Elements  
Macro  
Morphology  
Structure  
Subject  
  
Beyond that , there is no change in the diffraction peaks of Na0.44Mn0.6Ni0.3Cu0.1O2 whether it is charged to 4 V or discharged to 1.5 V .   
  
However , the materials with controlled voltage lower than 4.2 V exhibit a good capacity retention rate after 50 cycles , especially in the voltage range between 2 and 4 V .   
  
The main reason for the decrease in specific capacity is that copper is an inactive element in copper-substituted samples , which results in a significant reduction in the theoretical capacity when the amount of copper content is superabundant .   
  
However , the high-voltage discharge plateaus also gradually disappear with the decrease of the ratio of nickel .   
  
Thus , it would be important to control the proportion of copper to 0.1 , with both advantages of high capacity and high cycle retention .   
  
Compared to the copper-free Na0.44Mn0.6Ni0.4O2 , there is a significant reduction in Rct for the copper-substituted electrodes .   
  
The total cell resistance with Na0.44Mn0.6Ni0.3Cu0.1O2 ( 264.9 O ) is obviously lower than the resistance observed with Na0.44Mn0.6Ni0.4O2 ( 343.7 O ) , which is mostly due to the reduction of Rf .   
  
The poor cycle performance of P2-Na0.44Mn0.6Ni0.4O2 cathode is the result of unstable structure and the Jahn-Teller effect .   
  
It can be observed that the substitution of copper does not affect the position of the discharge plateaus , indicating that Cu is not involved in redox reaction during charging and discharging .   
  
The D values in each charging/discharging plateau are clearly lower than that between plateaus , which is due to the intermolecular resistance caused by the deintercalation/intercalation of sodium ions in the crystal lattice .   
  
Compared with Na0.44Mn0.6Ni0.4O2 electrode , copper-substituted Na0.44Mn0.6Ni 0.3Cu0.1O2 shows a lower total cell resistance , which is mainly reduced by the irreversible resistance and the charge transfer resistance .   
  
Moreover , charge transfer resistance decreased from 125.8 O to 100.6 O , showing a reduction of resistance in deintercalation/intercalation process .   
  
Similarly for NCM/MgO , no reflections associated with MgO were detected , thereby suggesting that MgO coating on the surface might be either ultrathin or amorphous .   
  
The remaining voltage plateau below 4.0 V vs. Na was due to the presence of Na+/vacancy ordering and the stalking faults arising from transition metal layer gliding .   
  
It was evident that a small amount of Cu in the lattice was sufficient to smoothen the plateau at higher voltages at the expense of a small capacity due to the electrochemically inactive nature of the Cu ion .   
  
The long-term cycling performance of NM can be best described by its higher initial discharge capacity along with a high capacity fade until the tenth cycle , followed by more stable long-term cycling .   
  
The capacity fade at initial voltages can be attributed to several phenomena like ( i ) electrolyte decomposition , which resulted in the formation of a solid-electrolyte interface ( SEI ) layer , ( ii ) Jahn-Teller distortion resulting in Mn2+ dissolution into the electrolyte , ( iii ) severe internal stress with a significant volume change , resulting from the accommodation of larger sized Na ions , and ( iv ) insertion of solvated ions into the metal oxide layers .   
  
This lower value can be attributed to the presence of electrochemically inactive Cu species .   
  
However , substitution by copper smoothens the voltage plateau above 3.5 V vs. Na , thereby reducing the phase gliding due to deep extraction of Na at higher voltages .   
  
It can be noted that phase transitions alone can not be responsible for the capacity fade at high cut-off voltages , indicating the existence of other driving forces mentioned above .   
  
Hence , surface coating was a good strategy to prevent direct contact of the cathode material with electrolyte and improve its interfacial properties .   
  
Moreover , the smooth voltage curve of MgO-coated NCM ( Fig . 4d ) indicated suppression of the partially irreversible P2-O2 phase transition at 4.2 V vs. Na , which was very important for P2-Na-Ni-Mn-O based cathodes at higher cut-off voltages .   
  
However , this study did not address the P2-O2 phase transition of cathode that occurs above 4.2 V .   
  
When bare NCM was charged to high voltage , more Na ions were extracted from the lattice , initiating the exfoliation of the layered structure and resulted in a capacity fade over prolonged cycles .   
  
The separations between anodic and cathodic peaks were significantly reduced for Cu-doped samples , thereby proving the improved stability of the cathode .   
  
Although , a small reduction in the initial capacity was observed for MgO coated NM , it rendered better stability with high capacity retention characteristics after 15 cycles ( Fig . S7+ ) .   
  
Further analysis of structure using in situ monitoring techniques would provide a deeper understanding of the mechanism behind MgO coating .   
  
The cathode capacity decreased with increasing current density due to improper utilization of active materials at high input currents .   
  
Even the high-capacity Na0.5Ni0.23Fe0.13Mn0.63O2 cathode reported by Hasa et al . could only deliver a capacity of 60 mA h g-1 at a rate of 5C .   
  
Clearly , the charge transfer resistance was very much reduced for Cu-doped sample , compared to that of the pristine material .   
  
Moreover , the absence of a proper semicircle in the high-frequency region of the doped material denoted negligible role of resistance caused by diffusion of Na+ ions in SEI layer .   
  
The appearance of a single semicircle in high-frequency region for MgO-coated sample indicates its reduced charge transfer resistance and the negligible role of interfacial resistance caused by SEI layer formation , which very well accounts for the long-term cycling performance of this sample .   
  
One is that the large relative atomic mass of copper than that of nickel leads to the decrease of theoretical capacity .   
  
Another is that when copper is used as the active element , the number of electrons transferred in the electrochemical process is half of that when an equal molar amount of nickel is the active element , and then a smaller amount of Na is extracted from the Cu-doped materials compared to the higher amount of Na extracted from the undoped material .   
  
Irreversible phase transition at a higher potential ( > 4.2 V ) is an important cause of severe capacity decay .   
  
When extensive sodium is being deintercalated from the interlayer , the phase transition from P2 to O2 occurs , which results from the structural instability of the layered oxides and finally results in severe voltage and capacity decay after a few cycles .   
  
After the current is gradually reduced to 0.1C , the specific capacity does not completely return to the initial capacity .   
  
More noteworthy , even when the Na0.67Ni0.1Cu0.2Mn0.7O2 electrode was charged and discharged at 5C , it could still deliver significantly higher capacities than others .   
  
The mechanisms responsible for capacity loss and poor reversibility in NaxMO2 cathodes are different from those observed in lithium systems .   
  
There is no Na+/vacancy ordered structure in the electrode with a large amount of Cu based on the ex situ XRD analysis , as the limitations in electron delocalization caused by Mn is reduced by the Cu substitution .   
  
Na+/vacancy-ordering is exhibited in most P2-type layered oxides , which limits the Na-ion transport kinetics and cycle performance in rechargeable batteries .   
  
Choosing the transition metal ions with similar ionic radii and different redox potentials is a strategy to prevent this .   
  
The weakening of the characteristic diffraction peak of P2-type materials indicates that the structure of the electrode has been irreversibly damaged by cycling tests .   
  
In contrast , the copper-substituted Na0.67Ni0.1Cu0.2Mn0.7O2 electrodes exhibit excellent structural stability and maintain the P2 phase ( Fig . 6d ) , although there is weak attenuation in the intensity of some diffraction peaks after Na+ constant deintercalation/intercalation .