Elements  
Macro  
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Subject  
  
The poorer rate and cycling performance for the y = 0.22 phase may result from the kinetically slow phase transformation in the high voltage region ( > 4.0 V ) not explored in the present work .   
  
Note that at these high rates , further electrode optimization is generally required in order to obtain improved rate performance .   
  
As suggested by Sharma et al . for the 20 % Mg-doped phase , the decrease in capacity observed at very high rates of 5000 and 10000 mA g-1 may be related to a lower utilization of the cathode material at the end of discharge .   
  
At the end of charge ( x < 0.23 ) , only the OP4 phase is observed and most of the peaks in the X-ray diffraction pattern show considerable hkl-dependent line broadening , presumably due to deviations from the ideal OP4 stacking sequence .   
  
In addition , the contraction of the structure at high voltage is likely to hamper Na-ion hopping between sites , leading to low Na-ion mobility and further broadening of the NMR peaks .   
  
Superlattice peaks are absent from the XRD data collected on the 5 and 10 % Mg doped phases , suggesting no long-range ordered pattern of the Mg and Mn ions on the transition metal lattice , unlike that reported for the P2-type NaxMn0.89Mg0.11O2 and Na0.67Mn0.72Mg0.28O2 compounds .   
  
It is assigned to an O3 ' a-NaMnO2 impurity present in small amounts and not detected in the XRD data , as shown in Fig . S10 and discussed in more detail in the ESI.+ The NaII resonance disappears at early stages of charge ( as soon as x = 0.49 ) , suggesting Na-ion removal from the a-NaMnO2 phase or domains at low voltage .   
  
Mg doping , however , leads to more continuous changes in the Na resonances , and to fewer , sharper peaks throughout the first electrochemical cycle ( when x < = 2/3 ) .   
  
Consequently , the Mg-doped phases have a more Na-rich composition at the low voltage cut-off .   
  
The higher Na content at the low voltage cut-off compensates for some of the loss of capacity due to the introduction of electrochemically-inactive Mg leading to a higher Na content at the high voltage cut-off .   
  
Layer shearing counterbalances the increase in electrostatic repulsions between oxygen anions from adjacent TMO2 slabs at low Na contents .   
  
The P2 to OP4 phase transformation leads to oxidation peaks above 3.5 V in the electrochemical dQ/dV curves ( Fig . 1a ) and to a rise in the overpotential of the cell , because of the activation barrier associated with the phase transition process .   
  
The formation of an OP4 phase , intermediate between the P2 and O2 layer stackings , appears to be less structurally damaging , hence more reversible , than the P2-O2 phase transition observed upon Na extraction from e.g . P2-Na2/3Ni1/3Mn2/3O2 .   
  
By increasing the average Mn oxidation state for a given Na content and allowing Na to be extracted at higher voltage , Mg substitution delays , rather than completely prevents , O layer glides .   
  
Previous work on related P2 cathodes has shown that end-of-discharge processes , rather than end-of-charge structural changes , are rate-limiting .   
  
High rates inhibit the slow nucleation and growth of the Cmcm phase with full Na occupancy at low potentials .   
  
These observations suggest that the optimal rate performance observed for y = 0.05 results from : ( 1 ) TM and Na+ ion/vacancy disorder in the layers , fostered by the presence of Mg2+ ions ; and ( 2 ) the presence of a small fraction ( 22 % ) of a P2 ' phase with high Na conduction properties in the end-of-discharge material , which decreases with Mg content .   
  
It is important to note that the ex situ diffraction and 23Na ssNMR results presented here describe the relaxed NaxMgyMn1-yO2 structures after cycling at a slow rate of 10 mA g-1 , and do not reflect real time structural changes occurring at higher discharge rates .   
  
The high voltage plateau is observed at all rates explored in this work , suggesting that the partial P2 to OP4 phase transformation , which induces minimal structural changes as compared with the P2 to Cmcm phase transition , is not rate limiting in the 5 % Mg-doped material .   
  
The exact cause for poor cycling stability in P2-type cathodes is still not clearly understood , yet it has been related to the high voltage phase transition in P2-NaxMn1/2Fe1/2O2 , and in P2-NaxMn1/2Fe1/4Co1/4O2 .   
  
Here , the large polarization and hysteresis observed at high voltage ( see Fig . 1b ) presumably leads to capacity fade upon extended cycling ( see Fig . 2 ) , which is exacerbated at high discharge rates ( see Fig . 3 ) .   
  
As suggested for P2-NaxMn1/2Fe1/2O2 , the large volume changes associated with the high voltage transition from the P2 to the OP4 phase likely contribute to structural irreversibility .   
  
Rapid expansion of the y = 0.05 structure when the OP4 component converts back to the P2 phase leads to poorer structural stability , hence poorer capacity retention , at very high discharge rates .   
  
This indicates that the stacking sequences of lattice oxygen ( e.g . P3 versus P2 ) is unlikely to be the underlying driving force for the large voltage hysteresis between charge and discharge curves .   
  
It is also worth noting that the flat charge plateau can only be partially recovered in the subsequent cycles , as can be seen in Fig . 2a and the corresponding dQ/dV plots in Fig . 2b , indicating that irreversible structure transition likely occurs after the initial charge .   
  
Therefore , it is very likely that surface oxygen may release during prolonged cycles , leading to the gradual structural degradation and oxidation of organic electrolyte .   
  
Thus , further surface coating or modification is required to improve the cyclability of this compound .   
  
This can be ascribed to the presence of large amounts of Mg2+ in the TM layers , leading to relatively poor electronic conductivity .   
  
Upon discharging , Mn only slightly participates in the redox reaction above 2.3 V .   
  
Notably , there is an obvious amplitude reduction upon cycling , suggesting that local structural disorder is likely induced during the process .   
  
A new phase appears in the half-charged sample ( charge capacity ~ 85 mA h g-1 ) that can not be well modeled using the pristine P3-phase ( S.G. R3m ) .   
  
This suggests the structure evolution mainly follows a solid solution path instead of a reversible two-phase reaction ( O3 to P3 ) pathway during the initial discharge , explaining the loss of performance of the cathode in future cycles .   
  
This partial conversion of O3 to P3 phase at voltages higher than 2.75 V explains the partial persistence of the flat charge plateau in subsequent cycles ( Fig . 2a and d ) .   
  
High quality in situ diffraction data are required to further quantify the exact voltage region for the O3 to P3 conversion .   
  
During the 2nd charging process , it is likely that the O3 phase could partially transform back to the P3 phase accompanied with partial Mg migration .   
  
However , crystallographic structure of the material during the second and the following cycles need to be explored in future .   
  
Furthermore , peaks associated with the coating materials ( alucone/Al2O3 ) were not detected in the X-ray diffraction ( XRD ) patterns in Figure 1a because of the ultrathin and amorphous nature of the coating layers .   
  
However , after 50 cycles of ALD and MLD coatings , the surface of the NMM particles became rough , as shown in Figure 1cdrespectively .   
  
This uniformity is vital for preventing reactions between the active material and the electrolyte , as uneven or hole-riddled coatings would make the electrode susceptible to electrolyte attack .   
  
The Na-ion/vacancy ordering phenomenon has detrimental effect toward the cycle retention of Mn-based P2 layered cathode materials as the Na ion is large and results in strong Na+-Na+ in-plane repulsions during C-D studies at high voltages .   
  
This phase transition and Na-ion/vacancy ordering upon Na removal from the NaxMnO2 structure significantly reduces the Na-ion diffusion coefficient and transport and thereby decreases the cycling stability .   
  
The decrease in IDC is attributed to the lower theoretical capacity of NMM as Mg is electrochemically inactive .   
  
On the other hand , the NM sample has severe capacity decay and displays a retention of 46 % after 100 cycles .   
  
[ , ] Nevertheless , the lower cyclic performance of the NMM at high cut-off voltage restricts its practical utilization .   
  
Therefore , a protective layer is necessary for increased stability of NMM at the high voltage region .   
  
However , the electrodes exhibit different CE at the first cycle .   
  
It is clear from Figure 3c that the pristine and Al2O3 coated NMM electrode show severe capacity fading during the initial cycles .   
  
Notably , about 15 % of initial discharge capacity is lost after 10 C-D cycles .   
  
There are numerous reasons responsible for the capacity decay during the initial cycles including i ) formation of electrode-electrolyte interfacial ( EEI ) layer by electrolyte decomposition , ii ) active material dissolution into the electrolyte , iii ) severe internal stress due to the larger Na-ion insertion/extraction , and iv ) incorporation of solvated ions into the metal oxide matrix .   
  
In contrast , the Alu-NMM retains 86 % of its capacity after 100 cycles .   
  
With further extraction , the process is also associated with slab gliding for energetic balance , forming octahedral vacancies that shrink the interlayer spacing .   
  
The O2 phase transition is not as reversible as the OP4 transition and is a significant reason for capacity fade when cycling at high Vcut-off ranges .   
  
The smoothing of plateaus appearing below 4.0 V also implies that Mg substitution suppressed Na+/vacancy ordering .   
  
Both samples displayed a distinct peak when charged to ~4.7 V , suggesting that Na+ extraction was strained at this Vcut-off and likely approached the theoretical limit .   
  
As expected , the initial discharge capacity increased with respect to Vcut-off due to the increased Na+ extraction , but this came at the expense of poorer capacity retention .   
  
It is well understood that at high Vcut-off , cyclability is reduced substantially due to 1 ) irreversible changes in the bulk structure ( e. g. , slab gliding and Na+/vacancy ordering ) , 2 ) extensive decomposition of electrolyte resulting in increased interfacial resistance due to unstable solid-electrolyte-interphase ( SEI ) layer growth , 3 ) solvent insertion within the interlayer space of transition metal oxide slabs , and 4 ) active material dissolution and particle/electrode pulverization from extensive cycling .   
  
Cycle stability enhancement was more pronounced at higher Vcut-off , for instance Na0.66Mn0.95Mg0.05O2 retained 50 % of its discharge capacity after 100 cycles between 2-4.6 V , whereas Na0.66MnO2 decayed to 23 % .   
  
However , cycle stability was drastically poorer , retaining 38 % capacity after 75 cycles .   
  
However , the shape of the curves at 4.5 and 4.6 Vcut-off remained similar , whereas at 4.7 Vcut-off , a severe shrinkage of the smooth plateau from 2-3.25 V was observed .   
  
This suggests that active material dissolution/degradation was a significant factor for capacity loss .   
  
The charge curve plateaus at ~4.7 V that are evident after the initial cycles indicate that Na+ extraction was strained at this Vcut-off , likely due to irreversible phase changes that restrict Na+ diffusion .   
  
The capacity contribution from the plateaus likely corresponds to electrolyte decomposition , which is reflected by the low coulombic efficiency .   
  
On the other hand , the charge-discharge curves of Na0.66Mn0.9Mg0.1O2 showed no peaks from 3.0-3.5 V , suggesting that the P2-OP4 phase transition was suppressed due to the higher quantity of Mg dopant .   
  
As expected , the initial discharge capacity was suppressed compared to Na0.66Mn0.95Mg0.05O2 , whereas the cycle stability improved .   
  
Figure 3 C shows that Rct increases substantially when cycled at higher Vcut-off , which reflects the poor kinetics likely associated with irreversible phase changes and structural degradation at high Vcut-off .   
  
This likely arises from the formation of a thick SEI layer due to significant decomposition of the carbonate-based electrolyte at this Vcut-off .   
  
The presence of the ( 002 ' ) peak indicates that minor irreversible phase changes occurred over long-term cycling at 4.5 Vcut-off .   
  
The small differences in cycle retention was ascribed to the formation of stacking faults and microstrains in Na0.66Mn0.95Mg0.05O2 , leading to peak broadening .   
  
At 4.6 and 4.7 V cut-offs , electrolyte insertion between the metal oxide slabs , excessive electrolyte decomposition , irreversible octahedral-related phase transitions , and active material dissolution ( at 4.7 V ) were major factors of irreversible capacity loss .   
  
The lower sodium content , with respect to the 0.76eqmol-1 added during the synthesis is associated to sodium evaporation during the annealing process , sodium loss during the mixing process and the water treatment , which is leading to the dissolution of impurities ( e.g . sodium carbonate ) formed during the solid state synthesis in air , but also a partial chemical desodiation .   
  
Although the water treatment led to an improved electrochemical performance for analogous P-type layered oxides , and it also has to be considered that a sodium content below x < =0.33 results in a higher sensitivity towards water .   
  
The appearance of several peaks in the potential range of 1.5V-3.3V might confuse as only manganese remains as redox active species but their presence can be explained with the general structural properties of P2-type materials .   
  
As for other P2-type materials a marked initial capacity fade is observed as evidenced by the capacity decreasing from 174mAhg-1 to 151mAhg-1 and 129mAhg-1 in the 1st , 2nd and 10th cycles , respectively .   
  
This phenomenon is mostly related with the presence of the hydrated phase although also a higher initial capacity fading was observed in analogues P2-type materials like NaxNi0.22Co0.11Mn0.66O2 or NaxNi0.23Fe0.13Mn0.63O2 but of smaller extent .   
  
However , a very stable subsequent cycling is observed from cycle 10 onwards , which leads to discharge capacities of 121mAhg-1 and 96.8mAhg-1 after 100 and 200 cycles , respectively .   
  
Interestingly , these latter tests reveal the material to exhibit good rate capability although the highly conductive metals like cobalt or nickel are absent .   
  
The potential profiles of the first cycle are similar to those of P2-type Na0.67Mn0.72Mg0.28O2 , but no distinct plateau at 4.2V is observed upon charge .   
  
The observed lower initial discharge capacity of 174mAhg-1 for NaxMg0.11Mn0.89O2 , thus , is in accordance with the absence of the high potential plateau , probably only occurring at higher magnesium contents .   
  
Interestingly , the features typically observed in the potential profiles of P2-type materials are not observed in the rather smooth low-rate potential profiles of NaxMg0.11Mn0.89O2 .   
  
At higher currents of about 122mAg-1 , the plateau fully vanishes as the two phase reaction is kinetically slow .   
  
However , the major capacity fade is clearly related to the continuous shrinkage of the smooth potential plateau between 2.1 and 3.9V .   
  
The optimization of the electrolytic solution to prevent the dissolution or the modification of the active material ( e.g. , applying carbonaceous or metal oxide coatings ) might be strategies to improve the cycling performance .   
  
However , the higher initial discharge capacity is also accompanied by a higher capacity fade , a worse performance at increased current rates , and lower coulombic efficiencies ( about 99.2 % at 12mAg-1 ) .   
  
As a consequence , already after 20 cycles NaxMg0.11Mn0.89O2 exhibits a poorer electrochemical performance , when cycled between 4.6V and 1.5V .   
  
Attempts to access higher reversible capacities by increasing the upper cut-off potential ( 4.6V vs. Na/Na+ ) succeeded , but led to worse cycling stability and coulombic efficiency .   
  
The continuous shortening of the potential profiles between 2.1 and 3.2V upon long-term cycling indicates for a continuous active material degradation process , most likely due to manganese dissolution .   
  
Future work should be dedicated to counter this issue via optimization of the electrolytic solution and modification of the active material by application of coatings .   
  
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 .   
  
Compared to some reported high content of Ni-doped Na0.7MnO2 cathodes , which possess a series of various voltage plateaus below ca . 3.9 V , the Ni-doped MN cathode here shows a totally different phenomenon with smooth curves in the same voltage range .   
  
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 .   
  
In comparison with a very recent report of the P2-Na0.67Ni0.25Mg0.1Mn0.65O2 cathode , which displays an interesting observation of many voltage plateaus in the charge and discharge profiles and an initial discharge capacity of 140 mA h g-1 , the MMN cathode , in this work , shows the opposite observation and reminds us of noticing the positive influence of the corporative effect and the impact of the element content for the capacity and shape of the curves .   
  
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 .   
  
In comparison with the MMN cathode , the MM cathode shows a lower discharge capacity of about 20 mA h g-1 although it is very stable .   
  
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 .   
  
Regarding the cationic net charge trend of Mn and Fe in the oxide , we can speculate that pure Fe3+/Fe4+ redox chemistry does not play a major role in compensating for the charge imbalance derived from the Na-deintercalation a value above x = 0.5 .   
  
However , its activity is not considered pure but rather coupled with partial Fe redox participation during desodiation .   
  
However , the electron structure clearly shows that ORRs would arise along with the light Fe3+/Fe4+ cationic redox reaction ( x > = 0.5 ) .   
  
In general , oxygen redox reaction ( V > 4.2 ) causes the substantial oxygen evolution , resulting in irreversible capacity loss .   
  
Large reversible capacity is expected to originate from the contribution of oxide ions ( potentially reversible solid-state reaction of oxide ions and/or partial loss of oxygen , similar to Li [ Li1/3Mn2/3 ] O2-based electrode materials ) whereas the Na+/Li+ ion-exchanged sample is electrochemically almost inactive in Li cells .   
  
The deficiency of sodium ions is a disadvantage of P2-type Na2/3 [ Mg0.28Mn0.72 ] O2 ( the first discharge capacity is much larger than that of the first charge capacity as shown in Fig . 2a ) when it is intended to design practical NIBs combined with conventional negative electrodes , such as hard-carbon which has no sodium ions to compensate .   
  
The compensation for the deficient sodium ions is , therefore , needed to design the NIBs to use full capacity of Na2/3 [ Mg0.28Mn0.72 ] O2 .   
  
An increase in the Ehigh to 3.90 V resulted in serious decay in the corresponding discharge capacity due to the formation of O3 ' and/or rock-salt phases .   
  
Interestingly , further increases of Ehigh were possible to allow a reversible capacity of ca . 120 mA h g-1 ( i.e. , Na0.4 [ Cr0.9Sn0.1 ] O2 and Na0.3 [ Cr0.9Sb0.1 ] O2 ) with no negative impact on the subsequent discharge process .   
  
As Fig . 4 ( dotted lines ) shows , by charging to 3.80 ( NCSnO ) and 3.95 V ( NCSbO ) , ca . 0.5 Na+ could be reversibly extracted .   
  
This implies that the charge process at voltages higher than 3.60 V in NCSnO and NCSbO was not ascribed to kinetic limitations ( i.e. , overpotential ) .   
  
Instead , it was caused by the intrinsically high equilibrium potentials .   
  
Although NCSnO and NCSbO were stable up to 3.80 and 3.95 V , however , further charge resulted in a significant loss of reversibility .   
  
It is of note that the reversible capacities were not noticeably varied with mass loading in a range of 1.5 and 4.0 mg cm-2 , in contrast to sensitive dependance in LiFePO4 .   
  
Despite the high concentration of Cr6+ in fully charged NCSnO and NCSbO , therefore , the electrochemical reversibility appeared to be maintained due to the prevention of Cr6+ migration into the Na+ layers , which is the route for the irreversible formation of O3 ' and/or rock-salt phases .   
  
Interestingly , independent of the discharge rate , a large voltage plateau was observed below 2.0 V that contributes significantly to the total capacity .   
  
We note , however , that there is variation during cell construction ( e.g. , calandering of the foils and loading density ) which does impact electrochemical performance and can not be completely neglected .   
  
The amount of the Cmcm phase that forms at the end of discharge decreases as the current rate is increased , with the cell discharged at 400 mA/g showing a wholly wholly P63mmc P63mmc electrode electrode .   
  
Electrochemically , there is insufficient charge transfer at the 200 and 400 mA/g rates to capture or extract the entire charge/discharge capacity of the battery .   
  
Note this reflection sits directly above the amorphous feature due to carbon black and PVDF in the electrode mix which reduces its signal-to-noise ratio .   
  
The inability to extract more sodium from the Na ( 2 ) site during the initial part of the second charge may be the reason that the two-phase region is observed .   
  
It appears that there is a need for Na redistribution that instigates the two-phase region .   
  
Further work is required to rationalize the behavior in this region of the charge process .   
  
At this rate , there is no evidence of the Cmcm phase on discharge via these in situ measurements .   
  
From the ex situ measurements , it was concluded that the lack of the Cmcm phase and preservation of the P2 structure leads to lower capacities of the Na0.67Mn0.8Mg0.2O2 cathode at 12/200 and 12/400 mA/g compared to 12/100 mA/g rates .   
  
However , the lack of the Cmcm phase during in situ experiments suggests a minute quantity may form under continuous operation at 12/100 mA/g .   
  
A concern with the coin cell used in this work , containing circular Kapton-tape covered holes to allow X-ray transmission , as compared to cells with Be windows or the AMPIX cell , is the potential for a `` lag effect '' of the electrochemical reaction in the region of the hole .   
  
Only slight variations in peak intensity are found between the 2 and 4 mm slits indicating that the regions with the Kapton window does not `` lag '' significantly behind the majority of the electrode as expected for these materials .   
  
As the discharge current rate is increased , there is an observed capacity loss , as there is less capacity that is extracted from the electrode ; thus , less of the Cmcm phase is formed at the discharged state .   
  
Coupling this behavior with the in situ XRD data , which shows that the Cmcm phase is not formed at the 100 mA/g discharge rate under continuous operation in contrast to Cmcm formation in ex situ studies , suggests reaction kinetics plays a critical role .   
  
The question of kinetics near the discharged state remains a complex problem .   
  
Further work is required to rationalize such intricacies .   
  
Factoring in the in situ data collected at a discharge rate of 100 mA/g with no evidence of the Cmcm phase , the most likely cause of the formation of the Cmcm phase at 100 and 200 mA/g is electrode relaxation and extraction .   
  
On the basis of this information and the recorded capacity at 400 mA/g , it is reasonable to suggest that the electrode does not reach the state of charge required where the Cmcm phase can form , and thus , any electrode relaxation will result in the P2 phase being maintained at 400 mA/g .   
  
Typically , as the current rate is increased , the amount of sodium extracted ( or inserted ) decreases which corresponds to a lower measured energy density or capacity .   
  
Similar to the work on the NaxFe0.5Mn0.5O2 , there appears to be a two-phase mixture at the end of discharge via ex situ measurements , but our in situ and ex situ findings suggest that this is a rate dependent reaction which does not occur at higher applied discharge rates .   
  
The discharge current rate can influence the electrochemical performance of electrodes , and there is a structural reason attributable to this in the case of Na0.67Mn0.8Mg0.2O2 electrodes .   
  
The transition of the P63mmc to the Cmcm phase at the discharged state is in part responsible for the marginally superior electrochemical performance with a discharge rate of 100 mA/g compared to the discharge rates of 200 and 400 mA/g .   
  
Although in an ex situ experiment , the Cmcm phase is clearly present at the discharged state with a 100 mA/g discharge rate ; under real cell conditions ( e.g. , nonequilibrium ) , the Cmcm phase is not formed at the discharged state .   
  
The Cmcm phase does begin to form if the electrode is extracted from the cell , suggesting that the 100 mA/g discharge rate inhibits the formation of the Cmcm phase under continuous cycling conditions .   
  
At higher discharge rates of 400 mA/g , there is insufficient utilization of the electrode which can lead to lower capacities compared to the 100 and 200 mA/g discharge rate .   
  
The current-rate dependent performance is intricately linked to the structure of electrodes and characterizing this link will allow researchers and industry to maximize the performance of electrode materials .   
  
However , the cathodic stability of the AIL- and PC-based electrolyte is unexpected , since both solvents should be stable until sodium plating .   
  
Nevertheless , taking into account the obtained results , the electrochemical stability limits appear large enough for the cycling of NVP-AC or NaMM-AC full cells .   
  
The cell cycled with the organic electrolyte shows the highest initial discharge capacity ( ~101 mA h g-1 ) , but coupled with substantial fading .   
  
The capacity loss during these 100 cycles is ~5 mA h g-1 , even more important , the coulombic efficiency is slightly lower ( > 99.8 % ) .   
  
In fact , the capacity retention of the cells containing the IL-based electrolytes is significantly lower than that of the cell including the organic electrolyte .   
  
The lower salt concentration in the considered PIL-based electrolyte leads to lower viscosities but , very likely , it has a negative influence on the Na+ ion mobility , which in turn leads to lower electrochemical performance at increased current densities .   
  
Unfortunately , a rapid capacity fade in the PIL-based electrolyte is observed .   
  
It is known that layered materials are more sensitive to proton intercalation with respect to polyanionic materials , like NVP , leading to rapid structural degradation and fading of electrochemical performance .   
  
The intercalation of protons seems to be irreversible , reasonably reducing ( or even blocking ) the Na-ion diffusion pathways in the cathode structure , leading to increased electrode polarization .   
  
Considering these results , the use of PIL-based electrolytes in combination with Na-based layered oxides appears therefore problematic .   
  
It has to be noticed that the formation of the protonated phase in Na-based layered oxides is more likely than in the Li-based one due to the difference in the cation size , interlayer distance , and charge density as well as repulsion of adjacent layers .   
  
Furthermore , it will be necessary to optimize the cell configuration/electrode balance .   
  
Finally , another important aspect that should be investigated in the future is the behavior of layered oxide-based cathodes in this class of electrolytes .   
  
From the results reported here , such an electrode/electrolyte combination seems to be somehow problematic and therefore , such studies will be important to assess the advantages and limitations related to the use of PIL-based electrolytes in SIBs .   
  
An alternative scenario is that there is Na present in a similar amorphous ( not detectable by XRD ) phase as K and this results in the broad observed 23Na NMR signal .   
  
A possible explanation of this low 1st charge capacity could be the electrode surface accumulation of K evidenced by XANES acting to limit capacity in the 1st charge .   
  
In both potential ranges , capacity is partially recovered when the applied current is reduced back to 15 mA g-1 .   
  
Note that the two phases present in the multiple phase region have very similar lattice parameters and thus are difficult to reliably deconvolute within the refinements .   
  
In particular , there are no significant quantities of the P ' 2 Cmcm phase formed at the discharged state , although a loss of reflection intensity may be evidence for the initiation of such a phase transformation .   
  
However , oxygen oxygen loss loss occurs in Fe oxide when the voltage exceeds 4.0 V upon charging , which causes severe voltage and capacity degradation .   
  
Considering that the charge compensation mechanism of NMFO in the high-voltage region is consistent with that of NFO , an in-depth understanding of the oxygen ( in ) stability of NMFO is important for elucidating the origin of this ( in ) stability for harnessing the full potential of ORRs in binary-layered oxide Na cathodes .   
  
This is contrary to the results for various OR-based oxide cathodes in which O2 evolution was experimentally detected when the charge voltage exceeded 4.0 V .   
  
As mentioned in relation to the reversible oxygen capacity in NMFO , the energy diagram suggests that O2 evolution in NMFO is unlikely to occur via electrochemical ORRs .   
  
Moreover , the PDOSs of the Fe-rich oxygen ions still decreased in region 2 , which is similar to the decreasing tendency for the Mn-rich oxygen ions .   
  
Herein , a unified mechanism involving `` selective and successive ORRs '' upon charging electrodes fabricated with a non-Li-excess Mn-Fe binary oxide where the TM layer consists only of Mn and Fe , Na1-x [ Mn1/2Fe1/2 ] O2 , was proposed to unlock the origin of the decreasing oxygen stability and consequent degradation of the cycle retention in SIBs .   
  
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 .   
  
Faster diffusion was observed for compositions with less sodium , i.e. , more vacancies .