

Lithium-ion Active Materials

Dr. Jerry Barker

Jerry Barker Consultants, Oxfordshire, United Kingdom

Introduction

The great majority of today's lithium-ion batteries typically utilize active materials of lithium cobalt oxide, LiCoO_2 and crystalline graphite. Although commercially this has proven a highly successful cell chemistry, there remains a general requirement for new positive and negative electrode materials to facilitate production of the next generation of these energy storage devices. These materials will improve the performance of current applications (e.g. cell phones, laptops, personal electronics etc.) as well as allowing the penetration of new market opportunities such as power tools, standby power applications, electric vehicles and hybrid electric vehicles.

Positive Electrode Materials

1. Oxides

Positive electrode technology for lithium-ion cells is currently dominated by the layered lithium cobalt oxide. Recent developments in this area have indicated that the mixed metal oxides $\text{LiNi}_x\text{Co}_{1-2x}\text{Mn}_x\text{O}_2$ may offer some significant performance enhancements, especially in terms of specific capacity. In compositions where the transition metal layers contain Ni^{2+} , Co^{3+} and Mn^{4+} , the layered α - NaFeO_2 structure is maintained (Lu *et al* 2001). Of particular note is the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ material which demonstrates outstanding electrochemical performance, characterized by a reversible specific capacity approaching 200 mAh/g (Koyama *et al.* 2004). This development has facilitated the commercial production of lithium-ion batteries with energy density superior to current technology. Importantly, diffraction studies on this phase indicate negligible inter-site mixing of the lithium and transition metals. Other layered oxide materials of note include the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ (Ohzuku and Makimura, 2001), which operates with high reversible capacity and low polarization.

The manganese spinel, LiMn_2O_4 has been used in commercial lithium-ion batteries for some years (e.g. Amatucci and Tarsacon, 2002). This active material has some negative performance characteristics, including rapid capacity fade, and poor storage properties, these factors been acerbated at elevated temperatures. Strategies to improve these properties have included stoichiometry control, cation substitution, surface coatings and partial fluorine/oxygen replacement. The effect of fluorine substitution in cation substituted (Ti, Ni) manganese spinels has recently been described in some detail (Choi and Manthiram, 2007).

One unambiguous option for improving the energy density of lithium-ion batteries is to work with positive electrode materials with higher operating voltages. For example, a number of 5 V lithium insertion materials based on the manganese spinel, $\text{LiM}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($M = 3d$ transition metal), have been proposed (Ohzuku *et al.*, 1999). In all these iterations the

manganese remains in the tetravalent state, thus avoiding complications associated with the Jahn-Teller distortion of Mn^{3+} in the six-coordinate sites. The $LiNi_{0.5}Mn_{1.5}O_4$ spinel has received particular attention, delivering a reversible capacity of around 140 mAh/g at 4.7 V vs. Li. On a general note, it should be stressed that due to the higher operating voltages, these 5 V materials do not perform well in current lithium-ion configurations and improvements to other parts of the cell infrastructure (e.g. electrolyte formulations) will be required prior to commercial success.

2. Phosphates

Following the discovery of phosphates as positive electrode materials (Padhi *et al.* 1997, Barker and Saidi, 1999) there has been steady and concerted research effort in this area. One of the key attributes of these phases is the relative thermal stability of the phosphate anion which thereby imparts improved safety characteristics on the resultant lithium-ion cell.

The iron olivine, $LiFePO_4$ and its substituted variants (e.g. $LiFe_{1-x}Mg_xPO_4$) operate at around 3.5 V vs. Li and can now be found in a variety of applications. Improvements to the electronic conductivity of the $LiFePO_4$ material were necessary before commercial success – this being achieved through novel preparative approaches, or by post synthesis surface coating technology, typically involving carbon. Preliminary indications suggested that the manganese analogue, $LiMnPO_4$ would provide improved lithium-ion performance due to its higher operating potential. To date these enhancements have not been realized, due primarily to the high intrinsic resistivity of $LiMnPO_4$, although recent results have suggested that crystalline nano-particles of this material may be suitable for certain low rate applications (Drezen *et al.* 2006). The insertion properties of $LiCoPO_4$ have also been established, but the 4.8 V vs. Li operating potential is considered incompatible with conventional organic electrolytes (Bramnik *et al.*, 2004).

The $Li_3V_2(PO_4)_3$ Nasicon phase is currently under development, and this material (and its derivatives) demonstrates enough beneficial electrochemical properties to suggest significant future success (Barker *et al.*, 2007a). The initial testing of this material was restricted to the cycling of two alkali ions per formula unit, thereby limiting the specific capacity to around 130 mAh/g. Recent data have confirmed that, in fact, all three Li ions may be successfully extracted from the $Li_3V_2(PO_4)_3$ thereby revealing a reversible material utilization close to the theoretical figure of 197 mAh/g (Yin *et al.* 2003, Barker *et al.*, 2007a) (see Fig. 1). Other phosphate active phases of note include vanadyl phosphates, $LiVOPO_4$ (Gaubicher *et al.* 1999) and diphosphates such as $LiMP_2O_7$ (M= V, Fe) (Wurm *et al.* 2002), and most recently $LiFe_{1.5}P_2O_7$ (Ramana *et al.* 2007), all of which may find use in selected, low rate applications.

3. Fluorophosphates

This represents a relatively new area of exploration. The electrochemical insertion properties of the lithium vanadium fluorophosphate phase, $LiVPO_4F$ have been described in some detail, including its use in full lithium-ion cells (Barker *et al.* 2005a). The $LiVPO_4F$ adopts a triclinic symmetry, (space group *P-1*) and is iso-structural with the naturally occurring mineral amblygonite, $LiAlPO_4F$. The three dimensional framework structure comprises $[VO_4F_2]$ octahedra and $[PO_4]$ tetrahedra with the oxygen atoms shared between the two environments. The optimized material operates at close to theoretical performance (ca. 150 mAh/g, 4.2 V vs. Li) with high coulombic efficiency, making it near ideal for inclusion in current lithium-ion

technology, without the requirement to adjust other components of the cell infrastructure such as the electrolyte chemistry (see Fig. 2).

The lithium insertion and structural properties of $\text{Li}_5\text{M}(\text{PO}_4)_2\text{F}_2$ ($\text{M} = \text{V}, \text{Cr}$) phases have been reported (Yin *et al.* 2006). These phases possess a highly anisotropic, two dimensional layered structure comprising interleaved layers of lithium ions and M-P-O(F) sheets. The alkali ions reside in the channels along the a axis and in the interstitial space within the framework. The vanadium analogue offers a reversible specific capacity of around 70 mAh/g at 4.15 V vs. Li.

$\text{Li}_2\text{MPO}_4\text{F}$ ($\text{M} = \text{Co}, \text{Ni}$) phases adopt an ordered anionic framework structure comprising of $[\text{MO}_4\text{F}_2]$ octahedra and $[\text{PO}_4]$ tetrahedral with two crystallographic sites for the Li ions. The Ni phase is electrochemically inactive while the Co material shows reversible lithium insertion at around 4.8 V vs. Li (Barker *et al.*, 2005b). Due to the high operating potential only around 0.5 Li ions per formula unit are accessible (Okada *et al.*, 2005).

An interesting recent development is the use of a sodium based active material, sodium vanadium fluorophosphate, $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$, in lithium-ion cells (Gover *et al.*, 2006). The reversible cycling of two alkali ions per formula unit was achieved, corresponding to a material utilization of around 120 mAh/g and an average insertion voltage of 4.1 vs. Li (see Fig 3). These kinds of material may find application in sodium-ion cells or in hybrid (mixed lithium and sodium) systems.

4. Silicates

The Li_2MSiO_4 materials ($\text{M} = \text{Fe}, \text{Mn}$) show some promise as inexpensive positive electrode materials. One of the major obstacles to be overcome with these materials is the very low intrinsic electronic conductivity. Carbon coating methods (similarly to those used for the LiMPO_4 olivine described above) have been attempted. The preliminary electrochemical of $\text{Li}_2\text{FeSiO}_4$ was reported (Nyten *et al.* 2005), indicating that at low rates a stabilized specific capacity around 140 mAh/g could be achieved at an average voltage of around 2.8 V vs. Li. The crystal structure of the $\text{Li}_2\text{FeSiO}_4$ was shown to be orthorhombic, space group $Pmn21$, although the active material undergoes a transition to a more stable phase during the initial charge-discharge cycle.

The $\text{Li}_2\text{MnSiO}_4$ phase is iso-structural with the Fe analogue and the first report of its electrochemical performance has recently been described (Domionko *et al.* 2006). The deliverable capacity for this material is around 120 mAh/g, and is characterized by a sloping discharge voltage centred at 3.2 V vs. Li. This performance is accompanied by a large voltage polarization even at low charge-discharge rates. A recent development (Kokalj *et al.* 2007) has discussed the possibility of using mixed transition metal phases, $\text{Li}_2\text{Mn}_x\text{Fe}_{1-x}\text{SiO}_4$ in an attempt to boost the electrochemical performance.

The lithium insertion behaviour of $\text{Li}_2\text{VOSiO}_4$ has recently been reported (Prakash *et al.* 2006). By ball milling this vanadyl silicate in the presence of carbon this material allows about 0.7 Li ions per formula unit to be reversibly cycled at C/50 rate at an operating potential of around 3.6 V vs. Li.

Negative Electrode Materials

1. Oxides

The lithium titanium oxide spinel, $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ is a zero-strain insertion material that provides a specific capacity of around 160 mAh/g and a flat operating voltage of 1.55 V vs. Li (Colbow *et al*, 1989). This electrode material has been utilized in prototype lithium-ion cells, using positive electrodes materials including LiMn_2O_4 (Ferg *et al*, 1994), LiFePO_4 (Reale *et al*, 2004) and LiVPO_4F (Barker *et al* 2007b). Compared to conventional graphite based systems, these cells offer some enhancements to cycle life, rate capability and safety characteristics. The lower operating voltage adversely affects the battery energy density. Lithium insertion into TiO_2 -B nanowires and nanotubes has also been described recently (Armstrong *et al*, 2005).

2. Alloys

Alloy based electrodes materials are being promoted as potential replacements to graphite negative electrodes. Of particular emphasis is the fabrication of composite nanostructures, an approach which generally improves the specific capacity and cycle life performance of these electrode systems.

Due to the high theoretical capacity, Sn based electrode materials have been studied in considerable detail. The approach has focussed on the incorporation of the Sn in an oxide composite matrix, thereby limiting the impact of the large unit cells volume expansion experienced during Li insertion. For example, Sony recently announced the commercial introduction of a lithium-ion battery, Nexelion, in which a tin-based negative electrode is employed (Inoue, 2006). Other notable advances in this area have included the use of composite nanotubes of SnO_2 and carbon (Wang *et al*, 2006).

Lithium insertion into silicon-metal (M) alloys has received some recent attention. Much of this work has focussed on binary alloys where $M = \text{Fe}, \text{Mn}, \text{Cr}, \text{Ni}$ etc., where the electrochemically active material (Si), which is in an amorphous or nanocrystalline form, is embedded in an inert matrix (Si-M) (Fleischauer *et al*, 2005). Initial specific material capacities of more than 1000 mAh/g have been described, although this is generally accompanied by poor cycle stability associated with the large volume expansion experienced during the Li insertion process. Systematic testing and fabrications protocols have been proposed to establish the optimum performance of Si-C composites (Timmons *et al*, 2007).

3. Silicon

Recent developments have indicated the promise of silicon based negative electrode materials (Chan *et al*, 2008). Electrodes fabricated from bulk films and large particles of silicon demonstrate poor reversibility, primarily associated with the large volume expansion experienced during lithium insertion. Morphological control – such as production of Si nanowires and other nano-structured forms – show some encouraging performance characteristics. Long term cycling in Li-ion format and the detailed safety properties of highly lithiated Si will need to be assessed prior to commercial success.

4. Others

A number of recent publications (e.g. Poizot *et al*, 2002) indicated that simple binary metal oxides (MO, M = Fe, Co, Ni, Cu etc) could reversibly react with appreciable amounts of lithium at low operating potentials. These results suggest that these oxides may have some potential as negative electrode materials. For example, specific capacities as high as 700 mAh/g were reported for the Li//CoO system. In an extension of this approach a prototype CoO//LiCoO₂ cell was produced (Badway *et al*, 2002), which demonstrated a stable reversible specific energy of 120 Wh/kg and an average discharge voltage of 2 V. The major drawbacks with these types of material are the poor first cycle charge efficiency and the significant voltage hysteresis encountered during insertion/extraction cycles.

Bibliography

- Amatucci G, Tarascon J-M 2002 *Optimization of insertion compounds such as LiMn₂O₄ for lithium-ion batteries* J. Electrochem. Soc. **149**, K31-K46
- Armstrong A R, Armstrong G, Canales J, Bruce P G, 2005 *TiO₂-B nanowires as negative electrodes for rechargeable lithium batteries* J. Power Sources **146**, 501-506.
- Badway F, Plitz I, Grugeon S, Laruelle S, Dolle M, Gozdz A S, Tarascon J-M 2002 *Metal oxides as negative electrode materials in Li-ion cells* Electrochem. Solid-State Lett. **5**, A115-A118
- Barker J, Gover R K B, Burns P, Bryan A 2007a *The effect of Al substitution on the electrochemical insertion properties of the lithium vanadium phosphate, Li₃V₂(PO₄)₃* J. Electrochem. Soc. **154**, A307-A313
- Barker J, Gover R K B, Burns P, Bryan A J 2007b *A lithium-ion cell based on Li_{4/3}Ti_{5/3}O₄ and LiVPO₄F* Electrochem. Solid-State Lett. **10**, A130-A133
- Barker J, Gover R K B, Burns P, Bryan A, Saidi M Y, Swoyer J L 2005a *Performance evaluation of lithium vanadium fluorophosphate in lithium metal and lithium-ion cells* J. Electrochem. Soc. **152**, A1776-A1779
- Barker J, Saidi M Y 1999 US patent 5,871,866 *Lithium-containing phosphates, method of preparation and uses thereof*
- Barker J, Saidi M Y, Swoyer J L 2005b, US Patent 6,964,827 *Alkali/transition metal halo- and hydroxyl-phosphates and related electrode active materials*
- Bramnik N, Bramnik K G, Buhrmester T, Baecht C, Ehrenberg H, Fuess H 2004 *Electrochemical and structural study of LiCoPO₄-based electrodes* J. Solid State Electrochem. **8**, 558-564.
- Chan C K, Peng H, Liu, G, McIlwrath, Zhang X F, Huggins R A, Cui Y 2008 *High-performance lithium battery anodes using silicon nanowires* Nature Nanotechnology **3**, 31-35

- Choi W, Manthiram A 2007 *Factors controlling the fluorine content and electrochemical performance of spinel oxyfluoride cathodes* J. Electrochem. Soc. **154**, A792-A797
- Colbow K M, Dahn J R, Haering R R, 1989 *Structure and electrochemistry of the spinel oxides LiTi_2O_4 and $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$* J. Power Sources **26**, 397-402
- Dominko R, Bele M, Gaberscek M, Meden A, Remskar M, Jamnik J 2006 *Structure and electrochemical performance of $\text{Li}_2\text{MnSiO}_4$ and $\text{Li}_2\text{FeSiO}_4$ as potential Li-battery cathode materials* Electrochem. Comm. **8**, 217-222
- Drezen T, Kwon N H, Crouzet M, Teerlinck I, Isono M, Exnar I 2006 *Enhanced electrochemical performance of nanosized LiMnPO_4 for lithium ion batteries* Abstract #195, International Meeting on Lithium Batteries June 18-23, Biarritz, France.
- Ferg E, Gummow R J, de Kock A, Thackeray M M 1994 *Spinel anodes for lithium-ion batteries* J. Electrochem. Soc. **141** L147-L150
- Fleischauer M D, Topple J M, Dahn J R 2005 *Combinatorial investigations of Si-M ($M = \text{Cr} + \text{Ni}, \text{Fe}, \text{Mn}$) thin film negative electrode materials* Electrochem. Solid-State Lett. **8**, A137-A140
- Gaubicher J, Le Mercier T, Chabre Y, Angenault J, Quarton M 1999 *$\text{Li}/\beta\text{-VOPO}_4$: A new 4 V system for lithium batteries* J. Electrochem. Soc. **146**, 4375-4379
- Gover R K B, Bryan A, Burns P, Barker J 2006 *The electrochemical insertion properties of sodium vanadium fluorophosphates, $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$* Solid State Ionics **177**, 1495-1500
- Inoue H 2006 *High capacity negative-electrode materials next to carbon: Nexelion* Presented at the International Meeting on Lithium Batteries 2006, Biarritz, France, June 18-23, 2006 Abstract No. 228
- Kokalj A, Dominko R, Mali G, Meden A, Gaberscek, Jamnik J 2007 *Beyond one-electron reaction in Li cathode materials: designing $\text{Li}_2\text{Mn}_x\text{Fe}_{1-x}\text{SiO}_4$* Chem. Mater. **19**, 3633-3640
- Koyama Y, Yabuuchi N, Tanaka I, Adachi H, Ohzuku T 2004 *Solid state chemistry and electrochemistry of $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ for advanced lithium-ion batteries* J. Electrochem. Soc. **151**, A1545-A1551
- Lu Z, MacNeil D D, Dahn J R 2001 *Layered $\text{Li}[\text{Ni}_x\text{Co}_{1-2x}\text{Mn}_x]\text{O}_2$ cathode materials for lithium-ion batteries* Electrochem. Solid State Lett. **4**, A200-A203
- Nyten A, Abouimrane, Armand M, Gustafsson T, Thomas J O 2005 *Electrochemical performance of $\text{Li}_2\text{FeSiO}_4$ as a new Li-battery cathode material* Electrochem. Comm. **7**, 156-160
- Ohzuku T, Makimura Y 2001 *Layered lithium insertion materials of $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$: A possible alternative to LiCoO_2 for advanced lithium-ion batteries* Chem. Lett., **30**, 744-746
- Ohzuku T, Takeda S, Iwanaga M 1999 *Solid-state redox potentials for $\text{Li}[\text{Me}_{1/2}\text{Mn}_{3/2}]\text{O}_4$ ($\text{Me} = 3d\text{-transition metal}$) having spinel-framework structures: a series of 5 volt materials for advanced lithium-ion batteries* J. Power Sources **81-82**, 90-94

- Okada S, Ueno M, Uebou Y, Yamali J-I, 2005 *Fluoride phosphate $\text{Li}_2\text{CoPO}_4\text{F}$ as a high-voltage cathode in Li-ion batteries* J. Power Sources **146**, 565-569
- Padhi A K, Nanjundaswamy K S, Goodenough J B 1997 *Phospho-olivines as positive-electrode materials for rechargeable lithium batteries* J. Electrochem. Soc., **144**, 1188
- Poizot P, Laruelle S, Grugeon S, Tarascon J-M, 2002 *Rationalization of the low potential reactivity of 3d-metal-based inorganic compounds toward Li* J. Electrochem. Soc. **149**, A1212-A1217
- Prakash A S, Rozier P, Dupont L, Vezin H, Sauvage F, Tarascon J-M, 2006 *Electrochemical Reactivity of $\text{Li}_2\text{VOSiO}_4$ toward Li* Chem. Mater. **18**, 407-412
- Ramana C V, Ait-Salah A, Utsunomiya S, Mauger A, Gendron F, Julien C M 2007 *Novel lithium ion pyrophosphate ($\text{LiFe}_{1.5}\text{P}_2\text{O}_7$) as a positive electrode for Li-ion batteries* Chem. Mater. Web Release date October 9, 2007
- Reale P, Panero S, Scrosati B, Garche J, Wohlfahrt-Mehrans M, 2004 *A safe, low-cost, and sustainable lithium-ion polymer battery* J. Electrochem. Soc. **151**, A2138-A2142
- Timmons A, Todd A D W, Mead S D, Carey G H, Sanderson R J, Mar R E, Dahn J R 2007 *Studies of $\text{Si}_{1-x}\text{C}_x$ electrode materials prepared by high energy mechanical milling and combinatorial sputter deposition*. J. Electrochem. Soc. **154**, A865-A874
- Wang Y, Zeng H C, Lee J Y 2006 *Highly Reversible Lithium Storage in Porous SnO_2 Nanotubes with Coaxially Grown Carbon Nanotube Overlayers* Adv. Mater. **18**, 645-649
- Wurm C, Morcrette M, Rousse G, Dupont L, Masquelier C 2002 *Lithium insertion/extraction into/from LiMX_2O_7 compositions ($M = \text{Fe, V}$; $X = \text{P, As}$) prepared via solution method* Chem. Mater. **14**, 2701-2710
- Yin S-C, Grondy H, Strobel P, Huang H, Nazar L 2003 *Charge ordering in lithium vanadium phosphates: electrode materials for lithium-ion batteries* J. Am. Chem. Soc. **125**, 326-327

J. Barker

Jerry Barker Consultants, Oxfordshire, UK

June 2008

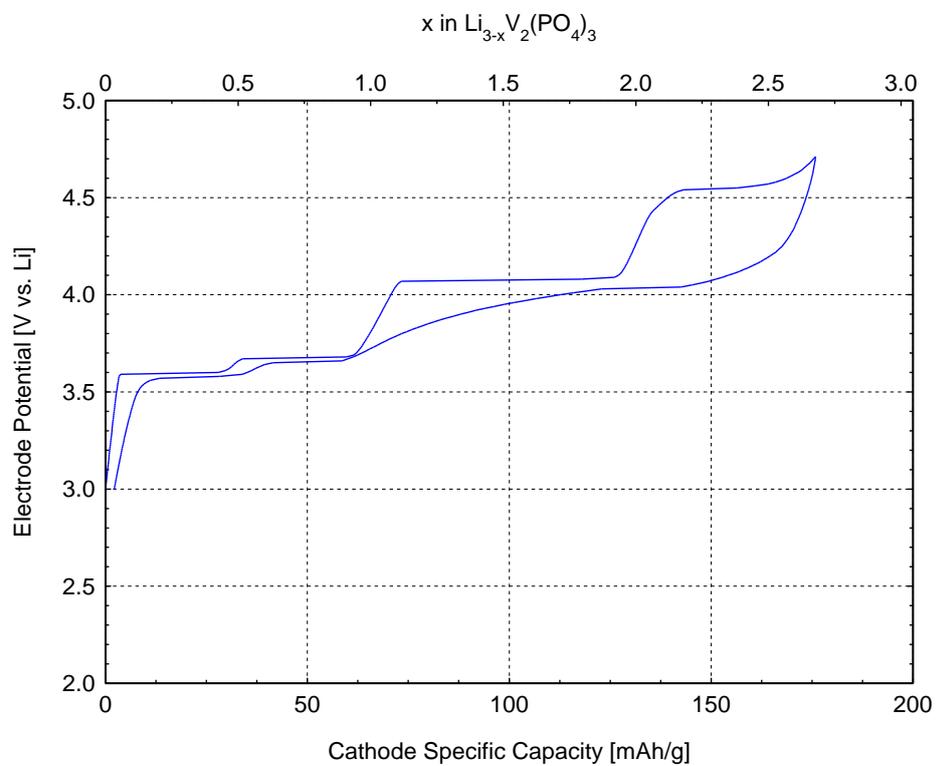


Figure 1

Electrode potential versus specific capacity relationship for the $\text{Li}/\text{Li}_3\text{V}_2(\text{PO}_4)_3$ system. These data were collected at 23°C using an approximate C/10 charge/discharge rate.

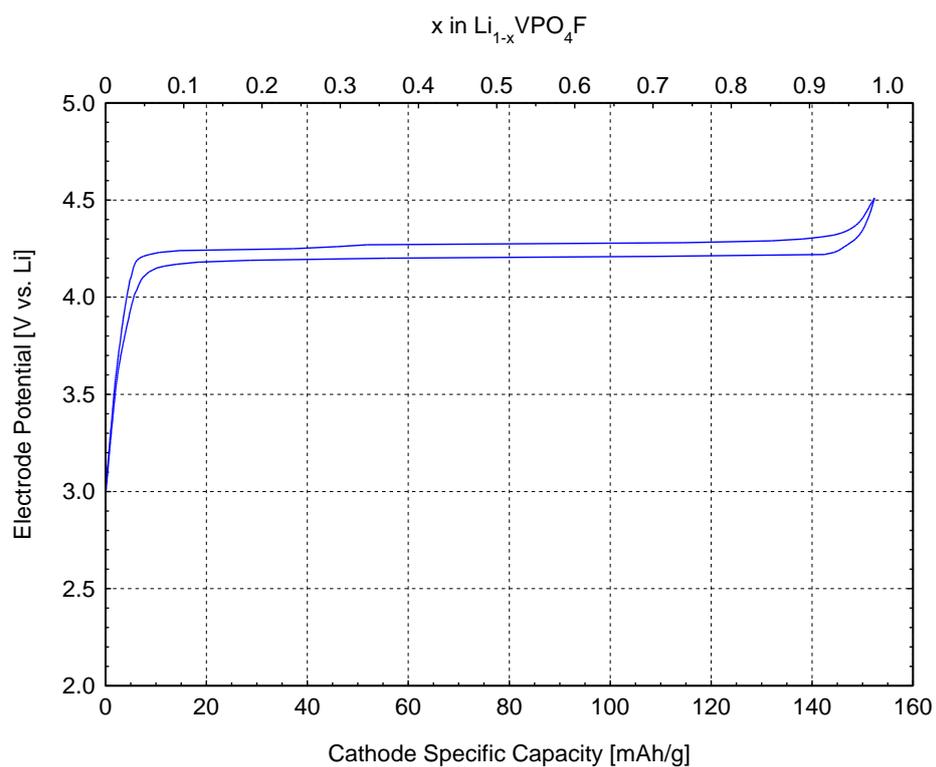


Figure 2

Electrode potential versus specific capacity relationship for the $\text{Li}/\text{LiVPO}_4\text{F}$ system. These data were collected at 23°C using an approximate C/10 charge/discharge rate.

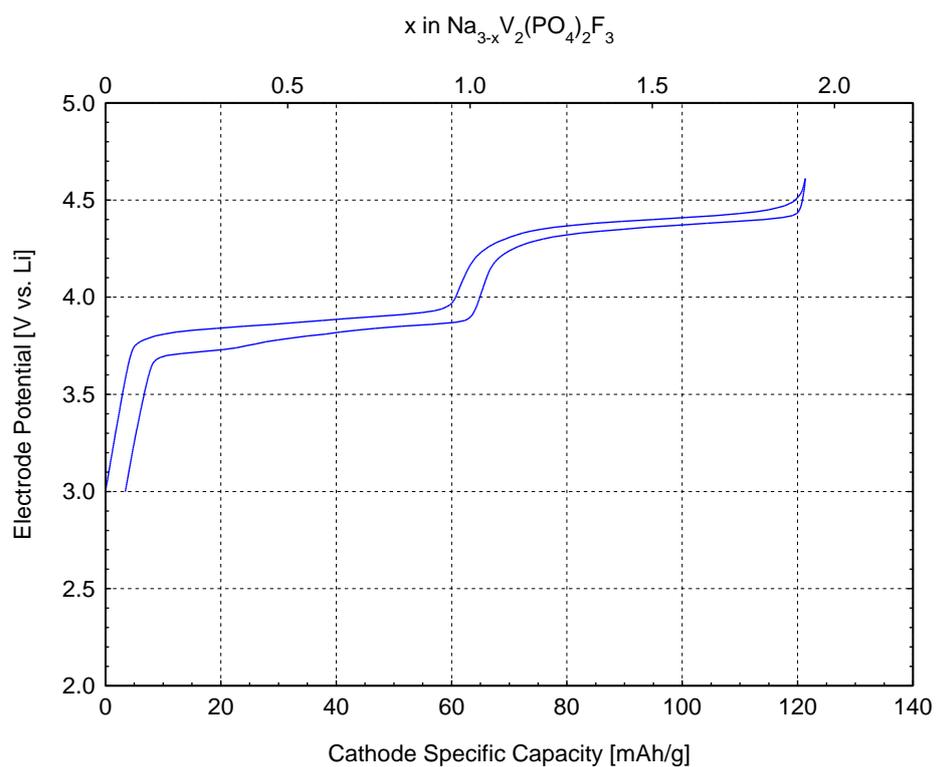


Figure 3

Electrode potential versus specific capacity relationship for the $\text{Li}/\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ system using a lithium based electrolyte. These data were collected at 23°C using an approximate C/10 charge/discharge rate.