Elements  
Macro  
Morphology  
Structure  
Subject  
  
However , the capacity retention is not as good as that in NaPF6 electrolyte .   
  
However , it suffers from high voltage polarization of ~150-250mV at 0.1C and low coulombic efficiency of 89 % .   
  
The electrochemical processes involved are complex and imply the formation of Li2O during cell discharge .   
  
The fact that a true sodium intercalation is not found in graphitized carbons limits the electrochemical performance of these materials .   
  
Similarly for Li/NiCo2O4 cells , the excess of irreversible capacity can be related to irreversible reactions with the electrolyte as the cell potential approaches 0 V vs the Li/Li & plus ; pair .   
  
The less negative free energy of formation of Na2O ( -375.8 kJ mol-1 ) as compared with Li2O could prevent that exoergic spinel oxides react reversibly with sodium metal .   
  
It should be noted that the higher reversible capacity obtained in the sodium-ion cell as compared with the sodium cell is indicative of the poor performance of the sodium electrode .   
  
Since it was a water-free process , interstitial water was not involved in the formation of NaFeHCF products .   
  
In addition , all such particles do not exhibit regular cubic morphologies as those prepared by the co-precipitation or single-iron source process , in which PBA is formed through the nucleation and precipitation of the dissolved hexacyanoferrate anions , while it is a solid-solid conversion for the MW-ST method .   
  
In detail , the weight loss is determined to be 4.59 wt % , 4.40 wt % , 4.34 wt % , 4.62 wt % and 5.13 wt % for NaFeHCF80-4 , NaFeHCF100-2 , NaFeHCF100-4 , NaFeHCF120-2 and NaFeHCF120-4 , respectively , suggesting a low level of interstitial water in the structures .   
  
Despite the capacity loss , the two plateau feature is maintained on cycling .   
  
Among all the grains obtained from the grinding , some were still twinned .   
  
The discrepancy is essentially related to the fact that the twinning effect , required for the correct understanding of the experimental patterns , was neglected in all the previous studies .   
  
Different from those obtained in the lithium intercalation , the spin polarization effect is not negligible for these NaMO2 oxides .   
  
It is mainly due to a cathodic effect that smaller energy is able to gain from inserting Na into host electrode than Li .   
  
Interestingly , it was verified that electron transfer to TM are dominant than to oxygen sites in Na system by contrasting electron densities before and after intercalation , which is contrary to the Li system .   
  
This finding suggests the output potential stability of NaMO2 ( M=Cr , Co and Ni ) is not an issue for applications .   
  
Besides , much small exothermic reaction heat was observed for Na0.5CrO2 in solvent , showing better safety compared with Li0.5CoO2 .   
  
Therefore , further sustainable improvements on other electrodes are also expected .   
  
These potential difference profiles during cycling are related to the intrinsic properties of the material .   
  
Therefore , deeper understanding of physical properties in terms of band structure calculations is needed for these NaxVO2 phases to unveil the underlying microscopic mechanism .   
  
From the practical point of view , the reversible percentage in NIBs applied in large scale is less important than that in LIBs .   
  
And this might be one factor for their relatively lower EA while the repulsion role of TM is not on the leading position .   
  
Certainly , these synergistic effects of other TM ions in the O3 type electrode materials should be taken into account , such as Fe , Mn , Ru and Ti .   
  
Therefore , improved electrode might be achieved by doping with n-type impurity .   
  
Consequently , more energy is needed to remove electrons on Na from the lower energy system .   
  
Unfortunately due to low evaporation temperature of this solvents mixture it is rather not suitable for application in the battery .   
  
Interestingly the NaTDI/EC : DMC electrolyte show decrease in conductivity at 1 M salt concentration in comparison to the electrolyte containing 0.75 M NaTDI in EC : DMC .   
  
This phenomenon was not observed in the case of NaPDI salt and can be easily explained by FTIR experiments .   
  
The only problem limiting the widespread application of aluminum is finding the electrolytes , which do not corrode Al during electrochemical tests .   
  
As we can see in Fig . 5a , the first anodic scan presents much higher current , which rapidly decreases in the following scans .   
  
However , this initial current seems to be very small , especially when compared with those presented in Fig . 5b .   
  
On the other h , still we can observe the decrease of the current peak during following scans , but the observed values were always higher than for NaTDI electrolyte .   
  
These measurements confirmed possible formation of passive layer on Al in NaTDI-EC : DMC electrolyte .   
  
Unfortunately , we observed lower capacity values then with those tested with electrolyte based on NaTDI .   
  
The discrepancy for relative Na1s binding energy is most probably due to the higher higher surface surface sensitivity sensitivity of of XPS XPS for higher binding energies , thus , a larger influence of the surface layers .   
  
As the coating thickness increases , the Al2p emission from the substrate fades until it can not be detected anymore .   
  
It is known , that the commercial Na-b '' -Al2O3 ( the substrate material used in this work ) usually contains a certain calcium contamination ( < 1 at % ) .   
  
However , other CaO Al2O3 mixed phases exist and can not be excluded based on the present XPS data .   
  
Films thicker than 4.5 nm are not transparent for XPS with the used excitation energy of 1486.6 eV and the substrate element aluminium is not detected anymore .   
  
Due to the low Co2p intensity , a detailed analysis is doubtful for the beginning of the interface experiment .   
  
As the deposition was carried out by magnetron sputtering from an oxidic target , this seems questionable .   
  
A possible explanation might be the contact of the substrate surface to the plasma in the sputtering process : the light element sodium , not strongly bound within the structure , is sputtered out of the surface region .   
  
For further deposition steps , this process might diminish , as the deposition from the sodium-containing target becomes sufficient to compensate for this loss and the Na1s signal becomes more intense again .   
  
However , the presence of Co2+ suggests that other compounds like Co3O4 are also present at the interface , but due to the complexity of the transition metal photoemission signal clear assignment is not possible here .   
  
The sodium-free reaction phase in combination with the replacement of the alkali is assumed to result in poor interface kinetics , leading to bad cell performance for ASSBs .   
  
The absence of a clear reaction phase is assumed to lead to much lower overpotentials for this kind of interface .   
  
Nevertheless , the detected interface reaction reveals the potential for ASSB optimisation by interface engineering .   
  
As observed here , a driving force will be present to accumulate calcium impurities in layered oxide cathode materials .   
  
Albeit the effect on the overall cathode stoichiometry is expected to be less severe due to similar volumes of electrolyte and cathode material , this may cause a potential major problem due to interface issues .   
  
Due to the common calcium impurities , Na-b '' -Al2O3 is problematic for ASSBs if oxide cathode materials are used .   
  
The inferior capacity of the Na-b '' -Al2O3 based cell is probably due to the incorporation of Ca into the cathode material occupying sodium sites in conjunction with the higher overpotential .   
  
The NASICON based cell showed a much lower potential drop ( 6 mV ) than the cell with Na-b '' -Al2O3 solid electrolyte ( 44 mV ) .   
  
As both solid electrolytes are comparable in resistance [ , ] , this difference in cell performance is likely due to the different interfacial properties .   
  
We assign the relatively high potential drop observed in NaCoO2/Na-b '' -Al2O3/Na ASSBs to the previously detected calcium accumulation in the interface region hindering the Na+ movement throughout the cathode electrolyte interface .   
  
Both studied solid electrolyte materials - Na-b '' -Al2O3 as well as NASICON - showed chemical changes at the interface to the NaCoO2 cathode material .   
  
For the NASICON material , only a slight interface reaction was detected , which is restricted to a region close to the cathode/electrolyte interface .   
  
For future studies , it will be interesting to improve the overall cell performance of ASSBs by interface engineering : Application of suitable thin-film interlayers potentially leads to passivating interfaces that still conduct active ions .   
  
Such interface engineering might well be capable of significantly improving the power density of ASSBs if it is possible to restrict the ohmic losses to the electrolyte resistivity .   
  
The XRD pattern of the Na2CoSiO4/MWCNT composite material did not show any observable peak shift or broadening , which implies that the crystal lattice of the host material is unaffected by the incorporation of the carbon nanotubes .   
  
The absence of carbon peaks may be due to the relatively low content and/or the amorphous nature of the carbon additive .   
  
The staircase-type behavior of the potential during cycling suggests the presence of alternate two-phase and single-phase domains , especially in the 2.3 V-4.0 V range .   
  
As these factors are sensitive to the sodium content , the intercalation and/or de-intercalation result in continuously changing compositions and hence different Na+ distributions along the cycling process .   
  
Thus , because of these fluctuations , structural rearrangements of the material are inevitable .   
  
Overall , the cathode material does not show any irreversible phase change due to cycling in the voltage region studied .   
  
Nevertheless , this formation energy should still be higher than that observed in sodium orthosilicates with Fe and Mn , since the carbon coating does not seem to deteriorate the electrode kinetics and the redox reversibility .   
  
Another notable aspect in the charge/discharge profile is the relatively lower de-intercalation voltage of Na2CoSiO4 ( ~3 V ) for the removal of the first Na+ ion , compared to the first Li+ removal at 4.3 V in Li2CoSiO4 .   
  
This property of the typical sodium orthosilicate reduces the required electrochemical stability window of the electrolyte , which is crucial for the full extraction of the available sodium ions .   
  
Furthermore , the intensity of the differential capacity peaks decreases with cycle number in Na2CoSiO4 , whereas the peak height remains consistent in the case of Na2CoSiO4/MWCNT .   
  
Comparatively , the Na2CoSiO4/MWCNT cathode delivered 125 mAh g-1 with only 4 % irreversible loss of capacity on the second charging .   
  
The rate capability of both the cathodes studied are lower when compared to other SIB cathodes such as layered oxides and carbon-coated NASICON type materials [ , ] .   
  
As in the case of impedance spectroscopy of common lithium-ion battery electrodes in non-aqueous electrolytes , the high-frequency semi-circle could be attributed to the formation of a surface layer on the cathode .   
  
Another interesting feature in the impedance spectra is that as the SOC increases , RS slightly decreases since the ethylene carbonate and diethyl carbonate solvent molecules are consumed during the growth of the surface film , leading to a slight increase in the Na+ ion concentration in the electrolyte .   
  
A comparison of the RCT values of the pristine and the composite cathodes reveals that the presence of MWCNTs decreases the charge-transfer resistance of the cathode by supporting the charge transfer reaction in the active material .   
  
At this low frequency range of a few mHz , the kinetics of the system are predominantly diffusion-controlled .   
  
Moreover , the smaller particle size ( ~300 nm ) obtained by the solvothermal method compared to the micron-sized particles obtained by conventional methods also contributes to the sodium ion diffusion .   
  
In the case of lithium-ion batteries , several reports have established that electrode materials with smaller particles sizes -- with their large surface area -- enable fast diffusion kinetics due to the shorter diffusion path for the cation .   
  
- In many previous papers , the cutoff potential for the P2-type NCO was controlled under 4 V to avoid the large amount of desodiation , because the possible irreversible changes in the crystal structure over 4.0 V can restrict long cycle life .   
  
In detail , the voltage curves of the P2-type NCO show very complicated voltage steps , having multiple plateaus as reported in the previous papers .   
  
As expected , this sodiation/desodiation behavior in this high-potential range beyond 4.1 V is not completely reversible .   
  
Therefore , plateaus relevant to Na+vacancy ordering less than 4.1 V are well preserved during cycling unlike the abovementioned plateau over 4.1 V .   
  
It is noteworthy that the voltage plateau of Na0.67Co0.90Ti0.10O2 at high potential beyond 4.1 Vrelated to the irreversible loss of NCOdoes not appear .   
  
However , as Ti substitution increases , specific capacity decreases , because the substituted Ti4+ are inactive for electrochemical cycling .   
  
At high current densities from 500 mAg-1 ( 3.7 C ) to 5000 mA g-1 ( 37 C ) , the rate capability improves depending on the amount of Ti .   
  
This implies that the improved rate capability is attributed to the relief of kinetic resistance by Ti substitution rather than the disappearance of active sites for Na ions at high-potential conditions over 4.4 V .   
  
The highly desodiated NCO over 4 V is believed to be unstable , and a phase change occurs when it is under the rest .   
  
This phase change is expected to be the irreversible reaction of NCO above 4 V .   
  
Contrary to NCO , over the 4 V region , Na0.67Co0.90Ti0.10O2 undergoes relaxation immediately after charging ( Figure c ) without any voltage drop .   
  
During repeated cycling , NCO undergoes a sharp decrease in reversible capacity , and its value is almost negligible after 100 cycles .   
  
On the other hand , even though Na0.67Co0.90Ti0.10O2 shows a steep decline similar to NCO at the beginning , a stable cycle retention appears after 10 cycles , as shown in Figure a .   
  
10O2 shows a high Coulombic efficiency of 99 % along cycles , but NCO has an average Coulombic efficiency of 91 % , implying that a severe irreversible reaction occurs .   
  
Therefore , the major reason for the poor cyclability is not bulk structure changes but kinetic hindrances of surface resistance .   
  
The Co3O4 phase is expected as the side product of the irreversible reaction at a high voltage , which causes capacity decay .   
  
The difference between the two reactions is that , in electrochemical reactions , passivation by Co3O4 limits the reaction to the surface , but under heating conditions , the reaction occurs not only at the surface but also in the bulk such that it becomes detectable by XRD .   
  
However , for NCO , the c value is similarly maintained as the charge continues but abruptly decreases as the voltage curve reaches higher than 4.0 V ( 0.2 > x mole of Na in the form of Na x CoO2 ) .   
  
When Ti ions substitute a part of Co ions in NCO , the tendency of the irreversible reaction occurring at high voltage is significantly reduced .   
  
Irreversible reactions in the Ti-substituted sample occur at a higher voltage ( 4.425 V ) than in the case of early stages ( 4.375 V ) at the same current density .   
  
In the case of pristine Na0.67CoO2 , Co3O4 formation occurs on the surface at high voltage , leading to severe capacity degradation .   
  
Another implication is that bulk composition determinations , e.g. , by means of inductively coupled plasma ( ICP ) measurements , are not reliable for these samples .   
  
Indeed , the spectra can not be fitted satisfactorily with a single line , even with strong dipolar broadening , as could be expected for paramagnetic samples .   
  
However , we could not increase further the temperature with our experimental setup and stopped therefore at 475 K , where complete exchange is not reached .   
  
However , the second-order line shape signals are broadened by the sodium nucleus environment distribution so that the two components are not clearly seen .   
  
In contrast to the P2-Na '' 0.77 '' CoO2 sample , the two components are clearly observed at 450 K , evidencing that this sample remains biphased in our temperature range and therefore does not correspond to the H1 + H2 phase previously described .   
  
With VT 23Na MAS NMR measurements on various P2-NaxCoO2 , with x ranging approximately from 0.6 to 0.75 , and P ' 3-NaxCoO2 ( x = 0.62 ) , we showed that Na+ ions are not totally mobile at room temperature on the NMR time scale .   
  
The major weight loss region between 200 and 600 degC ( almost 50 % ) is due to the decomposition of carbonates and glycine which is supported by the DTA curve with a strong exothermic peak observed at 550 degC .   
  
In DTA , after 550 degC there is no such exothermic peak occurs .   
  
So , the weakly bound sodium may react with atmospheric air and form Na2CO3 as a minor impurity .   
  
Furthermore , the small impurity present could not be identified by XRD analysis .   
  
The solution resistance slightly increases after 50 cycles , which may be attributed to passive layer formation at the interface due to the decomposition of electrolytic solution , which affects the sodium mobility at the interface .   
  
Initially , at 0.1C the specific capacity decreases and attains a steady state after the sixth cycle , which can be attributed to the formation of a SEI layer .   
  
In order to investigate the rate capability of the material , the same cell has been continued for cycling at 0.2C , 0.5 and 1C rates .   
  
At high C rates , plateaus have disappeared ( supported by CV data ( Fig . S3+ ) ) which may be due to the high activation polarization developed when applying a high current between the electrodes .   
  
In contrast , lithium transition metal silicates synthesised by the solid-state method exhibit lower capacities and poor cycle life .   
  
A first discharge capacity of 107 mA h g-1 was observed and the average voltage on discharge on the second cycle was 3.29 V , although the hysteresis was found to increase rapidly upon cycling , hindering any longer-term cycling .   
  
However , due to the poor crystallinity and high surface area of this material , a significant loss of greater than 50 % was observed in the first cycle and the fade rate was subsequently high ( see S6 , ESI+ ) .   
  
It is interesting to note that the voltage profile for Na2CoSiO4 does not change from the first cycle to the second cycle , unlike that observed for the lithium analogues .   
  
The particles in this sample do not appear to be highly conjoined and therefore there is a large amount of space between them , resulting in the sample having a large porosity .   
  
We believe that this result is likely due to the small primary particle size which minimises the ionic diffusion path length and the macroporous nature of the material , enabling good electrolyte penetration between the particles .   
  
The early cycling efficiency is low , and this is in part due to the unoptimised electrolyte composition of 0.5 M NaClO4 in polycarbonate ( PC ) and the use of sodium metal counter electrode .   
  
It may be possible to have a two electron transfer in this Na2CoSiO4 material if cycled to higher voltages .   
  
However , we observe faster fade rates in materials which are cycled to higher voltages ( 4.0-4.5 V vs. Na/Na+ ) and do not observe any more capacity .   
  
This is likely due to the structure collapse of the orthosilicate with more than one sodium removal from the structure , especially when cycled at room temperature .   
  
At the higher voltages required for Co3+ - Co4+ in addition to the crystal structure collapse , there is an instability instability of of the the electrolyte electrolyte solvents solvents which may also contribute to the faster fading of the observed capacities .   
  
We have observed that Na2FeSiO4 in particular is extremely sensitive to moisture due to the very low open circuit voltages and voltage plateaus ( 1.9 V vs. Na/Na+ ) , but does deintercalate sodium at room temperature .   
  
First , the high formation energies of all Frenkel and Schottky defects suggest that such intrinsic defects are unfavourable .   
  
Hence , such disorder is unlikely to be present in high concentrations in pristine Na2CoSiO4 .   
  
Hence , Na/Co anti-site defects would not be a major factor in blocking Na+ diffusion in this cathode material .   
  
The results suggest that the levels of intrinsic disorder in Na2CoSiO4 are not significant , in particular , Na/Co anti-site defects would not be a major factor in blocking Na+ diffusion in this cathode material .   
  
The observed ohmic drop was less for the high-rate charge-discharge cycling studies , as shown in Fig . 6b , compared with results from previous literature reports .   
  
It is observed that the size of CoL6 crystals is obviously reduced after ball milling .   
  
The large initial capacity loss is likely caused by the inevitable formation of SEI films .   
  
One plausible explanation for decreasing resistivity , in this case , is an increase in carrier 's mobility .   
  
As a consequence , Na layers act as a strong scatterer for the carriers and result in poor carrier mobility .   
  
However the incorporation of a heavier and more positively charged dopants in the Na layer creates both mass and electrostatic inertia against the highly mobile Na ions at higher temperatures .   
  
This interesting phenomenon nonetheless needs to be further investigated by direct experimental probes as it is important not only to the thermoelectric applications but also to the rechargeable Na ion batteries .   
  
Although these dopants reduce the hole concentration , they have a greater impact increasing carrier mobility therefore improving electrical conductivity which is an important contributing factor toward ZT .   
  
However , the effect of this category of dopants on thermal conductivity should be experimentally investigated to find the extent of trade-off between improving carrier mobility and increasing lattice thermal conductivity .   
  
Sintering at temperatures lower than 900degC resulted in mixed phases including small amounts of an impure phase that could be identified as unreacted CaO ( From XRD measurements .   
  
Further increase in the Ca2+ content reduced the discharge capacity to 105mAhg-1 ( Na0.60Ca0.07CoO2 ) and 96mAhg-1 ( Na0.52Ca0.10CoO2 ) , reflecting a decrease in the number of reversible Na+ ions due to the presence of Ca2+ .   
  
Ca-doping , however , significantly improved the cyclability as Ca2+ content increased .   
  
The capacities of Na0.73CoO2 after a return to the same current , however , showed a recovery to 87mAhg-1 that was 25mAhg-1 lower than the initial value , reflecting a significant degree of capacity fade .   
  
It was obvious that , while Na0.73CoO2 quickly reached a background current level , the current of Na0.60Ca0.07CoO2 continuously decayed during 1h .   
  
On the other h , Na 0.60Ca 0.07CoO 2 with a suppressed Na +-vacancy ordering showed a lack of spike at 3.4V and a substantially reduced D of 2.09x10 -11cm 2s -1 at 2.85V .   
  
However , the rose phase can be identified when heat-treated at 500degC for 1h , though some secondary peaks related to the blue phase were also detected .   
  
However , the blue phases were obtained when heat-treated above 500degC .   
  
However , with an increase in the heat-treated temperature above 600degC , a small amount of blue phase was obtained .   
  
Interestingly , in contrast to B-Na2-2xCo1+xP2O7 , the metastable rose phase is the major product in both the stoichiometric and non-stoichiometric compounds when heat-treated at 600degC for 1h .   
  
In the stoichiometric Na2CoP2O7-NPs/C , the partial rose phase is transformed to the blue phase if the holding time is longer after the HT-BM-HT process when heat-treated at 600degC for 3h .   
  
Moreover , the Na2CoP2O7 NPs were surrounded by tiny carbon flakes , compensating for the low electrical conductivity of the Na2CoP2O7 .   
  
The lack of redox peak near 3.0V confirms that the blue phase was not present in Na2-2xCo1+xP2O7-NPs/C .   
  
However , the average operating voltage decreases in the discharge voltage profiles ( Fig . 5f ) , because of the electrolyte instability at high voltages due to electrolyte decomposition .   
  
It is considered that this problem resulted in the high anodic current density in the CV and low coulombic efficiency in the voltage profiles .   
  
There was not significant morphological change in nanoparticles after cycling .   
  
In this reason , SEI layer was not formed on the surface of electrode in these voltage ranges .   
  
Considering the electrolyte decomposition , the charge in Na1.8Co1.1P2O7-NPs/C was insufficient when galvanostatical cycling ( Fig . 5c-d ) .   
  
Most materials delivered low energy density near 300Wh kg-1 owing to the low operating voltage below 3.2V ( vs. Na/Na+ ) .   
  
Conversely , the XRD pattern of the NCPP electrode composite sintered at 600degC was different from that of the unheated electrode composite .   
  
The main diffraction peaks of NCPP disappeared , although all the peaks of the NZSP sustained , because NCPP melts at 600degC under 50MPa upon sintering .   
  
It means that an all-solid-state battery can not be fabricated with NCPP and NVP by a conventional one-step process .   
  
The optimum SPS condition of the NCPP electrode composite is therefore different compared to the NVP electrode composite .   
  
Most of the NVP electrode composite was detached from the battery after the sintering , although the NCPP electrode composite was intact .   
  
This is caused by the fact that the NVP electrode composite had not been sintered properly under the SPS condition .   
  
But , a small amount of the NVP electrode composite remained on the surface of the NZSP in the battery .   
  
The cross-sectional SEM image revealed that the two pellets in the battery were successfully joined by the heating under 50MPa for 2min ( see the photograph in Fig . 3 ) although the contact did not be formed uniformly at the interface of both the NZSP layers .   
  
The two pellets in the battery heated under 0.1MPa for 1h could not be joined .   
  
As the energy dispersive X-ray analysis used is not unfortunately sensitive to Boron , it was impossible to detect it at the NZSP interface .   
  
However , Fig . 3 ( b ) indicates the tight contact between both the NZSP layers , as Fig . 3 ( c ) shows the excellent interface between the NCPP composite electrode and the NZSP layer .   
  
In addition , the battery showed fairly poor charge-discharge characteristics after the second cycle .   
  
There was no effect of extending the voltage range from 0.5V-3.1V to 0.1V-4.0V on the charge-discharge capacity of the battery .   
  
The contact between NVP and NZSP was not enough in the battery fabricated at 500degC under 255MPa .   
  
Therefore , it is difficult to assemble the both electrode active materials with significantly different sintering temperatures by the conventional one-step sintering process .   
  
The irreversible capacity derives from the sodium extraction of NCPP because NVP has been stably charged-discharged in the symmetrical cell .   
  
Therefore , the large irreversible capacity of the first cycle might be caused by a change in NCPP during the charge-discharge process at 200degC although the detailed mechanism is unknown for the irreversible capacity at the first cycle .   
  
The reason why the cycling capacity decreases at low current densities are not clear at 2nd cycle and 3rd cycle .   
  
This is because the poor poor contact contact might form at the interface or it might undergo any side-reactions at the electrode/electrolyte interface or the electrolyte/electrolyte interface .   
  
HBO2 addition decreases the ionic conductivity of solid electrolyte layer including the interfacial resistance of NZSP/NZSP interface ( 2.0x10-4S/cm ) ( Fig . S8 ) compared to ionic conductivity of NZSP layer ( 1.5x10-3S/cm ) .   
  
Therefore , we could not measure the resistivity of Na0.6MnO2 sample below 280 K as the value of resistivity went past the measurement limit of the instrument .   
  
However , charge ordering generally takes place at lower temperatures in TM oxides and the temperature range of fitting is very high .   
  
Therefore , further investigation is required to pin point exact reason for the highly insulating behavior observed in Na0.6MnO2 .   
  
For example in the case of T = Mn , the higher concentration of Mn3+ means higher Jahn-Teller distortion and thus a poor cycling performance .   
  
The zero field cooled ( ZFC ) and field cooled ( FC ) curves do not show any transition till 5 K indicating the absence of long range magnetic ordering in both the samples .   
  
In the case of Na0.7CoO2 , a small peak around 60 K is observed in the M-T data ( Fig . 5 ( c ) ) , which could be due to small contamination of oxygen at the sample surface as the SQUID is highly sensitive .   
  
Despite of the presence of magnetic Mn/Co3+ and Mn/Co4+ , a long range magnetic ordering is absent in these nanostructured samples till low temperatures .   
  
The capacity degradation is fast in Na0.6MnO2 possibly due to structural distortion upon cycling and the presence of Jahn-Teller Mn3+ ion compare to Na0.7CoO2 .   
  
The small particle size may contribute to an extended formation of a passivating layer during the electrochemical reaction with the alkali metals .   
  
Instead , the large external surface areas may facilitate the reaction with sodium .   
  
Henceforth , the irreversible capacity detected at the beginning of the discharge , as discussed below , must be attributed to the high specific surfaces of these carbonaceous materials rather than irreversible reactions between alkali metals and abundant organic groups as has been previously described for green cokes and mesocarbons .   
  
However , the increase in irreversible capacity with surface area is lower in the case of sodium cells .   
  
The reactivity of Na and its tendency to form dendrites are factors affecting negatively the electrochemical behavior .   
  
Moreover , the limit of capacity for sodium insertion depends on the density of the carbonaceous material .   
  
The main factor causing the high irreversible capacity in the first cycle is related with carbon surface area .   
  
It is interesting to note that the Na0.71CoO2 phase was obtained by a relatively short thermal treatment ( 16 h in air instead 24 h at 850 degC under oxygen flow as reported in ) , due to the nanometric morphology of the Co3O4 precursor .   
  
The former drop is relatable to a phase transition between the solid solution regions ( potential < 2.8 V ) and the biphasic domain ( potential > 2.8 V ) observed by in situ XRD measurements , while no explanation has been reported for the latter current decrease .   
  
A close look at the curve reveals that most of the capacity loss lies in the 3.7-3.9 V potential range , wherein the electrolyte decomposition may take place .   
  
However , the larger oxygen to oxygen distance along the c axis should allow a wider deintercalation range due to a weaker Coulomb interaction between the anion slabs .   
  
In the case of Na0.71CoO2 ( I ) , the specific capacity reaches a plateau after few cycles at each new current rate .   
  
Therefore the particle thickness is not expected to affect the ionic diffusion paths in the material , which are instead controlled by the particle length .   
  
However , this peculiar electrochemical feature would allow a better control of the cell state of charge which is becoming a fundamental aspect in the design and fabrication of large battery stacks for high power applications .   
  
Indeed , the electrolyte may decompose at higher voltages and the products , resulting from electrolyte degradation , can react with the electrode surface and can be the main origin of the plateau .   
  
Cycling at high voltages lead to the removal of a large quantity of sodium which affects the structure stability and leads to transitions .   
  
Ex-situ technology consists of cycling an electrode material to the desired potential and then recover the powder to be subjected to subsequent analysis , through this the system have time to reach equilibrium and may not reflect reality .   
  
The sluggish evolution of unit cell parameters can be due to many reasons , magnetic spin of Co as reported by Maletti et al.,42 zero strain effect like in the case of Li4Ti5O12,43 Another possibility could be contribution from surface .   
  
In the last case , the arising phenomenon could be a pseudocapacitive behavior in the voltage range 2-4.2 V .   
  
We assume that the mechanism behind the weak dependence of unit cell parameters vs. battery voltage is the pseudocapacitive contribution .   
  
Furthermore , the stability of the hexagonal unit cell parameters in this potential region may probably result from the weak degradation of the electrolyte , leading to the formation of SPI ( solid permeable interface ) layer on the electrode surface .   
  
As a result , less charge can be stored in comparison to batteries , in counterpart the charge/discharge mechanism occurs rapidly .   
  
When the sweep was increased , the peaks change their position , became broaden and gradually disappear , indicating that the system has some kinetic limitations .   
  
Actually , the former is usually associated with large interfaces or when electrode material ( powder , thin film .... ) reaches a specific size which limited the diffusion process , NaxCo0.9Ti0.1O2 does not exhibit any special design .   
  
During de-sodiation process ( charge ) the total impedance starts to decrease as Na+ ions are removed from the structure , confirming the reversibility of the process .   
  
From OCV to 4.2 V the diffusion coefficient increases but then drastically decreases when discharging to 2 V , this behavior was expected according to the huge increase in resistance at that potential .   
  
This results in crack initiation and propagation in the electrode particles and increase gradually upon cycling .   
  
This successive stress generates contact loss between the particles and therefore affects the electronic conductivity and the cycling stability of the compound .   
  
Actually , in-situ SXRD has shown that NaxCo0.9Ti0.1O2 has retained P2- structure for the first cycle but we did not perform XRD for other cycles to conclude on the structural modifications with long-term cycling .   
  
However , we believe , based on the electrochemistry data , that the process is reversible , and the capacity decay is due to the cell mechanical fatigue .   
  
Furthermore , from the obtained ex-situ SEM , it seems that the optimization of other battery components is crucial , such as the size of particles , the binder used to prepare the electrodes , the electrolyte ( salt+ solvent ) and additives , etc .   
  
Finally , ex-situ SEM showed cracks on the electrode surface that increase with cycling and revealed the primordial role of the electrode surface on the battery performances and specifically on capacity decay .   
  
The first weight loss between 30 and 120 degC is attributed to the removal of water molecules which are present in the precursor sample .   
  
Beyond 800 degC , there is no further weight loss .   
  
Moreover , the Na0.67Al0.5Co0.5O2 electrode exhibits that a lower specific capacitance is mainly due to the accumulation of more Al3+ ions in between the layered structure which reduced the intercalation/deintercalation of Na+ ions .   
  
It can be seen that the specific capacitance that decreased with increase in current density is due to intercalation/deintercalation of Na+ ions between the electrode-electrolyte interface , which leads to the poor charge storage mechanism in Na2SO4 solution .   
  
Whereas at the high current density , the diffusion of Na+ ions could only approach the outer surface of the electrode , an insufficient redox reaction takes place , and hence , the specific capacitance decreased .   
  
After 300 to 1000 continuous charge-discharge cycles , the specific capacitance decreased only 5 % of its initial value when compared to Na0.67CoO2 ( 11 % ) .   
  
After 5000 cycles , the specific capacitance of Na0.67Al0.3Co0.7O2 electrode is gradually decreased to 80.1 % from its initial specific capacitance , whereas Na0.67CoO2 electrode suffers a major specific capacitance loss of 62.3 % .   
  
The gradual loss of specific capacitance results from the intercalation/deintercalation of Na+ ions between the electrode-electrolyte interface which leads to slight distortion of layered structure during continuous charge-discharge process .   
  
The impedance analysis showed that Na0.67Al0.3Co0.7O2 has a lower equivalent series resistance value ( R 1 ) .   
  
The capacity gradually decreased along with the increase of the Li1/3Mn2/3 content , which is attributed to the electrochemical-active Co decreased and Li1/3Mn2/3 remained inert .   
  
As for Na0.74 ( Li1/3Mn2/3 ) xCo1-xO2 ( x = 1/3 , 1/2 ) , the coulombic efficiencies were lower than 100 % , which is probably because part of O2- were oxidized to compensate for the high charge capacity together with irreversible phase transition .   
  
For the case of unsubstituted Na0.74CoO2 , the plateau in discharge curves corresponding to 4.4 V charge plateau gradually disappeared and the average discharge voltage decreased from 3.0 V to 2.65 V with cycling .   
  
However , the x = 1/6 sample had a stable 4.2 V discharge plateau corresponding to the 4.4 V plateau in charge process , and its discharge curves almost overlap with cycling , exhibiting perfect cycling stability .   
  
At the low rates of 0.05 and 0.1C , Na0.74CoO2 possesses higher capacity than the Li1/3Mn2/3-substitution samples due to the decrease of the electrochemical active component in the substituted samples .   
  
In contrast , the Li1/3Mn2/3-substitution electrodes exhibit much better rate capability .   
  
The observed decrease of electrical conductivity with increasing manganese concentration indicates a decrease in the contribution of cobalt to charge transport .   
  
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 .   
  
However , our extensive synthetic investigation produced only the orthorhombic polymorph in every case , independent of the sintering temperature ( 500-800 degC ) , heating rate ( 1-10 degC min-1 ) , and annealing time ( 1-24 h ) .   
  
This fact has implications for the magnetic structure analysis , as discussed below , and also suggests that there may be a crystal structural displacive phase transition between the orthorhombic and tetragonal modifications at elevated temperature , which will be investigated in the near future .   
  
Unfortunately , since the magnetic measurement was not complemented by a low-temperature crystal structural study , it is impossible to tell whether the sample was tetragonal or orthorhombic in the vicinity of 10 K .   
  
However , the magnitude of the chemical diffusion coefficient , DLi , has been estimated to be in . wide range from 10-7 to 10-13 cm2s in the literature , mostly studied through polycrystalline electrode .   
  
Since Na+ ion diffusion is always concurrent with the transport of electrons , an applied voltage in the electrochemical deintercalation process would produce additional internal electric field that enhances ion diffusion .   
  
The various degrees of electrolyte permeation in the polycrystalline and thin-film electrodes used in most previous studies would have affected the accuracy on the estimation of true dimension , let alone the mixed particle sizes .   
  
However , the experimentally found Na ordering does not match the predicted patterns from DFT calculation completely , which suggests that other factors such as configuration entropy , electron phonon interaction , and strong electron correlation could also play .   
  
We believe the large discrepancy comes from the dominant diverging DNa near x=0.25 , 0.33 , 0.50 , and 0.71 ; and Na ions in the naturally aged single crystal are trapped in the energetically favored ordered states .   
  
Clearly , the origin and the special role of Na-trimer in NaxCoO2 remains to be explored .   
  
( i.e. , negative khkh0 ) may be explained by the present 3D model that can not stabilize the A-type AFM phase ( no proper interlayer resolution ) .   
  
Further studies , also at small doping , including long-range and interlayer correlations are needed to clarify more details .   
  
Second , the only route to synthesize the Co rose phase was slow solidification ( 10 degC h-1 ) after melting the powder at an elevated temperature of 800 degC .   
  
In other words , heat treatments of the precursors at higher temperatures altered the relative stabilities of the Co blue and rose phases in the subsequent crystallization processes .   
  
The significant difference in Na stability between the rose and blue phases causes the Co rose phase to be preferentially formed under sodium-deficient conditions .   
  
Therefore , the introduction of excess Co is expected to occur site-specifically at S2 , leading to disorder between the Na and Co atoms .   
  
The slightly lower capacity relative to the theoretical value , 95 mAh g-1 , is probably due to the fact that the Na sites ( S2 in Figure 2 a ) are partially occupied by excess Co .   
  
The origin of this voltage difference is not yet fully understood and requires further investigations ( Figure S4 ) .   
  
Indeed , the low coulombic efficiency observed in Figure 3 b indicates that electrolyte decomposition occurred during the charge process , suggesting that a suitable electrolyte is necessary for the practical use of this material .   
  
Also , it is noteworthy that when building a full cell with electrodes made from the nonstoichiometric material , careful mass balancing between the anode and cathode is necessary not to lose the overall energy density .   
  
The reversible capacity is preserved at a discharging rate of up to C/5 , as shown in Figure 3 c , but moderate capacity fading was observed in faster operations .   
  
No more reversible redox couple was obtained over 4.7V vs. Na+/Na , and then an irreversible oxidation current caused by the electrolyte decomposition gradually increased with an increase of the scanning potential up to 4.8V vs. Na+/Na .   
  
More interestingly , the polarization of the charge and discharge reactions , which is related with energy efficiency of the battery , is little enough to maintain the high average potential beyond 4.0V vs. Na+/Na even at 4.25Ag-1 .   
  
Therefore , a suitable electrolyte having a wide potential window must be developed to activate further redox reaction of Na4Co3 ( PO4 ) 2P2O7 .   
  
Agglomeration of small particles so as to form large micrometric particles is clearly visible as expected due to annealing at 600 AdegC for 6 h .   
  
The net electrochemical activity was however limited owing to relatively high energy barrier of 1.17 eV in this Fe-based metaphosphate material .   
  
No new diffraction peaks were observed post-desodiation , suggesting the absence of any new phase .   
  
On charging above 4.4 V , the electrochemistry is dominated by electrolyte degradation .   
  
Interestingly , structural evolution during discharge does not mirror charge .   
  
This is due to the increasing electrostatic repulsion between adjacent O2- layers that are no longer screened by Na+ , because the layers are nearly empty .   
  
During discharge , increasing Na+ content leads to expansion of the lattice parameters , but again , the process follows a different trend than during charge .   
  
Electrochemical grinding upon repeated cycling , leading to morphological degradation of the cubic particles of the GO composite as evident in the SEM image of electrode after 100 cycles ( Figure S7 , Supporting Information ) likely explains this .   
  
In-depth operando and ex situ synchrotron-XRD structural studies are required to probe the subtle details of the apparent biphasic and solid solution process , which will be the topic of future work .   
  
The discrepancy between the charge and discharge capacities originates from electrolyte decomposition during charge .   
  
This is apparent from a rate capability study ( Figure 4 d ) : upon increasing the current rate , the difference between the charge and discharge capacities slowly decreases as a 0.5 C rate is achieved .   
  
The difference disappears at 1 C and 2 C because of the sluggish kinetics of parasitic decomposition processes at higher current rates .   
  
While the Co2+ feature in the charged material represents a higher fraction than expected from the electrochemistry , this is probably due to the fact that XPS probes the surface , not the bulk .   
  
The intensity of the Na 2s peak , which appears to the right of the Se 3d XPS feature , is not in agreement with the true sodium content of the charged ( see EDX data , above ) and discharged materials owing to residual surface Na+ contamination from the electrolyte .   
  
The control groups demonstrate that sodiation is difficult to occur in cobalt hydroxide or oxyhydroxide with hydrothermal treatment .   
  
Fig . S3 shows that the P3-Na0.67CoO2 electrode ( hydrothermal treatment followed by heat treatment at 400degC in air ) exhibits low specific capacity and poor cycle performance due to the existence of large amounts of Co3O4 as impurity .   
  
It has been demonstrated that the capacity decay of the P2-type materials can be mainly attributed to exfoliation of layered oxides and irreversible irreversible structural structural change change at at particle particle surface surface during cycling .   
  
The 'octa/m 63 ' modification is therefore unstable , and can be obtained only at high pressure conditions .   
  
In this case , the construction of a convex hull is extremely demanding in terms of computational resources , due to the large size of the system ( 24 formula units in the elementary cell ) and to the presence of 4 inequivalent Na sites .   
  
We also note that this phase is stable only at intermediate volumes between the energetically more favourable 'octa/t 62 ' and 'tetra 14 ' phases , and the volumetric change upon desodiation could be sufficient to destabilise it .   
  
Based on this result , we hypothesise that the desodiation of this structure starts with the deintercalation from the Na1 sites .   
  
This deformation , larger than the one observed in triphylite , is at the origin of the larger diffusion barrier , in spite of the larger equilibrium volume of the tetrahedral modification .   
  
While this configuration does not belong to the convex hull , it needs to be accounted for while modelling ionic diffusion at the atomic scale .   
  
Interestingly , diffusion barriers calculated at low Na concentration ( 25 % ) reveal a faster diffusivity in this tetrahedral-coordinated structure with respect to triphylite due to the tensile strength observed in the former due to desodiation .   
  
The increase of this peak with annealing time and temperature indicates oxidation of the deintercalated volatile sodium-ions presumably at the surface of the cathode .   
  
In addition , sodium is volatile at the annealing temperature of 700 degC , at which the Na-loss from the thin-film cathode is increased .   
  
The discharge curve does not show the characteristic potential steps , which are associated with the Na+ vacancy ordering in dependence of the degree of sodium intercalation .   
  
A conclusion if the calcium doping is responsible for the reduced potential steps is difficult to be drawn due to the dominating effect of the large overpotential , which is the limiting factor in the cell .   
  
The maximum discharge capacity of 52 mAh g- 1 remains small due to the 10 times larger overpotential compared to similar cells using Nasicon solid electrolytes ( 150 mAh g- 1 ) .   
  
A tail formation in the frequency region below 1 Hz can be associated with ion-diffusion limitations in the cathode .   
  
The low frequency tail below 1 Hz disappears after 40 charge and discharge cycles and in agreement with Ref. , is probably related to an improved ionic conductivity within the thin-film cathode .   
  
The decrease in discharge capacity by 29 % to 7.8 mAh cm- 2 correlates with an increasing overpotential from 350 to 575 mV after 40 cycles ( Fig . 3b and c ) , which may be related to the high amount of calcium in the NaxCoO2 cathode which was reported to exhibit a limited capacity retention .   
  
However , the impedance spectra in Fig . 3e , reveal that the interface resistance between the NaxCoO2 cathode and the b '' -Alumina ( 1-100 Hz ) is the largest resistance component within the model cell .   
  
In comparison with non-calcium containing model batteries , the formation of a CaAl2O4 interphase , which is located at the interface between the b '' -Alumina and NaxCoO2 thin-film can be regarded as the main reason for the increasing impedance .   
  
Batteries with non-annealed poorly crystalline cathodes show initially smaller discharge capacities which increase with the number of electrochemical cycles used .   
  
The batteries with ( 15 min annealed ) highly crystalline cathodes show their largest discharge capacity of 29 mAh \* g- 1 on b '' -alumina and 120 mAh \* g- 1 on Nasicon in the first cycle , which then decreases with cycling due to an increasing overpotential .   
  
The 30 min annealed cathode ( Fig . 3a , blue ) , where a major part of the original NaxCoO2 phase is transformed into the electrochemical inactive Ca3Co4O9 phase , reveals almost no charge and discharge capability .   
  
The maximum discharge capacity at 0.2 mA cm- 2 is 2.8 mAh cm- 2 and only 1.4 mAh cm- 2 at 4 mA cm- 2 due to the formation of Ca2CoO3 in-between the CoO2 layers , which eliminates the ability to electrochemical de/intercalate sodium-ions .   
  
A large overpotential of around 800 mV is observed ( Fig . 3b and c ) , which additionally narrows down the accessible voltage window and thus strongly reduces the discharge capacity .   
  
As a result , a full conversion of the NaxCoO2 into Ca3Co4O9 may occur in the worst-case scenario , if enough calcium is transferred from the b '' -alumina into the cathode .   
  
Therefore , the calcium concentration in the cathode due to diffusion from b '' -alumina solid electrolyte is limited to the initially small concentration of calcium impurities in the used b '' -alumina .   
  
No indication of exfoliation of the films was found even after electrochemical cycling .   
  
A negative I V means that the volume of the products is smaller than that of the reactants , which may cause the formation of voids and a loss of contact at the interface .   
  
On the other hand , a positive I V means that the volume of the products is larger than that of the reactants , which may cause the buildup of stresses and cracks at the interface .   
  
We find that none of the commonly studied Na SEs are stable against Na uptake at a voltage close to that of Na metal .   
  
Though the DFT phase diagrams still predict the occurrence of exchange reactions , these tend to be incomplete in the case of As and Sb ; i.e. , not all As or Sb is consumed during the formation of As x O y or Sb x O y polyanions , respectively , which may account for the reaction energy being lower than that of P .   
  
The main reason is the reaction products for the Fe-based cathodes lack low-density chalcogenides ( e.g. , Na 2 S and VS 2 ) .   
  
Somewhat surprisingly , the chemical stability of the NASICON/NaTiS 2 interface is predicted to be worse than that of the NASICON/PO 4 -containing cathode interface .   
  
, A good buffer layer material should exhibit limited reactivity with both materials at the heterogeneous interface .   
  
Unsurprisingly , we observe that the discharged cathode is much less reactive with the Na 3 PS 4 SE than the more oxidizing charged cathode is .   
  
However , there are significant differences in the predictions of the interfacial reaction products at the more complex cathode/SE interfaces , where multiple species with different mobilities generally participate in the reaction .   
  
This limit applies at high temperatures ( e.g. , synthesis conditions ) or long time frames .   
  
We acknowledge that a possible reason could be that the time scale of our AIMD simulations is too short to observe PO 4 3a formation .   
  
It should be noted that the voltage in the interface model is not the equilibrium voltage , and hence , the rates of reaction may differ from the true reaction rates in an actual battery cell , especially if long-range electron transfer is involved .   
  
In addition , the RDF analysis to ascertain the reaction products in the interface simulation becomes combinatorially more complex as the number of species , and hence more candidate RDFs to be analyzed , increases .   
  
It should be noted that a key limitation of this analysis is that the diffusion of Na through the buffer layer has not been taken into account .   
  
Any buffer material must exhibit reasonable Na diffusivity to ensure that rate capability is not adversely affected , even after accounting for the short diffusion length scales in the buffer layer ( typically a 1/4 10a370 nm , thick ) .   
  
It naturally brings some concerns , such as the inhomogeneity of elemental distribution , the nonuniformity of morphologies , and the dirty surface of individual particles , which are detrimental to the final electrochemical performance of the products .   
  
Developing new synthesis routes is essential to provide opportunities to solve these issues , thereby enhancing the electrochemical performance .   
  
Further observation and understanding of superstructures at different concentrations , and of the relevant transitions , will lead to greater insight into the overall control exerted on the system by the ionic ordering .   
  
The possibility of producing single domains using electric fields or by thin-film deposition should be investigated since the electrical conductivity will be higher along the stripes than for multidomain samples , increasing the figure of merit for thermoelectric applications .   
  
To better describe the Coulomb parameters , one should account for the intertwined physics from the electron occupation , screening , and structural details , which are highly system dependent .   
  
However , it would be still interesting to check whether other advanced DFT methods , for example , DFT+DMFT , can predict the lower voltage for NaCoO2 , which can be .   
  
As there are still ongoing discussions on the SCAN functional , especially on its capability when cooperated with vdW or +U scheme , the concrete consensus is still to come .   
  
Furthermore , hybrid functional overestimates the intercalation voltages of LiCoO2 and LiNiO2 and one needs manually adjust the mixing parameter .   
  
For the product of Ni foam reacting with NaOH , no diffraction peaks can be observed according to the XRD patterns , demonstrating that Ni hardly reacting with NaOH in the hydrothermal reaction .   
  
This capacity augment in the initial 40 cycles might be largely ascribed to the activation process .   
  
It is noted that the voltage plateaus are related to the existence of biphasic domains during Na+ ions insertion/extraction process .   
  
The decreased charge transfer resistance might be ascribed to the enhanced electronic conductivity in the activation process for the initial 100 cycles .   
  
The investigation of the sodium deintercalation properties should be of great importance in assessing the possible applications of NaNi1/3Co1/3Mn1/3O2 as Na-ion batteries cathode material .   
  
In contrast , full deintercalation of the sodium from NaNi1/3Co1/3Mn1/3O2 leads to dramatic decreasing of the layer distance of metal oxide , which will cause the structural instability of the materials and poor electrochemical performance .   
  
In certain applications of rechargeable batteries , such as grid storage , high rate capability is more critical than energy capacity .   
  
In addition , a spatially separated crystalline impurity phase was detected ; its amount is , however , below 0.1vol % ; in our opinion this phase will have only little effect on dynamic properties seen via impedance spectroscopy .   
  
The contaminant is inherently present in the sample and does not form during milling ; presumably , the reflection at ca . 38deg could be a hydroxide .   
  
Ball Ball milling milling produces nanocrystalline Na2O2 , the corresponding XRD peak widths are broadened due to size effects and lattice strain .   
  
Obviously , this feature , which should not be mixed with the increase of background signal below 30deg because of the glass capillary used , implies the presence of some amorphous material that is formed during mechanical treatment .   
  
Considering isotherms recorded at sufficiently low T , i.e. , considering those for which the second bulk process ( see above ) can not be resolved , the dc plateau seems to pass directly over into an NCL-type dispersive behavior .   
  
An explanation could be that the number density of charge carriers in Na2O2 is extremely low , which would result in very low conductivities .   
  
Therefore , in our case , the electrical response of the overall relaxation process in ball-milled Na2O2 might mainly reflect the bulk response but is also influenced by interfacial effects .   
  
Thus , one might assume that the first process is slightly influenced by interfacial or grain boundary processes while the other one reflects an electrical relaxation process taking place solely in the bulk regions .   
  
Point defects and dislocations , also influencing the effective charge carrier concentration , need be considered to explain the differences between theoretical and experimental studies on microcrystalline Na2O2 .   
  
If we assume that the associated activation energy is similar to that found for sdc , the corresponding diffusion coefficient D would be in the order of 10-25m2s-1 at room temperature -- still illustrating extremely poor conductivity .   
  
In structurally disordered Na2O2 , as it is obtained by high-energy ball-milling , the number of charge carriers as well as the number of available positions for the mobile species might be enhanced .   
  
Conductivity measurements revealed extremely low overall electrical conductivity following Arrhenius-type behavior with an activation energy of ca . 1eV .   
  
Nevertheless , the fully discharged compound ( x = 0.8 ) shows smaller thermal contraction of the Co-O bond if compared with the charged samples .   
  
Therefore , similar to LixCoO2 the charging/discharging of Na-batteries affects the configurational disorder in the Co-O sublattice , affecting the battery characteristics such as reversible diffusion ; however , the bond bond strength strength changes more prominently with desodiation , which may be the key factor for the limited battery capacity for NaxCoO2 cathodes .   
  
Instead , the temperature dependent MSRD reveal that the local Co-O bond are softer for the fully discharged cathode ( i.e. , in the sodiated cathode ) , while the Co-Co bond strength appears to remain unaltered .   
  
Recalling the faster diffusion rate for Na+ with respect to the Li+ ions , it is likely that local Co-O atomic disorder and bond strength are limiting factors in the diffusion capacity in the Na-ion batteries .   
  
Although microwave synthesis can produce very crystalline materials in rapid times , we were unable to produce any Red-phase until the reaction was held for at least 30 min .   
  
Additionally , we found that a minimum molar concentration of 0.3 M had to be used in order to produce the target phase .   
  
Second , the XRD data that were collected for this work was done on an instrument that does not rotate the sample during data collection , which is frequently used to remove the problem of preferred orientation .   
  
As mentioned above , our sample most likely has cobalt phosphate mixed in with the target phase and has a lower amount of available sodium for ( de ) -intercalation if we assume a sodium deficient model for the compound ( i.e. , Na0.76Co0.97PO4 ) .   
  
As mentioned above , one way to improve the energy density of sodium-ion batteries is to ensure that the capacity is delivered at the highest possible voltage without exceeding the stability of the electrolyte .   
  
If the transition metal polyhedra ( i.e. , FeO4 in Li2FeSiO4 ) share an edge with a counteraction with less formal charge ( i.e. , Li+ ) then the electrostatic repulsion felt by the transition metal is not strong enough to reduce the Madelung electric field and edge-sharing does not result in a higher voltage .   
  
Because this analysis was conducted ex-situ , it is difficult to determine if the peak at ~31.3 ( in the pristine electrode ) simply shifts and splits during charging or if it merges with the peak at 32.0 ( pristine electrode ) to give the resultant pattern seen in the charged electrode .   
  
The origin of this peak needs to be further investigated with combination of inductively coupled plasma-optical emission spectroscopy and high resolution neutron diffraction in the near future .   
  
However , the absence of the Co3O4 characteristic phonon peak at 700 cm-1 from our spectra rules out the existence of Co3O4 as a secondary phase .   
  
Therefore , the origin of the observed reduction in the resistivity for y > = 0.03 should be attributed to improved carrier mobility rather than higher carrier concentration .   
  
An immediate consequence is a subtle reduction of hole concentration due to electron-hole recombination , as mentioned in the previous section .   
  
At higher temperatures , the motion of Na+ ions in the Na layer is highly disordered ( i.e. , amorphous ) due to the high ionic mobility of Na+ .   
  
However , when a heavier and more positively charged ion is doped in the Na layer , it creates both mass and electrostatic inertia against the mobile Na+ ions at higher temperatures .   
  
It should be emphasized that the incorporation of ions with higher oxidation states ( i.e. , tri , tetra , pentavalent ) in the Na layers may not necessarily lead to an overall enhancement in performance due to higher degree of electron-hole recombination , which is caused by their higher electron contributions to the conduction band .   
  
Nevertheless , these SO4-alluaudites are metastable in nature with a tendency to deviate from stoichiometry to form AA'-excess and MM'-deficient compositions .   
  
Similar to the cases of Fe and Mn , despite several attempts , we were unable to stabilize single-phase Na2Co2 ( SO4 ) 3 often containing some amount of unreacted CoSO4 precursor .   
  
It is worth noting that while the BVS values of Na1 ( 1.185 ) and Na2 ( 1.184 ) are close to the expected value ( i.e . 1 ) , the slightly lower BVS value of Na3 ( i.e . 0.818 ) indicates shallow site potential for Na+ occupation in Na3 sites , favouring fast Na+ ion diffusion during cathode operation .   
  
There was no sign of any moisture content either in the bulk or surface , as confirmed by the absence of any band in the vicinity of 3500 cm-1 assigned to symmetric/asymmetric stretching of OH- species .   
  
While the Fe-alluaudite is stable up to 500 degC , the Co-alluaudite was found to undergo step-wise weight loss , followed by drastic weight loss at 750 degC .   
  
Nonetheless , the Fe-Co solid-solution alluaudite phases underwent sharp weight loss due to two-step decomposition at 250 degC and 500 degC .   
  
Nevertheless , we did not observe any redox activity in the safe operating potential window ( 2-4.6 V vs. Na/Na+ ) of some well-known organic electrolytes ( e.g . NaClO4/NaPF6 : PC ) despite repeated attempts with various cathode optimizations , carbon content , electrode thicknesses and galvanostatic cycling rates .   
  
For even smaller Vd , it becomes difficult for our finite size numerical calculations to discern the localized states and the values of Eb , leaving open the possibility of self-trapped , spontaneous local moment formation without the Na potential .   
  
Our study suggests another possible scenario where the in-plane FM order associated with the 3D A-type AF order does not develop on the 2D surface at finite temperatures .   
  
Naively thinking , the diffusion velocity of Na+ ions is very slow at such low temperatures .   
  
Thus , the Na+ distribution does not reach to a ground state within measurement time ( ~20 min ) below 200 K .   
  
The Madelung site energy calculation based on the structural data at 100 K fails to explain the significant difference in between Na0.52MnO2 and Na0.59CoO2 .   
  
Even though the mass loading for the powdered Na0 \* 74CoO2 can attain as high as 5.68 mg cm-2 , the low utilization rate of the active materials brings on the limited capacity ( 65 mAh g-1 ) and thereafter the low areal capacity .   
  
Although the i-Na0.7CoO2 electrode possesses an initial capacity of 126.3 mAh g-1 , a severe capacity decay is detected with the capacity retention of only 23.1 % .   
  
Compared to the Na0.7CoO2 nanosheet array electrode , the i-Na0.7CoO2 electrode prepared with traditional high temperature solid-state method and coating strategy shows obviously inferior electrochemical performance .   
  
It is considered that the traditional coating strategy via the isolated binders severely blocks Na+ ions diffusion pathways .   
  
In addition , the weak adhesion between active materials and substrates especially with high mass loading leads to drastic capacity loss .   
  
As expected , even through successive ultrasonic test for 30 min for the Na0.7CoO2 film , only a negligible amount of Na0.7CoO2 was peeled off from the substrate .   
  
Nevertheless , penetration of the graphite disk by the electrolyte is not observed .   
  
As a result , reactions between the electrolyte and both of these carbon working electrodes can only occur at the carbon-electrolyte interface .   
  
Upon further increasing the salt content , the conductivity of the electrolyte falls off significantly due to increasing ion interaction .   
  
However , in the case of NaPF6 , an insoluble fraction of conducting salt could be observed by eyes when exceeding concentrations of 0.4 M .   
  
A deviation from the VTF behavior is found below around -5 degC , which can be explained by partial solidification of EC once entering the two phase region of the phase diagram upon cooling .   
  
Consecutively also solidification of DMC might occur ( the eutectic mixture in the absence of the conductive salt freezes at -7.6 degC ) .   
  
As expected , the ionic conductivity rises with increasing temperature which can be attributed to thermally aided ion-dissociation and decrease in viscosity of the electrolyte solution .   
  
At low temperatures , NaOTf and NaClO4 based electrolytes are outside this regime , so overall NaPF6 is the preferred electrolyte over the whole temperature range .   
  
As seen from Fig . 5 ( b ) , considerably larger currents are found for the graphite sample during anodic sweep , especially when exceeding potentials above 4.3 V vs. Na/Na+ .   
  
Nevertheless , steel could be a good choice for certain combinations of active materials and electrolytes and their stability with sodium electrolytes has not yet been reported .   
  
In contrast to this , the CV profile of the above electrolyte with a SS316 grade shows an additional reduction peak at around 1.8 -2.0 V vs. Na/Na+ .   
  
However , this peak re-appears upon further scanning cycles .   
  
In these electrolytes , HF can be found as common impurity which may instantly react with oxides on the metal surfaces , resulting in the formation of fresh water molecules .   
  
For the NaClO4 based electrolyte ( Fig . 6 ( b ) ) irrespective of the type of current collector , a small hump was observed starting at potentials around 3.0 V vs. Na/Na+ .   
  
This behavior is likely to be related to the poorer stability of the ClO4- anion compared to PF6- and indicates that the perchlorate salt might be unstable even at potentials exceeding 3.0 V vs. Na/Na+ .   
  
However , a comparison on the hump observed at around 3.0 V vs. Na/Na+ could not be made for NaClO4-EC : DMC alone due to limited resolution data .   
  
For the NaOTf based electrolytes , side reactions during positive sweep occur even at potentials below 3 V vs. Na/Na+ ( SS304 ) , but peak positions and current density strongly depend on the type of current collector .   
  
Aluminium shows anodic instabilities at potentials beyond 3.2 V vs. Na/Na+ and no reduction process is observed during negative sweep .   
  
But excellent stability is found when cycled below that value .   
  
However side reactions start to occur at potentials around 3 V vs. Na/Na+ when less stable anions such as ClO4- and triflate are used .   
  
For the cells utilizing NaOTf and NaClO4 based electrolytes , the CV profiles exhibit a tendency for more pronounced irreversible electrochemical reactions .   
  
Even though the overall reversibility of sodium intercalation is mainly preserved , the large shift in reaction potentials ( i.e . appearance of overpotentials ) indicates fading of the electrode kinetics due to the formation of surface films with high resistivity .   
  
The NaPF6 based electrolyte shows a single , slightly flattened semi-circle in the Nyquist plot as the spectral information contains both RSEI and Rct related processes .   
  
However , no significant enhancement in the magnitude of RSEI and Rct is observed upon subsequent CV measurements .   
  
A similar trend was observed for the cell utilizing the NaClO4 based electrolyte with the exception of a gradual increase in contributions of RSEI and Rct upon each CV measurement .   
  
In summary , a stable surface film of low resistivity is formed in the NaPF6 based electrolyte , while both NaClO4 and NaOTf based electrolytes cause a steady increase in resistivity which is highly unfavorable for cycling Na0.7CoO2 .   
  
The increase in resistivity can be attributed to passivation of the electrode surface and formation of an electrochemically unfavorable solid electrolyte interphase film which causes attenuation of intercalation kinetics and electrochemical reactions .   
  
In the case of NaClO4 , severe decomposition is found at potentials exceeding 4.5 V vs. Na/Na+ , however , first reactions occur even at potentials as low as 3.0 V vs. Na/Na+ .   
  
Copper current collectors suffer from degradation beyond an operating potential of 3.2 V vs. Na/Na+ .   
  
The XRD patterns ( Fig . 4A ) exhibit no notable difference , which indicates good structural stability during repeated cycling , while the peak position of ( 002 ) slightly shifts to a lower degree ( Fig . S8 , ESI+ ) ; this may be due to the structural deterioration caused by deep Na+ intercalation/deintercalation after long-term cycling , corresponding to slight capacity fading ( ~3 % ) .   
  
It is very hard to approach the exact stoichiometry of x=0.763 as described by this ideal superstructure model electrochemically , partly due to the fact that 0.77 sits very close to the 0.77-0.82 miscibility gap boundary , stage ordering of defects would also contribute to the slight deviation from the ideal arrangement .   
  
However , the unusually high Curie constant can not be explained as coming from Co4+ of low-spin state t2g5eg0 s=12 only while at most 23 % of total Co ions can be Co4+ , unless the existence of higher-spin state is considered like that found in LixCoO2 .   
  
Frequency-dependence study of Tg using ac susceptibility measurement is not conclusive due to instrument resolution and temperature limit .   
  
The Stoner mechanism may not survive for x=0.77 and 0.71 of higher carrier density as suggested by its absence of A-AF ordering .   
  
Since the Na content has been tuned electrochemically at room temperature , we started the measurement with cooling cycle first in order not to produce any irreversible behavior due to overheating .   
  
However , the target Na concentration for Na23CoO2 is very hard to obtain precisely , partly because of its metastable nature .   
  
In any case , based on our findings it is clear that the role of oxygen deficiencies need to be accounted for in the modeling of the x=23 material .   
  
However , such deviation from the T-linear dependence at low temperature is evident and more significant in Na23CoO2 .   
  
We also remark that the extraction of carrier density from Hall coefficient data is not possible because of its strong temperature dependence due to strongly correlated nature .   
  
Studies on Na ion ordering based on screened intersodium interaction without considering the involved oxygen deficiency could result in misleading prediction or interpretation .   
  
The nanorod-assembled urchin-like architecture is not completely formed until 24 h .   
  
As with many transition-metal oxides and sulfides , the CoSe2 turns into nanoparticles , which shortens the Na+ transport path .   
  
According to previous reports , the carbonate-based electrolytes react with the intermediate products of transition-metal disulfides and diselenides , resulting in prompt depletion of active materials .   
  
In addition , although excellent cycling performance is obtained when testing in a voltage range of 1.0-3.0 V , the capacity is only 0.131 Ah g-1 , which is always lower than that of 0.5-3.0 V .   
  
According to previous reports , the irreversible capacity in the initial cycles mainly originates from the discharge capacity in the voltage below 1.0 V , which is attributed to electrolyte decomposition and irreversible reactions with conductive carbon .   
  
Although good cycling performance is achieved when enhancing the terminal voltage , it is indispensible to balance between the maximum Na-storage capacity of CoSe2 and cycling performance .   
  
One is to testify it after 50 cycles at 1 A g-1 to avoid the interference of initial decay .   
  
Unlike common ionic diffusion , the peak current ( i ) is not well proportional to the square root of the scan rate ( v ) ( Figure S14 , Supporting Information ) , indicating that the charge-discharge process is composed of non-faradaic and faradaic behaviors .   
  
The irreversible capacity gradually decreased with an increase in the cycle number and was negligible at 10th cycle .   
  
While 1.33 electron reactions should be required to deliver the theoretical capacity , the reversible capacity of 110 mAh g- 1 was limited to ca . 0.86 electron reactions .   
  
In general , organic electrolytes are unstable in the high potential region and the electrolyte decomposition would occur .   
  
The polarization of the charge/discharge reaction was little enough to maintain high discharge potential above 4.0 V at 5 C rate .   
  
The tiny shifts of the absorption energies above charge capacity of 136 mAh g- 1 indicate charge compensation by Co , Mn and Ni ions could not work well , because the irreversible side reaction such as electrolyte decomposition occurred .   
  
If the SEI layer , which was washed away before the XPS measurement was made , contains Ni2+ , the remaining product would be a little Ni3+-rich .   
  
Hence , the initial fade in the specific capacity at 0.03C rate appears to be the result of formation of a solid-electrolyte interphase ( SEI ) layer .   
  
With an increasing rate of charge/discharge , the limited diffusion rate of Na+ reduces the specific capacity .   
  
Since the plateau at 4.4V in the charge curve of Fig.2 corresponds to the formation of an SEI layer , we attribute the small peaks in Fig.5 at ca . 4.3 and 4.0V on , respectively , the anodic and cathodic sweeps to a surface structural reorganization occurring as a prelude to the formation of the SEI layer .   
  
But from the rate study , it is evident that after charging to 4.3V ( or higher ) vs Na+/Na ( see Fig.2 ) , Na extraction/insertion is rather slow .   
  
However , the replacement of a fraction of the Na+ ions with Sr2+ should prevent the in-plane Na+ ordering .   
  
However , several small plateaus indicate that although long-range ordering of Na+ ions has been suppressed , short-range orderings probably persist .   
  
We also tried to make a similar electrochemical test for a Na2Co2TeO6 coin-cell with sodium as the negative electrode ; Na+ could not be reversibly extracted/intercalated in this case , and electrolyte reduction was observed , rendering the coin-cell dead for subsequent cycles ( see Fig.8 ) .   
  
At a voltage greater than 4.0V vs Na+/Na , the electrolyte used can be oxidized with the formation of an SEI layer ; the capacity fade at fast cycling rate does not appear to be the result of an SEI-layer formation .   
  
On the other hand , XRD results of samples with a mixture of Co , Mn , and Ni were sensitive to the calcination temperature .   
  
However , with the same rate , we could not achieve a pure P2 phase for the other compositions ( y = 1/2 and 2/3 ) , for which both P2 and P3 phases were detected at 800 degC , whereas NiO impurities were identified at 850 degC .   
  
The introduction of Mn and Ni in P2-Na x Co ( 1-y ) Mn2y3Ni y3O2 reduces the Co content , leading to a decrease of the Co4+ formation rate .   
  
In addition , nonstoichiometric oxygen is expected in this type of material when synthesized in air .   
  
However , an attempt to increase the pH to 7 , in our case , resulted in the appearance of a small impurity of nickel oxide in the XRD patterns .   
  
The samples with a combination of Co , Mn , and Ni ions have only three peaks , and their intensity decreases with increasing x , which is manifested in lower specific capacity values .   
  
- However , it is clear that these ordering phases are also strongly related to the electronic composition of the ( MO2 ) n layers , where the presence of Co4+ appears to accentuate the intensity of the potential jumps .   
  
For P2-Na x Co1/3Mn4/9Ni2/9O2 ( y = 2/3 ) and Na x Mn2/3Ni1/3O2 ( y = 1 ) , however , it is difficult to point out the start of the potential jump .   
  
In addition to the reaction of these materials with air , they react with the binder ( PVDF ) to form NaF during electrode manufacturing , making it difficult to identify the exact sodium content .   
  
However , the Coulombic efficiency of Na x CoO2 decreased slightly from 99.5 % in cycle 20-98.8 % in cycle 50 .   
  
On the other hand , the capacity for Na x Mn2/3Ni1/3O2 increased slightly from 100.8 to 102 mAh g-1 in the 25th cycle and then dramatically decreased afterward to only 93.92 mAh g-1 in the 50th cycle .   
  
On the other hand , despite a specific discharge capacity of 136.57 mAh g-1 , Na x CoO2 ( y = 0 ) completely lost its voltage profile during the first discharge .   
  
Although Na x CoO2 ( y = 0 ) delivered better electrochemical performance than that from Na x Mn2/3Ni1/3O2 ( y = 1 ) when cycled between 2.0 and 4.2 V versus Na+Na , no reversibility was possible when the sample was cycled up to 4.5 V versus Na+Na , leading to a very low capacity retention of only 28 % after 20 cycles .   
  
In conclusion , despite the higher capacity values achieved , the capacity retention was lower when we cycled the materials up to 4.5 V versus Na+Na with the appearance of a new plateau .   
  
Because we had cycled the three samples at high voltages , electrolyte decomposition is one of the main causes of the irreversibility .   
  
Although each sample might react differently with the same electrolyte , we believe that the strange behavior of Na x CoO2 ( y = 0 ) is caused by a much more complex phenomenon and more studies need to be addressed to understand the structural evolution of this material at high voltage .   
  
According to our electrochemical results , more sodium ions are inserted into P2-Na x Co1/2Mn1/3Ni1/6O2 during the first discharge ( 0.4 Na+ ) and then are extracted during the first charge ( 0.3 Na+ ) because we cycled it beyond its OCV value .   
  
This allows the material to deliver a higher discharge capacity during the first cycle , and the difference needs to be compensated by reduction of transition metals beyond their first state .   
  
Their counterparts ( lithium carbonates ) decompose due to electrochemical oxidation , but they are not reversibly formed by electrochemical reduction , suggesting that they can be formed as a byproduct of the oxygen reduction reaction .   
  
Also , only one potential jump was observed in their voltage profiles , and its intensity decreased with decreasing Co content .   
  
Even though increasing y ( Mn2/3Ni1/3 ) lowered the discharge capacity , it remarkably increased the capacity retention .   
  
However , the three materials ( y = 0 , 1/2 , 1 ) showed lower stability with cycling , where Na x CoO2 ( y = 0 ) completely lost its voltage profile during the first discharge , and the capacity retention dropped to less than 94 % for the other samples after only 20 cycles .   
  
This new finding raises questions about the origin of the high-voltage plateau and the phase transition that accompanies it , and further studies are needed to understand and improve the stability of P2-type materials at high voltages .   
  
Though at first we expected a higher Co redox potential , the presence of the strongly covalent CoO4 tetrahedral building unit can be considered as the root cause behind the relatively lower redox potential of 3.0 V .   
  
However , the initial steady cycling stability slowly fades after 20 cycles ( ESI+ ) , the reason being unclear at this point .   
  
Owing to the high operating potential ( 4.5 V ) close to the stability limit , the electrolyte may undergo slow but steady decomposition .   
  
Secondly , the prolonged electrochemical cycling leads to the gradual decomposition and accumulation of organic components at the surface of the positive electrode ( Na2CoP2O7 ) side .   
  
Though the addition of FEC additives restricts this problem , it can not eradicate it completely .   
  
As a function of time , however , gradual formation of undesirable organic products ( at the Na metal counter electrode ) and their accumulation on the Na2CoP2O7 particles leads to gradual capacity fading .   
  
Looking into the near linear voltage profiles , one may wonder if the net capacity arises owing to capacitive contribution from the carbon additives in the cathode composites .   
  
Comparative X-ray diffraction patterns showed peaks shifting towards lower angles in the Na2-xCoP2O7 ( ESI+ ) , suggesting possible lattice expansion upon desodiation while retaining the pristine structure .   
  
However , the presence of a modulating structure accommodating lattice strain , e.g . large inter/intra-layer Co-Co distances and limited ( de ) insertion of Na atoms , may minimize the strain involved during electrochemical cycling .   
  
Nevertheless the need for prolonged heat treatment in the solid-state route leads to aggressive grain growth and agglomeration , hence forming large micrometric particles .   
  
However , the values of b2 decrease with increase in doping suggesting that there is an increase of crystallographic distortion .   
  
However , this variation could also be due to the creation of some in-gap states which would change with doping .   
  
We anticipate that concentration of Co4+ ions would decrease with increase increase in in doping doping of of W6+ W6+ ions ions resulting in increase of hopping distance and therefore increase in activation energies with doping .   
  
With further increase in doping content ( x ) , structural distortions and electron-doping like behavior of W6+ ions , due to the higher valence state of W6+ than Co3+ and Co4+ ions , start to dominate and result in decrease of carrier concentration .   
  
However , x = 0.0 sample does not follow this trend suggesting that the electronic specific heat ( Ce ) and second term in above equation are the dominated factors here .   
  
However , we can not rule out some other unexplained microstructural aspects of these materials that can also be responsible for irregular behavior in thermal conductivity of doped samples .   
  
Such abundant porous structures can promote electrolyte permeation , thus affecting the electrode 's rate performance .   
  
In other words , moderate amounts of Al doping can facilitate the electrochemical performances of NCPP , while excessive Al doping is adverse because of the inactive Al3+ , leading to reversible capacity reduction .   
  
The overlapping CV reduction curves imply that the capacity decay of the Al0.15-NCPP electrode can be neglected and it has excellent reversibility .   
  
In contrast , NCPP has a capacity retention of only 80.3 % , showing inferior cycling stability .   
  
Obviously , at current densities of 5C and 10C , the cycling performance of Al0.15-NCPP is far superior to that of NCPP .   
  
The smaller voltage drop implies that lower electrochemical polarization of Al0.15-NCPP can be achieved with successive Na+ ion intercalation and deintercalation at a high discharge current density of 30C .   
  
Moreover , too much Al doping may induce large changes in the structure and cause phase instability , hindering the Na+ ion diffusion and thus leading to inferior electrochemical performance for Al0.2-NCPP .   
  
From the SEM images ( Fig . S12+ ) , it is clear that the Al0.15-NCPP electrode material maintained its original microspherical morphology , and the structural deterioration is not obvious , whereas serious serious structural structural collapse collapse occurred for the NCPP electrode material , showing serious pulverization .   
  
Al0.15-NCPP exhibits superior performance in the half-cell system , and demonstrating the prospects for application of this promising high voltage material by a full battery test is more important .   
  
On the other h , it is also important to spell out some modeling limitations for this method , which must be understood carefully to overcome them in the future .   
  
In addition , the present RM method is not optimized for studying electron tunneling reactions .   
  
The SEI layer formation occurs from the reduction of electrolytes at the anode surface due to the electron electron leakage leakage from from the the anode anode during the first charging cycle .   
  
However , it is challenging to directly capture the reactions at the electrode/electrolyte interface experimentally , as some could occur at the picosecond ( ps ) timescale .   
  
In contrast , the less favorable decomposition of DFEC could promote the presence of inactive DFEC molecules , which should cause large cavities during the SEI film formation and reduce the stability of SEI film .   
  
Accordingly , the dissolute PC-derived products must aggregate toward the bulk electrolyte through a `` near-shore aggregation mechanism '' .   
  
On the other h , some high peaks of dissoluted products appear in the bulk electrolyte solution due to the high transport properties of Na+ cation .   
  
To overcome such limitations , many investigations were focused on suppressing such dissolution of SEI components and optimizing the NIB electrolyte with appropriate additives .   
  
In fact , the use of VC , ES , and DFEC as additives in NaPF6/PC solution deteriorated the initial reversible capacity .   
  
In contrast , no apparent deposit was shown in FEC-free PC-based electrolytes .   
  
Such bridge formation could be essential to suppress the dissolution of SEI products leading to the formation of compact SEI film .   
  
As results , the FEC addition must lead to a compact and dense SEI film regardless of whether or not FEC reduction reactions take place .   
  
Selecting the appropriate additive is essential to enhance the cycling performance of NIBs .   
  
The increase of reduction plateau indicated the suppression of the reduction process in FEC-added electrolytes .   
  
A possible explanation was that FEC is adhered to the surface and adsorbed at the electrolyte/electrode interface before its being reduced ; FEC molecules are instantly electrochemically reduced at the electrode surface when the potential is driven to low values .   
  
However , an open question was why such positive effect of FEC was optimum at a lower concentration , while the negative effect was appeared by increasing FEC amount showing a deterioration of NIBs performance at higher concentration .   
  
Regardless of the FEC additive concentration , the dissolution amounts of SEI film products were numerically found lower in the FEC-added electrolytes , even when the concentration is quite small , in comparison to those in the FEC-free one .   
  
On the other h , due to the dependency of the SEI film structures on the FEC concentration , the formation of dimer products ( Na2DMBDC ) was clearly increased at the lower concentration of FEC , and decreased by increasing FEC concentration .   
  
Thus , the increase in the organic products made the cavity size decrease , leading to the formation of denser SEI film at low FEC concentration .   
  
In addition , the formation of inorganic products as NaF and Na2CO3 decreased at the lower FEC concentration ( Fig . 8b ) , reducing the production of the gas molecules such as C3H6 and CO2 .   
  
In contrast , by increasing the FEC concentration , the cavity sizes increased to make the interaction energy decrease among SEI film compounds leading to the smaller stability of porous SEI film .   
  
Consequently , its durability should reduce under any mechanical impact , e.g. , the collision of Na+ cations and electrolyte solvent molecules .   
  
However , such treatment remains limited for evaluation of the SEI stability because only the organic products were considered and not the whole SEI layers .   
  
By increasing FEC concentration , the increase in the number of bridges prevented the direct contact between NaPCs so as to decrease the reaction frequency of the dimer formation .   
  
In addition , it was found that the increase in the FEC amount decreases the diffusion of NaPCs due to the higher viscosity of the FEC-added PC solvent than the FEC-free one .   
  
It was , therefore , concluded that these two effects at the higher FEC concentration lead to the decrease in the organic dimer formation and unstable SEI film by reducing the collision frequency between NaPCs .   
  
However , the SEI film should become unstable by another negative factor due to the insufficient organic dimer formation .   
  
However , PC-based electrolyte itself showed less efficiency to form a stable SEI film in LIBs with the graphite anode contrary to ethylene carbonate ( EC ) -based electrolyte , despite the close structural similarity between EC and PC solvents .   
  
Such contradictory behavior , especially between EC and PC solvents , opened mysterious questions since both EC and PC commonly undergo reductive ring-opening reactions to form similar dimerized products .   
  
However , the question of why PC-derived products are unable to form a good SEI layer remains .   
  
In the PC-based electrolyte ( Fig . 10c and d ) , the aggregation of the reduction products was clearly weaker than in the EC system ( Fig . 10a and b ) , leading to the higher dissolution of SEI film products in the PC-based electrolyte .   
  
Such a high presence of gas could generate the graphite exfoliation observed experimentally in a PC-based solvent .   
  
Furthermore , the RM simulation reveals that in addition to the familiar role of FEC decomposition to form a NaF-rich SEI film , the intact FECs themselves play a role in suppressing the dissolution of SEI film products .   
  
At the same time , it decreased with the increase in the FEC amount , leading to a decrease in the NIB lifetime during charge-discharge cycles .   
  
According to RM simulation results , it was verified that the SEI film should become unstable due to the insufficient organic dimer formation .   
  
The lower capacity during first charge in the upgraded electrolyte , already observed in a previous work , may be most likely attributed to the formation of a passivation layer at the cathode surface partially hindering the de-sodiation process .   
  
However , both the carbonate-based electrolytes revealed a very poor behavior , with very limited signs of sodium intercalation process in the sodium cell .   
  
The poor electrochemical performance may be ascribed to the unfavorable graphitic interlayer distance compared to the ionic radio of sodium ions in carbonate-based electrolyte media that hinders the formation of binary GICs , which should enable the Na-intercalation process .   
  
The cell completely recovers its initial capacity when the current is lowered back to 1C .   
  
The voltage profile during the test reported in Fig.4d evidences relevant capacity retention and almost no effect of the increasing current on the polarization , thus further accounting for the high rate capability of the cell .   
  
However , prior to combining anode and cathode , the high performance of the P2-Na0.7CoO2 should be confirmed in the TEGDME-based solution , that is , the most suitable electrolyte for the anode .   
  
The first cycle reveals the expected lower charge capacity in respect to the discharge ascribed to the above discussed sodium deficiency in the cathode that is used without any activation ( compare with Fig.S1b in SI section ) .   
  
Certainly , we are aware that our SIB still requires optimization , especially in terms of overall cell balancing so as to properly address the initial irreversible capacity and finally increase its overall electrochemical behavior .   
  
For electrostatic reasons , Naf is expected to be less stable than Nae , thus , will be emptied first during the desodiation reaction .   
  
A structural ordering in the interslab space between sodium and vacancies could be expected as the origin of this potential jump .   
  
Loss of initial capacity after 50 cycles was only 2 % , and the coulombic efficiency approached 98 % .   
  
Nevertheless , when the deintercalated sodium exceeds 0.3 , the NaxTiO2 system with O3-type structure suffers from an irreversible structural transition , resulting from titanium ions migration from the slab to the interslab space .   
  
Consequently , high cell polarization is observed , leading to a low stability of NaxTiO2 in O3 stacking .   
  
The cathode material P2-NaxCo1/2Ti1/2O2 seems to overcome this issue .   
  
The first possible one , is the low concentration of Ti3+ present in the expected Na2/3 ( Co3+ ) 1/2 ( Ti4+ ) 1/3 ( Ti3+ ) 1/6O2 starting material that reduces the titanium migration .   
  
The other is that the sodium environment in P2-Na2/3Co1/2Ti1/2O2 is dissimilar to that in O3-type .   
  
Nevertheless , the continuous evolution of the polarization in the studied composition range ( without abrupt change ) indicates no first-order structural transition .   
  
At the end of the charge process , it seems that a potential plateau starts to form , but this could be a result of electrolyte degradation at such high potential .   
  
This phenomenon leads to an open structure and layered oxide with high interslab space at the end of charging .   
  
It should be noticed that an irreversible plateau at high voltage ( 4.3V ) appears during the first cycle , in addition to obvious polarization .   
  
This transition induces a change in the sodium environment , which could be the reason for obtaining the irreversible plateau .   
  
However , similar compounds showed that , when the same plateau is present but at lower voltages , the reversibility is greater .   
  
Therefore , we believe that the decomposition of the electrolyte at high voltages might be the main cause of the irreversibility of the plateau and the deterioration of the electrode performance ( polarization ) .   
  
However , the low resistivity of the cathode prepared through solid state reaction can be attributed to the well connected grains when compared to agglomerated/porous sample obtained by ball milling and sol gel techniques .   
  
The cells have not been subjected to charge-discharge cycles due to low value of Na+ diffusion coefficient of about 10-12cm2/s when compared to that of value 10-8cm2/s for Li+ in the LiCoO2 based systems and low ionic conductivity of the electrolyte ( 10-6S/cm ) when compared to that of conventional liquid electrolyte .   
  
However , for the cobalt ( II ) ions the coordination to the sulfonate groups is weak and the intercalation of MV2+ dication into the cavity of p-sulfonatothaicalix [ 4 ] arene can easily break the potential layer arrangement .   
  
However , the charge disproportionation induced by 8 % mole divalent Mg doping in NaCoO2 affects both Co and O simultaneously .   
  
However , divalent Mg ion doping in Na ( Co0.92Mg0.08 ) O2 will lead to charge disproportionation , which affect simultaneously the electronic structure of both Co and O .   
  
The OCP is slightly higher than Vapp for x > 0.5 , but is significantly lower than Vapp for x < 0.5 due to the side reaction .   
  
Whether such 3/7 superlattice ordering exists within the bulk requires further Laue transmission diffraction analysis .   
  
One of the major concerns in the experimental study of NaxCoO2 compounds is the question of phase homogeneity .   
  
No other samples exhibited two-phase signatures regardless of whether Vapp falls in the dx/dVapp=0 plateau range .   
  
axis , it is possible that in-plane ordering may yield potential microscopic phase separated domains as commonly found in this series .   
  
We can not rule out the possibility of phase segregation below room temperature .   
  
The significant thermal hysteresis found below ~27K for Na0.5CoO2 strongly implies its weak ferromagnetic nature .   
  
much higher charging rate may yield metastable phases of Na0.55CoO2 of higher weak FM moment , and these may eventually fall into .   
  
Clearly more work is required to investigate the effects of Na order across the NaxCoO2 phase diagram .