frontiers in
ENERGY RESEARCH

REVIEW ARTICLE
published: 01 September 2014
doi: 10.3389/fenrg.2014.00036

Recent developments in synthesis of $xLi_2MnO_3 \cdot (1 - x)LiMO_2$ (M = Ni, Co, Mn) cathode powders for high-energy lithium rechargeable batteries

The Nam Long Doan, Kimoon Yoo, Tuan K. A. Hoang and P. Chen*

Department of Chemical Engineering and Waterloo Institute for Nanotechnology, University of Waterloo, Waterloo, ON, Canada

Edited by:
Xueliang Sun, Western University, Canada

Reviewed by:
Reza Younesi, Technical University of Denmark, Denmark
Zhaoxiang Wang, Chinese Academy of Sciences, China
Hao Liu, Chinese Academy of Engineering Physics, China

Correspondence:
P. Chen, Department of Chemical Engineering and Waterloo Institute for Nanotechnology, University of Waterloo, 200 University Avenue West, Waterloo, ON N2L3G1, Canada
e-mail: p4chen@uwaterloo.ca

Lithium-rich layered powders, Li_2MnO_3-stabilized $LiMO_2$ (M = Ni, Co, Mn), are attractive cathode candidates for the next generations of high-energy lithium-ion batteries. However, most of the state-of-the-art preparation procedures are complicated and require multiple energy-intensive reaction steps. Thus, elucidating a low-cost synthetic protocol is important for the application of these materials in future lithium-ion batteries. Recent developments in the synthesis procedures of lithium-rich layered powders are discussed and future directions are pointed out in this review.

Keywords: cathode materials, lithium-rich layered oxides, powders, lithium-ion batteries, synthesis

INTRODUCTION

From its first commercial introduction by Sony in 1991, the $LiCoO_2$ cathode has been widely used in portable electronics due to its excellent rate capability, cyclability, and high-tap density (Ying et al., 2004; He et al., 2006). Although the theoretical specific capacity of $LiCoO_2$ electrodes is 273 mAh g^{-1}, the practical specific capacity is ~140 mAh g^{-1} due to high-surface reactivity and instability of the delithiated $Li_{1-x}CoO_2$ ($x > 0.5$) (Thackeray et al., 2007; Nagai et al., 2011). Cobalt, however, is relatively expensive and somewhat toxic, thus, there is a great need to find new cathode materials with superior capacity, energy, safety, and lower cost.

Argonne National Laboratory initiated research to develop a family of Li_2MnO_3-stabilized $LiMO_2$ (M = Mn, Ni, Co) cathodes for lithium-ion batteries (Kim et al., 2002, 2004; Thackeray et al., 2005). These electrode materials have similar layered structure to $LiCoO_2$, but possess superior stability, which allows the extraction of higher quantities of lithium ions during charge over a wider operating potential range, such as 2.0–4.6 V. As a result, practical specific discharge capacity of more than 200 mAh g^{-1} can be achieved at an average discharge potential of ~3.6 V vs. $Li^+/Li°$. In addition, thermal stability of these electrodes is significantly greater than that of $LiCoO_2$. Furthermore, less cobalt usage leads to lower material cost and environmental hazard.

There are excellent reviews (Thackeray et al., 2005, 2007; He et al., 2012; Yu and Zhou, 2013) describing molecular structure, thermal stability, electrochemistry, cycling stability, and other physical as well as electrochemical properties of $xLi_2MnO_3 \cdot (1 - x)LiMO_2$ for cathode application. However, there is no review, which explains the synthetic procedures of these cathode materials. Because the synthesis method greatly determines the material properties and its commercial feasibility, a systematic review of synthesis procedures of $xLi_2MnO_3 \cdot (1 - x)LiMO_2$ powders is crucial, especially for researchers who are entering high-energy lithium-ion battery research. In this review, we discuss many synthesis pathways of $xLi_2MnO_3 \cdot (1 - x)LiMO_2$ powders for cathode application in high-energy lithium-ion batteries.

SOLID-STATE SYNTHESIS

Solid-state synthesis is a conventional method for the preparation of electrochemically active materials for lithium-ion batteries. It is considered as a simple and scalable method. However, several choices of precursors, temperature profiles, cooling modes... should be identified and optimized. The solid-state process includes several successive steps such as mixing, milling, grinding, pelletizing, annealing, and quenching. In many cases, ball milling devices may be used for the purpose of fast and effective mixing and grinding. However, simple grinding and mixing by mortar and pestle are effective and widely accepted. Since reactions are controlled by solid-state diffusion, time, and energy consumption are important factors. For preparation of $xLi_2MnO_3 \cdot (1 - x)LiMO_2$ (M = Ni, Co, Mn), the precursors consist of transition metal salts (acetates of Ni^{2+}, Co^{2+}, Mn^{2+}) (Wang et al., 2012; Yu and Zhou, 2012; Yu et al., 2012a,b, 2013a), manganese–nickel–cobalt hydroxides (Kim et al., 2002, 2004; Johnson et al., 2007; Li et al., 2011; Xu et al., 2011; Zhang et al., 2012), or carbonates (Deng et al., 2010; Croy et al., 2011; Koenig et al., 2011; Wang et al., 2011), and a lithium-containing compound (usually lithium hydroxide). The stoichiometric mixture is initially decomposed at 480–600°C for 3–15 h, then pelletized and calcined at 850–1000°C for 10–24 h in air. The sample can be rapidly quenched (in air or liquid nitrogen) (Kim et al., 2002; Ito et al., 2008; Wu and Manthiram, 2009; Madhu et al., 2010; Li et al., 2011; Zhang et al., 2012) or furnace cooled (Wang et al., 2012).

SOLID-STATE REACTION IN COMBINATION WITH CO-PRECIPITATION

Most $xLi_2MnO_3 \cdot (1-x)LiMO_2$ samples are prepared by a combination of co-precipitation and solid-state reactions (or mixed hydroxide method), following the pioneer work at Argonne National Laboratory (Kim et al., 2002, 2004). Scanning electron microscopy images of a typical product is shown in **Figure 1** (Li et al., 2011), which represent the non-uniformity of the solid-state synthetic products. The manganese–nickel–cobalt hydroxide precursor is prepared by co-precipitation of transition metal aqueous solutions (nitrate or acetate of Ni^{2+}, Co^{2+}, Mn^{2+}) in a basic aqueous solution (sodium, potassium, or lithium hydroxide) (Kim et al., 2002; Kang et al., 2006; Johnson et al., 2007, 2008; Park et al., 2007a; Wu and Manthiram, 2009; Li et al., 2011; Xu et al., 2011). In order to prepare the hydroxide precursor with uniform particle size, polyvinylpyrrolidone (PVP) and ethylene glycol (EG) are used as dispersants (Xiang et al., 2013). PVP hinders the growth space of particles due to micelle formation. EG limits the growth rate of particles because of the high viscosity. Subsequently, the dried material is mixed with lithium hydroxide to produce the starting mixture for solid-state reactions.

Deng et al. (2010) reported the preparation of $Li_{(1+x)}Ni_{0.25}Mn_{0.75}O_{(2.25+x/2)}$ (where $x = 0.32$–0.65), which contains the Li_2MnO_3 phase, by using all carbonate precursors. A spherical $Ni_{0.25}Mn_{0.75}CO_3$ precursor is first prepared by co-precipitation, followed by solid-state reaction between that precursor and a stoichiometric amount of Li_2CO_3. Similarly, $0.5Li_2MnO_3$ $0.5LiCoO_2$ is synthesized by solid-state reaction between $(Co_{0.5}Mn_{0.5})CO_3$ and Li_2CO_3 (Croy et al., 2011). $(Co_{0.5}Mn_{0.5})CO_3$ is prepared beforehand by mixing a solution of cobalt and manganese sulfate with ammonium bicarbonate solution. In addition, $Ni_xMn_{1-x}CO_3$ can be prepared from nickel and manganese sulfate, sodium carbonate, and ammonium hydroxide (Lee et al., 2006; Ito et al., 2008; Koenig et al., 2011; Wang et al., 2011). Another transition metal precursor is $NiMnO_3$, which can be prepared by heating nickel manganese double hydroxides at 600°C for 4 h, then $NiMnO_3$ is mixed with lithium hydroxide for the subsequent solid-state reactions (Ohzuku et al., 2011). Using a combination of co-precipitation and solid-state reaction techniques, higher homogeneity is achieved, thus, improved discharge capacity such as 270 mAh g^{-1} at 0.1 C in the voltage range of 2–4.6 V was reported (Lee et al., 2006). However, adding several steps to the conventional solid-state reaction leads to time and cost increases that may hinder scale-up and commercialization.

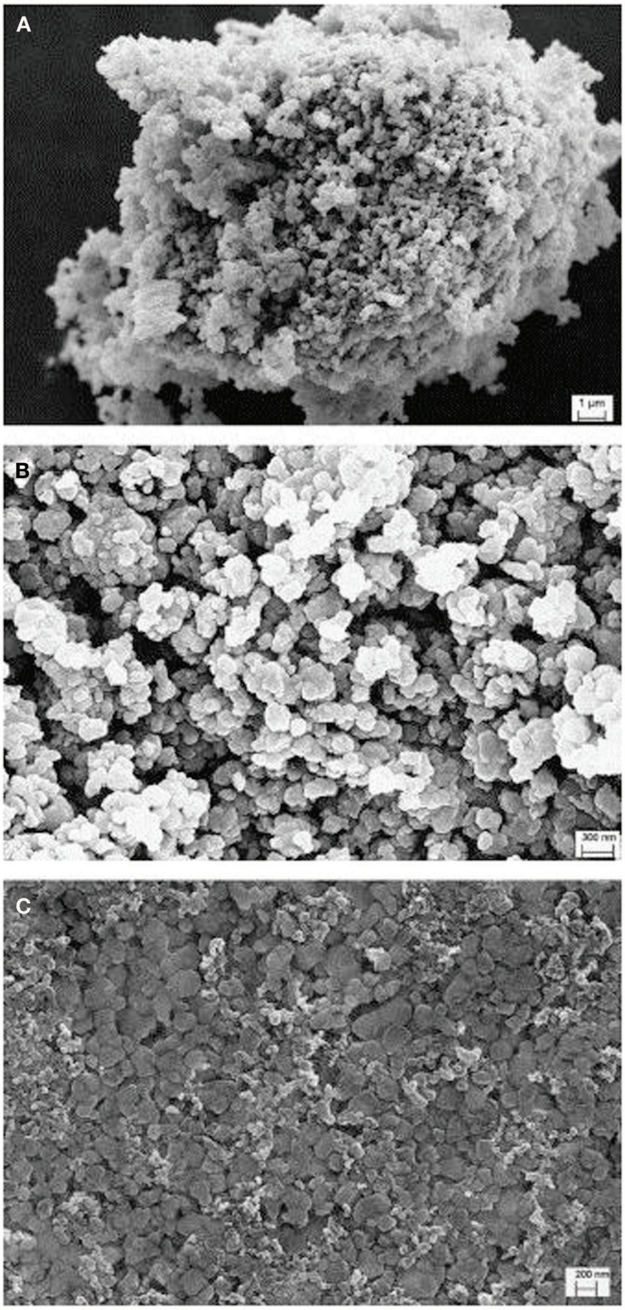

FIGURE 1 | SEM pictures of $Li[Li_{0.2}Mn_{0.56}Ni_{0.16}Co_{0.08}]O_2$ materials at different magnifications. **(A)** ×5k; **(B,C)** ×50k. Reproduced with permission from Li et al. (2011).

SOLID-STATE REACTION

Pure solid-state preparation of $xLi_2MnO_3 \cdot (1-x)LiMO_2$ has been practised by Zhou's group (AIST, Japan). By simple solid-state reactions of lithium hydroxide and transition metal acetates, cathode materials with sufficient high-specific capacity (~225 mAh g^{-1} at 0.1 C, 2–4.8 V) can be achieved (Yu et al., 2012b). $(1-x-y)LiNiO_2 \cdot xLi_2MnO_3 \cdot yLiCoO_2$ samples can be synthesized by solid-state reactions of all acetate precursors (Madhu et al., 2010). The optimized sample exhibits a discharge capacity of 244 mAh g^{-1} at C/15 rate in the potential range of 2–4.6 V. Oxalic acid can be used as a precipitant in the precursor mixture in order to produce dry precursor and to obtain higher homogeneous distributions of transition metal ions (Wang et al., 2012).

SOL-GEL METHOD

The sol-gel method appears to be the another good choice for the preparation of $xLi_2MnO_3\cdot(1-x)LiMO_2$ cathode materials. This method produces high purity and homogeneous products but is time consuming due to aging and drying. Stoichiometric amounts of lithium acetate, nickel acetate, cobalt acetate, and manganese acetate (or nitrate salts) are dissolved in distilled water (Wu et al., 2010; Jarvis et al., 2012; Jiang et al., 2013). An additional solution containing chelating agent such as citric acid (Wu et al., 2010), glycolic/tartaric acid (Kang et al., 2007), or citric acid/ethylenediaminetetraacetic acid (EDTA) (Jarvis et al., 2012) is added to the acetate solution under vigorous stirring to form a highly viscous gel. The solution pH is adjusted to ~7.5 using ammonium hydroxide. Water is evaporated at 70–80°C. The gel is decomposed at 450–500°C for 5–12 h and the solid product is ground after cooling. The resulting powders are pressed into pellets, heat treated at 800–900°C for 10–12 h. The final powder consists of nanosized primary particles, which are ~200–500 nm.

COMBUSTION METHOD

Simple combustion is a popular method to prepare the lithium-rich layered cathode materials (Park et al., 2003, 2007b; Wu et al., 2004; Hong et al., 2005; Fu et al., 2014; Shen et al., 2014). In comparison with mixed hydroxide (solid-state reaction in combination with co-precipitation) and sol-gel method, combustion method is simpler and less expensive (Park et al., 2003). Precursors must contain at least one acetate salt, other precursors can be nitrate (Park et al., 2003, 2007b; Hong et al., 2005) or hydroxide (Wu et al., 2004). Stoichiometric amounts of Li, Ni, Mn, and Co sources are dissolved in distilled water under continuous stirring and evaporating at 80–100°C on a hot plate. The molar ratio of acetate to nitrate can be adjusted to 3:1 to keep the combustion condition stable (Hong et al., 2005). A viscous gel is obtained after evaporation of excess water. In case all precursors are acetates (Fu et al., 2014), mannitol can be added and pH is adjusted to 2 using concentrated nitric acid to assist the gel formation. The resulting gel is fired at 400°C for 30 min to 1 h in air. The obtaining ash-like powder is ground and heated at 500–700°C for 3 h in air, then reground and heated again at 900°C in air for 5–12 h. Finally, it is quenched to room temperature.

OTHER SYNTHESIS ROUTES

CO-PRECIPITATION

Similar to the sol-gel method, co-precipitation offers uniform particle size distribution as well as high-phase purity. However, few papers (Gim et al., 2012; Min et al., 2013; Yu et al., 2013b) described this method, which may be due to the complicated procedure and the difficulty in controlling the chemical composition. In a typical synthesis, transition metal acetate precursors and lithium hydroxide are dissolved separately in distilled water. The hydroxide co-precipitation of the transition metals is facilitated by slowly combining the aqueous lithium hydroxide solution with the solution containing transition metal precursors at room temperature over an extended period of time (e.g., 24 h) (Gim et al., 2012). The resulting precipitate is dried between 85 and 120°C, followed by a grinding period. The powders are then heated at 600°C for 3 h to decompose the organic compounds, then calcined at 900°C for 12 h to promote crystallization, and finally quenched (Min et al., 2013).

If lithium carbonate is used as the lithium source instead of lithium hydroxide (Yu et al., 2013a,b), the precursors are mixed in a basic solution containing ammonium heptamolybdate tetrahydrate. The precipitate is dried at 100°C and annealed at 950°C for 5 h in air.

SPRAY PYROLYSIS

Spray pyrolysis (SP) is well known as a continuous and single-step preparation method for the synthesis of fine homogeneous and multicomponent powders. In comparison with the solid-state and sol-gel methods, SP is simpler and faster. In addition, the particle size distribution is typically narrow and controllable from the micrometer to submicrometer order, the purities of the products are high and the compositions of powders are easily controllable. Recently, the first paper reporting the preparation of $xLi_2MnO_3\cdot(1-x)LiMO_2$ by SP (Zhang and Axelbaum, 2012) was published. It is expected that more reports employing this method of synthesis will be available since it requires time to master this relatively new and special technique.

In a typical synthesis, the precursor solution is prepared by dissolving stoichiometric amounts of lithium nitrate and transition metal nitrates in deionized water. An air-assisted nebulizer aerosolizes the precursor solution to produce fine micrometer droplets. The droplets are transferred into a tubular furnace by a constant flow of air. Temperature of the furnace is held at 700°C to ensure full decomposition of the nitrate precursors. The powders are collected by a filter, and then annealed at 700–800°C for 2 h.

ELECTROSPINNING

This method was adapted by Hosono et al. (2013) to prepare hollow nanowires of $0.5Li_2MnO_3\cdot0.5LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$. An aqueous solution containing lithium acetate, transition metal acetate precursors, and polyvinyl alcohol are dissolved and then aged at 90°C for 1 h in an aqueous solution containing methanol and acid acetic. The precursor solution is loaded on a syringe, which connects to a metal needle. Under a voltage of 20 kV across the aluminum foil collector and the metal needle, polymer wires containing the metal salts can be obtained. Then, the desired material with wire structure could be achieved by heat treatment at 800°C in air. This method may be good for laboratory experiments to produce one-dimensional materials, but may require sophisticated high-voltage instruments for scale-up purposes.

REACTIVE MECHANOCHEMICAL SYNTHESIS

The previously described solid-state method often delivers products with large particle sizes (up to micrometer) with broad distribution, uncontrollable particle growth, and agglomeration. To overcome this problem, reactive mechanochemical synthesis is included in the synthetic procedure. This method is effective to prepare composite with a more uniform distribution of precursor components. There are several parameters (e.g., mass of balls/sample, rotation speed, pressure, temperature, the presence of wetting agents…) that can be controlled to deliver effective synthesis.

Mechanochemical process was utilized by Kim et al. (2012) to prepare the $xLi_2MnO_3\cdot(1-x)LiMO_2$ (M = Mn, Ni, Co).

Li_2MnO_3 and $LiMO_2$ (M = Ni, Mn, Co) can be incorporated together with controlled molar ratio thanks to the mechanochemical process (**Figure 2**). This incorporation of the two phases is apparently important because $LiMO_2$ can be stabilized and Li_2MnO_3 is the source of excess lithium.

In a typical synthesis, precursors (Li_2MnO_3 and $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$) and acetone are well mixed by using a planetary mill running at 350 rpm for 3 h. The composites are then heated at 1000°C for 10 h. Heat treated secondary particles are spherical. The performance of batteries prepared from this cathode material (discharge capacity is ~200 mAh g^{-1}) is lower than those prepared by the solid-state reaction. The reasons are not yet clear, but it may be due to the lack of the pelletization step, and the use of the stable precursors.

HYDROTHERMAL METHOD

Hydrothermal synthesis is performed at relatively low temperatures, thus, it is a low cost and energy-saving method to prepare fine particles. Lee et al. (2008) reported the preparation of layered $Li_{0.88}[Li_{0.18}Co_{0.33}Mn_{0.49}]O_2$ nanowires via hydrothermal processing at 200°C. As prepared $K_{0.3}MnO_2$ is dispersed in a solution of $Co(NO_3)_2$ in distilled water, then kept in an autoclave at 200°C for 5 days, and washed thoroughly with water to remove residues and dissolved potassium ions. The obtained powders are $Co_{0.4}Mn_{0.6}O_2$ nanowires. Finally, $Co_{0.4}Mn_{0.6}O_2$ nanowires are mixed with $LiNO_3\cdot H_2O$ (wt/wt ratio is 4:1) in 100 ml of distilled water, and maintained in an autoclave at 200°C for 2 days. As-prepared powders are rinsed with water, and vacuum dried at 120°C. The materials exhibit excellent rate capability (220 mAh g^{-1} at 1 C charge and 15 C discharge between 2 and 4.8 V), but poor cyclability (capacity retention of 92% after 50 cycles at 1 C) due to the high-specific areas of the nanowires, which reduce the diffusion path (increases the rate capacity) and increase the electrode/electrolyte contact area (accelerates side reactions, especially at high-charge potentials). In addition, the procedure is complicated and time consuming.

Wei et al. (2013) proposed a simpler hydrothermal route for preparation of $Li[Li_{0.2}Co_{0.4}Mn_{0.4}]O_2$. A suspension containing stoichiometric amounts of lithium, manganese, cobalt acetates is prepared, with oxalic acid as a precipitating agent and acetic acid as an additive. This suspension is heated in a Teflon container at 150°C for 3 h, then dried, pelletized, preheated at 450–500°C, and finally calcined at 750°C in air. The cathode material exhibits relatively low-specific discharge capacity of 180 mAh g^{-1} between 2 and 4.6 V vs. $Li^+/Li°$ at 100 mA g^{-1}. Moreover, high-temperature heat treatment is another disadvantage of this preparation route.

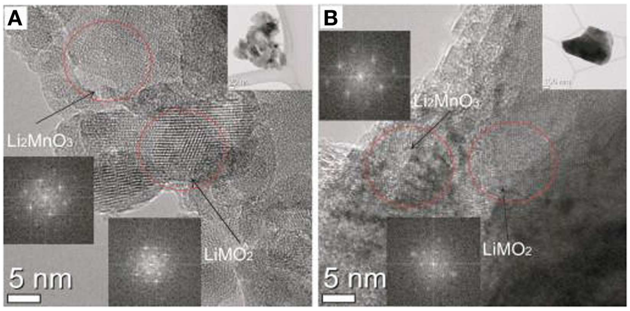

FIGURE 2 | HRTEM images: (A) $0.5Li_2MnO_3\cdot0.5LiMO_2$ (B) heat treated $0.5Li_2MnO_3\cdot0.5LiMO_2$. Reproduced with permission of Kim et al. (2012).

SURFACE MODIFICATIONS

Surface of high-energy materials can be modified with Al_2O_3, CeO_2, ZnO_2, or ZnO (3 wt% in the final product) (Wu and Manthiram, 2009), TiO_2 (Zheng et al., 2008), $FePO_4$ (Wang et al., 2013), or treated with 0.1 M HNO_3 (Kang et al., 2006). The surface modified cathodes with oxides (Wu and Manthiram, 2009) or $FePO_4$ (Wang et al., 2013) show higher first coulombic efficiency, discharge capacity, and capacity retention than the unmodified samples due to the retention of higher number of oxide ion vacancies in the lattice after the first charge (Wu and Manthiram, 2009; Wang et al., 2013). In addition, it was reported that TiO_2-coated $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ has enhanced thermal stability and cyclability (Zheng et al., 2008). The authors proposed that coating layer prevents the direct contact between active material and electrolyte, thus, reduces the side reactions between them at high-charge voltage region. On the other hand, it is suggested that acid treatment eliminates the first cycle irreversible capacity loss (first coulombic efficiency is close to 100%) by chemical activation of the Li_2MnO_3 phase. However, the acid treatment significantly reduces the cyclability and rate capability because of the H^+-exchange process and water entrapment inside the cathode powder (Kang et al., 2006). Immersion of the $xLi_2MnO_3\cdot(1-x)LiMO_2$ powders in a Li–Ni–PO_4 solution using sol-gel method, followed by a heat treatment period, leads to the formation of new materials with enhanced rate capability (Kang and Thackeray, 2009). Such treatment creates a stable protective Li–Ni–PO_4 layer, which exhibits high-lithium-ion conductivity at high-working potentials (4.6 V vs. Li^+/Li). Sun et al. (2012) reported that coating the high-energy cathode particles with AlF_3 could improve their electrochemical performance, both rate capability and cyclability. It is proposed by the authors that the Li_2MnO_3 phase is selectively converted to the spinel structure by chemical leaching of Li from Li_2MnO_3 due to the presence of the AlF_3 coating. Liu et al. (2010) introduced surface coating of $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ cathodes by aluminum using a thermal evaporation technique. Aluminum coating increases the first discharge capacity and coulombic efficiency, improves the cyclability, and enhances the rate capability. The suppression of oxygen vacancy elimination at the end of first charge results in the increase in first discharge capacity, while the suppression of oxygen vacancy elimination and side reactions in the subsequent cycles leads to cyclability improvement. Rate capability enhancement can be explained by the increase in the surface conductivity. Zhao et al. (2011) reported that coating $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ particles with manganese oxide (4 wt%) could significantly improve the cyclability and rate capability, although the reasons are not clear yet. Similar material was prepared by Wu et al. (2012), which exhibits lower charge transfer resistance in comparison with the uncoated one. In the study of Kang et al. (2005), $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ is coated with amorphous $Al(OH)_3$ created from the hydrolysis reaction of $Al(C_3H_7O)_3$. The $Al(OH)_3$

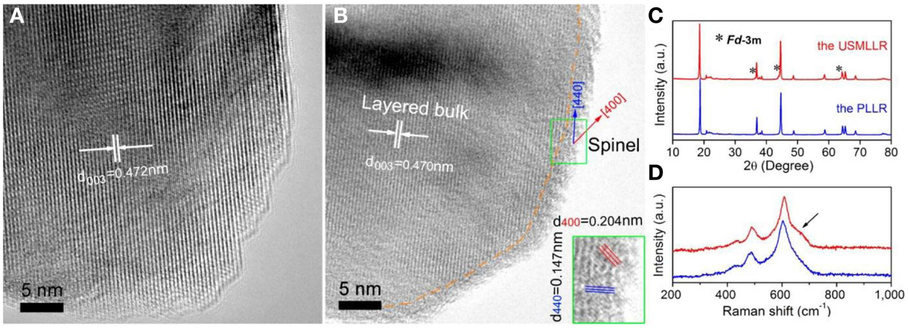

FIGURE 3 | HRTEM images of the pristine layered lithium-rich materials (PLLR) sample (A) and the ultrathin spinel membrane encapsulated-layered lithium-rich cathode (USMLLR) sample (B). The inset is two times enlarged view in green rectangle of **(B)**. XRD patterns (using Cu Kα radiation) **(C)** and Raman spectroscopies **(D)** of the PLLR sample and the USMLLR sample. Reproduced with permission from Wu et al. (2014).

coated cathode has a lower charge transfer resistance than the uncoated one, thus, has better rate capability. Moreover, the $Al(OH)_3$ coating also improves the thermal stability of the cathode powders.

Recently, Wu et al. (2014) proposed the coating of $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ by an ultrathin $Li_{1+x}Mn_2O_4$ layer. Polyvinylpyrrolidone is simply dispersed on the $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ materials, and the mixture is heat treated at 750°C to form an ultrathin $Li_{1+x}Mn_2O_4$ membrane on the surface (**Figure 3**). This high-lithium conductive membrane promotes the lithium transportation between electrolyte and the layered active material, and stabilizes the layered bulk during high-voltage cycling. As a result, rate capability, cyclability, and thermal stability are all improved.

CONCLUSION

Successful preparation of $xLi_2MnO_3·(1-x)LiMO_2$ cathode materials that exhibit a specific discharge capacity of 200 mAh g^{-1} or higher at 0.1 C rate between a potential range of 2–4.8 V vs. Li^+/Li is crucial to the development of high-energy lithium-ion batteries. There may be a number of ways to achieve the challenge in research laboratories. From an engineering point of view, choosing a feasible preparation method for straightforward commercialization is the challenge since most of the current state-of-the-art methods require significant heating and long-processing times. Many research groups follow the initiation of researchers at the Argonne National Laboratory to prepare the cathode materials by the combination of co-precipitation and solid-state reactions. However, complicated procedures, long-heat treatment times and high-heat treatment temperatures are current drawbacks, which cloud the competitiveness of the high-energy cathode technology. It is believed that solid-state reaction, combustion, sol-gel, and co-precipitation methods will be further optimized and modified to deliver more promising battery performance (both specific capacity and cyclability), together with shortening the preparation times, reduction of heat treatment durations, and temperatures.

ACKNOWLEDGMENTS

This work was financially supported by Positec, Natural Sciences and Engineering Research Council of Canada (NSERC), Canadian Foundation for Innovation (CFI), and the Canada Research Chairs (CRC) program. The authors would like to thank Dr. J. Byerley for assistance in editing the manuscript.

REFERENCES

Croy, J. R., Balasubramanian, M., Kim, D., Kang, S.-H., and Thackeray, M. M. (2011). Designing high-capacity, lithium-ion cathodes using X-ray absorption spectroscopy. *Chem. Mater.* 23, 5415–5424. doi:10.1021/cm2026703

Deng, H., Belharouak, I., Cook, R. E., Wu, H., Sun, Y.-K., and Amine, K. (2010). Nanostructured lithium nickel manganese oxides for lithium-ion batteries. *J. Electrochem. Soc.* 157, A447–A452. doi:10.1149/1.3308598

Fu, C., Li, G., Luo, D., Zheng, J., and Li, L. (2014). Gel-combustion synthesis of $Li_{1.2}Mn_{0.4}Co_{0.4}O_2$ composites with a high capacity and superior rate capability for lithium-ion batteries. *J. Mater. Chem. A* 2, 1471–1483. doi:10.1039/c3ta13920d

Gim, J., Song, J., Park, H., Kang, J., Kim, K., Mathew, V., et al. (2012). Synthesis and characterization of integrated layered nanocomposites for lithium ion batteries. *Nanoscale Res. Lett.* 7, 60–68. doi:10.1186/1556-276X-7-60

He, P., Wang, H., Qi, L., and Osaka, T. (2006). Synthetic optimization of spherical $LiCoO_2$ and precursor via uniform-phase precipitation. *J. Power Sources* 158, 529–534. doi:10.1016/j.jpowsour.2005.08.044

He, P., Yu, H., Li, D., and Zhou, H. (2012). Layered lithium transition metal oxide cathodes towards high energy lithium-ion batteries. *J. Mater. Chem.* 22, 3680–3695. doi:10.1039/c2jm14305d

Hong, Y.-S., Park, Y. J., Ryu, K. S., Chang, S. H., and Shin, Y.-J. (2005). Structural and electrochemical properties of $(1-x)Li[Ni_{0.20}Li_{0.20}Mn_{0.60}]O_2$-$xLi[Co_{0.50}Li_{0.167}Mn_{0.333}]O_2$ for lithium secondary batteries. *J. Power Sources* 147, 214–219. doi:10.1016/j.jpowsour.2004.11.018

Hosono, E., Saito, T., Hoshino, J., Mizuno, Y., Okubo, M., Asakura, D., et al. (2013). Synthesis of $LiNi_{0.5}Mn_{1.5}O_4$ and $0.5Li_2MnO_3$-$0.5LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ hollow nanowires by electrospinning. *CrystEngComm* 15, 2592–2597. doi:10.1039/c3ce26972h

Ito, A., Li, D., Ohsawa, Y., and Sato, Y. (2008). A new approach to improve the high-voltage cyclic performance of Li-rich layered cathode material by electrochemical pre-treatment. *J. Power Sources* 183, 344–346. doi:10.1016/j.jpowsour.2008.04.086

Jarvis, K. A., Deng, Z., Allard, L. F., Manthirama, A., and Ferreira, P. J. (2012). Understanding structural defects in lithium-rich layered oxide cathodes. *J. Mater. Chem.* 22, 11550–11555. doi:10.1039/c2jm30575e

Jiang, Y., Yang, Z., Luo, W., Hu, X., and Huang, Y. (2013). Hollow $0.3Li_2MnO_3$ $0.7LiNi_{0.5}Mn_{0.5}O_2$ microspheres as a high-performance cathode material for lithium-ion batteries. *Phys. Chem. Chem. Phys.* 15, 2954–2960. doi:10.1039/c2cp44394e

Johnson, C. S., Li, N., Lefief, C., and Thackeray, M. M. (2007). Anomalous capacity and cycling stability of $xLi_2MnO_3·(1-x)LiMO_2$ electrodes (M = Mn, Ni, Co) in lithium batteries at 50°C. *Electrochem. Commun.* 9, 787–795. doi:10.1016/j.elecom.2006.11.006

Johnson, C. S., Li, N., Lefief, C., Vaughey, J. T., and Thackeray, M. M. (2008). Synthesis, characterization and electrochemistry of lithium battery electrodes: xLi_2MnO_3 $(1\text{-}x)LiMn_{0.333}Ni_{0.333}Co_{0.333}O_2$ $(0 \leq x \leq 0.7)$. *Chem. Mater.* 20, 6095–6106. doi:10.1021/cm801245r

Kang, S.-H., Johnson, C. S., Vaughey, J. T., Amine, K., and Thackeray, M. M. (2006). The effects of acid treatment on the electrochemical properties of 0.5 $Li_2MnO_3{\cdot}0.5$ $LiNi_{0.44}Co_{0.25}Mn_{0.31}O_2$ electrodes in lithium cells. *J. Electrochem. Soc.* 153, A1186–A1192. doi:10.1149/1.2194764

Kang, S.-H., Kempgens, P., Greenbaum, S., Kropf, A. J., Amine, K., and Thackeray, M. M. (2007). Interpreting the structural and electrochemical complexity of $0.5Li_2MnO_3$ $0.5LiMO_2$ electrodes for lithium batteries ($M = Mn_{0.5\text{-}x}Ni_{0.5\text{-}x}Co_{2x}$, $0 \leq x \leq 0.5$). *J. Mater. Chem.* 17, 2069–2077. doi:10.1039/b618715c

Kang, S.-H., and Thackeray, M. M. (2009). Enhancing the rate capability of high capacity xLi_2MnO_3 $(1\text{-}x)LiMO_2$ (M = Mn, Ni, Co) electrodes by Li-Ni-PO_4 treatment. *Electrochem. Commun.* 11, 748–751. doi:10.1016/j.elecom.2009.01.025

Kang, Y.-J., Kim, J.-H., Lee, S.-W., and Sun, Y.-K. (2005). The effect of $Al(OH)_3$ coating on the $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ cathode material for lithium secondary battery. *Electrochim. Acta* 50, 4784–4791. doi:10.1016/j.electacta.2005.02.032

Kim, J.-S., Johnson, C. S., Vaughey, J. T., and Thackeray, M. M. (2002). Layered $xLiMO_2{\cdot}(1\text{-}x)Li_2MO_3$ electrodes for lithium batteries: a study of $0.95LiMn_{0.5}Ni_{0.5}O_2{\cdot}0.05Li_2TiO_3$. *Electrochem. Commun.* 4, 205–209. doi:10.1016/S1388-2481(02)00251-5

Kim, J.-S., Johnson, C. S., Vaughey, J. T., Thackeray, M. M., Hackney, S. A., Yoon, W., et al. (2004). Electrochemical and structural properties of $xLi_2M'O_3{\cdot}(1\text{-}x)LiMn_{0.5}Ni_{0.5}O_2$ electrodes for lithium batteries (M' = Ti, Mn, Zr; $0 \leq x \leq 0.3$). *Chem. Mater.* 16, 1996–2006. doi:10.1021/cm0306461

Kim, S., Kim, C., Noh, J.-K., Yu, S., Kim, S.-J., Chang, W., et al. (2012). Synthesis of layered-layered xLi_2MnO_3 $(1\text{-}x)LiMO_2$ (M = Mn, Ni, Co) nanocomposite electrodes materials by mechanochemical process. *J. Power Sources* 220, 422–429. doi:10.1016/j.jpowsour.2012.07.135

Koenig, G. M., Belharouak, I., Deng, H., Sun, Y.-K., and Amine, K. (2011). Composition-tailored synthesis of gradient transition metal precursor particles for lithium-ion battery cathode materials. *Chem. Mater.* 23, 1954–1963. doi:10.1021/cm200058c

Lee, D.-K., Park, S.-H., Amine, K., Bang, H. J., Parakash, J., and Sun, Y.-K. (2006). High capacity $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ cathode materials via a carbonate co-precipitation method. *J. Power Sources* 162, 1346–1350. doi:10.1016/j.jpowsour.2006.07.064

Lee, Y., Kim, M. G., and Cho, J. (2008). Layered $Li_{0.88}[Li_{0.18}Co_{0.33}Mn_{0.49}]O_2$ nanowires for fast and high capacity Li-ion storage material. *Nano Lett.* 8, 957–961. doi:10.1021/nl0731466

Li, J., Klöpsch, R., Stan, M. C., Nowak, S., Kunze, M., Winter, M., et al. (2011). Synthesis and electrochemical performance of the high voltage cathode material $Li[Li_{0.2}Mn_{0.56}Ni_{0.16}Co_{0.08}]O_2$ with improved rate capability. *J. Power Sources* 196, 4821–4825. doi:10.1016/j.jpowsour.2011.01.006

Liu, J., Reeja-Jayan, B., and Manthiram, A. (2010). Conductive surface modification with aluminum of high capacity layered $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ cathodes. *J. Phys. Chem. C* 114, 9528–9533. doi:10.1021/jp102050s

Madhu, C., Garrett, J., and Manivannan, V. (2010). Synthesis and characterization of oxide cathode materials of the system $(1\text{-}x\text{-}y)LiNiO_2{\cdot}xLi_2MnO_3{\cdot}yLiCoO_2$. *Ionics* 16, 591–602. doi:10.1007/s11581-010-0454-x

Min, J. W., Gim, J., Song, J., Ryu, W.-H., Lee, J.-W., Kim, Y.-I., et al. (2013). Simple, robust metal fluoride coating on layered $Li_{1.23}Ni_{0.13}Co_{0.14}Mn_{0.56}O_2$ and its effects on enhanced electrochemical properties. *Electrochim. Acta* 100, 10–17. doi:10.1016/j.electacta.2013.03.085

Nagai, R., Kita, F., Yamada, M., and Katayama, H. (2011). Development of highly reliable high-capacity batteries for mobile devices and small- to medium-sized batteries for industrial applications. *Hitachi Rev.* 60, 28–32.

Ohzuku, T., Nagayama, M., Tsujia, K., and Ariyoshi, K. (2011). High-capacity lithium insertion materials of lithium nickel manganese oxides for advanced lithium-ion batteries: toward rechargeable capacity more than 300 mA h g^{-1}. *J. Mater. Chem.* 21, 10179–10188. doi:10.1039/c0jm04325g

Park, S.-H., Kang, S.-H., Johnson, C. S., Amine, K., and Thackeray, M. M. (2007a). Lithium-manganese-nickel-oxide electrodes with integrated layered-spinel structures for lithium batteries. *Electrochem. Commun.* 9, 262–268. doi:10.1002/adma.201104106

Park, Y. J., Kim, M. G., Hong, Y.-S., Wu, X., Ryu, K. S., and Chang, S. H. (2003). Electrochemical behavior of Li intercalation processes into a $Li[Ni_xLi_{(1/3\text{-}2x/3)}Mn_{(2/3\text{-}x/3)}]O_2$ cathode. *Solid State Commun.* 127, 509–514. doi:10.1016/S0038-1098(03)00432-0

Park, Y. J., Lee, J. W., Lee, Y.-G., Kim, K. M., Kang, M. G., and Lee, Y. (2007b). The structural and electrochemical properties of thermally aged $Li[Co_{0.1}Ni_{0.15}Li_{0.2}Mn_{0.55}]O_2$ cathodes. *Bull. Korean Chem. Soc.* 28, 2226–2230. doi:10.5012/bkcs.2007.28.12.2226

Shen, C.-H., Wang, Q., Fu, F., Huang, L., Lin, Z., Shen, S.-Y., et al. (2014). Facile synthesis of the Li-rich layered oxide $Li_{1.23}Ni_{0.09}Co_{0.12}Mn_{0.56}O_2$ with superior lithium storage performance and new insights into structural transformation of the layered oxide material during charge-discharge cycle: in situ XRD characterization. *ACS Appl. Mater. Interfaces* 6, 5516–5524. doi:10.1021/am405844b

Sun, Y.-K., Lee, M.-J., Yoon, C. S., Hassoun, J., Amine, K., and Scrosati, B. (2012). The role of AlF_3 coatings in improving electrochemical cycling of Li-enriched nickel-manganese oxide electrodes for Li-ion batteries. *Adv. Mater.* 24, 1192–1196. doi:10.1002/adma.201104106

Thackeray, M., Kang, S.-H., Johnson, C. S., Vaughey, J. T., Benedek, R., and Hackney, S. A. (2007). Li_2MnO_3-stabilized $LiMO_2$ (M = Mn, Ni, Co) electrodes for lithium-ion batteries. *J. Mater. Chem.* 17, 3112–3125. doi:10.1039/b702425h

Thackeray, M. M., Johnson, C. S., Vaughey, J. T., Li, N., and Hackney, S. A. (2005). Advances in manganese-oxide 'composite' electrodes for lithium-ion batteries. *J. Mater. Chem.* 15, 2257–2267. doi:10.1039/b417616m

Wang, D., Belharouak, I., Koenig, G. M., Zhou, G., and Amine, K. (2011). Growth mechanism of $Ni_{0.3}Mn_{0.7}CO_3$ precursor for high capacity Li-ion battery cathodes. *J. Mater. Chem.* 21, 9290–9295. doi:10.1039/c1jm11077b

Wang, J., Qiu, B., Cao, H., Xia, Y., and Liu, Z. (2012). Electrochemical properties of 0.6 $Li[Li_{1/3}Mn_{2/3}]O_2\text{-}0.4LiNi_xMn_yCo_{1\text{-}x\text{-}y}O_2$ cathode materials for lithium-ion batteries. *J. Power Sources.* 218, 128–133. doi:10.1016/j.jpowsour.2012.06.067

Wang, Z., Liu, E., He, C., Shi, C., Li, J., and Zhao, N. (2013). Effect of amorphous $FePO_4$ coating on structure and electrochemical performance of $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$ as cathode material for Li-ion batteries. *J. Power Sources* 236, 25–32. doi:10.1016/j.jpowsour.2013.02.022

Wei, X., Zhang, S., He, L., Liu, G., and Yang, P. (2013). Structure, morphology and electrochemical properties of $Li[Li_{0.2}Co_{0.4}Mn_{0.4}]O_2$ cathode material synthesized by a simple hydrothermal method. *Int. J. Electrochem. Sci.* 8, 1885–1894.

Wu, F., Li, N., Su, Y., Lu, H., Zhang, L., An, R., et al. (2012). Can surface modification be more effective to enhance the electrochemical performance of lithium rich materials? *J. Mater. Chem.* 22, 1489–1497. doi:10.1039/c1jm14459f

Wu, F., Li, N., Su, Y., Zhang, L., Bao, L., Wang, J., et al. (2014). Ultrathin spinel membrane-encapsulated layered lithium-rich cathode material for advanced Li-ion batteries. *Nano Lett.* 14, 3550–3555. doi:10.1021/nl501164y

Wu, F., Lu, H., Su, Y., Li, N., Bao, L., and Chen, S. (2010). Preparation and electrochemical performance of Li-rich layered cathode material, $Li[Ni_{0.2}Li_{0.2}Mn_{0.6}]O_2$, for lithium-ion batteries. *J. Appl. Electrochem.* 40, 783–789. doi:10.1007/s10800-009-0057-2

Wu, X., Ryu, K. S., Hong, Y.-S., Park, Y. J., and Chang, S. H. (2004). Properties of $Li[Cr_xLi_{(1\text{-}x)/3}Mn_{2(1\text{-}x)/3}]O_2$ $(0.1 \leq x \leq 0.2)$ material prepared by quenching. *J. Power Sources* 132, 219–224. doi:10.1016/j.jpowsour.2003.12.030

Wu, Y., and Manthiram, A. (2009). Effect of surface modifications on the layered solid solution cathodes $(1\text{-}z)Li[Li_{1/3}Mn_{2/3}]O_2\text{-}(z)$ $Li[Mn_{0.5\text{ - }y}Ni_{0.5\text{ - }y}Co_{2y}]O_2$. *Solid State Ionics* 180, 50–56. doi:10.1016/j.ssi.2008.11.002

Xiang, X., Li, X., and Li, W. (2013). Preparation and characterization of size-uniform $Li[Li_{0.131}Ni_{0.304}Mn_{0.565}]O_2$ particles as cathode materials for high energy lithium ion battery. *J. Power Sources* 230, 89–95. doi:10.1016/j.jpowsour.2012.12.050

Xu, B., Fell, C. R., Chic, M., and Meng, Y. S. (2011). Identifying surface structural changes in layered Li-excess nickel manganese oxides in high voltage lithium ion batteries: a joint experimental and theoretical study. *Energy Environ. Sci.* 4, 2223–2233. doi:10.1039/c1ee01131f

Ying, J., Jiang, C., and Wan, C. (2004). Preparation and characterization of high-density spherical $LiCoO_2$ cathode material for lithium ion batteries. *J. Power Sources* 129, 264–269. doi:10.1016/j.jpowsour.2003.10.007

Yu, H., Ishikawa, R., So, Y.-G., Shibata, N., Kudo, T., Zhou, H., et al. (2013a). Direct atomic-resolution observation of two phases in the $Li_{1.2}Mn_{0.567}Ni_{0.166}Co_{0.067}O_2$ cathode material for lithium-ion batteries. *Angew. Chem.* 125, 6085–6089. doi:10.1002/anie.201301236

Yu, H., Wang, Y., Asakura, D., Hosono, E., Zhang, T., and Zhou, H. (2012a). Electrochemical kinetics of the $0.5Li_2MnO_3.0.5LiMn_{0.42}Ni_{0.42}Co_{0.16}O_2$ 'composite' layered cathode material for lithium-ion batteries. *RSC Adv.* 2, 8797–8807. doi:10.1039/c2ra20772a

Yu, H., Kim, H., Wang, Y., He, P., Asakura, D., Nakamura, Y., et al. (2012b). High-energy 'composite' layered manganese-rich cathode materials via controlling Li_2MnO_3 phase activation for lithium-ion batteries. *Phys. Chem. Chem. Phys.* 14, 6584–6595. doi:10.1039/c2cp40745k

Yu, H., and Zhou, H. (2012). Initial coulombic efficiency improvement of the $Li_{1.2}Mn_{0.567}Ni_{0.166}Co_{0.067}O_2$ lithium-rich material by ruthenium substitution for manganese. *J. Mater. Chem.* 22, 15507–15510. doi:10.1039/c2jm33484d

Yu, H., and Zhou, H. (2013). High-energy cathode materials (Li_2MnO_3-$LiMO_2$) for lithium-ion batteries. *J. Phys. Chem. Lett.* 4, 1268–1280. doi:10.1002/chem.201402727

Yu, S.-H., Yoon, T., Mun, J., Park, S., Kang, Y.-S., Park, J.-H., et al. (2013b). Continuous activation of Li_2MnO_3 component upon cycling in $Li_{1.167}Ni_{0.233}Co_{0.100}Mn_{0.467}Mo_{0.033}O_2$ cathode material for lithium ion batteries. *J. Mater. Chem. A* 1, 2833–2839. doi:10.1039/c2ta00309k

Zhang, H. Z., Qiao, Q. Q., Li, G. R., Ye, S. H., and Gao, X. P. (2012). Surface nitridation of Li-rich layered $Li(Li_{0.17}Ni_{0.25}Mn_{0.58})O_2$ oxide as cathode material for lithium-ion battery. *J. Mater. Chem.* 22, 13104–13109. doi:10.1039/c2jm30989k

Zhang, X., and Axelbaum, R. L. (2012). Spray pyrolysis synthesis of mesoporous lithium-nickel-manganese-oxides for high energy Li-ion batteries. *J. Electrochem. Soc.* 159, A834–A842. doi:10.1149/2.079206jes

Zhao, Y., Zhao, C., Feng, H., Sun, Z., and Xia, D. (2011). Enhanced electrochemical performance of $Li[Li_{0.2}Ni_{0.2}Mn_{0.6}]O_2$ modified by manganese oxide coating for lithium-ion batteries. *Electrochem. Solid State Lett.* 14, A1–A5. doi:10.1149/1.3496402

Zheng, J. M., Li, J., Zhang, Z. R., Guo, X. J., and Yang, Y. (2008). The effects of TiO_2 coating on the electrochemical performance of $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ cathode material for lithium-ion battery. *Solid State Ionics* 179, 1794–1799. doi:10.1016/j.ssi.2008.01.091

Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Received: 12 June 2014; paper pending published: 03 July 2014; accepted: 16 August 2014; published online: 01 September 2014.

Citation: Doan TNL, Yoo K, Hoang TKA and Chen P (2014) Recent developments in synthesis of $xLi_2MnO_3 \cdot (1-x)LiMO_2$ (M = Ni, Co, Mn) cathode powders for high-energy lithium rechargeable batteries. Front. Energy Res. ***2****:36. doi: 10.3389/fenrg.2014.00036*

This article was submitted to Energy Storage, a section of the journal Frontiers in Energy Research.