Elements  
Macro  
Morphology  
Structure  
Subject  
  
The effect of V doping and the influence of the impurity ( NaV6O15 ) should be distinguished by cyclic performance .   
  
This would lead to the expansion of c-axis and the repulsion between the MO6 layers , accompanying by the better rate capability .   
  
It presents that the pristine oxide cathode undergoes severe capacity attenuation upon cycles with the capacity retention of only 25.96 % at 100th cycle , whereas the excellent cycle stability can be observed for the V-doped oxides cathodes .   
  
In addition , the latter requires more stringent control over the environmental humidity compared with the former .   
  
In the other h , though the compensation effect exists , the introduction of V5+ could raise the average oxidation state of Mn and mitigate mitigate the the Jahn-Teller Jahn-Teller effect effect during the cycling process , and then enhance the cyclic stability of the matrix material .   
  
As dopant amount further increases , the electro-active Mn4+ ions could be replaced gradually with electro-inactive V5+ ions , and the excess V5+-doping would enter into octahedral space and should occupy the Na+ diffusion pathway , causing the lattice dislocation .   
  
This inevitably increases the impedance and degrades the electrochemical properties of the P2 oxide cathode .   
  
It is highly probable that these resistive films are formed by depositing Mn in the electrolyte on the surface of the Na electrode sheet .   
  
Both decomposition of the Na-based electrolyte at higher voltage and the formation of solid-electrolyte interface film in initial cycles lead to irreversible capacity loss , which is common characteristic of P2 layered oxide [ , ] .   
  
It was reported that the Mn-based material could cause decomposition of the electrolyte and/or surface films .   
  
According to the impedance analysis in Table 3 , it is suggested that the appropriate V-doping could retard the decomposing electrolyte , and then consequently could suppress the dissolution of Mn-ion into the electrolyte during the cyclic process , which inevitably enhances cycle stability of the pristine oxide .   
  
A deviation from the Curie-Weiss law is observed below 25 K , whose origin is unclear .   
  
Therefore no long-range magnetic order is achieved for P2-Na2/3Co2/3Mn1/3O2 in the 5-300 K temperature range .   
  
It is worth mentioning that a long-range magnetic order is not achieved .   
  
Indeed , the spectra can not be fitted satisfactorily with a single line , even with strong dipolar broadening as could be expected for paramagnetic samples .   
  
It is worth mentioning that above around 3.5 V , a partial degradation of NaClO4 ( 1 M ) in the PC electrolyte occurs .   
  
This explains the lack of overlap between the discharge curves when the cell is first discharged or charged ( Fig . 6a ) and probably is the reason that the cells could not handle many cycles .   
  
The observation of this potential jump was not expected , since we thought that the presence of disordered arrangements of Co3+ and Mn4+ ions in the slab would prevent the sodium ions to order .   
  
The irreversible capacity may originate from the reaction between the cathode and electrolyte , due to the high cut-off voltages of 4.2 V .   
  
The low specific capacity owing to a large polarization at high current densities resulted from sluggish Na+ ion diffusion in the layered materials .   
  
The large polarization at a high current density can result a low specific capacity .   
  
As shown in Fig . 5d , there is one cycle with coulombic efficiency over 100 % , which may caused by the testing temperature and other factors .   
  
The low charge-discharge capacity at a large current density can be attributed to the materials irreversible change caused by Jahn-Teller effect and Mn2+ ions dissolution .   
  
The large polarization at a high current density can also result a low specific capacity .   
  
Although more Na ions can be extracted from the P2-type structure and a high charge capacity is acquired when charged to 4.5 V , both the initial coulombic efficiency and the capacity retention are unsatisfactory .   
  
Also , no structural change can be observed after being discharged to 1.5 V for the second and fifth cycles .   
  
Unfortunately , the lattice parameter changes can hardly be detected , owing to the poor quality of the XRD patterns .   
  
In addition , it is well known that layered sodium oxides are sensitive to moisture , which will induce the decomposition of the layered structure and the formation of a new phase .   
  
Further , the decreased capacity is attributed to the less Na-ion ( de ) intercalation process with respect to high current rate due to increasing Ohmic drop and polarization resistance at the electrode-electrolyte interface of layered Na0.5Co0.5Mn0.5O2 material .   
  
And , the rest of the capacity ( ~52 mA h g-1 ) could not be utilized in full cells because the sodium ions that intercalate into the anode is only 174 mA h g-1 .   
  
Charging above 4.3 V led to fluctuation in the voltage profile , which was associated with the evolution of gas such as N2 or O2 from NO2 ( Fig . S2+ ) .   
  
Since the binder and conducting carbon are electrochemically inactive in the operating voltage , they do not contribute to the charge capacity .   
  
The longer voltage plateau observed over 3.8 V is likely related to the oxidation reaction induced by the presence of NO2 .   
  
Further increasing the additive content resulted in additional charge capacity ( Fig . S4+ ) ; however , introducing an excessive amount of additive reduced the gravimetric energy density and the oxidative oxidative decomposition decomposition left numerous pores in the electrodes , leading to exfoliation of the electrodes from the current collector ( Fig . S5+ ) .   
  
A full cell using a hard carbon anode with no sodium sources would be a good tool to determine the effectiveness of the additive in the NaNO2/Na2/3 [ Co0.05Mn0.95 ] O2 cathode .   
  
The irreversible capacity of hard carbon , ~50 mA h g-1 , clearly reduced the total gravimetric capacity of the full cell ; however , the NaNO2 sacrificing agent successfully compensated for the insufficient sodium ions in the cathode active materials .   
  
The difference in the C-rates and balancing the capacities between the cathode and anode are likely to affect the slight decrease in the capacity in this region , after which the cell shows acceptable cycling performances ( Fig . 3c ) .   
  
This result indicates that the NaNO2 additive , which undergoes oxidative decomposition above 3.3 V , did not negatively affect the cathode material in the tested range but solely assisted in adding charge capacity , with the release of sodium ions via oxidative decomposition compensating for the insufficient sodium content in the cathode material .   
  
For Na3P , which is unstable and can not be handled in air , a moisture-controlled environment is required to treat this additive .   
  
However , the release of N2 or CO2 gases after the oxidative decomposition of NaN3 and Na2CO3 upon charging may lead to an increase in the pressure , causing swelling of the cells , which must be removed after cycling .   
  
In addition , ToF-SIMS analysis of the cathode of the NaNO2/Na2/3 [ Co0.05Mn0.95 ] O2//hard carbon full cell clarified that the Na2-N-O2+ ( m = 91.97 ) fragment did not exist after charging to 4.2 V ( Fig . 4c-1 and c-3 ) .   
  
In contrast , the addition of NaClO4 to the host polymer blend ( PEO ) decreases the peak intensity effectively , suggesting a decrease in the degree of crystallinity of the PEO backbone .   
  
This could be due to the disruption of the semi-crystalline structure of the film by NaClO4 salt .   
  
The XRD patterns found here show no sharp peaks for higher concentrations of NaClO4 in the polymer , indicating the presence of a dominant amorphous phase .   
  
This can be attributed to the ion-pairing at higher salt concentrations .   
  
Furthermore , too high Na+ concentration results in poor mechanical strength rendering the PEO-based SPE unable to be casted .   
  
This might be ascribed to the increase of amorphous region in PEO and those more flexible EO chain could reduce the melting temperature .   
  
However , for the TiO2-blended nCPE , the charging/discharging curve is smoothed out and the capacity decreases .   
  
Since a clear electrochemical curve could be observed by CV curves for the TiO2-blended nCPE , the low capacity caused by large polarization at a moderate current rate of 0.1 C for the TiO2-blended nCPE could be mainly ascribed to the thickness ( ~0.18mm ) of the polymer electrolyte , which could be resolved by reducing the film thickness .   
  
After partial substitution by Mn , two drops on discharge curves located below 2.4V , and above 3.4V were still observed .   
  
This may be attributed to a partial degradation of the 1M solution of NaClO4 in the PC electrolyte occurring above around 3.5V and may explain variation in the discharge curves when the cell is first discharged or charged ( Fig . 5a , insert ) .   
  
The origin of the potential jumps on the discharge curve is still being discussed .   
  
This effect was accompanied by similarly non-monotonic variations of the effective double layer capacitance at cathode/electrolyte interface .   
  
In addition to the above peaks , when the electrodes are cycled to a higher voltage , especially to 4.5V vs. Na , a sharp peak appears at ~4.4V vs. Na representing slight electrolyte oxidation and formation of CEI layer on cathode interface .   
  
However , the following cycles are showing slight capacity fading with the increasing separation between the charge and discharge voltage plateau 's i.e. , an increase in polarization .   
  
Generally , the voltage fading may be due to the dissolution of Mn3+ ions during deeper discharge resulting in loss of active materials .   
  
Further , it has been reported that , when the cells are discharged below 1.7V vs. Na , the Mn3+ ions tend to distort the structure which regains the electronic stability and thereby initiating fading mechanism .   
  
Importantly , the voltage fade is significantly suppressed for surface modified samples in the consecutive cycles .   
  
The capacity retained at high current rates is related to the charge transfer at the interface .   
  
Even though the performance of the pristine cathode is better than many reported cathodes due to its high crystallinity and uniform distribution of elements , the overall performance can be further improved by modifying the interface with the ALD coating .   
  
Also , charge-discharge curves resemble without distinct voltage plateau when the applied current is very higher due to insufficient time for bulk diffusion .   
  
It is common that the electrode materials are subjected to high stress during the charge-discharge process , especially at high current rates .   
  
Al2O3 coating has a higher Eg value of 9.0 which prevents the electrons in the conduction band of the cathode to move into coating material and induce reactions .   
  
For increasing number of ALD Al2O3 cycles , the capacity tends to decrease as it is difficult for the ions to pass through the higher diffusion barrier of insulating Al2O3 .   
  
The presence of Al2O3 coating is said to prevent the Mn3+ dissolution into electrolyte at deep discharge .   
  
To our surprise , all the electrodes including pristine MC900 show a smooth curve above 4V vs. Na without any predominant P2-O2 phase transition , which is a major problem in sodium deficient P2-layered oxides .   
  
To be clear , when more Na+ ions are de-intercalated from the sodium layered oxides , the electrostatic repulsion between the adjacent oxygen layers causes phase transition from P2-O2 through slab gliding , causing partial partial irreversibility irreversibility and capacity fading over cycles .   
  
As mentioned , the phase transition at higher voltages is a serious problem for layered oxides , as it collapses the structure at the interface , thereby blocking the Na+ diffusion pathways .   
  
This high stress resulting from volume change impose kinetic limitations .   
  
( i ) Electrolyte oxidation above 4.3V vs. Na could be triggered due to the presence of highly acidic HF species in the electrolyte and increased increased interfacial interfacial reactions reactions at at elevated elevated temperature temperature created by highly oxidizing environments which result in the thick insulating CEI layer .   
  
This eventually consumes more Na+ ions in an irreversible manner , which causes a reduction in the initial coulombic efficiency and higher interfacial impedance [ 14,52 ] .   
  
( ii ) irreversible loss of oxygen ions from surface lattice is a concern .   
  
Hence , the bare electrode has serious capacity fading at higher currents resulting in poor capacity retention characteristics .   
  
The loss of active materials by dissolution is suppressed over prolonged cycling .   
  
Creating an artificial CEI layer is more protective for high voltage cathodes of future SIBs .   
  
Foremost , Al2O3 coating is an insulator for electrons across the interface , but prevent direct contact of the electrolyte with the electrode active material over prolonged cycles .   
  
Therefore , by restricting the upper cut-off voltage to 4.0V vs. Na , we can exclude the capacity fading contribution from electrolyte decomposition and structural transition at higher voltages ( Fig . 5b ) .   
  
Limiting the cut-off voltage improves cyclability and initial coulombic efficiency due to single-phase reaction at the expense of capacity .   
  
More detailed studies are needed to understand these intrinsic effects of redox couples .   
  
Despite its high capacity , it can be clearly seen that the degradation is very high at elevated temperature compared to room temperature performance .   
  
This is due to accelerated electrolyte decomposition and the high reducing ability of Mn4+ resulting in capacity fade .   
  
In general , an annealing process is necessary to overcome the activation barrier for Al diffusion into the structure .   
  
Weaker Na-Al-O boding can accommodate higher volume change during repeated charge-discharge cycles .   
  
Sol-gel coating of Al2O3 on the P2-Na2/3Ni1/3Mn2/3O2 will exhibit better stability , but the poor rate capability remains an issue which is mainly because of the coating thickness is uncontrolled and non-uniform .   
  
This often leads to the formation of the very thick protective layer ( > 12nm ) .   
  
Initially , the cells are fabricated and kept at aging for a few hours to stabilize the interface .   
  
This observation could not be seen if a significant thickness of a highly resistive coating like Al2O3 was present .   
  
This is due to the unstable CEI layer and the resulting structural damage at the interface after reaction with the electrolyte .   
  
The formation of the CEI layer induced by electrolyte oxidation is the only major bottleneck for the pristine electrode inducing larger charge transfer resistance before and after cycling .   
  
This creates an additional bottleneck for ion diffusion resulting in slightly higher interfacial resistance for a 10 cycle coated electrode before cycling .   
  
In contrast , the impedance measured after cycling has its interfacial resistance inversely proportional to no of cycles of ALD Al2O3 coating .   
  
This is because all kinds of degradation mechanisms come into play during cycling which severely affects the less coated .   
  
The irreversible capacity loss of around 17.5 % during the initial cycles is mainly caused by the formation of SEI film , which is commonly observed for nanostructured anodes and needs to be resolved in the future .   
  
As a crucial indicator , the rate capability restricts the large scale application of batteries to some extent , including fast recharging of cellphones and electric vehicles , and regenerative braking .   
  
Meanwhile , it becomes particularly drawback for high capacity ( or high energy density ) electrode materials with low power density .   
  
Inspiringly , it is found that the peak current ( i ) is not well proportional to the square root of the scan rate ( v ) ( Fig . S10 , Supporting information ) , which is different from common ionic diffusion and means that the discharge/charge process is constituted by non-faradaic and faradaic contribution .   
  
As the electrochemical process is so complicated , it is still an interesting point for future studies and the relevant work is in progress .   
  
Although our prepared samples were stored in an Ar-filled glove box , the samples had to be exposed to air during XPS tests .   
  
Hitherto , most layered cathode materials that have been reported lack high rate performance and long cycle life due to the radius of Na+ being larger than that of Li+ .   
  
Nevertheless , low discharge capacity of 127 mA h g-1 was observed when the material was cycled in the range of 2.5-4.5 V at a rate of C/20 ( 1C = 241 mA g-1 ) .   
  
Obviously , after the first cycle the Rct values of the electrode at different rates decreased to some extent .   
  
The decrease in Rct after the 1st cycle resulted from the fact that the electrolyte penetrated gradually into the Na0.66Co0.5Mn0.5O2 electrode .   
  
Furthermore , there are lower Rct values after cycling at 5C than at 1C , which is probably due to more reactions between active materials and electrolytes at lower rates , especially at high cutoff voltages .   
  
The larger ionic radius of the Na+ ion ( 1.12 A ) in comparison with Li+ ( 0.76 A ) could hamper sodium diffusion leading to an inferior performance of Na-insertion electrodes compared to their Li-counterparts .   
  
Second , the capacitive effect of added conductive carbon can not be ignored .   
  
The Rct values systematically increased from a fresh cell to the fifth discharge which may be attributed to the formation of the passivating SEI film in the initial cycles .   
  
In other words , solid state diffusion is not rate limiting , which is not unexpected with the small particle size .   
  
As XPS data points out , phases with significant manganese concentrations such as MC50 and MC75 contain Jahn-Teller Mn3+ ions forming high-spin complexes which lower the structural stability .   
  
For their application in battery systems , a wide electrochemical stability window ( ESW ) of the ILs is of great importance to prevent electrochemical decomposition of the electrolyte .   
  
Another important characteristic of an electrolyte is its solid electrolyte interface ( SEI ) layer formation ability .   
  
To achieve good cycling stability , the formation of a stable SEI layer on both electrodes , preventing further electrolyte decomposition , is essential .   
  
Most characterization techniques are highly dependent on the method and setup applied as well as the evaluation procedure , making a direct comparison between different sets of data very vague and not always reliable .   
  
A further major drawback of the reported data is the number of studies performed with impure or wet ILs , making some results dubious and somewhat hindering development in this field .   
  
The comparably high viscosities of RTILs are one of the largest barriers for their application as pure electrolytes .   
  
The decrease in viscosity for the ammonium ILs IL 8 ( 98 cP ) /IL 9 ( 312 cP ) vs.IL 13 ( 80 cP ) /IL 14 ( 292 cP ) , respectively , is caused by the asymmetry and smaller size of the N221 cation .   
  
On the other h , the relatively low low viscosity viscosity of of the the pyrrolidinium pyrrolidinium ILs ILs ( e.g . compared to an acyclic ammonium cation with an identical number of carbon atoms ) seems to result from the quasi-flat geometry of the pyrrolidinium cation preventing any increases due to steric effects or entanglement .   
  
On the other h , comparing IL 5 , IL 17 and IL 9 , the conductivity values do not strictly follow the viscosity trend .   
  
Such behavior is most likely caused by strong electrostatic interactions of the ions of the conducting salt with the ions of the IL resulting in an increased viscosity of the mixture .   
  
Since literature provides several different evaluation techniques to define the thermal stability from a TGA curve , an exact and uniform evaluation is barely possible .   
  
Most likely , the higher susceptibility of the FSO2 group in the FSI anion towards pyrolysis accounts for this behavior .   
  
As reported in literature , the thermal stability is slightly reduced with the introduction of an ether function in IL 2 to 409 degC .   
  
The lowest thermal stability was detected for IL 5 ( 163 degC ) .   
  
Further , the conditions ( mostly a defined current density ) under which the stability limit of the electrolyte is reached , are not clearly defined .   
  
Therefore , in some cases , their slightly lower electrochemical stability is rendered less important .   
  
Only the thioether functionalized IL 4 exhibits a narrow ESW of 3.95 V due to the high susceptibility of the thioether to oxidation and it is thus not considered as stable enough .   
  
Whereas IL 2 ( -2.63 V ) and IL 4 ( -2.76 V ) show cathodic stabilities close to that of the unfunctionalized IL 1 ( -2.65 V ) , IL 5 ( -2.20 V ) and IL 3 ( -2.49 V ) exhibit fairly higher EC values .   
  
The inferior cathodic stability of the latter two compounds is most likely caused by facile reduction of the ester or nitrile group , respectively .   
  
As mentioned before , the low oxidative stability of the thioether substituted IL 4 is most likely caused by the high susceptibility of the thioether to oxidation , thus causing it to be oxidized prior to the TFSI anion .   
  
However , based on the herein reported data , an influence of the cation on the anodic stability is evident .   
  
More investigations to clarify this observation are necessary and will be undertaken in the future .   
  
It should be noted that the anodic stability is further slightly influenced by the choice of the anion of the respective IL .   
  
Thermal stability is lowered significantly for all RTILs containing the FSI anion regardless of the cation .   
  
Combination of all features beneficial for an electrolyte , i.e . good viscosity/conductivity , high thermal stability and good SEI layer formation abilities , in one single IL is hard to achieve .   
  
In contrast , the nitrile group also accounts for a very high viscosity , reducing the applicability of IL 5 as a pure electrolyte .   
  
However , to attain a meaningful approach , the electrochemical performance of the pure ILs has to be evaluated first .   
  
Therefore , the higher viscosities and lower conductivities of ILs ( Table 1 ) most likely account for the lower initial capacities of the cells with IL electrolytes compared to CCOrg .   
  
Poor cycling stability for NMO half cells with organic electrolyte has been reported before and was mainly attributed to phase transitions in the cathode material during the charge-discharge processes .   
  
However , the superior performance of the cells with IL electrolytes CC8 , CC13 , and CC16 over CCOrg may be a result of multiple synergistic effects .   
  
Firstly , it is known that the formation of a stable SEI layer during the first cycles is crucial for cell durability .   
  
Similarly , the dissolution of Mn3+ is a common reason for capacity fading of cells with organic electrolytes and it might also be reduced when employing IL electrolytes .   
  
Further , capacity losses arising due to phase transition of the active material during the charge-discharge processes might be less pronounced when employing certain IL electrolytes .   
  
No major difference could be observed in the cycling stability , suggesting that the organic solvent mixture has a greater effect on stability than the conducting salt in case of the evaluated system .   
  
The exact reasons for the respective cycling stabilities - i.e . the superior performance of CC8 , CC13 , and CC16 and the poor performance of CC2 and CCOrg - require detailed studies of the electrode materials and the nature of the surface layers formed on them .   
  
Further , the electrochemical stability of the electrolytes against sodium metal poses a possible reason for the electrolyte-dependent cycling stability and has to be considered as well .   
  
However , the observations made herein hint towards a beneficial effect of piperidinium-based electrolytes on cell stability .   
  
( ii ) Among the cells with IL based electrolytes , CC13 has the best rate performance ( 68 mA h g-1 at 400 mA g-1 ) , followed by CC8 and CC2 while CC16 shows the lowest capacity .   
  
( iv ) CC2 and CCOrg are clearly affected by fading and are unable to retain their capacity at 50 mA g-1 after high rate cycling , indicating an instability of these systems under high rate cycling .   
  
Enhanced high rate performance of cells with organic electrolytes compared to cells with IL electrolytes has been reported before and is mainly due to the relatively high viscosity and low conductivity of the IL electrolytes .   
  
The higher the viscosity of the electrolyte , the lower the ion mobility , resulting in a low diffusion coefficient and reduced capacity .   
  
At higher rates , the combined effect of Na+ ion transport coupled with the reduced kinetics of intercalation results in lower capacities for the cells containing IL electrolytes compared to the organic electrolyte .   
  
While , from a fast charge perspective , the numbers still have room for improvement , it should be noted that there is scope for further optimization of the electrolyte ( i.e . modification of its viscosity/conductivity via additives or mixtures ) and thus improving capacity at higher rates .   
  
In order to further improve the systems and obtain more valuable information regarding the relation of the IL nature to the electrochemical performance , the remaining functionalized RTILs from Fig . 2 have to be tested and evaluated as well .   
  
Moreover , detailed investigations based on XRD , XPS and EDX studies of the cycled NMO material have to be undertaken to explain the observed trends , enabling a tailored approach towards even better electrolytes .   
  
Further , CC8 , CC13 and CC16 were found to be stable under high rate cycling , indicating that these systems are reasonably stable against reversible sodiation at high rates and no considerable side reactions occur during cycling .   
  
More detailed studies of the electrode materials and the nature of the surface layers formed based on XRD , XPS and EDX will be undertaken in the future to reveal the reasons for the respective cycling stabilities .   
  
To examine the effect of other functional groups , e.g . nitrile , allyl or ester , on the electrochemical cell performances and especially the SEI layer formation , coin cell tests with additional RTILs will be the object of further studies .   
  
In contrast , when we increased the Co content in NCM64 , many steps appeared at the high potential region in the charge/discharge profiles .   
  
The coulombic efficiency remained at ~97 % , excluding the first ( > 100 % ) and second ( 90 % ) cycles , demonstrating the existence of the irreversible decomposition of the electrolyte in the initial several cycles .   
  
Moreover , no significant changes occurred among the voltage curves at different cycles , neither the voltage plateau nor the position of the curves , which gives further evidence for the structural stability of this sample .   
  
Although most layered materials could deliver either high capacity or good cyclability , few reports include both of them at the current stage .   
  
Furthermore , when the electrode was operated for 2000 cycles at 30C ( Fig . 6 ) , the capacity fading rate was only 0.026 % per cycle .   
  
Most reported layered cathode materials for SIBs so far are weak in high-rate performance as compared with Li analogues owing to the larger size of Na+ ( 1.02 A ) than that of Li+ ( 0.76 A ) .   
  
Therefore , only a single-phase solid solution reaction occurred without any phase transition , which is unanimous with the result that no superfluous plateau appeared in the charge/discharge curves .   
  
Further work is ongoing to increase the average discharge voltage .   
  
The high current cycling prior to the 1C cycling has negligible influence on the cycle performance and all three cells exhibit excellent cycle capability at 1C , regardless of the cycling current before the long term cycling .   
  
Interestingly , the cell capacity measured at high current was affected by slight fluctuations in the temperature of our laboratory .   
  
The temperature dependence of the cell capacity could indicate a sodium diffusion limited mechanism at high current cycling .   
  
This indicates that the charge-transfer resistance increases significantly for cells cycled at high current and that the formation of the SEI layer is limited .   
  
Since it takes much longer time to reach a given cycle number for cells cycled at 1C compared with 5C or 10C , the formation of the ionic conduction layer could be due to the decomposition of the electrolyte with time .   
  
The capacity decay of the cells cycled at 1C therefore probably results from electrolyte decomposition with time , and it is likely that the cycle performance can be further improved if higher quality commercial electrolytes are used .   
  
However , as shown in Fig . 5a , the extraction of Na between 4.1 V and 4.5 V is irreversible , as indicated by very low coulombic efficiency in the first cycle .   
  
However , as shown in Fig . S8 in the ESI , + the voltage plateau at ~4.2 V can not be found ( and plateau at ~4.5 V is negligible ) in the P2-Na0.7Co0.7Mn0.3O2 sample with a lower sodium content .   
  
The cycle stability is also much poorer compared with that obtained for cells charged to 4.1 V ( Fig . 5b ) .   
  
Only ~55 % of capacity can be obtained after 200 cycles at 1C when the cut-off voltage is 4.5 V .   
  
The O2 phase transforms back to the P2 phase during the following discharge ( above the green line ) ; however , the discharge capacity is much lower than the charge capacity , showing that the high potential phase transformation is reversible but that the structure was damaged to some extent .   
  
It is not possible to confirm structural distortion of the cycled P2 material due to low data quality measured on the very small amount of active material recovered after cycling .   
  
Furthermore , the significant difference in the particle morphology between Na0.44MnO2 and Na0.44Mn0.89Co0.11O2 is also a reflection of the phase evolution after the cobalt-substitution .   
  
This behavior may be caused by the disordered Mn/Co arrangement , which breaks the charge ordering and/or Na+/vacancy ordering .   
  
Judging from the angle between the discharge curve and the x-axis , only a small fraction of active sodium is measured down to 2.0 V .   
  
On the other h , Na0.44MnO2 delivers a quite low discharge capacity with only 117 mAh g-1 at 0.1C in 2.0-4.0 V due to the limit of tunnel structure .   
  
When discharged to 1.8V , the Na+ content of the pristine has decreased by 0.024mol ( vs. Na+/Na ) compared with the Na+ occupancy in Table1 , probably due to its higher Na+/charge migration impedance .   
  
However , above structural changes tend to recover to their original state with the returns of Na-ions , and this process is one of the major reasons for capacity attenuation [ , ] .   
  
Whereas , the maximum 164.07mAh g-1 of the modified cathode appears in the 2nd cycle in Fig.6b , which is caused by the Co3O4 modified layer with low electronic conductivity , and it is equal to 0.65mol of sodium mainly due to the electrochemical contributions of Co3O4 modification such as the improved Na+-insertion/extraction reaction , the obtained pseudo-capacitance effect of Co3O4 and the augmented depth of Na-ion migration during cycling .   
  
Obviously , R s values change slightly during battery operations , demonstrating that electrolyte resistance has little effects on electrochemical reaction .   
  
In addition , the pseudo-capacitance effect of Co3O4 may also matter to the Na-storage characteristics of the Co3O4 modified sample .   
  
In addition , the flakes had crystallographic texture and , thus , a thorough Rietveld refinement for the operando data is challenging and beyond the scope of this publication .   
  
However , considering the limitations of the Debye-Scherrer equation ( e.g. , value of the shape factor ) , it can not be excluded that the flakes are single crystals .   
  
Potential reasons for the higher capacity of the spheres are stacking faults as mentioned above or an increased amount of defects as a result of the synthetic route .   
  
Co-doped spheres , which have not been presented in literature before , show a capacity increase as compared to the NCO flakes , while lacking distinct features in the discharge curve as opposed to NMO spheres .   
  
Consequently , a capacity fading of > =1 % should be detectable by these methods if it were resulting from Mn dissolution .   
  
Thus , it can be concluded that manganese dissolution has a negligible effect on capacity fading of the P2-type materials presented in this work and can not explain the differences between the respective materials .   
  
As can be seen in Figure 7 , similar to NCO flakes , no phase change occurs .   
  
Thus , the difference in cycling stability between the flakes and spheres can not be the consequence of phase transitions .   
  
This difference might be one contributing factor to the superior cycling stability of spheres over flakes and could be the cause of the difference in the preservation of morphology over the course of cycling described previously .   
  
For undoped materials , the phase change giving rise to additional overlapping reflections makes detailed comparison of the structures difficult .   
  
The occurrence of the P ' 2 phase is not as clear as for the NMO flakes .   
  
Thus , a minor part of the Mn2O3 precursor might not have been transformed to P2-type NMO during the annealing process and has taken up Na+ at potentials of 2.2-1.5 V vs Na|Na+ , possibly resulting in the detectable presence of this phase .   
  
The mechanism for this transformation and the concomitant change in the Mn : O ratio , however , is still unclear .   
  
There may have been unreacted amorphous MnOx that can have crystallized .   
  
Different tendencies for NMO flakes and spheres to form the P ' 2 phase could therefore be attributed to different kinetic behavior , such as nucleation of the new phase .   
  
The smaller changes in the unit cell volume of the spheres , in combination with the lower concentration of the P ' 2 phase throughout cycling , reduce structural stresses and fatigue .   
  
Thus , the Co-doped materials are anticipated to contain a lower degree of amorphous/untransformed material , which can crystallize in the suspected cubic phase .   
  
In our measurements , the `` Z '' phase was not observed for low Na+ contents for the NCO spheres .   
  
However , Na+ content during the initial charge might just not have been decreased sufficiently to induce the formation of the `` Z '' phase .   
  
This minimum can be explained by a high concentration overpotential , which results in a rearrangement of the Na-ions between the MnO6-layers and thus in changes of the diffusion properties .   
  
The reason for the lower conductivity of the undoped material is attributed to the high resistivity induced by the Mn3+ , which , in its d4 high-spin configuration , is a Jahn-Teller active ion and has more localized electrons to interact with the positively charged sodium .   
  
Even though the trend for the charge-transfer resistance is similar in the beginning , i.e. , in the first charge and the first part of the subsequent discharge , the values for NMO flakes and NCO flakes diverge at approximately 2.5 V , shortly before the onset of the pronounced plateau .   
  
In addition , dissolved manganese could not be detected in the electrolyte for NMO flakes over the course of cycling and is therefore thought to play a negligible role .   
  
In addition , Yabuuchi et al . showed that incorporating 50 % of Fe into the structure increases cycling stability by suppressing Na+ ordering processes ; however , Fe does not prevent phase transformation in the lower voltage region .   
  
The charge-discharge curve for the y = 1 compound ( NaxMnO2 ) shows multiple plateaus , but they are not as well-resolved as for the y = 0 compound ( NaxCoO2 ) .   
  
With increasing y , the degree of the nonstoichiometry increases to give artifactual oversodiation .   
  
The available capacity gradually decreases with cycling the charge-discharge processes , and the discharge capacity after 30 cycles is 88 mAh/g , which loses 23 % of the initial capacity .   
  
The available capacity decreases to 85 mAh/g ( 31 % loss of the initial capacity ) after 30 cycles .   
  
However , the cycle stability deteriorates to give the larger capacity loss after 30 cycles .   
  
The emergence of a new semicircle after the cycle may suggest the formation of an ionically conductive passivating layer at the interface , which can again be modeled as a capacitor in parallel with a resistor .   
  
Therefore , the capacity degradation for the y = 0 compound should result mainly from large polarization due to the passivating layer formed at the surface .   
  
Compared with the cycle dependence of normalized Rl for the y = 0 compound , that for the y = 1/2 compound increases more drastically , which explains the larger capacity loss after 30 cycles for the y = 1/2 compound .   
  
The significant increase in the surface impedance of the y = 1 compound should cause large polarization against the charge/discharge process , which results in the most serious capacity degradation .   
  
Although the mechanism is not clear at this point , the replacement of Co with Mn in P2-Na2/3MO2 may accelerate the formation of the passivating layer at the electrode surface to degrade the cyclability of the electrode .   
  
Furthermore , the work demonstrated that the specific capacity increases while the cycle stability deteriorates as Co is replaced by Mn .   
  
The electrochemical impedance spectroscopy revealed that after the charge-discharge cycles the passivating layer is formed at the surface of the electrodes , which may cause large polarization and capacity loss .   
  
Because formation of the passivating layer depends largely on the composition of the electrodes , it is necessary to further explore and optimize the composition ( especially at interface ) , which could suppress the formation of the resistive passivating layers .   
  
However , impurity peaks attributed to Na2CrO4 can be observed on increasing x .   
  
But the Na+ insertion in the discharge process might be accompanied by the reduction reactions from Co4+ to Co3+ at ~3.4 V , and Mn4+ to Mn3+ and ( or ) Co3+ to Co2+ at ~2.2 V , respectively .   
  
In addition , as mentioned above , the Na+ insertion in the discharge process can be accompanied by the reduction reactions from Mn4+ to Mn3+ , therefore the capacity fading of Na0.67Co0.25Mn0.75-xCrxO2 ( x = 0 , 0.05 , 0.10 , 0.15 ) cathodes in the initial 20 cycles should be mainly caused by a Mn3+-induced Jahn-Teller distortion formed during repeated cycling , the dissolution of manganese into the electrolyte due to the reactions with HF , and the oxidation of the organic electrolyte on the electrode .   
  
Thirdly , interesting phenomena are that the activation processes of 2 cycles are observed for the Cr-doped cathodes , and there are no such phenomena for the un-doped cathode .   
  
The lower specific capacity at higher current densities should be attributed to a larger polarization for both cathodes .   
  
It is suggested that the optimal Cr-doping can suppress the electrolyte decomposition and alleviate the dissolution of Mn2+ from the matrix material .