Insight into Ca-substitution effects on O3-type $NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$ as cathode materials for sodium ion batteries

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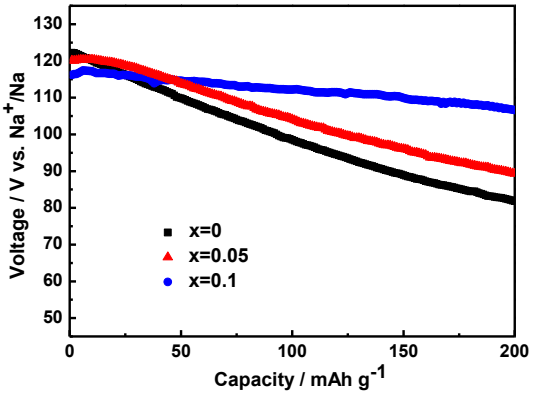
O3-type Layered oxide $NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$ (NaNFM) has been well investigated as promising cathode material for sodium ion batteries[1]. In this work, the effect of Ca-substitution in Na sites on the structural and electrochemical properties of $Na_{1-x}Ca_{x/2}Ni_{1/3}Fe_{1/3}Mn_{1/3}O_2$ ($Na_{1-x}Ca_{x/2}$NFM, x=0, 0.05, 0.1) were investigated. All the prepared $Na_{1-x}Ca_{x/2}$NFM samples showed single α-$NaFeO_2$ type phase with slightly increased alkali-layer distance as Ca content increased. The enlarged alkali-layer distance might benefit Na+ diffusion. However, the advantage was offset by the immobility of Ca^{2+}. The Ca-substituted samples show slightly decreased specific capacities. However, cycling stabilities of Ca-substituted samples were remarkably improved. In situ XRD measurement indicate that the $Na_{0.9}Ca_{0.05}$NFM cathode presented reversible structural evolution through an O3-P3-P3-O3 sequence during cycling just like the pristine NaNFM[2]. $Na_{0.9}Ca_{0.05}$NFM show wider voltage range in pure P3 phase state during charge/discharge, and exhibit better structure recoverability after cycling compared with NaNMF. The $Na_{0.9}Ca_{0.05}$NFM cathode delivered capacities of 116.3 mAh g-1(1C) 102.1 mAh g-1 (5C) and 86.2 mAh g-1 (10C) with capacity retention of 92% (1C) after 200cycles, compared to the 67% (1C) of NaNFM. The superior cycling stability of $Na_{0.9}Ca_{0.05}$NFM makes it a promising material for practical applications.



Cycling performance of $Na_{1-x}Ca_{x/2}Ni_{1/3}Fe_{1/3}Mn_{1/3}O_2$ (x=0, 0.05, 0.1) samples

References:

[1] D. Kim, E. Lee, M. Slater, W. Lu, S. Rood and C.S. Johnson, Electrochem. Commun., 18 (2012), 66.
[2] Y. Xie, H. Wang, G. Xu, J. Wang, H. Sheng, Z. Chen,Y. Ren, C. J. Sun, J. Wen, J. Wang, D. J. Miller, J. Lu, K. Amine and Z. F. Ma, Adv. Energy Mater., 1 (2016), 1601306.