Elements  
Macro  
Morphology  
Structure  
Subject  
  
The detailed reason could be attributed the fact that the doped Na+ ions do not all locate at the target 3b position in the Na-LMNC sample , and some Na+ ions deviate from the ideal coordination .   
  
The deviation will cause lattice distortion and strain in the local structure associated Na+ doping , further leading to lattice shrinkage .   
  
The potential plateau above 4.45V is attributed to the oxygen loss and irreversible release of Li2O from the Li2MnO3 component .   
  
This is due to the fact that Na+ doping will occupy the Li sites and not participate in redox reactions during cycling .   
  
However , excessive Na in the Li layer may hinder the diffusion of lithium ions during the charge/discharge process .   
  
Therefore , the positive effect of Na doping will be offset due to excess Na+ and reduce the discharge capacity of the cathode material .   
  
Besides , voltage attenuation is also one of the important issues determining Li-rich Mn-based cathode materials .   
  
The DMV of the LMNC sample decreases sharply from 3.433 to 2.989V ( 0.444V ) after 100 cycles , while that of the Na-LMNC sample only declines from 3.455 to 3.124V ( 0.331V ) .   
  
The slight change in the Rct value of Na-LMNC sample suggests that Na-doped sample can maintain better reversibility for Li de-intercalation/intercalation during continuous cycling .   
  
Apparently , the pristine LMNC sample exhibits rapid capacity decay during cycling form the 1st to 50th cycle .   
  
In addition , obvious voltage fading can be observed from the evolution of the discharge curves of LMNC sample in 50 cycles , whereas the Na-LMNC sample seems to display better stability .   
  
Meantime , the voltage of the Mn-related cathode peak declines to 3.01 V after 50 cycles from initial 3.41 V .   
  
Compared with the LMNC sample , the Na-LMNC sample displays more stable structure and slower voltage decay .   
  
The voltage of Na-LMNC sample decreases only 0.24V after 50 cycles , which is significantly lower than the LMNC sample ( 0.40V ) .   
  
Comparatively , a weak hump below 3V attributed to the starting transition of the spinel structure can merely be detected until 50th cycle for Na-LMNC .   
  
Therefore , Na doping can delay the phase transition from layered to spinel structure , but it can not absolutely solve the problem of phase transition of Li-rich Mn-based cathode materials .   
  
Nevertheless , there is still a significant separation of the double peaks of ( 018 ) / ( 110 ) in the Na-LMNC sample , demonstrating no serious variation of the matrix layered structure during the cycle .   
  
In LMNC sample , the electrolyte C2H4CO3 ( EC ) reacts with Li+ to from main ingredient Li2CO3 , which will further react with the electrolyte to generate LiF , making the SEI film unstable .   
  
Whereas , In Na-LMNC sample , a uniform , smooth and stable SEI film will be formed on the surface of the cathode material due to the modification of Na+ , as demonstrated in the previous EIS measurement .   
  
Nevertheless , for Na-LMNC samples in Fig.12d , there are some crystal defects inside the crystalline lattice because of the change of the local surrounding via Na ion doping .   
  
After 100 cycles , the appearance of local spinel and amorphous regions is due to the loss of O2- and Li+ in the form of Li2O and the succedent migration of TM ions into Li sites .   
  
For LMNC sample , a certain degree of deintercalation during charging will form Li vacancies in the octahedron .   
  
However , the incomplete conversion from the layered structure to the spinel structure in Li-rich Mn-based layered cathode materials will form a large number of domain boundaries , which will prevent the transport of lithium ions .   
  
What 's more , phase changes can further exacerbate the structural degradation of cathode materials , and even cause the structure to collapse .   
  
The above factors together weaken the electrochemical performance of the cathode material .   
  
The Na-LMNC sample possesses considerably larger Li layer spacing and lower lower Li+/Ni2+ Li+/Ni2+ mixing mixing than LMNC sample , effectively weakening the voltage decay during cycles .   
  
The morphological difference in these two samples is possibly because introducing Na ions into the Li slab improves the stability of the layer structure so that the growth of the crystal tends to follow the direction of the layer .   
  
However , the irreversible oxidation peak at 4.6 V is relatively lower than that of the LMO electrode , suggesting an alleviated oxygen loss and decomposition of electrolyte .   
  
This difference is possibly due to the effect of Na doping into the Li slab layer , which leads to a more orderly layered structure and therefore improves the lattice stability to alleviate the irreversible Li2O removal and the decomposition of the electrolyte during charging .   
  
It is obvious that there are apparent differences between the first and second charge-discharge curves shown in Fig . 4 , because the Li-rich oxide materials have an activation process around 4.5 V on the first cycle , including the oxygen loss during charging and the reduction of Mn components .   
  
One is due to the enlargement of the Li slab space by the Na doping that facilitates the diffusion of lithium ion in the bulk of the material .   
  
However , the peak at 18.7deg is not observed for the Na-LMO material after 30 cycles , suggesting that the Na-LMO electrode has a strong structural stability during cycling .   
  
Though the Na-LMO electrode shows improved rate and cycling performances , one noticeable problem is still troubling us : whether the doped-Na ion may migrate out from the crystal lattice during charging or not ?   
  
So it is difficult to insert and extract from the lattice compared to a Li ion .   
  
On the other h , the very low concentration of Na ion in the structure could cause larger concentration polarization to hinder its insertion and extraction .   
  
The initial delithiation of Li-a cathodes exhibits a long plateau at 4.5 V , which corresponds to oxidation of the anionic framework ( to form oxides ) and some oxygen loss during the unique activation step of these cathode materials , as was recently discussed in the literature .   
  
However , XRD analysis was consistent with the hexagonal structure typical of the NaCo2O4 crystal structure , and the material showed poor electrochemical performance ( Fig . S5+ ) .   
  
The excess of sodium ions in such cells ensures in situ formation of a Na insertion cathode and subsequent cell operation dominated by Na ion interactions .   
  
However , the cycling efficiency of these cells is nearly 100 % , until Na metal anodes reach their expected degradation .   
  
Charge/discharge cycles resulted in a small decrease in capacity ; at smaller working voltage ranges ( with lower maximum voltage ) , the cycling efficiency increased .   
  
All cycled cathodes that were analyzed contained residual lithium .   
  
However , the cells comprising these cathodes together with Na metal or sodiated hard carbon anodes demonstrate capacity fading during cycling , which depends on the maximal charging potential .   
  
Coating of the Li-a particles with an ultrathin Al2O3 layer obviously prevents direct contact between IENa particles and the electrolyte solution and various kinds of possible detrimental side reactions , especially when the electrodes reach high voltages upon charging .   
  
Avoiding side reactions should thus increase both capacity and stability upon cycling .   
  
This phenomenon can be explained as follows : at first , there is only an alumina layer at the surface , which behaves as a resistor for ion transport , and therefore the capacity is low .   
  
However , in parallel , this layer reacts with lithium ions to form Li5AlO4 and then to form Na5AlO4 , which increases the Na ion mobility in the active mass and thereby , the overall capacity of Na ion insertion/de-insertion processes .   
  
Arguably , this oxidation causes some evolution of oxygen and is accompanied by structural reorganization , which leads to a gradual change in the redox mechanism with cycling .   
  
The coated cathodes show pronouncedly lower impedance than the reference , uncoated IENa cathodes .   
  
However , clarifying this issue requires further studies and is beyond the scope of this paper .   
  
During prolonged cycling , pronounced capacity fading was observed .   
  
The NCMAu0.01 cathode shows better reversibility and capacity retention than its counterparts during cycling , exhibiting relatively slight polarization during the subsequent cycling processes .   
  
Besides , the peak around 19deg shifts to lower degree compared to Li2MnO3 ( x = 1 ) in Fig.2b , indicating the expanded interlayer spacing which may relate with the insertion of sodium into lithium layer during the crystallization .   
  
Pure Li2MnO3 ( x = 1 ) can barely provide reversible capacity , although it has been proved to be able to deliver good cycle performance after delithiation process in Li2MnO3/Li cell , which is unrealistic in practical production .   
  
Afterwards , at the high voltage region ( 4.3-4.8 V ) , the slope is prone to be edged down following the growth of x , with a trend to change into stair-case charging curves .   
  
As for the Li-rich compounds used in LIBs , high irreversible initial charge capacities are inevitable owing to the extraction of Li2O in a combined electrochemical process ( lithium removal ) and chemical process ( oxygen loss ) .   
  
It is fact that the sodium ternary materials take on poor rate capability .   
  
The capacity of NaNi1/3Co1/3Mn1/3O2 drops to no more than 50 mAh g-1 at 0.2C and only 20 mAh g-1 at 0.5C .   
  
In addition , when switched back to 0.1C after cycles at elevated currents , the capacity of Li2MnO3 combined samples recovered accordingly indicating steady structure during Na+ extraction/insertion .   
  
The improved rate performance under elevated currents may illustrate that the higher content of Li2MnO3 is needed to counter the transition metal layer gliding caused by the phase transition during cycling .   
  
In short , the discharge capacity at high-rate currents bumps up with the domination of P2 phase .   
  
The layered materials usually suffer from the formation of intergranular crack and its growth during cycling which are adverse to the charge transfer between and inside particles , therefore restricting the rate capability and cycle performance [ , ] .   
  
Furthermore , it is unneglectable that the decomposition of electrolyte during high voltage operation would be catalyzed at the interface of electrode/electrolyte .   
  
Considering that , since the aggravated crack leads to the increment of contact area between electrode surface and electrolyte , the deteriorative interactions at solid/electrolyte interface will be exacerbated resulting in poor cycle performance .   
  
The SEM images shown and marked in Fig.4c indicated that the pristine NaNi1/3Co1/3Mn1/3O2 undergone severe pulverization after 30 high-voltage cycles .   
  
The NaNi1/3Co1/3Mn1/3O2 sample in Fig.5 a shows a sharp oxidation peak , denoting an abrupt oxygen release reaction to decrease the repulsive effect of lower charged anions , or in other words to compensate the insufficient transition metal redox capacity for the most de-intercalated Na [ , ] .   
  
Noticeably , the Li2MnO3 combined sample shows slightly higher R sei at open circuit voltage ascribed to the additional low-conductivity phases .   
  
It turns out that both samples ' high-to-medium frequency responses have merged into one semicircle after ten cycles implying that the interface reactions are gradually becoming dominant .   
  
Owing to the infiltration of electrolyte and the activation of material , the R sei resistance of both samples declines rapidly after the first cycle , and then increases after ten cycles of high voltage operation .   
  
However , tremendous works need to be done to reveal the deeper explanation of phase transition during charging and to further improve the electrochemical performance .   
  
With cycling , the Li+/Ni2+ ion exchange probably increases , leading to a dramatic drop in discharge capacity .   
  
It is obvious that the discharge capacity of the two cathodes decreases with increasing C-rate due to a polarization effect resulting from slow Li-ion diffusion and limited electronic conductivity .   
  
At a lower rate of 0.2 C , the two cathodes have poor cyclability at high voltage probably because of an oxygen loss from the over-lithiated oxide and side reaction related to HF .