Surface modification and characterization of nanocrystalline LiNi$_{0.5}$Co$_{0.5}$VO$_4$ with Dy$_2$O$_3$ by polymeric resin process

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Abstract
A poly acrylic acid and ethylene glycol mediated polymeric resin process has been demonstrated for the fabrication of functional Dy$_2$O$_3$ layer on the nanocrystalline LiNi$_{0.5}$Co$_{0.5}$VO$_4$ surfaces. Polymeric resin helps in the uniform distribution as well as the stabilization of Dy$^{3+}$ ions on the LiNi$_{0.5}$Co$_{0.5}$VO$_4$ surfaces. The thermal degradation of Dy$^{3+}$ distributed polymeric resin at 500 °C results in the formation of Dy$_2$O$_3$ on the surface of LiNi$_{0.5}$Co$_{0.5}$VO$_4$ particles, which was confirmed by TG/DTA and FTIR analysis. Excellent homogeneity of the Dy$_2$O$_3$ layer with a controlled thickness on the surface of LiNi$_{0.5}$Co$_{0.5}$VO$_4$ has been confirmed by SEM-EDS and TEM analysis.

Keywords Polymeric resin, Cathode, Inverse spinel, Surface modification, Dy$_2$O$_3$

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Introduction
An ever increasing energy demand, the recent growth in commercial electric vehicle technology and mobile electronics, and emerging environmental concerns have motivated many researchers to explore portable/alternate energy solutions. As a result, extensive research activities have been devoted to rechargeable lithium ion batteries in last three decades with the ultimate aim of identifying suitable material combinations for improved charge and energy transfer performance. In particular, various types of cathode materials with layer (e.g. LiCoO$_2$ and LiNiO$_2$), spinel (e.g. LiTi$_2$O$_4$ and LiMn$_2$O$_4$), inverse spinel (e.g. LiNiVO$_4$, LiCoVO$_4$), and olivine structures (e.g. LiFePO$_4$) have been investigated and reported in literature. In addition to this, significant research efforts have been made in order to enhance the energy density of lithium batteries by manipulating the cathode intercalation voltage. LiNi$_{0.5}$Co$_{0.5}$O$_2$, LiCoO$_2$, and LiNi$_{0.5}$Co$_{0.5}$VO$_4$ are very attractive due to their higher potential of ~5V vs. Li+/Li. The challenge for these inverse spinel structured cathode materials in lithium ion batteries is their lower initial capacity and drastic capacity loss upon cycles.

Numerous efforts have been made in order to overcome these disadvantages including nanofabrication, metal ion doping, and surface modifications. Surface modification of cathode materials receives major attention due to their advantages such as enhanced structural stability during lithium intercalation, prevention of unwanted interaction of cathode surfaces with electrolytes, and the thermal stability. Moreover, the coating of metal oxides over cathode materials suppresses possibility of phase transition and enhances their structural stability and also reduces the cat ion disorder in its crystalline sites. As a result, side reactions and heat generation during cycling are decreased. Different types of metal oxides including ZrO$_2$, Al$_2$O$_3$, SiO$_2$, TiO$_2$, ZnO, and SnO$_2$ have been used for the surface coating of cathode materials. An extensive literature work has been performed on the surface modification of cathode materials by Li et al. In addition to that, Yi et al. summarized the surface modification of LiMn$_2$O$_4$ by various types of oxide layers. In addition to these reviews, Myung et al. also reported the surface modification of cathode materials by different materials. Comparing the various types of oxide materials, which have been used for the surface modification of cathode materials, rare earth oxides are unique due to their electrical performance as well as improved thermal stability. Ha et al. demonstrated the surface modification of LiNi$_{0.5}$Co$_{0.5}$O$_2$ with CeO$_2$ and showed the improved cell performance. In addition to that, Fey et al. employed La$_2$O$_3$ to modify the surface of LiCoO$_2$ and reported the enhanced cycled performance. Arumugam et al. investigated the surface modification of LiMn$_2$O$_4$ by La$_2$O$_3$. Recently, Kim and Park introduced Sm$_2$O$_3$-coated...
Dysprosium nitrate (metal ion source), GR grade Merck-India; polyacrylic acid (chelating and resin forming agent), AR grade, Merck-India; ethylene glycol (polymerizing agent) - SQ grade Qualigens-India were used in this process for the coating of Dy$_2$O$_3$ layer on the surface of nanocrystalline LiNi$_{0.5}$Co$_{0.5}$VO$_4$ particles. Pristine LiNi$_{0.5}$Co$_{0.5}$VO$_4$ particles were prepared by employing ethylene glycol assisted Pechini process, which is reported earlier. The synthesized nanocrystalline LiNi$_{0.5}$Co$_{0.5}$VO$_4$ with the average particle size of ~80 nm were dispersed in distilled water and the obtained dispersion was termed as A. A mixture of polyacrylic acid, ethylene glycol, and dysprosium nitrate solutions was prepared and evaporated at 80 °C under constant stirring. The molar ratio between polyacrylic acid and ethylene glycol was fixed as 10:2 and the amount of dysprosium nitrate was calculated for 1wt % of Dy$_2$O$_3$ to the LiNi$_{0.5}$Co$_{0.5}$VO$_4$. The resulted transparent solution was continuously evaporated, causing the polymerization between polyacrylic acid and ethylene glycol and led to the formation of polymeric resin B. Uniform dispersion of Dy$^{3+}$ ions in the resin matrix was achieved through their chelation by polyacrylic acid. The mixture of A and B was evaporated at 60 °C under vigorous stirring for 6 h in order to remove the remaining water. The resulted black colored solid mass has been calcined at 500 °C for 6 h to fabricate Dy$_2$O$_3$-coated nanocrystalline LiNi$_{0.5}$Co$_{0.5}$VO$_4$ particles. Schematic representation of resin-coated LiNi$_{0.5}$Co$_{0.5}$VO$_4$ is shown in Fig. 1.

Thermal degradation of polymeric resin with Dy$^{3+}$ dispersion coated on the surface of LiNi$_{0.5}$Co$_{0.5}$VO$_4$ particles was investigated in the simultaneous thermo gravimetric/differential thermal analyzer (TG/DTA) from Setaram, France. Approximately 3 mg of dried sample was heated between 30 °C and 600 °C at a rate of 10 °C min$^{-1}$ under the flowing oxygen. The structural coordination of the pristine, polymeric resin and Dy$_2$O$_3$-coated nanocrystalline LiNi$_{0.5}$Co$_{0.5}$VO$_4$ particles were studied using an FTIR-8000 spectrometer of Shimadzu, Japan. FTIR spectra of the KBr diluted LiNi$_{0.5}$Co$_{0.5}$VO$_4$ thin pellets were recorded between 400 and 4000 cm$^{-1}$. Powder X-ray diffraction (XRD) patterns were recorded by using an X Pert PRO MPD, PANalytical (Philips) X-ray powder diffractometer employing Cu-K$_\alpha$ radiation. The diffraction patterns of the LiNi$_{0.5}$Co$_{0.5}$VO$_4$ samples have been recorded between 10 and 80° 2θ values at the scan rate of 2° min$^{-1}$. Microstructure of the Dy$_2$O$_3$-coated nanocrystalline LiNi$_{0.5}$Co$_{0.5}$VO$_4$ particles was investigated using a scanning electron microscope, S-3400 from Hitachi, Japan employing a 25kv electron beam. The samples were dispersed in acetone under sonication and a drop of the dispersion was spread on the carbon tape pasted onto the aluminum stub prior to analysis. TEM analysis of the sonicated and well dispersed Dy$_2$O$_3$-coated nanocrystalline LiNi$_{0.5}$Co$_{0.5}$VO$_4$ particles has been performed employing JEOL-2010F transmission electron microscope with 200 kV accelerating voltage.
Results and discussion

The layer of Dy₂O₃ has been stabilized on the surface of LiNi₀.₅Co₀.₅VO₄ by degrading the polymeric intermediate matrix at an optimized temperature. Hence, the temperature-dependent degradation behavior of the polymeric intermediate coated with Dyⁿ⁺ chelation on the LiNi₀.₅Co₀.₅VO₄ surfaces at 500 °C leads to the formation of a Dy₂O₃ layer over the LiNi₀.₅Co₀.₅VO₄ particles. Also, the XRD pattern of pristine Dy₂O₃ is presented in Fig. 4 for the comparison.

The XRD patterns of the pristine, polymeric resin, and Dy₂O₃-coated nanocrystalline LiNi₀.₅Co₀.₅VO₄ are shown in Fig. 4. The strong diffraction peaks observed for the pristine LiNi₀.₅Co₀.₅VO₄ at 18.67 (111), 30.73 (220), 36.17 (311), 43.95 (400), 54.51 (422), 58.13 (511), and 63.85 (440) indicate the structural features of a phase pure cubic structure. The observed weak (111) and the strong (220) Bragg peaks indicate the predominant inverse spinel with no phase impurities. Coating of polymeric resin with chelated Dyⁿ⁺ ions over the LiNi₀.₅Co₀.₅VO₄ surfaces does not exhibit any significant peaks, which indicates that the polymeric resin exists in an amorphous phase. As confirmed by TG/DTA and FTIR analysis, thermal decomposition of the polymeric resin coated on the LiNi₀.₅Co₀.₅VO₄ surfaces at 500 °C leads to the formation of Dy₂O₃ structures. However, the functional Dy₂O₃ layer does not show any noticeable peaks in the XRD pattern, which indicates that Dy₂O₃ exists in a non-crystalline phase. Also, the lattice parameter a of the pristine, polymeric resin and Dy₂O₃-coated
Figure 5 (a) SEM image and (b) the relevant EDS spectrum of the Dy$_2$O$_3$-coated nanocrystalline LiNi$_{0.5}$Co$_{0.5}$VO$_4$.

Figure 6 SEM-EDS elemental mapping of the Dy$_2$O$_3$-coated nanocrystalline LiNi$_{0.5}$Co$_{0.5}$VO$_4$. 
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with the improved thermal stability, which could exhibit better electrochemical performance. Further, this process can be used for the fabrication of metal oxide-coated metal oxide nanostructures.

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