Elements  
Macro  
Morphology  
Structure  
Subject  
  
Unfortunately , the capacity retention was poor , which is most likely associated with the Jahn-Teller distortion in the oxide matrix .   
  
Notably , the charge profiles of the Zn-doped Na2/3 [ Mn1-xZnx ] O2 electrodes differed from that of the Zn-free electrode for the initial cycle .   
  
Because of the very low intensity of the OP4 phase , it was not possible to detect the OP4 phase during the O-XRD measurement .   
  
Again , we can not explain the variation of the oxidation for Mn above 4+ on charge ; specifically , the oxidation state of Mn is given as 4.51+ at the second charge , which is not valid considering the oxidation limit of Mn4+ based on the Mn3+/4+ redox pair .   
  
The C1s and O1s spectra did not change during charge/discharge , indicating that they do not participate in the electrochemical reaction .   
  
Surprisingly , there was no evident change in the oxidation state of Mn during charge , although a capacity of 120 mAh g-1 was delivered .   
  
The discrepancy in the oxidation state of Mn at the first charge arises because the charge capacity should have been less than 26 mAh g-1 based on the oxidation state of Mn , 3.9+ , for Na2/3 [ Mn0.7Zn0.3 ] O2 with consideration of the Mn3+/4+ redox .   
  
As observed in the XPS spectra , there was a change in the C1s and O1s regions unlike for the Z0 electrode .   
  
However , Na2O+ ( m = 61.98 ) was detected in the discharged electrode .   
  
The oxygen redox reaction is likely to be interrupted by surface resistance of the electrode caused by the many types of sediment produced by oxidative decomposition of the electrolytic salt and solvents and dissolution of manganese during prolonged high-voltage operation .   
  
Moreover , the HF attack was presumably prevented by the high oxidation state of Mn .   
  
Notably , the initial charge profile of the Zn-doped electrodes differs from that of the Zn-free electrode , which is associated with oxygen redox .   
  
Ex situ XRD analysis of the Z3 electrodes after different cycles shows that no structural arrangements occurs , unlike in the Li-rich system .   
  
In addition , ICP analysis of the pristine and charged electrodes confirms that Zn ions are not extracted from the structure .   
  
Usually , P2-type electrodes suffers from the abnormal low Coulombic efficiency ( CE ) at the initial cycle , however , the P2-Na2/3 [ Zn0.3Mn0.7 ] O2 electrode exhibited high CE , which benefits in full cell configuration .   
  
From the discharge profile , it is thought that the Mn4+/3+ redox may not be available in this operation condition , such that the effect of Jahn-Teller distortion over Mn3+O6 octahedra , which emerges when deeply sodiated to 1.5 V , can be excluded for the present work .   
  
The ac-impedance studies presented that the slight increase in the impedance would be associated with decomposition of electrolyte during high voltage operation ( Figure S2 , Supporting Information ) .   
  
In addition , it is possible that the oxidation of transition metals reduced the NiO distance , as Mn4+ is inactive on oxidation , resulting in a decrease of the a-axis parameter during desodiation .   
  
Upon charging to 4.6 V , there was no change in the oxidation state of Mn , as oxidation beyond 4+ is not possible in the operation window of 2.3-4.6 V .   
  
Discharging to 2.3 V did not alter the oxidation state of Mn , as the Mn4+/3+ redox is inactive in this voltage range .   
  
As observed in Figure 3cit is interesting that the calculated a-axis parameter gradually decreased even above 4.2 V , even though Mn was inactive at the first charge .