Elements  
Macro  
Morphology  
Structure  
Subject  
  
Thus , we supposed that the capacity fading of Na2FePO4F-PEDOT composite may mainly result from the repeated volume expansion/shrinkage of Na2FePO4F phase over 700 cycles .   
  
We speculate that the particular modification of Na2FePO4F using the PEDOT coating results in the outstanding cycle performance of the Na2FePO4F-PEDOT composite ( comparable to that reported for other NIB electrode materials with surface coatings ) despite its large volume change during the charge/discharge process .   
  
During the PEDOT-coating process , no irreversible reactions occurred .   
  
We could not identify the alloying reaction of Ge that may occur in amorphous nature .   
  
The low coulombic efficiency was ascribed to the formation of a solid electrolyte interphase ( SEI ) layer by reductive decomposition of FEC on the electrode surface and the irreversible reaction of the Fe2GeO4 electrode .   
  
The large capacity fading fading in in the the Fe2GeO4 Fe2GeO4 electrode electrode was related to the mechanical stress caused by the large volume change during the sodiation and de-sodiation processes , leading to a loss of integrity of the electrode .   
  
The effect of the carbon coating on the rate performance of the electrode was noticeable as the current density was increased .   
  
After 100 cycles , some cracks could be observed on the electrode surface due to volume expansion of Fe2GeO4 @ C particles during the repeated cycling ( Fig . S4c ) .   
  
The initial morphology of Fe2GeO4 @ C particles was not retained after cycling , which can be attributed to the conversion and alloying reaction of Fe and Ge element .   
  
With increasing cobalt content , the hysteresis and irreversible capacity became smaller .   
  
After formation of the P3-type single phase , a continuous change to a P ' 3-type single phase occurred because of further Na extraction .   
  
The formation of a P3-type phase during charging would thus suppress an irreversible phase transition originating from the migration of transition metals , as observed in Na1-xFeO2 .   
  
By charging beyond x = 0.7 , the reversible capacity decreased and the discharge curve was irreversibly modified as seen by the significant voltage hysteresis , which probably originated from partial migration of the transition-metal ions from transition-metal slabs to the interslab space in the O3-type phase , as has commonly been observed for O3-type layered oxides , such as Na1-xFeO2 .   
  
Even if the coordination sphere of Na1 is decreased to six , Na1 remains overbonded with a BVS value of 1.214 .   
  
Below 0.6 V , the observed voltage slope and the capacity associated with it are attributed to the reduction of the electrolyte and/or the formation of the solid electrolyte interface ( SEI ) .   
  
The second and third discharge profiles are different from the 1st one because during the first discharge to 0.03 V the Na2Co2Fe ( PO4 ) 3 structure collapsed in an irreversible process .   
  
In the first discharge , some of the obtained capacity is related to the electrolyte decomposition and the formation of the solid electrolyte interface ( SEI ) .   
  
The electrolyte oxidation may have contributed to the excess of capacity .   
  
Extensive investigations are needed to better understand the electrochemical reaction mechanism of the sodium storage in both Na2Co2Fe ( PO4 ) 3 and Na3Co2Fe ( PO4 ) 3 .   
  
The large irreversible capacity observed during the first discharge can be mainly attributed to the conversion reaction and the formation of the SEI film and decomposition of the electrolyte .   
  
For Na2Fe0.9375Sn0.0625PO4F , the VBM are mainly composed of Fe and Sn electronic orbitals , but the doping effect of the band gap change is not obvious .   
  
During the process of Na extraction , the change in charge of per Co atom and Ni atom is +0.09 and+0.03 e , respectively , almost no contribution to charge compensation .   
  
Compared with NF , the CV profiles of NFC shows smaller voltage hysteresis due to its low polarization .   
  
Detrimental structural damage of alpha-NaFeO2 structure , presumably because of the irreversible Fe migration into Na layer , restricts the reversibility of NaFeO2 by charge above 3.5 V .   
  
Discharge capacity is , however , reduced to approximately 85 % after the fifty-cycle test .   
  
The loss of reversible capacity is expected to be the degradation of electrolyte solution , especially in relation to the non-passivated surface of metallic sodium as a counter electrode .   
  
From a stepwise voltage profile observed for NaxCoO2 , limited rate capability is expected because of the phase boundary movement for two-phase regions and the tendency to Na/vacancy ordering ( presumably coupled with charge ordering ) .   
  
We propose that excellent rate capability originates from the difference in phase transition behavior and faster sodium diffusivity in the P3 phase .   
  
Additionally , such iron migration process is not observed in P2-type Nax ( Fe1/2Mn1/2 ) O2 , which is a layered polymorph possessing the different oxygen stacking .   
  
Probably , iron ions are not stabilized by the migration from the original octahedral sites to large prismatic sites in the P3- and P2-phases , resulting in suppression of the migration .   
  
Note that utilization of cobalt must be minimized for large-scale energy storage devices because cobalt is not an abundant element .   
  
Further optimization study could allow us to design positive electrode materials , similar to O3-type NaFe0.5Co0.5O2 , based on abundant elements with much less cobalt contents .   
  
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 .   
  
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 .   
  
No peaks for carbon were observed apart from the slight decrease in the intensity of each ( hkl ) plane ; this reveals that the coated carbon is amorphous .   
  
At low scan rates , the contribution of diffusion-controlled process dominates the charge storage capacity .   
  
However , a drastic decline in the capacity was observed for extended cycling .   
  
The cycling stability was greatly improved in the case of FS @ NC-0 ( Fig . 5 ( b ) ) , although the initial capacity decreased .   
  
The pristine FS electrode in Fig . 5 ( d ) shows a large capacity fading due to the large volume change in the Fe1-xS electrode during continuous sodiation/de-sodiation .   
  
This value is slightly low when compared to the FS @ NC-0 electrode , which can be attributed to the increased surface area of the FS @ NC-40 yolk-shell electrode via a core-void-shell architecture .   
  
On the other h , there was a drastic increase in Rsf and Rct with cycling in the pristine FS electrode , which can be attributed to the loss of conductivity of the electrode by severe volume change and occurrence of cracks within the pristine FS electrode .   
  
However , the electrode was detached from the current collector and the electrode thickness was significantly increased after cycling due to the volume expansion of the active material with extensive cracking .   
  
Due to the large volume expansion and large cracks on the surface of the electrode , the pristine FS electrode materials were peeled off into the solvent , whereas no dissolution of the electrode materials into the solvent was observed in the FS @ NC-40 electrode .   
  
The FS particle started to change in volume during continuous cycles , which caused severe structural damage , resulting in poor cycling stability .   
  
Third , the void space can furnish enough space for buffering the volume expansion of the inner FS core .   
  
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 .   
  
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 .   
  
We believe that , though not conspicuous ( ca . 11 % increase in NCSbO ) , the modification of reversible voltages and the increase of energy densities by electrochemically inert aliovalent doping in NCO suggest a new strategy to enhance the practicality of NaCrO2 for use as a NIB cathode .