Recently, Li-ion batteries with a high rate capability have received much attention from researchers due to their uses in power tools and hybrid electric vehicles. To fulfill these usages, among the various cathode materials, LiMn$_2$O$_4$ spinel has received much attention due to its good thermal stability and fast Li- ion diffusivity. However, dissolution of Mn$^{3+}$ from the Li$_{x}$Mn$_{2-x}$O$_4$ spinel structure leads to the destruction of the structure initiating at the electrode and electrolyte interfaces, resulting in rapid capacity fade. To improve this structural instability, substitution of transition metals (M = transition metals) into the Mn sites in Li$_{x}$Mn$_{2-x}$O$_4$ has been investigated intensively. Among the transition metals, Li$_{1-x}$Mn$_{1+x}$O$_4$ spinel exhibited an additional $-4.7 \, \text{V}$ plateau due to the presence of a Ni$^{3+}$/Ni$^{2+}$ redox pair, thus delivering $>100 \, \text{mAh/g}$ reversible capacity.

To meet the rate characteristics of the batteries, although cell design is an important factor that affects rate capability (power), the most essential factor that determines the rate is the electrode material. The purpose of these materials is to achieve a decrease in the diffusion length of the Li ion in the electrode particle, thus decreasing the kinetic barrier and in turn reducing the polarization factor at higher C rates. One means of achieving high rate capability is to manipulate the particle morphology into mesoporous nanowires, coating the materials with high electronic conducting materials. However, these bulky nanoparticles lead to a decreased energy density (Wh/cm$^3$) due to the much lower electrode density as the nanoparticles require higher amounts of binder and conducting agent compared to the bulk particles. In consequence, the best approach to improve the rate capability without losing the electrode density is to use clustered nanoparticles with a bulk size of $\approx 5 \, \mu$m.

In this study, the synthesis and electrochemical properties of nanoparticle-nanorod core–shell Li$_{0.5}$Mn$_{1.5}$O$_4$ spinel particles with a high energy density and high power were investigated using a hollow nanowire MnO$_2$ cluster precursor. The core–shell showed a reversible capacity of 121 mAh/g and a capacity retention ratio of 83% even at a cycling rate of 7C. Moreover, its power density was improved by 52% compared to analogous nanoparticles prepared by a sol–gel method.

Experimental

To prepare hollow MnO$_2$ nanorod clustered precursors, a 1:1 molar ratio of MnSO$_4$·5H$_2$O and (NH$_4$)$_2$SO$_4$ was dissolved in distilled water and transferred into the autoclave and then reacted for 12 h at 120°C. After the reaction, the mixture was rinsed five times with distilled water and was vacuum-dried at 120°C. An as-prepared MnO$_2$ template was used to prepare Li$_{0.5}$Mn$_{1.5}$O$_4$, and appropriate amounts of LiC$_2$H$_3$O$_2$·H$_2$O and Ni(NO$_3$)$_2$·6H$_2$O were completely dissolved in distilled water and mixed with MnO$_2$ in a molar ratio of 1:0.5:1.5 [LiC$_2$H$_3$O$_2$·H$_2$O:Ni(NO$_3$)$_2$·6H$_2$O:MnO$_2$]. After drying it in an oven, the product was ground using mortar and pestle, followed by firing at 400 and 700°C for 2 and 8 h, respectively. For comparison, the cathode powder was obtained using the sol–gel process, LiC$_2$H$_3$O$_2$·H$_2$O was first dissolved in distilled water, and then MnC$_2$H$_3$O$_2$·4H$_2$O and Ni(NO$_3$)$_2$·6H$_2$O were continuously dissolved into it with a molar ratio of 1:1:3:0.5 (Li:Mn:Ni). Finally, poly(vinylpyrroliodene) as a chelating agent was mixed together, and NH$_3$OH was added to adjust pH 8.5 to 9.0. The solution was dried at 90°C and fired at 850°C for 10 h.

To test the cycle-life performance of each cathode material, a slurry was prepared by mixing the active material, Super P carbon black, and a poly(vinylidene fluoride) binder with weight ratios of 60:20:20 in N-methyl-2-pyrrolidene in a homogenizer (Youjung Corp., Korea). Electrode density was measured under porosities of 20–23%. The pore volume of the electrodes was obtained with a mercury porosimeter (Micromeritics Pore Sizer S920). To adjust for such volume fractions, the electrode composition was adjusted to the electrode composition described above, and the roll-pressing frequency was varied. A coin-type half-cell (2016 size) contained a test electrode, a lithium-metal counter and reference electrodes, a 15 \mu m thick microporous polyethylene separator, and an electrolyte solution of 1 M LiPF$_6$ in ethylene carbonate/dimethyl carbonate (1:1 vol %) (LG Chem., Korea). Cell tests were carried out at various C rates under 21 and 60°C.

Powder X-ray diffraction (XRD, D/MAX-2200V, Rigaku) measurements using Cu Kα radiation were employed to identify the crystalline phase of the synthesized materials. A field-emission scanning electron microscope (NanoSem 230) and a transmission electron microscope (TEM) (JEM-2100) were used to assess the morphology of the obtained samples. Cross-section images were obtained with a focused ion beam (Quanta 3D FEG) using a Ga source. Electrochemical impedance spectroscopy (EIS) data were collected before and after 20 cycles at a rate of 7C (after discharging to 3.5 V) with an ac amplitude of 10 mV in the frequency range of 0.5 MHz–10 mHz by an Ivium impedance analyzer. The specific surface areas of the samples were measured using N$_2$ physisorption at –196°C by the Brunauer–Emmett–Teller (BET) method using an automatic surface analyzer (Quantachrome Autosorbs-1).

Results and Discussion

The XRD pattern of the MnO$_2$ precursor indicates the formation of the $\alpha$-MnO$_2$ tetragonal phase with a minor $\gamma$-MnO$_2$ phase (Fig.
Its XRD pattern exhibits the formation of the cubic spinel \( Fd\bar{3}m \) phase \([\text{the lattice constant was } 8.170(6) \text{ Å}]\) and a minor NiO impurity phase. Figure 2a shows scanning electron microscopy (SEM) images of MnO, which consist of nanowire clustered particles with a wire length of \( \sim 3 \text{ μm} \). In particular, the cross-sectioned image of the powder (Fig. 2b) shows a hollow urchin-like morphology with three different regions of hollow, porous, and dense. Figures 3a and b show SEM images of \( \text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) spinels obtained using a MnO precursor after annealing. The hollow region of the precursor was filled with \( \sim 100 \text{ nm} \) nanoparticles that are directly adjacent to the nanorod clusters (its morphology is quite similar to a sunflower). The high resolution TEM image (Fig. 3d) clearly shows the presence of the lattice fringe of the (111) plane of the spinel, corresponding to a d-spacing value of 4.7 Å; the inset of the selected area diffraction pattern (Fig. 2f) of the spinel particle confirms the single-crystalline phase.

Overall, the core–shell spinel particle size ranges from 7 to 10 μm with a spherical-like morphology (Fig. 4a), and even after electrode pressing, the core–shell morphology appears to be maintained (Fig. 4b). For spinel particles prepared by the sol–gel method, <1 μm particles resulted (see Fig. 5). The BET surface area of the hollow spinel particles prepared by the MnO precursor was 17 m²/g, whereas that prepared by sol–gel was 9 m²/g. The BET surface area of MnO precursors was 45 m²/g.

Figure 6 shows voltage profiles of the spinels obtained from the MnO template and a sol–gel method as a function of the cycle number with C rates increasing from 0.1C to 7C (identical charge and discharge rates were used). Figure 7 shows the discharge capacity of the spinels obtained from the MnO precursor and those of the hollow MnO precursor are 36 and 25%, respectively, which correspond to 67 and 75% coulombic efficiencies, respectively.

0.1C and 7C, respectively, with capacity retention at 7C of 83%. Furthermore, there is no capacity fade under continuous cycles at 7C up to 20 cycles (see Fig. 7). The spinel cathode prepared by the sol–gel method exhibits a similar trend to the core–shell particles, and its capacities were 99 and 80 mAh/g, respectively, at the two aforementioned rates. The irreversible capacity ratios of the \( \text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) electrode prepared by the sol–gel method and those of the hollow MnO precursor are 36 and 25%, respectively, which correspond to 67 and 75% coulombic efficiencies, respectively.
A sol–gel method was prepared by obtaining from the sol–gel method were electrode thickness and a pure loading amount of the spinel particles core–shell particles had a density of previous studies in which the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ spinel particle size method. However, the uncoated cathode showed rapid capacity fading at a rate of 7C of <50%.

A spinel nanoparticle prepared by poly(ethylene glycol) as a chelating agent showed a particle size of 79 nm that had a reversible capacity of ~98 mAh/g upon rate cycling at 8C. Compared to previous studies in which the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ spinel particle size was <1 μm (the particle size is similar to our sample prepared by a sol–gel method), the electrode density is expected to be much smaller than the core–shell spinels. The spinel particles prepared by a sol–gel method had an electrode density of ~1.9 g/cm$^3$, while the core–shell particles had a density of ~2.9 g/cm$^3$. An average electrode thickness and a pure loading amount of the spinel particles obtained from the sol–gel method were 20 μm and 7.2 mg, respectively (the electrode dimension was 1.9 cm$^2$). However, those from MnO$_2$ precursors were 15 μm and 8.3 mg, respectively. Porosity ranged between 20 and 23%. When these were converted to the volumetric energy density (the volumetric energy density was calculated from just the active material), the core–shell particles showed 1.6 Wh/cm$^3$, while those prepared by the sol–gel method showed 0.9 Wh/cm$^3$. Accordingly, the core–shell spinels demonstrated a 78% enhanced electrode density value compared to the analogy prepared by the sol–gel method. After 7C rate cycling, the core–shell showed a value of 1.3 Wh/cm$^3$, whereas nanoparticles prepared by the sol–gel method showed a value of only 0.7 Wh/cm$^3$ (Fig. 7b).

All Ni-containing spinel cathodes show voltage plateaus at ~4.7 V associated with the Ni$^{2+}$ to Ni$^{4+}$ redox reaction. In the ideal LiNi$_{0.5}$Mn$_{1.5}$O$_4$ structure, the oxidation state of manganese is fixed at +4. As the calcination temperature is increased to 700°C, however, an oxygen deficiency appears in LiNi$_{0.5}$Mn$_{1.5}$O$_4$, which partly lowers the manganese oxidation state from Mn$^{4+}$ to Mn$^{3+}$. This implies that a small portion of the manganese remains as Mn$^{3+}$ for the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cathode. Figure 8 shows differential capacity curves of the first cycle at a rate of 0.1C in spinel powder prepared by the sol–gel method. The two dominant peaks at 4.67 and 4.73 V are due to the Ni$^{2+}$ to Ni$^{4+}$ redox reactions. These two peaks are associated with oxygen-deficient LiNi$_{0.5}$Mn$_{1.5}$O$_{4-x}$ with a space group of Fd$ar{3}$m (face-centered cubic). However, the core–shell spinel nanoclusters show an additional peak at 4.7 V, which is associated with the presence of minor LiNi$_{0.5}$Mn$_{1.5}$O$_4$ with a space group of P4$_1$32 (primitive simple cubic).

Compared to LiNi$_{0.5}$Mn$_{1.5}$O$_{4-x}$, which has a one-step phase transition between two cubic phases, LiNi$_{0.5}$Mn$_{1.5}$O$_4$ with two-step phase transitions between three cubic phases should have shown greatly deteriorated capacity retention at higher C rates due to the larger degree of strain generated by the high rate cycling. However, the result in this study showed no capacity fade at the 7C rate, indicating that a nanostructure with a higher surface area may accommodate the strains during phase transitions. In addition, the differential capacity profiles of both spinel electrodes clearly exhibit 4 V plateaus. This plateau is related to the redox reactions between
Mn$^{3+}$ and Mn$^{4+}$. With increasing nickel content in LiNi$_x$Mn$_{2-x}$O$_4$, the intensity of the 4.1 V plateau gradually decreases conversely due to the decreased amount of Mn$^{3+}$. Because both spinel samples contain an impurity of NiO, the presence of the plateau at 4.1 V is reasonable.

To see any interfacial impedance changes between the two samples, EIS data were collected before and after 20 cycles at a rate of 7C after discharging to 3.5 V, as shown in Fig. 9. An equivalent circuit was used to interpret the impedance results inset of Fig. 9. $R_o$ is the ohmic resistance of the cell, and its value is 10$^3$ in both electrodes. $R_{ct}$ is the charge-transfer resistance at the electrode and electrolyte, and $R_{sf}$ is the surface film resistance, which correspond to a semicircle at high frequency. Before cycling, $R_{ct}$ and $R_{sf}$ in the spinel electrode obtained from the MnO$_2$ precursor are quite smaller than those obtained from the sol–gel method. After cycling, the resistance of the cathode electrode obtained from the sol–gel method is 580 $\Omega$, while that obtained from the MnO$_2$ precursor is 429 $\Omega$. This impedance spectra result shows that a nanostructured core–shell spinel lends faster Li-ion and electron transport at the interfaces between the electrolytes and the electrode.

Finally, the preliminary cycling test results of the core–shell spinel cathode at 60°C are presented in Fig. 10. The capacity decay of the core–shell spinel cathode at 60°C are presented in Fig. 10. The capacity decay of the core–shell spinel cathode at 60°C is not severe compared to that of the LiMn$_2$O$_4$-type spinel because most redox reactions come from Ni$^{2+}$ and Ni$^{4+}$. No dissolution of Mn and Ni ions in the electrolytes obtained from the cells after cycling at room temperature was observed based upon inductively coupled plasma–mass spectroscopy analysis. However, the amount of Mn ion dissolution at 60°C was 30 ppm, and this amount did not result in fast capacity fade in LiMn$_2$O$_4$-type spinels (dissolution of Ni ions was not detected at 60°C). Hence, it is expected that accelerated electrolyte oxidations at 5 V might lead to capacity fade.
Conclusions

In summary, nanoparticle–nanorod core–shell LiNi$_{0.5}$Mn$_{1.5}$O$_4$ spinel cathodes for Li-ion batteries were successfully prepared using a MnO$_2$ precursor with identical morphology. The cathodes demonstrated a reversible capacity of 100 mAh/g at a rate of 7C and no capacity fading. In addition, the energy density of the core–shell particles was 1.56 Wh/cm$^3$, which was an improvement of 56% over nanoparticles prepared by a sol–gel method.

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