Elements  
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All of these samples show a reversible phase transition from a monoclinic to a rhombohedral phase around room temperature , implying that the substitution of V in Na3V2 ( PO4 ) 3 by Cr has little effect on this phase transition .   
  
With specific regard to the Na3VCr ( PO4 ) 3 electrode , its S-shaped profile during the first cycle is evidently different from the dominant potential plateau for the other three kinds of electrode .   
  
The observed S-shaped curve of Na3VCr ( PO4 ) 3 electrode is consistent with previous reports showing irreversibility of the phase change during initial cycles and fast capacity fade at room temperature .   
  
As is known , an excessive oxidation can induce highly toxic Cr6+ , which is recognized as a possible risk .   
  
The presodiation treatment is necessary for Na3V1.5Cr0.5 ( PO4 ) 3 to deliver its full sodium storage capacity based on the three-electron redox reactions .   
  
However , it should be pointed out that the overpotential between the major charge/discharge plateau increases as the current density is increased .   
  
As a result , some energy loss is inevitable at high current densities .   
  
In situ XRD analysis will be necessary to provide more detailed information .   
  
Rct was prominently reduced upon charging , especially at the high cutoff voltage of 4.4 V , which is ascribed to a high cathode Na-ion diffusion after initial extraction of sodium .   
  
In Step # 2 , mechanical stirring could be implemented to prepare larger sodium particles ; however , preliminary result suggests that ultrasonication is needed to form fine sodium particles .   
  
While the majority of the particles appear spherical , some irregular sheet-like particles are observed that may have resulted from localized rapid cooling ( likely near the reactor wall ) , that preventing the molten sodium particles from solidifying into the preferred spherical shape .   
  
The fabrication of smaller particles is likely possible by reducing the ratio of sodium to mineral oil in the reaction vessel and may be more desirable to provide better penetration into the porous electrodes , to improve uniformity of electrode pre-sodiation .   
  
The presence of NaOH may originate from the reaction of metallic sodium and trace water present in hexane or from potential potential air air penetration penetration into into the the sample sample holder holder during XRD analysis .   
  
However , the heat of fusion ( melting ) for sodium powder is about 20 % lower than sodium reference , suggesting the presence of fine sodium particles or possible low-level NaOH impurities .   
  
More importantly , the OCV of the NaMP-coated cell is about 1 V lower than that of the uncoated cell , suggesting that partial sodiation of the active material occurs during the aging process , as sodiated carbon exhibits lower potentials .   
  
In full cell configuration , such improvement in the first cycle loss would translate to a reduction of `` sacrificial '' cathode active materials for increased specific cell capacity .   
  
The low first cycle Coulombic efficiency of the full cells can be attributed to the low first cycle efficiency ( ~55 % ) of the NaCrO2 cathode ( see Fig . S5 ) .   
  
Further optimization effort could improve the Coulombic efficiencies of the NaCrO2 cathode and the full cells .   
  
The polarization likely originates from the shift of the potential windows for the cathode and anode in the full cell due to unfavorable electrochemical side reactions that consume available alkaline ions .   
  
In comparison to the NaMP coated cell , the broader charge and discharge peaks and the larger reduction in peak intensity from cycle 30 to 70 in the uncoated cell provides further evidence of electrode degradation arising from the depletion of available sodium .   
  
Consequently , future work will focus on the development of surface protection layer on NaMP to enhance its air and water stability .   
  
Mechanical compression of the NaMP-coated NaMP-coated electrodes electrodes is found to be beneficial to activate the sodium powder .   
  
With the addition of sodium powder , GC1100 electrodes show reduction in first cycle capacity loss .   
  
Future work on reducing impurity contents in sodium powder and stabilizing sodium powder in air should yield further improvement in cell performance .   
  
However , it is noted that the new peak at 6.3 degree disappears on further heating to 527 degC , which suggests that P3 CrO2 is a thermodynamically metastable phase .   
  
Phase transitions with voltage plateaus were also observed at 150 degC in Na cells even though it was less pronounced compared with voltage profiles collected at the room temperature .   
  
Although the Na/vacancy ordering is lost at 207 degC , oxygen loss and phase segregation are not evidenced from the HT-SXRD pattern .   
  
Therefore , sodium batteries would be operated at 200 degC if a thermally stable negative electrode and electrolyte at 200 degC exist .   
  
However , such three-phase coexistence is hypothesized to originate from the kinetic limitation on the layered-layered phase transition ( P3-O3 phase transition ) and/or sodium diffusion across the CrO2 slabs , namely the kinetic limitation for the phase segregation in individual particles .   
  
Moreover , the ARC study clearly revealed that Na0.5CrO2 is stable even with electrolyte solvent as a reduction agent .   
  
Nevertheless , when the sodium content is further reduced to x < 0.5 in Na x CrO2 by electrochemical oxidation , the structural characters are being similar to those of the lithium system , leading to unavoidable irreversible phase transition .   
  
On further heating , two metastable oxides , presumably Na-rich and Na-free P3 phases , are formed probably because of the phase segregation on heating to 287-477 degC .   
  
Secondly , the AEP of Na-based battery is somewhat lower than Li counterparts , in view of our calculated AEP for NaCoO2 ( 2.84V ) and LiCoO2 ( 3.36V ) .   
  
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 .   
  
After some Li ions are extracted from the host , c-axis elongates consequently , which will facilitate the ion diffusion between these oxygen layers and decrease their motion barrier ultimately .   
  
Consequently , more energy is needed to remove electrons on Na from the lower energy system .   
  
Cubic Na3PS4 is crystallized via mechanochemical treatment in this study , while impurity components such as Na2SO3 in reagent Na2S used in the previous paper may play an important role on amorphization of electrolytes .   
  
The FWHM becomes larger with increasing milling periods of time , resulting in decreasing conductivity and increasing activation energy .   
  
Therefore , detailed structural analysis by high-resolution TEM observation is further needed for clarifying the effects of cubic Na3PS4 component on conductivity of glass-ceramic electrolytes .   
  
The sulfide glass with impurities such as Na2SO3 probably has a lower conductivity than the glass with less-impurity because the additional anion species act as a trap for Na+ cations , resulting in prevention of Na+ ion conduction .   
  
A large irreversible capacity is observed at the initial cycle .   
  
The capacity gradually decreases with initial three cycles and then almost constant capacity of 60mAhg-1 is retained after the 7th cycle .   
  
A potential reason for the initial irreversible capacity and capacity fading is the increase of cell resistance .   
  
In the all-solid-state lithium cell with LiCoO2 positive electrode and Li2S-P2S5 sulfide electrolyte , a large resistive layer was formed at the interface between the electrode and the electrolyte during the charging process .   
  
Detailed structural analyses are important for clarifying stability of the glass-ceramic electrolyte under a high oxidative state in contact with the charged NaCrO2 active material .   
  
Surface coating of NaCrO2 with oxide thin films must be effective in developing cell performance and will be examined in the near future .   
  
Slight decrease in weight was observed even after 20-h heating , suggesting minor further decomposition or vaporization of remaining CrO3 .   
  
It is worth noting that when the 10-h sample was dispersed in distilled water , the filtered solution exhibited an orange color ( Fig . S1 ) , which is an indication of residual CrO3 .   
  
The slow rate performance is a result of poor electronic conductivity of Cr2O5 and can be improved by increasing the content of conductive carbon matrix in the cathode .   
  
The Cr2O5/Na battery exhibited a broad redox peak with the center at 1.55V during discharge , and no clear peak was observed during charge .   
  
However , this sharp resonance is short-lived as the discharge process proceeds further .   
  
The sharp resonance disappears completely in electrodes discharged below 1.8V , with the broad component dominants the spectra at low voltages .   
  
Below 1.8V , a dramatic increase in fraction of the diamagnetic component at 0ppm is observed , indicating a significant amount of SEI formation at low voltages , while the amount of Na ions in the bulk remains nearly constant .   
  
Minor Na remains in both the SEI and bulk even at the top of charge ( 4.0V ) .   
  
The 23Na paramagnetic shift of the residual bulk Na at the top of charge is much smaller than that of Na ions intercalated at the beginning of discharge .   
  
The lack of significant change in the paramagnetic shift of the bulk Na in the crystalline Cr2O5 indicates a two-phase reaction at the early stage of discharge , i.e . the conversion of the crystalline to the amorphous Cr2O5 as more Na is intercalated .   
  
The greater charge transfer resistance is likely due to the loss of electric contact among chromium oxide particles in the electrode as they were broken down with extended cycling .   
  
Slower Na+ ion diffusion may be a result of reduced electrolyte concentration , as the electrolyte decomposition occurs to form solid electrolyte interphase ( SEI ) , which in turn blocks Na+ pathway .   
  
The continuously thickening SEI layer inevitably blocks Na transfer into the bulk and increases the impedance .   
  
Based on all the experimental evidence , the capacity fading in the Cr2O5/Na batteries may be caused by the following factors : 1 ) loss of electric contact resulting from particle break-down ; 2 ) generation of strong oxidizing CrO3 , which leads to catalytic electrolyte decomposition and thick thick SEI SEI formation formation that depletes Na electrolyte as well as blocks Na intercalation .   
  
However , minor Na remains in the bulk structure and SEI after each cycle , which leads to gradual capacity fading .   
  
Impedance spectroscopy , 23Na NMR , and powder-XRD data on cycled batteries have suggested that loss of electric contact due to structural amorphization and CrO3-catalyzed electrolyte decomposition are among the major reasons for gradual capacity degradation .   
  
However , only 87 mAh g-1 of reversible discharge capacity can be obtained , which indicates the serious irreversible capacity decline .   
  
This obvious capacity loss during initial cycle of NCO can be rationally ascribed to an irreversible structural distortion .   
  
From the dQ/dV curve of NCRO in Fig . S3b , the irreversible oxidation peak around 3.8 V disappears .   
  
Moreover , during the following 50 cycles , there is an obvious irreversible capacity fade of NCO , which is confined to a low capacity retention ( 52.3 % ) presented in Fig . 2c .   
  
In comparison , the reversible capacities of NCO demonstrate remarkable decline at constant current rates , which implies poor rate capability .   
  
On the other side , changes of the Rct of NCRO sample after 10 and 50 cycles are not obvious , corresponding to its superior reversibility over 50 cycles .   
  
However , the Ru-doping NCRO possesses good reversibility , which is in striking contrast to NCO .   
  
The much lower Cr/Na content of NCRO than NCO demonstrates chromium ions in Na layer is almost nonexistent during desodiation .   
  
The chromium ions in sodium layers would inhibit Na insertion into the collapsed structure during discharge , responsible for serious capacity loss .   
  
In summary , O3-type NCO suffers from a significant capacity decrease by charging to 3.8 V on account of the migration of Cr ions from CrO6 slabs to sodium layers during the initial charge process .   
  
The migration process is irreversible and hinders Na insertion into the layer oxide , leading to the loss of capacity .   
  
Although an emulsion is easily separated into water and oil phases , the addition of an emulsifying agent prevents this separation and stabilizes the emulsion .   
  
Even more seriously , the formed NaOH and Na2CO3 are electrical insulators ; this , in turn , increases the resistance resistance of of the the active active mass mass .   
  
Therefore , the crystal structure did not change even after exposure to air for 48 h , whereas bare NaCrO2 underwent phase separation into Na-deficient NaxCrO2 and NaOH ( Fig . S4a , ESI+ ) after even a brief exposure to air .   
  
However , the resulting electrochemical performance was disappointing for bare NaCrO2 .   
  
We proved that the excellent performance of this cathode material is intrinsic and does not relate to the solution used .   
  
Hence , the poor cycling performance can be understood ( Fig . 2b ) .   
  
It is interesting that the only difference between the two types of electrodes is the presence of a carbon coating layer .   
  
The cycling performance and rate capability of cells with bare NaCrO2 cathodes were disappointing ( 70 % at the 100th cycle ) .   
  
Thermal stability is another important parameter that should be investigated before these electrode materials are considered for use in practical power sources .   
  
Another interesting feature is that de-sodiated Na0.5CrO2 does not produce a cubic spinel phase such as that formed by de-lithiated transition metal oxides even after release of oxygen from the parent oxide .   
  
In addition , the observed exothermic heat produced from the phase separation process was also greatly reduced because of the slow evolution of oxygen from the crystal structure .   
  
Even after the exothermic reaction was complete , the weight loss was smaller for C-Na0.5CrO2 material up to 400 degC .   
  
In addition , the generation of heat from de-sodiated C-NaxCrO2 is relatively small due to the suppression of the evolution of oxygen during the exothermic reaction as a result of the presence of the carbon coating layer .   
  
Evidently , the presence of the nonelectrochemical active or lower performance NaMn1-yCryO2 phase decreases the overall properties of the electrode .   
  
The difference between the materials obtained from the in situ XRD and synthesis experiments may be due to the longer dwell time at 1000 degC in the latter , which provides enough time for NaMnO2 to be consumed .   
  
The trend of the continuous increment in the lattice parameter c for both O3 and P3 phases during charging was reversed during discharging .   
  
This small volume change only introduces a small amount of stress during the O3 - P3 phase transition , which is advantageous for the phase stability and cyclability of the cathode .   
  
Minimal shifts occurred during the discharging process , which is probably due to the reduced state in the pristine samples .   
  
However , the bond lengths of the second coordination ( Mn-Cr or Cr-Cr ) for both the Mn K-edge and Cr K-edge shortened slightly during the charging process , which could be due to the loss of sodium ions .   
  
Similar features could be seen in the discharge process as well , indicating the discrepant Na extraction/insertion process among different cycles .   
  
The overall capacity drops quickly from 90 to 77.6 mA h/g in five cycles , which is mainly due to the loss of high-voltage capacity .   
  
Obviously , if the upper limit is 4.0 V , NVCP shows a negligible capacity loss during cycling .   
  
- However , the shift of the edge indicates that V4+ is not completely oxidized to V5+ when charged to 4.3 V , which may be caused by the relatively sluggish kinetics of the active material and the competitive oxidation of the electrolyte in the high-voltage region .   
  
However , the intensity of the pre-edge of the sample at the end of discharge is higher than that of the pristine one , indicating that the local environments of vanadium ions are not completely recovered .   
  
More importantly , as shown in Figure S5b , the diffraction peaks do not completely shift back to their original positions at the end point of discharge , revealing an irreversible phase transformation process during Na extraction/insertion .   
  
Regarding the second charge process , it is apparent that the pattern features are quite different from that of the first charge , meaning that irreversible transformation of the structure has occurred in the first charge process .   
  
On the basis of the aforementioned analysis , we conclude that the irreversible bulk structure transformation coupled with the unrecovered local environment of vanadium atoms causes the loss of the high-voltage capacity , thus leading to the decrease of the overall capacity of deep desodiated NVCP during cycling .   
  
It is worth noticing that the irreversible transitions are possibly kinetically slow and that the desodiated species Na2-y V y 5+V1-y 4+Cr ( PO4 ) 3 is metastable because the Na ( 1 ) site is immediately depopulated with the onset of the high-voltage plateau , whereas the NVCP electrode still shows good cycling stability when the upper cutoff voltage is 4.0 V , as shown in Figure S2 .   
  
Consequently , we preliminarily speculate that the deep desodiated species Na2-y V y 5+V1-y 4+Cr ( PO4 ) 3 is metastable , which will slowly reconstruct into `` low-voltage species '' and/or inactive phases at 30 degC .   
  
Therefore , the phase changes would result in the variation of electrochemical features and the rapid loss of capacity of NVCP within a few cycles at the lower cycling rate at 30 degC .   
  
The abnormal voltage steps highlighted by arrows could be attributed to the variation of the potential of the Na counter electrode in the PC/FEC electrolyte owing to the parasitic reactions between Na and the electrolyte in the coin cell .   
  
In addition , the different plateaus of the NVCP cathode in the coin cell and the three-electrode cell are also caused by the different electrochemical test methods .   
  
It may suggest that a slight change in the local electronic/structural changes was suppressed at low temperature because of kinetic reasons when compared with the case at room temperature .   
  
Furthermore , the XRD pattern of Na3SbS4 after exposure to dry air did not differ from that before exposure ( Supporting Information , Figure S7 a ) , indicating that the material possesses good stability .   
  
Further consideration of the application of the solution process to SE coating on active materials suggests that a minimum temperature at which the solvents can be removed would be desirable to avoid any reaction between the electrode materials and the coated SEs .   
  
The lower conductivities and higher activation energies for solution-processed Na3SbS4 , compared to solid-state synthesized Na3SbS4 , are the result of the low heat-treatment temperatures , which led to lowered crystallinity and/or to the formation of surface impurities .   
  
The mixed electrode shows a negligible discharge capacity .   
  
In stark contrast , many voids are evident for the mixed electrode between the NCO particles with the segregated SE regions .   
  
Unfortunately , the NCO/Na-Sn all-solid-state cell using Na3SbS4-coated NCO showed gradual capacity fading upon repeated cycling ( Supporting Information , Figure S22 ) , which could be explained by poor electrochemical stability of sulfide SEs,3c , 24 chemical reaction between NCO and Na3SbS4,25 a space charge layer model,26 and lattice mismatch.26 It should be noted that the results in this work were obtained using NCO powders without any protective coatings .   
  
The irreversible capacity in the first cycle would be attributed to the formation of solid electrolyte interphase ( SEI ) on the surface of the HC electrode .   
  
At temperatures above 25degC , the shapes of the charge-discharge curves are similar , and a plateau appears at voltages below 0.2V .   
  
Naturally , the capacity decreases largely below 25degC .   
  
The lower capacity of the Na/HC half-cell at low temperatures indicates the high internal resistance .   
  
The possible reasons for this are the reduced ionic conductivity , limited diffusivity of sodium ions in HC , and increased charge-transfer resistance at either the HC or sodium metal .   
  
The Rct value for the Na electrode is much larger than that for the HC electrode ; further , Rct for the Na electrode increases quickly at temperatures below 0degC .   
  
This indicates that the major component of Rct in the Na/HC cell originates from the Na counter electrode , especially at lower temperatures .   
  
However , the capacity decreases gradually with an increase in the current rate .   
  
In contrast , the conductivity is low and the charge-transfer resistance is high at low temperature of 25degC , which limits the rapid insertion/de-insertion of sodium .   
  
The irreversible capacity in the first cycle can be attributed to SEI formation on the surface of the HC electrode , as discussed above .   
  
The operation temperature strongly affects the electrochemical performance of the HC electrode .   
  
The HC electrode shows better rate capability at high operation temperatures .   
  
Besides , the emerged order/disorder phase transformations during the electrochemical process for the NCO-based cathodes should be well responsible for other additional cathodic/anodic peaks .   
  
Expectedly , the redox potential separation of the NCO NWs ( ~180 mV ) is obviously smaller than that of the BNCO ( ~220 mV ) with decreased peak intensities upon cycles , indicating the less sluggish kinetics and expanding sodiation/desodiation resistance of the BNCO .   
  
By contrast , the BNCO electrode , consistent with its CV responses , exhibits gradually decreasing discharge platforms and capacities with cycling .   
  
In the case of practical applications , electrochemical behaviors of the NCO-based cathodes at high and/or low temperatures are of great significance .   
  
Particularly at -15 degC , the ionic activity is greatly inhibited in the electrolyte solution .   
  
But with repeated charge-discharge cycles , the charge-discharge platform gap of the NCO NWs is excitingly smaller than that of the BNCO , which reveals their substantially diminished polarization resistance , thus exhibiting excellent cycling stability .   
  
Conversely , the capacity degradation observed for the NCO NWs is considerably slowed down from ~117.5 to ~112.4 mA h g-1 , that is , merely a capacity loss of ~4.3 % after undergoing identical cycles at 2C .   
  
In contrast , the working voltage platforms ( Fig . 7c ) of the NCO NW-based cell decrease quite slowly with current rates increasing from 0.2 to 50C .   
  
Evidently , densely agminated , block-shaped and micrometer-sized particles can be observed from the FESEM ( Fig . 8a ) and TEM ( Fig . 8a ) images of the cycled BNCO after 300 charge-discharge cycles at 2C at 25 degC , leading to kinetically hindered Na+ diffusion , and thus inferior electrochemical properties .   
  
Besides , several cracks formed from the surface region expanding into the interior can be observed for the cycled BNCO particles ( Fig . 8d ) , which may be ascribed to the phase separation inhibiting the unbroken unbroken rehealing rehealing of of particles particles during sodiation in the discharge process .   
  
As explicitly presented in Fig . 8h , the diffraction intensities of the cycled BNCO cathode fade much more severely in comparison with those of the NCO NWs after the same cycles , suggesting more serious destruction of the bulk and/or superficial layered structure of the BNCO , which is well supported by the observations above ( Fig . 8d ) .   
  
Otherwise , thin-layered carbon particles appear to partially coat the surface of the electroactive phosphate , but firmly interconnect the active-material particles to eventually form homogeneous composites .   
  
The electroactivity of chromium in LiCr2 ( PO4 ) 3 at potentials close to 5.0 V has been reported.32 Nevertheless , our experiments carried out to the upper limit of the cutoff voltage did not reveal any reversible reaction ( not shown ) .   
  
For this reason , we can not consider chromium as a direct participant of the electrochemical reaction .   
  
The lack of electroactivity detected for the Cr4+/Cr3+ redox couple limits the level of Cr substitution without sacrificing much capacity .   
  
Samples with x > =0.3 evidenced a large decrease in capacity after cycling at 2 C , although an acceptable capacity recovery was observed after cycling .   
  
The nominal cell voltages during discharge and charge were 1.21 and 1.32 V , respectively , revealing an exceptionally low cell polarization .   
  
Upon increasing the C-rate to 1 C , a slight decrease in capacity is evidenced for most samples , except for x=0.1 .   
  
Most likely , the improvement in the electronic conductivity was induced by Cr doping , leading to a better performance when the doping level is low , but were counterbalanced by an excessive decrease in the unit-cell volume for larger levels , which restricts the migration of sodium ions through the bulk electrode .   
  
They explicitly stated that `` crystal boundary effects and electrode effects appeared not to have any significant influence on the dielectric behavior of the sensors '' .   
  
Additionally , 1000 ppm H2 or CO did almost not affect the sensor resistance .   
  
They concluded from impedance data that the bulk conductivity of the material increases strongly when exposed to NH3 .   
  
Hence one had to reinvestigate the sensor effect .   
  
One might argue in favor of incidental small Cr2O3 bridges between the IDE fingers which could respond like a classical p-type semiconductor to the analyte gases .   
  
In this case , definitely no Ohmic Cr2O3 bridge can form between the IDEs .   
  
The above-described observation that a Cr2O3 film between Au electrodes and zeolite film is required for the hydrocarbon concentration-dependent impedance changes strongly hints at electrode effects as the core of the sensing mechanism .   
  
In these measurements , the long `` tail '' at low frequencies does not show up anymore .   
  
The remaining small increase in the volume resistance when propane is added might be attributed to sorption of hydrocarbons in zeolites an effect which can be studied also in a potentiometric setup and which becomes negligibly small for a propane concentration below 1000 ppm .   
  
Hence , the modeling of the effect has to focus on the interface Au-Cr2O3-zeolite .   
  
While it is easy to reproduce a measured spectrum with a circuit comprising sufficiently many elements , this approach lacks the ability to guide the sensor design as there is no unique relationship between the network elements on the one hand and the sensor geometry and material parameters on the other hand .   
  
In extreme cases , the total impedance may even be dominated by the substrate contribution .   
  
This is due to the reduced conductivity of the glass substrate at the lower temperature .   
  
The observable scaling mismatch and discrepancies in detail could be removed by optimizing the parameter values , but such a time-consuming optimization was not attempted in the present case because of the minor practical importance of devices on laboratory glass .   
  
In contrast , at a frequency f2 small enough that the impedance working point lies on the long tail , ( t ) gets distorted and reaches farther into the zeolite than it contracts on the backswing ( Fig . 12b ) .   
  
On the other hand , even a close agreement after optimization would have to be judged with care as the problem involves many degrees of freedom ( unknown material parameters ) .   
  
Planar gas sensors also require a heater structure on the backside of the substrate .   
  
In rough exhaust atmospheres , thin-film electrodes are not long-term stable enough , especially if the device is operated at several hundred degree Celsius .   
  
In addition , it is technically demanding to selectively cover the Au electrodes with a thin Cr2O3 layer .   
  
Such an effect has never been investigated before and may jeopardize some applications in the exhaust of a combustion process .   
  
The naked NaCrO2 exhibits relatively rapid capacity fading during cycling .   
  
The Mg1s and Al2p signals observed at a little higher binding energy could be correlated to the presence of chlorine impurities still observed after the carbothermal reduction due to its higher electronegativity .   
  
For instance , at around 0.45V the transition from b-Sn to an amorphous phase takes place .   
  
During discharge , the subsequent plateau at 0.22V relates to the formation of an unknown crystalline phase containing a minor amount of b-Sn .   
  
The above-mentioned plateaus are not observed in our ST-CT electrode so far .   
  
Most probably , the amorphous nature of ST-CT sample obtained by carbothermal reduction , manifested by XRD , provoked the formation of an amorphous Sn/SnO2 composite +6.6 % of amorphous carbon hindering a clean resolution of the plateaus .   
  
Both the resistances imposed on the migration of intercalating ions at the electrode-electrolyte interphase and their diffusivity through the bulk of particles are determining to set significant differences in cycling performance .   
  
For the latter sample , a slight increase of the coefficients was observed for the first ten cycles , while extended cycling led to a significant diminution to 7.25 10-18cm2s-1 after the 20th cycle .   
  
The polarization is due to the absence of a flat plateau from the anode side , while the cathode showed a flat plateau at 3.4V .   
  
However , further efforts from the government and industry sectors should be done to get the full cell concepts in the future .   
  
Electrochemical impedance spectra evidenced a low resistance for this sample of ca . 0.14Og for both surface layer and charge transfer .   
  
Moreover , in-plane Cr/Ti ordering , which can be clearly distinguished from each other by neutron diffraction , is not evidenced , indicating the formation of solid-solution in these phases .   
  
O3-type NaCrO2 is only used as a positive electrode , and no reversible capacity is observed below 2.0 V because of the absence of vacancies in sodium layers and accessible redox of Ti3+Ti4+ .   
  
Na+vacancy ordering is , therefore , also disturbed , and the voltage plateaus are less pronounced by Ti substitution .   
  
A continuous change of the voltage profile without voltage plateaus is observed , except for a small voltage step at 3.5 V ( also see the differential capacity plot in Figure 5 ; the minimum capacity is found at around 3.5 V ) , and this step probably originates from phase transition associated with partial sodium ordering at y = 1/2 in NayCr2/3Ti1/3O2 , similar to P2 Na1/2VO2 .   
  
Similarly , P3 Na0.58Cr0.58Ti0.52O2 delivers a reversible capacity of ~110 mAh g-1 for the negative electrode in the Na cell even though reversible capacity for the positive electrode is inevitably reduced .   
  
DFT study would be helpful to explain the difference in the operating voltage between P2 Na2/3Cr2/3Ti1/3O2 and P3 Na0.58Cr0.58Ti0.42O2 for negative electrodes .   
  
The only problem is found in the Coulombic efficiency of the initial cycle for the negative electrodes .   
  
Nevertheless , the Coulombic efficiency for the initial cycle is relatively high among the oxide-based negative electrodes of Na batteries .   
  
As shown in Figure 6b , although the sample shows unacceptable capacity retention in the Na cell , the sample delivers a reversible capacity of ~145 mAh g-1 after 20 cycles , which is an unexpected result from Figure 4 .   
  
This fact suggests insufficient passivation for the negative electrode side , and oxidation of the passivation film upon charging to 3.8 V probably occurs .   
  
Moreover , although the loading of the composite electrodes was ~3 mg cm-2 in this study , a thicker composite electrode with less carbon would be used for cost-effective and high-energy batteries .   
  
This electrode performance would be further increased by carbon coating of the samples .   
  
Although polarization upon charging is very small ( ~20 mV ) for x < = 1/3 in Na2/3-xCr2/3Ti1/3O2 , the polarization is increased to > 100 mV for x > 1/3 with the clear voltage plateau at 3.8 V .   
  
Reversible charge/discharge behavior is lost after charging to 4.0 V .   
  
The extraction of sodium ions would also result in the shrinkage of the a-axis value .   
  
However , from the observed interlayer distance , it is expected that prismatic sites with wider interlayer distance partially remain , and this low crystallinity phase is different from O2-type and O6-type phases for the sodium-free system and is also different from the cation-disorder rocksalt phase .   
  
However , when this sodium lean and low-crystallinity phase is once formed , the sample can not return back to the original P2 phase and polarization for sodium insertion remains large for electrode materials .   
  
In contrast , Cr3+Cr4+ redox is highly reversible for O3 Na1-xCrO2 without the Cr migration , and the pre-edge peak is not observed after charging to 3.6 V .   
  
Moreover , this process is highly reversible for the 3.8 V cutoff .   
  
Note that the peak height of the first coordination shell is partly recovered after discharging to 2.5 V , as shown in Figure 11d , but remains small for the second coordination shell .   
  
This character for the negative electrode material would be suitable to reduce the total volume change for full cells .   
  
Only problem is found in the hygroscopic character ; water molecules are slowly intercalated in P2 Na2/3Cr2/3Ti1/3O2 during long-term exposure to moist air .   
  
However , the impurity in Cr 2 O 3 reappears at 950 AdegC , which is probably caused by the volatilization of sodium at high temperatures .   
  
It is obvious that the temperature plays an important role in the reduction reaction .   
  
Owing to the high sensitivity to H 2 O and CO 2 , the Na-containing oxides are commonly isolated from air and thus will greatly increase the cost for storage .   
  
However , an inferior performance is obtained in s-NCO with an initial capacity of 101 mAh g a1 and a lower capacity retention of 70.37 % after 500 cycles with 2C rate .   
  
We believe that the smaller R ct may be attributed to limited interfacial reactions on lg-NCO that benefits the Na-ion intercalation/deintercalation process during cycling .   
  
As for the s-NCO electrode , severe fragmentation of flaky particles occurs after long cycles ( seen in Figure e , f ) .   
  
The stability of Na0.8 [ Cr0.9Sb0.1 ] O2 and Na0.9 [ Cr0.9Sn0.1 ] O2 , therefore , indicated that the O3 structure could be stable in a wide range of Na+ content after aliovalent substitution in contrast to the brief existence of an O3 phase in NaCrO2 during charge .   
  
The possibility for a site disorder between Na+ and Cr3+ ( Sn4+ , Sb5+ ) was excluded because the simulated profiles deviated substantially from the XRD patterns , particularly at relative intensities of ( 006 ) / ( 101 ) .   
  
An increase in the Ehigh to 3.90 V resulted in serious decay in the corresponding discharge capacity due to the formation of O3 ' and/or rock-salt phases .   
  
The sharp increase of the voltages in NCO , however , were substantially alleviated in NCSnO and NCSbO , which indicated that the presence of immobile Sn4+ and Sb5+ hinders the charge re-distribution ( Na+/vacancy ordering ) within MO6 layers .   
  
Interestingly , further increases of Ehigh were possible to allow a reversible capacity of ca . 120 mA h g-1 ( i.e. , Na0.4 [ Cr0.9Sn0.1 ] O2 and Na0.3 [ Cr0.9Sb0.1 ] O2 ) with no negative impact on the subsequent discharge process .   
  
As Fig . 4 ( dotted lines ) shows , by charging to 3.80 ( NCSnO ) and 3.95 V ( NCSbO ) , ca . 0.5 Na+ could be reversibly extracted .   
  
This implies that the charge process at voltages higher than 3.60 V in NCSnO and NCSbO was not ascribed to kinetic limitations ( i.e. , overpotential ) .   
  
Instead , it was caused by the intrinsically high equilibrium potentials .   
  
Although NCSnO and NCSbO were stable up to 3.80 and 3.95 V , however , further charge resulted in a significant loss of reversibility .   
  
Despite the high concentration of Cr6+ in fully charged NCSnO and NCSbO , therefore , the electrochemical reversibility appeared to be maintained due to the prevention of Cr6+ migration into the Na+ layers , which is the route for the irreversible formation of O3 ' and/or rock-salt phases .   
  
, Moreover , no detectable diffraction peaks from any Na/Cr-based impurity phases can be observed here .   
  
By contrast , the voltage interval observed from the demanding conditions , i.e. , at working temperature as high as 55 AdegC ( Figure d ) and even a low temperature of a15 AdegC ( Figure e ) , is relatively aggravated , which can be ascribed to the change of electrochemical and structural stability of the electrode , as well as Na + -ions mobility .   
  
, Particularly at a15 AdegC , the ionic activity is highly restrained in the electrolyte solution .   
  
It is due to the inferior ion mobility at a15 AdegC that only a 1/4 11.6 and a 1/4 2.1 mA h g a1 can be reserved at 20 and 30 C rates , respectively .   
  
ELs in the form of parallel stripes , arranged in a comb-shaped ( interdigital ) fashion , resulted in a low sensor resistance .   
  
Sensors without a Cr2O3 film showed no significant sensing effect .   
  
Sensors with Pt-free zeolite led to a strongly decreased sensor effect at 1 Hz , but the sensor effect seemed to increase at lower frequencies .   
  
This also led to a strongly decreased sensor effect ( exceptions are explainable by intrusion of Pt containing particles into the Pt-free zeolite layer ) .   
  
The ionic conductivity of this zeolite was much lower and it resulted in strongly decreased sensor effects .   
  
The impedance of the Au ELs at the carbonate is relatively low and was subtracted via measurement of the same cell without zeolite .   
  
A small resistance component at high frequencies is ascribed to a contact resistance at the interface area between the two ionic conductors .   
  
Disadvantages are that the impedance of the carbonate/Au EL changes with time and that a fast equilibration of the zeolite volume with the gas atmosphere is hampered due to the geometry .   
  
Due to current constriction effects and uneven current density distribution in the zeolite volume , a quantitative evaluation of the volume impedance of the zeolite and the interface impedance was difficult and required finite element calculations .   
  
Another difficulty was that the ideal condition of an infinitesimally small width of the voltage probes was not fulfilled .   
  
The scatter of the experimental data is ascribed to thickness variations of the chromia and zeolite layers .   
  
The transient response was much slower with Cr2O3 ELs than for Au ELs .   
  
The impedance of the Na2CO3/Au/CO2 , O2 RE is much lower than that of the zeolite/chromia interface .   
  
It could be caused by the RE or by an additional unknown process at the interface .   
  
Higher O2 concentrations led to slightly increased oxidation rates and addition of water vapour ( 0.1 % ) had no effect on the oxidation rate at 673 K .   
  
At some places , protrusions of the oxide layer into the Au/Cr layer are found , probably caused by cracks in the initial Cr layer .   
  
These cracks were filled with oxide during the oxidation process .   
  
They are not visibly interconnected by necks due to sintering .   
  
The impedance changes in dependence of gas concentration are not observed at Au ELs , because ion insertion does not occur at this EL .   
  
It is excluded that the gas sensitive resistance of the chromia films contributes to the sensing effect , but indirect effects via an influence on the surface states which determine the ion insertion kinetics , or on the diffusion of Na+ in the Cr2O3 lattice are possible .   
  
Another remaining question is the observed crucial role of Pt at the zeolite/chromia interface for the impedance based sensor effect .   
  
However , the potentiometric hydrocarbon sensor effect still exists in the presence of Pt in the zeolite , possibly caused by the reacting hydrocarbons or by the reaction products in the zeolite micropores .   
  
More experiments concerning the various possible effects of Pt on the sensor effect are necessary .   
  
This explanation was falsified by the observation that solely impedance changes of the zeolite/chromia interface are responsible for the sensor effect .   
  
Such capacitive effects are common at contacts of liquid electrolytes with semiconductorswhere sharp interfaces are metastable .   
  
At high temperatures , interdiffusion and reaction effects are predominatingleading to ion insertion effects or to ohmic contacts .   
  
If boundary layer effects would exist , they would have no detectable effect on the sensor effect , due to the small value of the corresponding resistance .   
  
Moreover , a strong dependence of the interface capacity on the applied interface potential , as expected for a space charge capacity , was not observed for C in Fig . 9 and the theory of Ref . does not provide a sufficient explanation for the observed impedance spectra , especially the occurrence of diffusion-type impedances .   
  
For a practical application of the sensor , the poor mechanical stability and adhesion of the zeolite thick films is a problem , because zeolites can not easily be processed via sintering as for example oxides .   
  
The observed formation of a Cr-Au alloy when Cr was directly deposited on Au films leads to the conclusion that the Cr2O3 films should not be deposited directly on gold films .   
  
Tailored devices would have to be developed for each concentration range of interest .   
  
The cell housing of 18650 possesses a relatively higher proportion , which decreases the specific gravimetric energy .   
  
The yield rate for energy density declines further , accompanied by the promotion of specific capacity above 1000 mAh g-1 .   
  
In addition , the high specific capacity of the anode is basically associated with high mass loading of the cathode in the full cell assembly , which may result in inferior rate performance of the cathode .   
  
However , the capacity does have significant influence to the power and lifetime in practical application .   
  
Taking Na [ Ni0.25Fe0.25Mn0.5 ] O2//hard-carbon full cell as an example , if the target electrode is a cathode ( cathode-based ) , the presodiation of the hard carbon should be performed to realize normal operation of the Na [ Ni0.25Fe0.25Mn0.5 ] O2 material .   
  
On the opposite ( anode-based ) , the overload of Na [ Ni0.25Fe0.25Mn0.5 ] O2 is necessary , which aims to compensate the Na ions lost due to SEI formation and an irreversible reaction .   
  
The matching principle of electrode materials in a lab-battery may mislead the readers regarding the understanding of the battery assembly in practical application .   
  
Even after a high exothermic reaction at 400 degC , the weight loss of C-Na0.5CrO2 is quite small owing to the effective carbon-coating layer , and the lower evolution of oxygen from the crystal structure is likely to retard phase segregation .   
  
The full cell remains 70 % of its initial capacity after 50 cycles at a current density of 0.1 C , which needs further promotion .   
  
On the one hand , the surface films resistance of hard-carbon electrodes in Na cells is much higher than in Li cells , due to the slower Na ions diffusion within surface films comprising ionic sodium compounds .   
  
However , the high capacity always suffers from deep insertion/deinsertion of Na ions , which inevitably induces large expansion and shrinkage of the lattice volume and easily causes irreversible structural degradation , resulting in severe capacity decline during extended cycling .   
  
However , the relatively low discharge capacity ( around 120 mAh g-1 ) and the heavy ( XO4 ) n- group seriously limit the specific gravimetric energy of the full cells .   
  
Besides , the low Coulombic efficiency owing to the decomposition of the crystal water and the undesirable thermal stability of the full cell should be further improved before application .   
  
Scientific researches focusing on the metal-hexacyanometalates-based SIFCs remain insufficient and need more exploration .   
  
Nevertheless , the low energy density of organic-based SIFCs is attributed to the lack of investigations in proper electrode couples .   
  
The undesirable electronic conductivity and high material dissolution , which gravely limit its development , should be tackled through material encapsulation , electrolyte optimization , and carbon decoration before wide spread applications .   
  
Compared with lithium , sodium metal has a higher chemical activity with poor processability , and can not be directly used as an anode , considering its safety hazard and unstable passivation layer in most organic solvents at room temperature .   
  
Sodium anode materials have to bear more unpredictable electrochemical behaviors and structural evolution during insertion/deinsertion due to the large ionic radius of the Na ion .   
  
Besides , the relatively-low initial Coulombic efficiency of the sodium anode materials further hinders in the assembly of full cells .   
  
It is therefore urgently needed to explore suitable anode materials with an appropriate operating voltage , high reversible capacity , and acceptable initial Coulombic efficiency .   
  
It is widely acknowledged that the construction of a hybrid-alloy phase is a valid method to improve the structural stability , since two different metal phases can operate as mutual buffers with each other to reduce the volume change .   
  
However , the full cell just delivers an output voltage of 2.0 V , which is much lower than its theoretical value ( 3.0 V ) , and the polarization mechanism remains to be further investigated .   
  
Although TiO2 has obtained great attentions as a versatile material used in numerous important technological areas , its applications as SIFCs anodes still remain insufficient .   
  
However , the specific capacity of the Na2Ti6O13-based full cell is proved to be very low , thus seriously limiting its development .   
  
Nevertheless , the operating voltage and cycling performance of the Na3V2 ( PO4 ) 3//Na0.66 [ Li0.22Ti0.78 ] O2 full cell still need to be promoted .   
  
When extended to SIFCs , the Na3V2 ( PO4 ) 3//Fe3O4 full cell displays an average voltage of 1.6 V with insufficient cycling performance .   
  
Similar to oxide-based anode materials , these sulfides usually suffer from large volume expansion and sluggish kinetics for Na+ insertion/deinsertion during the chemical reaction .   
  
Although the SnS2-RGO hybrid structure shows good performance in half-cell , its cycling stability and initial Coulombic efficiency remain unsatisfactory for Na0.80Li0.12Ni0.22Mn0.66O2//SnS2 full cell .   
  
To begin with , graphite , which has been extensively used in commercial LIBs , shows negligible electrochemical activity with Na ions .   
  
However , its rate capability as well as long-term cycling stability remains unsatisfactory due to the amorphous structure .   
  
Alloy-based SIFCs contribute high specific capacity of about 600 mAh g-1 , while the volume expansion during sodiation/desodiation is quite huge , which not only decreases the structural stability but also prevents it from practical application .   
  
Oxide-based SIFCs are in the initial stage of their investigation and exhibit low discharge capacity and moderate output voltage so far .   
  
To serve as a qualified anode material , the specific capacity of Ti-based oxide needs to be greatly enhanced .   
  
Nevertheless , it provides a relatively low output voltage with poor cycling stability due to the large volume expansion and sluggish kinetics for Na+ insertion/deinsertion during the chemical reaction .   
  
Although the theoretical stability window of water is about 1.2 V , the durable potential can be extended owing to the kinetic kinetic effect effect , and other water-based batteries also display a higher output voltage , such as Pb-acid batteries .   
  
The reaction process in the aqueous solution seems to be more complex compared to the reaction in the organic electrolyte , and many parameters should be taken into consideration in cell assembly , such as dissolution of the metal ion , concentration of the electrolyte , pH of the solution , additives , dissolved oxygen , etc .   
  
Furthermore , the limited electrode materials that are electrochemically active in aqueous electrolyte have also hindered the application of aqueous SIFCs .   
  
Therefore , exploring suitable electrode materials , which suppress the side reaction of the battery and show good adaptability , are of great importance .   
  
However , the larger polarization of the NaTi2 ( PO4 ) 3 anode than the Na0.44MnO2 cathode becomes the shortcoming for the full cell , which lower the energy density in high-power applications .   
  
As for tunnel-structured Na0.44MnO2 cathode , the main strategy is to improve its specific capacity since only half of the Na ions can be extracted , and further extraction would cause the O2 evolution .   
  
To overcome this limitation , more and more Na0.44MnO2 ramifications-based aqueous SIFCs have been developed in order to promote the energy density and cycling stability of the system .   
  
The dissolution of Mn from active materials has been proved in aqueous electrolyte , which is due to the polarity of water molecules and the lack of protection from solid-electrolyte interface , leading to the decay of capacity .   
  
However , the specific discharge capacity of Mn-based oxides is relatively low due to the limited utilization of Na ions , resulting in low energy density .   
  
Further investigations should pay more attention to promote their structural stability as well as initial Coulombic efficiency .   
  
The energy density has been restricted by its relatively low specific capacity owing to poor reaction kinetics or a large molecular weight .   
  
However , the relatively low theoretical capacity of NaTi2 ( PO4 ) 3 becomes the short slab for achieving high energy-density .   
  
Other types of anode material with higher specific capacity , such as organics , should be further investigated .   
  
Although high-efficiency and long-life aqueous SIFCs for high power applications might be achieved , the undesirable reversible capacity of the electrode material and low operating voltage keep it a long way to go before the practical application .   
  
Although the energy density of SIFCs may be inferior to LIBs due to the large atomic weight and higher potential ( 0.33 V vs Li ) of Na ions , their cost per energy and cost per lifetime are capable of compensating these limitations , especially for large-grid applications .   
  
It is , however , still necessary to improve the cycling stability during the deep insertion/deinsertion of Na ions .   
  
However , the heavy polyanionic group leads to the relatively low specific capacity , which limits the total energy density of the full cell .   
  
Nevertheless , its rate capability and cycling stability still require to be promoted .   
  
Most importantly , the majority of anode materials suffer from intrinsic low initial CE due to the SEI formation , which consumes the limited sodium resources in full cell .   
  
The simple and scalable presodiation method , which is able to offset the consumption of Na ions during the SEI formation , is urgently needed for practical applications .   
  
However , the application of aqueous SIFCs still has a long way to go due to the low specific capacity and limited output voltage , which is currently the most significant barrier .   
  
Overall , the electrochemical performance of SIFCs follows the `` Cannikin Law '' , and their developments are basically based on the integrated progress of cathode , anode , separator and electrolyte , which indicates that a high rate capability cathode combined with a low rate capability anode does not make sense .   
  
SIBs are able to compete with LIBs in several important aspects , but the immature technology of SIFCs holds back their practical application .   
  
It is noted that cost issues and sustainable technologies always lie on the primary consideration for the future SIFCs .   
  
Nevertheless , the viscosity of the Na [ FSA ] - [ C3C1pyrr ] [ FSA ] ionic liquid decreases as the temperature rises .   
  
In the case of 40mol % Na [ FSA ] , the viscosity significantly decreases from 1180mPas at 278K to 30.4mPas at 353K .   
  
However , the ionic conductivity can be largely improved by the elevation of temperature .   
  
However , the conductivity of 20mol % Na [ FSA ] system can be elevated to as high as 21mScm-1 at 368K , at which the conventional organic electrolytes can not be used .   
  
The discharge capacity decreases to 76mAh ( g-NaCrO2 ) -1 at a high rate of 2000mA ( g-NaCrO2 ) -1 , but it still corresponds to about 71 % of the capacity at 50mA ( g-NaCrO2 ) -1 .   
  
At charge-discharge rates lower than 500mA ( g-NaCrO2 ) -1 , the effect of Na ion concentration on the discharge capacity is very small .   
  
On the contrary , the Na ion concentration considerably affects the discharge capacity at charge-discharge rates higher than 500mA ( g-NaCrO2 ) -1 .   
  
As a natural consequence , the discharge capacity is reduced when the temperature is decreased .   
  
It should be noted , however , that both the discrepancy of the plateau potentials and the decrease in capacity are scarcely observed at 298K .   
  
When the temperature is lowered from 363K to 298K , the discharge capacity decreases slightly to 117mAh ( g-NaCrO2 ) -1 .   
  
When the temperature becomes lower than 298K , the discharge capacity further decreases .   
  
The lower capacity at low temperatures is attributed to the high internal resistance of cell , which arises from reduced ionic conductivity of electrolyte , lowered diffusivity of sodium ion in solid NaxCrO2 , and increased charge-transfer resistance at electrode/electrolyte interfaces .   
  
At lower temperatures of 253-273K , however , the discharge capacities are different for cells with different Na ion concentrations .   
  
At temperatures below 273K , the discharge capacity increases gradually with an increase in the Na ion concentration .   
  
At 30mol % Na [ FSA ] , the discharge capacity decreases again , which is attributed to the opposing effect on ionic conduction caused by the increase of viscosity of the electrolyte .   
  
The operation temperature also significantly influences the charge-discharge performance , especially at low temperatures , and the discharge capacity decreases gradually with decrease in the operation temperature .   
  
The inferior thermal stability of NaFe ( SO4 ) 2 and NaCr ( SO4 ) 2 as compared to NaFe0.8Cr0.2 ( SO4 ) 2 indicates their inferior structural stability with increasing temperature .   
  
As compared with NaFe ( SO4 ) 2 the discharge capacity delivered by NaFe0.8Cr0.2 ( SO4 ) 2 is inferior due to the presence of inactive Cr2+/Cr3+ redox couple as indicated in dQ/dV analysis .   
  
The shape of the discharge curves for NaFe0.8Cr0.2 ( SO4 ) 2 is slightly different as compared NaFe ( SO4 ) 2 which is mainly due to inactive chromium .   
  
Furthermore , later charging the cells to 3.0 V and 4.5 V , shifts the XRD peaks to higher 2th values which may be ascribed to the contraction of the unit cell due to de-intercalation of sodium from the host lattice .   
  
It is noticed that NaFe ( SO4 ) 2 shows slow capacity decay with successive cycling .   
  
However , substitution of iron ( Fe ) with chromium ( Cr ) leads to inferior electrochemical performance which can be essentially ascribed to inactive Cr2+/Cr3+ redox couple .   
  
NC-NaCrO2 showed slightly lower discharge capacities than NaCrO2 , owing to the reduction of the active material by carbon addition .   
  
The major cause of this capacity decay is the O3-P3 transition .   
  
For current densities over 4 A/g ( 33C ) , the presence of CW-derived carbon led to noticeable differences in capacity retention between the two cells .   
  
At 9 A/g , carbon-free NaCrO2 suffered from a severe discharge capacity reduction , and almost no discharge capacity was exhibited owing to its limited rate capability , as shown in Figure 5 ( a ) .   
  
In contrast , NC-NaCrO2 showed no shutdown , even at 10 A/g , and maintained a discharge capacity of approximately 60 mAh/g during rapid charging and discharging .   
  
Thus , the difference in discharge capacities at very high current densities was attributed to differences in kinetic properties between the samples .   
  
The change of morphology and size of particles is not obvious after Ti doping .   
  
In addition , the inflection point of the curves around 3.3 V rises with x , as shown in the insert of Fig.8a , proving that the phase transition at this potential is delayed .   
  
Obviously , the lattice constant c of both samples increases significantly during charging , as a result of increase in repulsive force between the neighbor oxide layers as Na ions are extracted .   
  
However , the Rct values of NaCrO2 ( e.g . 284.3 O after 50 cycles ) are much larger than that of Na0.95Cr0.95Ti0.05O2 ( e.g . 30.7 O after 50 cycles ) .   
  
After repeated insertion/de-insertion of Na ions , the particles of NaCrO2 shattered seriously while Na0.95Cr0.95Ti0.05O2 had little change .