

Short communication

Theoretical evaluation of high-energy lithium metal phosphate cathode materials in Li-ion batteries

Wilmont F. Howard^{a,*}, Robert M. Spotnitz^b

^a Howard Battery Consulting, 2313 Laurelwood Terrace, Silver Spring, MD 20905, United States

^b Battery Design LLC, 2277 DeLucchi Drive, Pleasanton, CA 94588, United States

Received 3 December 2006; received in revised form 15 December 2006; accepted 19 December 2006

Available online 30 December 2006

Abstract

Lithium metal phosphates (olivines) are emerging as long-lived, safe cathode materials in Li-ion batteries. Nano-LiFePO₄ already appears in high-power applications, and LiMnPO₄ development is underway. Current and emerging Fe- and Mn-based intercalants, however, are low-energy producers compared to Ni and Co compounds. LiNiPO₄, a high voltage olivine, has the potential for superior energy output (>10.7 Wh in 18650 batteries), compared with commercial Li(Co,Ni)O₂ derivatives (up to 9.9 Wh). Speculative Co and Ni olivine cathode materials charged to above 4.5 V will require significant advances in electrolyte compositions and nanotechnology before commercialization. The major drivers toward 5 V battery chemistries are the inherent abuse tolerance of phosphates and the economic benefit of LiNiPO₄: it can produce 34% greater energy per dollar of cell material cost than LiAl_{0.05}Co_{0.15}Ni_{0.8}O₂, today's "standard" cathode intercalant in Li-ion batteries.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Li-ion battery; Olivine cathode material

1. Introduction

Since the commercialization of battery-active LiCoO₂ in 1980 [1], the breadth of cathode intercalation materials for Li-ion batteries has expanded to meet increasingly stringent demands for performance and safety. The layered rock-salt structures (including LiNiO₂ [2] and LiCo_xNi_{1-x}O₂ [3,4] derivatives) exhibit problematic stability with overcharge, are environmentally unfriendly, and have a relatively high cost. At first, spinel (Li_{1+x}Mn_{2-x}O₄, 0.05 ≤ x ≤ 0.13) seemed a viable alternative [5], but extensive industry evaluation revealed low capacities and rapid fade with cycling, especially above room temperature. Next-generation composite structures (solid solutions) of Li₂MnO₃ and Li(Co,Ni)O₂ [6–8] show high-energy output and improved thermal stability, although recent Co and Ni price escalations are worrisome.

A new class of intercalation compounds, phosphates (olivine structure) rather than oxides, has emerged that overcome many

of the weaknesses inherent to earlier cathode candidates. First defined by Goodenough's team in 1997 [9], these species, of general formula LiMPO₄, are characterized by nearly flat oxidation-reduction voltage curves, a distinct advantage in circuitry design. Further, olivines are resistant to overcharge and thermal degradation, and are inherently safer than oxides that may release oxygen at inopportune times. The robust covalent bonding of PO₄³⁻, however, reduces the compounds' ionic conductivities, and olivines require additional treatment with conductive aids to perform at reasonable capacities. In fact, LiFePO₄ is classified as a semiconductor, while LiMnPO₄ is an insulator [10].

Table 1 lists physical and electrochemical properties of existing and candidate battery-active intercalants. LiFePO₄ is the only commercial olivine, and must be calcined in an oxygen-free environment while particle surfaces are modified to incorporate a conductive layer of carbon [11] or Fe₃P [12]. This difficult synthesis has slowed process scale-up, thus restricting wide-spread evaluation and acceptance by the battery industry. LiMnPO₄ suffers from anisotropic Jahn-Teller distortion with delithiation [13], which reduces an already low conductivity and results in rapid capacity fade with cycling. Both LiCoPO₄ and LiNiPO₄ have upper charge voltage limits incompatible with present-day

* Corresponding author. Tel.: +1 3013840371.

E-mail addresses: batmatman@comcast.net (W.F. Howard), rspotnitz@batdesign.com (R.M. Spotnitz).

Table 1
Physical and electrochemical properties of Li-ion cathode intercalation materials [10,14,15]

Cathode material	Discharge voltage, V vs. Li ⁰	Theoretical capacity (mAh g ⁻¹)	True density (g cm ⁻³)	Diffusivity (cm ² s ⁻¹)
LiMnPO ₄	4.1	171	3.43	10 ⁻⁷
LiFePO ₄	3.4	170	3.60	10 ⁻⁸
LiCoPO ₄	4.8	167	3.70	10 ⁻⁹
LiNiPO ₄	5.1	167	3.89	10 ⁻⁵
Li _{1.07} Mn _{1.93} O ₄	3.9	117	4.15	~10 ⁻¹⁰
LiAl _{0.05} Co _{0.15} Ni _{0.8} O ₂	3.6	265	4.73	~10 ⁻⁸
LiCoO ₂	3.6	274	5.05	~10 ⁻⁸

electrolytes. Olivines offer attractive electrochemical performances: what can be done to reduce the barriers to utilization, especially in large-format batteries?

If diffusivity were the measure of cathode capability, the listings in Table 1 indicate LiNiPO₄ would be the optimum intercalant. Remember, however, that olivines allow only slow one-dimensional Li⁺ diffusion, layered Co/Ni compounds have diffusion planes (two-dimensional), and cubic spinels permit rapid three-dimensional Li⁺ transport. Delacourt et al. [16] made a critical observation when they prepared LiMnPO₄ by precipitation from aqueous solution: the resulting small particles (~100 nm) had significantly greater capacity at selected discharge rates than calcined size-classified material (5–10 μm). This is attributed to the shortened diffusion pathways in nanoparticles. More elegantly stated, a particle surface undergoes structural relaxation in response to the local environment (in this case, the electrolyte), and nanoparticle properties may be governed by the distance between the top and bottom surfaces [17].

Nanomaterials are widely touted as the solution to numerous problems associated with micron-sized cathode powders. Not only are near-theoretical capacities expected, possibly doubling energy output, but nano-sizing should enhance rate capability and reduce structural degradation, which translates into extended cathode working life. Li-ion batteries for power applications from A123 Systems and Altair Nano feature nano-intercalants in both electrodes: this paper is restricted to high-energy comparisons, including consideration of speculative olivine cathodes operating above 4.5 V.

2. Analysis

To assess the potential of lithium metal phosphate cathodes as a disruptive technology versus lithium metal oxide

cathodes in lithium-ion batteries, a theoretical comparison was made based on 18650-sized cells using Battery Design Studio[®] software (www.batdesign.com). For this analysis, we held the graphitic anode thickness constant at 172 μm (includes 12 μm thick copper foil), assigned a porosity of 25% for both electrodes, assumed an irreversible capacity loss of 10% during the first charge–discharge cycle, and allocated diameters of 4.9 mm for the mandrel and 17.8 mm for the jellyroll (i.e., the 18650 cell without the can). Equilibrium discharge curves for cathode materials were either estimated (metal phosphates) or provided by Battery Design Studio[®].

Cathode loadings were calculated using the true densities (from crystallographic data) and theoretical capacities of the intercalants (Table 1). The results for 18650 battery electrode parameters, from Battery Design Studio[®] software, are detailed in Tables 2 and 3. LiCoO₂ batteries provide the benchmark data. Table 4 contains cost information about cell materials, including chemicals and container components. Our cost estimations are loosely based on a 2000 study [18] from Argonne National Laboratory, updated to accommodate increasing Co and Ni prices and the gradual decrease of separator and electrolyte pricing.

Table 5 summarizes the major cost items associated with each cell chemistry, excluding the header, by combining pricing information with material weights from previous calculations. The four most costly cell items (cathode, anode, electrolyte and separator) account for 68–79% of the total cell cost, and the cathode (Co, Ni-based materials) or electrolyte (with Fe or Mn intercalants) are always the most expensive components. The cathode portion ranged from a low of 11.5% of the total materials cost (LiMnPO₄) to a high of 41% (LiCoO₂), while the electrolyte cost extended from 16% (with LiCoO₂) to 27% (with LiMnPO₄).

Cell electrochemical and cost figures are presented in Table 6, based on results in the previous five tables. Note that the average

Table 2
Calculated cathode properties of 18650 cells, assuming 25% coating porosity and 18 μm thick Cu current collector

Cathode parameters	Cathode material						
	NCA ^a	LiCoO ₂	LiMn ₂ O ₄	LiFePO ₄	LiMnPO ₄	LiNiPO ₄	LiCoPO ₄
Unit capacity (mAh cm ⁻²)	4.63	4.63	4.42	4.63	4.51	4.61	4.52
Thickness w/collector (μm)	159.2	208.6	304.9	258.3	267.0	247.4	257.5
Coated length (cm)	117.6	103.3	81.6	91.5	85.0	92.8	91.4
Coating thickness (μm)	70.6	95.3	143.4	120.2	124.5	114.7	119.7
Coating weight (g)	15.70	19.76	19.72	15.80	14.59	16.31	16.09
Total length (cm)	60.20	53.12	42.26	47.71	44.46	48.36	47.67

^a LiAl_{0.05}Co_{0.15}Ni_{0.80}O₂.

Table 3

Calculated anode properties of 18650 cells, assuming 25% coating porosity, 160 μm coating thickness and 12 μm thick Cu current collector

Parameters	Cathode material						
	NCA	LiCoO ₂	LiMn ₂ O ₄	LiFePO ₄	LiMnPO ₄	LiNiPO ₄	LiCoPO ₄
Unit capacity (mAh cm ⁻²)	4.17	4.17	3.96	4.17	4.05	4.15	4.06
Coated length (cm)	118.3	104.0	82.3	94.2	87.7	95.5	94.1
Coating weight (g)	9.31	8.19	6.48	7.42	6.91	7.52	7.41
Total length (cm)	64.24	57.12	46.26	52.21	48.96	52.86	52.17

Table 4

Material prices used for cell costing

Material	Units	US\$ Unit ⁻¹
LiMnPO ₄	kg	10.00
LiFePO ₄	kg	15.00
LiCoPO ₄	kg	25.00
LiNiPO ₄	kg	20.00
Li _{1.07} Mn _{1.93} O ₄	kg	10.00
LiAl _{0.05} Co _{0.15} Ni _{0.8} O ₂	kg	35.00
LiCoO ₂	kg	40.00
PVDF binder	kg	46.00
Carbon black	kg	10.00
Al foil	kg	20.00
Separator	m ²	2.00
Electrolyte	kg	60.00
Graphitic anode	kg	30.00
CMC binder	kg	5.00
Electrolytic Cu foil	kg	25.00
Can	Each	0.08
Header/misc	Each	0.15

PVDF, polyvinylidene fluoride; CMC, carboxymethylcellulose. Separator density = 11 g cm⁻².

Table 5

Major cost components of 18650 cells (excluding header)

Material	18650 Cell component cost (US\$)						
	NCA	LiCoO ₂	Spinel	LiFePO ₄	LiMnPO ₄	LiNiPO ₄	LiCoPO ₄
Cathode	0.523	0.751	0.187	0.213	0.131	0.294	0.362
Anode	0.274	0.240	0.191	0.218	0.203	0.221	0.218
Electrolyte	0.267	0.296	0.296	0.276	0.309	0.281	0.278
Separator	0.174	0.156	0.130	0.140	0.134	0.144	0.140

Table 6

Comparison of olivine and Li metal oxide systems in 18650 (16.53 cc) batteries and jellyroll cells (12.62cc)

18650 Cell properties	NCA	LiCoO ₂	LiMn ₂ O ₄	LiFePO ₄	LiMnPO ₄	LiNiPO ₄	LiCoPO ₄
Avg. voltage (V)	3.65	3.84	3.86	3.22	3.90	4.91	4.59
Capacity (Ah)	2.71	2.40	1.79	2.13	1.94	2.19	2.10
Energy (Wh)	9.90	9.22	6.92	6.86	7.57	10.73	9.65
Energy density (Wh kg ⁻¹)	219.8	193.3	154.3	162.9	186.4	250.2	227.4
Energy density (Wh L ⁻¹)	598.9	557.8	418.6	415.0	458.0	649.1	583.8
Weight (g)	45.05	47.69	44.84	42.12	40.61	42.89	42.43
Materials' cost (US\$)	1.628	1.824	1.159	1.219	1.139	1.314	1.370
Energy cost (Wh US\$ ⁻¹)	6.08	5.05	5.97	6.31	6.65	8.16	7.04
Jellyroll properties							
Energy density (Wh kg ⁻¹)	312.3	272.1	223.2	239.7	285.0	366.2	333.9
Energy density (Wh L ⁻¹)	784.5	730.6	548.3	543.6	599.8	850.2	764.7
Weight (g)	31.70	33.89	31.01	28.62	26.56	29.30	28.90

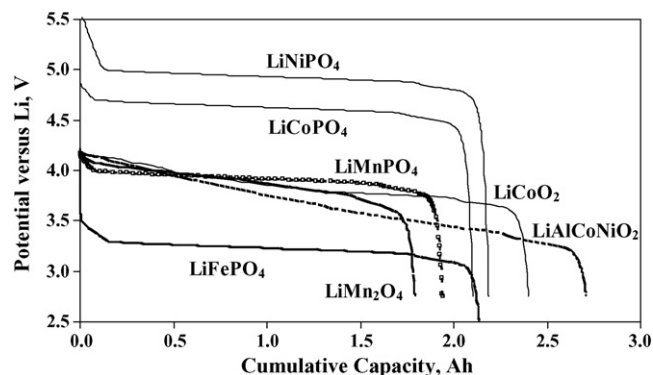


Fig. 1. Simulated discharge curves of various Li-ion cathode materials.

voltage entries are capacity-averaged potentials, as calculated by Battery Design Studio[®] software, and reflect the expected cell voltage, not the maximum potential. Jellyroll properties are included to highlight the reduction of cell energy density when container weights are included in the computations.

Figs. 1 and 2 visually compare the capacity and energy curves, respectively, for the seven cathode materials in this study.

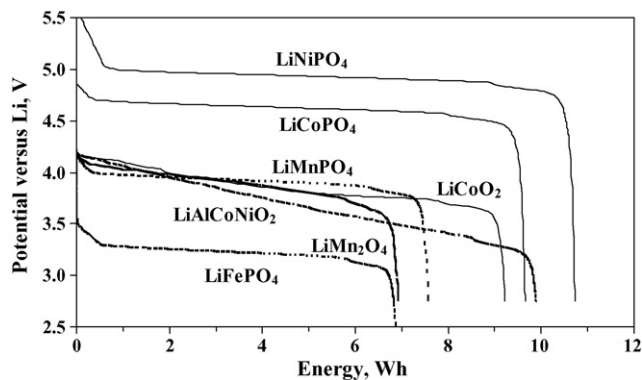


Fig. 2. Simulated voltage versus energy curves for 18650-size cells with selected Li-ion cathode materials.

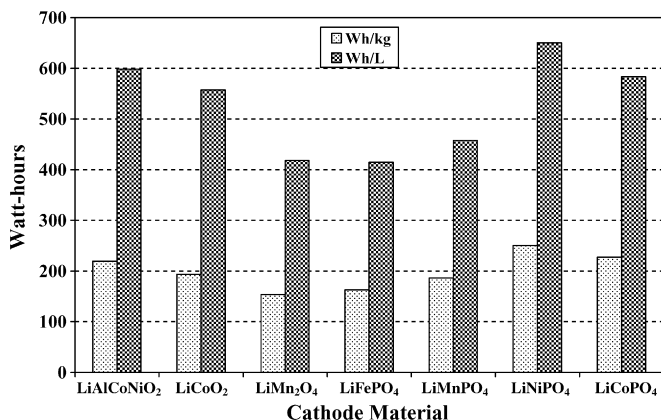


Fig. 3. Comparison of gravimetric and volumetric energy densities of 18650 batteries with commercial and next-generation cathodes.

Although batteries with $\text{LiAl}_{0.05}\text{Co}_{0.15}\text{Ni}_{0.8}\text{O}_2$ (NCA) cathodes have the highest capacity rating (2.7 Ah), projected LiNiPO_4 systems yield the greatest energy (10.7 Wh). Gravimetric and volumetric energy densities are presented in Fig. 3, clearly showing Co/Ni-based cathode materials with a substantial advantage over Mn/Fe intercalants. Finally, Fig. 4 compares energy output and costs for contemporary and speculative materials in 18650 formats. Cell materials costs were based on a 6-cell assembly to make the graph more readable.

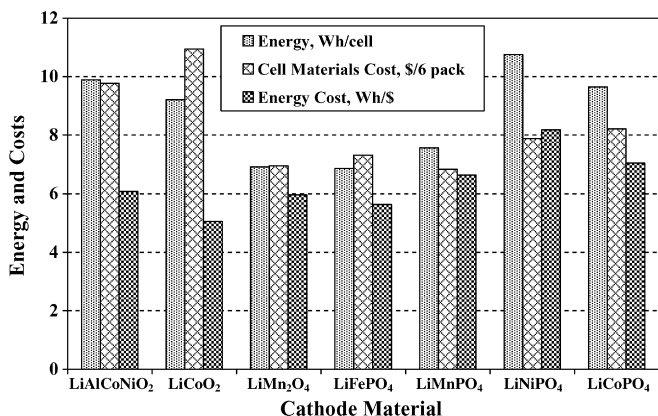


Fig. 4. Energy output and costs of 18650 batteries with targeted cathode materials.

3. Discussion

Cathode material capacity from each battery was computed from simulated low-rate discharges (Fig. 1), and ranged from 1.79 Ah ($\text{Li}_{1.07}\text{Mn}_{1.93}\text{O}_4$) to 2.71 Ah (NCA). The energies of the various 18650 cells were calculated by multiplying capacity-averaged cell voltage and capacity (Table 6), and are graphically presented in Fig. 2. Note that anode weights in Table 3 vary with the cathode, reflecting cell volume restrictions and the need to balance electrode capacities.

Interestingly, LiFePO_4 is energy-competitive with $\text{Li}_{1.07}\text{Mn}_{1.93}\text{O}_4$ (both ~ 6.9 Wh), due to the different discharge voltage plateaus. Given that spinel shows a lesser performance than LiCoO_2 in portable electronic applications, it is reasonable to speculate that LiFePO_4 will not compete for this application unless its superior abuse tolerance becomes an overriding positive. LiCoPO_4 cells were calculated to have 4.7% greater energy than LiCoO_2 batteries and 2.6% less than the lithium nickel cobalt aluminum oxide units. LiNiPO_4 , with 10.73 Wh, theoretically provides significantly more energy in 18650s than the layered NCA material. Of course, the high voltage of the LiCoPO_4 and LiNiPO_4 cells makes electrolyte stability problematic.

We also considered jellyroll electrodes alone to exclude the effect of the heavy packaging. Stated another way, a 12.62 cc jellyroll is the working portion of the battery and produces the same energy as a 16.53 cc 18650. As shown in Table 4, the gravimetric energy densities of jellyrolls average 45% more than the 18650s, while the volumetric densities are 31% greater. These calculations show the significant impact that cans and headers have on the energy ratings of 18650-size batteries.

If cell energy output were the only criterion, the Co/Ni-containing intercalants would be clear choices. Figs. 2 and 4 demonstrate the potential superiority of LiNiPO_4 cells (10.7 Wh). Even the worst of the group, LiCoO_2 (9.2 Wh), has substantially greater energy than the best of the Mn/Fe compounds (LiMnPO_4 , ~ 7.6 Wh). There are two constraints on these findings, however: electrochemical stability and material costs.

Safety is a primary concern with high-energy Li-ion cells: witness the extensive press over Sony's 2006 recall of laptop batteries. Phosphate olivines provide a tremendous advance in cathode stability, especially with overcharge. The oxygen atoms are strongly bound to phosphorous within the phosphate moiety and unavailable to oxidize the electrolyte solvents. Even though NCA and Li-rich spinel cathode materials are more stable than their predecessors, there is still the concern about thermal runaway and high-risk 'events' creating substantial liabilities for manufacturers. As these batteries increase in size, the potential for property damage and human injury increases, and charge voltage and thermal controls become essential. Such concerns are minimized with today's LiFePO_4 , and other battery-active olivines should have the same safety properties.

Judging a cathode material by its gravimetric capacity or energy output is misleading, however. Factoring in material density (and therefore cathode weight per each fixed volume cell) allows for a better metric, energy cost per unit ($\text{Wh US}\$^{-1}$,

based on the total cost of cell materials). This ratio permits price-conscious original equipment manufacturers to choose the most economic system. Fig. 4 indicates that LiFePO_4 is the optimum material ($6.3 \text{ Wh US}\$^{-1}$) in existing or emerging technologies, and although LiCoO_2 has relatively high-energy output, it is the least economical choice ($5.05 \text{ Wh US}\$^{-1}$). But what about next-generation systems?

Electrolytes stable from 0 to 5 V and beyond are already a possibility: asymmetric tetra-alkyl ammonium- $(\text{CF}_3\text{SO}_2)_2\text{N}$ ionic liquids are potential electrolyte solvents for high-energy Li-ion batteries [19]. Alternately, or perhaps in conjunction, cathode nanomaterials with minimal impedance may provide protection against electrochemical degradation above 4.5 V. The basis for this conjecture is that intercalation into nanoparticles is, *in extremis*, a surface reaction rather than a diffusion-limited process. Li-depleted (i.e., charged) cathode particles are essentially insulators, and the electron path of least resistance becomes the electrolyte solvent, which is reduced into various charged species that ultimately interfere with Li^+ transport at the anode. Nanomaterials, however, capably maintain electron flow across environmentally altered particle surfaces with minimal damage to surrounding species.

These arguments open up the possibility of LiCoPO_4 and LiNiPO_4 as high-energy but safe olivine cathodes. An 18650 cell containing 14.7 g of LiNiPO_4 could supply $>10.7 \text{ Wh}$ of energy, or over $8.1 \text{ Wh US}\$^{-1}$ of cell materials. This is 8% more energy produced at 34% less energy cost than today's standard, $\text{LiAl}_{0.05}\text{Co}_{0.15}\text{Ni}_{0.8}\text{O}_2$, and $>40\%$ cost advantage with 56% more energy compared to LiFePO_4 cells. Surprisingly, LiMnPO_4 , with 21.3% greater energy per gram, is not a strong displacement technology for LiFePO_4 . This is due to the substantially lower density of the Mn cathode material allowing less active ingredient per cell and the higher cost of Mn relative to Fe. Taking these factors into account, and assuming nearly complete Li de-intercalation during charge, LiMnPO_4 has only a 5.4% $\text{Wh US}\$^{-1}$ advantage over LiFePO_4 , while LiNiPO_4 stands to gain 30–55% over today's battery technologies.

4. Conclusions

Among current Li-ion battery systems, NCA outputs the most energy (9.9 Wh in 18650 units) while $\text{Li}_{1.07}\text{Mn}_{1.93}\text{O}_4$ and LiFePO_4 produce the least ($\sim 6.9 \text{ Wh}$). LiMnPO_4 , an olivine under development and with a theoretical capability of 7.6 Wh in an 18650 format, may be a disruptive technology against LiFePO_4 , although this is dependent on the manufacturing economics of phase-pure LiFePO_4 with a conductive coating versus nano-sized LiMnPO_4 . It is the yet to be developed LiNiPO_4 , however, that has the greatest potential energy performance

among the listed cathode materials, $\sim 10.7 \text{ Wh}$. This high voltage olivine will require significant advances in electrolytes (ionic liquids) and nanotechnology before attaining commercial acceptance.

A similar picture emerges when considering energy produced versus unit cost of materials in an 18650 cell. LiCoO_2 is the most costly cathode compound (only $5.05 \text{ Wh US}\$^{-1}$), but $\text{LiAl}_{0.05}\text{Co}_{0.15}\text{Ni}_{0.8}\text{O}_2$ is extremely competitive ($\sim 6.1 \text{ Wh US}\$^{-1}$) when compared to the other commercial materials, spinel ($\sim 6.0 \text{ Wh US}\$^{-1}$) and LiFePO_4 ($6.3 \text{ Wh US}\$^{-1}$). The greatest energy performance by a large margin is LiNiPO_4 , which we calculate at $8.16 \text{ Wh US}\$^{-1}$, albeit at a voltage outside the range of contemporary electrolytes. LiCoPO_4 , which operates at a slightly more forgiving charge profile, may be easier to commercialize, and the economics are superior to current 18650s (over $7 \text{ Wh US}\$^{-1}$). This, combined with the safety advantages of phosphates, should be sufficient incentives for strong development efforts in high-energy olivine-based batteries operating up to 5.1 V.

References

- [1] K. Mizushima, P.C. Jones, P.C. Wiseman, J.B. Goodenough, *Mater. Res. Bull.* 15 (1980) 783.
- [2] A. Nadiri, C. Delmas, R. Salmon, P. Hagenmuller, *Rev. Chim. Miner.* 21 (1984) 537.
- [3] C. Julien, *Ionics* 6 (2000) 30.
- [4] M. Kandi, Y. Tatebayashi, M. Sekino, Y. Isozaki, I. Mitsuishi, *Extended Abstracts of IMLB10 (2000) No. 231*.
- [5] M.M. Thackeray, P.J. Johnson, L.A. de Picciotto, P.G. Bruce, J.B. Goodenough, *Mater. Res. Bull.* 19 (1984) 179.
- [6] Z. Lu, D.D. MacNeil, J.R. Dahn, *Electrochem. Solid-State Lett.* 4 (2001) A191.
- [7] K. Numata, C. Sakaki, S. Yamanaka, *Chem. Lett.* (1997) 725.
- [8] M. Yoshio, H. Noguchi, J. Itoh, M. Okada, T. Mouri, *J. Power Sources* 90 (2000) 176.
- [9] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, *J. Electrochem. Soc.* 144 (1997) 1188.
- [10] A. Yamada, M. Hosoya, S.-C. Chung, Y. Kudo, K. Hinokuma, K.-Y. Liu, Y. Nishi, *J. Power Sources* 119 (2003) 232.
- [11] N. Ravet, Y. Chouinard, J.F. Magnan, S. Besner, M. Gauthier, M. Armand, *J. Power Sources* 97 (2001) 503.
- [12] P.S. Herle, B. Ellis, N. Coombs, L.F. Nazar, *Nat. Mater.* 3 (2004) 137.
- [13] A. Yamada, S.-C. Chung, *J. Electrochem. Soc.* 148 (2001) A960.
- [14] K. Amine, H. Yasuda, M. Yamachi, *Electrochem. Solid-State Lett.* 3 (2000) 178.
- [15] F. Zhou, M. Cococcioni, K. Kang, G. Ceder, *Electrochem. Commun.* 6 (2004) 1144.
- [16] C. Delacourt, P. Poizot, M. Morcrette, J.-M. Tarascon, C. Masquelier, *Chem. Mater.* 16 (2004) 93.
- [17] S. Kim, *Electrochem. Soc. Interface* 15 (2006) 28.
- [18] L. Gaines, R. Cuenca, "Costs of Lithium-Ion Batteries for Vehicles," Report #ANL/ESD-42, Argonne National Laboratory, May 2000.
- [19] J. Sun, D.R. MacFarlane, M. Forsyth, *Ionics* 3 (1997) 356.