



OPEN

SUBJECT AREAS:

BATTERIES

SYNTHESIS

Received
28 February 2014Accepted
11 April 2014Published
2 May 2014

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Mechanochemical Synthesis of Li_2MnO_3 Shell/ LiMO_2 ($M = \text{Ni}, \text{Co}, \text{Mn}$) Core-Structured Nanocomposites for Lithium-Ion Batteries

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Core/shell-like nanostructured $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($M = \text{Ni}, \text{Co}, \text{Mn}$) composite cathode materials are successfully synthesized through a simple solid-state reaction using a mechanochemical ball-milling process. The LiMO_2 core is designed to have a high-content of Ni, which increases the specific capacity. The detrimental surface effects arising from the high Ni-content are countered by the Li_2MnO_3 shell, which stabilizes the nanoparticles. The electrochemical performances and thermal stabilities of the synthesized nanocomposites are compared with those of bare LiMO_2 . In particular, the results of time-resolved X-ray diffraction (TR-XRD) analyses of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ nanocomposites as well as their differential scanning calorimetry (DSC) profiles demonstrate that the Li_2MnO_3 shell is effective in stabilizing the LiMO_2 core at high temperatures, making the nanocomposites highly suitable from a safety viewpoint.

As the application of lithium-ion batteries continues to expand to higher energy consumption devices, such as electric vehicles (EVs) and electrical energy storage (EES) systems, the development of higher energy density electrode materials is becoming more essential. For cathodes, materials with higher operating voltage windows and larger specific capacities are being intensively studied¹. As a part of these developments of advanced cathode materials, the layered transition metal oxide, which can accommodate more than one unit of Li per molecule, has been receiving the most attention in recent years^{2–6}.

Many studies have attempted to optimize the $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ composite system because its capacity can reach higher than 200 mA h g⁻¹. For these composites, the LiMO_2 component is primarily responsible for lithium deintercalation and intercalation at voltages lower than 4.5 V (vs. Li/Li⁺), and Li_2MnO_3 acts as the additional capacity reservoir when charging above 4.5 V (vs. Li/Li⁺)^{2–6}, where the irreversible activation of Li_2MnO_3 into Li_2O and MnO_2 occurs during the first charge cycle^{2–8}. Generally, the synthesis of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ (equivalently $\text{Li}_{1+x}\text{MO}_2$) or LiMO_2 has been performed via co-precipitation or sol-gel methods^{9–13}. However, the mechanical treatment of solids, such as the ball milling method, could offer a rather simple and highly efficient process with lower energy consumption and cost¹⁴, to prepare these electrode materials.

Recently, West *et al.* prepared the Li_2MnO_3 and LiMO_2 components separately and performed the synthesis using a ball-milling-annealing process¹⁵. These researchers observed that the synthesized composite material exhibited crystallographic characteristics and electrochemical performances similar to those of layered-layered $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ materials prepared by the conventional co-precipitation process¹⁵. This result proved that the Li_2MnO_3 and LiMO_2 components do not need to be connected at the atomic level to achieve anomalously high capacities (*i.e.*, capacities greater than 200 mA h g⁻¹). In our previous studies, we used the mechanochemical process to form alloys among nanoparticles^{16–20}. We have also recently demonstrated that Li_2MnO_3 and LiMO_2 can be closely integrated as a nanocomposite in a controlled mole ratio via a mechanochemical process^{21,22}. To increase the specific capacity of LiMO_2 ($M = \text{Ni}, \text{Co}, \text{Mn}$), a good strategy is to increase its Ni content^{23–26}. However, the cathode material may experience detrimental effects at the surface because the Ni at the surface of the material can be easily oxidized and destabilize the surface of the electrode, resulting in a poorer cycle life and thermal stability^{27–31}.



Sun *et al.* developed a cathode material $\text{Li}[(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})_{0.8}(\text{Ni}_{0.5}\text{Mn}_{0.5})_{0.2}]\text{O}_2$ with a microscale core-shell structure; the $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ core yielded a high capacity, while the $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2$ shell provided high thermal stability³². In addition, the material exhibited improved cycling performance, with a capacity retention of 98%³³. A similar cathode material with an average composition of $\text{Li}[\text{Ni}_{0.68}\text{Co}_{0.18}\text{Mn}_{0.18}]\text{O}_2$, fabricated by controlling the volume ratio of the core and shell components, also exhibited superior performance³⁴. The results reported by Sun and co-workers demonstrated that the core-shell structure is suitable for improving the electrochemical performance of microscale cathode materials. Thus, it is reasonable to assume that the core/shell-like structure would also be suitable at the nanoscale. If $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ nanocomposites were fabricated with a core/shell-like structure, not only would the stability of the material be high, but it would also exhibit anomalously high capacities.

In this study, we synthesized nanoscale core/shell-like structured $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ composites for use as cathode materials. The shell was Li_2MnO_3 , while the Ni-rich $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ component formed the core. The nanocomposites were fabricated via a solid-state reaction using a mechanochemical process. The uniform Li_2MnO_3 coating on the outer surface stabilized the Ni-rich LiMO_2 cores, as illustrated in Figure 1. We tested various mole ratios of the two components, Li_2MnO_3 and LiMO_2 , to optimize the amount of the surface-coating-forming component (Li_2MnO_3). We also tested various heat treatment temperatures to investigate whether the temperature had any effect on the structures and electrochemical performances of the nanocomposites. Finally, we investigated whether the thermal stabilities of electrodes formed using the nanocomposite materials were more stable than those of electrodes based on LiMO_2 alone.

Results

Morphologies of the synthesized nanocomposites. Figure 2 presents the bright field (BF) images of the $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMO}_2$ samples after they had been subjected to heat treatment temperatures at 400, 700, and 1000°C . Note that the scale bars in Figure 2 differ as the particle size of the sample was increased at higher heat treatment temperatures. The particles shown in Figure 2 are primary particles, separated from the secondary particles to obtain the transmission electron microscopy (TEM) images. Based on the TEM image in Figure 2 (a), it can be surmised that nanoscale Li_2MnO_3 formed at 400°C and completely covered the surface of the LiMO_2 particles.

Because the particles of the Li_2MnO_3 sample synthesized at 400°C are much smaller ($<50\text{ nm}$)⁷ than those of the starting material of LiMO_2 (average secondary particle size of $\sim 10\ \mu\text{m}$ before the mechanochemical process), we believe that the Li_2MnO_3 layer formed on the surfaces of the LiMO_2 primary particles after the mechanochemical process and the subsequent heat treatment. With an increase in the heat treatment temperature to 700°C , the particle size of Li_2MnO_3 increased, as observed in Figure 2 (b)⁷. The TEM image in Figure 2 (c) also reveals that larger Li_2MnO_3 particles existed on the surfaces of the LiMO_2 particles even after the heat treatment at 1000°C and that the overall particle size increased with the heat treatment temperature. In addition, scanning electron microscopy (SEM) images of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$, where x is 0.3, 0.5, or 0.7, are displayed in Figure S1 (Supplementary Information); the heat treatment temperature was 700°C . Because of the aggregation of the primary nanoparticles, secondary particles formed after the mechanochemical milling process and the subsequent high-temperature heat treatment; this result was consistent with those of our previous studies^{20–22}. To confirm whether the surface coating material was Li_2MnO_3 and the bulk material was $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$, we employed energy dispersive X-ray spectroscopy (EDS) to investigate the two materials.

The results of the elemental analysis of the $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMO}_2$ nanocomposite sample prepared at 1000°C are presented in Figures 3 (b), (c), and (d). The elements Ni, Co, and Mn are present at the centers of the particles of the nanocomposite material (see Figure 3 (b)). However, upon observing the surfaces of the particles, it was observed that the element Mn was present on the surfaces in the greatest amount, while Ni and Co were present in much smaller amounts (see Figures 3 (c) and (d)). We believe that this result occurred because during the high-temperature heat treatment at 1000°C , the mixing of the metal cations caused the movement of the transition metals between the Li_2MnO_3 surface and the LiMO_2 bulk; however, the shells of the synthesized electrode materials were designed to be Mn-rich to enhance stabilization.

We also performed elemental mapping for the $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMO}_2$ nanocomposite sample prepared at 1000°C ; the results are presented in Figs. 3 (e), (f), and (g). The elemental map shows the concentrations of Mn, Co, and Ni. It was evident that Co and Ni were present in smaller amounts at the surface than was Mn. Upon considering the results of the EDS analyses in combination with the elemental concentration maps, it could be surmised that the mechanochemical process was highly effective for synthesizing core/

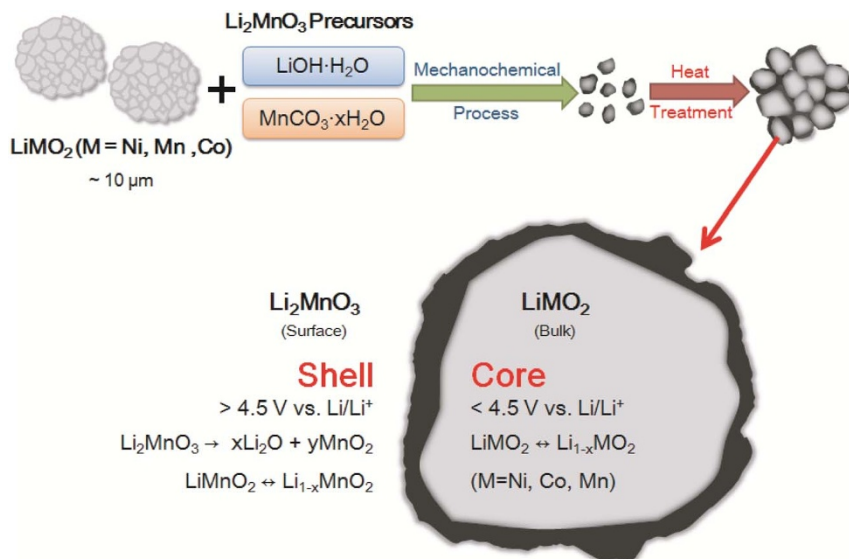


Figure 1 | Schematic of the core/shell-like nanostructure: Li_2MnO_3 surface coating on LiMO_2 (M = Ni, Co, Mn) bulk electrode materials.

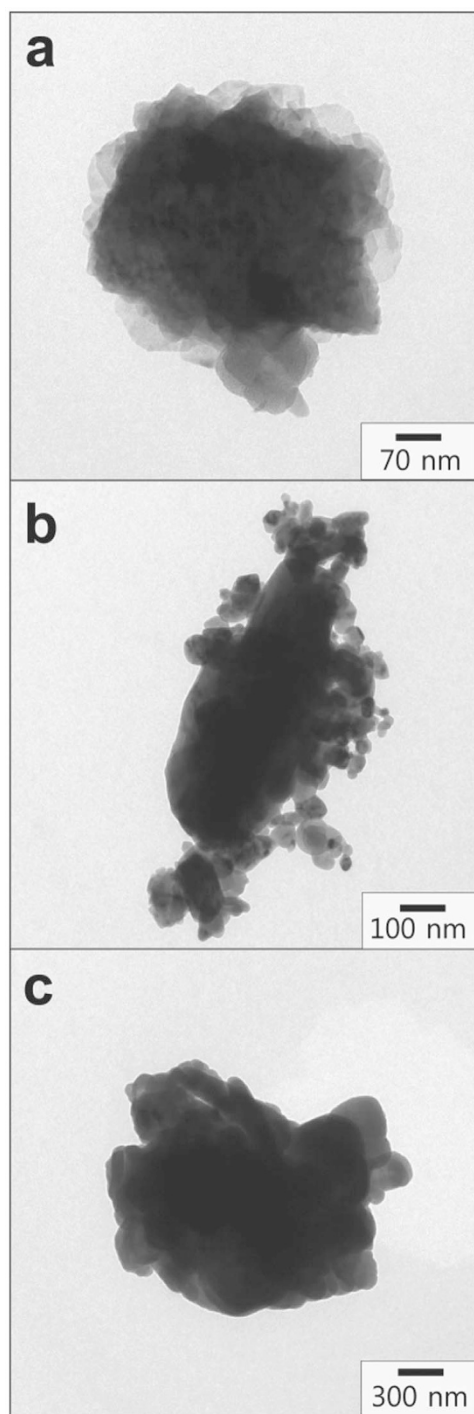


Figure 2 | BF images of $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ heat treated at (a) 400°C , (b) 700°C , and (c) 1000°C .

shell-like nanostructures. Furthermore, the nanostructures prepared were such that the Li_2MnO_3 played the role of stabilizing the LiMO_2 core. Finally, to further investigate the crystal structures of Li_2MnO_3 and LiMO_2 , high-resolution (HR) TEM was used to image the $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMO}_2$ nanocomposite sample prepared at 1000°C ; the image is presented in Figure S2 (Supplementary Information). The fast Fourier transform (FFT) patterns of the images confirmed the existence of both $C2/m$ Li_2MnO_3 and $R-3m$ LiMO_2 . This result confirmed that the two components closely integrated with each other at their interfacial region.

Structures of the synthesized nanocomposites. Figure 4 presents the X-ray diffraction (XRD) profiles of (a) Li_2MnO_3 , (b)

$\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$, and the $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMO}_2$ nanocomposite samples heat treated at (c) 400°C , (d) 700°C , and (e) 1000°C ; the values of 2θ range from 15 to 70° . The XRD patterns of all the nanocomposite samples consisted of overlapping peaks of Li_2MnO_3 and LiMO_2 . All the diffraction peaks could be indexed as being attributable to a hexagonal structure with the space group $R-3m$. The image on the right in Figure 4 (a) shows a magnified version of the XRD patterns for 2θ values ranging from 20 to 24° . The low-intensity peaks correspond to the cation ordering in the Li_2MnO_3 layer^{2–8}. With increases in the heat treatment temperature, the intensities of these peaks also increased. While the $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMO}_2$ nanocomposite sample heated at 400°C exhibited a single broad peak at 21.1° , a double peak ranging from 21.1 to 21.4° appeared for the sample heated at 700°C . In addition, slight shifts in the peaks at 21.1 and 21.7° were observed for the $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMO}_2$ sample heated at 1000°C . The fact that the (018) and (110) peaks appeared separately, at 64.7 and 65.7° , respectively, suggested that the cation ordering in the nanocomposites was of a high degree and that the nanocomposites exhibited a well-layer structure^{34,35}. Figure 4 (b) presents the XRD patterns of the $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ samples (where x is 0.3, 0.5, or 0.7) heat-treated at 1000°C . For these samples, low-intensity peaks also appeared at 21.1 and 21.7° . As a greater amount of Li_2MnO_3 was incorporated into the nanocomposite, the intensities of the peaks lying between 20° and 24° also increased. The diffraction patterns for the $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ samples heat treated at 400 and 700°C are presented in Figures S3 and S4, respectively.

To obtain additional structural information on the core-shell nanocomposite, we calculated the lattice parameters based on the space group $R-3m$, which are summarized in Table S1 (Supplementary Information). When the synthesis temperature was increased, the lattice parameters a and c decreased and increased, respectively, which implies that the overall c/a ratio was increased. This result indicates that the lithium ion can be easily de-/intercalated to the cathode hosts due to the expansion in the z -direction. In addition, we calculated the crystallite size for each sample using the Williamson-Hall method. At each synthesis temperature, as the amount of Li_2MnO_3 was increased, the overall crystallite size of the nanocomposite samples decreased. This result was consistent with our TEM results in Figure 2 and demonstrated that the particle sizes of the Li_2MnO_3 on the surface were smaller compared with those of the LiMO_2 particles. As the synthesis temperature increased, the crystallite size of our sample also increased⁷.

Electrochemical measurements and thermal stabilities. Galvanostatic charge and discharge measurements were performed using cells containing $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ as the active material. The 1st cycle charge and discharge profiles for the $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ samples (where $x = 0.3, 0.5$, or 0.7) heat treated at 400°C are shown in Figure 5 (a). The cell containing $0.7\text{Li}_2\text{MnO}_3 \cdot 0.3\text{LiMO}_2$ exhibited a charge capacity of $269.1 \text{ mA h g}^{-1}$; however, this cell also exhibited a large and irreversible capacity loss. The cell containing $0.3\text{Li}_2\text{MnO}_3 \cdot 0.7\text{LiMO}_2$ initially exhibited a lower charge capacity ($219.9 \text{ mA h g}^{-1}$) and lower irreversible capacity. Figure 5 (b) shows the 1st cycle charge and discharge profiles for the $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ samples heat treated at 700°C . It was observed that the specific capacity decreased as the amount of Li_2MnO_3 incorporated was increased. Typically, the discharge capacity of Li_2MnO_3 decreases with an increase in the synthesis temperature because of the resultant increase in the particle size and the decrease in the number of stacking faults in the Li_2MnO_3 structure⁷.

Figure 5 (c) shows the 1st cycle charge and discharge profiles for the $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ samples heat treated at 1000°C . The discharge capacities of all the samples were higher, and the samples exhibited significantly smaller losses in their irreversible capacities.

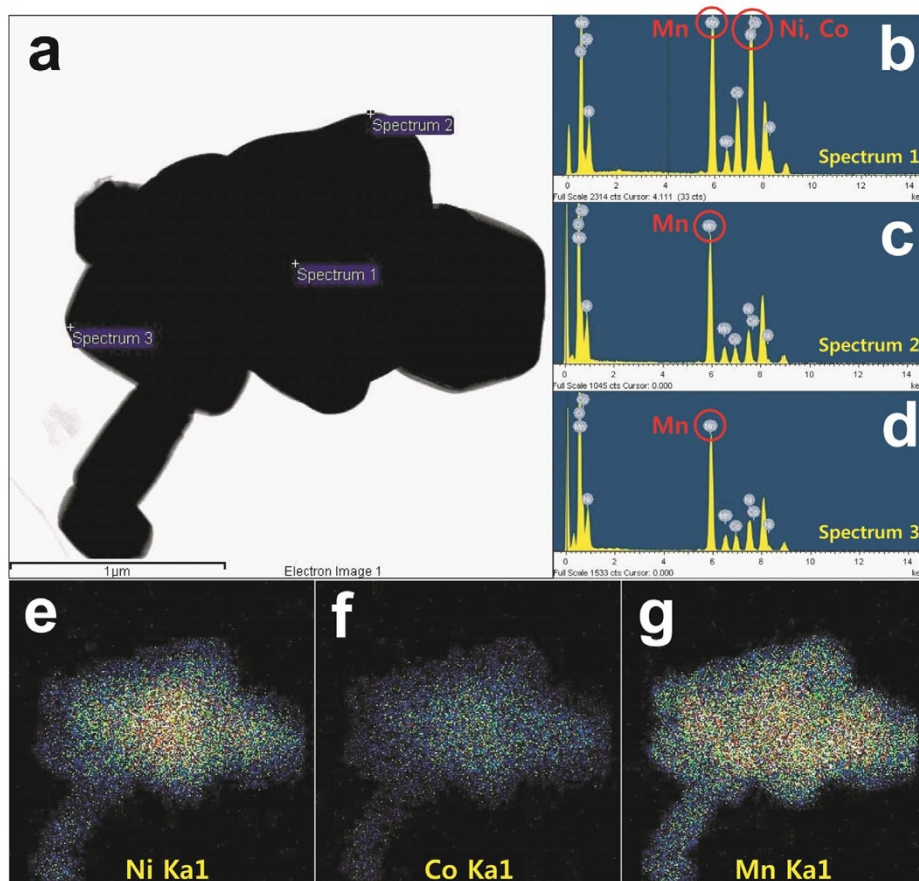


Figure 3 | EDS point elemental analysis and elemental mapping for $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (1000°C). (a) electron image, (b) spectrum 1 (bulk), (c) spectrum 2 (surface), (d) spectrum 3 (surface), and elemental maps for (e) Ni, (f) Co, and (g) Mn.

The cells containing $0.3\text{Li}_2\text{MnO}_3 \cdot 0.7\text{LiMO}_2$ and $0.7\text{Li}_2\text{MnO}_3 \cdot 0.3\text{LiMO}_2$ exhibited specific capacities of 207.2 and $206.3 \text{ mA h g}^{-1}$, respectively. In addition, the discharge capacity of the cell containing $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMO}_2$ was higher at $228.9 \text{ mA h g}^{-1}$. The 1st and 2nd cycle charge and discharge capacities and efficiencies of the various $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ nanocomposite samples, as well as those of Li_2MnO_3 and $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$, are listed in Table S2 (Supplementary Information). The nanocomposite cathode materials prepared at 700 and 1000°C exhibited higher 1st cycle efficiencies than those of Li_2MnO_3 and LiMO_2 . After Li_2MnO_3 activation resulting from charging during the 1st cycle, the nanocomposite samples synthesized at 700 and 1000°C exhibited efficiencies greater than 90% during the 2nd cycle. The rate capabilities of the coin cells containing the $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ samples heat treated at 1000°C are plotted in Figure 6 (a); the values correspond to different test current rates. The cell containing $0.3\text{Li}_2\text{MnO}_3 \cdot 0.7\text{LiMO}_2$ exhibited initial discharge capacities as high as 207.2 , 188.4 , 171.2 , and $147.4 \text{ mA h g}^{-1}$ for test current rates of 10 ($1/20 \text{ C}$), 20 ($1/10 \text{ C}$), 50 ($1/5 \text{ C}$), and 100 ($1/2 \text{ C}$) mA g^{-1} , respectively. The cell containing $0.7\text{Li}_2\text{MnO}_3 \cdot 0.3\text{LiMO}_2$ exhibited initial discharge capacities of as high as 217.5 , 197.1 , 175.8 , and $152.6 \text{ mA h g}^{-1}$ at current rates of 10, 20, 50, and 100 mA g^{-1} , respectively.

Finally, the cell containing $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMO}_2$ exhibited initial discharge capacities as high as 237.5 , 219.6 , 198.1 , and $174.3 \text{ mA h g}^{-1}$ at the current rates of 10, 20, 50, and 100 mA g^{-1} , respectively. Thus, when the $\text{Li}_2\text{MnO}_3/\text{LiMO}_2$ mole ratio was $0.5:0.5$, the nanocomposite sample heat treated at 1000°C exhibited specific capacities higher than those of the other materials. The cycling characteristics of the cell based on the $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMO}_2$ sample heat treated at 1000°C are shown in Figure 6 (b); the values correspond to 20 cycles,

initial discharge capacities of 2.0 to 4.8 V, and a current rate of 20 mA g^{-1} ($1/10 \text{ C}$). As mentioned earlier, for the heat treatment temperature of 1000°C , it was expected that the size of the Li_2MnO_3 particles would increase significantly. In the synthesized core/shell-like nanostructures, Li_2MnO_3 acts as a coating material. The high-temperature treatment results in the formation of an integrated structure at the interface between the surface layer and the bulk material, which improves the cycling performance. For the sample heat treated at 1000°C , the Li_2MnO_3 outer layer adheres more strongly to the LiMO_2 bulk material and increases the stability of the nanoparticles. Because the specific capacity of Li_2MnO_3 decreases significantly with the temperature⁷, it can be concluded that the role played by the Li_2MnO_3 layer in stabilization is of critical importance. In contrast to the results reported by West *et al.*, who prepared Li_2MnO_3 and LiMO_2 separately using ball-milling and subsequent annealing (the processes had to be repeated twice, once for each material), the synthesis technique employed in the current study is simple and robust.

Discussion

In the synthesized nanocomposites, the Li_2MnO_3 component plays a greater role in stabilization because of the core/shell-like structure. The Li_2MnO_3 coating, which is present on the outer surfaces of the LiMO_2 cores, effectively stabilizes the cores comprising the bulk, resulting in improved electrochemical performances. This result is consistent with those of our previous studies^{21,22}. In addition to the cost of the synthesis technique employed for fabricating the electrode materials, as well as their initial capacities, rate capabilities, and cyclability, the thermal stability of the materials is another important factor for determining their commercial potential.

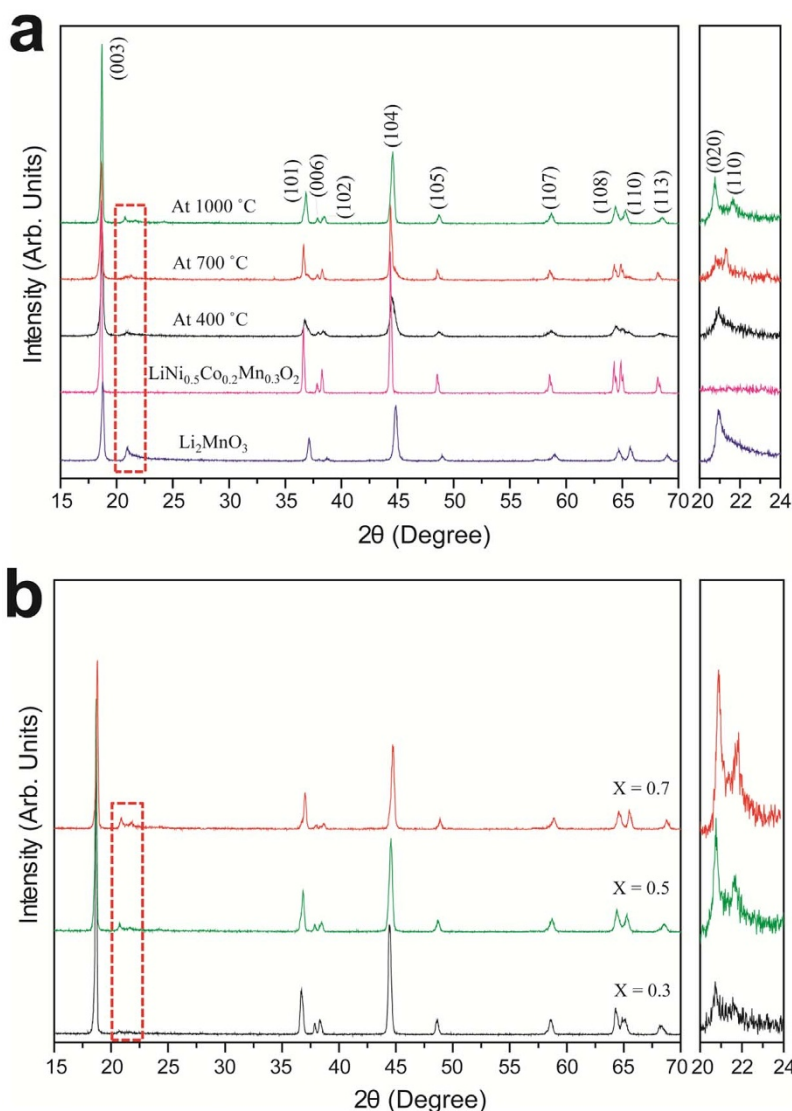


Figure 4 | X-ray diffraction patterns of (a) $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ heat treated at 400, 700, and 1000°C (temperature variation), (b) $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ for $x = 0.3, 0.5,$ or 0.7 and heat treated at 1000°C (mole ratio variation).

The thermal stabilities of the $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMO}_2$ and $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ nanocomposites after they had been charged to 4.8 V were compared using differential scanning calorimetry (DSC) in a manner similar to that employed by Park *et al.*³⁶ For $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMO}_2$, the sample heat treated at 1000°C was selected because this sample had exhibited the best electrochemical performance. It can be observed from Figure 7 that the 4.8-V-charged $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ sample, whose particles did not have an outer Li_2MnO_3 coating, exhibited exothermic peaks corresponding to a two-step dissociation reaction. The temperatures corresponding to the 1st and 2nd exothermic peaks were 228.68 and 268.52°C , respectively; this result indicated that the dissociation of the material occurred through a two-step process³⁶. The total heat generated during the dissociation reaction was 461.5 J g^{-1} . However, only one exothermic peak was observed for the 4.8-V-charged $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMO}_2$ sample, indicating a one-step dissociation reaction. The peak was positioned at 248.30°C , and the total heat generated during the reaction was 239.2 J g^{-1} , which was lower than that for the bare sample. This result is very similar to those reported by other research groups, who have reported that AlF_3 or FePO_4 -coated LiMO_2 can stabilize the cathode surface and start to decompose only at high temperatures^{37,38}. Thus, in addition to exhibiting a higher capacity and improved cyclability (see Figs. 5 and 6), the core/

shell-like structured $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMO}_2$ sample also exhibited a reduction in the total heat generated and an increase in the dissociation temperature. Therefore, the fact that a greater number of Ni ions were present in the bulk of the electrode resulted in a higher capacity, while the Li_2MnO_3 shell improved the overall thermal stability of the Li_2MnO_3 -coated materials³⁷. The results of the time-resolved (TR) XRD analyses were in good agreement with the DSC results and provided additional information regarding the changes induced in the various nanocomposite samples after heating. Figures 8 (a) and (b) present the TR-XRD patterns of the $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ and $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMO}_2$ samples heat treated at 1000°C in the absence of an electrolyte; the samples were subsequently heated from room temperature to 600°C and then charged to 4.8 V. The initial TR-XRD data were collected at 38°C because the X-ray generator required more than a few minutes to initialize.

We had previously observed that materials with a layered structure undergo phase transformations in the following sequence as the temperature is increased: $R\text{-}3m \rightarrow Fd3m \rightarrow Fm3m$. The amount of oxygen released during the phase transformation from $Fd3m$ to $Fm3m$ is higher than that generated during the transformation from $R\text{-}3m$ to $Fd3m$ ^{29,30}. Thus, it is important to suppress the phase transformation from $Fd3m$ to $Fm3m$ if one wishes to improve the thermal

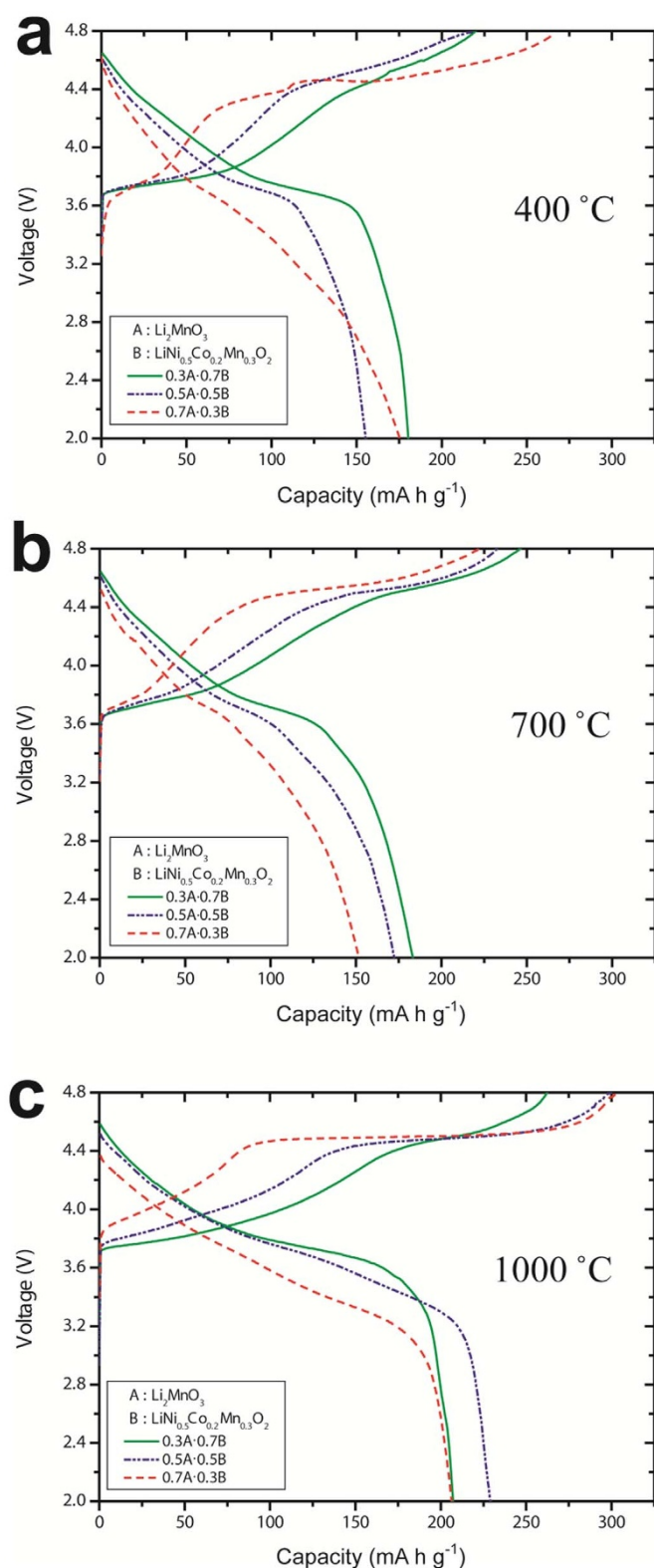


Figure 5 | 1st cycle charge and discharge curves at 10 mA g⁻¹ (1/20 C) between 2.0 and 4.8 V: (a) 400 °C, (b) 700 °C, and (c) 1000 °C.

stability of such cathode materials. It can be observed from Figure 8 (a) that, at 38 °C, the LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ sample exhibits a structure belonging to the *R-3m* space group^{35,39} (*i.e.*, it has a rhombohedral structure). The change in the structure of the sample commences at approximately 227 °C; this value agrees well with the DSC data, which is presented in Figure 7 (a). Over the temperature range of 200 to

260 °C, which also corresponds to the 1st exothermic peak, the (108) and (110) peaks corresponding to the layered structure merged into a (440) peak, which could be indexed to a disordered spinel structure with the space group *Fd3m*^{29-31,40}. This result indicated that cation mixing increased over this temperature range⁴⁰. With respect to the 2nd exothermic peak (corresponding to a temperature range extending from approximately 240 to 300 °C), the TR-XRD data suggested that the nanocomposite material underwent a phase transformation, with its structure changing from that corresponding to a disordered spinel to that of a rock salt. The (400) and (440) peaks corresponding to the disordered spinel structure disappeared and new (200) and (220) peaks appeared, which could be indexed to the rock salt structure (space group: *Fm3m*). This rock salt structure was preserved at temperatures as high as 600 °C. As observed in Figure 8 (b), the 0.5Li₂MnO₃·0.5LiMO₂ sample exhibited a higher thermal stability than that of the LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ sample.

At 38 °C, the 0.5Li₂MnO₃·0.5LiMO₂ sample was observed as having the same structure (*i.e.*, one corresponding to the *R-3m* space group) as the LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ sample. However, its structure started to change at approximately 244 °C, a temperature much higher than that for the LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ sample (~227 °C). This value agreed well with the DSC data, which is presented in Figure 7 (b). Further, this temperature is higher than all the previously reported values, which are 223 °C for Li_{0.33}Ni_{0.5}Co_{0.2}Mn_{0.3}O₂⁴⁰ and 236 °C for Li_{0.33}Ni_{1/3}Co_{1/3}Mn_{1/3}O₂⁴¹. It was evident that the layered structure dissociated based on the gradual decrease in the intensities of the (105), (107), and (113) peaks starting at approximately 244 °C. The appearance of the (311), (400), and (440) peaks confirmed the formation of a new phase starting at 339 °C. The formation of this new phase occurred over the range of 339 to 465 °C and was accompanied by the appearance of peaks corresponding to the LiM₂O₄-type spinel structure. Over the temperature range of 339 to 465 °C, in addition to the peaks corresponding to the layered structure, the spinel structure coexisted over this temperature range. These results indicate that the core/shell-like structure of the nanocomposite 0.5Li₂MnO₃·0.5LiMO₂ not only retarded the transformation of its structure to the spinel structure at high temperatures but also slowed down its dissociation, increasing its thermal stability. However, in contrast to the observations for LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂, for 0.5Li₂MnO₃·0.5LiMO₂, another change in structure, that into a Mn₃O₄-type spinel structure, was also observed. At approximately 490 °C, peaks attributed to Mn₃O₄ began to appear (these peaks are marked with an asterisk). It is highly likely that this Mn₃O₄-like phase was formed by the dissociation of the Li₂MnO₃ shells. At the end of the heating stage, that is, at 600 °C, 0.5Li₂MnO₃·0.5LiMO₂ exhibited a higher thermal stability than LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂.

To conclude, we mechanochemically synthesized xLi₂MnO₃·(1-x)LiMO₂ cathode materials with a core/shell-like nanostructure using a simple solid-state reaction. The synthesis process employed is an easy, one-step, and low-cost method and results in significant improvements in the electrochemical performance of the LiMO₂ component due to the presence of the stabilizing Li₂MnO₃ shell-like layer on the surfaces of the LiMO₂ particles. The presence of this Li₂MnO₃ layer was confirmed using TEM, energy-dispersive spectrometry, and elemental mapping. Furthermore, the presence of Li₂MnO₃ and LiMO₂ on the surfaces and in the bulk, respectively, was also confirmed based on the FFT patterns of the high-resolution transmission electron microscopy (HRTEM) images of the synthesized samples. Of the various samples synthesized, the 0.5Li₂MnO₃·0.5LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ sample synthesized through a heat treatment at 1000 °C exhibited the highest discharge capacity as well as the highest cyclability. The results of the TR-XRD and DSC analyses showed that the synthesized nanocomposite materials exhibited

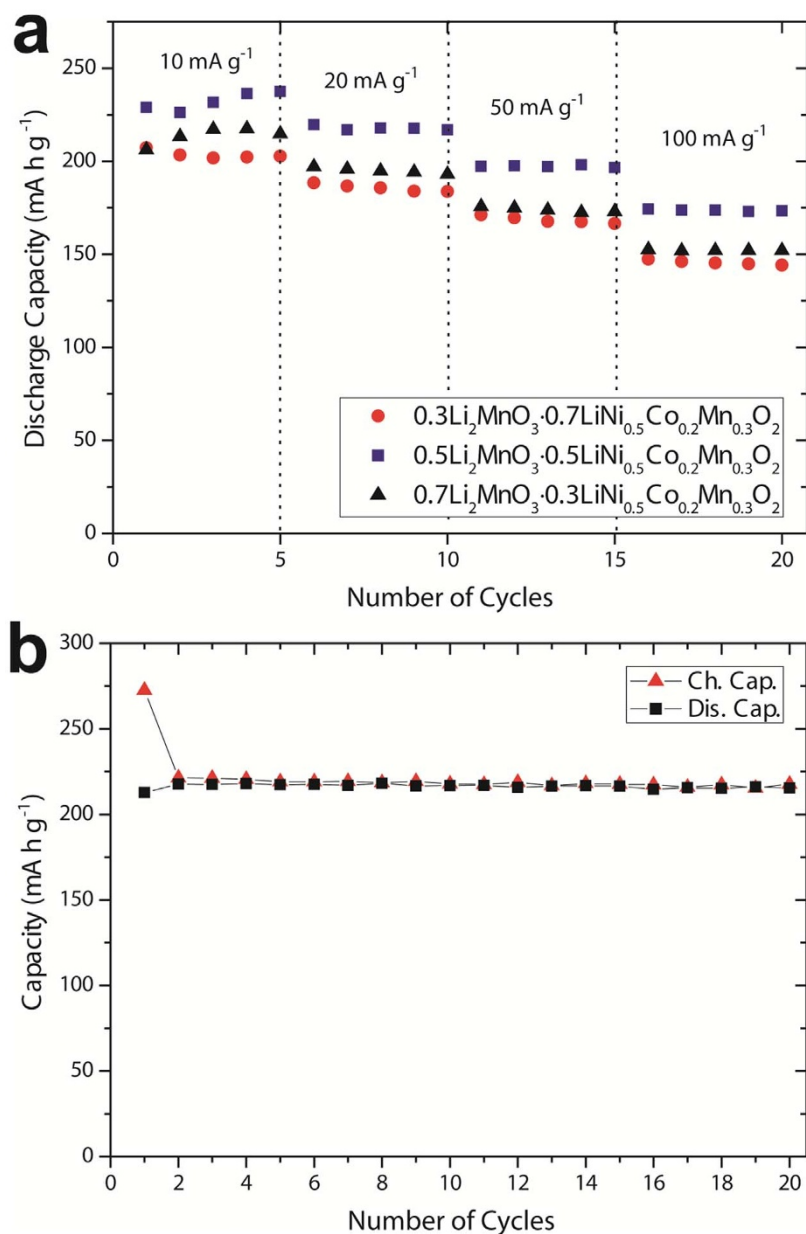


Figure 6 | (a) Discharge capacities at different C-rates at 1000 °C, (b) cycling performance at 20 mA g⁻¹ (1/10 C) between 2.0 and 4.8 V of the 0.5Li₂MnO₃·0.5LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ nanocomposite sample heat treated at 1000 °C.

higher thermal stabilities. We propose that the Li₂MnO₃ coating on the surfaces of the LiMO₂ particles effectively stabilized the electrodes consisting of the Ni-rich bulk material.

Methods

Material synthesis. Stoichiometric amounts of LiOH·H₂O (≥98%, Aldrich) and MnCO₃·xH₂O (≥98%, Aldrich) were used to form the Li₂MnO₃ shells. The precursors were mixed with LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ (~10 μm, L&F Materials Co., Ltd., Korea) using a planetary mill (Pulverisette 5, Fritsch) in the presence of acetone at 350 rpm for 3 h; the ball-to-powder weight ratio was 20:1^{16–22}. Li₂MnO₃-stabilized LiMO₂ core/shell-like nanocomposite materials with compositional ratios of 0.3Li₂MnO₃·0.7LiMO₂, 0.5Li₂MnO₃·0.5LiMO₂, and 0.7Li₂MnO₃·0.3LiMO₂ were prepared in this study. The heat treatment was performed at 400, 700, or 1000 °C in a box furnace; the heating time was 32 h for the treatment at 400 °C and 10 h for the treatments at 700 and 1000 °C.

Material characterization. FESEM (NOVA NanoSEM200, FEI) was used to characterize the morphologies of the prepared materials. Enhanced images were obtained using TEM (CM30, Philips). A TEM system (JEM2100F, JEOL) with an EDS attachment and elemental mapping functionality (Inca Energy, Oxford) was used to investigate the elements present on the surfaces and in the bulk of the synthesized cathode materials. HRTEM (Tecnaï G2, FEI) was used to investigate the crystal

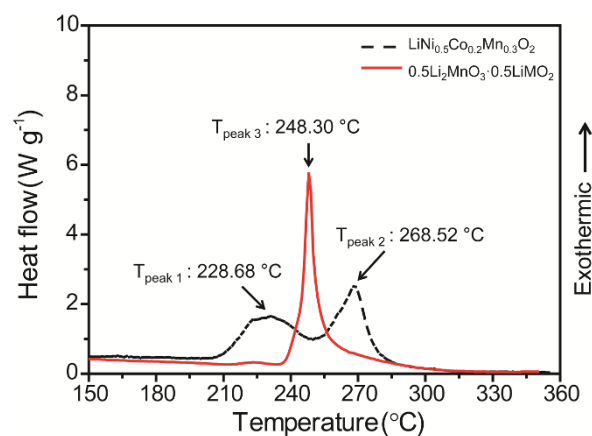


Figure 7 | DSC profiles for pristine LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ and the 0.5Li₂MnO₃·0.5LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ sample heat treated at 1000 °C after being charged to 4.8 V vs. Li/Li⁺.

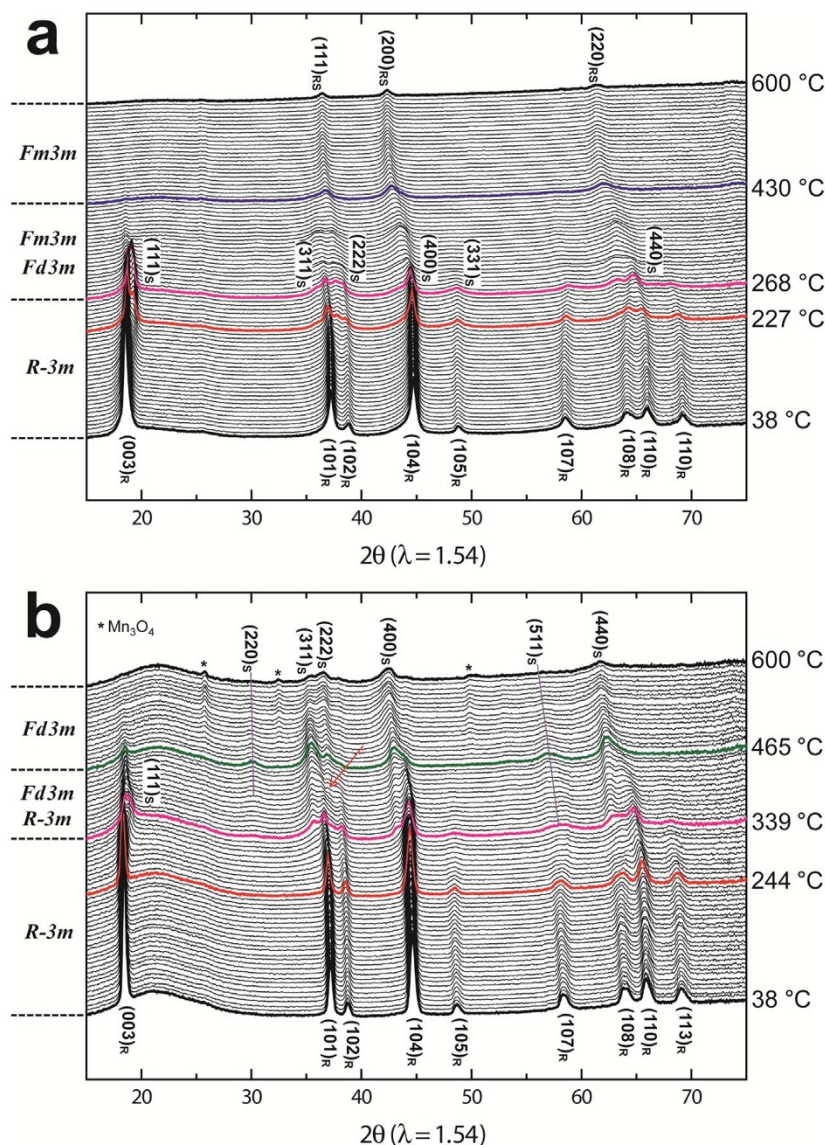


Figure 8 | TR-XRD patterns of the (a) $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ and (b) $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ samples heat treated at 1000°C (the temperature was raised to 600°C after being charged to 4.8 V vs. Li/Li^+).

structures of the materials based on their FFT patterns. XRD measurements were performed with a Rigaku X-ray diffractometer using monochromatic $\text{Cu-K}\alpha$ radiation (40 kV and 100 mA). A scan rate of 3°min^{-1} was selected to collect the diffraction data over 2θ values ranging from 15 to 70° .

Electrochemical measurements. For the electrochemical measurements, coin cells with the CR2032 configuration (Hoshen Corp., Japan) were used. The cells were assembled in a dry room using Li metal for the counter and reference electrodes; Celgard® 2400 was used as the separator. The cathode consisted of a mixture of the synthesized nanocomposite samples, Denka Black®, and polyvinylidene fluoride (PVDF) in 1-methyl-2-pyrrolidone at a weight ratio of 80 : 10 : 10. The electrolyte used was a 1 M solution of LiPF_6 in an EC : DMC : DEC mixture (1 : 1 : 1 by volume). The cells were stored for 24 h before being subjected to galvanostatic charge-discharge cycling tests. We used a multichannel battery tester (Model 4000, Maccor Inc.) in the constant current/constant voltage (CCCV) mode over potentials ranging from 2.0 to 4.8 V; the test current rate was 10 mA g^{-1} (1/20 C) unless noted otherwise.

Thermal stability analyses. To determine the thermal stabilities of the charged $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMO}_2$ (1000°C) electrodes, TR-XRD and DSC analyses were employed. The TR-XRD analyses were performed using an X-ray diffractometry system (R-Axis IV++, Rigaku) at the Korea Institute of Science and Technology (KIST) and at the 1D beamline at Pohang Light Source. Before the analyses, the electrodes were charged fully to 4.8 V. Then, the surfaces of the electrodes were scratched. The obtained powder samples were sealed completely and were mounted on the thermal stage of the TR-XRD system. $\text{Mo-K}\alpha$ radiation with a wavelength of 0.7107 \AA was used for the X-ray diffractometry system at KIST. To allow for a ready comparison of the obtained results with those reported in the

literature, the 2θ values over which the analyses were performed have been converted into values corresponding to $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). Using the DSC system (Auto Q20, TA Instruments), the thermal stabilities of the electrode materials $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMO}_2$ (1000°C) and $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ were then analyzed, and the capillaries were heated to 600°C at a heating rate of 3°C min^{-1} .

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Acknowledgments

This work was supported by the National Research Foundation of Korea Grant funded by the Korean Government (MEST) (NRF-2011-C1AAA001-0030538). This work was also supported by the KIST Institutional Program (Project No. 2E24663).

Author contributions

J.K.N., S.K., D.B., B.W.C. and K.Y.C. conceived, planned and designed the experiments. J.K.N. and S.K. synthesized the cathode materials and performed TEM, SEM, DSC and electrochemical tests. H.K. performed XRD analysis. W. Chang and W. Choi contributed to discussion TEM and DSC results. J.K.N., S.K. and K.Y.C. wrote the main manuscript. B.W.C. and K.Y.C. supervised the whole processes. All authors reviewed the manuscript.

Additional information

Supplementary information accompanies this paper at <http://www.nature.com/scientificreports>

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Noh, J.-K. *et al.* Mechanochemical Synthesis of Li_2MnO_3 Shell/ LiMO_2 ($\text{M} = \text{Ni, Co, Mn}$) Core-Structured Nanocomposites for Lithium-Ion Batteries. *Sci. Rep.* **4**, 4847; DOI:10.1038/srep04847 (2014).



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