SYNTHESIS AND CHARACTERIZATION OF Li TRANSITION-METAL OXIDE ELECTRODE MATERIALS, AND THEIR APPLICATIONS IN Li -ION BATTERIES

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$Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ is an important member of the $Li(Ni_yCo_{1-2y}Mn_y)O_2$ system (y = 1/3), which, has recently been investigated as a promising candidate for positive electrode materials in lithium ion rechargeable batteries (LIB). Further expansion of this ternary system by replacing costly and electrochemically insignificant, Co with other potential but cheaper elements such as Al, Fe, Mg, Zn is of great research interest.

In this study, $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ together with new material compositions of $Li(Ni_{1/3}Co_{[(1/3)-x]}Mn_{1/3}M_x)O_2$(M=Al, Fe, Mg, Zn and x= 0.11, 0.22, 0.33) and $Li(Ni_{1/3}Co_{1/3}Mn_{[(1/3)-x]}Mg_x)O_2$ (x= 0.11, 0.22, 0.33) were synthesized in the form of fine powders by Pechini method and calcined at 900 °C.

The phase analysis by XRD revealed the formation of solid solutions of appropriate α - $NaFeO_2$ layered structure (R3m layered structure) in all the compositions but with the presence of a secondary phase in trace amounts in some compositions. The d.c electrical conductivity, measured by four probe method, increases with temperature in an exponential manner for all the materials, except for the Zn substituted system. Most of the materials prepared by Pechini method in this study show appropriate particle size for LIB positive electrode. Selected oxide powders were mixed with polyvinylidene fluoride (PVDF) binder (KynarFlex 2801) and Super P Carbon Black in proportions 1:0.25:0.10 by weight to prepare the positive electrode. CR2016 type stainless steel coin cells, assembled in an argon-filled glove box were used for electrochemical testing. All the electrochemical testing was done at room temperature. Used anode is a metallic lithium foil and the electrolyte was 1.2 M $LiPF_6$ (lithium hexafluorophosphate) in 3:7 (weight ratio) ethylene carbonate:ethyl methyl carbonate (EC:EMC). The cells were tested using galvanostatic

charge / discharge mode using potential window of 3.0-4.5 V. For $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ a much better electrochemical performance is seen for the material calcined at 1000 °C, with a specific capacity close to 180 mA h g^{-1}. Conversely, the material calcined at 800 °C shows only a specific capacity of 140 mA h g^{-1}. In general some of the $Li(Ni_{1/3}Mn_{1/3}Co_{[(1/3)-x]}M_x)O_2$, M=Fe, Al and Mg materials show a considerably higher first cycle charge capacity than the state-of-art cathode material, $LiCoO_2$, of LIB.

The present study, shows the potential and the suitability of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ and $Li(Ni_{1/3}Mn_{1/3}Co_{[(1/3)-x]}M_x)O_2$, M=Fe, Al and Mg materials prepared by Pechini method, for application as electrode (cathode) material in lithium ion batteries.