

Short communication

Cathode materials: A personal perspective

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Abstract

A thermodynamically stable rechargeable battery has a voltage limited by the window of the electrolyte. An aqueous electrolyte has a window of 1.2 eV, which prevents achieving the high energy density desired for many applications. A non-aqueous electrolyte with a window of 5 eV requires Li^+ rather than H^+ as the working ion. Early experiments with Li_xTiS_2 cathodes showed competitive capacity and rate capability, but problems with a lithium anode made the voltage of a safe cell based on a sulfide cathode too low to be competitive with a nickel/metal-hydride battery. Transition-metal oxides can give voltages of 4.5 V versus Li^+/Li^0 . However, the challenge with oxides has been to obtain a competitive capacity and rate capability while retaining a high voltage with low-cost, environmentally friendly cathode materials. Comparisons will be made between layered $\text{Li}_{1-x}\text{MO}_2$, spinels $\text{Li}_{1-x}[\text{M}_2]\text{O}_4$, and olivines $\text{Li}_{1-x}\text{MPO}_4$ having $0 < x < 1$. Although higher capacities can be obtained with layered $\text{Li}_{1-x}\text{MO}_2$ compounds, which have enabled the wireless revolution, their metastability makes them unlikely to be used in power applications. The spinel and olivine framework structures have been shown to be capable of charge/discharge rates of over 10C with a suitable temperature range for plug-in hybrid vehicles. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

About 35 years ago, the price of oil jumped from \$8 per barrel to \$32 per barrel. This first energy crisis alerted everyone to the need for energy conservation and alternative energy technologies. However, the development of cost-competitive alternative technologies proved to be difficult, so the oil and automotive cartels were able soon to lull the politicians into complacency. Nevertheless, the scientific community was alerted, and with limited funding slow but steady progress has been made on several fronts.

The two principal alternatives to fossil fuels as an energy source are nuclear energy and solar/wind energy. Each of these requires energy storage, and the most versatile way to store energy is as chemical energy, which is why the nations are so addicted to fossil fuels. Although radiant solar energy can be stored biologically in plants and converted to a fuel such as ethanol, electrical energy from a nuclear, hydroelectric, or solar/wind power plant may be stored as chemical energy in the anode of a rechargeable battery or in H_2 by the electrolysis of water. If rechargeable batteries were to be distributed in plug-in hybrid electric cars, electrical energy could be stored in these

batteries during the off-peak power demand when commuters are sleeping; such a situation would provide an important alleviation of our dependence on oil. In pursuit of this goal, the development of the lithium rechargeable battery enabled the wireless revolution that now provides the funding for development of higher capacity and high-power batteries for a variety of applications that include the plug-in hybrid electric vehicle. The automotive industry that ignores this challenge will be swept aside as was the National Cash Register Co. by the advent of the digital computer.

My personal involvement with batteries began in the early 1970s when I was asked to referee a project of the Ford Motor Co. to develop a sodium–sulfur battery that used a ceramic Na^+ -ion electrolyte and liquid electrodes. While contemplating how to design a Na^+ -ion electrolyte, I came up with the idea of framework structures, which I called “skeleton” structures at the time [1]. One of the frameworks that I developed with Henry Hong [2] had as its framework the structure of hexagonal $\text{Fe}_2(\text{SO}_4)_3$; it is now known as the NASICON framework. I have used this framework to demonstrate the opening of the free volume for alkali-ion transport by polyanion substitution for the O^{2-} ion, the measurement of the relative positions of transition-metal redox couples, and the role of the Madelung energy and the inductive effect in determining these energies in a given solid [3]. However, I do not discuss these oxides here because cathodes with this framework do not appear to be competitive with those I do discuss,

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viz the layered LiMO_2 compounds, the spinels $\text{Li}[\text{M}_2]\text{O}_4$, and the olivines LiMPO_4 in which M is a transition-metal atom. Nevertheless, it was during these studies of polyanion substitution for the oxide ion that we came across the olivines [4], and $\text{Li}_{3-x}\text{V}_2(\text{PO}_4)_3$ is of potential interest as it has been reported to have a capacity of 170 mAh g^{-1} at a stepped insertion potential of 3.9–3.5 V versus Li at 0.5C [4a].

2. Why oxides

The working ion of a traditional rechargeable battery is the H^+ ion in an aqueous electrolyte, which restricts the range of thermodynamic stability to an open-circuit voltage of about 1.2 V. A non-aqueous Li^+ -ion electrolyte can sustain a thermodynamically stable open-circuit voltage of up to 5.0 V. In the early 1970s, Steele [5] suggested a reversible insertion/extraction of lithium into/from layered TiS_2 would make a feasible cathode material for a Li^+ -ion rechargeable battery, and in 1976 Whittingham demonstrated this concept in a landmark paper [6]. However, the voltage versus a lithium anode was only about 2.2 V, and it was quickly realized that elemental lithium cannot be used safely as the anode. If an insertion compound was also to be used as the anode in a so-called “rocking-chair” cell, the voltage would be lowered further, which would make the TiS_2 /lithium battery non-competitive with batteries using an aqueous electrolyte.

I noted that TiS_2 was either a small-gap semiconductor or a semi-metal, which meant that the voltage of the lithium battery could not be increased significantly with a sulfide as the cathode. Although an oxide is able to stabilize higher oxidation states of a transition-metal atom than a sulfide, layered MO_2 compounds are not formed. Only where vanadyl or molybdyl ions are formed, as in V_2O_5 or MoO_3 , are layered oxides stable. On the other hand, LiMO_2 oxides may be well ordered with Li^+ and M^{3+} ions in alternate (1 1 1) octahedral-site planes of a face-centered-cubic array of oxide ions. Therefore, I asked Mizushima, who had joined me at Oxford as a visiting scientist, to see how much lithium he could extract from LiCoO_2 and LiNiO_2 before they became unstable at room temperature [7,8]. We were able to demonstrate an open-circuit voltage versus lithium of 4.0 V, but the battery companies of Europe and the USA were not interested in manufacturing a battery with a discharged cathode. It was only an electronics company, the SONY Corporation of Japan, that appreciated this voltage would allow the use of a carbon anode to obtain a battery of high energy density for a cell telephone. It was thus that the $\text{Li}_{1-x}\text{Ni}_{1-y}\text{Co}_y\text{O}_2$ cathode materials were identified and the wireless revolution was launched. This history demonstrates the essential role of the customer in the realization of a new technology.

3. Layered LiMO_2 cathodes

Despite its commercial success, the $\text{Li}_{1-x}\text{Ni}_{1-y}\text{Co}_y\text{O}_2$ cathodes have two drawbacks: (1) Cobalt is expensive and toxic. (2) Only about half of the lithium can be extracted before the oxide begins to lose oxygen or to oxidize the electrolyte to replace the Li^+ ions by H^+ ions, which introduces safety issues for large batteries. There is, therefore, a strong incentive to remove the

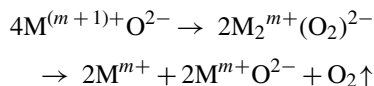
cobalt and to increase the capacity by allowing removal of more lithium before the oxide, which is metastable on removal of lithium, becomes unstable at room temperature.

Other transition-metal oxides with this layered structure tend to become disordered on removal of lithium. Transport of the M atom to the Li layer is through a tetrahedral site, and any ions stable in a tetrahedral site are driven by internal electric fields into the lithium layers on removal of lithium. Moreover, the disproportionation reactions $2\text{Mn}^{3+} = \text{Mn}^{4+} + \text{Mn}^{2+}$ and $3\text{Cr}^{4+} = 2\text{Cr}^{3+} + \text{Cr}^{6+}$ create ions with tetrahedral-site stability like the Fe^{3+} ion. However, Ni^{2+} is stable in the presence of Mn^{4+} , and both of these ions have a strong octahedral-site preference. Moreover, the $\text{Ni}^{3+}/\text{Ni}^{2+}$ and $\text{Ni}^{4+}/\text{Ni}^{3+}$ redox couples are both “pinned” at the top of the $\text{O}^{2-}:2p^6$ band, which means there should be no voltage step on passing from one redox couple to the next. Therefore, one could expect more than half of the lithium can be removed from $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ before the oxide becomes unstable.

Ohzuku and Makimura [9] were the first to prepare $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ material from $\text{Ni}(\text{OH})_2$, $\text{Mn}(\text{OH})_2$, and LiOH , but they found it extremely difficult to obtain well-ordered Li^+ ions. The driving force for ordering of the Li^+ ions includes a mismatch in the ionic radius of the alkali ion, Li^+ or Na^+ , and the transition-metal atom M^{3+} or $(\text{M}^{2+}, \text{M}^{4+})$ [10]. Schougaard et al. [11] determined that ordering of the M and Li required an ionic-radius ratio $(R_{\text{M}})/R_{\text{Li}} < 0.85$; and this ratio is 0.83 in $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$, which places it at the margin to be synthesized as a well-ordered structure. They used an oxalate method to prepare well-ordered $\text{LiNi}_{0.56}\text{Mn}_{0.44}\text{O}_2$. Subsequently Kang et al. [12] ion-exchanged $\text{NaNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ to obtain well-ordered $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$. Fig. 1 shows the voltage versus capacity and the retention of the capacity of a $\text{Li}_{1-x}\text{Ni}_{0.56}\text{Mn}_{0.44}\text{O}_2$ half-cell cycled at 0.1 mA cm^{-2} between 2.75 and 4.3 V. A capacity of over 110 mAh g^{-1} was retained at a 5C (12 min) discharge, and the full capacity was regained on lowering the charge/discharge rate. Thus a higher capacity has been achieved in a layered oxide that does not contain Co. Although the single cell was shown to be capable of a fast discharge, it has not yet been determined whether these metastable cathodes can withstand the inevitable heating that is expected if used in a hybrid electric vehicle.

Since low-spin Co^{3+} is a smaller ion than Ni^{3+} , an alternative approach has been to minimize the Co content in $\text{LiNi}_{0.5-\delta}\text{Mn}_{0.5-\delta}\text{Co}_{2\delta}\text{O}_2$ ($\delta \leq 1/6$) so as to allow easier fabrication of a well-ordered oxide.

In order to suppress O_2 evolution by the surface reaction:



or the oxidation of the electrolyte by the cathode, several workers [13] have coated the LiMO_2 particles with a main-group oxide. The strategy behind this work is an attempt to reduce the contact of cathode particles with the electrolyte while allowing the Li^+ ions to pass through the coat. No redox couple is pinned at the top of the $\text{O}^{2-}:2p^6$ band of a main-group oxide, so the holes in the redox couple of the cathode particle are located well above the top of the $\text{O}^{2-}:2p^6$ band of the coat, which blocks the holes

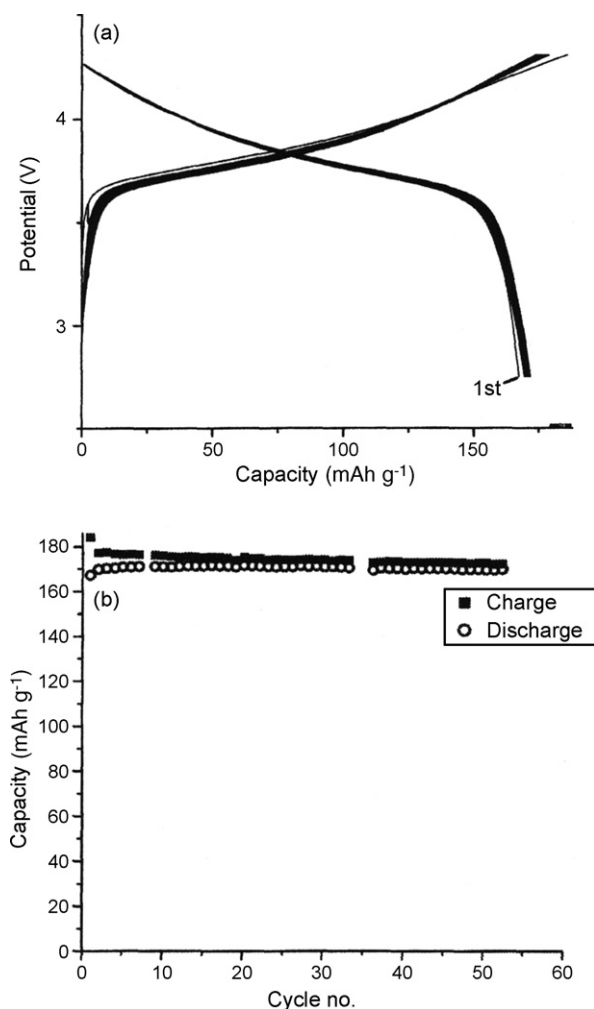


Fig. 1. (a) Galvanostatic cycles (2.75–4.3) vs. Li^+/Li , current density 0.1 mA cm^{-2} and (b) specific capacity vs. cycle number for $\text{LiNi}_{0.56}\text{Mn}_{0.44}\text{O}_2$ (after Ref. [11]).

from reaching the surface. Capacities as high as 280 mAh g^{-1} have been obtained with $\text{LiMn}_{0.5-\delta}\text{Ni}_{0.5-\delta}\text{Co}_{2\delta}\text{O}_2$ coated with Al_2O_3 [14].

4. The spinels $\text{Li}[\text{M}_2]\text{O}_4$

In the early 1980s, Bruno Scrosati gave a seminar at Oxford in which he claimed he was inserting lithium into magnetite, Fe_3O_4 . Two weeks later, Michael Thackeray came from South Africa to work with me. He told me he had been looking for an inexpensive oxide for a cathode and was inserting lithium into Fe_3O_4 . This finding surprised me as my previous experience with spinels showed they do not tolerate excess cations.

Fig. 2 shows the $\text{A}[\text{B}_2]\text{O}_4$ spinel structure. The tetrahedral-site A cations occupy the 8a sites, which form a diamond-like sub-array, and the octahedral-site B cations occupy the 16d sites. It turns out that the $[\text{B}_2]\text{O}_4$ array forms a strongly bonded, 3D framework in which the 8a tetrahedral sites and 16c octahedral sites form an interconnected interstitial space. I quickly realized that the inserted Li^+ ions must be displacing the tetrahedral-site Fe^{3+} ions of Fe_3O_4 into the empty 16c sites of the array to form

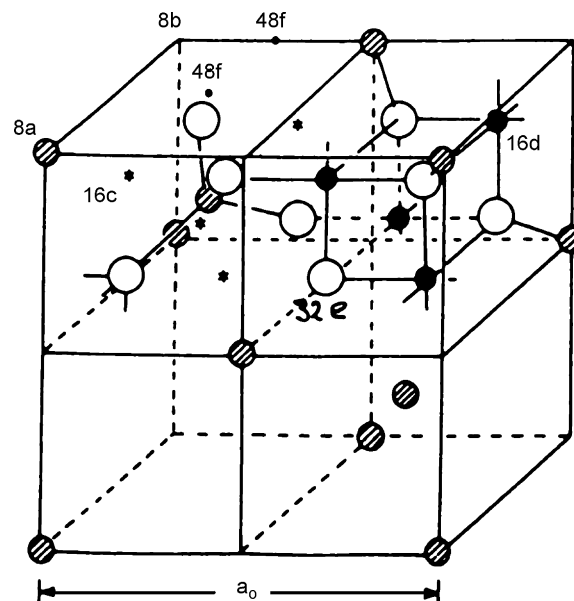


Fig. 2. Two quadrants of the $\text{A}[\text{B}_2]\text{O}_4$ spinel structure.

an ordered rock-salt structure. Therefore, I told Thackeray to insert Li into the spinel $\text{Li}[\text{Mn}_2]\text{O}_4$. We showed that with Li^+ ions on the 16c sites we obtained an open-circuit voltage of 3 V [15]. Thus it was demonstrated that the $[\text{B}_2]\text{O}_4$ spinel framework could be used as an insertion host for Li^+ ions.

At about the same time, Sinha and Murphy at the Bell Telephone Laboratories independently extracted Cu^+ from the thiospinel $\text{Cu}[\text{Ti}_2]\text{S}_4$ to give a cubic $[\text{Ti}_2]\text{S}_4$ framework [16]. Insertion of Li into this cubic framework gave a voltage output identical to that of the layered TiS_2 because the Li^+ ions occupy only the 16c sites in the thiospinel framework. In the oxide $\text{Li}[\text{Mn}_2]\text{O}_4$, on the other hand, the Li^+ ion occupies the 8a tetrahedral sites of the spinel structure, and extraction of the Li from the tetrahedral sites gives a voltage of 4 V versus lithium metal [17]. Thus a step of 1 V in the energy of the $\text{Mn}^{4+}/\text{Mn}^{3+}$ redox couple occurs on shifting the Li^+ ions from tetrahedral to octahedral sites. Although this shift is an interesting example of the inductive effect by a counter cation on the energy of a redox couple, it means that the capacity of the 3 V or the 4 V regimes is limited to half a Li^+ ion per Mn atom.

A cooperative orbital ordering at the Mn^{3+} ions gives a flat voltage versus Li content for the 3 V range, but the associated structural change gives capacity fade unless the oxide is ball milled so as to introduce stacking faults and microdomains within a crystallite [18].

Of more interest has been the stabilization of the 4 V range where Mn dissolution to the electrolyte tends to poison the surface of the anode. A correlation has been made between the Mn dissolution and a change Δa of the cubic lattice parameter in the range $0 < x < 0.5$ of $\text{Li}_x[\text{Mn}_2]\text{O}_4$ as a result of a phase segregation into Li-rich and Li-poor phases. Choi and Manthiram [19] have recently shown that substitution of 0.1 Li and 0.1 Ni per formula unit into the B sites of $\text{Li}[\text{Mn}_2]\text{O}_4$ reduces Δa to near zero. In order to restore the Mn^{3+} -ion concentration after this substitution, they introduced F^- ions in place of O^{2-} ions. Up to 0.2 F^- ions per formula unit could be introduced to give

$\text{Li}[\text{Mn}_{1.8}\text{Li}_{0.1}\text{Ni}_{0.1}]\text{O}_{3.8}\text{F}_{0.2}$. With this composition, the amount of Mn dissolved into the electrolyte on cycling is strongly reduced, and stable cycling was achieved with a capacity of 110 mAh g^{-1} at $C/10$ discharge rate or 100 mAh g^{-1} at $4C$ rate. The spinel framework remains stable to high temperatures and the 4 V versus lithium is attractive, but the capacity remains disappointingly low.

5. The olivines LiMPO_4

The olivine structure of LiFePO_4 is shown in Fig. 3. The FePO_4 3D framework, like the spinel framework, is stable to high temperatures. A subtle structural change between LiFePO_4 and FePO_4 leaves the 1D channels for Li^+ -ion motion intact, but the phase change provides a flat voltage versus state-of-charge curve of 3.4 V. This voltage is well-suited to a solid-polymer electrolyte. The existence of 1D channels for Li^+ -ion motion imposes two constraints: (1) the Li channels must not be blocked by either disorder of the Li and Fe atoms or by the presence of a foreign phase; (2) the cathode particle must be small without stacking faults that block the channels. Small LiFePO_4 particles are platelets with the Li channels oriented parallel to the short dimension, and recent experiments on the phase change that occurs on Li^+ -ion removal [20] suggest that this morphology allows the Li^+ ions to move cooperatively within channels in a successive wave to give a moving phase boundary between the two phases. Therefore, despite the 1D channel for Li^+ -ion motion, $10C$ charge and discharge rates can be achieved with LiFePO_4 cathodes. The specific capacity approaches 160 mAh g^{-1} for thousands of cycles at $C/5$ discharge rate, and

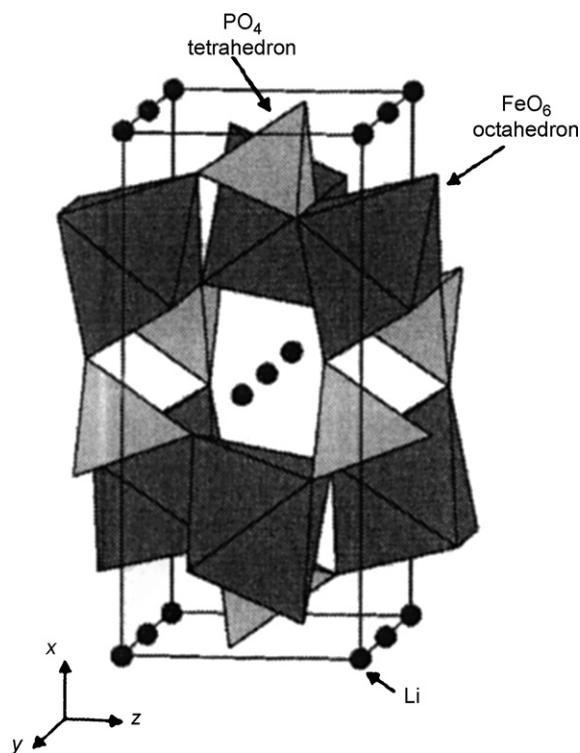


Fig. 3. The olivine structure of LiFePO_4 .

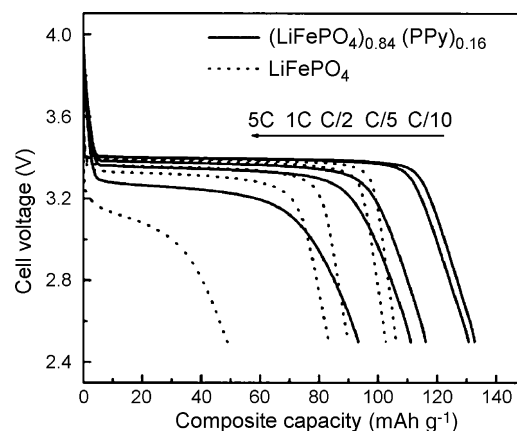


Fig. 4. Cell voltage vs. discharge composite capacity at various discharge rates for the $(\text{C-LiFePO}_4)_{0.84}(\text{PPy})_{0.16}$ composite cathode. The charge rate was fixed at $C/10$. The performance of a $(\text{C-LiFePO}_4)(\text{C} + \text{PTFE})$ composite cathode is also shown for comparison (after Ref. [23]).

the reversible capacity loss at higher discharge rates is small. Moreover, the cathode is environmentally benign and safe.

Salah et al. [21] have shown that firing small LiFePO_4 particles at 700°C in the presence of a sucrose or cellulose acetate carbon precursor creates a carbon-coated C-LiFePO_4 with about 1 wt% C. This carbothermal procedure reduces all the iron to Fe^{2+} , thus eliminating $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles that can block the 1D Li channels. These cathodes retain capacity down to -20°C [22].

We have recently shown that replacement of the inactive $\text{C} + \text{PTFE}$ additives in a composite cathode by an electronically conducting, electrochemically active polymer such as polypyrrole (PPy) enhances the capacity and rate capability of the composite cathode [23]. The PPy bonds to the carbon-coated

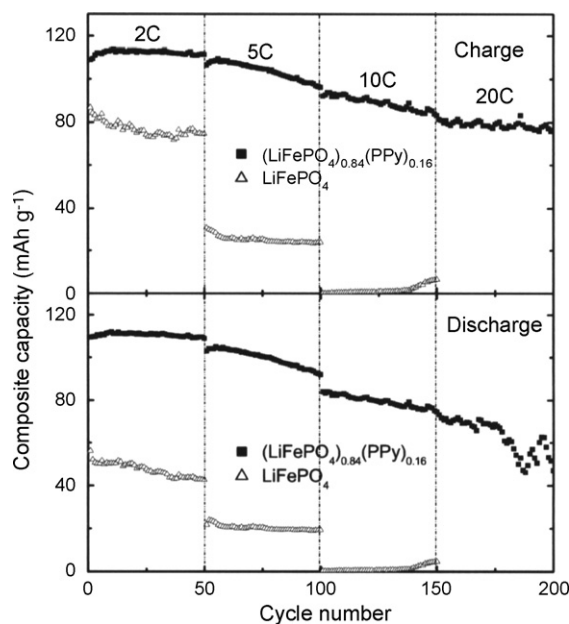


Fig. 5. Composite capacity vs. cycle number at high charge current for the $(\text{C-LiFePO}_4)_{0.84}(\text{PPy})_{0.16}$ composite cathode. (Discharge rate was $C/5$ for all cycles and discharge currents.) The performance of a $(\text{C-LiFePO}_4)(\text{C} + \text{PTFE})$ cathode is also shown for comparison (after Ref. [23]).

cathode particles as well as to the current collector during electrolytic deposition from a mixture of Py monomers and C-coated LiFePO₄. Thus good electronic contact is made between the redox couple of the oxide and the current collector. Moreover, elimination of the PTFE binder may enhance safety. Fig. 4 compares the cell voltage versus *composite* capacity for C-LiFePO₄ with 20 wt% C + PTFE versus C-LiFePO₄ with 16 wt% PPy, and Fig. 5 compares the capacities versus cycle number at different charge and discharge rate after discharge or recharge at C/5 rate for laboratory button half-cells.

The olivine LiMnPO₄ offers an open-circuit voltage of 4 V, but the preparation of small enough particles for extraction of lithium has yet to be demonstrated.

6. Conclusions

The spinel and olivine cathode materials have been shown capable of powering a plug-in hybrid vehicle. The spinel has a higher voltage and lower capacity than the LiFePO₄. The olivine has a voltage well-matched to a solid-polymer electrolyte and has been proven to be safe in large batteries. Layered oxides of higher capacity can be made, but it is doubtful that they will withstand the higher temperatures anticipated in an electric vehicle. However, they will continue to be the cathode of choice for the electronic applications of the wireless revolution.

Acknowledgements

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References

- [1] J.B. Goodenough, H.Y-P. Hong, J.A. Kafalas, *Mater. Res. Bull.* 11 (1976) 203.

- [2] J.B. Goodenough, in: P. Hagenmuller, W. van Gool (Eds.), *Solid Electrolytes*, Academic Press, New York, NY, 1998, p. 393 (Chapter 23).
- [3] A.K. Padhi, K.S. Najundaswamy, C. Masquelier, J.B. Goodenough, *J. Electrochem. Soc.* 144 (1997) 2581.
- [4] A.K. Padhi, K.S. Najundaswamy, J.B. Goodenough, *J. Electrochem. Soc.* 144 (1997) 1188;
(a) J. Barker, M.Y. Saidi, J.L. Swayer, *J. Electrochem. Soc.* 150 (2003) A684.
- [5] B.C.H. Steele, in: W. van Gool (Ed.), *Fast Ion Transport in Solids: Solid State Batteries and Devices*, North Holland/America Elsevier, Amsterdam/New York, 1973, p. 103.
- [6] M.S. Whittingham, *Science* 192 (1976) 1126.
- [7] K. Mizushima, P.C. Jones, P.J. Wiseman, J.B. Goodenough, *Mater. Res. Bull.* 15 (1980) 783.
- [8] J.B. Goodenough, K. Mizushima, T. Takada, *Jpn. J. Appl. Phys.* 19 (Suppl. 19-3) (1980) 305.
- [9] T. Ohzuku, Y. Makimura, *Chem. Lett.* (2001) 744.
- [10] S. Venkatraman, J. Choi, A. Manthiram, *Electrochem. Commun.* 6 (2004) 832.
- [11] S.B. Schougaard, J. Bréger, M. Jiang, C.P. Grey, J.B. Goodenough, *Adv. Mater.* 18 (2006) 905.
- [12] K. Kang, Y.S. Meng, J. Bréger, C.P. Grey, G. Ceder, *Science* 311 (2006) 977.
- [13] C. Li, H.P. Zhang, L.J. Fu, H. Liu, Y.P. Wu, E. Rahm, R. Holze, H.Q. Wu, *Electrochim. Acta* 51 (2006) 3872.
- [14] Y. Wu, A. Manthiram, *Electrochem. Solid State Lett.* 9 (2006) A221.
- [15] M.M. Thackeray, W.I.F. David, P.G. Bruce, J.B. Goodenough, *Mater. Res. Bull.* 18 (1983) 961.
- [16] S. Sinha, D.W. Murphy, *Solid State Ionics* 20 (1986) 81.
- [17] M.M. Thackeray, P.J. Johnson, L.A. De Picciotto, P.G. Bruce, J.B. Goodenough, *Mater. Res. Bull.* 19 (1989) 179.
- [18] S.-H. Kang, J.B. Goodenough, L.K. Rabenberg, *Chem. Mater.* 13 (2001) 1758.
- [19] W. Choi, A. Manthiram, *Electrochem. Solid State Lett.* 9 (2006) A245.
- [20] G. Chen, X. Song, T.J. Richardson, *Proceedings of the Int. Meeting on Lithium Batteries*, Biarritz, France, June 18–23, 2006 (Abstract 361).
- [21] A.A. Salah, A. Mauger, K. Zagrib, J.B. Goodenough, N. Ravet, M. Gauthier, F. Gendron, C.M. Julien, *J. Electrochem. Soc.* 153 (2006) A1692.
- [22] M. Gauthier, *Phostec Communication*.
- [23] Y.-H. Huang, K.-S. Park, J.B. Goodenough, *J. Electrochem. Soc.* 153 (12) (2006) A2282–A2286.