Short communication

Preparation of high quality layered-layered composite Li_2MnO_3–$LiMO_2$ (M = Ni, Mn, Co) Li-ion cathodes by a ball milling–annealing process

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ABSTRACT

Cathode powders based on the layered-layered composite Li_2MnO_3–$LiMO_2$ (M = Mn, Co, Ni) have been prepared by a ball milling and annealing process. In principle, this easily scalable and simple process allows for the variation of the stoichiometry, degree of intermixing, and crystallite size by varying the ratio of Li_2MnO_3 and $LiMO_2$ parent compounds, milling time, and annealing time and temperature. The resultant cathode powder composition of $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ (M = Mn, Co, Ni) has been shown to have the same crystallographic and electrochemical features as those prepared by conventional sol–gel or co-precipitation methods, with specific discharge capacity of about 250 mAh g^{-1} between 4.7 and 2 V. Improvements in specific discharge capacity were demonstrated by the addition of an $AlPO_4$ coating on the cathode powder following the mill-anneal synthesis method. In addition to providing a new means to vary the properties of this cathode system in a more controlled fashion, this synthesis approach also can be used to examine the hypothesis of electrochemical stabilization of the Li_2MnO_3 by the substitutional $LiMO_2$ structural unit.

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1. Introduction

The materials system based on the layered-layered compositions of Li_2MnO_3–$LiMO_2$ (M = Mn, Co, Ni) is of significant interest as cathodes for advanced lithium-ion cells due to their high specific capacity of about 240–280 mAh g^{-1} between 4.8 V and 2 V [1–4]. However, there are numerous serious issues with this class of cathode materials, namely their high first cycle irreversible capacity and inherently low rate capability, especially at low temperatures. These cathode materials are typically prepared by sol–gel or co-precipitation approaches, and depending on the synthesis conditions can result in a wide range of powder properties (e.g. tap density and surface area) and electrochemical properties (e.g. rate capability and irreversible capacity). For example, given the similar ionic radii for Li^+ and Ni^{2+}, it is often the case that transition metal oxides have considerable cation disorder, with Ni ions occupying sites in Li layers, which can severely hinder facile Li^+ motion and hence lower the practical rate capability [5]. Thus, we have explored alternative synthesis methodologies to improve the electrochemical performance of this materials system while not sacrificing important powder properties such as surface area and tap density.

We report herein a new process to prepare layered-layered compositions of Li_2MnO_3–$LiMO_2$ in the exemplary case of 1:1 of Li_2MnO_3:$LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$ (equivalently $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$) by ball milling and annealing mixtures of the parent compounds. This approach represents a novel alternative to conventional synthetic approaches. Further, the method is readily tailorable to a wide range of stoichiometries and in principle can reduce cation disorder provided starting materials have low disorder given the unlikely diffusion of the transition metals during the annealing process. It is also conceivable that the process could be extended for the straightforward preparation of other immiscible (e.g. spinel + layered) cathode compositions as well.

In a broader sense, the technique may allow for the ability to test the hypothesis that the Li_2MnO_3 is electrochemically stabilized by solid solution substitution by the $LiMO_2$ structural unit [6]. By adjusting the milling time, the degree of homogenization and intermixing of the parent compounds can be varied, and thus short range order of the resultant powder can be varied. The ability to tailor the intermixing and degree of "dissolution" of the LMO_2 into the Li_2MnO_3 lattice cannot be offered by other conventional synthesis methods.

2. Experimental

The Li_2MnO_3 cathode powder was prepared by a sol–gel approach, where stoichiometric amounts of lithium acetate

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(Aldrich) and manganese acetate (Aldrich) were dissolved in deionized water. The resultant liquid was stirred while heating at 120 °C to a dried gel. The dried gel was ground and further heated sequentially for 1 h in room air at 300 °C, 400 °C, 500 °C, grinding and remixing the powder between each successive firing step. The powder was then fired at 800 °C for 16 h and then cooled to room temperature in the furnace.

In order to prepare the layered-layered composite cathode powders, the above described Li_2MnO_3 and numerous layered cathode materials such as $LiCoO_2$, $LiNiO_2$, $LiNi_{0.8}Co_{0.2}O_2$, and $LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$ were tested in varying compositions. Of the different variations, the 1:1 ratio of Li_2MnO_3:$LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$ (equivalently $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$) was found to have the highest specific discharge capacity. As such, subsequent materials characterization and electrochemical studies were performed exclusively on this stoichiometry.

The Li_2MnO_3 and $LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$ (supplied by Quallion) powders were added in 1:1 molar ratios to a steel ball mill. The powders were dry milled with steel balls for a total of 6 h with a ball-powder mass ratio of 1.5–2.7. Following milling, the powders were fired in air at 800 °C for 24 h and then quenched on copper plates to room temperature. These powders were then re-milled for 6 h and re-fired in air at 800 °C for 24 h and quenched to room temperature. The annealing time and temperature were not optimized, but it should be noted that these variables will strongly impact the degree of diffusion of the cations within the lithium and transition metal layers. The quench procedure was included in the synthesis process following literature reports for this class of layered-layered composite oxides [7].

X-Ray diffraction (XRD) measurements were carried out using a Siemens D500 diffractometer run in the theta-2 theta geometry, with a Cu anode ($\lambda = 1.541$ Å) at an accelerating voltage of 40 kV and a tube current of 20 mA. Crystalline Si powder was added as a standard to the cathode powder for the XRD measurements. Tap density measurements were performed with a Quantachrome Autotap instrument, with 1000 taps per sample.

In some cases, the milled – annealed cathode powders were prepared with a 2 wt% $AlPO_4$ coating following the mill-anneal synthesis. For these cathode powders, separate stoichiometric solutions of aluminum nitrate (EM) and dibasic ammonium phosphate (J.T. Baker) were prepared by dissolving the salts in deionized water. The dibasic ammonium phosphate solution was then added dropwise to the aluminum nitrate solution to form a colloidal suspension to which the milled-annealed cathode powder was slowly added. The suspension was then filtered, dried, and fired in room air at 400 °C for 4 h and allowed to cool to room temperature in the furnace. The weight percent of $AlPO_4$ was based on stoichiometric calculations of the precursors.

Cathodes were prepared by spray coating Al foil substrates with slurries of 80 wt% cathode powder, 10 wt% C black (Shawinigan), and 10 wt% poly(vinylene difluoride) (PVDF) binder (Sigma Aldrich, $MW_{avg} = 534,000$) in N-methyl-2-pyrrolidinone (NMP) (Sigma–Aldrich). The cathode active mass loading was 5–10 mg cm^{-2}. Coin cell studies were performed by assembling the above electrodes in stainless steel CR2032 coin cell hardware, with Al clad Ni-plated stainless steel cases at the cathode terminal, with 100 μl of 1 M $LiPF_6$ in ethylene carbonate:dimethyl carbonate:diethyl carbonate (EC:DMC:DEC) (1:1:1, vol%) electrolyte. Multiple cell replicants (at least four cells per formulation) were used to validate the reproducibility of the cell data. Statistical comparisons between the specific discharge capacity of the uncoated milled-annealed cathode powders and the 2 wt% $AlPO_4$ coated milled-annealed powders were performed using an unpaired t-test calculation tool [8].
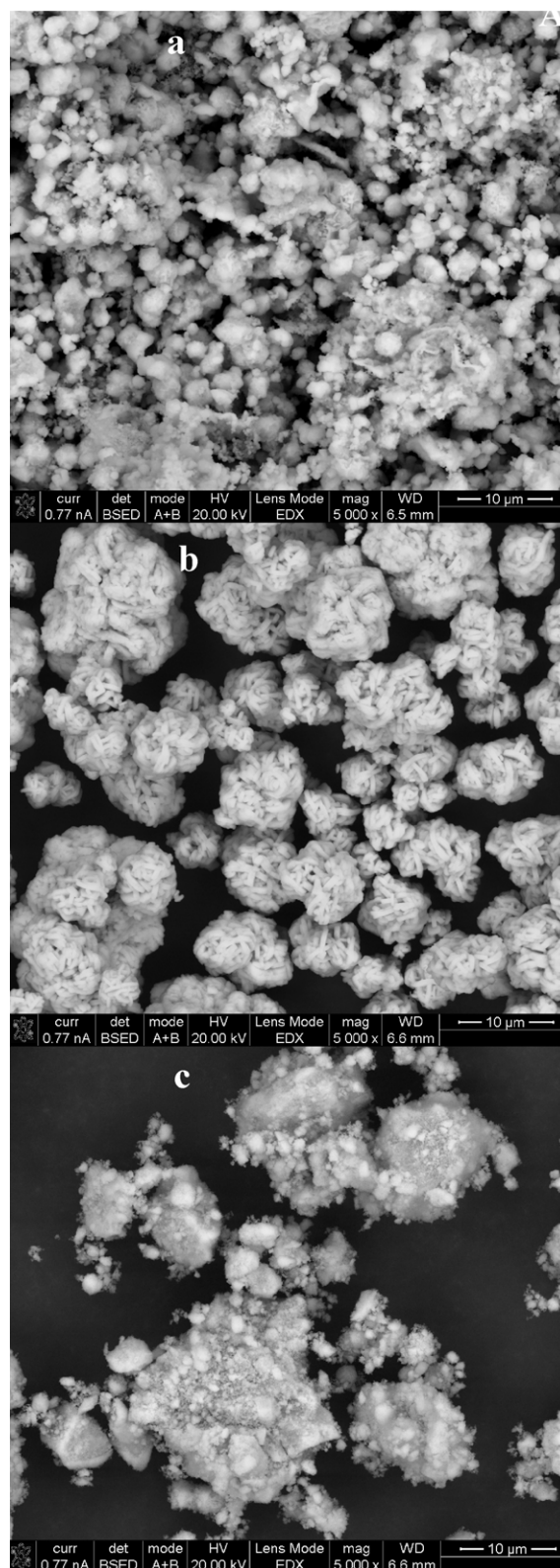

Fig. 1. Scanning electron micrographs of (a) as-prepared Li_2MnO_3, (b) as-received $LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$, and (c) milled and annealed 0.5 M Li_2MnO_3–0.5 M $LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$.

3. Results and discussion

The microstructure of the Li_2MnO_3, $LiMn_{0.33}Ni_{.33}Co_{0.33}O_2$, and the resultant milled-annealed 0.5 M Li_2MnO_3–0.5 M $LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$ ($Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$) are shown
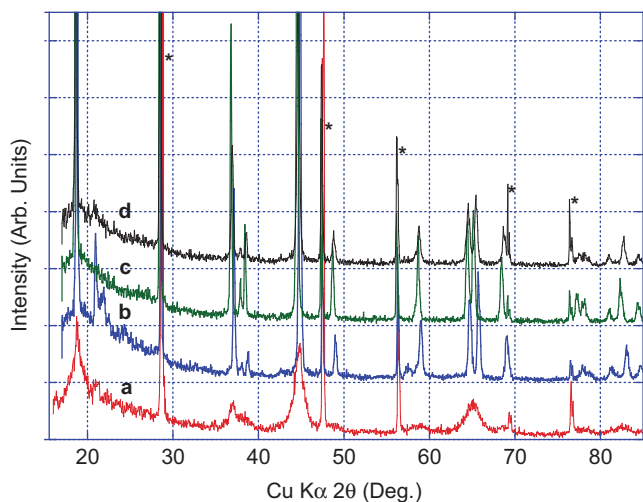
Fig. 2. X-Ray diffraction patterns of (a) milled and pre-annealed 0.5 M Li_2MnO_3–0.5 M Li $Mn_{0.33}Ni_{0.33}Co_{0.33}O_2$ (b) as-prepared Li_2MnO_3, (c) as-received $LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$, and (d) milled and annealed 0.5 M Li_2MnO_3–0.5 M $LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$. Asterisks indicate reflections associated with Si standard.

Fig. 3. X-Ray diffraction patterns of (a) $Li_{1.17}Mn_{0.56}Ni_{0.135}Co_{0.135}O_2$ prepared by conventional carbonate synthesis route, and (b) milled and annealed 0.5 M Li_2MnO_3–0.5 M $LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$ (resultant $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$). Asterisks indicate reflections associated with Si standard.

in Fig. 1a–c, respectively. The milling and annealing of the Li_2MnO_3 and $LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$ resulted in a destruction of the fairly narrow size distribution of both of the parent compounds and lead to a bimodal type microstructure of the resultant compound that consisted of submicron primary particles agglomerated into a wide size distribution of secondary particles. The tap density of the resultant milled-annealed cathode powder was 2.0 g cm^{-3}, whereas the tap densities of the parent Li_2MnO_3 and $LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$ powders were 1.2 and 2.4 g cm^{-3}, respectively. The tap density of 2.0 g cm^{-3} of the resultant cathode powder compares favorably to the tap density of 1.4–1.8 g cm^{-3} often observed for this cathode materials system prepared by sol–gel, co-precipitation, or other analogous approaches [9]. However this tap density is somewhat lower than that of about 2.4 g cm^{-3} for commercialized $LiCoO_2$ or $LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$ [10].

The X-Ray diffraction patterns are shown in Fig. 2 for the parent Li_2MnO_3, $LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$ powders, the milled-annealed 0.5 M Li_2MnO_3–0.5 M $LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$, as well as the milled but pre-annealed 0.5 M Li_2MnO_3–0.5 M $LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$. The milling of the Li_2MnO_3 and $LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$ powders resulted in significant broadening and decrease in intensity of the reflections as expected as the average grain size of the parent crystallites is reduced due to the high energy milling process. Upon annealing, the XRD reflections narrow and increase in intensity, indicative of re-crystallization of the previously nanocrystalline unannealed powders.

The X-ray diffraction pattern of the milled-annealed 0.5 M Li_2MnO_3–0.5 M $LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$ was compared with a previously reported layered-layered Li_2MnO_3–$LiMO_2$ (M = Ni, Mn, Co), with a composition of $Li_{1.17}Mn_{0.56}Ni_{0.135}Co_{0.135}O_2$ that was prepared by a conventional carbonate synthesis route [11]. The two powders were well indexed to the layered-layered composite Li_2MnO_3–$LiMO_2$ with no additional diffraction peaks observed (Fig. 3). Weak peaks at 2θ of 21–25° that were not indexed to the $R\bar{3}$ m symmetry were consistent with cation ordering that occurs in the transition metal layer [12]. The two diffraction patterns overlay nearly identically, clearly demonstrating the mill-anneal synthesis approach yielded the desired layered-layered transition metal oxide.

In order to assess the efficacy of the milled-annealed cathode synthesis approach, four cells were constructed using a cathode made from simple mixture (without any milling or annealing)
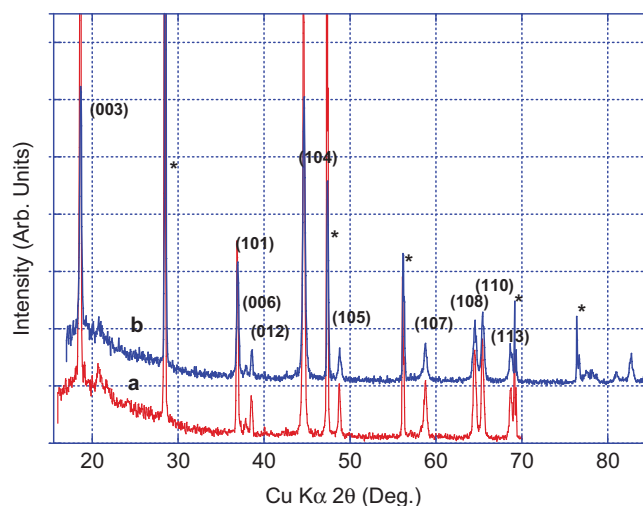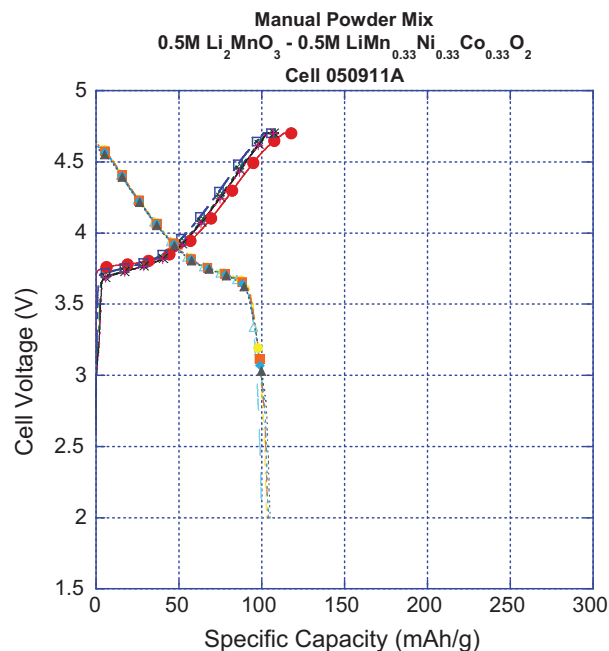

Fig. 4. Representative cell data of specific charge and discharge capacities at C/20 charge/discharge rate for the first five cycles of a cathode prepared from a simple mixture (without ball milling and annealing) of 0.5 M Li_2MnO_3–0.5 M $LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$.

of 1:1 ratio of Li_2MnO_3:$LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$ powders blended by hand. Representative charge and discharge specific capacities for five cycles at room temperature and at approximately C/20 charge/discharge rate are shown in Fig. 4. The specific discharge capacity even at the comparatively low rate yields no more than about 100 mAh g^{-1}, well below that of 240–280 mAh g^{-1} typically observed for the layered-layered Li_2MnO_3–$LiMO_2$ cathode systems. The charge and discharge curves have a sloping profile between 3.7–4.7 V, and weak plateau at about 3.7 V, not unlike what could be expected for a simple 1:1 mixture of the generally inactive Li_2MnO_3 and the $LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$ with a charge/discharge plateau near 3.9 V. These cycling data demonstrates that a simple
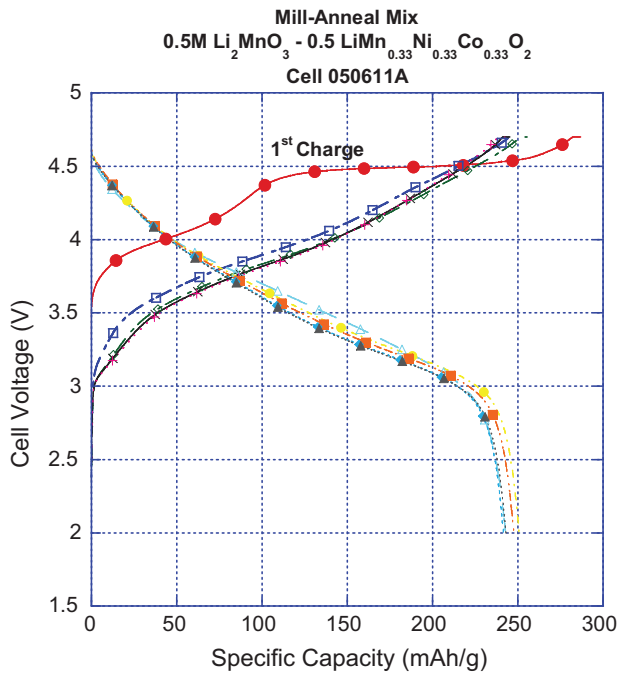
Fig. 5. Representative cell data of specific charge and discharge capacities at $C/25$ for the first five cycles of a cathode prepared by ball milling and annealing of 0.5 M Li_2MnO_3–0.5 M $LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$.

Fig. 6. Specific discharge capacity as a function of temperature and charge/discharge rate of uncoated milled-annealed 0.5 M Li_2MnO_3–0.5 M $LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$ and 2 wt% $AlPO_4$ coated milled-annealed 0.5 M Li_2MnO_3–0.5 M $LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$. Cell data represent an average of four cells for the uncoated cathodes and an average of five cells for the $AlPO_4$ coated cathodes.

mixture of the two parent compounds does not afford the desired electrochemically active cathode material.

In contrast, cells constructed using a cathode made from a milled and annealed 1:1 ratio of Li_2MnO_3:$LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$ had markedly different charge/discharge profiles and much greater specific capacities. As shown in Fig. 5, on the first charge cycle there was a well-defined 4.5 V charge plateau that did not appear on any subsequent charging cycles. This first cycle 4.5 V charge plateau is a characteristic feature of the layered-layered composite Li_2MnO_3–$LiMO_2$ material system, and is widely attributed to the removal of oxygen from the cathode accompanied by diffusion of transition metal ions from surface to bulk where they occupy vacancies created by lithium removal [13]. The discharge specific capacity at approximately $C/25$ rate was about 250 mAh g^{-1}, commensurate with that of the targeted composition $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ as prepared by conventional synthesis approaches.

Based on the above promising results demonstrating that the mill-anneal synthesis could provide the targeted tap density, crystal structure, and electrochemical performance, further improvements in the material were sought by means of adding a passive coating to the milled-annealed cathode powders. It has been widely reported that adding a coating of metal oxides, phosphates, fluorides on the layered-layered composite
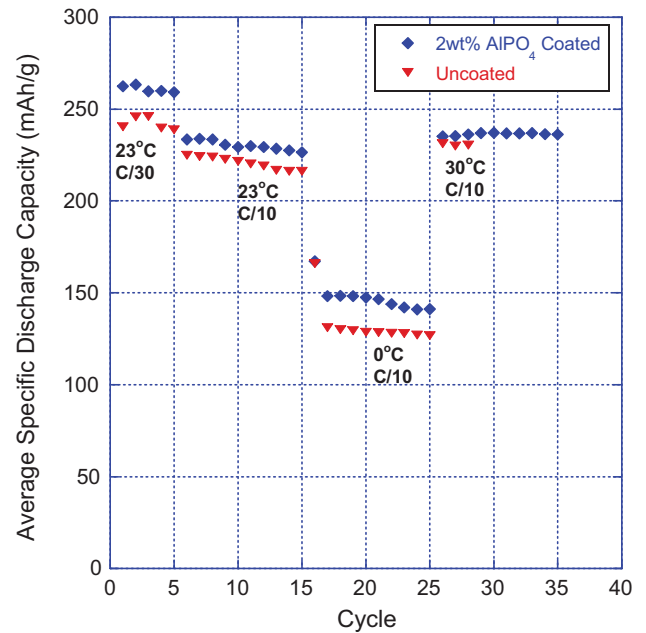
Li_2MnO_3–$LiMO_2$ cathode materials can result in reduction of the first cycle irreversible capacity as well as improved low temperature performance, rate capability, and cycle life [14–18]. Cells were built using cathodes prepared from powders with and without 2 wt% $AlPO_4$, all from cathode powders synthesized by the milled-annealed process with the 0.5 M Li_2MnO_3–0.5 M $LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$ stoichiometry. These cells were cycled through a range of temperatures and rates to directly compare the performance of the cathodes with and without the $AlPO_4$ coating.

Fig. 6 summarizes the comparison in performance in terms of discharge specific capacity of the uncoated and $AlPO_4$ cathode powders. These data represent the numeric average of four cells for the uncoated variant and five cells for the $AlPO_4$ coated variant as the cells were cycled through room temperature low rate formation conditions, $C/10$ rate at room temperature, $0 °C$ $C/10$ rate cycling, and $30 °C$ $C/10$ rate cycling. This cycling routine was employed to assess the sensitivity of the cathode performance to active thermal cycling. Based on these data, clear improvements appear to have been achieved at all temperatures and rates when the $AlPO_4$ coating was employed. To validate this trend, quantitative statistical tests (unpaired t-test) were carried out to eliminate observer bias and to assess the statistical significance of the trends. These data are summarized in Table 1. In all cases, the P value of the t-test was

Table 1
Summary of cycling statistical data for cells incorporating milled-annealed cathodes with and without $AlPO_4$ coatings.

Charge/discharge rate	Test temperature (°C)	Mean specific discharge capacity (mAh g^{-1})	Unpaired t test P-value
≈$C/30$	23	Uncoated: 242 2 wt% $AlPO_4$ Coated: 261	<0.0001
$C/10$	23	Uncoated: 221 2 wt% $AlPO_4$ Coated: 230	<0.0001
$C/10$	0	Uncoated: 129 2 wt% $AlPO_4$ Coated: 145	<0.0001
$C/10$	30	Uncoated: 231 2 wt% $AlPO_4$ Coated: 236	<0.0039

less than 0.0039 which showed the improvement associated with the $AlPO_4$ can be considered a statistically significant effect.

4. Conclusions

Layered-layered composite Li_2MnO_3–$LiMn_{0.33}Ni_{0.33}Co_{0.33}O_2$ cathode powders have been prepared by a ball milling and annealing process. Resultant cathode powders have been characterized in terms of crystallography and powder morphology relative to the parent compounds, and electrochemically evaluated in comparison to simple mixtures of the parent compounds. The milled-annealed powders have the layered-layered crystal structure, first cycle 4.5 V charge plateau, and specific capacity of about 250 mAh g^{-1} between 4.7 and 2 V. These characteristics are entirely consistent with the formation of the layered-layered composite Li_2MnO_3–$LiMO_2$ cathode system as prepared by conventional sol–gel or co-precipitation methods. Further improvements in the cathode performance in terms of specific discharge capacity could be obtained by the addition of a 2 wt% $AlPO_4$ coating applied to the powder after synthesis. Furthermore, the mill-anneal process yields reasonably good tap density of 2.0 g cm^{-3} while providing a means to easily vary the composition, powder morphology, and degree of intermixing of the parent compounds.

Acknowledgements

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