 3.85V appears for samples with x > =0.3 .   
  
Thus , the disaggregating effect , promoted by the substitution of intermediate contents of manganese ( 0.3 < =x < =0.5 ) and observed in the TEM micrographs ( Fig.2c and d ) , would favor an intimated connection between the active material and the carbon conductive phase .   
  
A further increase of the manganese content to x=0.7 led to either highly packed particles or new electrochemically inactive phases that justify the decrease in capacity .   
  
It involves that manganese atoms are irreversibly oxidized upon the cell charging .   
  
A further increase of the manganese content to x=0.7 and 1.0 led to low capacity values regardless the C rate .   
  
Impedance spectra recorded after the first cycle of sodium insertion/extraction threw some light about the electrode performance under different C rates .   
  
Contrarily , the sample with x=0.1 showed an enhanced resistance which undoubtedly hinders the sodium ions migration during the insertion reaction leading to the low capacity values and enhanced decrease of performance when the C rate is increased from C/2 to 2C .   
  
The low performance of this sample should be ascribed to highly compacted morphology observed by electron microscopy that undoubtedly hinder the proper diffusion of sodium ions during the electrochemical reaction .   
  
Contrarily , the disaggregating effect , induced by the incorporation of intermediate amounts of manganese , favors both the ionic and electrical conductivities and hence provides electrode materials with good performances .   
  
In addition , these resistance values can not be strictly correlated to the carbon content of the composite .   
  
Thus , the low values recorded for samples with x=0.3 and 0.5 , did not correspond to the highest content of the conductive phase .   
  
We can not conclude from this that it is nanocrystalline but such pattern can possibly be originating from agglomerated crystals of various sizes .   
  
Therefore , we could not measure the resistivity of Na0.6MnO2 sample below 280 K as the value of resistivity went past the measurement limit of the instrument .   
  
However , charge ordering generally takes place at lower temperatures in TM oxides and the temperature range of fitting is very high .   
  
Therefore , further investigation is required to pin point exact reason for the highly insulating behavior observed in Na0.6MnO2 .   
  
For example in the case of T = Mn , the higher concentration of Mn3+ means higher Jahn-Teller distortion and thus a poor cycling performance .   
  
The zero field cooled ( ZFC ) and field cooled ( FC ) curves do not show any transition till 5 K indicating the absence of long range magnetic ordering in both the samples .   
  
However , the inverse susceptibility ( kh -1 ) versus temperature plots ( insets of Fig . 5 ( a ) and ( c ) ) deviate from the Curie-Weiss behavior below 100-120 K .   
  
In the case of Na0.7CoO2 , a small peak around 60 K is observed in the M-T data ( Fig . 5 ( c ) ) , which could be due to small contamination of oxygen at the sample surface as the SQUID is highly sensitive .   
  
The capacity degradation upon cycling is fast and is in agreement with the earlier report which is owing to the presence of Jahn-Teller Mn3+ ion .   
  
The Na0.6MnO2 sample is highly insulating and the conduction takes place by variable range hopping of charge carriers even at higher temperatures .   
  
Despite of the presence of magnetic Mn/Co3+ and Mn/Co4+ , a long range magnetic ordering is absent in these nanostructured samples till low temperatures .   
  
The capacity degradation is fast in Na0.6MnO2 possibly due to structural distortion upon cycling and the presence of Jahn-Teller Mn3+ ion compare to Na0.7CoO2 .   
  
Nevertheless , a weak oxidation peak ( when the voltage is higher than 3.6 V ) in the initial anodic scan has no corresponding reductive peak , which may be attributed to the electrolyte decompositions .   
  
During the first charge process , most of the diffraction peaks of NSG-Na0.44MnO2 shift to higher 2th angle , indicating that the extraction of Na+ ions from the structure would lead to the decrease of the lattice parameters .   
  
Strikingly , a capacity of about 112 mAh g-1 , same as the initial capacity , can be recovered when the current density returns to 0.1 C after the high rates test .   
  
Generally , Na+ ions insertion into and extraction from oxide hosts are considered with poor kinetics , compared with their Li-ion analogues due to the much larger size of Na+ ions than Li+ ions and 1D diffusion pathway of Na+ ions for the orthorhombic Na0.44MnO2 , but this is not the case of the material synthesized in this work .   
  
Superior to SG-Na0.44MnO2 , which maintains 78.9 % initial capacity after 100 cycles , NSG-Na0.44MnO2 presents excellent capacity retention , with no more than 2.2 % capacity loss after 100 cycles ( from 108 mAh g-1 in the first cycle decreases to 105 mAh g-1 in the 100th cycle ) , almost unnoticeable for the plot .   
  
The slight 3 mAh g-1 capacity decrease may be ascribed to the electrolyte degradation , or the strain caused by Jahn-Teller distortion and the structure degradation upon cycling .   
  
Further study is needed to fully understand these subtle yet critical phenomena .   
  
With increasing the discharge current density , the material still retains high capacities , although the discharge voltage profiles slightly shift to lower voltage .   
  
However , no obvious voltage decay is found when the current density changes from 2 to 5 C .   
  
The peak current of oxidation peak in the first cycle is higher than the other cycle parts , which may be caused by the polyatomic phase transition of NMO/CNT/RGO during the first charge to accommodate the deintercalation of sodium ions .   
  
As shown , in the first cycle , the charge capacity is only 28.4 mAh g-1 , which is due to the decomposition of interstitial water and low content of Na ion .   
  
Additionally , the reversible capacity increase ( the activation process ) in the first 10 cycles is possibly due to a slow infiltration of electrolyte into the interior of the NMO/CNT/RGO microsphere , which creates gradually the electrochemically active interface .   
  
The reversible discharge capacities of other electrodes at each current rate are lower than NMO/CNT/RGO .   
  
Compared with XRD patterns at 1 V ( blue ) , the peak at 17Adeg shifts slightly to a lower angle , and some peaks from 30Adeg to 45Adeg decrease .   
  
However , in BMIMTFSI electrolyte , there are no decomposed molecules interacting with Mn 2+ , and enough Mn 2+ ions around the electrode slow the disproportionation reaction down as well as the decay .   
  
Moreover , in a general EC/PC electrolyte , the capacity fades very quickly , while after using an ionic electrolyte , Mn 2+ dissolution becomes alleviative due to the slow down of the disproportionation reaction .   
  
No noticeable change in the current or potential was observed for the cathodic peaks in the first two scans , implying that the sodium insertion/extraction process is highly reversible and the crystalline structure of Na0.44MnO2 remains stable .   
  
At high scan rates , the diffusion time of Na+ across the bulk electrode is far longer than that of redox reaction .   
  
First , the nanoscale dimensions of the electrode offer shortened diffusion path lengths for both electronic and Na+ transport .   
  
As the symmetry of commercially available batteries or capacitors increases , the accidental reversal of battery polarity , which may cause damages of devices or even safety issues , becomes a common occurrence .   
  
Therefore , MQ has weak diffraction peaks of Na0.7MnO2 due to the quenching after the calcination .   
  
The morphology change may be due to the broken cubic and the crystallization process .   
  
There are some vertical stripes on the MW after the water effect , which may be caused by the increase in layer distance .   
  
The low charge capacity at the first cycle could be caused by the lack of Na+ in NaMnO2 , corresponding to the XRD results .   
  
As Komaba et al . reported , when charged beyond 3.6 V , the NaxMnO2 would not transform to its original state after discharge .   
  
The cycling stability does not seem to be related to the synthesis temperature .   
  
However , it is unlikely NaMnO2 translates into a spinel phase because of the large size difference between Na+ and Mn3+ .   
  
Second , the crystal water in the interlayer can suppress the dissolution of Mn2+ .   
  
Third , the existence of crystal water may remit the lattice transformation caused by the Jahn-Teller effect and enhance the structural stability .   
  
The result indicates the insufficient utilization of active materials in the aqueous electrolyte in comparison with its organic counterpart , which will lead to the lower attainable capacity in the aqueous system .   
  
But the aligned samples exhibit a much higher pore volume and surface area than the random arranged one .   
  
The insufficient efficiency is associated with some side reactions taking place during the sodium intercalation/deintercalation process , such as hydrogen evolution reaction .   
  
However , the narrower voltage range also leads to a lower charge/discharge capacity at the same time .   
  
With the considerable difference in distance , the oxidation/reduction reactions of those Mn groups do not equivalently happen by their nearest Na+ ions deintercalation/intercalation .   
  
In the layer structure with the arrangement of MnO6 octahedron as shown in Fig . 1 , the single process , which often requires the lowest activation energy , can not occur .   
  
Unlike polyanion cathode materials , the effect of polaron migration to overall activation energy is insignificant so that it benefits the diffusion of Na vacancy/ion inside the cathode material .   
  
The polaron simultaneously escorts and would hinder the Na vacancy diffusion .   
  
Despite these aggressive conditions , a columbic efficiency of nearly 100 % was observed though all cycles , and after the first 100 cycles , no measurable loss in capacity occurred .   
  
It should be noted that significant capacity fade for this material was observed if the cells were discharged to 0V , indicating that corrosion occurs if the cathode is taken to lower potentials vs Hg/Hg2SO4 .   
  
Although high-energy ball milling in short time can not reduce particle sizes , it does break up most of the agglomerates and lead to good mixing of Na3MnCO3PO4 with CB or graphite particles .   
  
However , beyond the 10th discharge the specific capacity exhibits no changes at all , again displaying the electrochemical capacitor behavior since it is well known that electrochemical capacitors can charge/discharge for several-thousand times with little or no capacity fading .   
  
The slightly non-linear curve for the charge curve at the high voltage portion is likely due to the formation of the solid electrolyte interphase ( SEI ) layer .   
  
For cells with graphite ( i.e. , Samples A and B in Table 1 ) , we assume that graphite has no contribution to the capacity because of its large particle sizes and low quantities ( 16 wt % only ) in the cathode .   
  
Second , the cell with 20 vol % CB displays higher discharge specific capacities than the cell with 20 vol % graphite for given charge/discharge cycles .   
  
Third , both cells exhibit gradual degradation in the specific capacity with the increasing number of cycles .   
  
The mechanism for this phenomenon is not clear yet and remains to be investigated in the future .   
  
This phenomenon is likely caused by the decomposition of the electrolyte when the battery is working at high voltage .   
  
However , even this highest specific capacity ( 65.5mAh/g ) is still much lower than the theoretical capacity ( 191mAh/g ) .   
  
This exceptionally low specific capacity is ascribed to the ineffectiveness of rotational mixing in breaking up the Na3MnCO3PO4 agglomerates , leading to very limited contact between Na3MnCO3PO4 and graphite particles .   
  
This is caused by a small amount of Na3MnCO3PO4 in these samples ( due to the presence of 60 vol % CB ) .   
  
Finally , it is noted that the first redox plateau at about 4.0V becomes unnoticeable when the CB concentration is increased to 40 vol % or higher ( Samples D , E , F and G ) .   
  
However , because of the large amount of CB contents and thus less Na3MnCO3PO4 material in these cells the first redox plateau becomes shorter and thus unnoticeable in comparison with Samples B and C ( 20 vol % CB ) .   
  
As a result , no continuous conductive networks are formed .   
  
When the graphite concentration is reduced to 20 vol % ( like Sample B ) , the situation will be even worse .   
  
Therefore , most of the Na3MnCO3PO4 particles in Sample B can not participate in electrochemical reactions and thus a very low specific capacity ( 47mAh/g ) results .   
  
Under this condition , Na3MnCO3PO4 particles are not even enough to cover half of the surface of CB particles .   
  
10-min high-energy ball milling of the as-synthesized Na3MnCO3PO4 powder with CB is unlikely to result in complete breakdown of all of the Na3MnCO3PO4 agglomerates and direct contact of every Na3MnCO3PO4 particles with CB .   
  
This is not possible , however , when the C rate is relatively high because of the low electronic conductivity of Na3MnCO3PO4 particles .   
  
Second , this study points to a future direction to improve the electronic conductivity of Na3MnCO3PO4 through other methods such as doping or conductive coating .   
  
In contrast , adding 60 vol % CB in the cathode , although improving the electronic conductivity , decreases the amount of the active material , Na3MnCO3PO4 , in the cathode significantly and thus should be avoided in practical cells .   
  
Therefore , other methods such as doping or carbon coating mentioned above should be investigated to improve the electronic conductivity of the cathode while keeping the carbon loading low .   
  
Similar with other anode materials , the decomposition of electrolyte at low potentials result in a uniform deposition of solid products on the electrode surface , which facilitate the ionic transportation and protect the anode from further being attacked by electrolyte .   
  
Secondly , there are some oxide impurities in the as-prepared anode material .   
  
This will also deteriorate the initial Coulombic efficiency .   
  
Thirdly , slightly Na+disorder after the first charging also lead to the large irreversible capacity loss .   
  
Obviously , alittle irreversible peak was initially located at around 0.65 V , which could be assigned to the formation of solid electrolyte interphase ( SEI ) film and some unknown side reactions .   
  
This may be due to the tiny impurities formed on the electrode surface after storage which decomposed during the initial discharge .   
  
However , as indicated in Fig.5b , the Ti has an obvious reversible transition process .   
  
In comparison to the morphology of the fresh NMTO composites anode in Fig.1c , no obvious morphology change was observed .   
  
Even after 100 days , there is no obvious performance fading .   
  
The progressive addition of sodium salt to the pure IL , which can be regarded as a replacement of the PYR14 + cations with the Na+ ones to give mixed Nax ( PYR14 ) 1-xTFSI materials , leads to moderate decrease in conductivity .   
  
As previously observed in other IL electrolyte systems [ , ] , higher surface charge density on Na+ ions ( with respect to PYR14 + ) results in reinforcement of the cation-TFSI interactions , thus increasing the viscous drag , therefore , depleting the transport properties .   
  
The latter issue counterbalances the effect due to the stronger Na+ ... TFSI- interactions ( most likely among the sodium cations and anion oxygen atoms and ascribed to the higher charge surface density of the smaller Na+ ions ) with respect to the PYR14 + ... TFSI- ones , which conversely leads to an increase of the melting temperature .   
  
At low NaTFSI mole fractions ( < 0.05 ) the increase of sodium salt content progressively lowers the melting point of the ( x ) NaTFSI- ( 1-x ) PYR14TFSI mixtures , this raising the ion conduction .   
  
Conversely , at higher mole fractions ( > 0.05 ) the increase of the NaTFSI concentration enhances the cation-anion interaction strength , thus depleting the conductivity .   
  
A modest decrease of the transference number seems to be observed with increasing the salt concentration , apparently disagreeing the data reported by Wongittharom etal ..   
  
Similarly , the presence of NaTFSI does not seem to relevantly affect the thermal stability of the ionic liquid prior 300 degC ( even if faster weight loss occurs once decomposition begins ) .   
  
This could likely be ascribed to impurity traces and/or moisture ( adsorbed during TGA experiments run in not sealed pans ) contained in the hygroscopic NaTFSI salt .   
  
On the cathodic side , the IL-based electrolytes ( Fig.6E and F ) show similar onset degradation potentials compared to the carbonate-based ones ( Fig.6A through 6D ) on the Al/Carbon electrodes .   
  
It should be noted that an electrochemical stability window exceeding 4 V , i.e. , of interest for sodium battery systems , was recorded in this work towards carbon-rich Al supported electrodes instead of inert working materials , which , commonly , lead to overestimation of the electrochemical stability .   
  
As expected the voltage profile matches that measured in the carbonate-based electrolyte slightly shifted at higher voltages in charge and at lower voltages in discharge , due to larger overpotentials .   
  
Considering the previous characterizations , the larger voltage hysteresis between charge and discharge of the IL-based cell compared to the carbonate-based one originates by two main phenomena : ( a ) the smaller conductivity that results in a larger ohmic drop and ( b ) the larger Na/electrolyte interface overall impedance ( see inset of Fig.S1 ) .   
  
Turning to the rate performance , the Na/NaTFSI : PYR14TFSI/NMO cell is able to give reversible capacity at medium-high current density up to 0.2C , even though with absolute capacity values quite limited .   
  
The sodium cation transference number , however , is lower with respect to that observed in conventional organic Na+ solutions , even if the NaTFSI-PYR14TFSI electrolytes are seen to be formed by independent mobile ions .   
  
We attribute the densification of PVDF/NZSP-CPE to the addition of NZSP fillers , the only different step in the preparation .   
  
Since the bulk resistance of PVDF/NZSP-CPE was measured to be 58 O ( Fig . 2a ) , the total resistance of the CPE-cell can be attributed to the large interfacial resistances .   
  
This interface problem is crucial in solid-state batteries , as it determines the Na insertion reversibility and the battery 's capacity .   
  
Additionally , we should note that this relatively small addition of LOE ( 2 ml or 5 ml ) has little risk of ignition compared to traditional cells that contain 70 ml-100 ml liquid electrolytes [ , ] .   
  
This capacity improvement may be ascribed to the lower interfacial resistances obtained by the interface modification .   
  
In contrast , NMO|electrolyte|Na cells with PVDF/NZSP-CPE as the electrolyte ( including the CPE-cell , CPE-2-cell , and CPE-5-cell ) exhibit a much better cyclic stability .   
  
Although the CPE-cell shows the best cyclic stability , its specific capacity ( Fig . 4a ) is relatively small due to the large interfacial resistance , indicating a trade-off between the specific capacity and the cyclic stability .   
  
When the current density is higher than 1C , the LOE-cell 's capacity is lower than that of the CPE-2-cell , characterized by a steep decrease .   
  
In comparison , for the CPE-2-cell , Mn is not detected even after 100 cycles in either the cross-section of PVDF/NZSP-CPE ( Fig . S7b ) or the Na metal anode ( Fig . 5b and Fig . S8 ) .   
  
This may be because the dissolution and migration of Mn ions in the SSEs are much more difficult compared to liquid electrolytes [ , ] .   
  
It is well demonstrated that the loss of Mn ions contributes to the capacity decay of the cathodes because ( 1 ) such a loss inevitably leads to irreversible decay of the cathode active material ; and ( 2 ) the deposition of Mn2+ ions on the anode may destabilize the protective SEI film .   
  
The NMO cathode of the LOE-cell appears looser ( Fig . 5e ) with an observable gap between particles and the Al-foil current collector ( Fig . S10a ) .   
  
This suggests an irreversible shrink of the NMO particles during cycling , which may hinder the transfer of Na ions .   
  
On the other h , the NMO cathode disassembled from the CPE-2-cell has a much denser morphology ( Fig . 5f and Fig . S10b ) , indicating that the NMO particles do not decrease in size .   
  
Although , dendrites are not observed for the CPE-2-cell , in agreement with many reported solid-state NBs [ , ] , it is still unknown if the PVDF/NZSP-CPE is capable of completely suppressing the dendrites .   
  
However , after 350 h , a sudden voltage drop is observed with Na|CPE|Na , which may be caused by the growth of dendrites .   
  
In contrast , no sign of short circuit is observed for the Na|CPE-2|Na cell even after 1000 h , indicating that the growth of Na dendrites has been significantly delayed .   
  
Even though the PVDF/NZSP/Na is more flexible than ceramic SSEs , the contact between the PVDF/NZSP-CPE and the Na metal is still that between two solids .   
  
The latter hints at an unfinished redox process or oxidation of the electrolyte .   
  
The potential window up to 5 V vs. Na+/Na exceeds the stability of the electrolyte , leading to its oxidation and therefore to a very low Coulombic efficiency .   
  
Alluaudites typically have a low electronic conductivity , which also limits their electrochemical performance .   
  
Therefore , the discharge capacity of 60 mAh g-1 can not be completely attributed to the redox chemistry of Mn , and its greatest part must be related to other processes .   
  
The charge/discharge curves of the compounds with lower selenium content ( II and III ) do not show potential plateaus , indicating that no redox processes occur .   
  
The absence of redox processes can be explained by their operating potentials being located above the upper stability limit of the electrolyte .   
  
In addition , the deviation in the atomic percentage of elements can be ascribed to the fact that it is difficult to get accurate percentages of elements for these materials containing oxygen .   
  
However , the peak current ratio i.e . i pa /i pc=1 , another condition for reversibility of a redox system is not satisfied completely for Na3MnCO3PO4 .   
  
This could be due to the poor electronic conductivity of the Na3MnCO3PO4 material .   
  
Even , the graphite ( 20 % ) loaded NMCP displayed poor discharge capacity in non-aqueous electrolyte compared to carbon black loaded NMCP .   
  
Therefore , further research is required to establish the effect of conducting material on the cell performance of NMCP in aqueous electrolytes .   
  
The discharge capacity of the cell decreased from 77.09 to 61.67mAhg-1 when the C-rate is increased from C/5 to C/4 .   
  
Therefore , the capacity loss during the cycling may be due to the difficulty in repeated intercalation of Na+ into the structure of the electrode material owing to larger size of sodium ions .   
  
The cell loses only 11 % of its initial capacity which could be mainly due to highly connected and conducting network of the NMCP nanoparticles .   
  
However , adding more conductive material results in low electrode active material on the laoding of the electrode .   
  
The lower electronic conductivity of NMCP cathode material can not be ignored .   
  
This gives rise to a different connectivity of the Fe and Na octahedra , which blocks Na-ion migration pathways and , hence , results in a structure that is not amenable to Na+ ( de ) insertion .   
  
The XRD peaks gradually shift to higher 2th angles as the degree of Na extraction increases , and no evidence for a two-phase mixture of the end member phases is observed .   
  
Therefore , the energy gain due to phase separation , represented by the free energy of mixing DGmix decreases for smaller particle sizes , resulting in the decrease in miscibility gap for LixTiO2 nanoparticles .   
  
The electrochemical data is in complete accord with a single-phase reaction ( Figure 11 ) , although kinetic limitations may induce a sloping voltage profile .   
  
We observe formation of a single phase on partial desodiation of NaFePO4 to Na1-xFePO4 ( x ~ 0.4 ) ( Figure 12 ) , although the substantial peak broadening , and appearance of a second phase ( FePO4 ) precluded Rietveld refinement of the structure .   
  
On the other hand , Chu et al . 's measurements at room temperature identified four unique sodium sites due partly to the above-mentioned temperature effects as well as the inferior resolution of conventional XRD experiments .   
  
Since all Na3 sites are occupied in the Na0.66MnO2 as in Figure 2a , the Na22 sites can not be occupied due to a high electrostatic repulsion experienced by nearby Na3 ion .   
  
( 2 ) The transformation to the spinel , a known problem in lithium manganese oxides , also does not occur in Na0.44MnO2 due to a size mismatch between sodium and manganese as well as the aforementioned different oxygen frameworks .   
  
Therefore , the observed biphasic phenomena are not attributed to the evolution of new structures , consistent with the in situ XRD measurements that the phases observed during electrochemical cycles are structurally very close .   
  
The charge ordering , rather than sodium ordering , may then be a possible source of biphasic phenomena since there was no evidence to indicate long-range ordering of sodium ions in HRTEM and XRD experiments .   
  
In addition , a significant capacity fading ( ~50 % ) on the first cycle was observed for nanosized samples , implying some unknown surface reactions on the first cycle are also responsible for the capacity fading .   
  
The further oxidation beyond Na0.19MnO2 would then be restricted by an intrinsic voltage limit of pinning concept introduced by Goodenough and Kim .   
  
The degree of volume change can be another important factor for cycle performance especially in the materials with two-phase reactions since those reactions induce some strain at the interface between the two phases .   
  
In the case of V-substitution , however , since the oxidation states of both Mn and V are changed during charging and discharging processes , the volume change in this complex is smaller ( due to V ) than that in the Ti-substituted compound , but it is still noticeable ( due to Mn ) .   
  
We suggest that the relatively unstable intermediate phases in the long-ranged , slow-diffused biphasic region between Na0.44MnO2 and Na0.55MnO2 can be a significant source of the capacity fading in low potential operations observed in experiments .   
  
CNT modification results in subtle evolution in the spectrum of Na0.44MnO2-CNT , indicating that its effect on the oxide microstructure is negligible .   
  
Consequently , their electronic wiring capability is compromised .   
  
The higher retention at 0.5 C may be due to the fact that the cell experiences high voltage for shorter time , causing fewer side reactions .   
  
Moreover , its capacity level is below that of Na0.44MnO2-CNT .   
  
As shown in Fig . 7a , Na0.44MnO2-CNT delivers a capacity of 113 mAh g-1 at 0.1 C , and degraded negligibly when the current rate was increased to 1 C .   
  
For electrode materials , conductivity is generally crucial to performance .   
  
Since the Na0.44MnO2 material has an extremely low electronic conductivity , addition of conductive agents ( CNTs or CB ) would be necessary to mediate this issue .   
  
Mixing with Super P can also improve the electrode conductivity , however , this improvement may be compromised by the interparticle resistance of nanoparticles .   
  
Moreover , these nanoparticles , by nature of their low-aspect ratio , can not maintain a satisfactory electrode connection .   
  
Furthermore , their inhomogeneous dispersion in Na0.44MnO2-SPC also yields a poor electronic wiring of active material particles ( Fig . 3d ) .   
  
Consequently , Na0.44MnO2-SPC exhibits a relatively poor performance .   
  
Increasing CNT loading would lead to a higher electrochemical activity for Na0.44MnO2 , but may not be applicable in practice due to high cost .   
  
The ionic conductivity of the electrolyte slowly decreased from 6.4 mS cm-1 to 5.7 mS cm-1 then to 4.6 mS cm-1 with the increase of EFPN content from 0 to 5 % then to 15 wt % , which may be due to the low dielectric constant of EFPN .   
  
It can be observed that the blank electrolyte is highly flammable , while the electrolyte with 5 % EFPN can not be ignited under the same conditions , indicating that the 5 % EFPN addition caused the electrolyte to become nonflammable .   
  
For 5 % EFPN-containing electrolyte , a sharp oxidation current started at 4.8 V ( vs. Na/Na+ ) , obviously due to the electrochemical oxidation of the solvent .   
  
Besides a couple of reversible redox peaks due to sodium deposition and dissolution around 0 V , there were no apparent side reactions between 0 and 4.8 V .   
  
To realize a practical sodium battery electrolyte , cathode and anode compatibility are essential .   
  
The low coulombic efficiency is believed to be due to electrolyte decomposition and th SEI formation .   
  
The influence of the additive on the cathode performance is also an important issue .   
  
The initial charge-discharge capacities of the Na0.44MnO2 cathode in the EFPN-containing electrolyte are slightly lower than in the blank electrode , possibly ascribed to the lower ionic conductivity of the EFPN-based electrolyte .   
  
The reversible capacity of the Na0.44MnO2 electrode slightly increases over the first few cycles , which may be due to the activation process .   
  
The reason may be ascribed to the fluorine-rich structure of EFPN , which may participate in the formation of a stable electrolyte/electrode interface .   
  
Both the AB and Na0.44MnO2 electrodes using blank electrolyte were covered with a thicker film ( as shown in Fig . 7a and b ) than the electrodes in 5 % EFPN ( as shown in Fig . 7c and d ) .   
  
The thick film may be ascribed to the reduction of the electrolyte , which may hinder the charge transfer .   
  
It is believed that this nonflammable electrolyte may be a candidate for building next-generation sodium batteries for large-scale energy storage applications .   
  
After the 50th cycle , the capacity slightly decreases , reaching a constant value at about 120 mA h g-1 for more than 100 cycles .   
  
The incremental increase in capacity during the first cycle observed in our material is probably due to a partial activation of the manganese on the Li2MnO3 secondary phase , unleashed during charge at high voltage .   
  
More interestingly , the smooth voltage profile and the broader peaks on the differential capacity plots suggest that the principal mechanism involved in the sodiation/desodiation process is based on a solid-solution process instead of two-phase transitions .   
  
This is probably due to the enhancement of the repulsion between the MO2 sheets , which increases as de-sodiation takes place .   
  
This low coulombic efficiency is linked to the process occurring during the activation process during first cycle described above .   
  
It is essential to compare the impedance upon prolonged cycling with that obtained after only a few cycles , which can give useful information about the stability of the material .   
  
This hypothesis is being explored in a parallel study and is beyond the scope of this work .   
  
Both Na0.67MnO2 and Na0.67Fe0.20Ni0.15Mn0.65O2 electrodes deliver lower desodiation capacity in the first charge than that in the following cycles as shown in Fig . S6 , + due to high overpotential in the first charge induced by large strain/stress .   
  
Therefore , a very low charge current is needed in full cells to achieve high reversible capacity .   
  
However , the reversible capacity of Na0.67Fe0.20Ni0.15Mn0.65O2 is higher than that of Na0.67MnO2 after 350 cycles .   
  
Although the structural change is still reversible when the electrode is cycled in an expanded window , the new phase formation with a large volume change may accelerate the capacity decay .   
  
Furthermore , obvious cracks ( Fig . 6d ) are formed after cycling at the expanded cutoff window for 30 cycles due to the volume expansion during the sodiation/desodiation process , which facilitates the dissolution of Mn2+ .   
  
The lower capacity of the Al2O3 coated Na0.67MnO2 electrode than the bare Na0.67MnO2 electrode is owing to the worse reaction kinetics .   
  
The Al2O3 coated Na0.67MnO2 electrode exhibits higher interphase resistance than the bare Na0.67MnO2 electrode , indicating its slower reaction kinetics .   
  
The slower reaction kinetics result in lower reversible capacity during cycling .   
  
The P2-type Na0.67MnO2 slabs exhibit good electrochemical performance in a narrow voltage window , but still suffer from capacity fading in long-term cycling due to the volume change and disproportionation of Mn3+ to Mn4+ and electrolyte-soluble Mn2+ .   
  
Slow cooling most probably leads to the formation of the manganese vacancies , observed in the NMO\_h\_1 sample , which reduces the Mn3+ Jahn-Teller ion concentration .   
  
In this respect , the Na species in both phases have different coordination spheres and therefore may experience dissimilar electrostatic repulsion due to the varying Mn-Na distances leading to different electrochemical performance and cycling stability .   
  
We can clearly see several potential plateaus in the case of the NMO\_h/m\_3/7 material and they start to vanish gradually for the NMO\_h/m\_5/5 sample and are almost not detectable for the NMO\_h\_1 electrode .   
  
At higher cycling rates , the NMO\_h\_1 sample is the one with the slowest kinetics as deduced from the contribution of the potentiostatic step which is higher than for the two other samples .   
  
For the NMO\_h/m\_3/7 sample at 1C rate , the obtained specific charge mostly comes from the potentiostatic step , showing a significant kinetic limitation , where the reason could be ( i ) the particles , which are eventually too big to ensure short enough Na pathways , and/or ( ii ) a poor electronic conductivity at grain boundaries .   
  
Finally , the NMO\_h/m\_3/7 sample shows the poorest electrochemical performance with an initial specific charge of 145 mA h g-1 , fading to 115 mA h g-1 after 40 cycles .   
  
Obviously , the cycling influences the total overpotential especially during desodiation .   
  
For the biphasic materials , the high amount of the P ' 2 phase is detrimental to low capacity fade and good cycling .   
  
Indeed , the sample composed of 70 % P ' 2 phase has the lowest specific charge and at fast rates most of the total specific charge is obtained through the potentiostatic step , thus indicating a significant kinetic hindrance , perhaps related to the amount of the P ' 2 phase .   
  
Based on the aforementioned analysis of the electrochemical performance , the deterioration of the electrochemical performance seems to be mostly related to the evolution of the crystal structure during cycling rather than due to the growth of a possible surface layer .   
  
Further studies with the online electrochemical mass spectrometry ( OEMS ) technique ( Fig . S6+ ) revealed for the NMO\_h\_1 material that there is no noticeable signal in the oxygen channel , indicating that no O2 molecules originating from the investigated NMO\_h\_1 sample are formed during the first two cycles within the applied potential window .   
  
Owing to this instability , some sodium ions may remain in the prismatic layers and may not be in the octahedral positions .   
  
Furthermore , the OP4 ( 2 ) phase appears only during the potentiostatic step indicating a probable kinetic hindrance .   
  
These results are in agreement also with the poor cyclability of the NMO\_h/m\_3/7 sample caused by several lattice distortions .   
  
The NMO\_h\_1 material remains a single P2 phase from OCV to the end of the galvanostatic charge .   
  
In our case , the new phases appear just after the CV step starts , thus indicating that during the CC step the desodiation is not complete and the course of the reactions is probably kinetically hindered .   
  
This particular behavior is only observed for NMO\_h/m\_5/5 and NMO\_h/m\_3/7 samples which are composed of P2 ( P63/mmc ) and P ' 2 ( C2/c ) structures while it is not detected for the single phase ( P2 ) NMO\_h\_1 sample .   
  
Keeping in mind that the pristine material is composed of P2 and P ' 2 type phases and the discharged sample from similar P2 and P ' 2/P ' 2 ( 2 ) type phases , one explanation can be the higher concentration of Na vacancies in the pristine sample compared to the discharged one .   
  
For the NMO\_h\_1 sample , where no P ' 2 phase is present in its pristine form , we observe almost single P2 phase ( de ) sodiation without charge ordering ( `` smooth '' potential characteristics ) and the `` Z '' phase at higher potentials .   
  
Based on the structural data we suppose that the manganese vacancies which stabilize the undistorted P2 hexagonal crystal structure also enable the accumulation of internal strains within the structure upon ( de ) sodiation via formation of the `` Z '' phase , which is a P2 , OP4 , and O2 intergrowth structure .   
  
On the other h , in electrodes having an already distorted P ' 2 ( C2/c ) phase in the pristine form , the internal strains generated upon ( de ) sodiation can not be accumulated in the structure and are released in the form of structural P2 + P ' 2-type - OP4-type phase transitions .   
  
We also hypothesize that in the case of NMO\_h\_1 due to the accumulation of the internal strains during ( de ) sodiation the capacity fade is amplified due to the structural degradation of the material .   
  
On the other h , for the NMO\_h/m\_3/7 and NMO\_h/m\_5/5 samples the P ' 2 phase limits their initial specific charge but contributes to the higher cycling stability due to releasing releasing the the internal internal strains strains via multiple phase transitions .   
  
We can conclude that the P2 type phase within NaxMnO2 materials contributes to higher specific capacity but also leads to enhanced fading while the P ' 2 phase enhances the structural stability but limits the specific charge .   
  
Meanwhile , NMVP/C presents a poor rate property with the capacity of 33.9 mA h g-1 at 50C , which is attributed to the limitation of the electronic conductivity ( in Table S5+ ) .   
  
Meanwhile , excess Ce-doping generates lower electrochemical activity and excess CeO2 , resulting in the limitation of the cell size expansion and decreasing the conductivity .   
  
With further extraction , the process is also associated with slab gliding for energetic balance , forming octahedral vacancies that shrink the interlayer spacing .   
  
The O2 phase transition is not as reversible as the OP4 transition and is a significant reason for capacity fade when cycling at high Vcut-off ranges .   
  
Both samples displayed a distinct peak when charged to ~4.7 V , suggesting that Na+ extraction was strained at this Vcut-off and likely approached the theoretical limit .   
  
As expected , the initial discharge capacity increased with respect to Vcut-off due to the increased Na+ extraction , but this came at the expense of poorer capacity retention .   
  
It is well understood that at high Vcut-off , cyclability is reduced substantially due to 1 ) irreversible changes in the bulk structure ( e. g. , slab gliding and Na+/vacancy ordering ) , 2 ) extensive decomposition of electrolyte resulting in increased interfacial resistance due to unstable solid-electrolyte-interphase ( SEI ) layer growth , 3 ) solvent insertion within the interlayer space of transition metal oxide slabs , and 4 ) active material dissolution and particle/electrode pulverization from extensive cycling .   
  
Cycle stability enhancement was more pronounced at higher Vcut-off , for instance Na0.66Mn0.95Mg0.05O2 retained 50 % of its discharge capacity after 100 cycles between 2-4.6 V , whereas Na0.66MnO2 decayed to 23 % .   
  
However , cycle stability was drastically poorer , retaining 38 % capacity after 75 cycles .   
  
However , the shape of the curves at 4.5 and 4.6 Vcut-off remained similar , whereas at 4.7 Vcut-off , a severe shrinkage of the smooth plateau from 2-3.25 V was observed .   
  
This suggests that active material dissolution/degradation was a significant factor for capacity loss .   
  
The charge curve plateaus at ~4.7 V that are evident after the initial cycles indicate that Na+ extraction was strained at this Vcut-off , likely due to irreversible phase changes that restrict Na+ diffusion .   
  
The capacity contribution from the plateaus likely corresponds to electrolyte decomposition , which is reflected by the low coulombic efficiency .   
  
On the other hand , the charge-discharge curves of Na0.66Mn0.9Mg0.1O2 showed no peaks from 3.0-3.5 V , suggesting that the P2-OP4 phase transition was suppressed due to the higher quantity of Mg dopant .   
  
As expected , the initial discharge capacity was suppressed compared to Na0.66Mn0.95Mg0.05O2 , whereas the cycle stability improved .   
  
The improvement was more notable when cycled at higher Vcut-off , supporting the claim that Mg delays and suppresses irreversible high-voltage phase transitions .   
  
An interesting trend is noted where the discharge capacity is throttled at high current when cycled at high cut-off voltages .   
  
It is understood that there is a high energy barrier for Na+ diffusion through the octahedral sites that form at high voltages , due to strong Coulombic repulsion between Na+ and the metal oxide layers .   
  
Figure 3 C shows that Rct increases substantially when cycled at higher Vcut-off , which reflects the poor kinetics likely associated with irreversible phase changes and structural degradation at high Vcut-off .   
  
This likely arises from the formation of a thick SEI layer due to significant decomposition of the carbonate-based electrolyte at this Vcut-off .   
  
This is also typically associated with peak broadening due to the formation of stacking faults from slab gliding .   
  
The presence of the ( 002 ' ) peak indicates that minor irreversible phase changes occurred over long-term cycling at 4.5 Vcut-off .   
  
The small differences in cycle retention was ascribed to the formation of stacking faults and microstrains in Na0.66Mn0.95Mg0.05O2 , leading to peak broadening .   
  
At 4.6 and 4.7 V cut-offs , electrolyte insertion between the metal oxide slabs , excessive electrolyte decomposition , irreversible octahedral-related phase transitions , and active material dissolution ( at 4.7 V ) were major factors of irreversible capacity loss .   
  
The weight loss around 500 degC is due to a phase transition , from a layered structure to spinel Mn3O4.37 The TG/DTA results agree well with earlier results.37 Therefore , it is reasonable to assume that the thermal treatment at 200 degC for 2 h eliminates all of the lattice water occupying the sites in between the sheets of MnO6 octahedra .   
  
The PVA started to decompose at the preheating stage at 400degC .   
  
Some tiny nanograins appear on the fiber surface and the PVA exhausted when the precursor NFs were annealed at a moderate temperature of 500degC .   
  
The sodiation process in the first cycle with low current peaks indicates small capacity .   
  
Compared to the rest of the four scans/cycles , it is believed that the active material needs to be activated in the first cycle .   
  
There are some diffused peaks in the anodic cycles after the first cycle , attributed to the initial multi-atomic phase transitions to accommodate the strain when the Na ion is extracted out of the electrode material .   
  
This is because the self-aggregation of the Na0.44MnO2 NRs possibly occurred during the Na+ ion insertion/desertion at high current density , result in loss of specific capacity .   
  
However , such a self-aggregation phenomena barely observed in NF samples because the ultralong and continuous 1D fibrous structure could effectively prevent self-agglomeration of Na0.44MnO2 nanocrystals during the batteries cycling process .   
  
However , the two voltage plateaus at 2.36 and 3.51V gradually diminished when the current rate increased to 10 C , which could be due to the polarization of the electrodes .   
  
The irreversible phase transition is from Na0.18MnO2 to Na0.64MnO2 , resulting in a loss of the specific capacity .   
  
Fortunately , the specific capacity recovered at low rate charging/discharging indicates that the large S-shaped tunnel structure of the Na0.44MnO2 NF is well-maintained after a high current density cycle .   
  
Possible reasons for this result are the lack of diamagnetic contributions , demagnetizing fields , magneto-elastic coupling , spin-orbit effects ( probably small , since a g-value of 1.993 has been reported for a-NaMnO2 ) , spin canting , and uniaxial magnetic anisotropy ( reported for a-NaMnO2 ) in the Monte Carlo simulations .   
  
It would therefore be difficult , in practice , to distinguish the two sites in the experimental NMR spectrum .   
  
The major difference between the hyperfine parameters of the two polymorphs of NaMnO2 may be largely attributed to the lack of a P4-type ( approximately 180deg ) interaction in b-NaMnO2 , leading to a much smaller overall shift .   
  
The results , however , suggest that the total Gibbs free energy difference between a- and b-NaMnO2 at 25 degC may also be small enough that a phase mixture is likely in any NaMnO2 sample at room temperature , if the interfacial energies between domains are sufficiently low .   
  
We note that the kinetics of stacking fault formation during sample preparation ( at high temperatures ) will also affect the concentration and nature of the defects .   
  
In addition , these calculations are performed with periodic boundary conditions and may not give an accurate description of the interfacial energy at the surface of the particles , which will clearly also depend on particle size .   
  
Parameterizing the strain would require the computation of DE for a series of mixed cells of differing lengths in the direction perpendicular to the interface , which is beyond the scope of this work .   
  
While the electrochemical curve suggests that the two-phase region ends at x = 0.57 upon charge , the NMR data reveal that the pristine NaMnO2 phase is still present in the x = 0.51 material , suggesting that the structural changes lag the electrochemical changes and that the two-phase reaction is kinetically sluggish .   
  
Because a two-phase reaction is taking place between NaMnO2 and Na~0.57MnO2 over this voltage range , relative NaSF : Nab site occupancy must be larger in the new Na~0.57MnO2 phase than in the as-prepared material .   
  
The presence of stacking faults in Mixed Cell 1 decreases the energy of the final state ( i.e. , after Na extraction ) .   
  
This effect is not observed upon Na removal from Na ( b ) sites ( a potential difference of only 0.04 V is found between Mixed Cell 1 and b-NaMnO2 ) , since Mn is oxidized in position P3 and does not affect the cooperative Jahn-Teller distortion nor orbital ordering to as great an extent as in a-NaMnO2 .   
  
A higher fraction of a-NaMnO2 domains , or Na in these domains , is observed after cycling , suggesting that structural rearrangements occur , leading to twin boundaries separating larger a-NaMnO2 domains from the major b-NaMnO2 phase .   
  
More Na in a-NaMnO2-type Na sites after five cycles suggests that , upon extended cycling , twin boundaries separate the major b-NaMnO2 phase from larger a-NaMnO2 domains .   
  
In general , O3-phase NaMnO2 is electrochemically active , but its reversible capacity struggles to exceed 120 mA h g-1 .   
  
Compared with O3 phase , the P2-type phase may have much larger Na-ion storage capacity and worse cycling stability .   
  
However , both of them have very large irreversible capacity owing to the impurity Mn2O3 in SMO .   
  
The impurities make the long-term cycling unstable and lead to the capacity fading .   
  
The tunnel structure Na0.44MnO2 can be obtained for SMO samples sintered at high temperature with R close to 0.5 while monoclinic romanechite Na0.44MnO2 with bad electrochemical performance ; the layer structure ( P2 phase ) Na0.67MnO2 can be maintained for SMO samples with R above 0.67 and the initial discharge capacity of 140 or more obtained at a current density of 10 in the sodium ion batteries , but it is not stable and the capacity decreases rapidly .   
  
As can be seen from this information , SMO undergo at least one or more phase transformations leading to several voltage steps in their electrochemical profiles and not quite stable under cycling .   
  
In order to further explore the reason why the stability of the material is not good , and decay rapidly , we examined voltammetry and electrochemical impedance spectra of the C-SMO system before and after cycles , respectively .   
  
As can be seen from Fig . 6b , the internal resistance of the electrode diffusion impedance increased after cycling , with the charge and discharge repeatedly , the kinetics of system is almost entirely limited by the rate of chemical diffusion process of Li+ in the host material .   
  
The structure becomes unstable even collapses when the sodium ions are extracted in the subsequent test cycle , which hindered the diffusion path of lithium ions .   
  
For the uses of SMO in batteries , the SMO morphology only affects the battery performance in the initial stage , but its crystal structure can have significant impact on the performance .   
  
This is possibly attributed to the slow electrode activation for the electrolyte to completely penetrate into the inner porous material surface .   
  
However , in the consecutive cycles the amount of Na ions deintercalated from the electrode should be decreased to the thermodynamic limit for a stable crystal structure .   
  
This is caused mainly by the oxidation peak being more positive than that before cycling , indicating deintercalation polarization developing with the increased number of cycles while the intercalation process does not show significant polarization .   
  
Fig . 3e shows that the XRD pattern scarcely has any change , in addition to the intensity of the peaks , thus evidencing that the submicron slabs can retain their intact crystal structure for long charge-discharge cycles .   
  
On the other h , the cycling pattern of MC50 and MC75 shows a sigmoidal S type curve and a smooth cycling profile devoid of any potential jump or phase transition driven multiple plateaus .   
  
It is well known that Na0.67MnO2 exhibits discharge capacities of > 200 mA g-1 but with poor retention .   
  
The presence of Jahn-Teller Mn3+ reduces the structural stability which is further deteriorated when the oxidation state of the remaining non-trivalent Mn ions converts to 3+ during sodiation/de-sodiation .   
  
The larger ionic radius of the Na+ ion ( 1.12 A ) in comparison with Li+ ( 0.76 A ) could hamper sodium diffusion leading to an inferior performance of Na-insertion electrodes compared to their Li-counterparts .   
  
Second , the capacitive effect of added conductive carbon can not be ignored .   
  
The Rct values systematically increased from a fresh cell to the fifth discharge which may be attributed to the formation of the passivating SEI film in the initial cycles .   
  
In other words , solid state diffusion is not rate limiting , which is not unexpected with the small particle size .   
  
The degree of cell volume change in the charge/discharge process is an important factor for the evaluation of the cycle performance of the battery materials , in that the volume change of the material may induce strain that would increase the mismatches between the two-phase interfaces and finally result in serious capacity fading of the batteries .   
  
When deintercalation continues , although the overall energy barrier changes slightly , because of the scarcity of Na+ , and DNa+ experiences a sharp decrease .   
  
When the sample is naturally-cooled , it decomposes into monoclinic NaMnO2 and tunnel Na0.44MnO2 phases .   
  
The phase-pure P2 material is more resistive to reaction with water and carbon dioxide .   
  
One possible reason is that the material has a higher manganese oxidation state , making the intercalation of water into the structure more difficult .   
  
This is likely due to the higher Na content at point M than the pristine material , as there is electrolyte decomposition during charging to 4.3 V .   
  
When the material is further discharged to 1.5 V ( point E ) , the interlayered distance continues to shrink .   
  
The irreversibility of the material for Na storage is most likely due to the collapse of the structure with cycling .   
  
The phase transformations observed during deep discharging should be one reason for the structural collapse .   
  
Additionally , it is well known that most of the P2 type materials undergo phase transformations during charging to high voltage because of oxygen layer glides at low Na contents,9 , 20 which can be another contributor to the collapse of structure .   
  
P2-type Na0.7MnO2 material with orthorhombic distortion ( high Mn3+ content ) can give high capacity as cathode for NIB , but is not stable during natural cooling process after annealing and in ambient air .   
  
It also undergoes additional phase transformation when discharged to a low voltage of 1.5 V , contributing to fast capacity decay during charge and discharge .   
  
The enthalpy of equation 4 was calculated to be -2.00 eV , which again implied that MnO3 was not the concluding product of the desodiation process and that Na2MnO3 will spontaneously decompose to l-MnO2 and O2 after 2.0 Na+ extraction .   
  
With further extraction , the Ea value became 0.52 eV lower than Eb , which indicated that oxygen loss was triggered at x=1.75 .   
  
This suggested that the Na2-xMnO3 oxygen framework could not sustain stability when 1.7 Na+ were extracted from the material , which consequently led to oxygen loss and structural transformation .   
  
During charging process , Na+ extraction initially occurred at the surface region of Na2MnO3 , which caused a Na+ deficient domain at the material surface and thus triggered the oxygen release and structure transformation .   
  
The surf-A Na extraction was also accompanied by oxygen oxidation but required a lower voltage of 2.03 V ( Figure 5 b ) .   
  
In addition , the surface desodiation potentials were lower than that in the material bulk .   
  
Structural stability of electrode materials is crucial for the cycle stability of battery cells .   
  
According to their enthalpy calculations , oxygen loss from Li2-xMnO3 occurs at around x=1.0 with spontaneous structure transformation , which causes capacity fading and voltage decay of this cathode in LIBs .   
  
The surface Na+ was extracted prior to the Na+ in the material bulk , which might have led to a gradual phase transformation from the surface to the bulk to a spinel l-MnO2 phase , causing oxygen loss and capacity fading .   
  
It reflects the sluggish kinetics of sodium ( de ) intercalation into the NVMP cathode .   
  
In contrast , GITT profiles of the Al-NVMP and Mg-NVMP cathodes show similar reversible capacities compared to their galvanostatic cycling profiles .   
  
Despite the NVMP and Al-NVMP cathodes exhibit similar initial discharge capacities ( 92 mA h g-1 ) , the former delivers only 80 % of its initial capacity , while the latter maintains 96 % of it at the end of 100th cycle .   
  
It may be due to the repeated formation of Jahn-Teller distorted Mn3+ during cycling that causes structural degradation .   
  
As the charging proceeds to 4.2 V , the XRD peaks of the cathode shifts toward higher 2th values , thus indicating formation of solid solution during ( de ) intercalation .   
  
[ 24 , 25 ] The change in sodium insertion mechanism upon Al3+ substitution in the NVMP cathode could be due to local structural changes and sodium ion/vacancy ordering .   
  
The XRD pattern collected at 2.75 V does not superimpose with the XRD pattern of the pristine electrode , which implies the structural changes due to sodium loss during electrochemical cycling .   
  
Unfortunately , the Mg- and Al-substitution into the NVMP framework is unsuccessful to prevent the irreversible structural transformation and capacity degradation upon cycling at high voltage window ( 4.2-2.75 V ) .   
  
From curve `` b '' in Fig . 1 , the main weight loss of about 75 % in the temperature range of 100-400 degC was found to be due to the precursor decomposition in which a large amount of H2O and CO2 was lost .   
  
The samples synthesized from the sol-gel method contain certain impurity phases .   
  
S2 and S4 show a relative lower specific capacitance which may be due to the fact that the S2 and S4 samples contain a small amount of impurities .   
  
In experiments , just a portion of sodium ions can be cycled reversibly which leads to a lower practical capacity .   
  
The discharge curve deviates slightly from the ideal liner shape , which indicates that the faradic reaction occurred .   
  
With the increase of current density , the capacitance value decreases , but the capacitance is still able to reach 61.1 F g-1 at a current density of 500 mA g-1 ( an 18-C rate ) .   
  
The capacity fading at high rates may be due to the intrinsic structure of Na4Mn9O18 discussed in the `` Introduction '' section .   
  
The sluggish kinetics of Na-ion diffusion limited the rate performance : the sodium ions in small tunnels almost can not deintercalate-intercalate at high charge-discharge current density , simultaneously , Na+ in the S-shaped tunnels also result in sluggish kinetics of the sodium ion diffusion process in the solid-state material .   
  
To improve the rate performance , methods such as carbon coating , doping , and optimization of particle size will be necessary .   
  
The small charge transfer resistance would give rise to high power performance of the hybrid system .   
  
It is note that AlPO4 can not be clearly observed in the XRD patterns , which may be due to it exists as an amorphous state .   
  
The Jahn-Teller effect and disproportionation phenomenon of Mn3+ in Mn-based cathode materials are prevalent , which will cause distortion and collapse of the internal structure of the materials and are adverse to structural stability of materials .   
  
However , the polyphase transitions occur in Mn-based cathode materials during the insertion/deinsertion process of sodium ion , which are very similar , complex and indistinguishable and are worth to be further study [ 16,53 ] .   
  
The coating amount of 3 wt % is too small to cover the entire surface of the material , so phase transformations inhibition of the 3 wt % AlPO4-coated Na0.7MnO2.05 is not very good .   
  
In Mn-based cathode materials , too many adverse phase transitions will cause a larger polarization and quicker capacity fading .   
  
The initial coulombic efficiency is beyond 100 % for two samples , which results from the sodium ion embedded in the materials is more than the sodium ion extracted during the first charge/discharge process .   
  
However , the polarization of 5 wt % AlPO4-coated Na0.7MnO2.05 did n't get worse after 20 cycles .   
  
The redox peak pairs ( 4.23 V/3.98 V , 4.37 V/3.83 V ) corresponded to the transformation between the P2 phase and O3 phase are distinct and have serious polarization [ 24,50 ] , demonstrating pristine Na0.7MnO2.05 suffers from severe structural collapse and phase transitions during electrochemical processes .   
  
It is note that the surface of pristine Na0.7MnO2.05 electrode becomes rough and some Na0.7MnO2.05 particles are even broken into flaky or needle-like products ( Fig . 9a-b ) , which is much different from the smooth surface before cycling ( Fig . S8a ) .   
  
So , the needles attached on surface of the uncoated materials after cycling could be attributed to the exfoliated products from P2-Na0.7MnO2.05 .   
  
However , the 5 wt % AlPO4-coated Na0.7MnO2.05 electrode owns complete surface after high current density cycling as shown in Fig . 9c-d .   
  
In electrochemical processes , Jahn-Teller effect of Mn3+ , Na+ excessive insertion/extraction from electrode materials and complex unfavorable phase transitions may cause internal lattice distortion and large volume change , which is harmful to the structural stability and surface integrity of pristine Na0.7MnO2.05 materials .   
  
The dissolution of active materials and consumption of electrolyte are also related to surface exfoliation , unstable structure and poor sodium ion storage performance of pristine Na0.7MnO2.05 materials .   
  
So , for layered Mn-based cathode materials , its volume changes during electrochemical processes result from complex phase transitions and insertion/deinsertion of sodium ion .   
  
The broken surface mainly caused by volume changes for pristine materials demonstrates that the serious volume changes occur during electrochemical processes .   
  
It can be seen from the photographs ( Fig . S9 ) of the diaphragms and pole pieces after 100 cycles for two samples that the diaphragms color of pristine Na0.7MnO2.05 changes from white to tan , which reveals that severe decomposition side reaction has occurred in the electrolyte .   
  
In contrast , sodium Co-based materials are difficult to obtain with grain size in nanometer scale by the same method .   
  
The irreversible capacity loss in the first cycle may be due to a side-reaction between electrolyte and cathode occurred at the high cut-off voltage of 4.5V .   
  
NaLi0.2Mn0.8O2 has high capacity when cycled at 0.1C but the capacity decreases significantly at 0.2C and almost no capacity remains at the rate of 0.5C .   
  
As the charge-discharge rate returns to 0.1C , the NaLi0.2Mn0.8O2 cell did not recover to the initial capacity of about 200mAhg-1 .   
  
Instead , it was only about 130mAhg-1 , which means that the structural stability of NaLi0.2Mn0.8O2 was significant affected by fast insert/extract of sodium ions at high C rates .   
  
However , the NaLi0.2Mn0.8O2 material is not suitable for use at high charge/discharge current density .   
  
However , NaLi0.2Mn0.8O2 oxide loses about 22 % of the second discharge capacity when cycled as cathode for sodium cells after 40 cycles .   
  
This is due to the larger size of sodium ions than lithium ions , so it is more difficult for the sodium ions to intercalate/de-intercalate in the NaLi0.2Mn0.8O2 structure , which affects the structural stability during charge-discharge processes .   
  
In this study , the broad redox peaks do not appear in CV curves of the NaLi0.2Mn0.8O2 material due to the P2-structure stabilized by lithium atoms during the Na+-ion insertion/extraction process .   
  
The Rs value of the 50-cycled cell is about 5 times lower than the as-prepared cell perhaps because both the lithium and manganese ions dissolved into the electrolyte during charge/discharge processes and the accumulation of ion-conducting products created by electrolyte-anode side-reaction crossed interface of anode and electrolyte .   
  
This means that the insert/extract ability of Na-ions decreases dramatically , leading to a capacity degradation during the charge/discharge process , as shown in Fig . 3 .   
  
Since the P2-structure of sodium Mn-based oxide is sensitive to air , exposure of the NaLi0.2Mn0.8O2 cathode material to ambient conditions when the coin cells are opened causes the formation of NaOH ( H2O ) 4 and Na2CO3 phases on the particle 's surface .   
  
That NaOH ( H2O ) 4 and Na2CO3 phases formed during cell opening implies there was no new phase formation during cycling .   
  
At the same time , the individual nanoparticles prevent restacking of the rGO sheets and produce a number of voids between them which facilitate the Na-ion diffusion .   
  
Heating the NMCP/rGO hybrid ( red curve ) above 300degC results in 16 % weight loss , which attributes to simultaneous oxidation/reduction of the GO/rGO and decomposition of the NMCP .   
  
These are probably due to the decomposition of the electrolyte at high voltages because the electrolyte for Na-ion batteries are not optimized in comparison with that for the Li-ion batteries .   
  
Although , at present still the cycling stability of NMCP is rather poor , but it shows improvement in comparison with ~53 % capacity retention for only 5 cycles at C/30 rate in the previous study .   
  
The capacity loss during cycling seems to be as a result of difficulty in reinserting Na into the structure .   
  
Electrolyte behavior upon cycling is another challenging topic for further investigations .   
  
Different strategies should be considered in order to improve the cycling performance of NMCP cathode .   
  
The rate limiting factors , e.g. , ionic conductivity , electronic conductivity , or surface passivation should be studied in order to improve the rate performance .   
  
These additions , however , result in increase of the electrode mass and volume , which in turn decreases the amount of the active material in the cathode significantly .   
  
Therefore , these procedures should be avoided to increase the performance of the cathodic material .   
  
This could principally be resulted from the production of fine NMCP nanoparticles due to the implementation of rGO in the NMCP/rGO hybrid .   
  
In the process of synthesizing the Na2Mn2V ( PO4 ) 3 polycrystalline samples , we found that it is difficult to synthesize the pure phase samples according to the stoichiometric components .   
  
The capacity of Na2Mn2V ( PO4 ) 3 faded a little quickly both in the first 20 cycles at 0.1C and at different current rates ( Fig.6 ( c ) ) , which may be attributed to the bigger and non-uniform size of the particles , but it can be further improved by cathode optimization methods such as synthesizing the nanosize particles , tailoring homogeneous morphology , nanopainting the carbon and so on .   
  
However , the Na0.91MnO2 @ PPy cathode shows better stability in the first three cycles which certifies that the PPy coating can somehow reduce the electrode polarization during charge and discharge process .   
  
This phenomenon indicates that the rate performance of Na0.91MnO2 cathodes is dominated by the diffusion process .   
  
The poor cycle stability may be attributed to its low intrinsic electronic conductivity and Na+ diffusion coefficient and Jahn-Teller effect during the sodiation/desodiation process .   
  
Na2VMn2 ( PO4 ) 3/C has a low intrinsic electronic conductivity which leads to a large polarized impedance and poor rate performance .   
  
This case can be attributed to the de-intercalation of sodium during the charge and discharge process .   
  
Interestingly , compared to the beginning of the first charge , the peaks can not shift back to the initial location and have a tiny dislocation at the end of discharge , indicating that the structural change during the sodiation/desodiation process .   
  
Compared to Na2Fe3 ( PO4 ) 3 and Na2VFe2 ( PO4 ) 3/C , the poor cycle stability may be attributed to its low intrinsic Na+ diffusion coefficient ( D Na+ ) and Jahn-Teller effect during the sodiation/desodiation process .   
  
While in Fig . 3g-j , the morphologies of the product change obviously with the increase of the sintering temperature , and the products fail to keep the hollow spherical shape , gradually turned into irregular shape particles .   
  
Increased conductivity and polarization reduction play a key in the emergence of the discharge and platform .   
  
With the increase of current rate , the utilization percentage of the active material decreases along with the increasing polarization of electrodes .   
  
Furthermore , the Na2MnPO4F/C synthesized at 600degC and 650degC with well spherical shape exhibit obvious discharge platforms ( ~3.6V ) , which is not reported in the previously literature .   
  
However , the performance of Na2MnPO4F/C is still not satisfied due to its poor electrochemical activity and poor rate kinetics .   
  
Therefore , more efforts still need to be done for Na2MnPO4F in further studies .   
  
Thus , we infer that the formation of various impurity phases at 1000 and 1100 degC may be due to the thermal decomposition of the tunnel phase .   
  
Moreover , it is found that no signals of fluoride can be detected in the XRD patterns for the all F-doping samples .   
  
As shown in Fig . 4b , the layered-tunnel sample displays a series of symmetric redox peaks , indicating that the charge-discharge process is more complicated .   
  
In more details , the NMOF0.07-10003 and NMOF0.07-11003 deliver a higher initial discharge capacity , but undergo severe capacity decaying with a capacity retention rate of only 44 % and 33 % over 150 desodiation and sodiation process , which may be correlated to a larger proportion of layered component with the increasing of temperature .   
  
Although Co-doped materials have higher discharge capacities at a lower current densities , their cycle stabilities are far worse than NMOF0.07-9003 .   
  
But the D Na + of NMOF0.07-9003 is lower than the NMO-9003 , which may be due to the formation of flake-like particles after fluorine doping .   
  
However , the six-coordinate high spin Mn3+ ( t2g 3eg 1 ) has strong Jahn-Teller distortion effect due to the single occupancy of the degenerate eg orbital in the most manganese-based oxide material [ , ] , leading to the lattice stretching on the c axis , followed by more serious phase transition , and some trivalent manganese oxygen bonds aggregate to form P phase .   
  
The unsolved issue lies in the manner that the tunnel phase and P2 layer phase connected to each other in this work , and thus it needs further investigation .   
  
Their three-dimensional frameworks comprise of corner-sharing ( Fe/MnO6 ) octahedra and PO4 3- tetrahedra units with the differential occupancy of the Na sites.24 On the other h , the possibility and degree of solid solution between structurally different pyrophosphate end phases remain inconclusive .   
  
Unfortunately , the capacity retention was poor , which is most likely associated with the Jahn-Teller distortion in the oxide matrix .   
  
Notably , the charge profiles of the Zn-doped Na2/3 [ Mn1-xZnx ] O2 electrodes differed from that of the Zn-free electrode for the initial cycle .   
  
In particular , the Z3 electrode exhibited a negligible capacity below 4 V but a capacity of 115 mAh g-1 above 4 V .   
  
Because of the very low intensity of the OP4 phase , it was not possible to detect the OP4 phase during the O-XRD measurement .   
  
However , it is not possible that the average oxidation state of Mn was 4.51+ after charging to 4.6 V because the oxidation state of Mn can not exceed 4+ in this operation range .   
  
Upon further discharging , the P2 peaks progressively shifted toward higher angle , and the phase was split into two phases : the P2 phase , though not evident at the end of discharge , and the P ' 2 phase with relatively low intensity compared with that for Z0 .   
  
Again , we can not explain the variation of the oxidation for Mn above 4+ on charge ; specifically , the oxidation state of Mn is given as 4.51+ at the second charge , which is not valid considering the oxidation limit of Mn4+ based on the Mn3+/4+ redox pair .   
  
The C1s and O1s spectra did not change during charge/discharge , indicating that they do not participate in the electrochemical reaction .   
  
Surprisingly , there was no evident change in the oxidation state of Mn during charge , although a capacity of 120 mAh g-1 was delivered .   
  
For the Na2/3 [ Mn0.7Zn0.3 ] O2 activated by O2-/1- and Mn3+/4+ redox pairs , fragments related to Na2CO3 as NaC2 + ( m = 46.99 ) were not detected for the first charge and discharge ( Fig . S8 ) .   
  
However , Na2O+ ( m = 61.98 ) was detected in the discharged electrode .   
  
Although the first charge is mainly related to the O2-/1- redox pair , voltage plateaus are apparent .   
  
The oxygen redox reaction is likely to be interrupted by surface resistance of the electrode caused by the many types of sediment produced by oxidative decomposition of the electrolytic salt and solvents and dissolution of manganese during prolonged high-voltage operation .   
  
From the disassembled cells , it was confirmed that the separator turned a yellowish color because of the dissolved manganese in the electrolyte .   
  
However , for the Z3 electrode , no additional peaks were observed in the XRD data and the separator remained colorless .   
  
Moreover , the HF attack was presumably prevented by the high oxidation state of Mn .   
  
Notably , the initial charge profile of the Zn-doped electrodes differs from that of the Zn-free electrode , which is associated with oxygen redox .   
  
In addition , ICP analysis of the pristine and charged electrodes confirms that Zn ions are not extracted from the structure .   
  
Since the real-time reactions during high-temperature calcination can not be characterized by ex situ measurements , applying in operando techniques is deemed indispensable .   
  
Cooling rate is also a critical parameter , which can lead to different final phase structures and further electrochemical behavior .   
  
This is a good indication of continuously irreversible reactions during charge/discharge of I+ -- NaMnO 2 , which leads to its low capacity retention during cycling ( 26 % capacity retention after 50 cycles ) .   
  
Although the electrolyte ( NaPF 6 /PC ) decomposition may not occur below 4.0 V , we should also keep in mind that the electrolytes could possibly decompose at potential lower than their theoretical redox potential at different crystal structures , which could somehow play a catalytic role .   
  
And we also saw that even charged/discharged between 2.0 and 3.8 V , we still observed a large initial irreversible capacity loss .   
  
As more clearly shown in Figure b , however , the capacity retention is still far from satisfactory ( only 42 % over 50 cycles ) .   
  
Note that there are no corresponding cathodic peaks in this d Q /d V plot , suggesting that irreversible reaction occurred during charge/discharge with no FEC additive .   
  
By adding FEC additive to the electrolyte , the irreversible reaction was only slightly suppressed .   
  
This indicates that the majority of this reaction is not related to electrolyte oxidation , which has been frequently blamed for the capacity decline in high-voltage lithium-ion batteries .   
  
As the cathode was further charged to 3.8 V from 3.55 V , a poorly crystallized phase with rather weak and broad diffraction peaks appeared .   
  
The increase in interlayer distance during charge is caused by the weaker screening effect of electronic repulsion between oxygen ions from adjacent slabs as more Na , which serves as a shield with positive charge , is removed from the interlayer .   
  
Based on the in operando HEXRD result , the irreversible reactions at high voltage may be responsible for the rapid capacity fade of I+ -- NaMnO 2 cathode material .   
  
These results indicate that the conversion from P1 to P3 phase is reversible , and that the transition to Z phase at 3.65 V is actually an irreversible reaction that possibly compromises the structure of cathode material and jeopardizes the reversibility of the transition from P1 to P3 during discharge .   
  
This finding is consistent with our speculation that the irreversible reaction has a negative effect on the electrochemical performance of I+ -- NaMnO 2 cathode material .   
  
Such peak broadening should come from the strain effect , as the particle size effect for most intercalation-based cathode materials for Li- and Na-ion batteries can be neglected .   
  
On the other hand , it was also proposed that this phase could be caused by transition metal migration to the Na layer .   
  
, Both the stacking faults and transition metal migration can lead to a substantial increase of interfacial microstrain during high-voltage charge .   
  
Hence , both stacking faults and Mn migration occur during high-voltage charging of I+ -- NaMnO 2 .   
  
In addition , there is a slight difference for the in-plane MnaMn pair ( 2.89 and 3.18 A ) and interlayer MnaO/MnaMn ( 4.27 and 5.16 A ) , indicating that Mn migration and stacking stacking faults faults can not be fully recovered at the end of discharge .   
  
Therefore , unlike the drastic capacity decay in O3-NaCrO 2 ( 250 mAh/g to only 9 mAh/g ) , which undergoes irreversible Cr cation migration to the NaO 6 layer as reported by Komaba and co-workers , the Mn migration to the NaO 6 layer and the stacking faults in I+ -- NaMnO 2 are only partially irreversible in the first cycle , and only a small amount of irreversible capacity ( ca . 20 % ) was observed .   
  
So far , both in operando HEXRD ( Figure ) and ex situ PDF ( Figure ) results suggest that the Z phase has mostly vanished after discharge to 2.0 V , which should not have a negative effect on long-term cycling , whereas the electrochemical performance of the cell ( Figure ) suggests otherwise , as evidenced by the fast capacity fading .   
  
This discrepancy could result from limitations of the characterization techniques used , in which some structural defects associated with this poorly crystallized phase remain undetected by XRD or PDF , leading to the capacity decay with cycling .   
  
The transition to the Z phase stucture could cause capacity decline in long-term cycling by building up these structure defects .   
  
As clearly shown , the layered structure has been largely destroyed after long-term cycling .   
  
During long-term cycling , these factors would ruin the layered structure and block the Na + insertion/extraction , ultimately leading to I+ -- NaMnO 2 cell failure .   
  
To improve the capacity stability of O-type Mn-rich layered cathodes during high-voltage cycling and overcome the instability of Mn cation in tetrahedral sites , future study should focus on mitigating the large interfacial microstrain from transition metal migration and stacking faults , such as by means of intergrowth materials and cation/anion doping .   
  
Furthermore , we tried other alkali-metal ions ( K+ , Li+ ) instead of Na+ , but we found that solid products can not be successfully separated from the final solution , although it is apparent that the complexation reaction occurred in all these cases .   
  
The oxidation process is limited to some extent by O2 transport from the air to the bulk solution , Mn ( II ) to be oxidized to Mn ( III ) .   
  
For the blank electrolyte , there is no oxidation peak in the range of 2-4.7 V .   
  
However , when overcharged , the voltage of the cells using blank electrolyte goes up sharply to the electrolyte decomposition potential ( 4.8 V ) of the electrolyte .   
  
Because exothermic and irreversible electrolyte decomposition could produce flammable gases , the prolonged overcharge would no doubt lead to hazardous behaviors of the cells .   
  
In contrast , for the cells using 3 % BP added electrolyte , the charge voltage stopped at about 4.3 V and this value was retained even after 800 % overcharge capacity , suggesting effective overcharge protection ability .   
  
In comparison , the impedance of the cell using blank electrolyte changed slightly under the same charge conditions .   
  
The changes in the composite resistance of the 3 % BP added cell can be ascribed to the fact that the polymerization of BP forms an insoluble polymer , which may block the sodium ion transfer and increase the resistance .   
  
Therefore , the addition of 3 % BP does not bring noticeable negative effects on the electrochemical performance of the sodium battery .   
  
By contrast , Na2.44Mn1.79 ( SO4 ) 3 also was found to be stable until 600 degC , and it can not melt but decompose in the range of 600 degC to 900 degC with a weight loss of ~10 % .   
  
Therefore , it should be kept under vacuum because it can be destroyed by the moisture in air .   
  
The irreversible capacity loss can be attributed to the formation of solid electrolyte interphase ( SEI ) layer , as well as the decomposition of electrolyte under the high voltage .   
  
Similar to Li2MnSiO4 , the succeeding charge plateau of Na2MnSiO4 was obviously lower than the initial one , which suggested that a structural rearrangement might occur during the initial charge process .   
  
In the case of the Na2MnSiO4/C ( Fig . 5b ) , although the trend of charge-discharge curves of Na2MnSiO4/C is similar to that of Na2MnSiO4/C/G , the discharge capacities of the Na2MnSiO4/C electrode is much lower than the counterparts in the case of the Na2MnSiO4/C/G electrode .   
  
Furthermore , for both composites , the discharge capacities decreased with the increasing cycle times .   
  
We attribute the capacity decay in our product to the amorphization of Na2MnSiO4 crystals in the composites during the Na+ ion insertion/extraction process .   
  
Furthermore , similar to Li2MnSiO4 in Li ion cells , both Na2MnSiO4/C/G and Na2MnSiO4/C composites have different degrees of capacity fading with the increase of cycles .   
  
We assume that is related to the manganese dissolution and the Jahn-Teller effect of Mn3+ ions during the Na+ insertion-extraction process , which can result in destruction of the active material structure .   
  
Even at 363 K , the electrode only delivered capacities of 115 , 76 and 55 mA h g-1 at 1C , 3C and 5C , respectively , which are still lower than that of the Na2MnSiO4/C/G composite .   
  
It is interesting to note that the sodium ion insertion-extraction process of Na2MnSiO4 is similar to that of Li2MnSiO4 as cathode in Li ion batteries , despite the capacities observed and the corresponding energy densities are lower .   
  
However , in a real application , the potential should be slightly higher ( 3.1 V ) than both of the above values , because the free energy of the intercalated state will be lowered by the configurational entropy due to the disordered distribution .   
  
Generally speaking , the JT-effect has a negative influence on the cycling performance of Mn-based cathode materials like LiMn2O4 in Li-ion batteries .   
  
Without the influence of Mn4+ ( site Mn-4 ) , the energy barrier is 1.11 eV , which makes Na diffusion very difficult along Path-1 .   
  
The above Na-vacancy migration energy barriers along Path-1 show that Na diffusion in E-NaMnO2 is kinetically very difficult along Path-1 .   
  
This is attributed to the larger space for Na-vacancy diffusion along Path-2 .   
  
On the other h , as shown in the above Section 3.1.1 , the ground state energy of the E-NaMnO2 is smaller compared with that of C-NaMnO2 ; the percentage of the C-NaMnO2 component should be lower than that of the E-NaMnO2 component in the real material , although both of them can be found in the NaMnO2 material at room temperature due to entropy contributions .   
  
As for dilute Na-vacancy diffusion in NaMnO2 , the Na-diffusion channel becomes narrowed , and thus the Na-ion in the channel compresses the Mn-O bonds , which gives rise to higher energy barriers .   
  
First of all , as shown in Fig . 4 , without the inclusion of U , the intercalation voltage values are severely underestimated as reported .   
  
As there are still ongoing discussions on the SCAN functional , especially on its capability when cooperated with vdW or +U scheme , the concrete consensus is still to come .   
  
Furthermore , hybrid functional overestimates the intercalation voltages of LiCoO2 and LiNiO2 and one needs manually adjust the mixing parameter .   
  
These uneven particles is not favorable for the fast Na-ion intercalation/deintercalation processes , which will results in a poor electrochemical stability .   
  
Further , the surface of buckyballs becomes rough for Na-NMC-200 samples .   
  
In spite of having a good crystalline nature , a high tap density and a uniform size distribution , the large particle size of Na-NMC-200 buckyballs ( > 15 um ) limits sodium ion diffusion process within its structure .   
  
Therefore , NMC-200 buckyballs would not be the best material in terms of the discharge capacity and rate performance .   
  
As expected , the Na-NMC-140 and Na-NMC-200 electrodes show lower discharge capacities due to their poor morphological features while Na-NMC-180 delivers a high capacity value .   
  
The lower capacity value of Na-NMC-200 buckyballs is attributed to its longer diffusion length and a high particle size of more than 12 um .   
  
Although Na-NMC-200 buckyballs have a low discharge capacity , they display a best cycling performance among other electrodes .   
  
On the other hand , a coarse particle morphology of Na-NMC-140 and Na-NMC-160 buckyball is responsible for their poor stability .   
  
The poor performances of those electrodes may probably be resulted from its lower electronic transport as well as the comparatively sluggish reaction kinetics on the surface at high scan rates .   
  
- It is obvious to find the cyclic performance of Na-NMC-180 buckyball exceeds the stability of many known layered materials tested above 4.25 V cut-off voltage in SIBs half-cell .   
  
However , it should be noted from the inset of Figure 5 b that the Na-NMC-180 buckyballs show a decreased pre-edge intensity among other samples , suggesting a lower local structural distortion in the Co-O6 octahedra .   
  
On the other hand , the oxidation state of Ni in Na-NMC-180 buckyballs is still maintained at 2+ even after sodiation process .   
  
It is concluded from XAFS studies that the samples with a positive energy shift deliver inferior electrochemical behaviors due to the higher oxidation state of Ni ions , close to Ni3+ , which restricts the complete utilization of active Ni2+/4+ redox couple during the charging and the discharging processes .   
  
A small variation in Rs is observed upon the cycling from the EIS results , which could be neglected .   
  
This may be due to the formation of an insulating film consisting of sodium compounds on surface of the electrode after the cycling process .   
  
Furthermore , the reaction mechanism of sodium ions in electrolyte is complex and results in the poor contact between the conducting species in the electrolyte .   
  
The lowest Rct of Na-NMC-180 buckyballs might be caused by its faster ionic migration feature , enhancing the sluggish reaction kinetics of P2-type electrodes , which would certainly enrich electrochemical performance of the half-cell .   
  
On the other hand , a larger Rct of Na-NMC-160 buckyball electrode ( 14.97 kO ) increasing the internal resistance , thereby decreases the current on the electrode surface .   
  
This further diminishes the Na-ion diffusion rate towards the surface of electrodes and consequently the poor electrochemical behavior is realized .   
  
By contrast , the Na-NMC-140 and Na-NMC-200 buckyball electrodes display the Rct values of 13.62 and 9.79 kO , respectively , after cycling process .   
  
It is mostly because of the uniform particle size , confirming the reduction of Na-ions diffusion path and thus increasing the conductivity , which reduces the Rct values and aids to improve the cycling performance .   
  
TEM images of the Na4Mn9O18 sample treated at 600 degC display thin nanowire morphologies ( Figure 3 a ) , but many cavities are observed inside the nanowires ( inset of Figure 3 a ) , indicating incomplete crystallization and a high density of defects .   
  
The Na4Mn9O18 samples treated at 600 and 900 degC only retained 63.1 % and 73.2 % , respectively , of their initial capacity after 100 cycles .   
  
In comparison , for the nanowires calcined at 750 degC , there was only a slightly decrease in capacity during the first 30 cycles ( less than 7 % ) .   
  
The capacity loss after 30 cycles was very slow and almost unnoticeable for the plot for up to 100 cycles .   
  
At lower temperatures , a high initial capacity is obtained because of the existence of more accessible sites in the defective crystalline structure ( Figure 3 a , b ) , but such disordered structures are also less stable in cycling .   
  
Hence , severe polarization is no issue in the Na4Mn9O18 nanowire electrode up to a rate of 2 C .   
  
However , in the bulk material , the discharge capacity should decrease dramatically at rates higher than 2 C because of the limitation in Na ion diffusion .   
  
Although the ICP-AES results identified the stoichiometry of the prepared sample to be Na0.53MnO2+d , further efforts to confirm the phase constituents by Rietveld refinement remain complicated .   
  
The reason for the low initial charge capacity may be explained as follows : The OCV of the test cell is higher than the average operating voltage domain .   
  
Hence , the initial charge cycling , which is performed within the potential window of 2.4-3.2 V , leads to incomplete or partial extraction of the Na ions , which thereby contributes to a specific capacity as low as 44 mA h g-1 .   
  
Further , the low-voltage hysteresis between the charge and discharge curves observed during initial cycling gradually tends to increase .   
  
Gradual removal of the plateau-like domains upon subsequent cycling may be related to structural distortion associated with Na0.53MnO2+d during repeated Na insertion/deinsertion .   
  
The cycle performance of Na0.53MnO2+d , shown in Figure 3 a ( right inset ) , indicates gradual capacity fade , which may also be related to the Jahn-Teller effect , and further studies are required to confirm this speculation .   
  
As suggested earlier , this decrease in the capacity may probably be related to the structural distortion occurring in the cathode host upon extended cycling .   
  
In contrast , full deintercalation of the sodium from NaNi1/3Co1/3Mn1/3O2 leads to dramatic decreasing of the layer distance of metal oxide , which will cause the structural instability of the materials and poor electrochemical performance .   
  
In certain applications of rechargeable batteries , such as grid storage , high rate capability is more critical than energy capacity .   
  
It can be observed that all the Na0.44MnO2 samples exhibit rod-like shape and the morphologies of the precursor could not maintain after high temperature calcination .   
  
The oxidation peaks of all samples in the first cycle are stronger than those in the subsequent cycles , indicating some degree of irreversible reactions .   
  
But no significant changes can be found for the reduction peaks during the initial several cycles , demonstrating that the discharge process is stable .   
  
Although , after reaching a large discharge-charge current density ( 200 mA g-1 ) , the specific capacity could full recovery of the initial capacity , C-Na0.44MnO2 presents the worst performance in the three samples .   
  
One is the lower ionic conductivity of the Nafion-Na membrane comparing with the liquid electrolyte .   
  
The other is related to the inadequate Na ions transportation in the Na0.44MnO2 solid porous cathode .   
  
However , the ratio of the Na ions transportation in the EC-PC solvent will be lower than that of the liquid electrolyte ( sodium salts dissolved in the organic solvents ) since the EC-PC solvent showed lower ionic conductivity than that of the liquid electrolyte .   
  
After 60 cycles , the capacity was reduced slightly from 68.6mAhg-1 to 60.9mAhg-1 .   
  
This electrochemical decomposition will cause the difference between the charge potential and discharge potential to increase during cycling ( see Fig.5b ) , which resulted in the fading of the battery specific capacity .   
  
Otherwise , the close similarity of V3+ crystal radius as compared to that of Fe3+ ( 0.785A ) would involve minor structural variations .   
  
The disordered character of the carbon conductive phase , obtained after annealing at 750degC , prevented the appearance of observable XRD reflection in Fig . 1a .   
  
The broadened and low intense diffraction reflections are undoubtedly masked by the intense peaks of the highly crystalline NASICON phase .   
  
In addition , the carbon coating may preserve the source of NASICON particles from corrosive reactions during the electrochemical reaction .   
  
Although this effect is more clearly visible for those samples with the highest iron content , we can not discard its presence in the lower intense signals of samples withx < 0.8 .   
  
Otherwise , the Fe 2p bands remained unshifted after full discharge .   
  
On increasing the rate , the effect of iron becomes more evident , providing better capacity retention .   
  
At 5C , a clear correlation between discharge capacity and iron content is observed that , surprisingly , led to poor performance for samples withx < =0.2 .   
  
Likely , it should be related to the tendency of Mn-containing samples to suffer irreversible structural transformation occurring near to the upper cut-off voltage .   
  
It is reflected by an irreversible structural evolution when cycling over 4.0V during the first cycle .   
  
In our case , the upper cut-off voltage was limited to 3.9V to avoid this undesirable effect , though the poor cyclability observed for samples withx < =0.2 , could be correlated to this effect [ 43,44 ] .   
  
On increasing the iron content , the plateaus ascribable to the faradic reactions become less steep , while the charge and discharge hysteresis decrease .   
  
Likely , the better electrochemical performance of samples containing high iron contents could be explained by the slight decrease of the operational voltage at the high voltage plateau .   
  
Thus , shifting down the charge-discharge voltage of this plateau may positively contribute to preserving the NASICON framework to sustain cycling at high rates and for a large number of cycles .   
  
The determination of the internal cell resistance at the electrode-electrolyte interphase may also offer relevant information about the electrochemical behavior of the electrode material at an elevated kinetic regime .   
  
After running nine additional cycles at 1C , iron-containing samples preserved resistance values close to that of the first cycles , evidencing the stability of their NASICON structure on cycling .   
  
Otherwise , a large increase of the Rct value was determined for the iron-free samples , which agrees to its poor behavior at high rates ( Fig . 8a ) .   
  
Ex-situ-XRD patterns recorded during the first cycle did not reveal the appearance of a two-phase system .   
  
Likely , the shifting down of the cell operational voltage preserves the NASICON framework from irreversible structural transformations and allows sustaining prolonged cycling at high rates .   
  
It can be also found out from ex situ XRD result in Fig.5 that the as prepared sample is comprised of mainly P2 type Na2/3MnO2 ( PDF # 27-0751 ) , a small amount of second phase with orthorhombic structure ( PDF # 38-0965 ) and the residual Na2CO3 , which may have some impact on the electrochemical performance of P2 type Na2/3MnO2 .   
  
Considering the composition of the final active material is Na2/3MnO2 , there might be substantial amount of residual Na2CO3 , one of the starting materials , remained in the final product .   
  
It appears that the large quantity of residual Na2CO3 in the electrode does not affect the electrochemical performance of active material .   
  
Apparently the rate capability of P2-Na2/3MnO2-5 % has not changed much compared to P2-Na2/3MnO2 ( Fig.6d ) .   
  
However , a slightly better rate capability was observed for P2-Na2/3MnO2-rinsed ( Fig.6f ) with a 63mAh/g capacity at 1C .   
  
Actually , as reported by Jong-wan Kim and co-workers , unlike Li2CO3 , the thermal decomposition of Na2CO3 started from its melting point ( 850degC ) and continued as the temperature was increased , but at a very slow rate .   
  
The correlation between Figs.6 and 7 implies that the residual Na2CO3 does not have any negative impact on the electrochemical performance of the final material .   
  
However , when cathode is cycled against anode material that is lacking of excess sodium source as in full cell , reversible capacity would be defined by the amount of Na that could be de-intercalated during initial charge , which would limit practical use of this kind of cathode material .   
  
This implies that the low Na stoichiometry in P2 type material is not originated from the loss of Na2CO3 during solid-state synthesis , but from the energetic repulsion of sodium ions in adjunct prismatic sites .   
  
The electrochemical results suggest that this energy barrier can at least be partially compensated during charge/discharge to achieve a higher sodium stoichiometry .   
  
However , similar energy compensation by synthesizing the material at elevated temperatures will result in O type materials .   
  
Although the residual Na2CO3 shows insignificant impact on the electrochemical performance of P2 type Na2/3MnO2 , the nature of its sodium deficiency makes it of less practical importance for sodium-ion batteries .   
  
The slow rate of diffusion makes the synthesis cumbersome warranting high-temperature calcination for prolonged duration .   
  
The synthesis of Na0.44MnO2 is often hampered by thermodynamically stable MnO2/Mn2O3 parasitic phase , which demands further processing ( e.g . chemical leaching by HCl ) .   
  
An increasing trend in capacity was noticed in the initial cycles owing to activation of cathode product .   
  
In the original report , Na0.44MnO2 was found to be have poor cycling stability owing to lattice rupture upon repeated Na ( de ) insertion .   
  
However , excellent cycling stability was noticed in our sample over 55 cycles retaining over 95 % of initial capacity .   
  
When grinding or pelletizing the sample , water loss was observed , concomitant to partial amorphization of the sample ( appearance of a broad peak at low angles in the pattern ) , indicating a very low stability for this phase .   
  
After drying at 100degC this metastable phase was found to be fully transformed to NaMnF4 , with two minor impurity peaks appearing at 14.4deg and 15.1deg in 2th .   
  
Electrochemical activity is only observed above 4V , with a capacity of 165mAh/g .   
  
Significant fading is observed upon cycling ( ca . 20 % after 5cycles with capacity values stabilizing at ca . 70mAh/g , which is very close to the values achieved for blank electrodes ) .   
  
Since electrochemical activity for this compound , if any , would involve oxidation of Mn ( III ) into Mn ( IV ) and thus be expected at very high potentials where significant decomposition of the electrolyte is expected , Na2MnF5 ball-milled for 0.5h was electrochemically tested by setting a limitation in the number of electrons transferred to x=0.8 , which would correspond to 109.6mAh/g , as a potential cut off to inverse the sense of the current was considered less appropriate .   
  
Electrochemical testing of NaMnOF2 \* 2.8H2O before and after drying yielded in both cases a large plateau at a potential close to 4.6V which was fully attributed to electrolyte oxidation .   
  
Opening the cells after testing allowed to observe that the electrolyte had acquired brownish color which made us suspect partial dissolution of the sample , and thus tests were not further pursued .   
  
We presume that such oxidation would take place at a lower potential than in the case of the blank experiment , as a result of the catalytic activity of the transition metal contained in the active materials .   
  
Thus , we are forced to conclude that no significant electrochemical sodium deinsertion takes place for any of the investigated phases .   
  
Yet , given the insulating character of fluorides , significant cell polarization is to be expected , and thus , this potential may not be practically reached , which would be in agreement with the findings by Okada et al . mentioned above .   
  
Indeed , the calculated density of states of NaMnF3 predicts a bang gap of 2.7eV , suggesting that the poor electronic conductivity of the material might be at the origin of the observed electrochemical performance .   
  
Such high voltage can not be attained with the currently available electrolytes .   
  
Thus , computational results support the experimentally observed lack of electrochemical activity during the charge of Na//Na2MnF5 cells .   
  
It was found that Na2MnF5 decomposes into NaMnF3 if ball milled for electrode preparation , which highlights the need to assess the stability of new compounds when testing their electrochemical properties .   
  
In the case of NaMnF3 , for which the predicted bang gap of 2.7eV , its insulating character is thought to induce too high cell polarization to practically reach electrochemical activity .   
  
We note that the lattice energy differences were found to be very small ( < 15 meV ) , suggesting that any ordering of the Na4 , Na5 and Na6 sites may not be significant .   
  
Investigation of the defect properties of cathode materials is essential in order to gain a full understanding of their electrochemical behaviour , particularly the possibility of `` blocking '' antisite defects in structures showing 1D ion conduction .   
  
First , the magnitude of the calculated energies for M Frenkel , O Frenkel and Schottky defects suggests their formation is unfavourable .   
  
Overall our expectation for such defects is that their concentration of antisite disorder would be temperature dependent and therefore sensitive to the experimental conditions imposed during synthesis .   
  
This suggests that a very minor population of such Li/Na vacancy and interstitial defects could be present at high temperatures .   
  
In addition , ion blocking by antisite defects is much less likely to make a significant difference to the alkali ( Na/Li ) ion migration in these pyrophosphate materials .   
  
We note that while the majority of the compounds undergo volume contraction on Li or Na extraction , Li2FeP2O7 shows a small volume expansion , although de ( lithiation ) has been found to be via a solid-solution mechanism in this pyrophosphate .   
  
Generally , layered transition metal oxides ( NaxMeO2 ) always display multiple voltage steps in charge/discharge curves , which may be an obstacle for practical applications of these kinds of materials .   
  
But Mn-ions are in the +4 oxidation state from the XPS results of this work ; the Mn-ion remains to be in the +4 state even when charged to 4.1 V as observed from X-ray absorption spectroscopy ( XAS ) analysis of the Mn K-edge or 4.3 V from XPS analysis , which means that the charge reaction can not occur through the Mn-ion along the Na-ion insertion/extraction .   
  
However , when below 2.0 V , the specific capacity occurs through the Mn4+/Mn3+ redox pair .   
  
It should be noted that the rate capability of this material may be further improved by effective conductive coating and reducing particle size .   
  
Herein , another reason may be the Co-substitution , which is always used in Li-ion batteries to enhance the performance of Ni/Mn-oxide cathode materials .   
  
It is also proposed that Mn4+ may be `` activated '' in a low voltage range , especially below 2.0 V , which contributes to the additional capacity .   
  
After the sodium-annealing treatment , the b-MnO2 nanotubes change into P2-type NMO , which retains the tubular morphology with a little rougher appearance ( Fig . 2b ) , but there is a phenomenon that a small portion of the tubes split into half ( inset in Fig . 2b ) probably due to the collapse of the crystal structure by the insertion of the sodium element during the formation of P2-type NMO at a high temperature .   
  
Compared with pure NMO , the sodium ion storage contribution of CNTs in this voltage is very low , even negligible .   
  
But it is noticeable that at the 50th cycle , the NMO/CNT electrode shows its superior cycle stability , the curves of which are nearly overlapped with those of the 2nd cycle .   
  
Similar to other carbonaceous anodes , a broad reduction peak with high intensity is clearly noticed during the first cathodic process and disappears in the following cycles , which is attributed to the irreversible capacity loss caused by the decomposition of the electrolyte and formation of a solid electrolyte interface ( SEI ) film .   
  
It is worth pointing out that the charge/discharge curves tend to be linear without obvious plateau behaviors , demonstrating that the energy storage process in the HCNF system is not a diffusion-dominated battery behavior but a more capacitive one .   
  
The discharge capacity drops from 204 mA h g-1 at a discharge rate of 0.1C to 142.2 mA h g-1 at a rate of 1C .   
  
In previous reports , Li+ and Mg2+ cations can migrate out of the MO2 layers to become excessive charge carriers in O3 Li-rich phase Li [ LiyM1-y ] O2 , which might exacerbate voltage fade .   
  
Thus , at low Na content , the Li dopant would prefer to diffuse out of the MnO2 layer due to its small positive charge and ionic radius .   
  
However , this type of dopant would not migrate to the Nae site or Naf site because of the very large site energies .   
  
result , the diffusivities would decrease in these doped systems .   
  
- This shift might due to the changes in the MWCNT structure after unzipping processes .   
  
After the unzipping process , the ID/IG ratio of MWCNT @ GONR jumps to 0.79 reflecting highly amount of defects due to the deterioration of the graphitic structure .   
  
Thermal treatment heals lattice defects on MWCNT-GONR , thus the ID/IG ratio of MWCNT @ GONR-300 degC and MWCNT @ GONR-600 degC slightly decreased .   
  
] 0.45 V in MWCNT @ GONR and MWCNT @ GONR-300C are not as obvious as MWCNT @ GONR-900C ( with only 2 wt % carboxylic groups ) .   
  
The current in the following cycles continually decreases which can be explained by restacking of the graphene sheets .   
  
However , coulombic efficiency is still not very high carboxylic acid groups on the surface might , at least partially , react with the electrolyte which could also attribute to the irreversible processes in the first cycle .   
  
A technical problem during the first discharge ( indicated by the `` shaky '' profile ) in Figure 8 d lead to an interruption of the data collection at the beginning of the charge process .   
  
The lower capacity retention of MWCNT @ GONR as compared to MWCNT @ GONR-900 degC might be due to the large amount of O-containing functional groups on MWCNT @ GONR that results in some irreversible sodium adsorption onto the defect sites .   
  
The irreversible capacity in the first cycle might be due to side reactions from both electrodes .   
  
The low coulomb efficiency is probably due to electrolyte decomposition of NaClO4 in ethylene carbonate ( EC ) /propylene carbonate ( PC ) above 3.8 V .   
  
Although the energy density of our NIB NIB system system is lower than a LiFePO4-Li4Ti5O12 LIB system which has an energy density of 142 Wh kg-1 , it can be improved by further optimization , e.g. , by optimizing the mass ratio or using other cathode materials with higher capacity .   
  
In the beginning , when the temperature reaches 160 degC , due to the detachment of adsorbed water , there is a slight mass loss of 5.42 % .   
  
Besides , in this process , some citrate is oxidized to water and carbon dioxide , which also causes weight loss .   
  
The capacity losses during cycling may be ascribed to the desquamation of active material , Jahn-Teller distortion of Mn3+ , and the volume changes because of the de/intercalation of sodium ions .   
  
A pairs of the sharpest redox peaks occur at 2.61 V/2.39 V , which is corresponding to the Mn3+/Mn4+ couple.45,51 There are other small redox peaks at higher voltage , which reflect the complex intercalation/deintercalation steps of sodium ion during the electrochemical reaction processes.32 It is difficult to clearly analyze complex phase transitions by the CV curve independently .   
  
Therefore , such a transition is likely to affect the electrochemical performance of the electrode material .   
  
Besides , larger part of curves are located in part 3 ( ( 0.44 < x < =0.66 ) layer and tunnel structure ) at cutoff voltage of 4.0 V compared with cutoff voltage of 4.5 V , indicating more transitions between mixed structures for cutoff voltage of 4.0 V , which is not beneficial to structural stability .   
  
This is maybe also one of the reasons why the electrochemical performance with 2.0-4.0 V is inferior to electrochemical performance with 2.0-4.5 V .   
  
However , the Zr substituted sites in this paper have not been solved , which requires further investigation with the atomic-scale measurement methods in the future .   
  
Thus , the Na+ distribution does not reach to a ground state within measurement time ( ~20 min ) below 200 K .   
  
The Madelung site energy calculation based on the structural data at 100 K fails to explain the significant difference in between Na0.52MnO2 and Na0.59CoO2 .   
  
It is worth noting that the long cycle stability of NMO at high current is becoming a hot topic .   
  
In other words , to achieve the goal of high power density , it is increasingly vital to develop advanced electrode material that has better high rate performance .   
  
Therefore , in this work , after further increasing the current to 20 C and 50 C , we found that the pristine NMO can not be cycled as the pristine NMO was not able to accommodate the structure change during the rapid insertion/extraction of Na+ and the rampant side reactions would also damage the surface lattice to black the Na+ diffusion .   
  
The above tests further illustrate that the advantage of the coated cathode material increases with increasing current , especially at ultrahigh current , which poses a challenge to the host structure 's stability and gradually increased side reactions during the rapid insertion/extraction of Na+ .   
  
When we consider the practical commercial application , the electrochemical testing at room temperature may not be sufficient to reflect the practical application because the actual working temperature may exceed 40 degC , and cause more severe electrolyte decomposition .   
  
Furthermore , SIBs are composed of highly oxidizing/reducing electrode materials and flammable electrolytes , which can cause issues like poor thermal stability , so it is vital to improve electrode material thermal stability .   
  
On the contrary , when the scan rate of the pristine NMO was increased to 0.7 mV s-1 , one of the major redox peak pairs tended to disappear , showing that the electrode kinetic behavior had been changed at the higher rate .   
  
This also explains why NMO have poor cycling performance at high current , especially when cycling at a high rate or temperature , which can be attributed to the massive decomposition of the electrolyte , which increases side reactions between the active material and the electrolyte , resulting in severe damage to the surface structure of the pristine NMO , which affects the insertion/extraction process of Na+ and thus causing the capacity decay rapidly .   
  
We see that the intensity of the pristine NMO sample 's redox peak decreased significantly after cycling .   
  
For the conventional SSR method , it is difficult to completely remove the impurity phase due to the insufficient mixing of Na and Mn source in their powder raw materials .   
  
Samples f1 and SSR contain some impurity phase of Mn2O3 , which might account for their low reversible capacities and low coulombic efficiency .   
  
Formation of small amount of hydrated phases still takes place in the modified samples , which is probably due to the incomplete coverage of NNMO .   
  
NNMO-coated samples show better cycle performance , especially for the NMO/20 wt % NNMO sample .   
  
This suggests that there is a significant loss of crystallinity after prolonged cycling .   
  
Peaks shift is not observed for NMO sample , probably due to the accumulation of stacking faults after long-term charge/discharge processes .   
  
This resistive film may originate from the electrolyte decomposition [ , ] and the deposition of Mn on the anode of Na metal [ , ] .   
  
The initial Rf and R ct values of NMO/20 wt % NNMO are significantly smaller than that of NMO , indicating that the coated material has lower impedance .   
  
The strategy is to use a coating material with similar structure as Na0.7MnO2 to minimize lattice strain at the interface .   
  
However , the absence of the ( 101 ) reflection at 23.3deg indicates the presence of stacking fault in the structure .   
  
Similarly , the 2nd peak of weight loss at 562 degC is due to phase transformation from a-type to b-type by inducing twinning in the a-phase .   
  
It was observed that mass change is less than 3 % during the process of phase change due to absence of any chemical reaction .   
  
It could be implied that liquid nitrogen quenching of the pellet helps in retaining the b-phase effectively .   
  
Similarly , during sodium insertion less pronounced plateaus are observed from 4 to 2.7 V while a prominent plateau is observed around 2.5 V .   
  
In case of NaMn0.89Al0.11O2 , the charge plateaus are less noticeable while discharge plateau around 2.5 V is also observed as other two cathodes .   
  
This results in decrease in discharge capacity though keeping cycling stability intact .   
  
However , these peaks in CV plots merge to form one peak at high scan rate .   
  
On the other h , NaMn0.89Al0.11O2 show diminished second peak and a long single peak which intimidate that loss of long range order mitigated to a certain extent .   
  
Since , Mn3+ ( ( t2g ) 3 ( eg ) 1 ) or Mn4+ ( ( t2g ) 3 ) does not contain spin down electrons it is highly probable that U parameter would overestimate formation energy values .   
  
Eventually Al doping reduces the band gap value .   
  
To further our research we intend to study structural modification to this class of material due to different dopants through experiment and DFT based simulations .   
  
However , this material looses long range order during charging .   
  
Therefore during fast charging show less capacity , low rate capability and fading .   
  
Clearly , sintering the sample at 250 and 450degC is not enough to form the Na0.44MnO2 , since it still contains Na2O2 ( PDF # 09-0075 ) and MnO2 ( PDF # 12-0141 ) phases as the main phases .   
  
So we assume that the bottoms of the rods on the main matrix are melted Na-rich region verified by EDX analysis and such low melting point of these two precursors may possibly cause high mobility of ions inducing the fast crystal growth .   
  
We suggest that there is partial melting ( due to the low melting points of the starting oxides ) during the heat treatment in the sample .   
  
Such melting can cause high mobility of the ions and supply free energy to the system triggering the rod formation .   
  
It is well known that the Nernst equation does not explain the thermodynamics of the battery due to solid state redox reaction .   
  
The obvious 12 % weight loss in the temperature range of 25-110degC is caused by the elimination of the absorbed water from the precursor .   
  
However , there is a weight gain as oxygen from air is involved in the reaction of Mn2O3 and Na2O .   
  
No obvious weight loss is observed between 740 and 900degC , indicating that Na0.7MnO2.05 is synthesized within this temperature region .   
  
However , the samples burned at 850 and 900degC contain a small amount of impurity , which is identified from the peaks at 12.7 and marked by `` \* '' .   
  
The behavior of the Na0.7MnO2.05 electrode deviates from the ideal rectangular shape , indicative of both the capacitive and the pseudocapacitive properties .   
  
However , there exist obvious aggregations for the S3 and S4 powders burned at higher temperatures , which is not favorable for Na+ transport .   
  
As a result , the oxidization reaction occurs at a higher potential while the corresponding reduction reaction takes place at a lower potential , causing increased potential difference between the oxidization and the reduction reactions .   
  
This is because the electrolyte permeation is quite slow .   
  
From the potential-time curves , the capacitance significantly fades with increasing the current density .   
  
This is because that a large number of ions could be adsorbed by the electrodes with the increase in current density , and the ion concentrations rapidly decrease between the electrode-electrolyte interfaces .   
  
Consequently , polarization loss at the electrodes increases and becomes the rate determining step , causing capacity loss .   
  
From the curves , the capacitance significantly fades with increasing the sintering temperature .   
  
Larger particle size is not conducive to increase the reaction rate due to the reduced contact area between the liquid and solid , and increased the internal resistance .   
  
However , after 1000 cycles , the structure of the particles becomes looser with the boundaries turning to be rough .   
  
The impedance behavior at the high frequency region is characteristic of the resistance at the oxide-electrolyte interface due to discontinuity in the charge transfer process at the solid oxide/liquid electrolyte interface which is a result of difference in the conductivity between solid oxide ( electronic conductivity ) and the aqueous electrolyte phase ( ionic conductivity ) .   
  
The impedance behavior in this region also involves contributing resistance from Faradaic redox processes , which is associated with the surface phenomena of the Na0.71MnO2.05 electrode .   
  
As can be seen from Figure 4b , for Na2.76Mn1.78 ( SO4 ) 3 , its BVS map is almost same with that of Na2Fe2 ( SO4 ) 3 , but different from that of .   
  
The irreversible capacity of 10 mA h/g ( 95 % charge-discharge efficiency ) may come from electrolyte decomposition when the cell was charged to high potential , 3.9 V ( vs Na+Na ) .   
  
The shapes of the load curves are almost invariant on cycling , and only exhibit a small but continuous reduction in capacity associated mainly with the voltage plateau .   
  
While the agreement between the experimental powder diffraction pattern and the simulation pattern with 25 % stacking faults is compelling , and certainly demonstrates that this material can not be described by a single structure , Diffax can not reveal the detailed nature of the structural complexity .   
  
However , the overriding conclusion from the in situ powder X-ray diffraction data is that there is a major collapse of the long-range structure at low sodium content , with many of the peaks disappearing and those that remain exhibiting significant broadening in most cases .   
  
The significant structural disorder at the end of the Na extraction process may result from an increase in the proportion of stacking faults upon Na removal , as indicated in the NMR data .   
  
While the collapse of long-range order on Na extraction inhibits a detailed understanding of the structure of the Na deficient materials , it is apparent that the structural changes observed when Na is extracted are reversed when Na is subsequently electrochemically reinserted in the cathode material .   
  
Our analysis of the changes in the structure of the cathode material upon cycling indicates that b-NaMnO2 has a complex intergrowth structure and that the long-range order present in the as-prepared material collapses when Na is extracted , and is then recovered when Na is reinserted , but with an increase in the proportion of twin boundaries .   
  
Although a small polarization ( 150 mV ) is observed along the 2.7 V plateau , the polarization reached a value of 600 mV below x = 0.4 .   
  
The large cell polarization at low Na content may result from the collapse of the long-range structure .   
  
Clearly , there is an irreversible loss of capacity on cycling , as the capacity does not return to its initial value .   
  
As noted previously , capacity fading at low rates is associated mainly with the voltage plateau at 2.6 V .   
  
It should also be recalled that Mn3+ containing electrodes are prone to some degree of Mn2+ dissolution in the electrolyte , something that will be more prominent near full Na insertion where the concentration of Mn3+ is greatest .   
  
Upon Na reinsertion , however , the structure is recovered , although exhibiting increased disorder .   
  
The coulombic efficiency rapidly rose up to ~100 % in the subsequent cycles and the reversible capacity of the PNP @ CNTs anode decreases slowly in the first 5 cycles and remains stable at ~125 mA h g-1 .   
  
The capacity decrease in the first few cycles can be ascribed to the slight solubility of the reduction products of the oligomers in aqueous electrolytes .   
  
As shown in Fig . 2e , the reversible capacity of the PNP @ CNTs anode decreases slowly during the first 10 cycles and then remains stable over the subsequent 500 cycles .   
  
Bragg peaks of impurity phases have not been detected , suggesting that low dose Mn2+-doping does not alter the structure of NVP .   
  
When recycled at the initial rates , there is almost no specific capacity loss .   
  
However , in Fig . S4 , + there is an additional voltage plateau around 3.85 V .   
  
As a result , an additional voltage plateau around 3.85 V is occurred in the in the charging process .   
  
But excess Mn2+ doping could worsen the crystal structure of Na3V2 ( PO4 ) 3 , therefore , when the Mn content increased to Mn0.035-NVP/C , the DNa+ and the electrochemical performance decreased ( Table 4 ) .   
  
In particular , the utilization of such methods to arrive at cathodes with uniquely defined morphologies is of great necessity as it will help to achieve mass-scale production in a short period .   
  
Further , the higher boiling point of TTEG ensures sustained polyol combustion for apparently longer durations that can facilitate the formation of hierarchical or secondary particles .   
  
However , several peaks were not completely grown in the as-obtained sample , demonstrating that the combustion deposits need heat treatment to yield the preferred product with high crystallinity .   
  
Moreover , amongst the three electrodes , NVMCP/C/NPs exhibits the least electrochemical polarization , signifying an enriched electronic conductivity due to the Cu doping .   
  
On the whole , after delivering a high initial discharge capacity ( 79 mA h g-1 ) , the cathode showed a small drop in the capacity ( 70 mA h g-1 ) up to the 40th cycle .   
  
It is worth noting that the high cathode mass ratio and slow-diffusion kinetics of Na+ ion in highly viscous diglyme electrolyte definitely affected the final productivities of the full cell .   
  
However , the reasonably good performance of the NVMCP/C/CC cathode along with the MnS2 anode in full-cell formations even in the high-viscosity electrolyte demonstrates their high suitability for real-world applications .   
  
It is to be noted that the explored research outputs for the NVMP cathode mainly uses hard carbon anode for full-cell construction .   
  
However , oxygen oxygen loss loss occurs in Fe oxide when the voltage exceeds 4.0 V upon charging , which causes severe voltage and capacity degradation .   
  
Considering that the charge compensation mechanism of NMFO in the high-voltage region is consistent with that of NFO , an in-depth understanding of the oxygen ( in ) stability of NMFO is important for elucidating the origin of this ( in ) stability for harnessing the full potential of ORRs in binary-layered oxide Na cathodes .   
  
This is contrary to the results for various OR-based oxide cathodes in which O2 evolution was experimentally detected when the charge voltage exceeded 4.0 V .   
  
As mentioned in relation to the reversible oxygen capacity in NMFO , the energy diagram suggests that O2 evolution in NMFO is unlikely to occur via electrochemical ORRs .   
  
In general , ORRs originate from labile oxygen 2p-electrons , the deep reactions of which provoke oxygen loss in OR-based oxide cathodes .   
  
That is , it is surmised that lattice oxygen coordinated with two Fe3+ ions exhibits inferior oxygen stability compared with that surrounded by a single redox-active Fe ion .   
  
However , at x = 0.75 , where the impact of an attractive electrostatic interaction derived from neighboring Na atom on the oxygen stability would be less prominent , Fe-rich oxygen exhibits inferior oxygen stability in comparison with Mn-rich oxygen .   
  
Despite the voltage and length of the ( de ) intercalation plateau ( at 3.37 V vs Na+/Na0 ) has remained same for the Na3V2 ( PO4 ) 3 cathode , additional charge and irreversible capacities are noticed which could be due to the electrolyte degradation .   
  
The slight change in the profile can be ascribed to the local structural changes during charging process .   
  
Interestingly , the appearance and amplitude associated with the second shell ( V/Mn ) -Na of the kh ( k ) signals of the discharged cathode at both V- and Mn-K edges do not reconcile with the pristine cathode ( Figure 4 c , f ) , thus confirming the irreversible losses occurred during the additional Na-ion extraction , which corroborates our ex situ XRD findings .   
  
The substituted Mn2+ is electrochemical inactive in the cathodes with lower concentration ( y < = 0.5 ) .   
  
At y = 1.00 , Mn and V electron densities are fairly high and almost equal , but lesser than that of y = 0.75 cathode , which accounts for the reduced redox activity .   
  
However , y = 0.75 and 1 cathodes undergo rapid capacity fade ( i.e. , only 61 % and 30 % of their initial values are retained at the end of 50th cycle ) .   
  
Although , such rapid decay could be ascribed to the structural changes occurring at higher voltages as previously discussed , it seems that the y = 0.75 cathode exhibit slower degradation in comparison with y = 1 sample .   
  
However , the discharge capacities of the Na4VMn ( PO4 ) 3 cathode have severely decreased at higher C-rates ( 69 and 44 mA h g-1 at 2C and 5C rates , respectively ) .   
  
As the C-rate increases to 5C , its capacities decline by 86 % along with moderate increase of polarizations .   
  
These observations clearly indicate that the kinetics of sodium ( de ) intercalation is relatively slower in the Na3.75V1.25Mn0.75 ( PO4 ) 3 cathode compared to the Na3V2 ( PO4 ) 3 at higher C-rates .   
  
On the other hand , despite their enhanced first charge capacity , the y = 0.75 and 1 cathodes show faster capacity degradation .   
  
However , this observation does not establish that all aluminum ions are confined near the vicinity of the particle surface .   
  
The initial charge-discharge curve of Na0.65MnO2 agrees well with previous reports on the charge-discharge behavior of Na0.44MnO2,26 , 27 with the exception of a short-range sloping voltage profile at the end of the discharge .   
  
At low current density ( rates < =0.1 C ) , the extent of the discharge capacity degradation of the sodium manganese oxides is not a function of aluminum incorporation .   
  
However , the extent of capacity loss at high current density ( > 1 C ) is suppressed by aluminum incorporation , indicative of facile sodium ion insertion/extraction into/out of the NaAl0.1Mn0.9O2 particles .   
  
Therefore , the superior cycling performance of NaAl0.1Mn0.9O2 as compared to Na0.65MnO2 ( at > 100 cycles ) indicates that capacity degradation in sodium manganese oxides is primarily associated with the structural stability on the surface of the Na0.65MnO2 particles .   
  
Therefore , the drastic capacity fading observed in NaAl0.1Mn0.9O2 during the early stages of cycling can probably be attributed to both its low electrical conductivity and the high activation energy required for sodium ion extraction with an increase in sodium content .   
  
The moisture exposure of the Mn-based oxide products for long time is easy to form protonated products [ 39-42 ] , which may be the main reason for Mn4+ reduction .   
  
Especially , the surface of the materials is liable to hydration and then forms few NaOH on the surface , even with brief exposure to air .   
  
The preparation of our samples requires calcination and cooling treatment in air , so the surface of samples is likely to be hygroscopic .   
  
At high voltage , the worse electrochemical stability may be attributed to the fact that more sodium ions are removed from the internal structure during charging , making the internal structure more difficult to recover in its initial structure after charging/discharging and then its degradation .   
  
The pristine Na0.44MnO2 suffers from serious capacity decay during cycling .   
  
With the rates increase , the pristine Na0.44MnO2 demonstrates quick capacity decay .   
  
Especially at 8C , it only delivers 65.2 mAh g-1 , which is only 59 % of the initial discharge capacity at 0.2C .   
  
However , the pristine Na0.44MnO2 obtains initial discharge capacity of 80 mAh g-1 at 4C and only keeps 45 % capacity retention after 500 cycles .   
  
The larger resistance for pristine Na0.44MnO2 may be ascribed to the internal structure distortion of active materials , surface surface exfoliation exfoliation of of electrode electrode materials materials and consumption decomposition of electrolyte during electrochemical processes .   
  
It is noted that an oxidation peak ( at 4.1 V ) is shown in CV curves of pristine Na0.44MnO2 and there is no corresponding reduction peak , which is related to consumption decomposition of electrolyte .   
  
In the different cycles CV curves of pristine Na0.44MnO2 ( Fig . 6b ) , the 5th cycle curve and the 100th cycle curve do not overlap well , which means that there is large irreversible capacity from the 5th cycle to the 100th cycle .   
  
However , under the same large voltage range and scanning rate of 0.1 mV s-1 , the curves ( Fig . 6c ) of the 5th cycle and the 100th cycle are slightly different from 2 wt % Al2O3-coated Na0.44MnO2 , which demonstrates that the slight capacity decay occurring from the 5th cycle to the 100th cycle for 2 wt % Al2O3-coated Na0.44MnO2 .   
  
From the images ( Fig . 7a-c ) of pristine Na0.44MnO2 , we can see that the surface of the submicron rods electrode is obviously broken .   
  
Broken submicron rods ( Fig . 7b ) and gaps on the surface of the submicron rods ( Fig . 7c ) indicate that the serious surface exfoliation of the pristine Na0.44MnO2 after cycling can be the main reason for capacity fading of pristine Na0.44MnO2 submicron rods .   
  
Some similar cathode materials have been reported for volume expansion and direct contact reaction between the electrolyte and the electrode during the electrochemical processes may cause the electrode materials to fall off under high voltage [ 20,55 ] .   
  
The pole pieces of modified Na0.44MnO2 and the diaphragms ( Fig . 7g ) do not change significantly , but the color of the pristine Na0.44MnO2 diaphragms ( Fig . 7h ) have changed from white to light yellow , indicating that the side reaction between pristine Na0.44MnO2 and electrolyte has occurred during the electrochemical processes .   
  
Therefore , part of the electrolyte and pristine Na0.44MnO2 electrode materials are consumed .   
  
However , the 4.1 V peak ca n't be found in CV curves of 2 wt % Al2O3-coated Na0.44MnO2 , which demonstrates consumption decomposition reaction of electrolyte is significantly decreased by Al2O3 coating and Al2O3-coated Na0.44MnO2 electrode did not suffer the corrosion from electrolyte .   
  
Although the locations of main diffraction peaks also correspond with the peaks locations of pristine Na0.44MnO2 before cycling , the intensities of the peaks are obviously weakened .   
  
During the first discharge process , the internal lattices structure of materials keeps expanding , which reduces the structure ordering , causing the gradual decreasing of ( 201 ) peak strength and then disappearing with the increase of cycling number .   
  
However , the poor structural stability/reversibility of the pristine Na0.44MnO2 during the sodium ions insertion/deinsertion processes makes it difficult for the internal structure of the materials to recover to the original state after cycling .   
  
On the contrary , the change change of of XRD XRD pattern pattern for Al2O3-coated Na0.44MnO2 electrode after cycling is not obvious .   
  
Due to multiple insertion/extrication of sodium ions , the internal crystal structure of the pristine Na0.44MnO2 collapses and distorts , which may result in an irreversible shift of the ( 350 ) peak .   
  
In addition , many changes of the internal structure of pristine Na0.44MnO2 may be irreversible because of the structural distortion and expansion , so the ( 350 ) peak of pristine Na0.44MnO2 has not undergone the reversible split and weakened change during cycling .   
  
In addition , volume expansion will also make the surface of the material unstable and fall off , so it also reduces the surface shedding to some extent .   
  
clear voltage plateau as observed for Li1.3Nb0.3Mn0.4O2 is not found for the Na system .   
  
Moreover , the cyclability of the sample in the Na cell is not acceptable for battery applications .   
  
In this voltage region , oxygen oxidation is not evidenced .   
  
Such side reaction can result in the oxygen loss and accumulation of carbonate species , which is expected to be accelerated for the nanosize Na1.3-xNb0.3Mn0.4O2 prepared by mechanical milling .   
  
This observation is also consistent with the fact insufficient cyclability as shown in Figure 2 , and the FSA additive probably suppresses such unfavorable side reaction with electrolyte solution and electrolyte consumption on electrochemical cycles .   
  
Note the oxygen loss and densification process can not fully explain the large initial reversible capacity .   
  
It is hypothesized this fact probably originates from the difference in surface area of the samples .   
  
Further systematic studies will contribute the development of high-energy rechargeable batteries for energy storage applications in the future .   
  
Nevertheless , it would be necessary to optimize the particle size in order to increase the Coulombic efficiency at elevated rate .   
  
Because the mother phase is described in . triclinic space group , it is rather difficult from powder X-ray diffraction to go further .   
  
More importantly , contrary to the reported studies on layered NaxMnO2 , no amorphization and/or increase of disordered and stacking faults is observed , which is due to the fact that the insertion process is occurring through only one biphasic process suggesting .   
  
A combined neutron diffraction , TEM and X-ray synchrotron study will be necessary to solve this structure with accuracy .   
  
This indicates that fewer phase transitions occur during sodiation and desodiation as x in b-Na0.7 [ Mn1-x Li x ] O2+y increases .   
  
Consequently , the disordered Li/Mn distribution caused inhomogeneous electrostatic repulsion between Mn and Na+ , leading to Na+vacancy disordering .   
  
Thereby , not all of the Mn4+ can be reduced to Mn3+ during the next sodiation , because some Na+ sites were still occupied even after full desodiation .   
  
This is because the P2-type Na-poor phases obtained after desodiation are metastable .   
  
This reveals that not being able to observe the OP4 phase during charging and discharging ( Figure ) is attributed to the phase transition from P2 to OP4 being kinetically hindered , although the OP4 phase is more thermodynamically stable than P2 for Na-poor phases .   
  
Over both voltage ranges , b-Na0.7MnO2+y delivered similar reversible capacities of approximately 112 and 135 mA h g-1 , respectively , but poorer cycle performance was observed in the higher voltage range despite the fact that Jahn-Teller distortion occurs in the lower voltage range .   
  
Therefore , the poor cycle performance of b-Na0.7MnO2+y is not due to the Jahn-Teller distortion or the formation of the OP4 phase during charging .   
  
However , the binary phase transition is known to be one of the principal factors causing the capacity fading of layered cathode materials ( i.e. , Li [ Ni1-x-y Co x Mn y ] O2 ) for Li-ion batteries because interfacial strain can lead to the formation of cracks at grain boundaries within a particle , resulting in increasing polarization .   
  
, Therefore , the poor cycle performance of b-Na0.7MnO2+y is considered more dependent on the binary reaction mechanism than the Jahn-Teller distortion or OP4 phase formation .   
  
Similar to the disordered Li distribution in b-Na0.7 [ Mn1-x Li x ] O2+y ( x = 0.07 ) , the random distribution of Mn vacancies in a-Na0.7MnO2+z also caused inhomogeneous electrostatic repulsion between Mn and Na+ , leading to the Na+vacancy disordering during sodiation and desodiation .   
  
Compared to b-Na0.7MnO2+y ( with its complex phase transitions during sodiation and desodiation ) , the more stable cycle performances of b-Na0.7 [ Mn1-x Li x ] O2+y ( x = 0.07 ) and a-Na0.7MnO2+z were attributed to their one-phase reaction mechanisms ( undergoing no phase transition during sodiation and desodiation ) .   
  
The poor cycle performance of b-Na0.7MnO2+y was not due to Jahn-Teller distortion or the formation of an OP4 phase during charging .   
  
In particular , the OP4 phase was not observed during charging and discharging , because the transition from the metastable P2 Na-poor phases to the OP4 phase was kinetically hindered .   
  
However , vacancies generated during cycling played the same role in phase transitions during charging and discharging .   
  
Stable cycle performance was observed , with 82 % capacity retention after 100 cycles .   
  
In addition , the edge-sharing geometry of Mn1-O6 and Mn3-O6 polyhedra is expected to lead to a strong Mn3+-Mn3+ repulsion in the desodiated structure , which destabilizes the charged state of the electrode , leading to an increased voltage .   
  
The multiple peaks in the dQ/dV profiles imply complex reactions during electrochemical cycling ; this will be discussed in detail later in the paper .   
  
This cycle stability is markedly superior to that of typical manganese-based cathodes at the elevated temperatures , which exhibit rapid capacity decay due to accelerated Mn dissolution .   
  
We speculate that the large lattice mismatch between the a- and b-phases is the cause of the significant distortion of the a and c lattice parameters of the a-phase during this stage , as well as the apparent phase separation .   
  
It is uncertain as to the origin of this d-phase during discharge ; however , we speculate that it may arise from specific Na-vacancy ordering , which occurs preferentially in the structure .   
  
The absence of a b-phase in the calculations may imply that the b-phase is a kinetically driven intermediate phase between the a- and g-phases , which is structurally similar to both the a- and g-phases , even though its origin is not clearly understood .   
  
One interesting point to note is that , unlike most reported manganese-based cathode materials , Na diffusion is not significantly retarded by the structural changes induced by the Jahn-Teller distortion .   
  
It is worthwhile to note that Na4Fe3 ( PO4 ) 2 ( P2O7 ) , which shows similar structural evolution to Na4Mn3 ( PO4 ) 2 ( P2O7 ) , exhibits slow slow Na Na kinetics kinetics in this state of charge because of the P2O7 distortion and atomic rearrangement which narrows the Na diffusion channels .   
  
After Fe oxidation , there are only limited plausible Na diffusion pathways remaining for NaFe3 ( PO4 ) 2 ( P2O7 ) , as activation barriers of Na1-Na4 , Na2-Na4 , Na3-Na2 , Na3-Na4 paths become higher than 500 eV .   
  
In particular , as the Na3-Na2 path closes down due to significantly higher barrier , the 3-dimensional diffusion channel of Na4Fe3 ( PO4 ) 2 ( P2O7 ) does not remain intact ( see Fig . S11 , ESI+ ) .   
  
With the crystal water extracted , the MO layer space shrinks which impedes the Na ion ( de ) intercalation from/into the interlayer space .   
  
That is to say , layered Na-Bir possesses a much smaller charge transfer resistance than heat treated Na-Bir .   
  
However , the characteristic diffraction peaks of heat treated Na-Bir vanish after 150 cycles , indicating that its structure collapsed .   
  
The whiff lattice expansion of Na-Bir suggests that there is a small amount of tension during Na ion extraction from the layer framework , with the crystal water acting as a cushion .   
  
Without crystal water , the structural integrity will decompose and the layer framework will be damaged .   
  
However , the dissolution of Mn for heat treated Na-Bir in aqueous electrolyte is very serious .   
  
The crystal water releases the structural strain during Na ion intercalation/extraction into/from the former framework , which dramatically suppresses the dissolution of Mn .   
  
It should be noted that the sol-gel preparation of such a kind of polyanion material usually leaves some residual carbon on the particles ' surface , which could effectively improve the material 's electronic conductivity .   
  
However , the cycling stability of the prepared Na4MnV ( PO4 ) 3 was not as good as those reported in the literature ( Fig . S4b+ ) .   
  
To meet the requirements for practical application , further effort in materials preparation such as nano-engineering and surface carbon coating should be made to improve the electrochemical performance of Na4MnV ( PO4 ) 3 .   
  
With further charging to 3.7 V , the resonance peak at -428 ppm was almost invisible .   
  
This indicated that Na+ could only migrate in a 1D channel along the c-axis during this charging process ( Fig . 7 ) , while migration along the a- and b-axis was hindered by high diffusion barriers > 0.8 eV .   
  
Moreover , the effective Na+ diffusion barrier was much smaller than those in the first voltage plateau , which resulted from the biphasic transition from Na ( 1 ) Na ( 2 ) 2-xMnV ( PO4 ) 3 to Na ( 2 ) Na ( 3 ) MnV ( PO4 ) 3 .   
  
Second , two new peaks appear and are fixed at 14.9deg and 28.8deg during the discharge process , and instantly disappeared at the end of the discharge process , respectively .   
  
A high mass loading is important for the cathodes to achieve high areal capacity in practice .   
  
The higher the charge voltage , the more favorable it is to release oxygen gas ( n=0 ) ; thus , the 4.5 V potential plateaus are not stable and tend to release oxygen , as indicated by the initial C.E . of the various cutoff curves ( Figures 3 h and 4 b ) .   
  
Owing to the zero-strain feature of Na2Mn3O7 , the fade-off capacities for the subsequent cycles are induced by oxygen gas release .   
  
For Na2Mn3O7 , an increase in the long-range order distribution of Mn vacancies indicates more accumulated stress owing to manganese-site vacancy shrinkage/expansion ; this makes it easy to release oxygen and leads to a low C.E . and poor cycling stability .   
  
In the heterojunction , Na2Mn3O7 is the main phase ( Na2Mn3O7/Na0.44MnO2 is 69:31 ) , but its potential plateaus ( 4.2 and 4.5 V ) are not clear in the charge/discharge curves ( Figure 3 d , g ) .   
  
To realize a workable aqueous Na-ion battery , it is necessary for the anode to be in a Na-deficient condition and cathode should be designed in a suitable Na-rich state , both of which have sufficient Na storage capacity , thus enabling a `` rocking-chair '' Na-ion battery .   
  
However , the typical diffraction peaks of the MWNTs were not observed in the XRD pattern , which might be caused by the low content of MWNTs and the highly crystalline nature of NaTi2 ( PO4 ) 3 .   
  
The low Na ion insertion/extraction potential was located at the lower limit of the electrochemical window of the aqueous electrolyte .   
  
In addition , the voltage difference between charge and discharge curves showed that polarizations occur , certainly due to low electronic conductivity , even after improving the electronic conductivity by adding MWNTs .   
  
The intrinsic causation of this phenomenon for the aqueous battery system is still unknown .   
  
However , possible causes include partial dissolution of electrode materials , active materials stripping from the current collector in the aqueous electrolyte , or hydrogen and oxygen being generated by water hydrolysis .   
  
Thus further investigation of these effects is needed , and the aqueous NaTi2 ( PO4 ) 3-Na0.44MnO2 system may be a candidate for safe , low-cost , high-power storage systems .   
  
The capacity decay could be ascribed to the loss of Na+ ions in the HC anode part .   
  
Such fast Na+ kinetics can be a key factor to account for the excellent rate capability .   
  
Nevertheless , the little cycling stability fading of the NMO material should be originated to the structural instability during repeatedly insertion/extraction of sodium ions .   
  
The strong Na+/e- binding increases the electronic localization and thereby decreases the diffusion coefficient to a certain degree .   
  
A small amount of capacity attenuation should be derived from the Jahn-Teller distortion of Mn3+ , the dissolving of Mn2+ into the electrolyte , and the volume changes due to the de/intercalation processes of large Na ions .   
  
From the comparison it is clear that the impedance at the Na/electrolyte interfaces ( Z3el-CR ) is not negligible , so the two electrode measurements ( Z2el-WC ) can not be used as representative of the working electrode impedance .   
  
In this frequency range , the impedance of lithium ion battery electrode is due to the complex electrochemical reactions taking place at the interfaces .   
  
On the contrary , the charge transfer resistance increases with the sodium amount in the phase .   
  
At the lowest frequencies ( below 1Hz ) , the contribution of the solid-state diffusion is present ( ZD in the equivalent circuit of Fig . 6 ) , i.e . Na ions moving into the bulk of active particle material .   
  
In this case , the presence of the metallic current collector blocks the diffusion of ions at the inner interface ( the stainless steel current collector does not alloy with Na ) .   
  
In this case , the measurement requires several hours and the external cell conditions have to be carefully controlled ( constant temperature ) .   
  
To our knowledge do not exist other data to compare with , however this behavior may be attribute to diffusion in the polymeric film formed on the particle surface .   
  
In the measurements performed at a higher rate the charge efficiency increases , indicating the presence of one side reaction during the anodic process : the less the time the system remains at oxidative potentials , the higher the efficiency .   
  
There are two chemical/physics processes , which contribute to the overall surface resistance : the well known charge transfer resistance and the presence of a passivating layer ( SEI ) on the particle surface .   
  
Unfortunately , the as-produced material although displays a highly suitable redox potential of ~3.7V ( versus Na/Na+ ) owing to Mn2+/Mn3+ redox , it shows a poor electrochemical performance of 19.9mAhg-1 under the rate of 0.1C ( 1C=120mAg-1 ) , which might be due to the Jahn-Teller effect [ , ] .   
  
Interestingly , due to the ionic radius of Fe ( 0.078nm ) smaller than that of Mn ( 0.083nm ) , the cell volume of Fe-doped samples would decrease slowly .   
  
However , the Na3Mn2P3O11 @ C electrode has a large potential gap ( ~630mV ) , which could be owing to the inherent low conductivity and Jahn-Teller effect .   
  
Although the undoped Na3Mn2P3O11 @ C manifested 87.4 % of the initial discharge capacity , it only presented a low specific capacity of 18.1mAhg-1 at 100th cycle .   
  
The undoped electrode material delivered a low capacity from 19.9mAhg-1 at 0.1C to 3.4mAhg-1 at 5C .   
  
Afterward , when fully discharged , there are still no obvious changes of the intensity and position of diffraction peaks , indicated a stable structure and negligible volume changes upon ( de- ) sodiation .   
  
Only imperceptible changes could be observed , suggesting a stable two-phase reaction ( Na-poor and Na-rich ) during the whole cycling .   
  
The excess capacity during the first charge process should mainly come from the high voltage region and is strongly affected by kinetic factors .   
  
Hence , the compositional dependence of chemical diffusion coefficients is difficult to obtain by the CV tests .   
  
Furthermore , in the GITT profiles of Fig.7 , there is an abrupt decrease of Na-ion mobility at the end of each charge/discharge process for all samples .   
  
This may be originated from the gliding of the ( MnO2 ) slabs , which can lead to the octahedral Na+ vacancies and more complex dynamics of electrochemical desodiation .   
  
Hence , one of the further investigations is to prevent the occurrence of such gliding , which is ongoing in our lab .   
  
Surprisingly , as cycling progresses , a charge plateau begins to appear at ~3.9V resulting in an increase in charge capacity .   
  
It is clearly seen that this control experiment does not exhibit the similar trend as described earlier with 5vol % VC even after 20 cycles .   
  
Notably , the electrode is able to regain 100 % of its initial capacity when cycling is reverted to 0.1C after its performance at 5C .   
  
Interestingly , when 5vol % VC is added , the diameter of the semicircle of the EIS plots decrease significantly during cycling ( Fig.5c ) .   
  
When 10vol % VC is added , a detrimental outcome is noted in the resistances associated with the storage processes ( Fig.5e ) , where the size of the depressed semicircle increases drastically after each cycle .   
  
However , as the VC concentration is increased above 5vol % , a decrease in discharge capacity is noticed .   
  
In other words , although inclusion of VC up to a certain limit ( 5vol % ) improves discharge capacity and decreases cell impedance as cycling progresses ( Fig.5 ) , excess additive beyond 5vol % leads to detrimental effect in cell impedance and subsequently on sodium storage performance .   
  
We believe that this passivation film dissolves during the course of cycling which reflects the decrease in passivation film and charge transfer resistances ( as demonstrated by a decrease in the diameter of the semicircle in the EIS plots ) , and the degree of dissolution depends largely on the amount of VC .   
  
On the other h , no such observation is made from the EIS measurement of the sodium counter electrode ( CE ) ( as seen in Fig.S8 ) for the 5vol % VC , which clearly reveals that the impedance changes arise only from the passivation film occurring on the surface of the Na2MnSiO4 WE .   
  
When less than 5vol % VC is used ( Fig.7a and b ) , the passivation film formed does not sufficiently wrap the entire electrode surface leading to high Mn dissolution .   
  
Please note that presently , the actual reason for the observed increase in both the charge and discharge capacities when 5vol % VC is added is still unclear ( as seen in Figs.2a and 4 ) .   
  
However , we are claiming that the reason leading to this increase in capacity might be due to a significantly suppressed suppressed manganese manganese dissolution dissolution , which is caused by an optimised passivation layer formed on the electrode surface .   
  
Nonetheless , more in-depth analysis has to be conducted to fully understand the role of this passivation layer .   
  
Another possible explanation for the observed increase in storage capacity in the first 10 cycles is that the liquid electrolyte might penetrate slowly into the bulk of the mesoporous electrode material investigated here as cycling progresses , thus promoting more electrochemically active sites with cycling .   
  
We recognise the fact that the XPS experiment is surface-sensitive and the results represent information only on surface processes during battery operation .   
  
The considerable polarization ( about 270mV ) observed for Na2Mn3 ( P2O7 ) 2 which can be usual seen in Mn-based LIBs and SIBs cathodes ( such as pyrophosphate Li2MnP2O7 and Na2MnP2O7 ) may due to the inherent low conductivity and Jahn-Teller effect and the resulting rate limitation .   
  
In terms of cyclic performance ( as shown in Fig . 4 ( f ) ) , only 34.33 % of the initial capacity ( 50.1mAh \* g-1 ) is preserved as reversible capacity for pure Na2Mn3 ( P2O7 ) 2 after 30 cycles , indicating the instability of the framework upon Na ion insertion/de-insertion .   
  
The discharge capacity of pure Na2Mn3 ( P2O7 ) 2 compound is dropped from 45.5mAh \* g-1 to 1.7mAh \* g-1 ( corresponding to only 3.74 % specific capacity retention ) when the C-rate is increased 20-fold from 0.1C to 2C , revealing very poor rate capability .   
  
It is worthwhile to note that the FePO4 \* 2H2O is not carbon-coated , thus , further optimization of rate performance could be possible if its electronic conductivity is enhanced .   
  
This puts our amorphous FePO4 \* 2H2O at high risk of side reactions if it is put in direct contact with water .   
  
Nevertheless , since the concentration of sodium ions is 1M and that the pH of the electrolyte is 7 , the equilibrium sodium intercalation voltage into FePO4 \* 2H2O must be over 2.30V vs. Na+/Na so as to prevent hydrogen evolution .   
  
One could see that the nano-crystals still exist among the amorphous structure .   
  
However , further increase of the Mn content above x=0.8 transforms the shape of the charge/discharge curve .   
  
For the low Mn contents ( x=0.2 , 0.4 ) the 3.9V plateau is reversible on discharge , however for x > =0.6 the 3.9V step vanishes on the first discharge and then does not reappear on either charge or discharge in case of lower cut-off voltage of 2.5V .   
  
However , even in a case of actual presence of a biphasic domain , the 2th positions of their reflections are too close to each other , so that they can hardly be resolved by standard laboratory X-ray diffraction methods .   
  
Most likely that on discharge Na+ is randomly inserted into available sites , but due to kinetic limitations Na+ does not fully reoccupy Na1 position , and certain amount of Na vacancies affect the ( de ) intercalation mechanism during subsequent cycling .   
  
Raising the voltage cut-off above 3.8V leads to an increase in reversible capacity due to extraction of the additional Na .   
  
However , low Coulombic efficiency resulted in returning of only 2 Na+ into the crystal structure of the phosphates .   
  
Authors attributed that to poor reversibility of the V4+/V5+ redox reaction .   
  
As it was reported for Na4MnV ( PO4 ) 3 [ , ] , rising the cut-off voltage above 3.8V leads to fast capacity fade during cycling .   
  
Yet stabilization of the practical energy density above 410Wh kg-1 observed for x > 0.4 samples ( Figs . 3 and 7c ) is still an important challenge .   
  
This improvement is sustained with cycling for Na3.4Mn0.4V1.6 ( PO4 ) 3 , however retaining this increase in case of higher Mn content is necessary towards the pragmatic utilization of NASICON-type cathodes in Na-ion batteries .   
  
Good rate performance of the cathode is a prerequisite for a high power full-cell device .   
  
There are also large particle agglomerates that do not show up in the TEM image .   
  
A structurally structurally stable stable and high high performance performance anode anode is as crucial as the cathode for the subsequent full-cell demonstration .   
  
At high charge-discharge current densities , both parts of the discharge capacity decrease greatly .   
  
However , the plateau around 0.1 V shortened more abruptly with the capacity below 0.1 V decreased from 111 mAh/g ( 0.2 C , 50 mA/g current density ) , to 70 mAh/g ( 0.5 C , 125 mA/g ) , 31 mAh/g ( 1 C , 250 mA/g ) , and 14 mAh/g ( 2 C , 500 mA/g ) .   
  
Because of the mixed electrochemical performance of hard carbon , which has high capacity and good cycling stability but poor Coulombic efficiency and poor rate performance , special attention is needed in terms of electrode balancing with a Na0.44MnO4 cathode for full-cell assembly .   
  
However , it was very difficult because the hard carbon was coated with a thick layer of SEI , which was from electrolyte decomposition over the hundreds of cycles .   
  
However , demonstration of a non-aqueous Na-ion battery full-cell with long cycle life and high energy is very challenging , even though highly stable cathode and anode materials such as Na0.44MnO2 and Na3V2 ( PO4 ) 3 have been demonstrated in half-cells .   
  
It is believed that the major obstacle is related to the low Coulombic efficiency that originates from the non-aqueous electrolyte and the wide voltage window .   
  
Yet in practice , cathodes and anodes usually have a first-cycle Coulombic efficiency much lower than 100 % .   
  
The non-aqueous electrolyte system has the advantages of large voltage window and high capacity , yet at the same time it presents problems/challenges .   
  
The solvents and salts in the non-aqueous electrolytes become oxidized at cathode surfaces at high charge voltage and reduced at anode surfaces at low discharge voltage , leading to the formation of SEI , low Coulombic efficiency in the first few cycles , large first-cycle irreversible capacity loss , and capacity fade in following cycles .   
  
A natural thought to address the challenge is to preform SEI layers on both cathode and anode before the full-cell assembly so that the side reactions and Na-ion Na-ion consumption consumption in subsequent full-cell cycling will be mitigated .   
  
It is known that an SEI layer forms on electrode surfaces when cycling the electrode in a half-cell against Na metal .   
  
The key is whether the SEI layer preformed in pre-cycle of a half-cell can help to improve the full-cell performance and whether the full-cell could be assembled without much damage to the preformed SEI .   
  
It is difficult to keep the pre-cycled working electrode intact when we collect it from the disassembled half-cell .   
  
An initial capacity of ~27 mAh/g was obtained , and it faded quickly to < 10 mAh/g .   
  
The first-cycle Coulombic efficiency of hard carbon in half-cells is even lower , ~70 % .   
  
Hence , it is believed that the low Coulombic efficiency of the cathode and the anode drained the limited Na ion stock in the Na0.44MnO2 cathode very quickly , resulting in low capacity , quick capacity fade , and poor Coulombic efficiency .   
  
SEM images in Fig . 4a and b show that the pre-cycled hard carbon anode ( Fig . 4a ) and the control hard carbon anode cycled in a full-cell without pre-cycling treatment ( Fig . 4b ) have amorphous coating on the surface indicating the formation of SEI on both hard carbon anodes .   
  
However , the SEI composition is different from that of the hard carbon anodes with pre-cycling treatment .   
  
The different SEI composition is ascribed to different electrolyte decomposition : the SEI formed on pre-cycled hard carbon is in a half-cell vs. Na metal and has unlimited Na ion stock , while the SEI formed on hard carbon in a full-cell without pre-cycling treatment has very limited Na ion stock and is formed vs. a Na0.44MnO2 cathode .   
  
The corresponding XPS Mn2p spectra of the pre-cycled Na0.44MnO2 cathode has almost no Mn2p signal ( Fig . 4f , red curve ) , indicating that a thick SEI layer was formed on the cathode surface during pre-cycling .   
  
It indicates that the SEI layer on the Na0.44MnO2 electrode cycled in a full-cell without pre-cycling treatment is either very thin or does not have a good coverage .   
  
It hence concluded that a good SEI layer was formed on the pre-cycled Na0.44MnO2 cathode while no or poor SEI on the cathode cycled in a full-cell without pre-cycling treatment .   
  
The performance of the control full-cell without pre-cycle treatment is very similar to the data shown in Fig . 3a : low capacity , fast capacity fade and low Coulombic efficiency .   
  
The full-cell is cathode limited below 2 C rate , yet it becomes anode limited at 4 C rate .   
  
Yet the cycling stability drops greatly with capacity retention of ~75 % over 1000 cycles ( Fig . 5e ) .   
  
It is believed that the excess anode capacity ( the capacity ratio between cathode and anode at 1 C rate ( 120 mA/g ) is ~1:1.5 ) and limited cycling stability of the hard carbon make the full-cell a bit distant from the optimum configuration .   
  
The full-cell has a poor long-term cycling stability at 4 C rate because it is anode limited at such a high rate and the over-charging of the hard carbon anode brings a quick cell failure .   
  
Full-cells tested in a wider voltage window such as 1-4.5 V have a significant reduction in cycling stability because of the instability of electrolyte at high voltage .   
  
It must be noted that the full-cell will have low capacity and poor cycling stability if either the cathode or anode surface layer is damaged during the disassembly of the pre-cycled half-cells or full-cell assembly .   
  
The goal for pre-cycling treatment of electrodes is to preform stable SEI layers on the electrode surfaces to reduce the consumption of Na ion stocks in full-cell cycling and hence achieve long stability .   
  
Damage of the surface layer usually leads to damage of the SEI layer and hence wastes the pre-cycle treatment .   
  
The critical role of a preformed intact SEI layer in achieving the best full-cell performance was elucidated , revealing that the low Coulombic efficiency of cathode and anode materials is a major deficiency in the development of Na-ion battery full-cells .   
  
The Na0.44MnO2-hard carbon full-cell chemistry is still distant towards satisfying the practical needs of Na-ion battery in many aspects .   
  
The pre-cycle treatment is not practical in industrial full-cell fabrication and also tricky to do in the lab .   
  
In addition , the flakes had crystallographic texture and , thus , a thorough Rietveld refinement for the operando data is challenging and beyond the scope of this publication .   
  
However , considering the limitations of the Debye-Scherrer equation ( e.g. , value of the shape factor ) , it can not be excluded that the flakes are single crystals .   
  
Potential reasons for the higher capacity of the spheres are stacking faults as mentioned above or an increased amount of defects as a result of the synthetic route .   
  
Consequently , a capacity fading of > =1 % should be detectable by these methods if it were resulting from Mn dissolution .   
  
Thus , the difference in cycling stability between the flakes and spheres can not be the consequence of phase transitions .   
  
This difference might be one contributing factor to the superior cycling stability of spheres over flakes and could be the cause of the difference in the preservation of morphology over the course of cycling described previously .   
  
For undoped materials , the phase change giving rise to additional overlapping reflections makes detailed comparison of the structures difficult .   
  
This suggests that although there is a lesser volume change for the spheres , a greater degree of strain distribution in the material is present at high and low Na+ loading , implying possible inhomogeneities in the distribution of Na+ concentration throughout the material .   
  
While it is not possible to observe such differences in the FWHM for NMO spheres for the aforementioned reasons , given the similar performance of the materials it is hypothesized that the same strain accommodation ability may also be one of the reasons for superior cycling stability and capacity of NMO spheres as compared to flakes .   
  
Thus , a minor part of the Mn2O3 precursor might not have been transformed to P2-type NMO during the annealing process and has taken up Na+ at potentials of 2.2-1.5 V vs Na|Na+ , possibly resulting in the detectable presence of this phase .   
  
The smaller changes in the unit cell volume of the spheres , in combination with the lower concentration of the P ' 2 phase throughout cycling , reduce structural stresses and fatigue .   
  
Thus , the Co-doped materials are anticipated to contain a lower degree of amorphous/untransformed material , which can crystallize in the suspected cubic phase .   
  
In our measurements , the `` Z '' phase was not observed for low Na+ contents for the NCO spheres .   
  
However , Na+ content during the initial charge might just not have been decreased sufficiently to induce the formation of the `` Z '' phase .   
  
Slower relaxation times during the major plateau at ~2.2-2.1 V as compared to the solid solution region ( e.g. , ~2.9 V ) are attributed to a decrease of electric and/or ionic conductivity ( Figure S4 ) .   
  
The reason for the lower conductivity of the undoped material is attributed to the high resistivity induced by the Mn3+ , which , in its d4 high-spin configuration , is a Jahn-Teller active ion and has more localized electrons to interact with the positively charged sodium .   
  
Moreover , the suppression of the Na+ ordering may further facilitate the Na+ transport between the layers .   
  
In addition , dissolved manganese could not be detected in the electrolyte for NMO flakes over the course of cycling and is therefore thought to play a negligible role .   
  
Moreover , the spherical material shows a higher capacity , which is attributed to structural defects .   
  
With the very rapid development of energy storage , the large-scale usage of LIBs will result in a shortage of the lithium sources in the near future .   
  
However , the radius of a sodium ion ( 102 pm ) is obviously larger than that of a lithium ion ( 76 pm ) , meaning that the crystalline lattices of most SIB electrode materials will encounter a much larger volume variation compared to those of LIBs during cycling .   
  
Hence , it is still a big challenge to develop practicable electrodes with superior electrochemical properties .   
  
The lower cycle stability should be originated from the undesirable Jahn-Teller distortion of Mn3+ and the severe volume changes due to the de/intercalation of large sodium ions .   
  
Note that , the delivered capacity could not recover well to the initial value when the current density returned to 0.2C .   
  
In the Na2SO4-MSO4 binary system , material synthesis leads to some unreacted MSO4 , which can be reduced by excess usage of Na2SO4 that invariably yields off-stoichiometric phases .   
  
Similar to the Fe-case , it was futile to conduct synthesis using stoichiometric amounts of precursors ( i.e . 1:2 molar ratio of Na2SO4 and MnSO4 ) , invariably forming a product rich with impurities ( e.g . MnSO4 ) .   
  
As the SO4-based compounds intrinsically suffer from rapid thermal decomposition above 400-450 degC releasing SOx ( x = 2 , 3 ) gases , we restricted the final annealing temperature to 350 degC .   
  
Further , it is prone to ambient poisoning over a prolonged period .   
  
Thus , these alluaudite phases should be kept under an inert atmosphere for safe handling .   
  
Owing to the lack of safe ( organic ) electrolytes , we were unable to experimentally observe the high Mn3+/Mn2+ redox activity in the target compound .   
  
Owing to the lack of electrolytes that are stable up to high-voltage ( ca . 5 V ) , it is difficult to currently implement Na2+2xMn2-x ( SO4 ) 3 in practice , but it attests to the richness of sulphate chemistry in designing novel insertion materials for rechargeable batteries .   
  
However , longer milling times can result in particle agglomeration and formation of big secondary particles .   
  
This might be due to the stirring effect during hydrothermal reduction of GO .   
  
Even at the rate of 1C , the specific discharge capacity of NMCP/rGO electrode corresponds to 56 % of its initial capacity , but the capacity of the pristine NMCP declined sharply .   
  
Nevertheless , the much higher practical charge-discharge capacities of the FC Na0.7MnO2 sample than those of the SC Na0.7MnO2 sample might stem from the enhanced Na-ion kinetics in P2-/O3-Na0.7MnO2 , which results from the increased amount of the P2-Na0.7MnO2 phase in the material .   
  
In general , the capacity fading of Na1-xMnO2 became more severe with increasing applied current density , primarily because of the drastic and substantial lattice changes in the Na1-xMnO2 layered crystal structure , which are accompanied by multiphase transitions during cycling .   
  
The increased number of vacancies could lead to strong Mn-O interactions and increased the structural stability of FC Na0.7MnO2 sample , even in the high-voltage region .   
  
Actually , no variation was found in all the anodic/cathodic peak positions of the FC Na0.7MnO2 in subsequent cycles , indicating low voltage polarization and suppressed irreversible structural changes upon cycling .   
  
Unfortunately , in the O3-NaMnO2 phase , which has a relatively low Mn4+/Mn3+ ratio , strong Jahn-Teller distortions occurred , which negatively affected the structural stability of Na0.7MnO2 during long-term cycling , despite its high initial charge-discharge capacity .