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COMMUNICATION

Novel Preparation of Core-shell Electrode Materials via Evaporation-Induced Self-Assembly of Nanoparticles for Advanced Li-Ion Batteries

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We report, for the first time, simple and novel synthesis of a Li-rich layered-spinel core-shell heterostructure (L@S core-shell) via evaporation-induced self-assembly (EISA) of Ni-doped Li$_{1,2}$Mn$_{0.8}$Ni$_{0.54}$O$_{2}$ nanoparticles (Li$_{1,2}$Mn$_{0.8}$Ni$_{0.54}$O$_{2}$) onto the surface of layered Li$_{1-x}$Mn$_{4,2}$Ni$_{6.13}$Co$_{0,13}$O$_{2}$ (LMNCO) without using any surfactant during the coating process. The resultant L@S core-shell as cathode in lithium ion batteries demonstrates significantly improved specific capacity, cycling performance and rate capability compared to pristine LMNCO.

The main drawbacks of commercial LiCoO$_2$ cathode material such as limited delivery capacity, toxicity as well as high cost have hindered its application in plug-in hybrid electric vehicles (PHEV) or electric vehicles (EV). In this regard, Li-rich layered oxides have attracted intensive attention due to its high specific capacity of ~250 mAh/g when cycled over a broad voltage range between 2.0 V and 4.8 V versus Li/Li$^+$ and other advantages such as environmental benignity, safety and relatively low cost. Among Li-rich layered oxides, Li$_{1-x}$Mn$_x$Ni$_{2}$O$_{2}$ (hereafter marked as LMNCO), has been reported to have an unsatisfactory cycling stability at room temperature. In addition, its 3D Li$^+$ ion diffusion pathways ensure rapid cycling stability and rate capability of Li-rich layered oxide cathode. However, preparation of core-shell heterostructures reported in literature required complex procedures and precise control of reaction conditions such as pH and concentration of the solutions, which poses challenges for large-scale production for high-energy high-power LIBs. Therefore, it can be expected to be a promising coating material to replace spinel Li$_{1-x}$Mn$_x$O$_2$. Herein, we report a simple and facile one-pot preparation of L@S core-shell...
structure (Li-rich layered-spinel core-shell heterostructure) via evaporation-induced self-assembly (EISA) of ultrafine Li$_4$Mn$_{12}$Ni$_6$O$_{12}$ nanoparticles onto the surface of Li-rich layered Li[(Li$_2$Mn$_{13}$Ni$_{10.5}$Co$_{0.5}$)$_3$O$_{10}$]O$_2$ (LMNCO) without using any surfactant during the coating process. In this study, we also introduce a simple route to prepare ultrafine Li$_4$Mn$_{12}$Ni$_6$O$_{12}$ nanoparticles (5–20 nm) from the spinel Li$_4$Mn$_{12}$Ni$_6$O$_{12}$ bulk by the so-called sonofragmentation. Sonofragmentation is a well-known one-step process to directly produce nanoparticles from large-grained powders.\textsuperscript{27, 28} It has been reported that even intrinsically strong carbon nanotubes can be fragmented by sonication.\textsuperscript{29} As a result, the as-prepared L@S core-shell material demonstrates significantly improved specific capacity, cycling performance and rate capability for application as cathode in new-generation LIBs compared to pristine LMNCO. Due to the structural and functional versatility of nanoparticles, the synthetic approach reported in this work can be generalized to other materials to form novel core-shell structures, for the application in LIBs or other fields.

![Schematic illustration of facile preparation of L@S core-shell heterostructure.](Fig. 1).

Fig. 1 presents a schematic illustrating the facile synthesis procedure of L@S core-shell heterostructure via EISA, which is different from existing methods such as “dip and dry”\textsuperscript{23} or co-precipitation.\textsuperscript{24} Briefly, simple top-down preparation of spinel Li$_4$Mn$_{12}$Ni$_6$O$_{12}$ nanoparticles is introduced by applying ultrasonication to larger Li$_4$Mn$_{12}$Ni$_6$O$_{12}$ particles in ethanol for two hours. The large-sized Li$_4$Mn$_{12}$Ni$_6$O$_{12}$ particles are broken into smaller nanoparticles due to mechanical energy of ultrasonic wave. Afterwards, as described in the experimental part, the resultant suspension of Li$_4$Mn$_{12}$Ni$_6$O$_{12}$ ultrafine nanoparticles in ethanol are mixed with Li[(Li$_2$Mn$_{13}$Ni$_{10.5}$Co$_{0.5}$)$_3$O$_{10}$]O$_2$ suspension in ethanol, followed by continuously stirring at 80°C until the solvent is completely evaporated. In this step, ultrafine nanoparticles of Li$_4$Mn$_{12}$Ni$_6$O$_{12}$ tend to self-assemble on the surface of large-sized Li[(Li$_2$Mn$_{13}$Ni$_{10.5}$Co$_{0.5}$)$_3$O$_{10}$]O$_2$ particles in order to drastically reduce surface energy. Finally, after post-annealing at 500°C for 3 hours, L@S core-shell heterostructure is successfully obtained.

The as-prepared spinel Li$_4$Mn$_{12}$Ni$_6$O$_{12}$ particles are characterized by both scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM image of Li$_4$Mn$_{12}$Ni$_6$O$_{12}$ particles before sonofragmentation in Figure S1 shows numerous highly-crystalline nanoparticles with smooth surfaces. Figure 2a and b display TEM and high-resolution TEM (HRTEM) images of spinel Li$_4$Mn$_{12}$Ni$_6$O$_{12}$ powders before and after sonofragmentation, respectively. Figure 2a reveals the average size of primary Li$_4$Mn$_{12}$Ni$_6$O$_{12}$ particles is ~500 nm. Interestingly, it is found in Figure 2b and c that sonication can effectively reduce the particle size of Li$_4$Mn$_{12}$Ni$_6$O$_{12}$ powders into nanoscale (5–20 nm). The lattice fringes of each nanoparticle in Figure 2c are clearly observed. The zoom-in view of two regions in green rectangles in Figure 2b is displayed in Figure 2c and d. The lattice fringes of the Li$_4$Mn$_{12}$Ni$_6$O$_{12}$ surface coating can be readily indexed to the planes of (222), (400) and (220), respectively, suggesting the efficient preparation of ultrafine monoclinic nanoparticles by using the sonication treatment. This approach demonstrates a promising way to produce various inorganic nanoparticles and will find wide potential applications in many fields such as nano-scale electronic devices.

As revealed in the SEM image of pristine layered LMNCO in Figure 3a, the sample is composed of nanoparticles (~200 nm) with smooth surface, indicating their highly crystalline nature. It is noted that L@S core-shell sample looks very similar to LMNCO particles under SEM since the ultrathin coating cannot be detected by SEM. Therefore, TEM is used to examine morphology of the core-shell structure as shown in Figure 3c and d. Crystal structures of the as-prepared pristine layered LMNCO, spinel Li$_4$Mn$_{12}$Ni$_6$O$_{12}$ and L@S core-shell samples are further identified using powder X-ray diffraction (XRD) as shown in Figure 3b. The main peaks from the Li$_4$Mn$_{12}$Ni$_6$O$_{12}$ sample can be readily indexed to Li$_4$Mn$_{12}$O$_{19}$ with spinel phase of face-centered cubic structure (ICDD: 46-0810). A secondary phase of monocrinic Li$_3$MnO$_2$ with C2/m symmetry (ICDD: 84-1634) is evidenced as well, which might be ascribed to decomposition of Li$_4$Mn$_{12}$O$_{19}$ spinel phase after post-heating treatment at 900°C. The strong peaks from both pristine LMNCO and L@S core-shell heterostructure samples can be indexed as a layered α-\textit{NaFeO}_2 structural type with space group R3m symmetry and some weak superstructure reflections (marked as * in Figure 3b) can be ascribed to monocrinic phase Li$_3$MnO$_2$. Compared to XRD patterns of pristine LMNCO and spinel Li$_4$Mn$_{12}$Ni$_6$O$_{12}$, the XRD pattern from the L@S core-shell heterostructure sample combines with the patterns of both layered structure and cubic spinel structure with weak shoulder peaks assigned to the spinel coating as pointed by the arrows in Figure 3b.

High-resolution TEM (HRTEM) is used to examine L@S core-shell sample to further identify its surface structure. As observed in Figure 3c, the bulk layered structure of pristine LMNCO is well-preserved in the L@S core-shell structure, displaying lattice fringes with an interplanar spacing of ca. 4.73 Å. It can also be seen that a homogeneous outer layer is uniformly coated on the surface of layered LMNCO bulk. The enlarged view in Figure 3d reveals a crystalline outer layer with lattice fringes showing an interplanar spacing of ca. 1.38 Å, which do not belong to the layered structure but are consistent with the (531) plane of the cubic spinel (Fd-3m), confirming that the outer layer is the spinel coating. Therefore, it can be concluded that novel L@S core-shell structure can be facilely
synthesized via evaporation-induced self-assembly of nanoparticles, which opens new route for achieving various core-shell structures for different applications.

Fig. 3. (a) SEM image of pristine layered LMNCO, (b) Powder XRD patterns of spinel Li$_{0.5}$Mn$_{2.5}$Ni$_{0.5}$O$_{4}$, pristine layered LMNCO, L@S core-shell heterostructured powders, (c) HRTEM images of L@S core-shell sample and (d) zoom-in view of the surface of L@S core-shell in the green rectangle in (c).

Fig. 4a and b compares initial three charge/discharge curves of pristine LMNCO and L@S core-shell heterostructured cathodes when cycled between 2.0 and 4.99 V vs. Li/Li$^+$ at 25 mA/g (~0.1 C). It is found that L@S core-shell heterostructured cathode is capable of providing a discharge capacity of ~272 mAh/g after three cycles, which is higher than pristine LMNCO that delivers a discharge capacity of ~248 mAh/g. Compared to the discharge plot of pristine LMNCO, two newly-formed plateaus at around 4.7 and 2.7 V are observed for L@S core-shell heterostructured sample, which is associated with the coating of spinel Li$_{0.5}$Mn$_{2.5}$Ni$_{0.5}$O$_{4}$-125.26 Therefore, lithium ions can be intercalated into the spinel coating at around 4.7 and 2.7 V (marked by arrows) during the discharge process, thereby leading to higher discharge capacities of L@S core-shell structure.

In order to compare cycling stability of L@S core-shell and pristine LMNCO cathodes, both samples are cycled at 0.1 and 0.5 C in the wide high-voltage range between 2.0 – 4.99 V vs. Li/Li$^+$, respectively, as shown in Fig. 4c and d. As observed in Fig. 4c, pristine LMNCO delivers a maximal capacity of ~258 mAh/g and maintains ~233 mAh/g after 60 cycles at 0.1 C. In contrast, L@S core-shell cathode delivers a maximal capacity of ~286 mAh/g and retains 273 mAh/g after 60 cycles exhibiting a higher capacity retention of 95.4 % than that of the pristine LMNCO (90.3%). Fig. 4d compares cycling performances of the two samples at a higher rate of 0.5 C. In this test, L@S core-shell delivers a maximal capacity of ~183 mAh/g and retains ~153 mAh/g after 100 cycles, which is much higher than that of pristine LMNCO giving ~125 mAh/g after 100 cycles. The improvement in cycling performance and specific capacity herein can be ascribed to the stabilizing effect of thin spinel phase coating, which not only helps to reduce the erosion from electrolyte under high voltage but also restrain the bulk LMNCO active-mass loss during long cycling.

Fig. 4e summarizes rate performances of pristine LMNCO and L@S cathodes at various charge/discharge rates, namely 0.1 C, 0.2 C, 0.5 C, 1 C, 2 C and 5 C at 2.0 – 4.99 V vs. Li/Li$^+$. It is found that pristine LMNCO shows a poor rate capability, with almost no discharge capacity at 5 C though a good recovery to ~225 mAh/g when cycled back to 0.1 C. On the contrary, L@S core-shell sample delivers initial discharge capacities of 126 mAh/g, 97 mAh/g and 37 mAh/g at 1 C, 2 C and 5 C, respectively; when cycled back to 0.1 C from 5 C, its discharge capacity reaches as high as 269 mAh/g, demonstrating an outstanding electrochemical reversibility. Such enhanced rate performance is resulted from the following factors. First, the spinel coating with excellent structural stability can effectively stabilize the surface structure of LMNCO core, thereby reducing the erosion from the electrolyte and the bulk active-mass lose. Second, the spinel coating facilitates fast Li ions diffusion from the electrolyte to the layered LMNCO core. In addition, due to structural compatibility between the layered LMNCO and spinel phase coating, L@S is expected to have high structural stability. It is also noted that the L@S core-shell cathode needs more charge-discharge cycles to reach its maximum capacity at 0.1 C than pristine LMNCO cathode. The reason for this difference can be attributed to the relatively uniform spinel Li$_{0.5}$Mn$_{2.5}$Ni$_{0.5}$O$_{4}$ coating at the outer surface of the LMNCO core, which leads to the gradual electrochemical activation of the Li$_2$MnO$_3$ component in LMNCO.
core during the initial several cycles. As a result, L@S core-shell composite cathode needs more electrochemical cycles to reach its maximum capacity in comparison with the pristine LMNCO.

Cyclic voltammetric (CV) measurements are then carried out to further explore electrochemical characteristics of the core, shell, and core-shell materials. Fig. S2 presents the first CV three cycles of pristine LMNCO and spinel \(Li_{3}Mn_{2+}Ni_{0.5}O_{4}\), respectively, at a scan rate of 0.1 mV/s in the voltage range of 2.0 - 4.99 V. As for the CV curve of pristine LMNCO (Fig. S2a), the first pair of redox peaks at 4.16/3.63 V in the first electrochemical cycle corresponds to the redox reactions of \(Ni^{3+}/Ni^{4+}\) followed by \(Co^{3+}/Co^{4+}\), while Mn still remains as tetravalent in \(Li_{3}Mn_{2+}Ni_{0.5}O_{4}\) structure.\(^{30,31}\) The anodic peak at 4.67 V is associated with decomposition of \(Li_{2}MnO_{3}\) to \(Li_{2}O\) and Li-active \(MnO_{2}\), the unavoidable decomposition of electrolyte and formation of solid electrolyte interphase (SEI) at such a high potential above 4.5 V.\(^{32}\) Such an electrochemical activation process of \(Li_{2}MnO_{3}\) would result in high capacity of LMNCO via simultaneously losing oxygen irreversibly as \(Li_{2}O\) and \(MnO_{2}\). Therefore, the cathodic peak at ~3.0 V becomes apparent after charging to 4.99 V and can be attributed to the redox reaction of \(Mn^{4+}/Mn^{2+}\) that may take place in the electrochemical reaction after the Li\(_{2}MnO_{3}\) component is electrochemically activated. It is also found that the anodic peak at 4.67 V in the first CV curve disappears in subsequent CV cycles. Fig. S2b displays a typical CV curve of spinel \(Li_{x}Mn_{2}Ni_{0.5}O_{4}\). It is clearly observed that the 2\(^{nd}\) and 3\(^{rd}\) curves of spinel \(Li_{x}Mn_{2}Ni_{0.5}O_{4}\) are almost identical, indicating outstanding electrochemical reversibility and structural stability during cycling over a wide voltage range between 2.0 and 4.99 V vs. Li/Li\(^{+}\), which is expected to be a promising surface coating for pristine LMNCO. In the CV curves of LMNCO coated with spinel \(Li_{x}Mn_{2}Ni_{0.5}O_{4}\) (L@S core-shell) as shown in Fig. 4f, it is found that the L@S core-shell cathode shows a slightly better electrochemical reversibility than pristine LMNCO. The redox peaks at 4.16/3.63 V are associated with oxidation of \(Co^{3+}/Co^{4+}\) redox only from LMNCO core and \(Ni^{3+}/Ni^{4+}\) redox from both LMNCO core and spinel \(Li_{x}Mn_{2}Ni_{0.5}O_{4}\) shell. Interestingly, the above redox peaks from L@S core-shell show higher corresponding current density than that of pristine LMNCO, probably attributed to the thin spinel coating that reduces the erosion from electrolyte and transition-metal ion dissolution. It is also noted that some peaks (pointed by arrows in the Fig.4f) and another extra peak at 4.88 V can be ascribed to the spinel phase coating, confirming the L@S core-shell heterostructure, which is consistent with the XRD and TEM results.

In conclusion, we report simple and novel synthesis of L@S core-shell structured electrode material via facile evaporation-induced self-assembly (EISA) of ultrafine crystalline \(Li_{3}Mn_{2}Ni_{0.5}O_{4}\) nanoparticles on the surface of Li-rich layered \(Li_{x}Mn_{2}Ni_{0.5}Co_{0.3}O_{4}\) particles. This L@S core-shell cathode material demonstrates significantly improved specific capacity, cycling performance and rate capability compared to pristine Li-rich layered cathode. Due to structural and functional versatility of nanoparticles, our study provides new insights into preparation of various core-shell structures via EISA of nanoparticles for applications in LIBs or other energy-related fields.

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Notes and references