Elements  
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Subject  
  
The poor cycling stability of Na [ Ni0.5Mn0.5 ] O2 is considered to be related to the severe structural changes arising from multiple phase transitions .   
  
The discharge capacity decreased as the cut-off voltage was lowered , resulting in 125.4 and 108.9 mAh g-1 for 3.58 and 3.35 V , respectively .   
  
However , when cycled at 4.0 V , all redox peaks after 100 cycles faded significantly and were largely polarized compared to the initial curve , indicating the poor reversibility of phase transitions .   
  
This anisotropic nature of the lattice change could greatly compromise the mechanical stability by imposing local stress on primary particles .   
  
[ 21 , 22 ] The nonuniform accumulation of stress on the secondary particles , depending on the orientation of primary particles , makes the cathode susceptible to microcracks and fracture of the secondary particles .   
  
Despite the rapid volume contraction during the initial phase transition from O3 to P3 , no discernible microcracks were observed on the secondary particle at 3.14 V .   
  
In addition , the following P3 to P ' 3 phase transition had a marginal effect on the particle integrity .   
  
However , although the unit cell volume was hardly changed at 3.58 V , some microcracks were nucleated near the particle core after the phase transition to the P3 ' structure ; but , the majority were arrested before they reached the particle surface .   
  
Even with a small change , the inversion of the stress field caused by the c-axis contraction critically exacerbated the mechanical stability , possibly by creating severe stress concentrations at largely desodiated states , and subsequently , led to the development of microcracks .   
  
[ 23-25 ] These microcracks along the grain boundaries persisted up to a fully charged state of 4.0 V , pulverizing the secondary particles .   
  
On the contrary , the prevalent microcracks closed upon discharging .   
  
Contrary to the case of 3.58 V where the unit cell is the hexagonal P3 ' structure during charging , the particle discharged to 3.5 V contained several channels extending to the surface , implying that microcracks do not close reversibly even during the first cycle .   
  
Microcracks are detrimental to the stability of the cathode because they significantly expose fresh inner particles and isolate the primary particles , accelerating the degradation of the abundant unstable Ni4+ species on the crack faces via parasitic electrolyte decomposition .   
  
[ 19 , 34 ] The abrupt P3 ' to O3 ' phase transition rendered the cathode susceptible to crack formation , resulting in the cycling stability fading at a much higher rate at 4.0 V cycling .   
  
However , when the P3 ' to O3 ' phase transition was avoided , capacity retention improved greatly by suppressing the severe microcrack formation , as we have demonstrated .   
  
The extent of this repeated opening and closure in the cathode was apparently sufficient to cause permanent structural damage to the material depending on the upper upper cut-off cut-off voltage voltage .   
  
The cathode particle cycled at 4.0 V showed significant mechanical damage with microcracks forming all along the grain boundaries , as expected .   
  
In comparison , at 3.58 V , the particle integrity was well preserved even after 100 cycles .   
  
However , the Rct of 4.0 V cycling rapidly increased from 2.7 to 96.4 O as the cycling proceeded , while the 3.58 V cycling exhibited a modest increase , reaching 14.1 O even after 100 cycles .   
  
A continuous voltage decay was recorded for 4.0 V cycling , which is consistent with the poor cycling performance and the polarized redox reaction by the gradual structural deterioration .   
  
However , no voltage decay was observed upon cycling at 3.58 V , indicating that the P3 ' to O3 ' phase transition is again responsible for the structural degradation .   
  
Although the SAED pattern verifies the overall remaining structure of the layer domain , the primary particle initiated tearing parallel to the ab planes ( marked by the red arrow ) , which is possibly owing to the fragmented dissolution of the cathode .   
  
As expected from the microcracks propagating to the surface , the exposed faces of the interior primary particles were heavily damaged by the subsequent electrolyte infiltration , as shown in the inset SAED image in Figure 6d .   
  
Thus , regardless of the position , the primary particles with an abundance of highly reactive Ni4+ species in the highly desodiated state were susceptible to surface degradation when in contact with the electrolyte .   
  
[ 19 , 34 ] The microcracks significantly increased the exposed surface and accelerated electrolyte penetration , resulting in the severe degradation of the cathode particle .   
  
However , the cycling stability deteriorated significantly , resulting in capacity retentions of 94.2 % at 3.35 V , 90.7 % at 3.58 V , and 75.5 % at 4.0 V after 100 cycles .   
  
Among the multiple phase transitions , the P3 ' to O3 ' phase transition above 3.6 V is mainly responsible for the loss of the structural stability of the O3-type Na [ Ni0.5Mn0.5 ] O2 cathode .   
  
The cross-sectional SEM observations indicate the strong dependence of the cycling stability on the extent of microcrack formation within the secondary particles caused by the severe phase transition .   
  
The appearance of the O3 ' phase in a largely desodiated state compromised the mechanical stability and the sudden collapse during the phase transition led to microcrack formation and fracture of the secondary particles .   
  
The microcracks allowed the penetration of the electrolyte into the secondary particle interior , resulting in chemical damage to the exposed internal primary particles via electrolyte electrolyte attack attack .   
  
These surface-degraded internal particles formed an electrochemically inactive NiO-like rock-salt phase , thereby accelerating capacity fading .   
  
Suppressing microcracks on the secondary particles is of prime importance for improving the cycling stability of hierarchical structured O3-type Na [ Ni0.5Mn0.5 ] O2 cathodes .   
  
However , the discharge capacity of NMN NMN 15 15 decays rapidly at high rate and almost reached 0 at high-rate 4 C and 8 C .   
  
This poor high-rate performance was mainly due to the longer sodium-ion diffusion path caused by the more P2 phase with large particles .   
  
In addition , the electrical conductivity of NMN 15 sample ( 2.88x10-2 ) is less than that of NMN 25 sample ( 7.66x10-2 ) in Table S5 , which imply the poor rate performance .   
  
The NMN 30 samples with more P3 phase with small particles showed lower capacity , moderate high-rate retention , indicating that excessive small particles of P3 phase and decreased layer spacing were not conducive to fast fast Na+ Na+ diffusion diffusion for high rate performance .   
  
Additionally , the P2/P3 composite material showed pseudo-capacitance phenomenon , which is beneficial for rate performance .   
  
This finding is attributed to the initial formation of the SEI layer on the carbon sheets due to electrolyte decomposition .   
  
Ideally , the chemical and structural stability of this SEI layer should be adequate to significantly reduce or prevent further decomposition of the electrolyte after the first few cycles .   
  
Consequently , the presence of native Na2CO3 on carbon sheets should reduce the amount of SEI formation .   
  
As evidenced by the overlapping CV curves after the first scan , the SEI formed in the 1st cycle is stable and prevents further reduction of electrolyte during subsequent cycles .   
  
The large surface area of the carbon sheets may not be fully covered by the native Na2CO3 , which results in the low coulombic efficiency .   
  
However , it is observed that the cell resistance exponentially decreases as the current density increases , indicating that Butler-Volmer kinetics are controlling the interfacial phenomena .   
  
The resistance in the electrolyte solution Rsol remains small and constant ( in the range of 4-4.6 O ) between cycles and at various potentials , suggesting the stability of the electrolyte upon cycling .   
  
The resistance of the SEI film Rsei shows slight increases after an additional 51 cycles , suggesting slow SEI growth during cycling ; the sudden increase in Rsei at 0.001 V is unexpected and may have its origin in the interaction between the sodium counter electrode and the electrolyte .   
  
However , such SEI growth is not deemed excessive to alter the sodiation behavior of the carbon sheets as evidenced in the dQ/dV plot .   
  
More importantly , no excessive SEI growth is observed in the cycled electrode ( comparing Figure 5 d Figure 5 b ) .   
  
A discharge capacity of 151.9 mAh g-1 is obtained between 2.0 V and 4.3 V , the capacity is lower than 173 mAh g-1 , which might be associated with the reduced Ni content in this work .   
  
Lowering the voltage cut-off can effectively suppress the structure collapse which is caused by too much sodium extraction at high voltage cut-off .   
  
Other reported layered materials deliver a relatively large discharge capacity of over 150 mAh g-1 , but with very limited capacity retention of over 20 or 30 cycles ; or exhibit a stable stable long-term long-term cycling cycling but at the tradeoff capacity .   
  
For this material , the coulombic efficiency at initial cycles of this P2-NNM electrode is close to 98.5 % , which is due to lack of degradation of electrolyte and excessive extraction of sodium ions in this voltage region .   
  
Moreover , the arrangements of tetragonally distorted M3+O6 octahedra in the material , that is Jahn-Teller distortion , lead to structural degradation on cycling and reduction of the distortion , thus reduction the presence of the Mn3+ ions is desirable from a stability perspective .   
  
The reduced interslab distance restricts Na+ ion diffusion within the layers of the material during charge-discharge cycles accounting for the poor C-rate performance of the Ti-doped materials in comparison with the pristine NNMO , esp .   
  
During the cathodic scan , this peak completely vanishes in the 2nd cycle due to the high irreversibility of this structural transition .   
  
This explains the poor capacity retention of Na0.67Ni0.17Ti0.16Mn0.67O2 electrode in the initial cycles in comparison with Na0.67Ni0.25Ti0.08Mn0.67O2 .   
  
The lower cut off voltage means the Mn3+/4+ redox will contribute more to the capacity but will have detrimental effects on cyclability and at voltages > 4.2V , P2-O2 transition shows a similar capacity fade on cycling .   
  
However , a huge capacity loss of 60mAhg-1 is observed in the first 10 cycles .   
  
However , the C- rate performance of the pristine material is better than the substituted materials at higher C-rates > C/2 .   
  
The faster Na+ diffusion ( at higher C-rates ) in the interlayer space is hindered as the interlayer spacing becomes narrower in the Ti-substituted samples .   
  
At lower C-rates , the Ti-substituted samples show better rate capability .   
  
In the case of Na0.67Ni0.17Ti0.16Mn0.67O2 cells , although the highest initial capacity was achieved , the cells suffer drastic capacity fade ( ~30 % capacity loss in first 10 cycles ) as found for the parent NNMO ( ~42 % loss in first 10 cycles ) .   
  
This large initial irreversibility of Na0.67Ni0.17Ti0.16Mn0.67O2 when charging above 4.2V , is due to the P2-O2 transition that reemerges in the higher substituted sample .   
  
The optimum amount of Ti- substitution ( x=0.08 ) that induces complete suppression of P2-O2 transition requires further studies as this behavior is reported in similar oxide systems [ , ] .   
  
However , added capacity from Mn3+/Mn4+ redox in Na0.67Ni0.17Ti0.16Mn0.67O2 can be utilized further by lowering the upper cut off voltage to 4.1V .   
  
The cycled charge-discharge voltage curve of the cell is observed to be slightly different from the initial cell .   
  
Although , the fade in capacity observed for the cathode at high voltage is inferred to be due to the P2-type phase not completely retaining its state at 0.5 C , as indicated by the irreversible irreversible phase phase transitions transitions in Figures a , b , cell resistance ( quantified high resistance of R 1 , R 2 , R 3 , and R 5 in Figure a and Table S2 ) is also observed to increase during cycling ( full cathode high voltage range ) , as shown in Figure a .   
  
On the other h , polyvinylidene fluoride ( PVDF ) has been used widely as a binder in electrode fabrication in the manufacturing process of commercial batteries , but the binder decreases its electrical conductivity .   
  
This may be due to the fact that Na2/3 [ Ni1/3Mn2/3 ] O2 particles are much larger than the gap distance between RGO sheets and can not be embedded into the gap effectively .   
  
After 1 month in this electrolyte , there was no decomposition of the electrode ( see S4 of ESI+ ) .   
  
With increasing charge-discharge rate , there is a large difference in discharge capacity between the GNNM and normal electrode .   
  
But in our experiments , it was difficult to control these three factors of the GNNM and normal electrode to keep them consistent simultaneously .   
  
This may be due to the fact that the PVDF in the normal electrode would limit the fast transfer of Na ions and thus change the ionic conductivity ( see S5 of ESI+ ) .   
  
The small particle size of Na2/3 [ Ni1/3Mn2/3 ] O2 and the strong connections between RGO and Na2/3 [ Ni1/3Mn2/3 ] O2 may be important factors .   
  
The distortion from the ideal hexagonal cell for these samples causes peak splitting of the h0l Bragg diffractions , e.g. , the 104hex .   
  
The relatively low coulombic efficiency ( 90 % ) may result from the formation of a SEI layer during the initial cycle under a low current density .   
  
Compared with the Na0.5Ni0.25Mn0.75O2 micro-sheets , the Na0.5Ni0.25Mn0.75O2 granular materials not only show a lower working voltage and capacity , but also display a worse cycling capability .   
  
In the case of the graphite electrode , the reversible capacity was negligible ( Figure S1 in Supporting Information ) .   
  
The capacity was , however , gradually reduced by the galvanostatic cycling in the NaClO4 EC : DMC .   
  
The hard-carbon electrode in the BC electrolyte showed a reversible capacity higher than 230 mAh g-1 in the early cycles ; however , the serious degradation began after the twentieth cycle .   
  
In this system , the cycle performance is constantly deteriorated from the early cycles .   
  
In the case of EC : ethyl methyl carbonate ( EMC ) , the irreversible decomposition around 0.5-0.2 V was suppressed .   
  
When the hard-carbon electrodes were also tested in the PC-based electrolyte solutions mixed with DMC , EMC , or DEC , they showed electrochemical activity ; however , severe degradation of the activity was observed in all electrolyte solutions ( Figure S2 ) .   
  
The VC addition , however , results in a negative effect on the Na insertion into the hard-carbon electrodes ( Figure S3 ) .   
  
This indicates that a different approach is required for the interfacial control for Na insertion electrodes .   
  
Even though the initial reversible capacity slightly decreases to ca . 230 mAh g-1 in the limited domain of 2.00-0.01 V , degradation of the capacity was not observed over 120 cycles .   
  
When the reversible capacity was limited by restricting the voltage domain above 0.05 , 0.10 , and 0.20 V vs. Na , no capacity degradation was observed during 200 cycles .   
  
In the case of lithium , the slopping curve with higher capacity appeared in the wider potential range between 0 and 1.2 V , and an ambiguous plateau appeared in the lower potential region near 0 V .   
  
The above results confirm that a passivation layer different from the lithium-based negative electrode exists for the sodium-based electrode .   
  
As is generally accepted , many organic solvents including carbonate esters are not thermodynamically stable at the standard potential of Na ; therefore , the interfacial passivation is essentially required for long-term cycling .   
  
Although all systems showed a high reversible capacity > 200 mAh g-1 ( negative electrode basis ) during the initial cycles , a decrease in the reversible capacity was observed in the NaClO4 system ( Figure S9 ) .   
  
This phenomenon indicates that the NaClO4 dissolved PC electrolyte was not sufficiently stable for the long term cycling of Na-ion batteries .   
  
Furthermore , when the Na-ion cell was tested at a higher rate of 300 mA g-1 , no significant decrease in capacity is observed , indicating that the hard-cabon/NaNi0.5Mn0.5O2 cell demonstrates a remarkable rate capability ( Figure 11 lower ) .   
  
In addition , as shown in Fig . 2 ( d ) , the surface of NaMN/Mg3 ( PO4 ) 2 is smooth and the nanosheet structure can not be observed .   
  
Generally speaking , the ( 0 0 2 ) lattice plane is considered as the fast Na-ion channel , and the ( 1 0 0 ) crystal plane is perpendicular to the ( 0 0 2 ) crystal plane , and the dominant growth of the ( 1 0 0 ) lattice plane will hinder the transmission of Na-ion , as a result , the electrochemical properties of the sample materials deteriorate after exposure to the air .   
  
As shown in Fig . 5 ( h ) , obviously , there is more surface oxygen on the surface of uncoated NaMN , it is possible that the bare layered oxide material easily absorbs moisture and oxygen from the air .   
  
The protective coating could prevent the electrolyte from directly contacting the active material , the reversible capacities of the samples are slightly reduced after metal phosphates coating .   
  
In contrast , the bare NaMN sample demonstrates a low coulombic efficiency in the first 5 cycles .   
  
The cells charged and discharged at various current rates ( 0.1-1 C ) are shown in Fig . 6 ( e ) , the results prove that the discharge capacity of NaMN could not recover to the initial value even though the current density return to 0.1 C again , which demonstrates an unsatisfactory rate performance of NaMN .   
  
Moreover , Mg3 ( PO4 ) 2 coating layer is tightly coated and poorly poorly conductive conductive , causing a slow electron and Na+ transfer in electrode materials , In summary , NaMN/Mg3 ( PO4 ) 2 shows a worse rate performance .   
  
As a comparison , the biggest Rct value of NaMN/Mg3 ( PO4 ) 2 demonstrates that the transfer of electrons is more difficult , it is probably the poor conductivity of Mg3 ( PO4 ) 2 coating .   
  
In addition , the transition metal ions in bare NaMN will dissolve in the electrolyte during the activation process and the original surface structure of NaMN is destroyed , hence , NaMN show a larger Rct value .   
  
This pair of reduction/oxidation peaks are not observed in the CV curves of NaMN/AlPO4 and NaMN/Mg3 ( PO4 ) 2 .   
  
This may be due to the fact that the bare material will directly contact the electrolyte and it could cause more defects on the surface of the particle , and resulting in the escape of surface oxygen ( O2- - O2 ) .   
  
As shown in Fig . 7 ( f ) , obviously , the discharge capacity of NaMN could not recover to the initial value when the current density return to 0.1 C again .   
  
Because of the great decrease of crystallinity , NaMN shows a significant voltage platform attenuation and capacity decay .   
  
Comparing with the cycle performance test results before exposure to the air , NaMN shows significant capacity decay after exposure to the air .   
  
In addition , the higher coulombic efficiencies of NaMN/AlPO4 and NaMN/Mg3 ( PO4 ) 2 indicate that no impurities will react with the electrolyte after exposure to the air .   
  
Nevertheless , as the plateau length at 4.2V becomes shortened during the charging process , it suffers from rapid capacity decay during the next two cycles .   
  
The long plateau at 4.2V in the charge profiles of the 0-NMTO electrode is attributed to the P2-O2 phase transition with the sliding and shrinking of the TMO2 layers , which is the main origin of irreversible capacity .   
  
And as the Ti content increases the better overlapping of the charge/discharge profiles is seen , but it will sacrifice some discharge capacity .   
  
Obviously , as the Ti content increases , the rate capability of the electrodes becomes better but with some sacrifice of the capacity .   
  
Although the 0-NMTO electrode exhibits the highest initial discharge capacity , it experiences severe capacity fading during subsequent cyclic process .   
  
In addition , the 0.3-NMTO electrode shows the best capacity retention of 86.6 % , but it shows a relatively low discharge capacity compared to the 0.2-NMTO electrode .   
  
It is well-known that the P2-type 0-NMTO not only suffers from a rapid capacity degradation but also a rapid voltage decay during the cyclic process at high voltage .   
  
It suggests that the 0-NMTO electrode experiences severe voltage decay .   
  
Compared to the 0-NMTO electrode , the Ti-substitution electrodes show a higher midpoint voltage , but the midpoint voltage decreases slightly with increasing Ti content in the Ti-substitution electrodes , which can probably attribute to the increase of the non-redox-active NiO content .   
  
[ 13,15 ] These massive cracks in the 0-NMTO particles will increase the contact area between the active material and the electrolyte at high voltage , leading to the increase of the side reaction between the active material and the electrolyte .   
  
Although the 0-NMTO particles restored their original morphology , they experienced drastic volume changes throughout the sodium removal and insertion process .   
  
This will cause exfoliation of the active material , affect the transport of electrons and deteriorate the life of battery .   
  
The huge increase in 0-NMTO electrode impedance after 100 cycles is mainly attributed to the particle exfoliation caused by dramatic volume changes during the cyclic process .   
  
Simultaneously , smaller Rct growth in the Ti-substitution electrodes means that Ti substitution can stable the active material/electrolyte interface and inhibit the increase of Rct .   
  
This result was obtained at a very small current density of 2mAg-1 and no long term cycling performance was provided in that paper .   
  
Herein , during the first charge , our prepared sample showed a Na+ extraction capacity of 75mAhg-1 when charged to 4.0V ( before the beginning of the higher voltage plateau around 4.25V ) , about 43 % Na+ of the Na2/3 [ Ni1/3Mn2/3 ] O2 formula was removed .   
  
However , it also can be seen that the charge and discharge capacities lose rapidly during subsequent cycling .   
  
The upper charge plateau around 4.25V and discharge plateau around 4.0V faded rapidly and disappeared after 10 cycles .   
  
The discharge capacity of 10th cycle was 103mAhg-1 ( 74 % ) and decreased to 40mAhg-1 ( 29 % ) at 100th cycle .   
  
It is clear that the anodic and cathodic peaks at higher potentials ( 4.36V/3.87V ) exhibited the worst stability , which disappeared after several cycles .   
  
It is obvious that the capacity decay was due to the change in the higher potential process .   
  
The CV results confirmed that the instability of the electrochemical behavior in 2.0-4.5V was due to the irreversible process in voltage range higher than 4.0V .   
  
The cycling performance was greatly affected by the P2-O2 phase transformation occurred above 4.0V .   
  
It seems that the stacking faults could not be completely eliminated in the discharge procedure when cycled with the current density of 17mAg-1 .   
  
The cycling stability between 1.6V and 3.8V is not as good as that between 2.0V and 4.0V .   
  
The Na|P2-Na2/3 [ Ni1/3Mn2/3 ] O2 cell delivered an initial discharge capacity of 140mAhg-1 ( 0.1C ) cycled between 2.0V and 4.5V , however the capacity decreased rapidly upon cycling .   
  
However , the cycling performance was not so stable in this voltage range .   
  
This means that the phase structure of the Na2/3 [ Ni1/3Mn2/3 ] O2 cathode could not be completely recovered to the original P2 phase during discharge process after charged to 4.5V .   
  
Combined with the obviously decayed electrode performance , we have to say that the electrode cycled between 2.0V and 4.5V suffered a significant alteration of the crystal structure .   
  
XRD analyses indicate that the crystal structure of P2-Na2/3 [ Ni1/3Mn2/3 ] O2 was irreversibly damaged due to the over extraction of Na+ during 4.0-4.5V charge process .   
  
The crystal spacing of the P2 phase in the biphasic material increases slightly , which may related to the replacement of a part of the smaller radius Mn by Sn with a larger radius .   
  
This may be associated with the Sn substitution in materials to produce different phase ratios .   
  
This phenomenon could be accounted for by the suppression of MO2 gliding and Na/vacancy ordering in the Na-intercalation process when Fe is introduced into the crystal lattice .   
  
The voltage plateau is attributed to the phase transformation between O3 and P3 phases , while the sloping profile at higher voltage must be resulted from a solid-solution reaction with P3-structure .   
  
Obviously , introducing Fe element into the NaNi0.5Mn0.5O2 lattice leads to a different Na-insertion mechanism due to the suppressed MO2 gliding and phase conversion .   
  
However , as the Fe amount was further increased , the decrease in electrochemically active Ni content led to a decreased capacity of this material .   
  
Because pure NaFeO2 can deliver only a reversible capacity of 92 mAh g-1 , much lower than NaNi0.5Mn0.5O2 , the Fe3+Fe4+ couple may have poorer electrochemical activity than that of the Ni2+Ni3+ couple in these composite oxide .   
  
In contrast , the NaFeO2 electrode exhibits very fast capacity degradation from 92 mAh g-1 in the first cycle to 42 mAh g-1 after 28 cycles , corresponding to only 46 % capacity retention .   
  
This poor cyclability is known to result from the Fe4+ migration from the transition-metal layer to sodium layer , arising from FeO6 octahedral distortion of Jahn-Teller effect .   
  
Additionally , the high Fe-substituted samples also show lower reversible capacity due to the poorer electrochemical activity of the Fe3+Fe4+ couple as discussed above and in previous work .   
  
However , these two electrodes show different CV feature at the high potential region : the oxidation peak of NaNi0.5Mn0.5O2 electrode at 4.1 V is much stronger than its reduction peak at 3.86 V , and the peak intensity fades quickly with subsequent cycles , indicating an irreversible electrochemical reaction .   
  
This irreversible reaction has been speculated to the co-insertion of the electrolyte solvent at high charge voltage due to the larger interslab distance of NaNi0.5Mn0.5O2 .   
  
However , the cycling capacities decrease gradually down to 144 mAh g-1 after 20 cycles , corresponding to 78 % capacity retention .   
  
This capacity decay occurs mainly at high voltage region , indicating an unstable phase transformation at high voltage charge .   
  
For comparison , the NaFe0.2Mn0.4Ni0.4O2 exhibits better capacity retention ( 87 % ) over 20 cycles , though its initial capacity ( 165 mAh g-1 ) is slightly lower .   
  
Besides , the areas of redox couples at the voltage above 4.0 V for bare P2-NaNMO in the second cycle decrease obviously compared with that of the first cycle .   
  
But there is no obvious variation of the areas of redox couples at the voltage above 4.0 V for the gradient Co3+ substituted P2-NaNMO in the initial two cycles .   
  
The gradient Co3+ substituted P2-NaNMO , because of the substitution of Co3+ , reveals a reduced discharge platform at a high voltage of ~4.2 V and a long discharge curve below 2.8 V , resulting in a reduced discharge voltage .   
  
Namely , the bare P2-NaNMO electrode only maintains a reversible capacity of 73.8 mA h g-1 with an inferior capacity retention of 46.2 % after 100 cycles at 0.1C , showing a rapid decay of capacity during cycles .   
  
Besides , the bare P2-NaNMO electrode exhibits a rapid decline of capacity at a high voltage of above 4.0 V , attributed to the unfavorable P2-O2 transition .   
  
But the bare P2-NaNMO exhibits a fast decline of average voltage , maintaining a low voltage of only 3.2 V after 100 cycles .   
  
Thus the bare P2-NaNMO presents a poor stability of energy density , only 40.1 % retention after 100 cycles .   
  
The continuous charge/discharge curves from 0.1C to 10C are exhibited in Fig . 4 ( c ) and ( d ) , wherein the bare electrode shows severe electrochemical polarization at the rates above 5C .   
  
Obviously , the gradient Co3+ substituted P2-NaNMO electrode has reduced Rct and Wo values compared to those of the bare electrode during the whole charge/discharge process in Table 1 , suggesting lower charge transfer resistance and Na+ diffusion impedance .   
  
Notably , the capacity in the high-voltage region above 4 V was largely retained for the coated electrode , whereas the bare electrode suffered from capacity fade , not only in the high-voltage region , but also in the low-voltage region below 2 V .   
  
Smaller charge transfer resistance was evident for the NaPO3-coated Na2/3 [ Ni1/3Mn2/3 ] O2 electrode , even for the fresh cell , and less impedance was generated for the coated electrode in comparison with the bare Na2/3 [ Ni1/3Mn2/3 ] O2 electrode , which implies that the environment in the interface is very different from the state of the fresh cell for the respective cells .   
  
Gradual structural deterioration of the active materials or oxidative decomposition of the electrolyte can be considered as possible reasons for the abrupt rise in the resistance .   
  
In comparison with the fresh electrodes , broadenings CO and CR bindings were observed after extensive cycles for the bare electrode , implying that sedimentation of byproducts was more progressed on the surface of the bare Na2/3 [ Ni1/3Mn2/3 ] O2 electrode .   
  
In comparison with Li cells , the environment in the Na cell is fairly corrosive because the amount of acidic HF generated in Li cells is usually lower than 300 ppm after extensive cycling .   
  
The above reactions suggest that the NaPO3 coating layer reacts with HF , a byproduct of decomposition of the NaPF6 salt in the electrolyte , and the layer is transformed into protonated NaxHyPO3 but leaves NaF as a byproduct .   
  
The reduced formation of the above-mentioned byproducts on the surface of NaPO3-coated Na2/3 [ Ni1/3Mn2/3 ] O2 was responsible for the low impedance during cycling , and this , in turn , contributed to the better electrode performance .   
  
These phenomena are likely to be isolation of active materials , which lost electric contact among particles so as to remain as less sodiated P2 phase .   
  
Thermal stability is another important issue that should be investigated before these electrode materials are considered for use in practical power sources .   
  
For the coated electrode , the coating layer that encapsulates the P2 particles would impede Na diffusion , such that development of the P2 structure was less dominant for the coated electrode ( Figure 8 d ) .   
  
Though slight , the encapsulating coating layer is likely to delay the evolution of oxygen from the oxide lattice , which was evidenced by less heat generation ( Figure 8 b ) .   
  
The lower HF level in the electrolyte prevented particle rupture and maintained the structural integrity of NaPO3-coated Na2/3 [ Ni1/3Mn2/3 ] O2 , whereas the bare active material exhibited serious morphological degradation , such as exfoliation of particles from the parent particle .   
  
The rapidly increasing polarization in fluorine-free carbonate-based electrolytes with cycling is attributed to successive decomposition of electrolyte and the formation of excessive CEI that blocks the Na+ transportation .   
  
The appearance of Na2/3Ni1/3Mn2/3O2 grains becomes more obscure with prolonged cycles as the CEI thickens ( as discussed below ) ( Figure 2b , c ) , which is attributed to the continuous decomposition of electrolyte .   
  
The continuous consumption of electrolyte and crack of Na2/3Ni1/3Mn2/3O2 grains accelerate the capacity decay of the cells with PC electrolyte .   
  
In contrast , the Na2/3Ni1/3Mn2/3O2 cathode cycled in the PC electrolyte shows a higher intensity of the peaks assigned to CO and CO groups , which is considered to be ascribed to the decomposition of electrolyte .   
  
Moreover , the slope of the linear region in the Nyquist curves of the cells with the FEC electrolyte slightly increased and then maintained unchanged after 100 cycles , indicating that the ion diffusivity does not change much .   
  
In contrast , the slope of the linear region in the Nyquist curves of the cells with the PC electrolyte gradually decreased with prolonged cycles , revealing a decrease in ion diffusivity .   
  
Herein , the continuous decomposition of the PC electrolyte on the Na2/3Ni1/3Mn2/3O2 surface results in a thick CEI layer that blocks Na+ transportation , finally causing sluggish kinetics and accelerating capacity decay ( Figure 4bbottom panel ) .   
  
In addition , the reaction becomes exothermic under the cathodic condition , which is energetically favorable .   
  
These results suggest that PC molecules are less stable than FEC molecules on the cathode side , and thus undergo severe decomposition .   
  
Since the electrolyte has minor effect on the electrochemical performance of the hard carbon anode based on results in half cells ( Figure S22Supporting Information ) , the improvement in the full cell performance is ascribed to the cathode side .   
  
One important characteristic of polymer-based SIBs is safety , as the liquid electrolyte will catch fire when the temperature of the battery is high .   
  
At first , the room temperature conductivity is approximately 10-7 S cm-1 , which is too poor to be used as an electrolyte .   
  
It is well known that interfacial stability is the most important issue in all types of all-solid-state batteries , so compatibility of NaFSI/PEO with Na metal has to be clarified before Na is used in a battery .   
  
This trend is similar to the PEO-based electrolyte in LIBs.23 The investigation of interfacial stability of NaTFSI/PEO was reported by Serra Moreno et al. , and they also found the interface to be stable without cycling.24 That is to say , the solid electrolyte interphase ( SEI ) formed in the initial cycles is very stable , and this result is quite important because PEO is not very stable in Li systems , with the polarization potential becoming larger at longer times.29 Further research is ongoing to clarify the mechanism .   
  
Another issue for real batteries is the cathode material .   
  
More importantly , good cycling performance was obtained , indicating a stable interface formed between cathode and this SPE .   
  
According to the comparison of these two structures , the P2 layered oxide NNM cathode material offers a better interfacial property , and we continue to work towards understanding the mechanism more deeply .   
  
Different from the P2 type structure , the Na-O octahedron in the O3-type structure is surrounded by tetrahedrons and it makes Na+-ion transportation difficult , which can account for the limited rate capability of O3-type structured materials .   
  
This plateau may correspond to electrolyte oxidation and an unknown phase transition that might be related to an ordering of the structure and needs to be further clarified in the future .   
  
A peak at around 4.2 V was only seen for the charging process , which is associated with the decomposition of the electrolyte and a lower cut-off voltage should be chosen for a higher initial Coulombic efficiency .   
  
It will be more beneficial to enhance electrolyte infiltration and improve coulombic efficiency .   
  
Similarly , no other peaks were observed in survey spectra of NaMNO-B , it proves that B0 is not existent in NaMNO-B .   
  
More lattice oxygen exposure is beneficial to improve the electrochemical activity of NaMNO-F .   
  
A large amount of surface oxygen accumulation on the material surface will inhibit the transformation of lattice oxygen to surface oxygen .   
  
It is known that the phase transition is apparently not beneficial to maintain the material structure stability during Na+ intercalation/deintercalation .   
  
It 's probably because the stronger M-F bonds can maintain the stability of the material , and thus the structural variation is difficult to occur .   
  
In contrast , because the introduction of boron inhibits the redox of oxygen , the NaMNO-B exhibits a lower discharge capacity .   
  
The extra charge capacity might be assigned to the oxidative decomposition of sodium propyl carbonate generated the formation of a solid electrolyte interphase or involving oxygen redox couples [ 39,40 ] .   
  
As shown in Fig . 6 ( i ) , NaMNO shows unsatisfactory rate performance .   
  
Moreover , NaMNO-B shows a capacity rising slightly since the material fully activated in the previous cycle .   
  
On the contrary , when using ethanol/water ( in a 4:1 vol ratio ) solvent , it turned turbid immediately once the two solutions are mixed .   
  
The conversion of internal material to crystal phase is therefore hindered by the surface layer and the further reaction requires the diffusion of atoms through the interface .   
  
Contrary to i-NNM , the charge/discharge profiles of b-NNM electrode become relatively smoother , implying a gentle phase transformation during Na+ deintercalation and intercalation .   
  
In contrast , with increasing current rates , the charge/discharge capacity of i-NNM cathode fades rapidly , indicating the low Na+ transport kinetics of i-NNM .   
  
The slow diffusion of Na+ in i-NNM therefore leads to lower specific capacity within a short time ( high current densities ) .   
  
It is well known that the cyclic stability of cathodes is vital to practical SIBs .   
  
The b-NNM cathode delivers a capacity retention of 77.3 % with a stable coulombic efficiency after 100 cycles , while the capacity retention of i-NNM cathode is only 57.7 % and the coulombic efficiency is fluctuating .   
  
The quick capacity degradation accompanying with voltage decay brings about the severe decline of energy density and energy efficiency ( Fig . S8a ) .   
  
In contrast , the capacity of the i-NNM cathode drops rapidly , and only 33.9 % of the initial capacity can be retained at the 500th cycle .   
  
However , when the content of molybdenum ion exceeds a critical value , e.g. , Na0.66Ni0.33Mn0.6Mo0.07O2 ( x=0.07 ) , the capacity will be decreased .   
  
This could be attributed to the fact that excess of sodium molybdate replaces part of the cathode material .   
  
Although two electrode materials exhibit a high initial discharge capacity , a fast capacity decay is observed in the first 10 cycles .   
  
After that , the cycling stability is slightly improved .   
  
Firstly , the Jahn-Teller distortion of the Mn3+ ion formed at the tail end of the discharge process affects the structural integrity of the layer framework .   
  
It is possible that the resistive layer mainly comes from irreversible structural degradation on the surface of the oxide particles , similar to that in previously reported lithium-based oxide materials .   
  
The surface roughness diminishes for the gel membrane , which can be credited to the decline in pore size and pore number .   
  
Additionally , we also found micropores in the surface capturing of the electrolyte solution is liable for fast ionic movement .   
  
The high electrolyte uptake behaviour of as-prepared P ( VdF-co-HFP ) fibrous membrane might increase the number of charge carriers and thus , lead to increase the ionic conductivity at ambient temperature .   
  
In the present study , the bulk resistance ( RGPE ) is significant and contributes to the total resistance and no semicircle was observed , indicating the charge carriers are only ions .   
  
Wettability is another important factor that can affect the cell resistance , rate capability and energy density of the battery .   
  
Furthermore , the difference in wettability is due to the difference in polarity of the Celgard membrane and liquid electrolyte .   
  
Here , in the conventional membrane ( Celgard ( r ) 2400 ) , the liquid electrolyte begins to dissipate at around 65 degC which is indicated by weight reduction in the TG curve as shown in Fig . 6 ( b ) .   
  
It is well-accepted that O3-type oxides have a lower reversible capacity .   
  
At 0.1C-rate , the charge/discharge profile of the Na/NaNi0.5Mn0.5O2 half-cell retained 97 % reversible capacity even after 50 cycles due to faster penetration of liquid electrolyte .   
  
The sloping voltage profiles indicate that a facile intercalation reaction might occur for these samples .   
  
However , substituted samples show improved capacity retention after 30 cycles .   
  
The discharge capacity of P2-Na2/3Ni1/3Mn2/3O2 decreased drastically with cycling .   
  
Unfortunately , we were unable to elucidate the reasons for the change in the voltage profiles of P2-Na2/3Ni2/9M1/9Mn2/3O2 at this juncture in the study .   
  
Therefore , it remains necessary to understand the origin of the voltage profile change and further study is in progress in determining the possible reasons .   
  
Metal ion substituted samples display sloping charge-discharge curves , which might be related to the different charge transfer mechanism .   
  
A slight increase in discharged specific capacities was observed in the first 20 cycles for the x > = 0.1 samples , although this effect is more pronounced in the x = 0.2 sample .   
  
This prevents the formation of consecutive empty Na layers and hence the transformation to the O2 structure is inhibited .   
  
These are more distinct at faster cycling rates , with clearer two-phase behaviour observed during charge at 100 mA g-1 than discharge at 8.5 mA g-1 .   
  
The absence of ordered structures or the insertion/extraction reactions via disordered states , especially in terms of Na+-vacancy disorder , have been related to high Na+ conductivity and excellent high-rate performance .   
  
It is therefore necessary to perform molecular dynamics simulations to probe such diffusion mechanisms and to complement the experimental measurements .   
  
Hence there is no structural re-arrangement in the c-axis upon Mg substitution .   
  
- O3-type cathodes , which can be described as octahedrally coordinated Na ions in between three ( TMO2 ) n slabs per unit cell , are sufficient sodium-ion reservoirs , especially in full cells .   
  
- However , in this type of layered structure , since direct hopping of Na ions from one octahedral site to an adjacent octahedral site requires high activation energy to overcome barriers , Na+ migrate through interstitial tetrahedral sites ( similar to O3-type LixCoO2 ) , which are considered to impose a high energy barrier for facile Na diffusion because the occupation of Na ions in the tetrahedral sites is unfavorable due to the size discrepancy .   
  
As a result , most O3-type cathodes exhibit complex phase transformations and several voltage plateaus during sodiation/desodiation leading to degradation of electrode properties .   
  
Hence , reducing phase transformation and extending solid solution zone during cycling are expected to enable higher rate charging and longer cycle life .   
  
- Thus , their capacity retention ( 75 % of the initial reversible capacity after 50 cycles ) and rate performance ( 10 mA h g-1 at 2C ) might limit their further practical application .   
  
Such deterioration of the electrode properties originates from the irreversible multiphase transitions in the high voltage region ( above 3 V ) .   
  
It is worth noting that the CV behavior for O3-NaNi0.5Ti0.5O2 electrode resembles that of capacitors when close to 4 V , which might be caused by the different different Na+/vacancy Na+/vacancy ordering ordering after Ti substitution .   
  
From a stepwise voltage profile observed for O3-NaNi0.5Mn0.5O2 , limited cell performance is obtained because the phase boundary movement for several two-phase regions is required .   
  
However , P2-Na2/3Ni1/3Mn2/3O2 plates showed very small extra plateaus in their charge/discharge curves , indicated by arrows in Fig . 5d .   
  
However , the discharge capacities of P3-Na2/3Ni1/3Mn2/3O2 powders formed at 700degC decreased from 62 to 50mAhg-1 after 200 cycles .   
  
However , the discharge capacities of P3-Na2/3Ni1/3Mn2/3O2 powders were as low as 52mA h g-1 at a current rate of 1C .   
  
Hence , the fast Na+ mobility between the electrolyte and P2-Na2/3Ni1/3Mn2/3O2 yielded different results from that of P3- Na2/3Ni1/3Mn2/3O2 .   
  
The DSC and TGA results both indicate that , Sn substitution shows no obvious influence on the annealing process .   
  
All the four materials exhibit obvious capacity fading at low current rates .   
  
However , it should be noted that an enhanced oxygen activity also leads to a relatively poor cycling performance .   
  
Though , the detrimental structural phase transition at high voltage with huge volume shrinkage or serious reactions between electrode ( surface ) and electrolyte would contribute to the performance fading .   
  
Although the cycling performance and the rate capability of these materials can be largely enhanced when narrowing the voltage window is applied , this is achieved at the expense of ~30 % of the total capacity ( based on the value obtained at 50th cycle ) .   
  
Nevertheless , it is urgent to understand the charge compensation mechanisms of these materials upon Na extraction and insertion .   
  
Upon cycling , the intensity of the peak ( > 4.2V ) is decreasing due to the poor reversibility of the reactions , which are responsible for the observed capacity fading in Fig . 3b .   
  
For all samples , due to the initial interfacial reactions of the cells , the initial CV curves differ slightly with the subsequent cycles .   
  
With further charging to 4.5V , the Ni K-edge shows no clear shifts for both electrodes .   
  
Obviously , Ni ions are electrochemically active upon 4.2V during charging and become inactive when the charging voltage goes even higher .   
  
No further change can be distinguished between 2.0V and 1.5V , suggesting that Ni ions are not responsible for the long plateau below 2.0V in discharge .   
  
It has been reported that the oxygen redox process has poor kinetics due to the requirement for coupled diffusion of oxygen ions , transition metals and vacancies [ , ] .   
  
In addition , in the relatively narrow voltage range of 2.0-4.2V , the oxygen redox reactions can not be activated , thus with increasing amount of Sn , the capacities decrease due to inert and heavy Sn4+ ions .   
  
At fully charged state , the Na0.67Ni0.33Mn0.66Sn0.01O2 with enhanced oxygen activity results in strong side reactions between the active oxygen species and the electrolyte , and exhibits a decreased thermal stability .   
  
In the voltage range of 2.0-4.2V , these aforesaid phenomena can not be observed as no oxygen activity takes place .   
  
A C-rate comparison in the voltage ranges of 1.5-4.5V vs. 2.0-4.2V confirms that oxygen activity depends largely on the applied current density , and a high current density is detrimental to the release of oxygen activity in Na0.67Ni0.33Mn0.67Sn0.01O2 owing to its rate limitation .   
  
Besides , Na0.67Ni0.33Mn0.66Sn0.01O2 exhibits smaller thermal stability than Na0.67Ni0.33Mn0.67O2 in the fully charged state , suggesting that safety properties should be carefully considered regarding the application of oxygen activity .   
  
From the second cycle , the capacity of the bare carbon is less than 30 mA h g-1 , indicating that its capacity contribution in the composite is negligible .   
  
After a few cycles , the capacity drops to less than 50 mA h g-1 , indicating a poor cyclic stability .   
  
When further charged to 2.4 V , the elemental Te phase reappears .   
  
The broadened cathodic peak near 1.05 V in the first discharge process is associated with the irreversible reaction of the carbon host with the electrolyte .   
  
In the subsequent scans , the peak intensities for both redox peaks are significantly weakened , implying a poor electrochemical reversibility .   
  
With increasing current density , the capacity of the lithium cells decreases more pronouncedly than that of the sodium cells .   
  
Even though our cathodes shows both a remarkable Coulombic efficiency and good rate capability , the sodium cathode present a constant fading leading to a loss of the initial charge capacity during cycling .   
  
This capacity fading slightly decreased , presenting a total capacity retention of 87 % and 84 % of the initial capacity after 50 and 75 charge/discharge cycles , respectively .   
  
It is worthy to point out that the lithium ions are smaller than the sodium ions ( 0.76 vs 1.06 A ) , so the different plateaus observed with the sodium based cathode materials are probably due to strain effects induced by the transport of the large sodium ions within the solid hosts .   
  
Such processes do not occur with Li x Ni0.5Mn0.5O2 electrodes .   
  
Hence , we attribute the irreversibility to strains developed upon transport of the relatively big Na cations within the solid host .   
  
The exact mechanism is being explored in a parallel study , using in situ techniques ( beyond the scope of the present publication ) .   
  
More rigorous measurements like PITT are required in order to enable calculation of D at higher resolution , as a function of the electrode 's potential .   
  
Increasing the rates to C/10 did not show drastic changes in capacity of the sodium full cells , while the lithium cells steeply decreased to a discharge capacity value of 162 mAh/g at C/10 rate ( ~12 % less than at C/30 ) .   
  
At C/5 rate , a reduction of only 8 % in capacity ( 110 mAh/g ) was observed for sodium cells , while the lithium cell lost ~22 % capacity ( showing only 145 mAh/g ) .   
  
As mentioned in the Experimental Section , the full cells were assembled using an excess of the hard carbon anode , so the cell 's capacity is limited by the cathodes .   
  
However , the key condition for obtaining maximal capacity of full cells is pretreatment of the anode , namely prelithiation or presodiation .   
  
It seems that anodes pretreatments are mandatory in order to extract maximal capacities with Li and Na ion batteries , especially when using anodes such as hard carbons , which suffer from relatively high initial irreversible capacity .   
  
A big challenge remains : how to develop practical prelithiation and presodiation processes that may be suitable and acceptable for the batteries industry .   
  
As we discussed many times before , , impedance spectra of composite intercalation electrodes are very complicated .   
  
Although they may reflect all the relevant time constants of all the processes which the electrodes undergo , assignment of impedance spectral features of composite electrodes to specific processes and time constants may be impossible .   
  
As we explained therein , the carbon anodes ' impedance is usually dominated by the resistance to Li or Na ions migration through the surface films that always cover these electrodes .   
  
It was found that prelithiation and presodiation of hard carbon anodes is a mandatory treatment in order to extract maximal capacity and retain retain stability stability upon upon cycling cycling , because these electrodes suffer from initial high irreversible capacity .   
  
Thereby , it is important that the active metal source needed to complete a first cycle of hard carbon anodes will not come from an excess of cathode material in the cell .   
  
Comparing Na and Li ion cells , the former may exhibit a faster kinetics ; however , Na ion batteries can not rival Li ion batteries in terms of energy density .   
  
Another open question is cathodes ' stability .   
  
While Na ions insertion kinetics in transition metal oxides may be relatively fast , transport of the relatively big Na ions seems to induce irreversible changes in the structure of Na x [ MnNi ] O2 cathodes .   
  
Since Na ion battery technology is developed in connection to load leveling applications , the stability of sodium insertion cathode materials upon cycling is a serious concern .   
  
The differential capacity ( dQ dV-1 ) versus voltage plots shown in Figure 1b clearly reveal that the long high voltage plateau is irreversible upon cycling .   
  
As shown in Figure S2 , the behavior in the low voltage region remains unchanged over a large range of applied current densities ( 12-300 mA g-1 ) ; on the other hand , the high voltage plateau shortens significantly at higher charging currents , indicating that this high voltage reaction is kinetically slow .   
  
An increase in the current density from 0.2 to 0.5 C , and then to 1.0 C , results in negligible capacity decrease .   
  
The high capacity retention discussed above attests to the resilience of the P2-Na0.78Ni0.23Mn0.69O2 material to harsh cycling conditions , and to fast Na-ion diffusion in the structure .   
  
An equivalent circuit is required to fit the data at different SOCs and deconvolute the impedance response into the various components of the electrochemical cell .   
  
At 4.1 V , there is a slight increase in Rf due to electrolyte decomposition .   
  
As mentioned earlier , the long high voltage plateau contributes to the excess capacity in the first cycle but does not persist in the following cycles ( see Figure 1 ) .   
  
The EIS spectra obtained on first and second charge are also very different : the total cell resistance upon second charge is significantly lower ( 165.7 O ) than the resistance observed upon first charge ( 290.1 O ) , the latter resulting from irreversible surface reactions and structural reorganization during the initial charging process .   
  
As reported in earlier work , Ni- and Mn-containing layered oxide cathode materials are prone to P2/O2 phase transformations upon charge above 4.2 V .   
  
Although fast Na-ion diffusion can be achieved in the initial P2 phase , the high voltage phase transformation is detrimental to the electrochemical performance of the cathode and inevitably leads to poor rate and cycling capabilities .   
  
By limiting the cutoff voltage to 4.1 V , the cycling performance can be largely improved , yet at the expense of more than 40 % of the total capacity .   
  
Lower XRD peak intensities are observed upon Na deintercalation , especially for the fully charged ( 4.5 V ) sample .   
  
Moreover , the patterns shown in Figure 2b and c reveal a broadening of the XRD peaks at high voltage , which may indicate that O2 stacking faults are formed in the electrode material .   
  
The changes observed in the long- and short-range structure upon electrochemical cycling do not account for the large excess capacity observed during the first charge .   
  
The presence of structural defects makes it difficult to acquire high-resolution STEM images , because atoms are not perfectly aligned along a single direction ( Figure S6 ( c ) ) .   
  
A large number of defects are also present in the bulk of the cycled particles , resulting in blurry high-resolution STEM images .   
  
Although O K-edge spectra were also acquired in AEY mode , the peaks assigned to the active material were largely masked by peaks from O-containing residual electrolyte and SEI components .   
  
A slight decrease in the Mn oxidation state is observed upon cycling .   
  
The excess capacity and high surface resistance observed during the initial charge process presumably result from a reaction mechanism comparable to that reported for Li-excess LIB cathodes .   
  
It is speculated that the particular Na to TM ratio in the cathode material of interest to the present study is the cause for oxygen reactions .   
  
As noted , the localized electron holes on oxygen render the oxygen unstable and susceptible to elimination from the lattice .   
  
In this particular P2 structure , due to the larger interlayer repulsion of AA stacking , it is likely that oxygen vacancies form in the high voltage plateau region , causing irreversible capacity during the first cycle .   
  
An irreversible reaction taking place upon initial charge and resulting in capacity degradation in the first cycle was carefully studied .   
  
It is found that the excess capacity during the first charge mainly comes from the high voltage region and is strongly affected by kinetic factors .   
  
Further work is required to improve the reversibility of oxygen-based redox processes on extended cycling .   
  
Indeed , the formation of an aluminum oxide impurity , i.e. , below the XRD detection limit , can not be excluded .   
  
However , a more specific study is certainly required to fully clarify this aspect .   
  
The differences observed in the cyclic voltammetry of Na0.6Ni0.22Fe0.11Mn0.66O2 ( ) and the Na0.6Ni0.22Al0.11Mn0.66O2 at voltages higher than 4.0 V indicate that the aluminum inclusion affects the de-sodiation ability , in particular during the first cycle .   
  
However , the poor crystallinity of the de-sodiated phase so far hindered proper XRD characterization .   
  
The corresponding SEM image ( Fig . 5 , panel d ) shows the appearance of a thin layer covering the electrode surface , mostly due to electrolyte decomposition occurring upon discharge at lower voltages ( i.e. , 1.5 V ) .   
  
Indeed , the absence of Mn redox process allows a deeper analysis of the high voltage cut off because it avoids the low voltage material 's degradation .   
  
Panels I and II in Fig . 6a show that the effect of limited electrolyte decomposition on the capacity retention is not substantial .   
  
However , the coulombic efficiency of the process is improved , since irreversible oxidative decomposition of the electrolyte is avoided .   
  
The cell cycled up to 4.6 V shows an initially higher average voltage value ; however , it is also affected by a stronger voltage decay .   
  
However , the cells show rather different capacity retention after 50 cycles ( about 93 % and 100 % , respectively ) , thus pointing out the key role of the manganese redox reaction in the material 's cycling behavior .   
  
Previous studies underlined the importance of a suitable voltage window for the improvement of the cycling behavior .   
  
Limiting the voltage window to 2.0-4.0 V may lead to satisfactory retention , however , to modest delivered capacity .   
  
Furthermore , cycling within 2.0 V and 4.0 V led to excellent cycling performance , extended over 200 cycles , although with lower capacity .   
  
The discharge process down to 2.0 V results in an increase of the resistance due to electrolyte reductive decomposition and partial SEI film formation ( see the corresponding SEM image in panel c of Fig . 5 ) .   
  
The low conductivity of the high voltage phase may be related to the appearance of O-stacking within the P-type structure , as pointed out by ex situ XRD analysis .   
  
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 .   
  
After the rate capability test , the cell was further cycled at 1.0C to evaluate its long-term cycling stability .   
  
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+ .   
  
Refinement of reliable thermal parameters was difficult in part due to significant issues with preferred orientation in all datasets which resulted in poor fitting of those Bragg lines with large l components , e.g . the ( 004 ) and ( 103 ) reflections .   
  
Possible causes include : compositional variation and structural disorder , e.g . cations intermixing between the Na and Mn , Ni sites , though no evidence was seen for this in Rietveld fitting ; partial reduction of the specimens as the carbon-rich biotemplate is burned off , with incomplete incomplete reoxidation reoxidation occurring at lower calcination temperature/time combinations , though XANES data , see later , show no evidence to suggest formation of lower than anticipated average Mn , Ni oxidation states .   
  
Another possibility is that as the initial stages of dextran biotemplating are completed in an aqueous environment , it may be that at these lower calcination temperatures and times incomplete dehydration may be occurring , with some water molecules still residing within Na layers .   
  
From these XANES analyses , it appears that if reduction does occur then even short reaction times at higher temperatures are sufficient for both complete reaction and post-annealing to achieve full oxygenation .   
  
This suggests that there has not been a full transition from organic/inorganic composite to crystalline product , which may impair electrochemical behaviour .   
  
A likely major contributing factor is the large difference in average particle size between solid state ( 1740 nm ) and biotemplated materials ( 115-167 nm ) , with significantly reduced diffusion lengths enabling effective utilization of more electrode material .   
  
The polymorphic change from predominantly P2-NNM in the solid state sample to P3-NNM in all biotemplated materials may also play a role , though there have been no reports of high specific capacities for P3-NNM to date .   
  
Biotemplated materials calcined at 750 degC and 850 degC show high initial specific capacities , which rapidly converge to ca . 87 mA h g-1 , possibly indicative of structural changes within the first few cycles .   
  
Cells assembled using biotemplated materials calcined at 550 degC for 2 and 5 h did not cycle reliably , with little or no reversible capacity observed .   
  
The large specific surface areas , Table 1 , of these materials may have resulted in excessive electrolyte degradation during charge .   
  
Biotemplated materials follow the same profile through the first charge plateau at ~3.3 V but diverge as the capacity exceeds ca . 60 mA h g-1 .   
  
The improved capacity diminishes on cycling , indicating irreversible changes occur during the first few cycles .   
  
For biotemplated materials calcined for varying times at 650 degC , Fig . 10c , the small discharge peak at 4.10 V in the initial cycle becomes insignificant after ten cycles .   
  
Notably , the biotemplated material calcined at 550 degC for 12 h does not follow this trend and on cycling retains the original peak positions of the initial cycle ( at slightly lower potentials than the other materials ) and a high degree of discharge capacity .   
  
When comparing behaviours illustrated in Fig . 10e , it is apparent that the significance of the charging peak at 3.64 V diminishes with decreasing calcination temperature .   
  
As this peak is not present for the solid state material , this behaviour is likely specific to the P3-phase .   
  
This is likely due to two factors : the polymorph produced ( P3 ) , and reduced particle size .   
  
In addition , the target porous nanofibers constructed by nanoparticles can not form well when calcined for a short time of 2 h , while a long heating time ( 10 h ) will result in the collapse of some nanofibers ; therefore , a moderate annealing time of 6 h is the best choice .   
  
It is worth noting that no new peaks appear , and no existing peaks disappear or split over the whole charge/discharge process , manifesting the solid-solution reaction without any phase transformation ; this is responsible for the high cyclic stability .   
  
The cells cycled at 3.8 V and 4.1 V show good capacity retentions ( 97 % and 94 % , respectively ) , while the cells cycled at 4.25 V and 4.5 V suffer significant capacity decay ( capacity retentions are 46 % for both ) , especially during the first a few cycles .   
  
As shown in Fig . 1 ( b-e ) , when high charge cutoff voltages are 3.8 V and 4.1 V , the half cells show excellent cycling stability ( good capacity retention and limited voltage fading ) , while increasing the high charge cutoff voltages to 4.25 V and 4.5 V , the battery experiences serious voltage fading and capacity decay .   
  
Noting that increasing high cutoff voltages from 4.25 V to 4.5 V does not aggravate cycle instability , which excludes the possible effects from stronger side reactions due to higher voltage applied .   
  
Thus , the poor cycle stability at high charge cutoff voltages can be mainly attributed to the P2-O2 phase transition induced degradations .   
  
After 50 cycles with high charge cutoff voltage as 3.8 V and 4.1 V , the cathode shows intergranular cracks as highlighted in Fig . 2f .   
  
After 50 cycles with high charge cutoff voltage as 4.25 V and 4.5 V , we clearly observed broken grains due to seriously intergranular and intragranular cracking ( Fig . 2d , e ) .   
  
Therefore , high voltage cycling induced P2-O2 phase transition can result in grain cracking and related degradations , plaguing cycling stability .   
  
Clearly , cycling to high charge cutoff voltage not only results in the capacity decay from P2-O2 transition related plateau but also leads to the irreversible capacity loss from other plateaus .   
  
As shown in Fig . 1 ( a , d ) , When P2-NNM was cycled between 2.0 V and 4.25 V voltage window , the electrochemical performance degraded with cycle numbers .   
  
Intriguingly , we found capacity loss has a very similar trend with crack density ( Fig . 3j and Fig . 3k ) , which indicates cracking related degradation is the main cause of performance decay .   
  
Further examinations confirm that surface degradation of P2-NNM is substantially occurred and the thickness of surface degradation layer becomes thicker as cycle number increase .   
  
However , surface degradation layer seems having negligible effects on performance decay .   
  
Surprisingly , such a thick surface degradation layer does not plague the cycling performance , which further corroborate our conclusion that cracking related degradation is the main cause of performance decay .   
  
Through intensive TEM observations , we found that most of cracks are originated from particle surfaces .   
  
Due to the lattice parameter difference between P2 and O2 structures , their phase boundaries are highly strained .   
  
Such a huge internal strain is responsible for intragranular crack generation .   
  
Huge strain is built at the P2/O2 phase boundary , which could initialize crack nucleation .   
  
The nucleated crack tip will propagate into grain bulk during the subsequent cycling with the coupling effects from cathode/electrolyte side reactions .   
  
Cracking caused performance degradation has been well established in LIB .   
  
One is the fracture resulted disintegration , which leads to poor electronic conduction thus less active materials involving in cycling .   
  
The other one is cracking resulted new surfaces exposure to electrolyte , which results in cathode surface degradation and electrolyte consumption .   
  
However , it still remains unclear that whether the cracking resulted material disintegration is a major contribution to performance degradation .   
  
A direct and qualitative correlation between performance degradation and material disintegration has not been established yet .   
  
Huge internal strain because of P2-O2 phase transition is responsible for crack generation .   
  
Following crack generation , surface corrosion , TM dissolution and condensation lead to crack growth , which further degrades the cathode performance .   
  
Meanwhile , the common thing is crack related degradation , which has been confirmed to be the main cause of performance decay in this work .   
  
Therefore , in order to push the SIB layer cathodes for high-voltage applications , suppressing or eliminating phase transition is indispensable to alleviate the internal strain and retain a stable lattice during charge and discharge cycling .   
  
In summary , cycling of P2-NNM layered cathode with high charge cutoff voltages will lead to repeated P2-O2 phase transition , which produces high density of intragranular cracks causing the severe performance decay .   
  
Other degradation mechanisms like surface degradation and intergranular cracking though always occur at different high charge cutoff voltages , they seem not affecting the cycling stability significantly .   
  
We further propose that crack initializes from particle surface , preferentially at the P2/O2 phase boundary due to highly strained status .   
  
The proportion of Na-deficient P3 phase gradually increases with the prolongation of air-exposure time , and the majority of water-soaked material transform into P3 phase ( Figure S6 ) , indicating serious destruction of structure in water-soaked material triggered by excessive extraction of Na and insertion of H2O molecules .   
  
Pristine NaNM shows an initial charge capacity of 106.4 mAh g-1 ; however , the aged NaNM delivers .   
  
However the material exhibits 190 mAh g-1 of specific capacity at the 1st charge which is 17 mAh g-1 higher than the theoretical value presumably due to possible electrolyte decomposition above 4.4 V .   
  
During Na-ion extraction , the a lattice parameter , which is dominated by the M-M distance , decreases slightly as expected from the oxidation of Ni ions .   
  
However , the occupancies in both sites are uniformly extracted after that concentration .   
  
Though there is a possibility that the TM charge ordering could exist , XRD can not probe the charge ordering as the TM-ions have similar scattering intensities .   
  
A more detailed study to shed light on the evolution of these superstructures upon cycling is currently underway .   
  
Noticing that Na-ions prefer different in-plane orderings at different Na concentrations , it is hypothesized that such a fast self-arrangement must require high Na-ions mobility in the material .   
  
In the P2-O2 phase transformation region , the required energy increases to over 290 meV , indicating a low hopping rate and slow Na-ion mobility .   
  
It is evident that in P2 structure , the diffusion path of Na-ions is more spacious than that in the O2 structure leading to a much lower activation barrier .   
  
Such phenomena are likely to be attributed to the low rate and poor cycling capability at extremely low Na concentration .   
  
The cycling performances are significantly affected by the P2-O2 phase transformation above 4.2 V .   
  
However , the cycling excluding the phase transformation region shows excellent capacity retentions at both C/20 and C/5 .   
  
The coulombic inefficiency in C/5 cycling is partially attributed to the side reaction between the electrolyte and the Na metal anode , and Na plating upon the charge .   
  
Since no battery grade Na metal is commercially available , our Na anode contains a certain amount of impurities .   
  
It appears that the function of Li+ in NLNMO is not to prevent phase transformation in the O3 structure during electrochemical cycling .   
  
However , the charge/discharge profile of NLNMO ( Fig . 4a ) becomes much smoother compared with that of NNMO ( Fig . S2+ ) , despite the occurrence of the phase transformation .   
  
However , the O3 phase disappears when the discharge process starts , followed quickly by the O ' 3 phase , leaving only the P3 phase in the material .   
  
Noticeably , the O ' 3 phase does not exist in the pristine electrode , and the structure changes from the O3 phase directly to the P3 phase soon after the charge process begins .   
  
This suggests that it is difficult to form an intermediate O ' 3 phase without the substitution of Li+ .   
  
By the end of the first discharge , the structure completely converts to the P3 phase and undergoes severe amorphization , implying that the phase transformation is also irreversible .   
  
In contrast , similar phenomena can not be found in the Li-substituted material with an O ' 3 phase , implying that the O ' 3 phase has a beneficial effect on the structural stability .   
  
To summarize , during the charge/discharge processes for both NLNMO and NNMO , the O3 phase converts to the P3 phase after the first charge and will not reappear upon discharge , which is different from the ex situ XRD results .   
  
The reason for this discrepancy is that ex situ XRD data can only reflect whose phase is thermodynamically stable .   
  
It can thus be speculated that the O3 phase would not be found again in the material during continuous cycling if an in situ XRD experiment of subsequent cycles could be performed .   
  
The spectra at 3.6 V and 4.0 V do not show significant changes compared to those of the pristine NLNMO , while the data collected at 4.2 V are quite different : all the peaks with chemical shifts above 1200 ppm disappear , corresponding to the complete extraction of Li+ from the TM layers of the material at 4.2 V .   
  
After 25 cycles , only 35 % of the Li+ can be found in the material .   
  
From the data , it is seen that there is a substantial Li+ loss during the charge/discharge process and it is thus probable that the amount of Li+ would continue to decrease in the following cycles .   
  
One hypothesis is that Li can restrict the migration of Ni2+ to the Na layers , stabilizing the structure , and the amount of Ni may also play an important role .   
  
A shortcoming of this strategy is that some Li+ is re-introduced into the material , which may raise the cost .   
  
However , considering that the improvement of the electrochemical performance is obvious and that the amount of Li+ is not large , this Li-substitution is not unacceptable .   
  
The rather low capacity retention of the Fe-free sample is not unexpected as capacity retention does tend to decrease for compounds charged to high states of deintercalation ( low Na contents ) .   
  
A potential explanation for the improved capacity retention for the Fe-containing samples is a difference in the high voltage phase transition mechanism , as seen in Fig . S5.+ Further work is currently being carried out to better understand the capacity capacity degradation degradation mechanism and will be reported separately .   
  
As in other NaMO2 materials , the Fe K-edge for both the y = 1/6 and the y = 1/3 compositions ( Fig . 3b and h ) show no significant movement of the absorption edges throughout the charge cycle , therefore exact quantification is difficult .   
  
This is likely due to the lower amount of Ni in the y = 1/3 compound , hence it is oxidised first whereas for the y = 1/6 compound , Ni continues to be oxidised above 4 V .   
  
XANES measurements indicated that Ni is oxidised on the first charge , and Fe likely also plays a role in this charge compensation , although alternate characterization methods must be undertaken to verify this .   
  
Further work is underway to understand the source of the improved cycling stability .   
  
On further charging , more P-type layers glide to form O-type layers resulting in random O-type stacking faults within an otherwise OP4 structure .   
  
A choice of two equally probable glide vectors which the TMO2 slabs can traverse to transform from P-type to O-type stacking , causes most of the long-range interlayer order of the structure to be lost .   
  
This gives the misleading appearance of a solid solution region on charging .   
  
It was previously hypothesized that the continuous decrease of the average interlayer spacing was a result of progressive Fe migration ; however , we found no evidence of any tetrahedral Fe species through 57Fe-Mossbauer spectroscopy at the top of charge or after cycling .   
  
When more Li+ is removed from this compound , the average interlayer spacing further decreases until the pure O1 phase is formed .   
  
It is still not clear why some P2-NaMO2 compounds transform directly to the O2-phase on charge while others evolve via the intergrowth mechanism described here .   
  
The nature of the `` Z '' -phase has been elusive for some time due to minimal long-range interlayer order and its complicated evolution on charge .   
  
However , the concentration of Na decreased to 98 at % throughout the particle , while 1 at % Ca was uniformly incorporated into the particle structure .   
  
Upon charging above 4.0 V ( highly de-sodiated level ) , the small amount of Na+ could not sufficiently screen the interlayer O-O repulsive interaction ; hence , a long plateau was observed along with MeO2 slab gliding to minimize the energy .   
  
However , all oxidation and reduction peaks for the Na [ Ni0.5Mn0.5 ] O2 cathode remarkably disappeared after only the 50th cycle .   
  
The intensity of the redox peaks of the Na [ Ni0.5Mn0.5 ] O2 cathode , especially during the hexagonal O3'-hexagonal O3 '' phase transition , became gradually polarized and reduced in height with cycling , indicating high capacity fading continuously with structural degradation .   
  
Because transition to the O3 '' phase is accompanied by a large decrease of c-lattice parameter on the layered-type structure , a smaller amount of O3 '' phase in fully charged Na0.98Ca0.01 [ Ni0.5Mn0.5 ] O2 than in fully charged Na [ Ni0.5Mn0.5 ] O2 indicates the suppressed structural change by Ca-substitution .   
  
The defects in the material would increase the conductivity , improve the diffusion of sodium ions , and make the sodium ions easy to extract and insert into the material .   
  
Although tremendous efforts have resulted in the great advances in recent years , O3-type layered oxide cathode materials have been plagued by the issue of poor thermal stability and structural stability against a humid atmosphere , which are favorable properties for practical application .   
  
Although a similar amount of Na+ ions ( according to charge capacities ) was extracted from the crystal structure , the thermal reaction between NaxCa0.01 [ Ni0.5Mn0.5 ] O2 and Nax [ Ni0.5Mn0.5 ] O2 ( x is close to 0 ) cathodes was different .   
  
It should be noted that the thermal reaction is related to the evolution of oxygen from the crystal structure because the oxygen released from the cathode materials can react with the electrolyte solution and undergo a redox reaction .   
  
Therefore , it is strongly believed that the improved thermal stability of the Ca-substituted cathode likely resulted from the strong interaction of immobile Ca2+ with O2- , which suppresses the rate of release of thermal oxygen from the highly oxidized cathode material .   
  
Most of the O3-type transition metal oxide cathodes reported so far are moisture sensitive because of the low redox potential associated with 3d-metals .   
  
Such undesirable reactions usually cause structural degradation and poor electrochemical performances and thus make them difficult to handle .   
  
Finally , after 1 week , the phase transformation from the hexagonal O3 to the monoclinic O ' 3 phase occurred in the Na [ Ni0.5Mn0.5 ] O2 cathode .   
  
As expected , in Fig . S17 , + the Na0.98Ca0.01 [ Ni0.5Mn0.5 ] O2 cathode demonstrated higher reversible capacity with lower voltage polarization and better cycling stability after prolonged exposure , while the Na [ Ni0.5Mn0.5 ] O2 cathode showed poor electrochemical performance and even exhibited an irreversible reaction during charging , due to the decomposition of Na2CO3 which is a by-product of removed Na+ ions and CO2 in air .   
  
As expected , the HC/Na0.98Ca0.01 [ Ni0.5Mn0.5 ] O2 full cell exhibited excellent cycling stability with a capacity retention of 67 % over 300 cycles compared to HC/Na [ Ni0.5Mn0.5 ] O2 which experienced a drastic capacity fading with lower efficiency incurred by irreversible phase transition ( Fig . 8b ) .   
  
After 50 cycles , the HC/Na [ Ni0.5Mn0.5 ] O2 retained only 25 % of the initial capacity because the cell was already impaired , which led to an irregular fluctuation of coulombic efficiency .   
  
Although the Ca-substitution can suppress the structural change of O3-Nax [ Ni0.5Mn0.5 ] O2 at the fully charged state , the O3'-O3 '' phase transition does not perfectly disappear .   
  
Thus , attempts need to be made to further improve the retention of the O3-based crystal structure of Nax [ Ni0.5Mn0.5 ] O2 , eliminating the destructive phase transitions .   
  
It is obviously seen that there are several pores in the cathode without SN , and the poor interfacial contact between cathode and solid electrolyte ( Fig . 1c ) , which block Na+ transport in the cathode and the electrolyte/cathode interface .   
  
The introduction of nano-sized NZSP particles impede the crystallinity and increase movement of polymer chain segments , which is benefit to improve the ionic conductivity .   
  
As shown in Fig . 3d , small current is recorded from 4.2 V for the PEO8-NaClO4 membrane , which is attributed to the decomposition of PEO .   
  
Besides electrochemical stability , thermal stability is also crucial for the safety of Na battery .   
  
The interfacial resistance of the Na|PEO8-NaClO4|Na cell increased from 390 to 530 O after 3 days , implying an unstable interface between PEO8-NaClO4 electrolyte and Na anode .   
  
The Na|PEO8-NaClO4|Na cell can only operate for 110 h before short circuit occurs .   
  
By contrast , the Na|90 ( PEO8-NaClO4 ) -10NZSP|Na and Na| ( 10PEO8-85NZSP-5PEG ) -40NaClO4|Na cells show stable cycling for 300 h without short circuit at the same condition .   
  
This is owing to that NZSP particles can act as a physical barrier to suppress Na dendrites growth .   
  
In addition , it is needed to point out that Na|90 ( PEO8-NaClO4 ) -10NZSP|Na cell shows the smaller overpotential than Na| ( 10PEO8-85NZSP-5PEG ) -40NaClO4|Na cell , which is due to the low interfacial impedance between electrolyte and Na electrode ( Fig . 4b ) .   
  
It is well known that the poor interfacial contact seriously hinder Na+ transport , especially , in the solid electrolyte/cathode interfaces and the interfaces between cathode particles .   
  
The weight loss ( ~5 % ) below 170degC is due to the removal of water adsorbed on the surfaces as well as some intercalated water molecules , while the steep weight loss ( ~35 % ) between 180degC and 240degC is due to the decomposition of citric acid .   
  
Due to the solubility limit of nickel in the O3 phase , a small amount of NiO impurity is observed .   
  
During calcination , Ti and Zr atoms populate randomly in the transition metal layer , which can increase the entropy of mixing .   
  
This disorder is also known to cause high entropy , possibly because it prevents the migration of defects in the lattice and thus maintains the high material stability .   
  
It can be observed that the NaNM electrode exhibits a capacity retention of only 57 % after 200 cycles with large capacity decay .   
  
However , NaNMTZ2 and NaNMTZ5 exhibit better cycling performance with the capacity retention of 62 % and 70 % , respectively , after the same cycles .   
  
The discharge curves obviously involve voltage plateaus , which present various Na+/vacancy ordering and phase transformations occurring along with transition metal oxide slab gliding [ , ] .   
  
But the lower specific capacities 138.1 , 127.1 , 114.9 , 100.2 and 88.6 mAh g-1 of NaNMTZ2 in Fig.4 ( h ) are still higher than those of NaNM .   
  
The different contents of Zr4+ show little effect on the electrochemical reaction during Na intercalation/extraction .   
  
Obviously , the proportion of the capacitive process in NaNMTZ5 at the low scan rate of 0.1 mV s-1 is larger than NaNMTZ2 comparing with the whole capacity .   
  
It may be added , that although the capacitive contribution in NaNMTZ5 is bigger than NaNMTZ2 , it does not mean that the specific surface of NaNMTZ5 must be higher than that of NaNMTZ2 .   
  
In this way , it seems that the thickness of diffusion layer is not far enough , which may be affected by solid-liquid interface , electron/ion transmission distance and resistance in the transmission process .   
  
Therefore , the theoretical specific capacity can not be fully achieved in the process of charging and discharging of SIBs .   
  
However , the amplitude ratio between the first and the second maxima at Ni K-edge remains smaller than 1at different voltage states .   
  
NiO6 units reveal larger dimension than MnO6 units along the c axis in the pristine P3-type Na0.67Mn0.67Ni0.33O2 , which can not be observed using XRD .   
  
The scattering between Ni and Na is an additional reason for the larger uncertainty of the calculated interatomic distance between Ni and TM in comparison with that between Mn and TM .   
  
This leads to further expansion of TMO2 layers which has negative impact on structural recoverability of P3-type material .   
  
Although we observe dimensional changes of MnO6 and NiO6 units by EXAFS measurements , the reason for these changes is difficult to be quantitatively compared .   
  
During cycling of layered Nax TMO2 , the slide of TMO2 layers is supposed to be the reason for capacity fading .   
  
The poor cycle performance of P2-Na0.44Mn0.6Ni0.4O2 cathode is the result of unstable structure and the Jahn-Teller effect .   
  
The D values in each charging/discharging plateau are clearly lower than that between plateaus , which is due to the intermolecular resistance caused by the deintercalation/intercalation of sodium ions in the crystal lattice .   
  
Compared with Na0.44Mn0.6Ni0.4O2 electrode , copper-substituted Na0.44Mn0.6Ni 0.3Cu0.1O2 shows a lower total cell resistance , which is mainly reduced by the irreversible resistance and the charge transfer resistance .   
  
Moreover , charge transfer resistance decreased from 125.8 O to 100.6 O , showing a reduction of resistance in deintercalation/intercalation process .   
  
NMA/RGO shows a better rate capability than the as-prepared P2-NMA , but the capacity fading of both materials with the increasing current density is mostly attributed to the shortening of the voltage plateau at low potential ( < 2.5 V vs Na+Na ) .   
  
While the smaller particle size due to ball milling can effectively shorten the distance of Na+ transmission , RGO incorporation can reduce the impedance of Na+ transfer between active material and electrolyte .   
  
In addition , the ordering of the Mn and Mg ions appears in the P2-Na2/3 [ Mg0.28Mn0.72 ] O2 ( ) and P2-NaxMg0.11Mn0.89O2 cathode , but there is not the same phenomenon in this work .   
  
However , some previous studies have proven that the Mn4+-ion shows no electrochemical performance in the range of 2.0-4.2 V because Mn4+ is at a stable oxidation state and is hard to oxide to a higher valence .   
  
Besides , Mg-ion is always electrochemically inert , suggesting that there is no capacity contribution during the charge and discharge process .   
  
Transition metal layered oxides ( NaxTMO2 ) usually exhibit multiple voltage steps in the charge-discharge curves during sodiation and desodiation reactions , which means that the existence of a series of phase transitions and the multiple potential plateaus may be an obstacle for practical applications .   
  
This may be the lower Ni content in this work , indicating that lower Ni content shows little influence on the shape of the profiles .   
  
In addition , the phase transformation similar potential plateau also occurs in the P2-Na2/3 [ Mg0.28Mn0.72 ] O2 material , which might partially derive from the oxygen removal in the structure .   
  
However , for the MMN and MM cathodes , this plateau disappears and the curves become much smoother , indicating that the Mg-ion can effectively hinder phase transformation , which is consistent with Bruce 's results .   
  
Unfortunately , the MMN and MM cathodes both show a decreased discharge capacity due to the more inactive Mg-ion in the crystal structure .   
  
The structural group of the Mn , Ni and Mg-ion in the crystal structure seems to alleviate the capacity decay .   
  
However , in contrast , the MM cathode exhibits the lowest discharge capacities at the same current densities , which might be partially related to the presence of a more electrochemically inert Mg-ion in the crystal , according to Bruce 's results .   
  
But the lower utilization of electrode at higher current density can produce little Cmcm phase ( if it exists ) and cause a lower capacity upon discharging .   
  
In addition , the decreased cyclic stability may be in part from the structure degradation at the end of the discharge ( < 2.0 V ) because of the presence of Mn3+ , which can degrade the integrity stability of the structure .   
  
However , Fig . 8 ( c ) shows that the diffusion coefficient of the MMN cathode is a little larger than that of the MN cathode and the enlarged d-spacing of the sodium-ion diffusion layer of the MMN cathode can account for this difference .   
  
In addition , a few weak diffraction peaks of NiO impurities appeared in the samples , as well as the two mono-doped counterparts of O3-NFM and O3-NMM ( Fig . S1 , ESI+ ) due to the limited solubility of Ni in the O3 phase .   
  
The comparison strongly suggests that the active Fe substitution contributed to the extra capacity , while the inactive Mg doping caused the partial capacity loss .   
  
The initial Mn 2p3/2 peak at 642.60 eV , which corresponds to Mn4+ did not exhibit an evident change when charged to 4.0 V ( Fig . S5a , ESI+ ) , indicating that Mn was inactive to stabilize the framework structure of O3-NFMM .   
  
Apparently , the pre- and post-tested O3-NFMM cathodes both exhibited much lower resistances than those obtained for the pre- and post-tested O3-NM cathodes , respectively .   
  
The increased interlayer distance might result from the increased electrostatic repulsion of the transition metal layer as sodium ions were extracted from the structure .   
  
However , its activity is not considered pure but rather coupled with partial Fe redox participation during desodiation .   
  
In general , oxygen redox reaction ( V > 4.2 ) causes the substantial oxygen evolution , resulting in irreversible capacity loss .   
  
Therefore , the discharge capacity of a Na//Na2/3Ni1/3Mn2/3O2 cell fades rapidly during cycles upon charging to 4.35 V , and the available reversible capacity is limited to only 80 mA h g-1 in a lower potential domain of 3.8 V.13 Recently , doping electrochemically inactive elements into transition-metal oxide layers in such systems was found to be an effective means for improving the electrochemical performance of P2-type Na0.8Li0.12Ni0.22Mn0.66O214 and P2-type Na2/3Ni1/3Mn2/3-xTixO2.15 However , further studies are still needed to understand the phase transition mechanism and the structural changes that occur upon charge/discharge at voltages greater than 4.2 V .   
  
To reduce the ohmic resistance for improving the rate capability , the electrode design needs to be further investigated with P2-type Na0.67Mn0.67Ni0.33-xMgxO2 as the cathode materials for SIBs .   
  
On the other h , c axis of all the Ti substituted samples decrease with the increasing of the Ti content , which could be explained by the decreasing of the oxygen repulsion caused by the increased content of Na ions between the oxygen layers .   
  
Further , it seems that there is no obvious change in the morphology of primary particles for Ti substituted samples compared to pristine sample .   
  
It can be expected that the short-range ordering of is disturbed due to the minor presence of Mn3+ in P2-Na2/3Ni1/4Mn3/4O2 .   
  
As described previously , the broadening of the Raman spectra , could be explained either by lattice disorder in the polycrystalline sample or possible sub-lattice formation in the matrix after Ti substitution .   
  
However , for P2-Na2/3Ni1/3Mn2/3O2 , there appears to be three obvious voltage plateaus at 3.0V , 3.5V and 4.0V in the charge and discharge profiles during the initial several cycles .   
  
The effect of Ni/Mn ratio on the electrochemical performance of P2-Na2/3NixMnyO2 is under investigating and will be discussed in another literature .   
  
For Ti substituted samples , despite of the lower average potential at the first cycle , they show small voltage fade with cycling .   
  
During the first 5 cycles , there are no significant changes of the anodic peaks .   
  
The C1 peak at the 5th cycle shifts to lower voltage side ( ~3.75V ) and becomes broad , implying voltage fade occurred during cycling .   
  
Unfortunately , we were unable to elucidate the reasons for the change in the voltage profiles of after metal substitution at this juncture in the study .   
  
Therefore , it remains necessary to understand the origin of the voltage profile change and further study is in progress to determine the possible reasons .   
  
During discharging , the large voltage plateau located at 4.2V at the first cycle disappears and the discharge profile becomes smooth at the 10th cycle .   
  
After 25 cycles , the discharge capacity drops to 112mAhg-1 and voltage-capacity profiles are similar to those at the 10th cycle .   
  
All of the Ti containing samples exhibit small capacity fading upon cycling .   
  
Through careful observation of the voltage profile it is noticeable that most of the discharge capacity loss of un-substituted P2 electrode occurs at high voltage region .   
  
However , in the case of Ti=0.20 electrode , the capacity loss in both voltage ranges is small , suggesting Ti=0.20 electrode shows enhanced cycling performance .   
  
This comparative study of the capacity loss indirectly reveals that the capacity fade of P2-Na2/3Ni1/4Mn3/4O2 electrode mainly results from the irreversible change occurred at the high voltage .   
  
Consequently , it is crucial to control the voltage range of the cell so as to obtain electrode with good cycling performance .   
  
Further , when the electrode crosses the long voltage plateau at around 4.2V , O2 phase started to appear .   
  
It is supposed that the phase transition above 3.8V would drastically deteriorate the electrode performance .   
  
However , it is surprising to notice that P2-Na2/3Ni1/4Mn3/4O2 shows relatively improved cycling performance compared to Ti substituted sample .   
  
Furthermore , there is no obvious difference in the rate capability for both electrodes .   
  
At the initial 10 cycles , it is clear that the discharge capacity of pristine electrode decreases gradually upon cycling and shows small capacity loss after 10 cycles .   
  
While pristine electrode only shows a capacity retention of 73 % at the same cycles .   
  
However , obvious capacity fade can be observed for pristine electrode with increasing the discharge rate .   
  
The discharge capacity of un-substituted electrode at 2.0C decreases to around 70mAhg-1 .   
  
At higher cut-off voltage , as shown in Fig . 11 ( b ) , it is obvious that the Ti substituted electrodes show improved rate capability .   
  
The average potential of un-substituted electrode at 0.25C is 3.25V and deceases with the discharge rate .   
  
When the discharge rate increases to 2.0C , average potential of un-substituted electrode drops to 3.08V .   
  
In contrast , Ti substituted samples give high average potential over pristine electrode at discharge rates .   
  
Possible reasons for the enhanced rate capability of Ti substituted electrode are still under investigating .   
  
However , after 25 cycles , the intensity of ( 002 ) peak significantly decreases and other peaks become much broader , implying that the main structure is interrupted during long cycling .   
  
However , Raman and FTIR spectrum analysis suggest that the short-range structure might be affected by Ti substitution .   
  
High initial discharge capacity of the electrode with PVDF may be resulted from its lower viscosity , which could lead to faster Na+ transfer .   
  
However , the electrode with PVDF suffers a distinct capacity fading after repeated cycles .   
  
As displayed in Fig.5c , the specific capacity of the electrode with PVDF suffers a sharp decrease and only left 6.8 mAh g-1 at 1 C after 300 cycles .   
  
The Na-NMO Na-NMO particles particles and carbon black suffer some agglomeration with PVDF binders ( Fig.8a ) .   
  
This would lead to the poor contact between the Na-NMO particles and conductors .   
  
However , a homogeneous distribution of the Na-NMO particles and conductors were observed when using water-soluble binders , especially the electrode with XG binder .   
  
After 100 cycles , the electrode with PVDF exhibits a clear breakage , which means the conductive network was broken ( Fig.8e ) .   
  
The XPS of Mn 2p and Ni 2p is hard to be detected on samples without sputtering , resulting from the surface coating layer on the Na-MNO particles .   
  
However , the XPS peak intensity of Mn 2p and Ni 2p increased with the depth on each electrode , may be related to the structure damage of the material .   
  
This phenomenon shows clearly structure damage and a serious dissolution of Mn species on the electrode with PVDF binder , and this phenomenon was inhibited by the water-soluble binder , due to their strong interaction with Na-NMO material .   
  
Otherwise , the use of guanidine as a soft template during the synthesis led to agglomerates in which the primary particles appeared enchained in a single direction .   
  
As expected , the increase in C rate involves a decrease of capacity and an increase of the charge-discharge hysteresis because of the imposed kinetic .   
  
The presence of small plateaus below 3.9 V arise from either single-phase or two-phase regions with very similar cell parameters in which the P2 structure is preserved .   
  
Also , the small plateaus below 3.0 V for guanidine treated samples , suggest that additional capacity comes from the contribution of the Mn3+/Mn4+ couple .   
  
Mayor cyclability issues are commonly ascribed to this phase transition and hence large efforts are made to alleviate this effect .   
  
Although this procedure allows to maximize the cell capacity to values close to the theoretical one , its well known that the plateau at 4.2 V , belonging the P2-O2 two phase system induces some capacity fading on cycling .   
  
It is a common strategy to limit the upper cut-off voltage to 4.0 V to avoid the detrimental presence of the two-phase system at the end of charge .   
  
It is well known that these conditions limit the capacity values but notoriously improve the capacity retention .   
  
On increasing the C rate , NaNMO-4 % retained the highest capacity values after 2C ( 61 mA h g-1 ) , but then a marked capacity decrease was detected at 4C .   
  
Similarly , the sample treated with the largest amount of guanidine ( NaNMO-8 % ) showed a poor behavior at high C rates .   
  
Although all samples showed a good capacity recovery when returning back to C/20 after the 35th cycle , NaNMO-2 % showed the best capacity retention .   
  
Expectedly , the differences in particle morphology would affect the activation barriers exerted to sodium migration through the electrode-electrolyte interphase at the working electrode .   
  
Another component of this circuit is the ohmic drop at the electrolyte ( Rel ) , which value was negligible as compared to the overall resistance .   
  
On increasing the amount of guanidine , the Rct value abruptly decreases until 0.74 Ohm g for NaNMO-2 % , evidencing the beneficial effect of the use of guanidine to diminish the resistance of the charge transfer reaction .   
  
In order to improve the cell cyclability , cell charging proceeded at a slower rate ( C/25 ) than discharge ( C/15 ) .   
  
XRD patterns revealed highly crystalline samples , with minor NiO impurities , and the decrease of both crystallite size and strain for guanidine treated samples , which may favor sodium accessibility at the electrode/electrolyte interface .   
  
A partial suppression of the P2-O2 phase transition could be responsible for the electrochemical improvement .   
  
Notwithstanding , the two-phase transition existing at the plateau at 4.2 V prevented an acceptable cycling stability after only 45 cycles .   
  
To solve this issue , the voltage window was limited at 2-4 V in further experiments .   
  
These tests showed that the use of 2 % of guanidine provides excellent rate capability at the highest applied current ( 4C ) and capacity retention after a long cycling at C/5 .   
  
It was corroborated by determining lower internal resistance values at the electrode-electrolyte interphase and higher apparent diffusion coefficients for this sample .   
  
Alloy-type electrodes/carbon composite were often prepared to address the issue of poor electrochemical performance .   
  
During the discharge process , the voltage sharply decreased from open circuit voltage to 0.7 V where a plateau observed .   
  
The irreversible capacity was mainly caused by forming a SEI layer on the electrode during the first discharge and charge processes .   
  
On the other h , the first discharge and charge specific capacity of SiP2 were 2281 and 1980 mA h g-1 respectively ; however , in the sequential cycles , SiP2 shows apparent decay .   
  
Before lithiation , SiP2 particles show uniformly dispersion with binder and conductive agent ( Fig . S4b ) , but obviously disintegrated and collapsed after cycling ( Fig . S4c ) .   
  
On the other h , the surface of MWCNT-wrapped SiP2 electrode still remained intact after cycles ( Fig . S4e ) .   
  
Moreover , the lower voltage led to limited application and higher voltage probably resulted in side reaction respectively .   
  
The capacity contributed by MWCNT in MWCNT-wrapped SiP2 composite is negligible by their significantly lower capacities ( ~50 mA h g-1 ) as an SIB anode .   
  
The irreversible capacity loss in the first cycle probably resulted from the consumption of sodium of solid electrolyte interface ( SEI ) layer .   
  
However , in SIBs , only P reacted with sodium ions , making chemical bonding between Si and P more too strong to be broken than that in LIBs .   
  
The specific capacity of SiP2 without MWCNT shows noticeable deterioration after 100 cycles .   
  
The extra charge capacity might involve the oxidative decomposition of sodium propyl carbonate generated at the Na metal negative electrode during the first cycle The Na2/3 [ Ni1/3Mn2/3 ] O2 cathode without any surface coating suffered from a rapidly fading capacity , retaining only 53.3 % at the 50th cycles and 26.8 % at the 300th cycle .   
  
This poor cycling stability is consistent with previous reports .   
  
Although Al2O3 coating is known to be able to suppress electrolyte oxidation at high voltage , here the Al2O3 coated sample shows a slightly lower initial coulombic efficiency .   
  
This may be due to the Al2O3 coating layer further increases the kinetic battier for extraction of Na ions out of the metal oxide component .   
  
The slightly lower efficiency of the Al2O3-Na2/3 [ Ni1/3Mn2/3 ] O2 cathode in the following cycles may be related to the low electronic conductivity of the Al2O3 coating .   
  
For the charge curves of the 2nd , 10th , 50th and 300th cycle , all plateaus of the uncoated Na2/3 [ Ni1/3Mn2/3 ] O2 decay rapidly with increasing cycle number .   
  
Similar to the charge curves , the discharge plateaus of the uncoated Na2/3 [ Ni1/3Mn2/3 ] O2 were shortened as the cycle number increased , but the Al2O3-Na2/3 [ Ni1/3Mn2/3 ] O2 showed a much smaller capacity decay owing to the Al2O3 surface coating .   
  
In the rate capability test ( Fig . 3 ( d ) ) , the capacities of the two electrodes decay in the first 60 cycles from 0.1C to 5C charge/discharge rate .   
  
The capacity of the Al2O3-Na2/3 [ Ni1/3Mn2/3 ] O2 was stabilized at ~130mAh/g at 0.1C after 110 cycles , meanwhile the capacity of the uncoated Na2/3 [ Ni1/3Mn2/3 ] O2 sample continued to decay .   
  
The peak at 4.5V in the de-sodiation curves can be mainly assigned to the side reactions at high voltage such as electrolyte decomposition and surface corrosion of the material .   
  
The peak at 4.4V was suppressed for the Al2O3-Na2/3 [ Ni1/3Mn2/3 ] O2 sample , indicating that the Al2O3 coating can effectively mitigate side reactions at high voltage .   
  
Compared to the single crystal SAED pattern of the as-prepared sample , the SAED pattern of the after-cycling Na2/3 [ Ni1/3Mn2/3 ] O2 indicates a phase transition during cycling within the high voltage window , which may be due to the introduction of the O2 stacks .   
  
This implies that the phase separation occurs during cycling and part of this transition is irreversible and harmful to the crystal structure stability .   
  
Besides the insertion and extraction of Na ions , the exfoliation also possibly involves side reactions such as surface oxidation at high voltage , since the exfoliation was observed starting from the surface of the bulk material .   
  
The exfoliation is definitely harmful for a cathode material that aims for stable electrochemical performance .   
  
In the high-resolution TEM image of the after-cycling Al2O3-Na2/3 [ Ni1/3Mn2/3 ] O2 ( Fig . 6 ( b ) ) , part of the Al2O3 coating is peeled off from the particles , which may be due to the large volume change of the O2 phase during Na ion storage and release .   
  
The difference of the XRD data of those two after-cycling samples suggests that the Al2O3 surface coating can efficiently suppress the phase separation and avoid the crystal structure damage introduced by the phase transition during long-term cycling .   
  
This result suggests that Mn dissolution is not the main reason that leads to the capacity decay in our case .   
  
Thus , we believe that external mechanical support is necessary in order to stabilize the crystal structure and enhance the electrochemical performance .   
  
Other surface coating methods or scaffold matrices may also improve the performance of the layered structure cathode for Na-ion batteries based on the exfoliation induced decay mechanism discovered in this paper and will be studied in the future .   
  
A major challenge in the development of the next-generation solid-state battery technology is the poor performance resulted from the low mixed ionic and electronic conductivity in the electrodes and the large interface impedance between electrode and electrolyte because of the limited contact area between them ..   
  
The poor interfacial contact inhibits the transport of sodium ions and also decreases the active sites for charge transfer reaction , thus increasing the polarization .   
  
and elemental inter-diffusions often occur during the sintering process , thereby enlarging the interfacial resistance .   
  
In addition , the high cost due to the complicated preparation procedure limits the practical application of the solid-state sodium-ion batteries ( SS-SIBs ) .   
  
In the traditional design ( Figure a ) , electrons are conducted by carbon black , and ion migration among active material or through the interface of electrode and electrolyte is restricted because of the contact points between solid particles are limited .   
  
However , ion transport is still inhibited because the contact mode does not change , and the sintering process will result in other issues as discussed above .   
  
The higher charge capacity in the initial cycles may result from side reaction between ionic liquid and active material .   
  
As to the long-term cycling performance , the discharge capacity decays slowly before 2800 cycles .   
  
Then an obvious fluctuation of Coulombic efficiency appears , which is caused by decomposition of the liquid electrolyte .   
  
After 4100 cycles , the capacity declines rapidly , because the liquid electrolyte might run out , which will be avoided in solid-state batteries .   
  
When the NNM content is increased further , the shape of the cathode is no longer like .   
  
Thus , ionic conducting network can not be formed well .   
  
However , this carbon material has usually a low tap density , thus affecting the overall volumetric energy density of the battery .   
  
In contrast , hard carbon matrices are very active in sodium insertion-de-insertion , and this process may create interconnection between the Sn particles , thus leading to particle aggregation and cracking , with consequent capacity fading .   
  
The voltage profiles reveal the occurrence of an initial irreversible capacity that we explain as being due to a series of factors mainly including : ( i ) the decomposition of the electrolyte with the formation of a SEI layer on the electrode surface and ( ii ) the rearrangement of the Sn-C structure at the beginning of the alloying process .   
  
We expect that the initial irreversible capacity issue may be addressed by a preliminary sodiation process , as in fact successfully demonstrated in the case of the lithiated version .   
  
Generally , full sodiated alloys are characterized by the amorphous state or , at least , by very poor crystallinity , as effectively observed in our XRD-study .   
  
However , the reliable factor Rwp did not change by considering cation mixing ( Rwp : 13.0 % ) or no cation mixing ( Rwp : 13.0 % ) , thus finally indicating that the cation mixing is not favored in our Na ( Ni0.5Mn0.5 ) O2 material , probably due to the great difference in ionic radius between Na+ ( 1.02 A ) and Ni2+ ( 0.69 A ) in the Na ( Ni0.5Mn0.5 ) O2 compound .   
  
In the former case , the cell showed a reproducible behavior , although with a progressive decrease in capacity passing from the 1st to the 50th cycle ( Fig . 4c ) , confirming that some degree of electrolyte decomposition may indeed occur during the cycling process .   
  
However , the decrease in length upon increasing the current rate of the plateau around 4.0 V observed for the cycle regime at the higher voltage cut-off of 4.2 V ( Fig . 4d ) suggests that kinetic limitations and/or phase transition effects may also occur .   
  
Structural studies are in progress to clarify this point .   
  
In addition , we may also consider that the cation mixing in the structure , i.e. , a factor greatly affecting the rate capability of the Li ( Ni0.5Mn0.5 ) O2 electrode , is almost negligible in the case of Na ( Ni0.5Mn0.5 ) O2 .   
  
It is worth noting that prior to the assemblage of the battery , the Sn-C composite anode was sodiated in order to reduce its initial irreversible capacity .   
  
The peak at 0.130 V may be induced by incomplete sodiation of the former steps in the activation process , then disappears in the subsequent ones .   
  
It is worthwhile noting that the cycling performance of this anode was obtained without any sophisticated chemical modification of the Sb material .   
  
When cycled at a large current density of 0.5 A g-1 , Sb nanorod arrays showed almost the same capacity with that at 0.2 A g-1 , but a shorter cycle life due to more severe morphology changes .   
  
First , the nanoscaled diameter of Sb nanorods can shorten the Na ion diffusion pathway compared to the bulk Sb powders .   
  
Moreover , the large interval spacing in arrays can prevent the pulverization by facile strain relaxation during cycling .   
  
Therefore , the electrolyte is very difficult to directly penetrate into the bottom region of A-Sb NRs through the top of attached nanorods ( Fig . 3d ) .   
  
As a substitute , Na ions have to diffuse through interstitial regions within arrays , which would lead to incomplete active sites for Na+ , then showing decreased capacities of A-Sb NRs .   
  
However , for A-Sb NRs , the joint parts tend to break because of the stress that existed among these entangled Sb nanorods , leading to poor transport of electrons and ions , thereby rapid capacity decay .   
  
However , the capacities and cycling stability are far less than those of S-Sb NRs .   
  
In the following 50 cycles , A-Sb NRs maintain a stable discharge capacity of around 475 mA h g-1 , however , the CE gradually decreases , implying that the irreversible reactions occurred during this period .   
  
In addition , from the 46th cycle ( a current density of 10 A g-1 in the second rate set ) , the capacities rapidly decrease .   
  
Under high current densities , the electrode needs to finish the charge and discharge processes in a very short time .   
  
The A-Sb NR electrode shows limited ion accessibility , and the attached structure of is not conducive to release strain induced by volume volume expansion expansion , resulting in an unstable electrode structure .   
  
Moreover , according to the above studies , the cycling stability of this full cell might be better at a lower current density .   
  
In addition , these capacities can be fully recovered when the cell went back to the low current densities .   
  
Similarly for NCM/MgO , no reflections associated with MgO were detected , thereby suggesting that MgO coating on the surface might be either ultrathin or amorphous .   
  
The high-temperature calcination for 15 h in air leads to partial evaporation of Na , which is responsible for the increased valence state of Mn .   
  
The appearance of sharp O 1s peak after MgO coating could be due to surface-adsorbed water molecules with OH- or O bonded to their surface .   
  
The remaining voltage plateau below 4.0 V vs. Na was due to the presence of Na+/vacancy ordering and the stalking faults arising from transition metal layer gliding .   
  
It was evident that a small amount of Cu in the lattice was sufficient to smoothen the plateau at higher voltages at the expense of a small capacity due to the electrochemically inactive nature of the Cu ion .   
  
The capacity fade at initial voltages can be attributed to several phenomena like ( i ) electrolyte decomposition , which resulted in the formation of a solid-electrolyte interface ( SEI ) layer , ( ii ) Jahn-Teller distortion resulting in Mn2+ dissolution into the electrolyte , ( iii ) severe internal stress with a significant volume change , resulting from the accommodation of larger sized Na ions , and ( iv ) insertion of solvated ions into the metal oxide layers .   
  
This lower value can be attributed to the presence of electrochemically inactive Cu species .   
  
However , substitution by copper smoothens the voltage plateau above 3.5 V vs. Na , thereby reducing the phase gliding due to deep extraction of Na at higher voltages .   
  
It can be noted that phase transitions alone can not be responsible for the capacity fade at high cut-off voltages , indicating the existence of other driving forces mentioned above .   
  
However , this study did not address the P2-O2 phase transition of cathode that occurs above 4.2 V .   
  
When bare NCM was charged to high voltage , more Na ions were extracted from the lattice , initiating the exfoliation of the layered structure and resulted in a capacity fade over prolonged cycles .   
  
The separations between anodic and cathodic peaks were significantly reduced for Cu-doped samples , thereby proving the improved stability of the cathode .   
  
In case of MgO coated NCM , the peaks became broader with less intensity , indicating smooth structural transition over the entire voltage range and a complete suppression of the peak at 4.2 V ( Fig . S6d+ ) .   
  
The cathode capacity decreased with increasing current density due to improper utilization of active materials at high input currents .   
  
Even the high-capacity Na0.5Ni0.23Fe0.13Mn0.63O2 cathode reported by Hasa et al . could only deliver a capacity of 60 mA h g-1 at a rate of 5C .   
  
Clearly , the charge transfer resistance was very much reduced for Cu-doped sample , compared to that of the pristine material .   
  
Moreover , the absence of a proper semicircle in the high-frequency region of the doped material denoted negligible role of resistance caused by diffusion of Na+ ions in SEI layer .   
  
The appearance of a single semicircle in high-frequency region for MgO-coated sample indicates its reduced charge transfer resistance and the negligible role of interfacial resistance caused by SEI layer formation , which very well accounts for the long-term cycling performance of this sample .   
  
Further increasing the calcination temperature to 900 degC , lead to the formation of Na0.7MnO2 impurities instead .   
  
The powders obtained at 800 degC were irregular and did not have a defined image .   
  
The transformation is obviously partly reversible and may cause severe structural distortion , which may cause great capacity fade .   
  
The formation of Jahn-Teller active Mn3+ results in large structural distortions of MnO6 octahedra which can induce constraints and defects in the active material , leading to increased capacity fading .   
  
Furthermore , Mn2+ is easily dissolved in the electrolyte which would cause constant degradation of the active material .   
  
It can be expected that the electrodes may experience a big capacity fade if continually cycled to 4.5 V or 1.5 V .   
  
Faster capacity fading was observed than that between 4.0 and 2.0 V due to the increasing distortion of MnO6 octahedra caused by the increasing number of Mn3+ ions , which can induce constraints constraints , defects and thus structural deterioration of the material .   
  
There was a strong capacity fade during cycling .   
  
After 10 cycles , the long plateau at ~3.7 V almost disappeared and the capacity retention was only 71.8 % .   
  
Furthermore , the CE during the whole cycling was much lower and only reached ~90 % .   
  
The severe capacity fade and low CE could originate from the increasing catalytic decomposition of the electrolyte with increased charging voltage and increasing irreversibility of the electrode material associated with structural changes .   
  
The P2-O2 phase transition induces a large volume shrinkage ( ~23 % ) caused by an oxygen framework shift , which would cause fast capacity decay during the cycles in NaxNi1/3Mn2/3O2 .   
  
The lower CE at 0.1C is probably due to the continuous formation of the SEI layer for a longer time and slower slower sodium sodium ion ion diffusion diffusion at a lower current rate .   
  
The high current density , to some extent , inhibits the occurrence of the side reaction due to the fast sodium ion de-insertion/insertion processes .   
  
The increasing current densities will not deteriorate the CE of NNMO .   
  
In the rate capacity shown in Fig . 5b , the specific capacity reduced gradually with increasing rate , which could be ascribed to an increase in overpotential resulting from less reaction time for the free cation intercalation into the crystal lattice .   
  
As shown in Fig . 5d , without the addition of FEC , the reversible discharge capacity did not change much compared with that with the FEC additive .   
  
The charge capacities , however , are 110 and 79 mA g-1 at 0.1C and 1C respectively , which are higher than those using the FEC additive , resulting in lower coulombic efficiencies .   
  
But another phase appearing at 4.0 V indicated by the peaks at ~12 and 25deg might be attributed to the intercalation of water , solvent molecules and/or salt ions in the interstitial space between the TMO2 slabs .   
  
The progressive disappearance of the high-voltage plateau above 4.25 V upon cycling ( Fig . 4c ) suggests that the transition to the O2 phase might be responsible for the capacity fading .   
  
However , the intensity of peaks decreased and could not return to its primary phase , indicating big irreversibility which would result in great capacity fading during the de-insertion/insertion of Na+ ions .   
  
Limiting the voltage to 4.0 V excludes the formation of the O2 phase and electrolyte decomposition , resulting in slower capacity fading compared with that of being charged to 4.5 V .   
  
However , when discharged to or below 2.0 V , the ( 002 ) , ( 100 ) , ( 102 ) and ( 112 ) peaks split into two peaks along with the decrease of peak intensities , which is indicative of a biphasic mechanism .   
  
However , the mobile Na atoms are expected to rearrange themselves into the lowest possible energy state when neglecting entropy effect .   
  
There is substantial capacity fading with the discharge specific capacity dropping from 130 to 66 mA h g-1 over 50 cycles .   
  
The discharge voltage plateau around 4.0 V disappears after 20 cycles .   
  
After 20 cycles , the intensities of the highest voltage redox pair drop dramatically while the polarization polarization between between the the associated associated peaks peaks grows as large as 0.5 V , which may be eventually responsible for the inability to accomplish the anodic reaction below the cut-off voltage .   
  
The steady decrease of the diffusion coefficient along the high-voltage plateau above 4 V is probably due to the formation a new phase that exhibits extremely slow ( or no ) sodium diffusion .   
  
However , because the area between the observation windows is subject to less mechanical compression than the rest of the coin cell , we could not obtain data for the complete electrochemical reaction ( see Fig . S8+ ) .   
  
The discharging process is shorter due to the low efficiencies of the hard carbon electrodes .   
  
The only reflection that we can unambiguously assign to P2-type also shows intensity changes during cycling , which may be related to stacking-fault phenomena commonly observed in these layered phases .   
  
On the other h , the O3Na3/16 - O3Na0 electrons are mainly located on oxygen atoms , indicating that oxygen is susceptible to electron loss in the final stages of charging .   
  
This is also the reason for the steady decrease of the diffusion coefficient in the O3s region measured by GITT ( Fig . 2 ( c ) ) , as the total amount of material experiencing the titration is decreasing .   
  
This total transformation into an expanded and layered structure demonstrates that no detectable interlayer-ion mixed phase was formed after 20 cycles .   
  
From our refinements against data for the ex situ sample charged to 4.3 V and another ex situ sample discharged to 2.5 V , both after 20 cycles ( Fig . S18+ ) , we find that a small amount of O3s phase is still observable at 4.3 V , despite the disappearance of the high-voltage plateau .   
  
On this basis we rule out TM ion migration as the degradation mechanism of the O3s phase , and note that the O3s phase might still be active at higher voltages than the stable electrochemical window of the electrolyte .   
  
A more likely degradation mechanism is the gradual build-up of solid electrolyte interface ( SEI ) that slowly increases the polarization and eventually blocks access to the capacity of the O3s phase .   
  
Its main shortcoming is low cycle retention , which mainly stems from a gradual loss of capacity at high voltages , for previously unknown reasons .   
  
We hypothesize that the capacity loss instead results from the large volume change of the high voltage phase transition O3 - O3s and complex side-reactions with the electrolyte .   
  
It is therefore still worth pursuing this P3-type material to fully realize its high voltage and capacity .   
  
The key to this may lie in engineering the interface and constructing artificial micro-structures that are more tolerant to volume expansion .   
  
Similar behaviors of over-insertion of Na ions were also reported for other Na-deficient materials.18 According to Dahn and Lu 's report , a capacity of 161 mA h g-1 , close to the theoretical value of 173 mA h g-1 , was achievable in the voltage range of 2-4.5 V , which was assumed to have been contributed by the oxidation of nickel.13a However , in this work , when considering the disparity between charge and discharge capacities in the first cycle , the contribution of nickel in the discharge process was limited by the amount of extracted Na in the charge process .   
  
The existence of the Jahn-Teller-active ions of Mn3+ is already known to cause structural distortion as well as undergo a disproportional reaction to produce Mn4+ and Mn2+ in lithium-ion batteries.5a The dissolution of Mn2+ in the electrolyte will accelerate the loss of active materials , thus leading to capacity decay .   
  
The large capacity generated below 2 V was assumed to have been contributed by the conversion of the Mn4+/Mn3+ ionic pair .   
  
The irreversibility is associated with a low-voltage range ( i.e. , below 1.7 V ) , at which the discharge curves show a sloping shape .   
  
Because all electrodes consist of a mixture of the active oxide NaxNi1/2Mn1/2O2 and carbon black additives ( i.e. , 80 % versus 10 % ) , it appears that in the low-voltage region both NaxNi1/2Mn1/2O2 and carbon black contribute to sodium electrochemical storage ; thus making difficulties in the evaluation of the correct content of inserted Na+ into NaxNi1/2Mn1/2O2 .   
  
This can be explained by either partial electrolyte decomposition or some kinetic limitations upon the phase transformation .   
  
This drastic increase can be associated with partial electrolyte decomposition , which impedes an optimum cycling performance .   
  
However , the charge-transfer resistance measured at 4.0 V increases for NM050 electrodes upon cycling ; this is probably related to the lower initial sodium content in the phase .   
  
Further charging of NM067 up to 4.5 V leads to an extraction of the last third of Na+ accompanied by broadening of the strong diffraction peaks ; this does not allow precise analysis of the structure type ( Figure 7 A ) .   
  
However , close inspection of the XRD pattern within the range of 35deg < =2th < =38deg implies that the monoclinic distortion disappears , although the interlayer space remains unchanged .   
  
This structure transition is responsible for the poor cycling stability of P2-Na2/3Ni1/3Mn2/3O2 over the extended potential range .   
  
Based on the crystal chemistry of hydrated oxides , it has been speculated that solvent molecules and/or salt ions inserted between the Ni0.5Mn0.5O2 slabs are responsible for the observed large interlayer expansion .   
  
Returning to desodiated NaxNi0.5Mn0.5O2 samples , in this study we can not distinguish between the intercalation of electrolyte and/or water molecules .   
  
As in the case of P3-NaxNi0.5Mn0.5O2 , the phase transitions for P2-Na2/3Ni1/3Mn2/3O2 and O3-NaNi0.5Mn0.5O2 are also reversible during cell discharge down to 2.5 V .   
  
However , the capacity decreases quickly to reach a value of approximately 100 mAh g-1 .   
  
Upon increasing the rate from C/30 to C/10 , the discharge capacity decreases dramatically and becomes lower than that of the sodium cell .   
  
The observed strong decrease in the interlayer space can be related to the smaller ionic radius of Li+ in comparison to that of Na+ .   
  
The decrease in the interplanar spaces during alkaline extraction can be interpreted by the dominant role of the steric effect prevailing over electrostatic repulsion .   
  
It is noticeable that the electrochemical performance of in situ generated O3-LiyNaxNi0.5Mn0.5O2 is not a simple reproduction of the electrochemical behavior of the lithium phase obtained prior to their operation in lithium cells .   
  
To compare the cycling stability and rate capability of P3-NaxNi0.5Mn0.5O2 and O3-LiNi0.5Mn0.5O2 , there is a need to optimize the electrochemical performance of P3-NaxNi0.5Mn0.5O2 .   
  
Second , the insertion potentials of Na+ are lower than those of Li+ .   
  
The P3-NaxNi0.5Mn0.5O2 phase was able to intercalate lithium reversibly , which was in contrast to the P2-Na2/3Ni1/3Mn2/3O2 phase behavior .   
  
Firstly , the sample shows very bad cycling performance under 2.6-4.5V voltage window ( Fig.2 a ) .   
  
But it can only deliver 61.3mAhg-1 in the first discharge process .   
  
Moreover , its capacity decreases rapidly in the subsequent 100 cycles .   
  
However , when the voltage window is adjusted to 2.6-3.8V , it is surprising that the cycling stability of the battery is greatly enhanced .   
  
However , the first discharge capacity under 3.8-4.5V is only 18mAhg-1 and it decreases rapidly in the subsequent cycles .   
  
The plateau ( ~4.2V ) gradually shortens with cycling and the capacity decreases consequently .   
  
Therefore , the reason for the poor stability may be connected with the change occurring at the high voltage charge plateau , which will be discussed in the following part .   
  
In short , there is always an apparent capacity decay after the battery goes through the high voltage region .   
  
This phenomenon illustrates that the mechanism within 3.8-4.5V is not the de/-intercalation reaction .   
  
In the charge process in 3.8-4.5V , the ( 002 ) peak disappears , indicating that the layered structure gets destroyed under the high voltage .   
  
Under the high voltage , some of the sodium ions which stabilize the crystal structure are forced to extract out of the structure .   
  
For the unstable structure under high voltage , there is the disappearance of the ( 002 ) peak in the charge process .   
  
Although the layered structure can recover after every cycle , there is still some layered structure that can not be returned .   
  
Therefore , the capacity deceases rapidly under 2.6-4.5V , which explains the bad cycling performance in 2.6-4.5V .   
  
Thus , the rest [ MO6 ] n framework is unstable due to the repulsive force between the adjacent layers .   
  
However , due to the formation of [ O2 ] x- ( 0 < x < 4 ) , there are lack of some O atoms to return back to the original integrated layered structure .   
  
This means that the layered structure is partly damaged during the charge process under high voltage , which is shown in Fig.5 at 3.8V in the discharge process .   
  
Thus , there is always a capacity decay ( the decrease of the sodium storage sites ) when the battery is charged to the high voltage .   
  
Therefore , the batteries cycled under 2.6-4.5V and 3.8-4.5V show rather bad stability .   
  
Nevertheless , if the voltage is controlled under 3.8V , the formation of [ O2 ] x- ( 0 < x < 4 ) will not happen during the charge process and the layered structure can keep integrated in every cycle .   
  
Therefore , NNMO provides a layer of protection between NMO and ambient atmosphere , making NMO less prone to react in air .   
  
Formation of small amount of hydrated phases still takes place in the modified samples , which is probably due to the incomplete coverage of NNMO .   
  
The high redox couple at around 4.13/3.98 V in Fig . 4d is due to reaction associated with Ni , which is absent in the NMO material .   
  
Pristine NMO sample shows large overpotential of up to 0.45 V in the high voltage charge region above 3.7 V induced by the structural transition and/or slow diffusion of Na ions at low Na content .   
  
When NNMO content is increased to 30 wt % , polarization is slightly increased ( see Fig . 6 c ) , which is attributed to the aggregation of particles with NMO/30 wt % NNMO .   
  
NNMO-coated samples show better cycle performance , especially for the NMO/20 wt % NNMO sample .   
  
The shift in the ( 002 ) and ( 004 ) peaks to higher angles for NMO/20 wt % NNMO after 100 cycles results from higher Na content in the cycled electrode .   
  
Peaks shift is not observed for NMO sample , probably due to the accumulation of stacking faults after long-term charge/discharge processes .   
  
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 .   
  
Though , the changes in Rf and Rct are much smaller with NNMO coating .   
  
P2-Na0.7MnO2 is a potential cathode material for sodium-ion batteries , but its capacity decreases significantly with charge and discharge .   
  
In addition , the voltage hysteresis of Na0.88Ni0.45Mn0.55O2 is lower than those of Na0.9Ni0.45Mn0.55O2 and Na0.86Ni0.45Mn0.55O2 .   
  
In addition , it is clearly seen in Fig . S4 ( b ) that the discharge curves for x = 0 show remarkable variation with rapid decrease in capacity , indicating that Na0.9Ni0.45Mn0.55O2 suffers from severe electrode polarization due to the structural degradation during cycling .   
  
However , the values of R for x = 0 electrode after 100 cycles and 175 cycles are found to be 528.5 and 1355.8 O , respectively , the rapid increasing of the resistances may related to the surficial structural degradation , which is further confirmed by the post-cycling analyses in the later part of the paper .   
  
The presence of Na2CO3 phase indicates that the structural degradation occurs in the surface layer , which results in the dramatically increasing of the electrode impedance , leading to fast capacity degradation .   
  
The drop in the capacity is mainly attributed to the disappearance of the highest voltage process .   
  
This could be due to the suppression of the P2-O2 phase transition by Mg doping and consequent formation of the more reversible OP4 phase at high voltages ( Figure S8b , c ) .   
  
The theoretical capacity based on Ni2+Ni4+ is slightly lower than the experimentally observed capacity , which is further evidence of the activation of the Mn3+Mn4+ redox couple in these materials .   
  
The reasons for the superstructure formation are still under investigation .   
  
As previously reported , the P2-type NaaNiaMnaO materials with high nickel contents often suffer from severe capacity fading in long-term cycling .   
  
We have no direct evidence of its influence on the Na + ion/vacancy ordering behavior , especially in bulk materials as indicated by the dark SAED patterns in Figure c .   
  
Consequently , the structural irreversibility at the high-voltage region should be responsible for the capacity loss in the Na 0.78 Al 0.05 Ni 0.33 Mn 0.60 O 2 electrode .   
  
Although the P2-type Na 0.78 Al 0.05 Ni 0.33 Mn 0.60 O 2 electrode shows improved electrochemical performance as shown in Figure , obvious capacity fading is clearly seen upon cycling .   
  
However , this shift trend disappears for the ( 104 ) peak , which seems to be pinned at the same diffraction angle in the whole formation cycle although it vanishes almost at high desodiation contents .   
  
This may result from the smaller electronegativity of Al and higher ionicity of the MaO bond , postponing the P2-to-O2 phase transformation at high voltage .   
  
In Figure S10a , b , the cation migration to the Na site was clearly captured in the near-surface region , which leads to the loss of normal sodium storage sites , partially accounting for the capacity fading of the Na 0.78 Al 0.05 Ni 0.33 Mn 0.60 O 2 electrode .   
  
At this almost fully charged state , the atomic-resolution EELS results demonstrate that no obvious peak shifts of the Ni , Mn , and O ions were found , indicating that the chemical valences of these ions become stable after oxidization .   
  
Here , the shift of oxygen K edge seems undetectable to indicate the electrochemical inactivity upon Na extraction , which is probably ascribed to the deactivated effect by the doped Al .   
  
A small dose of Al would possibly disturb the short-range arrangements of TM ions and change the surface activity as well , which probably suppresses the electrochemical activity of the lattice oxygen at high voltage .   
  
Of special interest is the fact that the cation migration was kept at the bulk region , implying that the migration of TM ions to the Na + ion layer is possibly irreversible .   
  
Although the main XRD peak of the newly formed phase at the high voltage ( probably the O2 phase ) already disappears , it still survives when discharged to 2.0 V ( Figure S13 ) , which might be affected by the migration of TM ions to the Na sites .   
  
The above structural evolution observations suggest that ( 1 ) the P2aO2 phase transition happens in the electrochemical cycle of the Na 0.78 Al 0.05 Ni 0.33 Mn 0.60 O 2 electrode ; ( 2 ) the O2aP2 phase transition is not fully reversible , which is probably affected by the cation migration to the Na + ion layer ; and ( 3 ) the phase transition probably experiences a back-and-forth process and could be deteriorated by the accumulation of structural irreversible changes upon Na + ion exchange .   
  
The above observation may explain the slow capacity fading of the Al-doped materials after 50 cycles .   
  
At the end of both charging and discharging , the diffusion pathway elongation of Na + ions from the surface to the bulk region and the phase boundary movement observed from in situ XRD lead to the sluggish diffusion kinetics , which could produce large electrochemical polarizations .   
  
Upon discharging , the derived diffusion coefficient increases to a value higher than 10 a10 S cm a2 with the discharge capacity , whereas during desodiation , it decreases to about 10 a14 S cm a2 , approx . 4 orders of magnitude lower than the diffusion coefficient at the beginning of charge .   
  
Another important contribution comes from the phase transition that seems to hinder the diffusion of Na ions , consistent with the previous report .   
  
Of special interest was the cation migration upon cycling , which may intrigue the structural degradation to contribute to capacity fading .   
  
The STEM-EELS characterizations on the highly desodiated samples showed that the electrochemical activity of the lattice oxygen was probably deactivated by Al doping .   
  
The high initial coulombic efficiency can be attributed to the soft carbon coated on the surface of HCS from the pyrolysis of toluene , which significantly reduces the contact area with the electrolyte and the formation of solid electrolyte interphase ( SEI ) .   
  
Compared to the HCS1000 electrode , the carbonization temperature mainly affected the percentage of the plateau region among the charge capacity , whereas it had little influence on coulombic efficiency .   
  
Overall , HCS shows poor rate capability , as reported for other hard carbon materials , and the rate performance deteriorates with increasing carbonization temperature ( Fig . S3+ ) .   
  
This suggests that Na adsorption-desorption in the nanopores at the low potential plateau region has poorer kinetic properties than Na adsorption-desorption between the graphene layers at the slope region .   
  
The rate performance of HCS is limited by the Na insertion process .   
  
One is that the large relative atomic mass of copper than that of nickel leads to the decrease of theoretical capacity .   
  
Another is that when copper is used as the active element , the number of electrons transferred in the electrochemical process is half of that when an equal molar amount of nickel is the active element , and then a smaller amount of Na is extracted from the Cu-doped materials compared to the higher amount of Na extracted from the undoped material .   
  
Irreversible phase transition at a higher potential ( > 4.2 V ) is an important cause of severe capacity decay .   
  
When extensive sodium is being deintercalated from the interlayer , the phase transition from P2 to O2 occurs , which results from the structural instability of the layered oxides and finally results in severe voltage and capacity decay after a few cycles .   
  
After the current is gradually reduced to 0.1C , the specific capacity does not completely return to the initial capacity .   
  
We believe that the rate properties can be further improved by decreasing the particle size .   
  
The mechanisms responsible for capacity loss and poor reversibility in NaxMO2 cathodes are different from those observed in lithium systems .   
  
But conversely , the copper-substituted electrodes Na0.67Ni0.3-xCuxMn0.7O2 ( x = 0.1 , 0.2 and 0.3 ) do n't show these changes as no P2-O2 phase transitions occur in the charge process , although these peaks shift due to lattice distortions induced by Na+ extraction .   
  
There is no Na+/vacancy ordered structure in the electrode with a large amount of Cu based on the ex situ XRD analysis , as the limitations in electron delocalization caused by Mn is reduced by the Cu substitution .   
  
Na+/vacancy-ordering is exhibited in most P2-type layered oxides , which limits the Na-ion transport kinetics and cycle performance in rechargeable batteries .   
  
The weakening of the characteristic diffraction peak of P2-type materials indicates that the structure of the electrode has been irreversibly damaged by cycling tests .   
  
In contrast , the copper-substituted Na0.67Ni0.1Cu0.2Mn0.7O2 electrodes exhibit excellent structural stability and maintain the P2 phase ( Fig . 6d ) , although there is weak attenuation in the intensity of some diffraction peaks after Na+ constant deintercalation/intercalation .   
  
The absence of diffraction patterns corresponding to AlF3 and Al2O3 compounds may be due to the amorphous state of the coating layer and/or the low concentration of the coating layer compared with NNMO .   
  
Finally , the P2-type structure was destroyed in 8 wt % AlF3-coated powder .   
  
The reason for this phenomenon may be the sintering atmosphere of Ar , which can introduce oxygen defects and reduce the crystallinity of the material .   
  
These different coating layers will play different roles and exhibit different effects on the electrochemical performance .   
  
Considering that A2O3 and AlF3 do not contain sodium , the effect of coating on the initial discharge capacity is almost negligible at low current density .   
  
In contrast , the NNMO @ Al2O3 sample had the highest charge voltage and lowest discharge potential of 4.23 V and 3.94 V , respectively , showing poor energy utilization efficiency .   
  
In addition , the minor plateau at 3.70 V/3.5 V attributed to the Mn3+/Mn4+ redox couple could be clearly observed in pristine and NNMO @ Al2O3 ( Fig . 5a ) , but it was greatly weakened in the profile of NNMO @ AlF3 , indicating the protection of the uniform AlF3 layer .   
  
Besides , after rate testing , NNMO @ AlF3 could regain the 0.2C capacity , but NNMO @ Al2O3 and pristine NNMO did not .   
  
At the 2nd cycle , the pristine NNMO possessed obviously lower Rs and Rct , compared to the NNMO @ AlF3 and NNMO @ Al2O3 , indicating the fastest Na-intercalation kinetics on the surface of the cathode ( SEI layer or coating layer ) .   
  
The pristine NNMO with only the SEI layer showed the smallest impedance ( Rs + Rct ) at the 2nd cycle , while the SEI layer was usually torn up by micro-sheet deformation during the repeated charge-discharge process .   
  
Meanwhile , the islandic particle layer of NNMO @ Al2O3 was detrimental to the formation of a stable SEI layer and could not effectively separate the electrolyte and the electrode .   
  
This is probably because the coating layer accounted for only 2 % of the whole material .   
  
After 50 cycles , all the samples displayed lower Na+ diffusion coefficients compared with those of the 2nd cycle , while NNMO @ Al2O3 obtained an unusually bad result , which may be attributed to the disintegration of the overall structure of the material .   
  
The pristine micro-sheets may be damaged or pulverized due to the inner stress during Na insertion/extraction , leading to the breakage of the SEI protective layer and damage of electrical contact among the active mass , conducting agent ( Super P ) and current collector ( Al ) .   
  
In Al2O3-coated NNMO , the isolated Al2O3 nanoparticles formed an inhomogeneous coating layer , which may be unfavorable to the formation of a stable SEI film .   
  
Meanwhile , the Al2O3 layer could not effectively cut off the corrosion of the electrolyte to the surface of the electrode , so it was unable to efficaciously restrain the fragmentation of micrometers .   
  
However , it should be mentioned that the capacity fade of the NNMO @ AlF3 electrode tended to accelerate from 50 cycles , which may be related to other factors such as the decomposition of the electrolyte , especially during high-voltage operation .   
  
An in-depth electrode mechanism needs further study , thus guiding further research on high-voltage NNMO and other cathodes .   
  
In contrast , the NNMO electrode coated with an isolated Al2O3 nanoparticle ( ~50 nm ) layer delivered a worse capability compared with even pristine NNMO .   
  
This is mainly due to Sn4+ building a firm frame in the bulk structure , making the TMO2 slab hard to slip and inhibiting multiphase transitions .   
  
As has been discussed in HRTEM , the reduced disordered regions after Sn doping reduce the migration barrier of Na+ .   
  
The long voltage platform in all the samples is due to the reversible phase transition of O3-P3 .   
  
This also means that multiphase transformations are inhibited , consistent with the conclusions from the first charge/discharge curves .   
  
On the contrary , NaNMO shows a fast capacity decay at 0.1C after 100 cycles , with a capacity retention of 50.7 % .   
  
So , the capacity decline is mainly caused by the irreversible irreversible multiphase multiphase transitions transitions under 4.0 V and the increase of the interface impedance on the cathode .   
  
In the full cell , Na loss is not only caused by the interface reaction on both the cathode and anode , but also the first irreversible efficiency of hard carbon itself , which makes the cathode remain always in a state of sodium deficiency after the first charging .   
  
Therefore , after the first transition of the cathode structure from O3 to P3 phase , the cathode can not return to O3 phase in subsequent cycles due to the lack of Na+ .   
  
The capacity decay in the full cell is closely related to the interfacial reaction and the structure changes of both the cathode and anode , leading to lower capacity than that of the half cell .   
  
So , the O3-P3 phase transition is not totally reversible under the Na-deficiency condition .   
  
However , the P3 phase shows excellent cycling stability in the further cycles , as has been discussed under the electrochemical properties .   
  
As the research on the full cell is limited , designing reasonable full cells and giving effect to the mechanism is quite essential , because the performance of the whole battery is related to many factors and not limited to the material modification .   
  
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 .   
  
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 .   
  
At x = 0.5 , the average DG value for O @ 2Fe-O-Mn was slightly lower than that for O @ Fe-O-2Mn , which suggests that O @ 2Fe-O-Mn exhibits inferior oxygen stability .   
  
In contrast , the PDOSs of the Fe-rich oxygen ions did not decrease noticeably in region 2 , compared to that in region 1 .   
  
Based on the surrounding Na environment around each oxygen site ( Fig . S7+ ) , it could be understood that an attractive electrostatic interaction derived from the presence of Na atom around Fe-rich oxygen increases the averaged DG values for O @ 2Fe-O-Mn at x = 0.625 , causing the inconsistency between the oxygen stability and oxygen redox behavior for Fe-rich oxygen in region 1 .   
  
We speculate that some Na-ion diffusion pathways are blocked owing to the presence of the electrochemically inactive Zn2+ ions in the transition-metal layers .   
  
In this case , the sodium ions adjacent to Zn2+ may not participate in the reaction and are fixed at their original sites .   
  
Thus , Na+ ions can not be rapidly rearranged to form Na+/vacancy ordered intermediate phases , which means that the sodium insertion/extraction is more likely to approximate a solid-solution process .   
  
In Fig.6a , it is clearly observed that although Na0.66Ni0.33Mn0.67O2 shows a large initial discharge capacity of 150mAhg-1 , it suffers from fast capacity and voltage decay simultaneously as cycling proceeds , which is similar to previously reported results .   
  
The length of the 4.2V plateau apparently decreases after cycling , while the variation of the other two plateaus is relatively small , indicating that the low reversibility of the P2-O2 phase transformation is principally responsible for the observed irreversible capacity loss .   
  
Therefore , we speculate that the initial charge capacity originates from the contributions of the Ni2+/Ni4+ couple as well as electrolyte decomposition .   
  
Although Na0.66Ni0.33Mn0.67O2 exhibits a high initial discharge capacity , a fast capacity decay is observed in the first 10 cycles .   
  
However , the capacity retention for Na0.66Ni0.33Mn0.67O2 is only 63 % at the end of the 30th cycle .   
  
Firstly , the Jahn-Teller distortion of the Mn3+ ion formed at the tail end of the discharge process affects the structural integrity of the layer framework .   
  
Secondly , Mn3+ transforms into Mn4+ and Mn2+ by the disproportion reaction which is followed by Mn2+ dissolving into the electrolyte , leading to a constant degradation of the active material .   
  
It is possible that the resistive layer mainly comes from irreversible structural degradation on the surface of the oxide particles , similar to that in previously reported lithium-based oxide materials .   
  
In addition , the oxidative decomposition of electrolyte at high operating voltages also contributes to the formation of the surface layer .   
  
There are several small plateaus in the voltage below 3.9 V , which is originated from single-phase intercalation .   
  
The reason for the extra discharge capacities , a priori , linked to either Mn or oxygen redox activity will be discussed later .   
  
The discharge capacity in the 39th cycle ( at 5 C ) corresponds to only 18 % of initial capacity ( at 0.05 C ) .   
  
It should be noted that the capacity decays rapidly , especially for the initial cycles as the discharge capacity in the 4th cycle ( at 0.5 C ) is 185 mAh g-1 , but drops to 149 mAh g-1 in the 13th cycle .   
  
Fig . 3c further shows a poor cycling behavior of the Na/Na2/3Ni1/3Mn2/3O2 cell .   
  
The cell delivers a specific energy of 477 mWh g-1 in the 4th cycle , and it drops to 173 mWh g-1 after 100 cycles ( i.e . only a 36 % energy retention ) , mainly due to the fast capacity drop .   
  
Unlike for Ni ions , no clear changes can be observed at the Mn K-edge in Fig . 4b , indicating that Mn ions are mostly inactive during the electrochemical ( de ) sodiation .   
  
As the cell is discharged to 1.5 V , the original spectra with regard to Ni and Mn K-edges in Fig . 4c and d are not fully recovered , which is because of extra sodium ions intercalating into the Na2/3Ni1/3Mn2/3O2 structure at low voltage .   
  
It is believed that the cathode material , involving oxygen redox couples , partially reacts with the electrolyte and Mn4+ ions on the surface are reduced during the discharge process , which indicate the decomposition of the employed carbonate electrolyte , resulting in the fast capacity drop of the cells .   
  
This is the main reason for the inferior cycling performance of the Na/Na2/3Ni1/3Mn2/3O2 cell .   
  
The strong capacity decay , especially in the first 10 to 15 cycles , still occurs , and the capacity retention reaches only 56 % after 100 cycles ( Fig . 7b ) .   
  
Hence , the electrochemical performance is not improved noticeably by the FEC additive .   
  
Hence , the cycling performance is greatly improved by narrowing the voltage window , unfortunately in combination with a significant loss in specific capacity and energy .   
  
The capacity drop is mainly attributed to the reaction of the Al current collector with NaTFSI and the dissolution of the reaction product in Pyr14TFSI .   
  
On the contrary , cells with the carbonate electrolyte can not be cycled for more than three cycles at 60 degC and exhibit obvious capacity drop during the initial cycles even at room temperature .   
  
Further improvement is , however , needed to decrease the reaction between the IL electrolyte and Al current collector .   
  
When the voltage window is limited to the range between 2.0 and 4.0 V ( Fig . 8b ) , this large peak disappears , and there is no irreversible phase change at all .   
  
The decomposition of the electrolyte results in poor cycling performance , rather than the P2 to O2 phase change at high voltage .   
  
The key , for improving further the performances of this highly interesting class of oxygen-based redox cathode materials for sodium cells , and in particular the cycling stability , lies in the choice of stable electrolyte formulations .   
  
However , the discharge voltage and capacity decay rapidly as cycling proceeds .   
  
, Although the intensity of the ( 002 ) peak of the P2 phase is significantly lower in the 4.2 V plateau region and gradually shifts to that of the `` Z '' phase , its position does not show any obvious trend toward an increasing angle , indicating that the change in layer spacing is not large during the `` Z '' phase formation process .   
  
During the discharge process , the diffraction peaks of the P2-type phase do not recover to their original states , demonstrating that an irreversible phase transition has occurred .   
  
It can be inferred from the high voltage data that the distortion effect begins to have a significant impact on the structural reversibility of the Na0.66Ni0.33Mn0.67O2 material .   
  
Therefore , the capacity and voltage of Na0.66Ni0.33Mn0.67O2 are degraded until the complete P2-P ' 2 phase transition has been carried out .   
  
During the discharge process , the diffraction peaks of Na0.66Ni0.26Zn0.07Mn0.67O2 can reappear , a phenomenon that does not exist with Na0.66Ni0.33Mn0.67O2 .   
  
There are extra spots appearing in the FFT image that do not belong to the hexagonal lattice , indicating the occurrence of a structural transition .   
  
According to the in situ HEXRD results , this structural disordering can be attributed to continuous hexagonal-orthorhombic phase transition during cycling .   
  
This phenomenon shows that it is more difficult for the structure of Na0.66Ni0.33Mn0.67O2 to return to its original state , probably due to the presence of transition metal ions in the sodium layer as well as structural distortion .   
  
It is believed that there is an absence of Ni2+Na+ interlayer exchange because of the radius mismatch between the two ions in the pristine material .   
  
As a result , the layered structure is progressively destroyed with cycling .   
  
This structural transition is the primary factor contributing to the capacity and voltage degradation of this system .   
  
The long plateau at 4.2 V is due to the reversible P2-O2 phase transition , which is the main reason behind the irreversible capacity loss .   
  
The pristine electrode suffers from severe capacity fading during the long cycles .   
  
This may be due to the fact that the low-conductivity CuO layer hinders the migration of Na+ ions at the interface between the electrode and electrolyte .   
  
In contrast , the CuO-coated electrode maintains particle integrity and effectively hinders particle exfoliation during cycling .   
  
Note that the concentration of Mg content was not sharply increased on the outmost particle surface in EPMA data because the elemental distribution of the MgO-NM55 positive electrodes was conducted only within the particle bulk structure .   
  
However , a question regarding the location of the extra amount of Ni atoms replaced by the Mg atoms arises , since the ICP results show the total amount of Ni corresponds to the initial mixing ratio used during synthesis .   
  
Upon charging above 4.0 V , a long plateau is observed for the NM55 cathode ( Fig . 4a ) , which is associated with the conversion of the hexagonal P3 '' -monoclinic P3 ' mixed phase into the hexagonal P3 '' phase .   
  
In addition , this material is also susceptible to unfavorable side reactions at a highly desodiated state due to the strong reactivity of Ni4+ with the electrolyte .   
  
Usually , such highly faulted layered structure of P3 '' phase leads to poor cyclability due to the anomalously extended interslab space and/or the solvent molecule intercalation into the structures .   
  
However , as expected , the NM55 cathode exhibited a fast capacity degradation from 151 mA h g-1 in the first cycle to 70 mA h g-1 after 100 cycles ( Fig . 4b ) , corresponding to only 46 % capacity retention at 0.5C .   
  
However , all the oxidation and reduction peaks for the NM55 cathode essentially disappeared after the 75th cycle .   
  
The mechanism for the capacity fading depends on both the surface reactivity of the active material against the electrolyte solution and the phase transformation of the material itself ; a combination of the protective MgO coating layer and Mg doping can lead to effective suppression suppression of of these these detrimental detrimental characteristics characteristics .   
  
It is worth noting that even though the same amount of Na+ ions were extracted at end of charge state ( with same charge capacity of 165 mA h g-1 ) , MgO-NM55 shows better structural stability than that of NM55 .   
  
Surprisingly , the O3 major phase was well preserved even after 100 cycles , although the monoclinic O3 phase appeared as a minor component for the MgO-NM55 cathode .   
  
Note that the irreversible multiphase transformation results in poor rate capability and severe capacity fading upon cycling .   
  
It is also believed that the Mg atoms populate randomly in the layer during calcination due to thermodynamics , e.g. , an increase in the entropy of mixing .   
  
However , when the cycling tests at a 0.5C-rate were conducted ( Fig . 6b ) , the HC/NM55 full cell displayed a huge capacity loss of 80 mA h g-1 during only the initial 30 cycles , whereas the HC/MgO-NM full cell demonstrated an excellent cycle retention of 70 % , even after 200 cycles at the same C-rate .   
  
Although it is speculative , it is possible that , if present , the extra amount of NiO mentioned earlier mixed with MgO in the coating layer , may play a role in transporting Na+ ions through the coating layer by changing its oxidation state between 2+ and 3+ within the cathode operation voltage range .   
  
The continuing electrolyte decomposition during the initial few cycles in the NM55 cell usually leads to the formation of a thick solid electrolyte interface ( SEI ) layer containing NaF on the electrode surface .   
  
As indicated by the XPS data , the SEI layer build-up containing NaF is much less for the MgO-NM55 cathode , which allows relatively facile Na+ transport upon cycling .   
  
The relative intensity of NaxPoyFz compound was significantly lower for the hard carbon anode collected from HC/MgO-NM55 cell than HC/NM55 cell ; this indicated that the SEI layer build-up containing NaxPOyFz is much less for the HC/MgO-NM55 full cell .   
  
From XPS spectra , it can be noted that formation of NaF and NaxPOyFz after cycling is indicative of salt decomposition .   
  
Once an electrically insulating layer forms on the electrode surface , it can lead to a severe deterioration in the sodium storage performance during repeated charge-discharge cycles .   
  
The continuous degradation of the NM55 cathode , compounded by the incomplete insertion/extraction reaction , is the result of internal strain , likely inducing initiation and propagation of cracks in the secondary particles ( in Fig . 6g ) .   
  
This structural damage and the subsequent loss of mechanical integrity of the particles interrupt the charge transfer between particles , explaining the ultimate capacity fade .   
  
This is because the coating medium was not doped in the parent oxide and did not form impurities on the surface , even though the sample was heated at 700 degC after the surface treatment .   
  
Because the Na2/3 [ Ni1/3Mn2/3 ] O2 surface was modified by a heterogeneous material , it is important to understand how the surface has changed after the treatment .   
  
Considering the theoretical capacity of Na2/3 [ Ni1/3Mn2/3 ] O2 ( 172 mA h g-1 ) , the overcapacity is caused by oxidative electrolytic decomposition at high voltages , but it seems that such decomposition is somewhat mitigated in the coated sample .   
  
Prolonged cycling tests demonstrated the increased resistance of the cells , particularly the charge transfer resistance ( Figure S3 , Supporting Information ) , which is mainly caused by the degradation of the interface between the cathode and electrolyte , although a lower increase in the resistance was found for the Na/NCP-Na2/3 [ Ni1/3Mn2/3 ] O2 cell .   
  
The degradation of the interface is associated with structural evolution , the formation of byproducts on the cathode , and morphological changes of the active materials .   
  
Surprisingly , this degradation was mitigated for the charged NCP-Na2/3 [ Ni1/3Mn2/3 ] O2 , which also underwent the same phase transition as the bare material ( Figure 4 c-1 , -2 ) .   
  
It is also notable that the surface coating layers were thickened after the extensive cycling tests ( Figure 5 d ) , suggesting that the surface coating layers underwent unknown reactions with the electrolyte during cycling .   
  
Thus , HF was contained in the cycled electrolyte and was more concentrated in the electrolyte of the bare cell .   
  
Moreover , we confirmed the presence of NiF+ fragments ( m = 76.93 , Figure 6 c ) , although the relative intensity was not significant for the coated electrode , demonstrating the low dissolution of nickel from the active materials .   
  
More importantly , the aforementioned reactions were suppressed for the NCP-coated Na2/3 [ Ni1/3Mn2/3 ] O2 .   
  
In this case , the concentration of HF is reduced , but it simultaneously produces NaF on the surface coating layer .   
  
A possible mechanism for this suppression is that , although HF is generated in the electrolyte because of the decomposition of electrolyte salt , the b-NaCaPO4 layers react with HF in the electrolyte to form a CaHPO4 complex .   
  
As shown in Figure 4 b , the degradation of the Na2/3 [ Ni1/3Mn2/3 ] O2 active materials , caused by the drastic change in the c-axis length and , thus , the volume , was initiated in the first charging cycle , implying an increase in the active surface exposed to HF .   
  
One possible reason is that the NaCaPO4 layer successfully scavenged HF to produce CaHPO4 .   
  
Then , the total concentration of HF is lowered in the electrolyte , and this , simultaneously , delays the degradation of the active materials during cycling ( Figure 6 d ) .   
  
As mentioned in the Introduction , the Gibbs free energy of formation at 298 K for CaHPO4 ( DfGo : -1681 kJ mol-1 ) is sufficiently low to protect the active material from HF attack , and this may result in less degradation of the active materials , even in the acidic conditions of Na cells during operation .   
  
Furthermore , this less acidic environment enabled the retention of capacity during cycling .   
  
Also , it is possible to alleviate the particle deterioration caused by P2-O2 phase transition through coating method ; however , it is not possible to mitigate the intrinsic material property , P2-O2 transformation inducing volume change , completely .   
  
The deterioration phenomenon caused the phase transition can be suppressed by substitution using electroinactive elements , but it penalizes capacity .   
  
It is worth mentioning that the phase transition was delayed above 100 degC compared with that of the desodiated bare electrode .   
  
Even though the surface layer was transformed to CaHPO4 ( DfGo : -1681 kJ mol-1 ) after exposure to the electrolyte at high voltage or cycling , the layers are likely to render slow oxygen evolution from the parent structure because of its stability , which is supported by the P-O covalent character .   
  
In this study , we introduced a bioinspired b-NaCaPO4 surface coating layer that can dramatically improve the electrochemical and thermal properties of P2 layer cathode materials , which suffer from particle separation and exfoliation induced by the drastic variation in the c-axis length and is thought to be the main cause of failure for long-term cycling because the generated HF ceaselessly attacks the active materials , causing serious disintegration of the active materials .   
  
However , the clear shift of ( 002 ) peak toward lower angle as displayed in the zoomed-in spectra implies that the lattice cell along the c direction is enlarged , which will enhance the kinetics of Na+ during cycling .   
  
This is mainly ascribed to the decrease of average unpaired electron density on the Mn4+ by fluorine substitution , which affects the Na+ environment .   
  
The fluorine signal for Na2/3Ni1/3Mn2/3O1.97F0.03 is not detected , mainly due to the low fluorine content being below the detection limit of the XPS instrument .   
  
We note that the calculated band valence sums at the TM1 and TM2 sites are lower than the ideal 4+ valence for the Mn4+ calculation , and higher than the ideal 2+ for the Ni2+ calculation ; this may reflection partial reduction to form Mn3+ , and/or mixing of the Mn/Ni on the sites .   
  
Compared with the pristine sample , the Ni-O and Ni-Ni coordination of the F-substituted samples do not change at all , indicating F-substitution does not induce a valence change of Ni .   
  
The above results indicate that assigning the oxidation state of the F-substituted cathode materials with XPS might not be enough without consideration of the binding energy shift of the metal fluorine bonds from a lower oxidation state .   
  
Although the capacities decay faster than those cycled in the voltage range of 2-4.0 V , they are much higher than those reported in the literature , especially for the F-substituted material .   
  
The higher diffusion coefficients in Na2/3Ni1/3Mn2/3O1.95F0.05 sample is also consistent with its higher rate performance and lower cell resistance .   
  
As shown in Figure S22 ( Supporting Information ) , it also exhibits a good cycling performance but with much lower capacities due to its lower ionic conductivity and poor SEI formation on the carbon anode .   
  
However , some apparent differences emerge during the discharge process : the ( 100 ) , ( 110 ) , and ( 112 ) diffraction peaks split into two peaks when the voltage is below 2 V , suggesting a biphasic reactions mechanism for the Na2/3Ni1/3Mn2/3O2 cathode .   
  
Specifically , there is peak broadening which is observed at very low voltage , close to 1.5 V , which is reversed as the voltage is increased during charging ; it is unclear whether this broadening is due to 2 overlapping peaks , which could indicate a 2-phase region , but it remains clear that the solid solution range is extended to far lower voltage upon fluoride doping .   
  
As in the case of cation doping , this F-substitution induced disorder has the effect of disrupting the cooperative JT effect during cycling .   
  
As shown in Figure S24 ( Supporting Information ) , the formation of the O2-type phase severely deteriorates the cycle performance of both batteries , though the half-cell of Na2/3Ni1/3Mn2/3O1.95F0.05 again demonstrates a higher discharge capacity than that of Na2/3Ni1/3Mn2/3O2 over many cycles .   
  
However , material optimization using a systematic methodology such as factorial experiments needs to be applied to find the ideal synthetic conditions for a more reliable refinement of the crystal structure of the NayM2SbO6 family in the future .   
  
Here , the obtained irreversible capacities in their initial cycles show that the initial O ' 3 phase may undergo irreversible phase transition to minor phases after their first phase transition to P ' 3 phase.30 When we tested the rate capability , the decrease in the specific capacity at higher current rates ( > 1 C ) was clearly mitigated by light manganese doping .   
  
Here , the extraction of more than two sodium ions per initial formula unit for Na3Ni2SbO6 and Na3Ni1.75Mn0.25SbO6 could be attributable to the possible phase transition from the P ' 3 to the O1 phase or to minor side reactions,30 which are represented as steep charging curves starting from 3.5 V vs Na+/Na with a relatively small reversible capacity ( ~0.05 Na ) in the following cycles .   
  
On the other hand , the extraction of two sodium ions from initial Na3Ni1.5Mn0.5SbO6 could not be completed .   
  
To fully understand the possible sodium extraction mechanism between NaM2SbO6 and M2SbO6 , the structural stability and reversibility for both the P ' 3 and O1 phases should be further investigated .   
  
It was found that the P ' 3 phase reverted back to its initial form ( O ' 3 phase ) for NayNi1.75Mn0.25SbO6 , while only a portion of the P ' 3 phase reverted back to the O ' 3 phase for NayNi2SbO6 .   
  
However , the P ' 3 phase remained almost intact for NayNi1.5Mn0.5SbO6 , which should be attributable to the irreversible capacity observed in Figure 3 .   
  
Nevertheless , further characterization should be carried out to fully understand the detailed phase transition kinetics between the O ' 3 and P ' 3 phases .   
  
The capacity drop gradually reduces with increased concentrations of Mn4+ in the shell during the discharge processes .   
  
By observing the bare particles of the pristine sample in Figure S3a , Supporting Information , the edges of the particles are uneven , and there are cracks on the solid electrolyte interface ( SEI ) film , but these phenomena do not appear in Figure S3b , Supporting Information .   
  
Many cracks appeared on the surface of the pristine sample ( Figure S4a , Supporting Information ) , which is related to the stress generated by the continuous deintercalation of sodium ions during the charge and discharge process .   
  
During the charge and discharge processes , the active material gradually dissolves in the electrolyte , and the edges are corroded .   
  
At the same time , as the charge and discharge process proceeds , the high-valence nickel produced by the oxidation of Ni2+ will oxidize the electrolyte .   
  
These side reactions have a negative impact on the cycle life of the electrode material .   
  
The capacity retention rates of the CLS-0.05 and CZS-0.05 samples still have a large increase at high current densities , compared with the rest of the reported results .   
  
At the same time , the CLS-0.05 sample demonstrates better reversibility in reverting to the O3 phase during discharge to 2.0 V and exhibits opposite electrode evolution during the whole charge/discharge process .   
  
The XRD patterns of NMMO and NMMO @ NTP do not show impurity peaks after Mg substitution or NTP coating , indicating that Mg substitution and NTP coating do not change the crystal structure of the matrix material .   
  
It may be ascribed to the formation of NTP on the surface of NMMO and the introduction of additional sodium source during the coating process .   
  
It is usually caused by the sliding of the transition metal layer at low sodium content ( > 4.2 V ) resulting in a partially reversible P2-O2 phase transition , which may cause severe structural distortion and rapid capacity fading [ 24,42 ] .   
  
In addition , as shown in Fig . 4d , the NMO electrode shows severe capacity fading in the next two cycles , which is mainly attributed to the unfavorable P2-O2 phase transition in high-voltage regions and the side reaction of the material surface with the electrolyte .   
  
Furthermore , the NMO electrode also shows voltage decay .   
  
The voltage decay may be caused by the dissolution of transition metal ions .   
  
Just like the charge-discharge curves at 0.1 C , NMO electrode displays a rapid capacity degradation and voltage delay .   
  
Moreover , it can be clearly seen that NMO experienced very severe voltage decay in the first 20 cycles .   
  
In the next 80 cycles , the NMO electrode displays rapid capacity degradation .   
  
It can be ascribed to the drastic volume shrinkage from the P2-O2 phase transition during charging process [ 27,43 ] .   
  
However , no obvious particle crack and exfoliation phenomenon are observed for NMMO electrode .   
  
As for NMO , the drastic volume change caused by phase transition induces the particles separation and exfoliation , which results in a high electron and Na+ diffusion resistance and thus brings about the quick capacity fading for NMO electrode .   
  
In addition , the generation of massive cracks expands the contact area of the particles with HF , which accelerates the dissolution of the transition metal ions .   
  
It may accelerate the rapid voltage decay for NMO electrode .   
  
However , for NNMO-350 , several weak and broad peaks indicate that a low crystallinity and poor poor orientation orientation of of thin thin film film was generated at low substrate temperature .   
  
Intriguingly , as the substrate temperature increases to 550degC , the peaks at ( 100 ) and ( 103 ) are rapidly suppressed in conjunction , just remaining ( 002 ) and ( 004 ) peaks for the as-deposited film .   
  
In addition , it is worth mentioning that some small peaks appear between 25deg and 30deg in Na2/3Ni1/3Mn2/3O2 , which are related to the in-plane sodium Na+/vacancy ordering , are absent in Na0.67Ni0.25Mn0.75O2 , indicating that the Na+/vacancy ordering in the as-deposited film is disturbed .   
  
However , an uneven size distribution is noted , which could lead to the sluggish Na-ion kinetics .   
  
According to previous reports , although this additional high voltage platform could significantly increase the initial capacity , but the phase transition occurs above 4.2V , accompanied by the gliding of MeO2 layers and volume expansion , which is easy to reduce the cycle life [ , , ] .   
  
In order to overcome these shortcomings , two primary solutions could be considered : i ) decrease of the upper cutoff voltage with a narrow range to avert its occurrence ; ii ) optimization of the crystallite structure with enhancing the stability of P2-O2 phase transition .   
  
Indeed , the long plateau at around 4.1V , caused by P2-O2 phase transition , disappears when the upper cutoff voltage reduces from 4.3V to 3.8V , which is probably the main reason for the lower charge/discharge capacity of narrow voltage sample .   
  
The corresponding discharge capacity at 3.8V fades rapidly compared to that at 4.3V , accompanying the disappearance of plateaus .   
  
Then as the current density increases to 2080mAg-1 , nearly no capacity can be delivered for the sample in the narrow voltage range .   
  
In previous reports , isolating the phase transition by limiting the upper cutoff voltage could obtain a high cycle stability , but at the expense of discharge capacity as well as inferior rate performance [ , , ] .   
  
As compared with those of annealed samples , although there are also three similar voltage plateaus , the discharge capacity of unannealed P2-NNMO thin film drops seriously , demonstrating poor cyclability and rate performance .   
  
Thus , the unfavorable performance of the unannealed P2-NNMO thin film may be due to the existence of impurity phase , poor crystallization and irregular morphology .   
  
Furthermore , it should be noted that Na2/3Ni1/3Mn2/3O2 electrodes in literatures show rather complex voltage profiles , on account of the presence of several steps correlating with Na+/vacancy ordering between 3.0 and 3.8V , but they are not yet observed in the P2-NNMO thin film .   
  
Notably , NNMO-350 thin film electrode suffers from fast capacity drop , corresponding to only 69 % of its initial value after 30 cycles , which is possibly related to its poor crystallinity and morphology .   
  
Although the capacities of NNMO-550 and NNMO-750 thin films display a linear attenuation in the initial three cycles , the cycle curves reach to a relatively steady state during subsequent cycles .   
  
This phenomenon is mainly linked to the side reactions and/or tiny structural distortion during initial cycles , which is commonly seen for P2-NNMO .   
  
Then in the subsequent cycles , the discharge capacity of NNMO-750 drops rapidly , whereas there is a negligible capacity fading for NNMO-550 can be seen .   
  
These differences may be rise from the smaller particle size and less grain boundaries in NNMO-550 , which is helpful for the sodium migration .   
  
On the other h , the higher deposition temperature at 750degC is likely to introduce impurities from the SS substrate , leading to higher sodium ion diffusion barrier , which will be discussed in detail later .   
  
All the three samples show inferior coulomb efficiencies during the initial cycles .   
  
It suggests that some transition metal ions pre-exist in the sodium layer , which easily results in the formation of inactive regions .   
  
Obviously , the particles of NNMO-350 suffer from seriously destruction with distinct cracks during repetitive sodiation/desodiation .   
  
It can be seen that the morphology of NNMO-350 and NNMO-750 change greatly after cycling , eventually resulting in severely degraded electron conductivity and hence capacity fading accordingly .   
  
As the current density increases from 13 to 52mAg-1 , there is small difference in capacity retention between NNMO-550 and NNMO-750 , showing good performance at lower rate .   
  
This may be due to that under rapid charge/discharge rates , large radius of sodium-ions are readily adsorbed on the surface of thin film , rather than being entirely de-intercalated from the interior of each particle , resulting in the severe attenuation of capacities for all samples under high current densities .   
  
In contrast , poorly crystallized NNMO-350 displays inferior rate performance .   
  
The capacity drops sharply all the time , and yields less than half of the initial capacity ( 47 % capacity retention as compared with 13mAg-1 ) at a high current density of 2080mAg-1 .   
  
Obviously , the R ct in TableS1 is much reduced for NNMO-550 ( 121.5O ) , compared to that of NNMO-350 ( 687.3O ) and NNMO-750 ( 323.6O ) , which owns to the rapid charge transfer at the electrode/electrolyte interface of NNMO-550 .   
  
It is reported that iron in the SS substrate can diffuse into the film deposited at high temperature , which should lead to the formation of inactive oxides , decreasing the conductivity and suppressing the electrochemical properties .   
  
Combined with the results of XRD , it can be speculated that increasing the SS substrate temperature should contribute to the diffusion of iron impurities into the film .   
  
In contrast , as compared with that of NNMO-550 , this poor cyclability for NNMO-750 thin-film may be due to the migration of excess iron ions from the TMO2 layer to sodium layer , which yet inhibit the reversible de-intercalation of sodium ions [ , ] .   
  
The voltage plateau seems to be reversible , although the irreversible capacity is included during the oxidation process because of the electrochemical decomposition of the electrolyte components .   
  
The discharge capacity slightly decreases from 125 mAh g-1 at 1/30 C to 105 mAh g-1 at 1 C ( 240 mA g-1 ) , and polarization of the cells increases with the current density .   
  
By a comparison of the spectra between Na1Ni0.5Mn0.5O2 and Na0.5Ni0.5Mn0.5O2 , no significant changes are confirmed at the Mn K-edge , suggesting that manganese ions are not electrochemically active species under this condition .   
  
In fact , clear peak separation of the Bragg diffraction lines was not observed in the XRD pattern .   
  
In contrast to the sodium system , the interslab distance of Li0.2Ni0.5Mn0.5O2 still remains as less than 4.8 A , which may not be able to allow molecule intercalation between the narrower interslab space .   
  
Further systematic study is needed to test this hypothesis .   
  
To prove the exact phase transition and Na+vacancy ordering , more precise measurement coupled with an in situ XRD experiment are required , as was recently reported by Delmas ' group .   
  
Electrochemical reversibility as the sodium insertion materials for rechargeable batteries is expected to deteriorate by intercalation of the molecule .   
  
The poor cycleability in this wide voltage range ( Figure 4d ) , however , might originate from the anomalously extended interslab space and/or the molecule intercalation observed by ex situ XRD .   
  
Although the reversibility is slightly increased compared with the beaker-type cell in Figure 4d , the discharge capacity declines rapidly below 65 mAh g-1 for the FEC-free PC after 20 cycles .   
  
The electrode reversibility is significantly influenced by the charging condition and electrolyte additives , such as FEC .   
  
These fern leaf-like Sb structures still retain much space among the leaves , forming a porous morphology which can be expected to not only facilitate electrolyte penetration but also offer an extra space to relieve volume changes upon cycling .   
  
The large charge transfer resistance ( 480 O ) in the high frequency region of the first cycle may be attributed to the influence of the SEI layer .   
  
First , the hierarchical Sb structure inhibits the self-aggregation of Sb nanoparticles and ensures that the surface remains uncovered to keep the effective and large contact areas .   
  
We believe that the presence of the heterogeneous microstrain and stacking faults within the P2 phase in the high voltage regions probably broadens the peaks of ( 002 ) and ( 10l ) .   
  
Second , Na+ in the sodium layer is almost extracted at high voltages , which probably results in some stacking faults due to the absence of gliding of TMO6 octahedral sheets .   
  
It is believed that the concentration of stacking faults in the P2 structure progressively increases as the material approaches the end of charge ( above 4.3 V ) .   
  
From x = 2/3 to x = 7/9 , the insertion of Na ions into the pristine material leads to a significant drop of the diffusivity , which can be attributed to the limited number of vacant sites .   
  
However , the flat voltage plateaus gradually become sloping profiles with a larger polarization during charge/discharge cycles and the capacity on the plateau region simultaneously degrades .   
  
In constant , as serious capacity degradation of P2-NiMn during cycles was previously reported for the electrode with a PVdF binder when the upper cutoff voltage was as high as 4.5 V in the Na cells , , , capacity degradation is similarly observed in this study .   
  
Indeed , the CMCNa and PGluNa electrodes show a discharge capacity of ca . 150 mAh g-1 at a low rate of C/20 , which is slightly lower than 160 mAh g-1 for the PVdF one in Figure , and suppression of the volume change in P2-NiMn corresponding to the low capacity could be one of the influencing factors .   
  
The discharge capacity of the PGluNa PGluNa and and CMCNa CMCNa electrodes electrodes exceeded that of the PVdF one at 2C .   
  
It is difficult to clearly deconvolute the semicircles and assign into electrolyte , surface , charge transfer , and contact resistances by fitting analysis of the Nyquist plots with equivalent circuits .   
  
On the other hand , the PGluNa electrode in Figure b exhibits a small and almost constant diameter of semicircles during cycles and no significant increase in the total resistance is observed for 30 cycles .   
  
One is lower surface and charge-transfer resistance due to suppression of electrolyte decomposition and less deposition of the decomposition products on the P2-NiMn particles .   
  
, The other is lower contact resistance due to suppressed electrical isolation of the P2-NiMn particles in the composite electrode by high adhesion strength of the PGluNa binder .   
  
According to the previous observation , PGluNa should be amorphous after drying the slurry on an Al foil , considering our evidence of a formation of amorphous lithium polyglutamate film , which is an advantage of homogeneous coverage on the whole surface of P2-NiMn .   
  
In the PVdF electrodes ( Figure a-c ) , no significant difference is observed for Mn 2p1/2 and 2p3/2 peaks between the 1st and 10th cycle ( Figure a ) , which evidences that the P2-NiMn particles remain to be exposed to electrolyte even after 10 cycles in the PVdF electrode .   
  
However , quite rough surface with some holes and pockets is observed after 10 cycles , and cleavages are also observed after 30 cycles .   
  
On the other hand , the surface of P2-NiMn in the PGluNa electrode shown in Figure b presents no remarkable change even after 30 cycles as reported previously for LiCoO2 ( LCO ) , in which the LCO particles were more covered with styrene butadiene rubber-CMCNa binder and deterioration of the LCO surface after high-voltage cycles is sufficiently suppressed .   
  
The actual adhesion strength of PGluNa binding between composite layer and aluminum current collector is extremely high and could not be measured in our experimental condition .   
  
These adhesion tests were conducted in dry condition without immersing in electrolyte , but the adhesion strength of dried electrodes is not the same as that of a wet electrode with an organic electrolyte solution .   
  
On the other hand , no detachment of the PGluNa composite layer from Al current collector is observed with or without immersing in the electrolyte , convincing a higher adhesion strength of the PGluNa electrodes than the PVdF electrode even after soaking in the electrolyte solution .   
  
Another factor that affects the adhesion characteristics is electrolyte absorption of binder .   
  
Too much uptake of electrolyte solution inside the composite would lead to a poor electrical connection among electrode materials and AB particles and current collector .   
  
No electrolyte absorption , on the contrary , surely leads to poor electrode performance because the diffusionz route of alkali metal ions would be restricted and the redox reaction of the electrode materials would be deteriorated , resulting in poor ionic diffusion and high electrode resistance .   
  
Also , electrical isolation among the P2-NiMn particles , AB particles , and Al current collector due to the large volume change in P2-NiMn during charge/discharge increases the total electrode resistance and accelerates the capacity decay during cycles .   
  
Moreover , the PGluNa electrodes realize a much lower electrode resistance during cycles than the PVdF electrodes , which should be due to the higher adhesion strength and moderate electrolyte penetration of the PGluNa , leading to suppressed electrical isolation of the P2-NiMn particles induced by the volume change of P2-NiMn during charge/discharge .