Preparation and Characterization of $LiNiVO_4$ and $LiNi_{1-x}Mn_xVO_4$ ($0 \leq x \leq 1$) Cathode Materials

Abstract

The inverse spinel lithium nickel vanadate, $LiNiVO_4$ and doped system lithium nickel manganese vanadate, $LiNi_{1-x}Mn_xVO_4$, x = 0.25 having cubic structure were successfully synthesized by the sol- gel (SG) and polymer precursor (PP) method. The citric acid was used as the chelating agent for both techniques. The TGA analysis was carried out to estimate the suitable firing temperature of the dried precursor and to investigate the chemical reaction during the synthesized process. All prepared system namely $LiNiVO_4$- SG, $LiNiVO_4$- PP, $LiNi_{0.75}Mn_{0.25}VO_4$- SG, and $LiNi_{0.75}Mn_{0.25}VO_4$- PP was calcined at temperature range from 500 °C to 800 °C for 3 hours separately in a furnace. The firing environment was done in air. The reducing agent used and the distilled water used as the solvent had made the synthesizing process simple and yet economical. The reaction mechanism of the $LiNiVO_4$- SG agrees with the thermal analysis for decomposition process. The XRD pattern of the $LiNiVO_4$- SG sample show an absence of the NiO impurities starting at 600 °C to 800 °C. The single phases of pure inverse spinel product were obtained at all sintering temperatures for $LiNiVO_4$- PP, $LiNi_{0.75}Mn_{0.25}VO_4$- SG, and $LiNi_{0.75}Mn_{0.25}VO_4$- PP systems. The Scherrer equation has been implemented to calculate the crystallite size of the obtained powder in this work. The obtained values from the equation satisfy the observed TEM results obtained in this work. The nanosized range particle was achieved between 42.94 nm to 68.07 nm for the $LiNiVO_4$- SG sample and 33.38 nm to 48.43 nm for the $LiNiVO_4$- PP system. The doped $LiNi_{0.75}Mn_{0.25}VO_4$- SG and $LiNi_{0.75}Mn_{0.25}VO_4$- PP system was found to be in the range of 23.65 nm to 33.54 nm and 19.82 nm to 39.53 nm respectively. It can be conclude that the doping material and additional of the polymer source inhibit the grain

growth of the particle in this work. The SEM morphology for the $LiNiVO_4$- SG system reveals that the particle distribution having porous morphology of the highest firing temperature at 800 °C. The formations of the polyhedral morphology were clearly seen as the samples were heated at elevated temperature for the $LiNiVO_4$- PP, $LiNi_{0.75}Mn_{0.25}VO_4$- SG, and $LiNi_{0.75}Mn_{0.25}VO_4$- PP systems. The elemental study, EDAX for this work also agrees stoichiometrically with the prepared cathodes. The open circuit voltage was obtained for undoped $LiNiVO_4$- SG and $LiNiVO_4$- PP system at around 3.0 V - 3.5 V for the both doped $LiNi_{0.75}Mn_{0.25}VO_4$- SG and $LiNi_{0.75}Mn_{0.25}VO_4$- PP systems. The cyclic voltammetry employed for the Li/ Li^+ system show reversible mechanism for the fabricated half- cell suggesting that the de/intercalation of Li^+ ion took place in the cell system. The de/intercalation peak using the $LiNiVO_4$- SG cathode demonstrate oxidation peak at 4.7 V and 4.3 V for the reduction peak. The anodic and cathodic peaks were observed at 4.4 V and 4.2 V respectively using the $LiNiVO_4$- PP cathode. The voltammogram of the cell using the $LiNi_{0.75}Mn_{0.25}VO_4$- SG show deintercalation peak at 4.3 V while at 3.7 V of reducing peak during the 1^{st} scan. The oxidation peak at 4.4 V for the forward scan were observed and at 3.7 V of the reduction peak for cell using the $LiNi_{0.75}Mn_{0.25}VO_4$- PP cathode.

Abstrak

Litium nikel vanadat, $LiNiVO_4$ dan sistem litium nikel vanadat dengan dopan mangan, $LiNi_{1-x}Mn_xVO_4$, x = 0.25 mempunyai struktur inverse spinel berjaya disintesis dengan jayanya menggunakan sintesis sol-gel dan kaedah polimer prekursor. Asid sitrik digunakan sebagai agen pengkelatan untuk kedua-dua teknik. Analisis TGA dilakukan untuk menganggarkan suhu pembakaran yang sesuai untuk prekursor dan untuk mengenalpasti reaksi kimia semasa proses sintesis. Semua sistem disintesis iaitu $LiNiVO_4$-SG, $LiNiVO_4$-PP, $LiNi_{0.75}Mn_{0.25}VO_4$- SG, dan $LiNi_{0.75}Mn_{0.25}VO_4$- PP dikalsinasi pada julat suhu dari 500 °C hingga 800 °C selama 3 jam secara berasingan dalam tungku pemanasan. Pemanasan sampel dilakukan di dalam persekitaran udara. Agen pengurangan dan air suling digunakan sebagai pelarut telah membuat proses sintesis mudah dan ekonomi. Reaksi mekanisme dari $LiNiVO_4$- SG mematuhi analisis terma untuk proses dikompos. Pola XRD sampel LiNiVO4- SG tanpa menunjukkan kehadiran bendasing NiO bermula pada 600 °C hingga 800 °C. Fasa tunggal produk inverse spinel diperoleh di semua suhu untuk $LiNiVO_4$- PP, $LiNi_{0.75}Mn_{0.25}VO_4$- SG, dan sistem $LiNi_{0.75}Mn_{0.25}VO_4$- PP. Persamaan Scherrer telah digunapakai untuk mengira saiz kristal serbuk yang diperolehi dalam kajian ini. Nilai yang diperolehi daripada persamaan memenuhi pemerhatian TEM yang diperolehi dalam kajian ini. Bahan katod bersaiz nano dapat dihasilkan dalam julat antara 42.94 nm hingga 68.07 nm untuk sistem $LiNiVO_4$- SG dan 33.38 nm ke 48.43 nm untuk sistem $LiNiVO_4$- PP. Saiz kristalit bagi katod $LiNi_{0.75}Mn_{0.25}VO_4$- SG ditemui berada dalam julat antara 23.65 nm ke 33.54 nm dan 19.82 nm ke 39.53 nm bagi katod $LiNi_{0.75}Mn_{0.25}VO_4$- PP. Dapat

disimpulkan bahawa bahan pengedopan mangan dan tambahan sumber polimer menghalang pertumbuhan kristal zarah dalam kajian ini. Morfologi SEM untuk sistem $LiNiVO_4$- SG menunjukkan morfologi berpori daripada suhu pembakaran tertinggi pada 800 °C. Formasi polyhedral jelas dilihat sebagai sampel dipanaskan pada suhu tinggi untuk $LiNiVO_4$- PP, $LiNi_{0.75}Mn_{0.25}VO_4$- SG, dan sistem $LiNi_{0.75}Mn_{0.25}VO_4$- PP. Analisis unsur, EDAX untuk kajian ini juga bersesuaian dengan stoikiometri dengan katod yang disintesis. Nilai voltan terbuka yang diperolehi untuk $LiNiVO_4$-SG dan sistem $LiNiVO_4$- PP adalah $\geq$ 3.0 V, manakala bagi kedua-dua system katod $LiNi_{0.75}Mn_{0.25}VO_4$- SG dan sistem $LiNi_{0.75}Mn_{0.25}VO_4$- PP adalah $\geq$ 3.5 V. Kitaran voltametri digunakan untuk mekanisme sistem Li/ Li^+ menunjukkan proses berbalik menunjukkan bahawa diinterkalasi Li^+ ion terjadi dalam sistem sel tersebut. Kelok redox menggunakan katod $LiNiVO_4$- SG menunjukkan puncak pengoksidaan pada 4.7 V dan 4.3 V untuk puncak penurunan. Kelok anodik dan katodik didapati pada 4.4 V dan 4.2 V masing-masing menggunakan katod $LiNiVO_4$-PP. Voltametri bagi sel menggunakan $LiNi_{0.75}Mn_{0.25}VO_4$- SG menunjukkan kelok pengoksidaan pada 4.3 V manakala pada 3.7 V pada kelok penurunan pada kitaran pertama. Kelok pengoksidaan didapati pada 4.4 V dan kelok penurunan pada 3.7 V bagi sel menggunakan katod $LiNi_{0.75}Mn_{0.25}VO_4$ - PP.