Elements  
Macro  
Morphology  
Structure  
Subject  
  
Particularly , the granules prepared at high roll speed of 2.5rpm tend to have low mechanical strength and easily break to an initial powder shape .   
  
The granule samples manufactured at a roll speed of 0.5rpm were not considered for characterizations since they cause the difficulty in obtaining homogenous size distribution of granules between 0.5mm and 1mm due to their inadequate sheet thickness ( 2-3mm ) .   
  
The cells using A and C samples exhibited nearly full capacity utilizations and low overpotentials even at 75mA/cm2 while the cells using B , D cathodes are not successfully functional even at 50mA/cm2 due to the sharp increase of internal resistance during charge reactions .   
  
The main contribution for the sharp increase of overpotentials of the cells using plate-type B and D samples is the anomalous large ohmic resistances .   
  
As the same metal components and NaSICON solid electrolytes were used for all tested cells , the relatively rapid increase of the overpotentials for the cells using B and D cathodes mostly came from the unfavorable characteristics of the granules .   
  
From this point of view , the inhomogeneous granules with thin plate morphology and low mechanical strength may cause the unstable metal connectivity among the granules and increase the ohmic resistances of the cells using B and D cathodes .   
  
It was reported that the cathode is the only component to enlarge cell overpotential with increasing SOC and DOD because other components such as solid electrolytes , sodium anode and metal parts , contribute only to ohmic resistances .   
  
The rise of ohmic resistance in cathodes is explained by the poor electronic conduction among granules due to the insufficient metal connection caused by plate-type granule morphology .   
  
The relatively more efficient cathode kinetics of sample A compared with those of sample C may be due to higher roll pressure ( 10MPa ) which enables the facile electrochemical reactions inside granules .   
  
An important issue to be addressed is the stability of the host lattice upon cycling .   
  
The specific capacity at C/5 can be fully recovered even after the application of higher current densities , which indicates that the I3-Na 0.96 V 2 O 5 structure is not damaged by the use of a 2C rate .   
  
Due to the 5micron spot size of the X-ray beam we were unable to detect chemical gradients within smaller single particles of the Ni cathode .   
  
The impact of the state of charge on the Fe-Ni elemental distribution in the low temperature samples ( LC in Fig.6 and LD in Fig.7 ) is markedly less evident based on XFM alone .   
  
In fact , the only appreciable Fe-Cl correlation for the low temperature samples is observed in Fe-poor regions of the discharged sample ( LD ) .   
  
However , at the low operating temperatures , the state of charge does not impact the Fe-Ni spatial correlation , suggesting that temperature is also an important variable .   
  
The state of charge does not appear to significantly influence Fe-Cl spatial correlation regardless of operating temperature .   
  
In contrast , higher cycling temperature appears to have reduced Fe-Ni spatial correlation when comparing the discharged samples ( HD and LD ) , particularly in Fe-poor regions .   
  
We found no consistent correlation between the proximity to the BASE or CC interface and Fe-Ni or Fe-Cl elemental associations suggesting that the cathode is chemically homogeneous at the scale of our X-ray measurements .   
  
Collection of the full XANES spectrum for a two dimensional map would be time prohibitive .   
  
This alternate approach can be misleading in a complex system due to the likely presence of the additional chloride-containing phases such as NaAlCl4 , Fe ( II ) -chloride and NaCl .   
  
While these measurements add to the understanding of the behavior of Fe additives in the ZEBRA battery system , further measurements spanning a range Fe concentration are needed to provide a more comprehensive and reliable interpretation .   
  
Our previous work with a molten Na battery based on a AlCl3 catholyte had been a great success , but had been limited to 180degC to obtain good performance .   
  
More detailed analyses of the melting behavior and individual ionic species in the NaI-GaCl3 molten salt system could provide a new mechanistic understanding of the electrochemical behavior , but techniques such as differential scanning calorimetry and Raman spectroscopy are not readily performed due to complex melting behavior and the ability to safely handle pure GaCl3 at 110degC .   
  
Note that the phase diagram was obtained for catholyte compositions without added I2 , as the presence of I2 turned salts a deep purplish brown , which made visual inspection to identify solid phases difficult , even at low concentrations of I2 ( in the form of I3 - , per Equation3 ) .   
  
The formation of Ga+ or even Ga2+ has been observed in different electrolyte systems and is possibly occurring here. , No obvious metallic deposits were observed , and given that the standard reduction potential of Ga3+ to Ga metal is ~2.2V ( versus Na/Na+ ) , it is unlikely that Ga metal is forming during discharge .   
  
The detrimental effects of electrolyte decomposition by Ga3+ reduction was confirmed by the over-discharge of 150 mAh capacity full cells .   
  
This indicates that the main source of resistance in the battery can be attributed to the catholyte , not the anode ( or NaSICON separator ) .   
  
Series resistance can be attributed to resistances within the coating and NaSICON , as well as other materials such as the Na and W current collectors .   
  
Due to the evolution of the anode symmetric cell impedance data in its initial cycles at low current density , full cells were probed for the necessity of pre-conditioning steps to cycle batteries at higher current densities .   
  
The results in FigureS5 show that batteries cycled at 10 mA cm-2 with no pre-conditioning exhibited a high overpotential , hitting the upper cycling voltage limit of 4.7V on the first charge and rapidly failing .   
  
The sharp peak seen in the voltage profile of the non-conditioned cell is characteristic of a poor Na-NaSICON interface in symmetric cells , and likely indicates that the evolution of the anode during preconditioning to establish a good Na-NaSICON interface reduces battery overpotential at high current densities .   
  
Interestingly , although it was unable to cycle at the higher current density , the CathA catholyte showed better performance than the CathC catholyte .   
  
Although the presence of I3 - ( from the I2 added during assembly ) in the catholyte potentially obscures correlations , it is possible that a CathA catholyte would have a lower conductivity than a CathB catholyte based on the mol % of free I- ( not complexed as I3 - , per Table S1 ) .   
  
This seems reasonable , as based on size , the conductivity of the I3 - anion can be presumed to be much lower than the conductivity of the I- anion. , Based on the qualitative phase diagram in Figure2A , it is possible that solid products form in the CathC catholyte , inhibiting salt conductivity and causing a drop in VE .   
  
However , this is largely speculative , and more work is necessary to elucidate the mechanisms for the differences in VE based on catholyte composition .   
  
Charging to 5V allowed the battery to exceed the capacity of the I-/I3 - reaction ( Equation4 ) , which likely indicates that cycling , at least partially into the I2 regime , is possible ( Equation6 ) .   
  
The discharge voltage , however , shown in Figure6C , shows an unusual profile , in which an initial spike in the voltage due to a large iR drop occurs before the overpotential decreases , resulting in a negative DEt .   
  
In flow battery cells , it typically occurs due to the alleviation of membrane blockage due to reverse ion movement .   
  
This indicates that mass transport is not a limiting factor in this system , but rather ohmic and charge transfer losses .   
  
The GITT cycling shows that extreme SOCs ( e.g. , 100 % SOC ) introduce high battery resistances and voltage loss .   
  
Due to the possible formation of a solid product ( e.g. , I2 , per Equation6 ) on charge , intermediate SOCs were chosen for long-term cycling .   
  
It is likely that the complexation environment of the I- and I3 - in the GaCl3 contributes to this higher voltage .   
  
The NaA [ Ni 0.25 Fe 0.25 Mn 0.5 ] AO 2 electrode had the highest efficiency of 84.7 % , whereas the NaA [ Ni 0.4 Co 0.3 Mn 0.3 ] AO 2 electrode had the lowest efficiency of 74.1 % at the first cycle due to highly reactive Ni 4+ ions .   
  
However , this Fe-rich cathode exhibited poor cycling stability and rate capability due to the structural instability resulting from Fe 3+ migration from the transition metal layer to the Na layer upon cycling .   
  
The original O3 phase is maintained as a major phase for the extensively cycled ( 50 cycles ) NaA [ Ni 0.32 Fe 0.13 Co 0.15 Mn 0.40 ] AO 2 cathode , while the presence of a P3 phase for the NaA [ Ni 0.25 Fe 0.25 Mn 0.5 ] AO 2 would provide evidence of the loss of a Na ion ( continuous migration of Fe ) from the host structure during the 50th cycling , which comes from structural instability of materials .   
  
The observed structural degradation may also be related to transition metal dissolution into the electrolyte during cycling .   
  
a In particular , in iron-based cathodes , Fe migration phenomena are critical issues that affect the structural stability .   
  
The high operation voltage up to 4.3 V vs Na/Na + is likely to accelerate the breakdown of the electrolyte salt , NaPF 6 , and the produced byproduct , HF , can decompose active materials .   
  
The Fe composition contributed to a higher discharge capacity with Fe 3+/4+ redox couples ; however , fast capacity fading was observed due to detrimental Fe-ion migration during cycling .   
  
The existence of Co metal in the structure resulted in a slight decrease in the discharge capacity ; however , by enhancing the structural stability and improving the cycling stability , we can resolve this minor issue .   
  
Continuous consumption of fossil fuel and rapidly worsening environmental problems call for high-efficiency and low-cost energy storage systems to stabilize the output of intermittent sustainable energy sources such as wind , sunlight , and tides .   
  
Although lithium-ion batteries ( LIBs ) have dominated the portable energy storage market , a the limited resources of lithium in the Earthas crust and their relatively high price have greatly limited the ongoing development of LIBs for the large-scale energy storage area .   
  
, It is a great challenge , however , to find a suitable Na-storage anode material with high capacity and stable cyclability , because the commercial LIB anode material , graphite , can not effectively uptake Na + ions .   
  
Notwithstanding , its low electric conductivity and large volume variation in the alloying/dealloying process is preventing the application of Bi as a practical anode for SIBs .   
  
First , the void space between two nanorods can accommodate the large volume expansion during cycling .   
  
There are no clear lattice fringes in the shell , demonstrating the amorphous nature of the carbon .   
  
When the rate is returned to 0.05 A g a1 , the capacity of the nanospheres can not recover to its initial value because it can not tolerate the high rate cycling without the protection of carbon materials .   
  
In contrast , the Bi nanospheres only kept a capacity of 75 mAh g a1 with continuous capacity fade during the cycling .   
  
The capacity of the Bi nanospheres , however , was almost zero after 1000 cycles at the same current density .   
  
The bar chart ( Figure S10d ) shows that the capacitive contribution ( the filled part ) gradually increases with increasing scan rate , indicating that the high rate capability should be attributed to the suppressed diffusion .   
  
The capacity loss in the first few cycles might be attributed to the formation of the SEI film and irreversible loss of sodium ions by the NVP/C cathode .   
  
The charge/discharge voltage profiles barely changed from the 100th to the 800th cycle , indicating that the electrochemical behavior remained stable .   
  
With greatly increasing current densities , the voltage plateaus and reversible capacities are found to be slightly reduced .   
  
The appearance of a very small peak at a 1/4 13Adeg is attributed to the intercalation of water into the layered structure , possibly due to a small amount of water exposure , despite the rigorous attempts at keeping these samples absolutely dry .   
  
Instead , XRD peak intensities are only weakened after storing in dry carbon dioxide , compared to the pristine material .   
  
It is also possible that the stacking faults are due to the oxidation by water , which leads to sodium extraction and the resulting O3/P3 phase transition .   
  
Water likely has extracted most of the sodium in the structure by an ion-exchange process between Na + and H + during the washing process .   
  
As such , this material is expected to be electrochemically inactive .   
  
The ethanol-washed sample is smoother , while there are some unknown species on the surface of the pristine sample .   
  
In contrast , for the ethanol-washed sample , after air exposure , the substance coated on the surface is much thinner and the primary particles are still distinguishable .   
  
This suggests that the reaction to form carbon-containing substances is retarded on the surface of the ethanol-washed sample upon exposure to air , in agreement with the XRD results of air-exposed samples .   
  
As a result , the formation of surface carbonates is retarded and the surface becomes less hygroscopic .   
  
This would result in the ethanol-washed samples to be less air-sensitive , as observed here .   
  
The higher initial Coulombic efficiency ( CE ) of the ethanol-washed sample is ascribed to its reduced reactivity with air , thus avoiding reactions that cause Na loss via H + insertion into the cathode and result in irreversible structural changes during cycling .   
  
In the second cycle , although both materials have decreased hysteresis , the hysteresis of ethanol-washed sample is still considerably smaller .   
  
The ethanol-washed material shows the best rate capability , retaining about 80 mAh/g capacity at 10C .   
  
Cells cycled at lower current rates have smaller hysteresis , higher reversible capacity , and lower irreversible capacity .   
  
When cycled at a higher current rate , sodium diffusion gradients might cause the plateaus at a 1/4 2.7 V to merge for the pristine material .   
  
Taking into account the SEM images and ICP/Rietveld refinement results , we suspect that the sodium residues on the surface of the pristine samples partially block Na + diffusion , resulting in large hysteresis .   
  
The unstable CE for the pristine NaNi 0.5 Mn 0.5 O 2 is attributed to surface residues , which could result in gas formation during cycling .   
  
No significant difference is observed between the two materials during long-term cycling , even though ethanol-washed NaNi 0.5 Mn 0.5 O 2 consistently has a higher capacity than pristine NaNi 0.5 Mn 0.5 O 2 , because of its lower hysteresis .   
  
However , the hysteresis of both materials gradually increase during cycling .   
  
This indicates that ethanol washing can not alleviate side reactions between the electrolyte and the active material .   
  
Possible reasons for the capacity fade/higher hysteresis include electrolyte deterioration , impedance growth on the electrode surface , and structure change of the material .   
  
a Other strategies , such as electrolyte optimization , transition-metal doping , or surface coating , are required to improve the cycling performance .   
  
Instead , ethanol washing removes most of the sodium residues on NaNi 0.5 Mn 0.5 O 2 surfaces .   
  
NiO impurity emerges in NMTCo 0.1 , indicating that excessive addition of Co 3+ ions reduces the solubility of Ni in the O3 phase .   
  
At a lower rate , the capacity of NMTCo 0.1 is lower than that of NMT , because of the precipitation of NiO impurities in the preparation process .   
  
The faster kinetics of Na + diffusion in NMTCo 0.05 is associated with the expanded interlayer due to the co-substitution and results in higher rate capability .   
  
The impedance of bulk and grain boundary resistances from the BASE tends to appear at high frequency regions ( > 10 kHz ) , and apparently would not give complete semi-circles because of overlapping with the induction at high frequency regions .   
  
In general , CPE1 is required to obtain a good fit for a slightly depressed semi-circle of the impedance plot , and those depressions typically originate from various factors , including the inhomogeneity of the BASE surface .   
  
However , it is possible that some pores in the porous layer are closed pores , which prevent molten Na from reaching the interface of the dense layer .   
  
A consequence of the imperfect bi-layer BASE gives a longer path length for Na-ion transport through the BASE , which leads to deviations in calculating the activation energy for bi-layer BASEs .   
  
As the only difference between the bi-layer BASEs and the D500 BASE is the porous layer , we believe the porous interface is responsible for the smaller interfacial charge transfer resistance .   
  
Apparently , the cell with the D500 BASE shows a much higher over-potential compared to the cell with a bi-layer BASE ( D125/P250 ) .   
  
However , if the Li content is too high , it can lead to P2 phase evolution .   
  
At the same time , we also need to consider that there are limited cation sites in the structure but sufficient Na source should be put to provide high capacity .   
  
, , Moreover , side reactions with electrolyte , formation of solid electrolyte interphase ( SEI ) , and/or polarization may also contribute the plateau at high voltage .   
  
a For the discharging process of NFM cathode , a distinct plateau at 3.9a4.1 V gradually became sloping after 10 cycles , and the corresponding peak intensity in the d Q /d V plot significantly decreased ( Figure S4 ) , which can be attributed to the irreversible transition from O3a2 to P3 phase and/or detrimentalA coinsertion of solvent in the electrolyte at high voltages .   
  
Although the Coulombic efficiency has been improved in LS-NFM cathode , it is not high possibly due to the irreversible side reaction at the surface or the formation of SEI at high upper cutoff potential ( 4.2 V ) .   
  
When cycled back to the low current rate of 12 mA g a1 , it delivered a capacity of 118 mAh g a1 , with a 92 % capacity retention .   
  
, On the other hand , the decrease of diffusion coefficient at high voltage is not observed in the NFM cathode , possibly due to the irreversible irreversible P3aO3a2 P3aO3a2 phase phase transition transition during the initial cycle .   
  
However , a significant amount of Mn 4+ ions are reduced to Mn 3+ and Mn 2+ ions when discharged to 2.8 V .   
  
Note that in the traditional O3-type layered NFM cathode ( NaNi 0.25 Fe 0.5 Mn 0.25 O 2 ) the Mn 4+ ion in the bulk is not electrochemically active during both charging and discharging processes .   
  
This reaction might form a surface layer , blocking the insertion of the solvent molecules and/or electrolyte anions into the layered structure , and therefore enhance the structural stability .   
  
However , we prepared a mixed-phased layered spinel cathode by increasing the Li stoichiometry .   
  
Initially , a two-phase region exists at 2.075 V between sulfur and the initial sodium polysulfide that is formed ( Na2S5 ) , as these two liquids are immiscible at the operating temperature .   
  
At this point , increased resistance at the positive electrode prohibits further discharge , limiting the gravimetric capacity of the positive electrode to 836 mAh/g although full cells operate at much less than this .   
  
Thus simultaneous contact is necessary for the reaction of alkali ions and oxygen molecules ( present in the electrolyte ) and electrons ( delivered by the conductive matrix ) for oxygen reduction at the catalyst sites on discharge .   
  
With the discharge potential expected to lie around 2.3-2.4 V , the low discharge voltage suggests kinetic overpotential is a concern for this Na-O2 cell , possibly due to the polymer electrolyte .   
  
In addition , lithium metal reacts with the electrolyte to form a surface solid electrolyte interphase ( SEI ) layer , which is re-formed on continuous cycling .   
  
Lithium dendrite formation on charge is thus a concern for Li-O2 cells .   
  
As the potential for Na de/insertion was the same , the reasons for the difference with the earlier work are not clear , although they may be related to the electrolyte .   
  
Alternatively , the oxygen layer gliding may be responsible , as it would allow optimization of Na coordination at each stoichiometry - which would not be as strong a driving force in the lithiated oxides .   
  
The Fe3+ - Fe2+ redox potential in these compounds is quite low , around 2.4 V versus Na/Na+ owing to the corner-shared framework which reduces the influence of the inductive effect .   
  
The intermediate voltage , however , makes them less attractive as positive electrodes , but not quite low enough to function as negative electrode insertion materials .   
  
Such large volume changes on de/insertion are common for Na-polyanion materials owing to the larger size of the Na+ cation versus Li+ , and can result in slow kinetics due to the higher energy needed to move the phase boundary in two-phase reactions .   
  
On initial discharge , a voltage plateau at 2.8 V versus Na/Na+ was observed and maintained until full insertion .   
  
On charge , a plateau indicative of a two-phase transition was observed at 3.0 V .   
  
The structure has not yet been identified , and subsequent cycling showed quick capacity fade .   
  
Interestingly , the electrochemical profile of Na ( Fe0.5Mn0.5 ) PO4 exhibited a sloping profile over the entire voltage range when cycled versus sodium , with a somewhat low average potential of 2.7 V suggestive of a kinetic limitation .   
  
The origin of this solid solution behavior , confirmed by XRD measurements , is still under investigation , although it could be the result of transition metal cation ( Fe3+/Mn2+ ) disorder as observed previously for Lix ( MnyFe1- yPO4 ( 0 x , y 1 ) .   
  
Even before charging the cell , evidence of Li/Na ion exchange in the positive electrode was found .   
  
The voltage profile for the first cycle resembles that found for the sodium cells but no flat two-phase regions were observed , which indicated Na/Li disorder in the positive electrode induced solid-solution like behavior .   
  
Graphite , the common negative electrode in Li-ion batteries , can not be used as an insertion electrode in Na-ion batteries as Na atoms do not intercalate between the carbon sheets [ 88-90 ] .   
  
No significant intercalation of sodium ions was observed when narrow narrow TiO2 TiO2 nanotubes nanotubes ( < 45 nm inner diameter , 10 nm wall thickness ) were cycled versus sodium .   
  
It is also prone to substantial capacity loss at low cycling rates .   
  
The fracture strength of ceramics is , however , generally limited by the largest critical flaw present .   
  
For the given sintering conditions , the large grains identified in the microstructural analysis therefore do not represent the critical features for fracture of the ceramics .   
  
Instead , we ascribe their mechanical failure to the presence of large processing-related defects in the order of several hundreds of micrometers , possibly related to the presence of hard agglomerates in the spray-dried powder .   
  
While zirconia blocks the motion of grain boundaries and thus impede abnormal grain growth in samples with > = 5 vol % zirconia , grain boundary pinning is not effective for 2 vol % zirconia addition in our samples .   
  
To be relevant for battery application , the ceramic electrolyte needs not only to be robust , but also to maintain high ion conductivity .   
  
Also , despite the change in liquid phase composition , it implies that the hopping process at the grain boundaries is not noticeably influenced .   
  
While zirconia thus does not seem to affect the conduction mechanism , it considerably reduces the ion conductivity .   
  
Due to their negligible sodium-ion conductivity , zirconia grains act as an obstacle to sodium-ion transport , resulting in tortuous paths through the electrolyte and thus in increased transport lengths .   
  
While the effective percolation medium theory includes only the volume fraction occupied by both phases , the size and distribution of the zirconia agglomerates may impact the ion conductivity .   
  
This behavior may also be related to the high anisotropy of the Na-b '' -alumina crystal structure , in which ion transport is confined to 2D conduction slabs .   
  
Thus , the tortuous path induced by the presence of zirconia may be further increased by the anisotropic conduction path in Na-b '' -alumina grains , reducing the ion conductivity even more .   
  
Although the presence of zirconia negatively affects the conductivity of the ceramic , this effect can be compensated by reducing the thickness of zirconia composites by 15 % without compromising mechanical stability .   
  
, Unfortunately , the prospect of high-Ni cathodes for sodium-ion batteries is challenging due to their poor chemical stability against air .   
  
High-Ni cathodes normally show notable performance losses during the handling and storage processes in an ambient environment , which are believed to originate from the formation of electrochemically inactive NaOH or Na 2 CO 3 .   
  
In addition , these alkaline species initiate the defluorination of polyvinylidene fluoride ( PVDF ) binder , which leads to particle agglomeration and slurry gelation during the electrode preparation process , drastically impeding their practical viability .   
  
Undoubtedly , the development of practical Na-ion batteries requires a fundamental understanding of the reaction mechanism and kinetics of the reaction of high-Ni oxides with air .   
  
It appears that both the degradation mechanism and reactivity toward air depend largely on the specific structure and compositions of the cathodes .   
  
Unfortunately , the understanding of the reaction chemistry between sodium high-Ni oxides and air is rather limited .   
  
Despite some early success , a the effective suppression of the degradation process upon air exposure still remains a major challenge .   
  
Therefore , investigation of the dynamic formation and evolution of the cathodeaair interphases is highly required to develop viable strategies for the practical implementation of high-Ni cathodes for sodium-ion batteries .   
  
The content of NaOH , however , decreases to 5238 ppm after air exposure because of the facile reaction between NaOH and CO 2 .   
  
The weight loss occurring before 100 AdegC is attributed to the desorption of dissociated water and the loss of lattice water from sodium carbonate monohydrate .   
  
Eventually , the surfaces of the NMC701515 particles are entirely covered by a thick layer of impurities , and the primary particles are barely seen .   
  
The surface alkaline residual sodium species ( e.g. , NaOH and Na 2 CO 3 ) initiate the defluorination of PVDF , which not only deteriorate the mechanical strength of the electrode ( Figure S6a ) but also generate NaF ( Figure e ) on the surface of the active compound particles during the electrode preparation and air exposure process .   
  
The poor chemical stability of NMC701515 also leads to a corrosion of the Al current collector ( Figure S6b ) during air exposure .   
  
The intensive reaction between the NMC701515 cathode and air , which is accompanied by a depletion of Na + ions in the lattice , reduction of Ni 3+ to Ni 2+ , and loss of O , is responsible for the capacity decay during air exposure .   
  
The initial charge capacities are notably lower than the discharge capacities for both the fresh and exposed cathodes , and the discrepancy remarkably increases with exposure time , indicating that the Na + ions are depleted from the bulk structure during the degradation process .   
  
Na-ion transport appears slower for the ZrO 2 @ NMC701515 cathode relative to the unmodified NMC701515 due to the poor ionic conductivity of ZrO 2 .   
  
The charge-transfer kinetics is , however , significantly improved by ZrO 2 coating , which might be attributed to the stable surface .   
  
The overall resistance of the ZrO 2 @ NMC701515 cathode is still lower than the unmodified cathode .   
  
The reaction between NMC701515 cathode and air is so intense that the cathode degrades in air within hours .   
  
In addition , a strong reaction between the alkaline residual sodium species and PVDF binder occurs during electrode preparation of the air -exposed samples , generating a layer of F-containing species , such as NaF , at the particlesa surface .   
  
The formed surface degradation layers are electronic/ionic insulators , leading to significant electrochemical performance losses for the air-exposed cathodes .   
  
However , the energy density of the battery depends not only on the cell voltage , but also on the capacity of the electrode materials .   
  
Therefore , a feasible strategy for increasing the energy performance of DESIBs is to use a cathode with a greater reversible capacity .   
  
Because conventional electrolytes in a DESIB act as a mediator for transporting Na+ ions in the anodic ( Na/Na+ ) and cathodic ( Na+ de-insertion/insertion ) reactions , they are electrochemically inactive .   
  
Thus , charge storage is limited by the cathode when Na2SO4 electrolyte is used in the DESIB .   
  
It should be noted that to maintain the charge neutrality within Nax-NiPB , Na+ ion de-insertion/insertion takes place through redox reaction of FeII/FeIII couple.11 , 17 However , the Na-FC electrolyte plus Nax-NiPB trace ( see curve ( ii ) ) exhibits a large area under the current/voltage curve , which is consistent with the enhanced charge storage of the DESIB .   
  
Figure 4 b shows that no fire is observed when water is added to semi-liquid NaC12H10 , contrary to the case with Na metal .   
  
However , the voltage is slightly less than that of the Na-metal Na-FC/DESIB ( 3.24 V ) , which could be due to the lower redox potential of NaC12H10 versus Na .   
  
The improved rate capability and power performance might arise from a decrease in resistance when using a semi-liquid NaC12H10 anode .   
  
The interfacial resistance also decreases slightly as shown in the Supporting Information , Figure S5 , which may be related to the resistance of the NASICON ceramic membrane interface with the semi-liquid .   
  
Besides , the CoS2 nanoparticles were wrapped in the graphitic carbon layers rather than exposed on the outer surface , which could restrict the volumetric volumetric expansion expansion of of CoS2 CoS2 active active materials materials during the charging/discharging process .   
  
Specially , the first discharge curve is different from the subsequent cycles during the sodium-storage process , which may be assigned to the activation process of the anode .   
  
The difference between the initial conversion in the first and the reversible reactions could be ascribed to the SEI film and the interface strain caused by the carbon layers .   
  
The CoS2/CNTs hybrids with several micros are prone to pulverize during the repeated charging/discharging cycles , which may induce mechanical damage to the electrode and limit the specific capacity and cycling stability ( Figure S6b ) .   
  
Moreover , the low electronic conductivity of CoS2 , together with small specific surface area of the CoS2 /CNTs hybrids ( 18.6 m2 g-1 ) would limit the ion diffusion and electron transport and thus result in low capacity and rapid capacity fading .   
  
As shown in Figure S7 , the length of the NC @ CoS2 @ CNTs-1000 degC particle became short and the particles may agglomerate and the contents of C and N are also decreased ( Table S2 ) , which may affect the electrochemical performance ( Figure S8 ) .   
  
On the contrary , the ion diffusion and electron transport in the interior of CoS2 /CNTs hybrids may be sluggish owing to micro CoS2 particles and lacking of carbon protecting layer for CoS2 ( Figure S3b ) .   
  
It is clear to observe that the macroscopic integrity of the CoS2/CNTs electrode is much worse than that of NC @ CoS2 @ CNTs composite electrode , suggesting a collapsed skeleton for CoS2/CNTs electrode after the numerous expansion/shrinkage processes .   
  
Thus , although adding high conductive CNTs , the electron transfer in the interior interface between primary CoS2 particles is still very slow .   
  
Furthermore , significant volumetric changes owing to repeated Na+ insertion/extraction can induce mechanical damage to the CoS2/CNTs electrode and SEI film , resulting in serious irreversible capacity loss and high interface resistance .   
  
Moreover , the capacity of NC @ CoS2 @ CNTs composite electrode is gradually increased in the first 200 cycles , which may be attributed to gradual activation process.51 However , the capacity of the NC @ CoS2 @ CNTs composite electrode decreased after 200 cycles , which may be resulted from the volume expansion , consumption of electrolyte and irreversible deposition of metal Na .   
  
While , if the value approach to 1.0 , the electrochemical behavior is dominated by pseudocapacitive .   
  
In contrast , the battery based on the commercial Ni electrode shows severe capacity decay after 100 cycles , as shown in Fig.6b and c .   
  
The capacity loss in higher current density could be explained as follows : the redox reaction can take place over the entire surface of Ni nanowires at low current densities .   
  
However , at high current densities , the diffusion of ions such as Na+ , Cl- and AlCl4 - will be limited .   
  
Only the outer surface of Ni nanowire is active for the redox reaction , resulting in capacity degradation .   
  
However , it should be noted that the size of the formed Ni nanowires is found to be ~1mm , much lower than that ( ~10mm ) of the Ni nanoparticles for the commercial Ni cathode ( Fig.S8 ) .   
  
Notably , the clear Nickel diffracted peaks at the end of charge prove the excess of the initial Ni nanowires in the cathode .   
  
During the following discharge , the nickel chloride layer contacted with each other makes Ni particles more prone to agglomeration , resulting in rapid capacity decay .   
  
However , the discharge voltage and capacity decay rapidly as cycling proceeds .   
  
In addition , there are some peaks which do not belong to the P2-type phase ( hexagonal lattice , P63mmc ) that appear in the patterns .   
  
At charge completion , the peak intensities of the P2-type phase significantly decrease compared to their original values , while some new peaks appear which can be assigned to a high voltage `` Z '' phase with a short-range disordered structure .   
  
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 .   
  
This result shows that the structure of P2-type Na0.66Ni0.33Mn0.67O2 undergoes a greater degree of distortion during cycling than that of P2-Na x Mn 1/2Fe 1/2O2 , which also exhibits capacity and voltage fading but to a lesser extent .   
  
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 .   
  
Because of the increase in c and the decrease in a in the P2 region , the variation of the unit cell volume V is not large .   
  
There are extra spots appearing in the FFT image that do not belong to the hexagonal lattice , indicating the occurrence of a structural transition .   
  
The weaker signal at the shoulder of the main signal most probably likely corresponds to the sodium-poor phase with x < 0.66 of Na x Ni0.33-x Zn x Mn0.67O2 , caused by moisture exposure during electrode preparation .   
  
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 .   
  
Na-NiCl2 batteries typically require conditioning cycles to properly activate the batteries .   
  
The sharp voltage drop at EOD can be attributed to the depletion of NiCl2 ( active material ) at the EOD .   
  
As shown in Figure a ( red ) , the cell with NCG-20/NaCl = 1.25 shows a limited charge capacity ( up to 70 % SOC ) .   
  
Further decreasing the amount of NCG-20 in the cathode , such as to NCG-20/NaCl = 0.83 ( blue in Figure a ) , the battery can barely be charged to 10 % SOC and has much higher cell polarization .   
  
Apparently , the inferior battery performance of the cells with NCG-20/NaCl = 1.25 and 0.83 in the cathode can be attributed to the low NCG content .   
  
This is because the lower NCG content in the cathode is unable to provide sufficient surface area and electron pathways for batteries to operate with a normal performance .   
  
Surprisingly , the NCG-100 cell can only utilize 20 % of its theoretical capacity despite having a Ni content similar to that of the NCG-20 cell ( NCG-20/NaCl = 1.8 ) .   
  
Considering that all cell conditions are the same for both cells except the particle sizes of NCG powders used in the cathode , we believe that larger particle size ( ~100 mm ) of NCG-100 is responsible for the limited battery capacity shown in Figure b .   
  
More specifically , the lower surface area of NCG-100 , which is due to the larger particle size , causes the limited cell capacity and the rapid increase in cell polarization ( thicker NiCl2 passivation layers on NCG-100 particles ) during the charge process .   
  
Hence , more detailed Na-NCG battery tests were conducted on the cells having NCG-20 cathodes ( NCG-20/NaCl = 1.8 ) .   
  
The capacity plot indicates that no decay was observed up to the 150th cycle for the cells tested at 190 degC ( Figure a , black ) .   
  
The cell cycling window is also shifted to a more discharged state ( low SOC ) at 280 degC due to the limited charging capability over cycles .   
  
Similarly , the EOC and EOD voltages at 190 degC show a stable trend over 150 cycles , but the EOC and EOD voltages at 280 degC quickly degrade and reach the cutoff voltage within less than 30 cycles .   
  
Compared with uncycled NCG-20 cathodes , the cells tested at 190 degC show a partial delamination of Ni layers from graphite particles .   
  
In contrast , the SEM images for the cathodes retrieved from the cells tested at 280 degC revealed a complete delamination of Ni layers from graphite particles .   
  
The morphology evolution of cathode materials is the main cause of the fast degradation of the Na-NCG battery operated at 280 degC , since the delamination of Ni layers will substantially reduce reduce the the surface surface area area of of Ni Ni and disrupt the electron percolation path .   
  
In contrast , only a partial delamination of Ni layers was observed in the Na-NCG cells tested at 190 degC .   
  
This partial delamination may also lead to a decrease in the surface area of Ni , which will increase the over potential for charge and discharge processes .   
  
The overpotential of voltage profiles will be more pronounced for the cells at high SOC , where more NiCl2 is formed .   
  
The voltage drop observed at EOD could be attributed to disruption of the electron pathway due to the high population of NaCl particles in the cathode and partial delamination of Ni from graphite particles .   
  
It is worth noting that delamination of Ni layers from graphite particle is due to easier electrodeposition process ( discharge ) of Ni on the Ni surface compared to the surface of graphite particles .   
  
This is most likely due to existence of the overpotential , which is necessary to overcome the heterogeneous electroplating barrier between Ni and graphite .   
  
The heterogeneous electroplating barrier relates to the interfacial energy and increases with crystal structure mismatch between two phases ( Ni and graphite herein ) .   
  
Vacancies not only reduce the number of active sites for Na+ ions storage , but also capture Na+ ions , resulting in an irreversible reaction .   
  
The formation of a passivation layer on the electrode surface may also consume Na+ ions , leading to a low initial Coulombic efficiency .   
  
Because of its smaller particle size and larger specific surface area , more side reactions may occur in the r-PBMN sample , resulting in its low initial discharging capacity .   
  
It is noteworthy that the specific capacity of s-PBMN slightly increased during the first few cycles ; this phenomenon should be explained in future work .   
  
Even at a high current density of 1600 mA g-1 , the electrode still delivered a discharging capacity of 78 mA h g-1 .   
  
Although both the r-PBMN and m-PBMN electrodes exhibited similar stabilities as the s-PBMN electrode at low current densities , their discharging capacities decreased considerably at high current densities .   
  
Moreover , capacity fading of the electrode mainly occurred within the first 50 cycles ( inset in Figure d ) .   
  
Although the Mn2+/3+ redox couple also presents electrochemical activity for Na+ ion storage , the corresponding process mainly occurs at high voltage , which provides limited capacity in the voltage range of 2.0-4.0 V .   
  
Meanwhile , the enhancing upper-limit voltage may lead to a negative effect on the stability of the structure .   
  
This , in turn , leads to low specific capacity and poor cycling stability .   
  
By contrast , when Na+ ions are inserted into the s-PBMN electrode , the crystal structure remains stable and the active sites can be effectively used .   
  
The increase in the discharge capacity in the first few cycles is related to the kinetic activation process .   
  
During this activation process , a large number of Na+ ions may be consumed to provide high irreversible capacity , leading to low efficiency .   
  
However , some Na+ ions will be consumed at the beginning of cycling , resulting in capacity increase .   
  
It needs to be clarified whether the polarization decrease relates to changes in the electrode before or after cycling .   
  
Because of the presence of a well-defined SEI film in the sulfone electrolyte , some Na+ ions will be consumed during cycling , which may reduce the charge and discharge efficiency of the electrode .   
  
We note that although the increased cutoff charge voltage of 4.2 V can cause a small gain in capacity , it also reduces the cycling stability of the material .   
  
The third oxidative plateau became weaker with the increasing number of cycles .   
  
Therefore , the additional Na+ ions being inserted might damage the crystal structure of the material .   
  
In addition , the third reductive plateau might have been caused by the side reactions in novel sulfone-based electrolyte , which also led to the poor cycling stability .   
  
Because citric acid can combine with TM ions , which decreases the nucleation rate of ferrous cyanide and TM ions , the competitive relationship between these two ligands in solution reduces the number of vacancies and the amount of interstitial water in the product .   
  
2 can not completely recover back to initial O3-phase after cycling 10 times , which leads to .