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OLIVINE COMPOSITE CATHODE MATERIALS FOR IMPROVED LITHIUM ION BATTERY PERFORMANCE

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ABSTRACT

Composite cathode materials in lithium ion batteries have become the subject of a great amount of research recently as cost and safety issues related to LiCoO_2 and other layered structures have been discovered. Alternatives to these layered materials include materials with the spinel and olivine structures, but these present different problems, e.g. spinels have low capacities and cycle poorly at elevated temperatures, and olivines exhibit extremely low intrinsic conductivity. Previous work has shown that composite structures containing spinel and layered materials have shown improved electrochemical properties. These types of composite structures have been studied in order to evaluate their performance and safety characteristics necessary for use in lithium ion batteries in portable electronic devices, particularly hybrid-electric vehicles. In this study, we extended that work to layered-olivine and spinel-olivine composites. These materials were synthesized from precursor salts using three methods: direct reaction, ball-milling, and a core-shell synthesis method. X-ray diffraction spectra and electrochemical cycling data show that the core-shell method was the most successful in forming the desired products. The electrochemical performance of the cells containing the composite cathodes varied dramatically, but the low overpotential and reasonable capacities of the spinel-olivine composites make them a promising class for the next generation of lithium ion battery cathodes.

INTRODUCTION

Lithium ion battery materials have recently become the subject of intense research interest. The use of these batteries in numerous portable devices, including mobile phones, laptop computers and medical devices has increased the demand for performance improvement. This demand is augmented by the potential use of lithium ion batteries for electric and hybrid electric vehicles where replacing the currently used nickel metal hydride batteries would provide the same performance but using only 20% of the space. For these large number of cell applications, the performance of lithium ion batteries is limited by abuse tolerance issues and the desire for higher energy storage capacities.

Attempts at improving the capacity of these batteries have historically focused on synthesizing and developing more lithium rich cathode materials. The presently used commercial cathode is a material with a layered structure, LiCoO_2 , and is shown in Figure 1. Layered structures are useful for applications requiring high energy

because they have a relatively high ratio of transition metal to lithium and they typically display good lithium diffusion properties. The energy of a cell is related to its ability to cycle large amounts of lithium over a long period, as opposed to the power of a cell, which is related to the rate at which lithium can be extracted. Most applications of the lithium ion batteries require high-energy batteries (e.g. laptops, mobile phones); however, the use of lithium ion batteries in

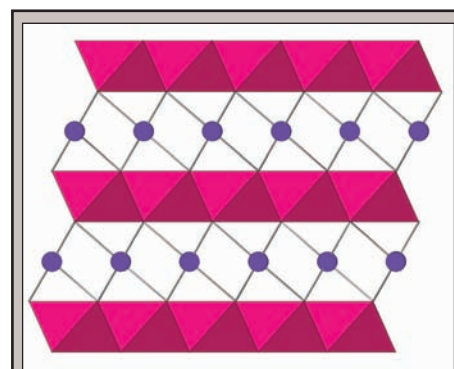


Figure 1. The structure of LiCoO_2 . The blue spheres are Li cations, the red polyhedra represent cobalt centered octahedra.

hybrid-electric vehicles would require a battery that can also deliver excellent power.

There are several issues related to the continued use of LiCoO_2 , specifically its relatively low cycling capacity of 140 mAh/g [1], and, more importantly, the rising price of cobalt. Structural analogues containing nickel, manganese, and several combinations thereof have been studied as possible alternatives to LiCoO_2 , but each of these materials presents different problems. LiNiO_2 has serious safety issues, namely at top of charge it can violently release oxygen. LiMnO_2 , due in part to the Jahn-Teller nature of the Mn(III) cation, is unstable to delithiation, rapidly converting on cycling to a material with the three-dimensional spinel structure [1].

Spinel provides much faster cycling (higher power) than layered structures because of the three-dimensional structure, which ushers lithium ions into and out of the cell more efficiently while maintaining electronic conduction via the three-dimensional lattice. The use of the spinel LiMn_2O_4 (or $\text{Li}_{1-x}\text{Mn}_{2-x}\text{O}_4$) as a cathode material offers a higher power alternative to layered structures. Figure 2 displays the structure of a spinel. Although it is a cheaper and more powerful alternative to LiCoO_2 , spinels have a lower capacity (100-120

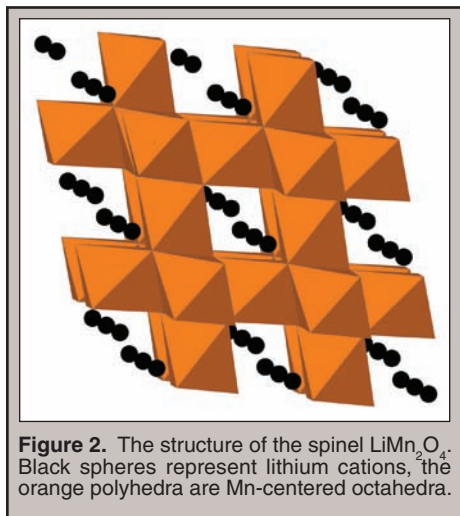


Figure 2. The structure of the spinel LiMn_2O_4 . Black spheres represent lithium cations, the orange polyhedra are Mn-centered octahedra.

mAh/g) and show poor cycling characteristics at elevated temperatures due to dissolution problems [2]. Another low-cost alternative to LiCoO_2 is the olivine LiFePO_4 , the structure is shown in Figure 3. It can be made using simple low cost starting materials and provides a higher energy alternative (LiFePO₄ typically delivers 160 mAh/g; a ~15% improvement) to the layered materials. Because of its three-dimensional structure, the volume change that occurs upon intercalation and deintercalation of lithium ions in olivine is smaller than in layered structures, resulting in increased electrode stability upon subsequent cycling. Additionally, there are less abuse tolerance concerns related to the energetic release of oxygen gas, as the $[\text{PO}_4]_3$ group will not release oxygen under operating conditions. Unfortunately, incorporating the phosphate anion also makes olivine a very poor electrical conductor in comparison to other electrode materials [3]. In order to promote its utility as a cathode material, the conductivity of olivine must be increased. This has been addressed mainly by surface coating nano-sized materials with a conductive carbon or slightly reducing the surface to create a coating of highly conductive FeP_x or Fe_3O_4 [3, 4].

The purpose of this study was to improve the limited capacity of lithium ion batteries by developing layered-olivine and spinel-olivine composites that could serve as safe, cheap and effective cathode

materials. The composite structures should produce a stabilizing effect on the cathode, allowing more lithium to be intercalated and deintercalated without encountering the thermodynamically driven structural collapse that occurs when too much lithium is extracted, while the spinel (or layered) component would increase the average conductivity of the sample. Three different approaches were taken in an attempt to synthesize these composites materials: direct reaction, ball milling and the core-shell approach. Materials were analyzed by X-Ray Diffraction and tested in half cells (vs. Li) for electrochemical performance.

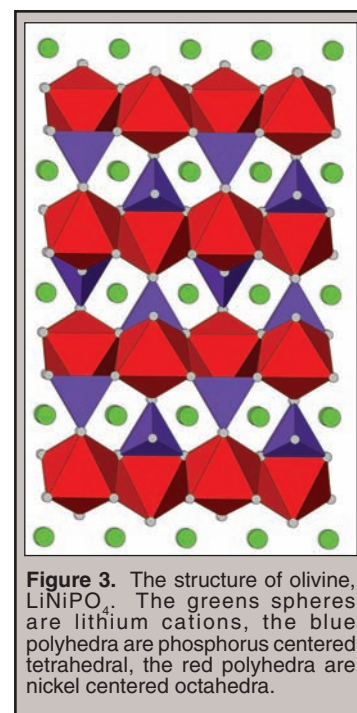


Figure 3. The structure of olivine, LiNiPO_4 . The green spheres are lithium cations, the blue polyhedra are phosphorus centered tetrahedral, the red polyhedra are nickel centered octahedra.

MATERIALS AND METHODS

The first method employed to synthesize layered-olivine composites was the direct reaction of precursor materials with the general stoichiometry $x\text{LiNiPO}_4 \cdot y\text{Li}(\text{Ni}_{0.5}\text{Mn}_{1.5})\text{O}_4$ and $x\text{LiNiPO}_4 \cdot y\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2$ ($x = 0.9, 0.5$; $y = 0.1, 0.5$). Physical mixtures of Li_2CO_3 , $\text{Ni}(\text{OH})_2$, MnCO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$, $(\text{CH}_3\text{CO}_2)_2\text{Mn} \cdot 4\text{H}_2\text{O}$ were prepared and ground by hand, and then fired to either 400 °C or 800 °C. The resultant powders were analyzed using X-Ray diffraction. Laminates containing the composite materials were made using 80% active material, 10% PVDF binder (Kureha), 5% acetylene black (Chevron C-55), and 5% carbon fiber (Osaka Gas) on aluminum foil. Cells were constructed in an argon-filled glovebox using a lithium metal anode, LP-40 electrolyte (50% EC (ethylene carbonate)/ 50% wt DEC (diethyl carbonate), 1 M LiPF_6 , Merck KG), and a Celgard polyethylene / polypropylene separator using methods described previously by the Argonne group [1].

The second technique utilized to prepare the same four composite stoichiometries outlined above was high energy ball milling. The same precursors were ground together and heated to 400 °C for 12 hrs in air. The materials were then broken down vigorously in the ballmill for approximately two hours. After processing, the materials were laminated and cells were constructed as described above.

The third procedure for producing composite materials was a core-shell synthetic method, which was used to synthesize both layered-olivine and spinel-olivine materials. The composites being made are listed in Table 1. Precursor salts, $(\text{CH}_3\text{CO}_2)_2\text{Co} \cdot 4\text{H}_2\text{O}$, $(\text{CH}_3\text{CO}_2)_2\text{Mn} \cdot 4\text{H}_2\text{O}$, $(\text{CH}_3\text{CO}_2)_2\text{Ni} \cdot 4\text{H}_2\text{O}$, $\text{CH}_3\text{CO}_2\text{Li} \cdot 2\text{H}_2\text{O}$, were dissolved in ethanol and stirred constantly using a magnetic stirring bar. The individual stoichiometries were set to yield the compounds LiCoO_2 , $\text{Li}_4\text{Mn}_5\text{O}_{12}$, and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. LiNiPO_4

Composite	XRD Analysis	Cycling Cap. (mAh/g)	Theoretical Cap. (mAh/g)
10% LiNiO ₂ / 90% LiNiPO ₄	(LiNi)O ₂ , LiNiPO ₄	40	30
10% LiMn ₂ O ₄ / 90% LiNiPO ₄	LiMn ₂ O ₄ , LiNiPO ₄	30	30
50% LiNiO ₂ / 50% LiNiPO ₄	(LiNi)O ₂ , LiNiPO ₄	125-150	150
50% LiMn ₂ O ₄ / 50% LiNiPO ₄	LiMn ₂ O ₄ , LiNiPO ₄	160	150
80% LiCoO ₂ / 20% LiNiPO ₄	LiCoO ₂ , LiNiPO ₄	20-40	120
80% Li ₄ Mn ₅ O ₁₂ / 20% LiNiPO ₄	Li ₄ Mn ₅ O ₁₂ , LiNiPO ₄	120-140	130
80% LiNi _{0.5} Mn _{1.5} O ₄ / 20% LiNiPO ₄	LiNi _{0.5} Mn _{1.5} O ₄ , LiNiPO ₄	120-130	120
50% LiCoO ₂ / 50% LiNiPO ₄	LiCoO ₂ , LiNiPO ₄	90	75
50% Li ₄ Mn ₅ O ₁₂ / 50% LiNiPO ₄	Li ₄ Mn ₅ O ₁₂ , LiNiPO ₄	90	85
50% LiNi _{0.5} Mn _{1.5} O ₄ / 50% LiNiPO ₄	LiNi _{0.5} Mn _{1.5} O ₄ , LiNiPO ₄	80	80

Table 1. Results of the core-shell method for synthesis of layered-olivine and spinel-olivine composite materials (assuming LiNiPO₄ is inactive in the testing window).

was made separately by heating a stoichiometric mixture of Li₂CO₃, (CH₃COO)₂Ni • 4H₂O, and NH₄H₂PO₄ at 800 °C for two days with one intermittent grinding. After analysis by powder XRD, the resulting material was then ground to a fine powder and sifted to remove any particles larger than 63 microns. This powder was added to the ethanol solution, stirred, and heated until dryness. The resultant powder was ground by hand and heated to 400 °C in air. Laminates and cells were constructed as described above.

Cells were tested on a Maccor battery cycling station, discharging and charging in a specified voltage window under constant current. A typical cycling window was 4.8 – 2.0 V (vs Li) using a 0.1 mA current. The amount of lithium passed between the electrodes as well as voltage profiles was monitored by the Maccor cycling software during charge and discharge of the electrochemical cell.

RESULTS AND DISCUSSION

Direct reaction synthesis and high energy ball milling — Several attempts were made to synthesize composite material with the general stoichiometry $x \text{LiNiPO}_4 \cdot y \text{Li}(\text{Ni}_{0.5}\text{Mn}_{1.5})\text{O}_4$ and $x \text{LiNiPO}_4 \cdot y \text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2$ ($x = 0.9, 0.5; y = 0.1, 0.5$). Lithium can only be extracted from LiNiPO₄ above 5.2 V (vs Li) but it was chosen for this study primarily because it is one of the few lithium olivine materials that can be synthesized in air. Analysis of powder X-Ray diffraction results for the composite direct reaction or ball milled samples revealed that all were a complex mixture of phases, rather than actual composites of an olivine (LiNiPO₄) and a layered or spinel structure. Figure 4 shows a typical XRD spectrum for these mixed phase materials, specifically the LiNiPO₄ / LiNi_{0.5}Mn_{0.5}O₂ (50/50%) for the 400 and 800 °C samples. All of the materials synthesized by this method were found to be physical mixtures of

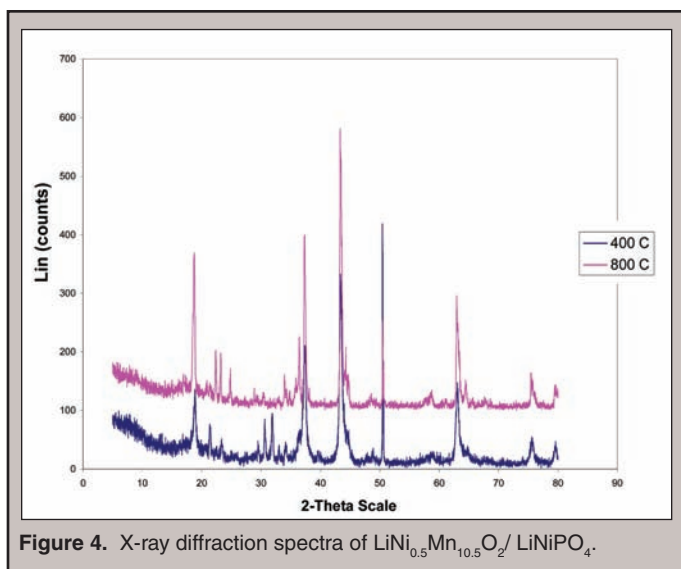


Figure 4. X-ray diffraction spectra of LiNi_{0.5}Mn_{0.5}O₂/LiNiPO₄.

(Li,Ni)O₂, Ni₃(PO₄)₂, Li₃PO₄, Li(Ni,Mn)O₂, MnP₂O₇, and Li₂CO₃. Electrochemical and powder XRD analysis of the materials subjected to high energy ball-milling showed no significant differences between those samples and the ones produced by direct reaction.

The limiting factor in the formation of the layered-olivine composites in the direct reaction method appeared to be the formation of LiNiPO₄. The complex reaction mixture placed in the oven had three cations and two anions, from which the layered-olivine composite was expected to form. It appears that binary phosphates are too stable with respect to ternary phosphates at the stoichiometries loaded, resulting in Li₃PO₄ and Ni₃(PO₄)₂ to be formed preferentially over the desired LiNiPO₄ in the presence of Mn and excess oxide. This physical mixture of components is responsible for the poor electrochemical performance of the cells. The disordered structure of the cathode and the uneven dispersal of compounds with different electrical and ionic conductivities caused poor cycling demonstrated by the cells.

Core-shell synthesis method — Table 1 presents information on the materials synthesized using the core-shell type method. The 50/50 LiNiO₂ and LiMn₂O₄ composites materials performed much better than the 10/90 composites, as expected, and is shown in Figure 5. Though the cycling efficiency of these cells was lower than for the 10/90 composites, the capacities were significantly

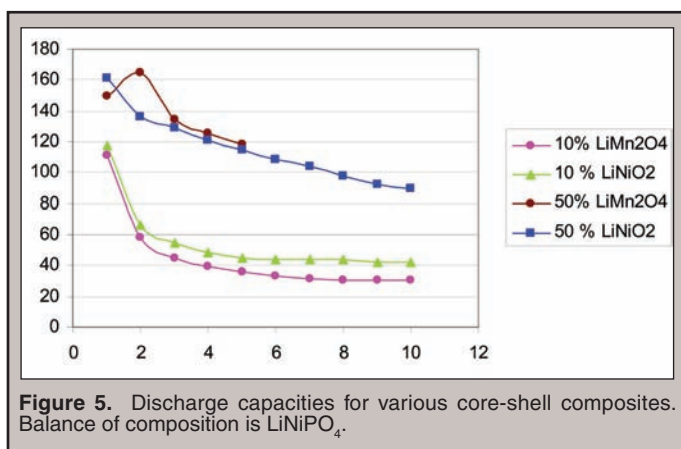


Figure 5. Discharge capacities for various core-shell composites. Balance of composition is LiNiPO₄.

higher. Both sets of materials cycled near their theoretical values, assuming the LiNiPO_4 component was electrochemically inactive in the voltage window used. The $\text{LiNiO}_2/\text{LiNiPO}_4$ cell had the highest capacity, ranging from 125-150 mAh/g, while the $\text{LiMn}_2\text{O}_4/\text{LiNiPO}_4$ performed the best, with an initial capacity of 160 mAh/g and a fade rate of only 3-4 % per cycle. The time profile for this sample is shown in Figure 6, during charge reveals two plateaus, one around 3 V corresponding to the extraction of the first Li-ion

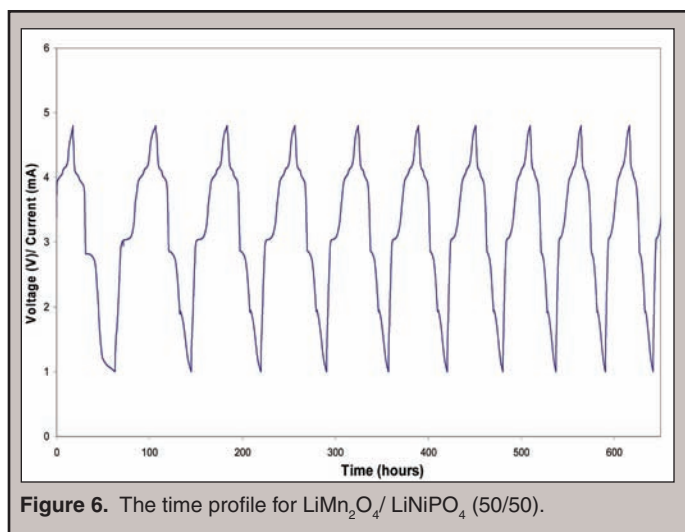


Figure 6. The time profile for $\text{LiMn}_2\text{O}_4/\text{LiNiPO}_4$ (50/50).

from the fully charged material $\text{Li}_2\text{Mn}_2\text{O}_4$, resulting in a LiMn_2O_4 cathode material, and the second around 4.2 V corresponding to the extraction of a second Li-ion, forming Mn_2O_4 [5]. The plateaus for intercalation and deintercalation occur at nearly the same voltages, representing a small overpotential, which suggests the electrical conductivity was not seriously hindered by the underlying insulating phosphate. For many of these materials the initial first cycle capacity exceeded theoretical capacity. This is usually associated with one time side reactions between the electrode and electrolyte, current collector passivation, and reactions between amorphous phases in the electrode and lithium.

The improved electrochemical performance of the samples prepared using the core-shell synthesis method as compared to those produced by the direct reaction method suggests more structured products. The x-ray diffraction patterns for the layered-olivine and spinel-olivine composites are featured in Figure 7 and 8, respectively. Figure 9 shows the hypothetical composite structure of the layered-olivine composite. Figures 10 and 11 show the first three cycles of some representative spinel-olivine composites. The lattice constants for all of the spinels formed in this study are shown alongside the literature lattice constants in Table 2. Lattice constants were determined by full pattern fitting and analysis using the Rietveld method. The lattice constants of the spinel coating help give a better idea of the exact Li/Mn distribution over the various possible lattice sites when compared to literature precedent.

In general the $\text{LiCoO}_2/\text{LiNiPO}_4$ composites, ideally layered-olivine composites, showed poor electrochemistry. Both the 80/20 and 50/50 composites showed poor capacity retention. Over 50 cycles, the capacity of the 80/20 sample dropped from 55 to

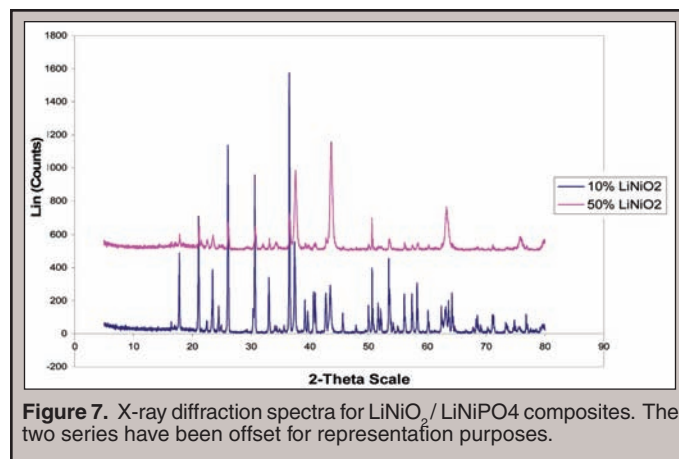


Figure 7. X-ray diffraction spectra for $\text{LiNiO}_2/\text{LiNiPO}_4$ composites. The two series have been offset for representation purposes.

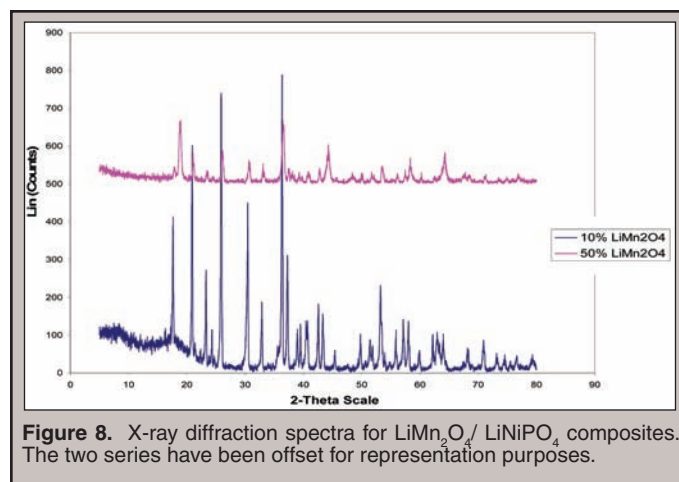


Figure 8. X-ray diffraction spectra for $\text{LiMn}_2\text{O}_4/\text{LiNiPO}_4$ composites. The two series have been offset for representation purposes.

20 mAh/g, while the 50/50 sample showed an initial capacity of 95 mAh/g, but faded quickly. The powder x-ray diffraction analysis for this material indicated that the synthesized material contained the expected product, LiCoO_2 coated with LiNiPO_4 , however some ambiguity exists in determining the exact form of the LiCoO_2 formed [6].

The poor performance of these cells could reflect the poor crystallinity of the coating material. The synthesis of LiCoO_2 , which involved the firing of the precursor materials to 400 °C, is well below the temperature at which LiCoO_2 is usually synthesized (700 °C), and can result in a poorly ordered sample. At these temperatures several other structures with inferior electrochemical properties have been reported with the same ratio of lithium to cobalt, notably $\text{Li}_2[\text{Co}_2]\text{O}_4$ or $(\text{Li},\text{Co})_2[\text{Co}_2]\text{O}_4$ spinels [6]. At the concentration levels used in this study, it would be difficult to distinguish a spinel structure from the desired layered structure by powder XRD as many of the main

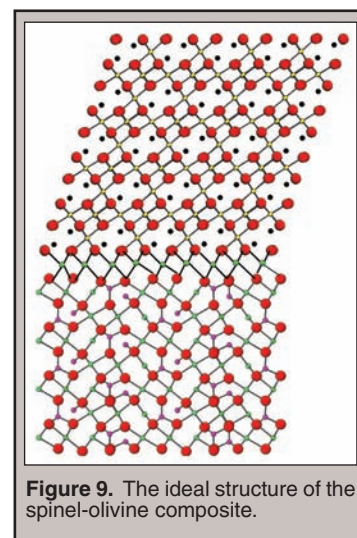


Figure 9. The ideal structure of the spinel-olivine composite.

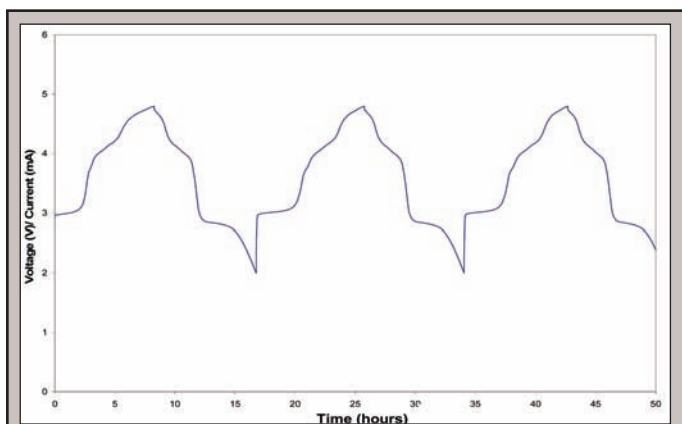


Figure 10. The time profile for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 / \text{LiNiPO}_4$ (80/20).

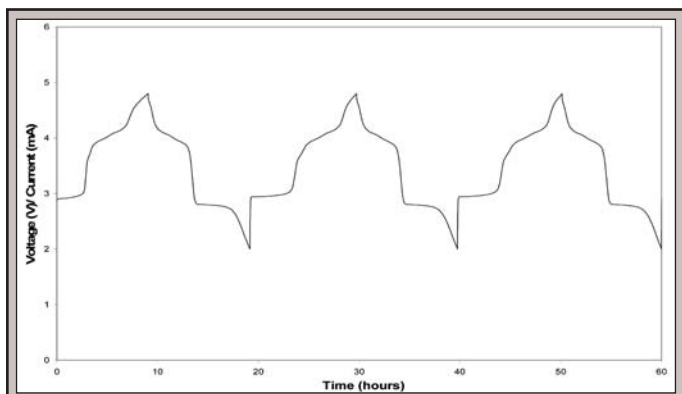


Figure 11. The time profile for $\text{Li}_4\text{Mn}_5\text{O}_{12} / \text{LiNiPO}_4$ (50/50).

diagnostic peaks overlap. The low-temperature synthetic method used may have yielded a disordered or non-uniform coating material, resulting in poor electrical and ionic conductivity. It is very possible that the optimization of this composite material could produce a good cathode material for Li-ion batteries, possibly by annealing the material at a higher temperature.

The $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 / \text{LiNiPO}_4$ composite produced using the core-shell synthesis method performed much better than the LiCoO_2 composite. The x-ray analysis for this data indicated that the product was the intended $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel coating on LiNiPO_4 . The time profile for the battery made with this composite material featured the two plateaus for the deinsertion of lithium at 3 V and 4 V, much like the LiMn_2O_4 composite, but with added capacity above 4.5 V (vs Li) indicative of the mixed Ni-Mn spinel and inclusion of some electrochemically active Ni(II) [7]. Figure 10 shows the time profile for the 80/20 composite. Furthermore, this material showed the same low overpotential as the spinel composite. The 50/50 composite showed a low but stable capacity, and the 80/20 composite had about the same capacity as a commercial LiCoO_2 cathode, but in a larger voltage window.

The final composite material synthesized and tested in this study was the $\text{Li}_4\text{Mn}_5\text{O}_{12} / \text{LiNiPO}_4$ composite [8]. This composite is another spinel-olivine composite, and had a time profile very similar to that of LiMn_2O_4 , as shown in Figure 11. This lithium rich Mn (IV) spinel is supposed to have all of its capacity at 3V, instead of a two plateaus at 3V and 4V as seen for LiMn_2O_4 . Although by XRD analysis it has a lattice constant closer to that reported for

Composite	Experimental Lattice Constant (Å)	Literature Lattice Constants (Å)
50% $\text{LiMn}_2\text{O}_4 / 50\% \text{LiNiPO}_4$	8.189(2)	8.244
80% $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 / 20\% \text{LiNiPO}_4$	8.148(1)	8.173
50% $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 / 50\% \text{LiNiPO}_4$	8.174(2)	8.173
80% $\text{Li}_4\text{Mn}_5\text{O}_{12} / 20\% \text{LiNiPO}_4$	8.139(2)	8.135
50% $\text{Li}_4\text{Mn}_5\text{O}_{12} / 50\% \text{LiNiPO}_4$	8.155(2)	8.135

Table 2. Table of spinel coating lattice constants.

$\text{Li}_4\text{Mn}_5\text{O}_{12}$, its electrochemistry is much more similar to LiMn_2O_4 . The exact reason for these discrepancies is not known at this time. The batteries produced using this $\text{Li}_4\text{Mn}_5\text{O}_{12} / \text{LiNiPO}_4$ composite as a cathode material behaved much like the batteries with the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 / \text{LiNiPO}_4$ composite cathode. The 50/50 composite showed a capacity just above that of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ 50/50, as did the 80/20 composite. Both the 50/50 and 80/20 composites had low overpotentials.

CONCLUSIONS

Of the two primary composite synthesis methods presented in this paper, direct reaction and core-shell, the core-shell synthesis method was far more successful. The direct reaction method proved inadequate for compounds with such a complex mixture of constituent anion and cations, especially when the synthesis required the anion to form a specific ternary compound within a collection of so many choices. The core-shell method was particularly effective for the synthesis of spinel-olivine materials. The synthesis of layered-olivine structures proved more problematic, though it was still successful the majority of the time.

The layered-olivine composites in general showed high overpotentials, suggesting the conductivity of the underlying olivine may have been an issue and the coating may have not been complete. The disordered nature of the layered compounds synthesized makes the intercalation / deintercalation of lithium ions much more difficult. This overpotential issue is a major problem that must be addressed before such composite materials can be seriously considered for use in commercial lithium ion batteries.

Unlike the layered-olivine composites, the spinel-olivine composites show low overpotentials, which suggests the excellent conductivity of the spinel structure compensates for the insulating nature of the phosphate group, producing a sufficiently conductive material. The spinel-olivine composite materials also show capacities ranging from 100-160 mAh/g, which will be a viable operating capacity if the fade rate can be reduced. A major problem these cells present is cycling efficiency, which is higher for the spinel composites than for the layered composites. Despite this shortcoming, the low overpotentials, capacity, safety benefits and ease of production of

spinel-olivine composite materials could make them an ideal class of materials from which to build the cathodes of next generation of lithium ion batteries.

ACKNOWLEDGMENTS

This research was conducted at Argonne National Laboratory. RW thanks the U.S. Department of Energy, Office of Science for funding and the organization of the SULI program. Financial support from the Office of Basic Energy Sciences and the Office of FreedomCar and Vehicle Technologies of the U.S. Department of Energy under Contract No. W31-109-Eng-38 is gratefully acknowledged.

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