Valence Technology Inc.

A Brief Review of Valence Technology's Phosphate Program (Saphion®)

by

Jerry Barker and Yazid Saidi

Pure PO4WER™

ICMAT2007: 4th International Conference on Materials for Advanced Technologies 2007, July 1–6, 2007, Singapore

Valence Technology Inc.

Valence Technology Inc.

Where Safety meets Power

12201 Technology Blvd., Suite 150,
Austin, Texas, 78727, USA

Pure PO4WER™

ICMAT2007: 4th International Conference on Materials for Advanced Technologies 2007, July 1–6, 2007, Singapore

Valence Technology Inc.

Jerry Barker Consultants

Specialists in Electrochemical and Solid-State Chemistry

www.jerrybarker.co.uk

Pure PO4WER™

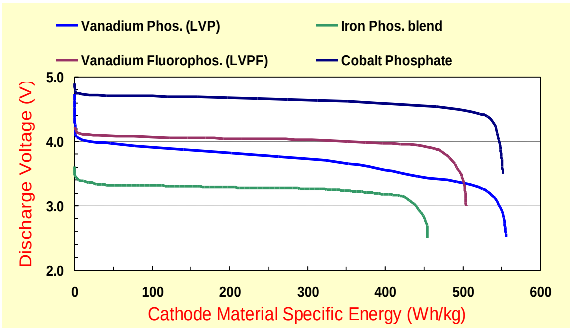
ICMAT2007: 4th International Conference on Materials for Advanced Technologies 2007, July 1–6, 2007, Singapore

Introduction– Valence Technology Inc.

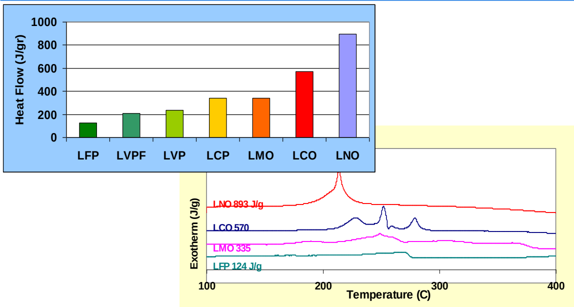
- **Valence Technology Inc. has been working on Phosphate Active materials since the early 1990's**
- **Has built up a large portfolio of lithium and sodium active materials – phosphates, condensed phosphates, fluorophosphates and other polyanions (100+ patents on active materials)**
- **Valence needed a cost-effective and scalable process for synthesizing these materials at a commercial level**
- **Developed the *Carbothermal Reduction (CTR)* method for the preparation of active materials**
- **Today Valence makes *all its active materials* using this CTR approach – at up to Metric Tonne/day scale**

Why Phosphates?

Discharge Characteristics of Phosphate Materials



Why Phosphates: DSC on Charged Cathodes



Theoretical basis for safety advantages of phosphates

Carbothermal Reduction

Carbothermal Reduction (CTR)

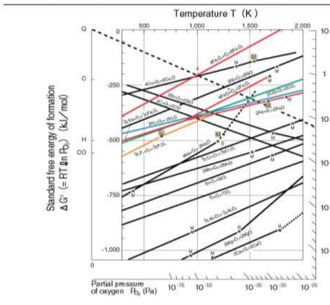
- 2C + O_2 → 2 CO = increase in volume and therefore entropy. Carbon is unique in that CO free energy of formation becomes increasingly negative as the temperature increases – i.e. more stable at high temperatures. *Implications: Carbon can reduce any oxide provided a high enough temperature can be reached.* Example: Na extraction:

  Na_2CO_3 (liquid) + 2 C (solid) → 2 Na (vapor) + 3 CO (gas)
- Carbothermal Reduction (CTR) technique utilizes an *in-situ* reducing agent while leaving behind an embedded conductive network.
- Carbon monoxide formed during the high temperature synthesis both promotes further reduction and deposits carbon "nanoparticles"
- Net result: precursor carbon is finely distributed throughout and on surface of final product.

$$C + O_2 \rightarrow CO_2$$
$$2\,C + O_2 \rightarrow 2\,CO$$

Free Energy or Ellingham Diagrams

2B(1) Standard Free Energy of Formation of Oxides



Top: Low affinity for oxygen – easy to reduce; Bottom: High affinity for oxygen – difficult to reduce

Determines the relative ease of reducing of a given metallic oxide to the metal using carbon

Determines the partial pressure of oxygen that is in equilibrium with a metal at a given temperature

But it tells us nothing about the kinetics of these reactions

Ref.: F.D.Richardson, JISI (1948)

Iron Blast Furnace

2D(2) Operating Conditions in Large Blast Furnace (BF)

Reaction Mechanisms:

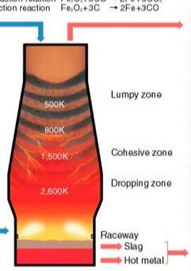
3 Fe_2O_3 + CO → 2 Fe_3O_4 + CO — *$Fe^{2+/3+}$*
Fe_3O_4 + CO → 3 FeO + CO_2 — *Fe^{2+}*
FeO + CO → Fe + CO_2 — *Fe^0*

Take Home Message:

Intermediate oxidation states:

- *Fe^{3+} → Fe^{2+}*
- *Mn^{3+} → Mn^{2+}*
- *V^{5+} → V^{3+}*
- *Mo^{6+} → Mo^{4+} etc.*

Indirect reduction reaction $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$
Direct reduction reaction $Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$



Top gas		
Dust (kg/t*)		16
Gas	Volume (Nm³/t*)	1,533
	Temperature (K)	430
	Pressure (MPa)	0.25
	CO (vol.%)	22.0
	CO_2 (vol.%)	22.8
	H_2 (vol.%)	4.2

Hot metal, Slag	
Hot metal temp. (K)	1,800
Slag / hot metal ratio	0.30

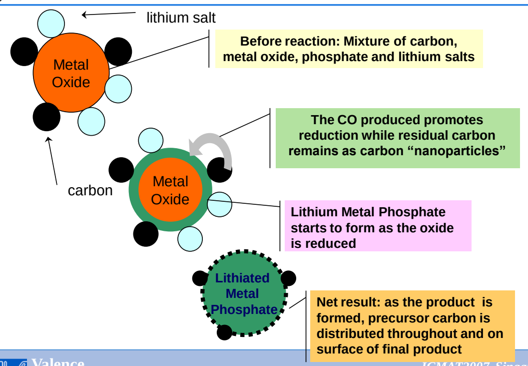
Composition (mass %)			
Hot metal		Slag	
C	4.50	SiO_2	33.8
Si	0.39	CaO	42.5
Mn	0.27	Al_2O_3	14.3
P	0.10	MgO	6.5
S	0.03	MnO	0.26
		S	0.96

Characteristics of Carbothermal Reduction

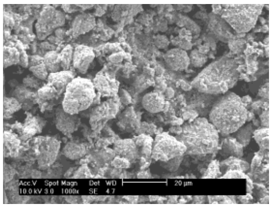
- Process 'borrowed' from the Extractive Metallurgy Industry
- Uses a particulate carbon to 'reduce in' the metal ion.
- Potential for use with cheap precursors (Fe_2O_3, V_2O_5, EMD etc)
- Residual carbon forms a highly conductive composite product
- Use same carbon as typical in Electrode Formulations (Super P)
- Valence Technology uses CTR to make all its active materials – at up to the Metric Tonne/day scale.
- Examples:

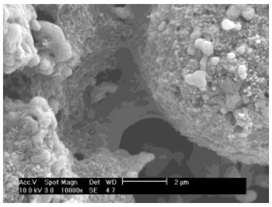
$$3\,LiH_2PO_4 + V_2O_5 + C \rightarrow Li_3V_2(PO_4)_3 + 3\,H_2O + CO$$
$$LiH_2PO_4 + 0.5\,Fe_2O_3 + 0.5\,C \rightarrow LiFePO_4 + H_2O + 0.5\,CO$$
$$LiH_2PO_4 + 0.5\,Mn_2O_3 + 0.5\,C \rightarrow LiMnPO_4 + H_2O + 0.5\,CO$$
$$0.5\,V_2O_5 + (NH_4)_2HPO_4 + C \rightarrow VPO_4 + 2\,NH_3 + H_2O + 0.5\,CO$$

CTR: A Schematic Representation

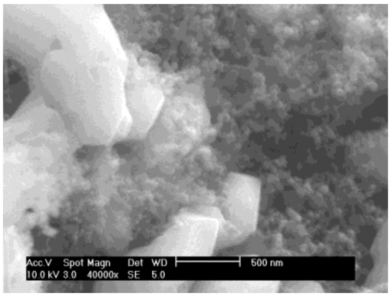


SEM of Carbothermal Material





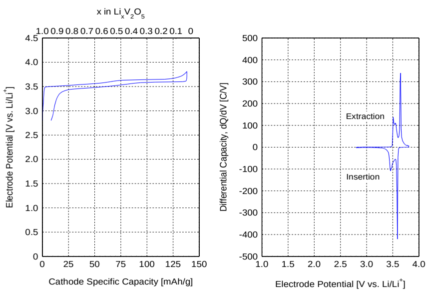
SEM of Carbothermal Material



γ–LiV_2O_5

$0.5\ Li_2CO_3 + 0.5\ V_2O_5 + 0.5\ C \rightarrow LiV_2O_5 + 0.5\ CO_2 + 0.5\ CO$

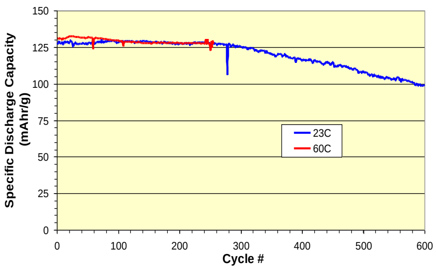
Li//γ–LiV_2O_5



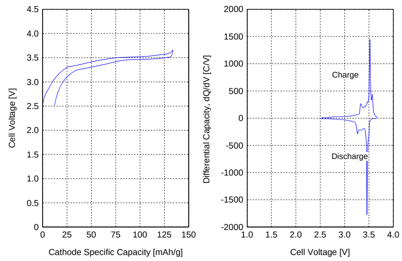
J. Barker et al. J. Electrochem. Soc. **150,** *A1267, (2003)*

Life Cycling of Li // γ–LiV_2O_5

C/5 Rate, 2.80–3.80 V



Graphite//γ-LiV_2O_5

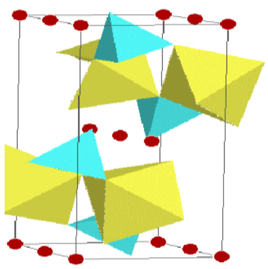


J. Barker et al. J. Electrochem. Soc. ***150****, A1267, (2003)*

$LiFe(Mg)PO_4$

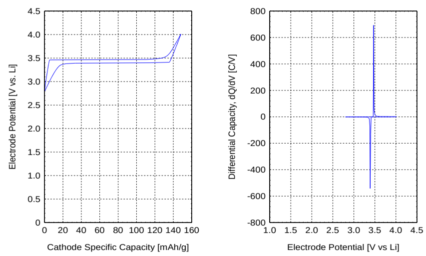
LiH_2PO_4 + 0.45 Fe_2O_3 + 0.1 $Mg(OH)_2$ + 0.45 C
→ $LiFe_{0.9}Mg_{0.1}PO_4$ + 1.1 H_2O + 0.45 CO

Olivine – $LiFe_{1-x}Mg_xPO_4$

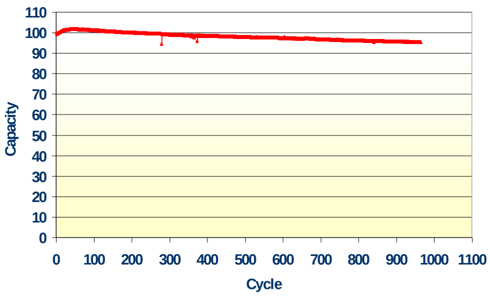


- 3- Dimensional Framework Structure
- Framework comprises PO_4 tetrahedra and MO_6 octahedra
- Fe and Mg occupy the same crystallographic position
- Controlled morphology and particle size give rise to fast electrode kinetics
- 150-170 mAh/g @ 3.45 V vs. Li
- Metric Tonne production

Li//$LiFe_{1-x}Mg_xPO_4$



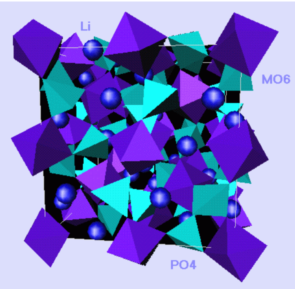
Graphite//$LiFe_{1-x}Mg_xPO_4$ – 18650 cycling



$Li_3V_2(PO_4)_3$

3 LiH_2PO_4 + V_2O_5 + C → $Li_3V_2(PO_4)_3$ + 3 H_2O + CO

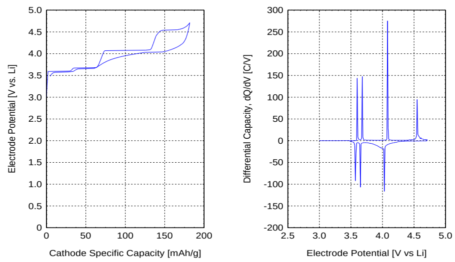
Structure of $Li_3V_2(PO_4)_3$



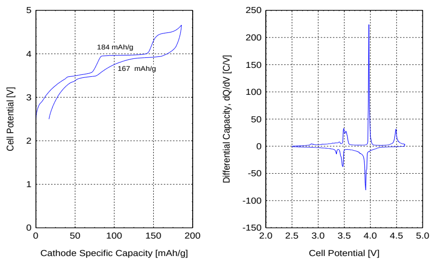
- 3- Dimensional Framework Structure
- Framework comprises PO_4 tetrahedra and slightly distorted MO_6 octahedra
- Three distinct crystallographic sites for Li^+
- High Li ion mobility gives rise to fast insertion kinetics
- All 3 Li ions extractable generating a specific capacity close to theoretical (197 mAh/g)

Acknowledgements: Profs. Goodenough, Delmas, Gopalakrishnan

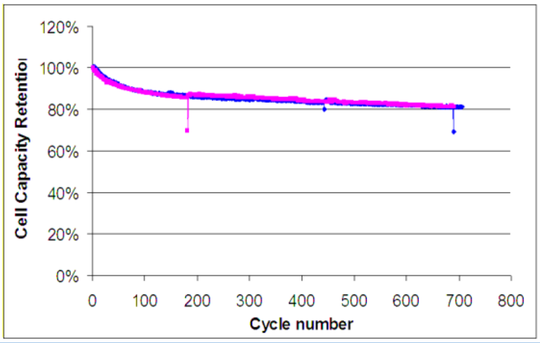
$Li//Li_3V_2(PO_4)_3$



$Graphite//Li_3V_2(PO_4)_3$



$Li_3V_2(PO_4)_3$ Lithium-ion cells: Cycling

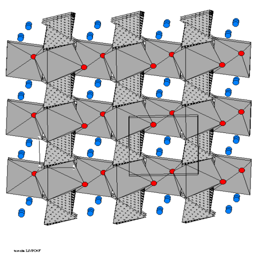


$LiVPO_4F$

$0.5\ V_2O_5 + (NH_4)_2HPO_4 + C \rightarrow VPO_4 + 2\ NH_3 + H_2O + 0.5\ CO$

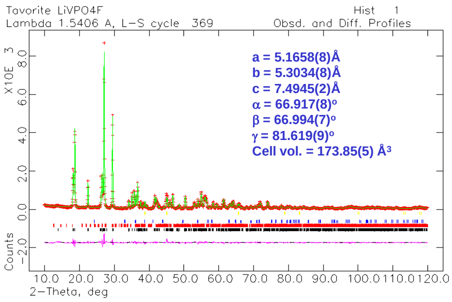
$LiF + VPO_4 \rightarrow LiVPO_4F$

Fluorophosphate – $LiVPO_4F$

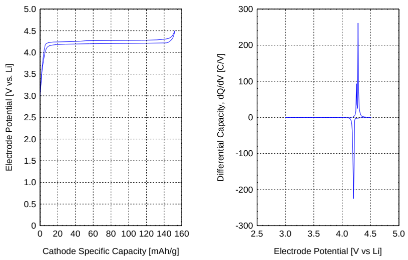


- Framework Triclinic Structure related to the minerals, Amblygonite $LiAlPO_4F$ and Tavorite $LiFePO_4OH$
- Structure comprises a 3D framework built up from PO_4 tetrahedra and MO_4F_2 octahedra
- Representation left is shown along the c-axis
- V located in the MO_4F_2 octahedra
- Electrochemistry suggests 2 sites for the Li ions

Refined XRD Data for $LiVPO_4F$ (Triclinic)

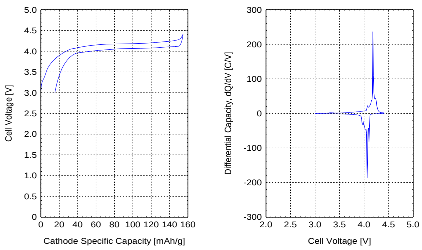


Li//$LiVPO_4F$



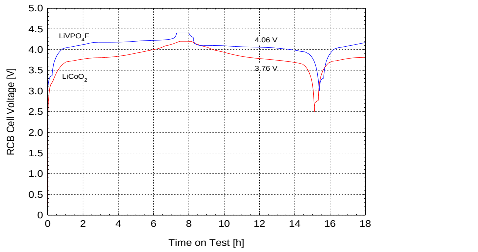
Theoretical Capacity - 155 mAh/g Reversible Specific Capacity!!

Graphite//$LiVPO_4F$



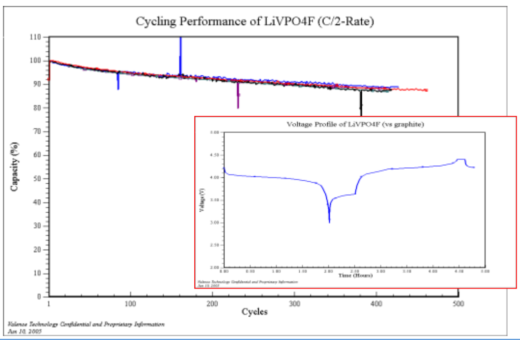
140 mAh/g Reversible Specific Capacity!!

$LiVPO_4F$ vs. LCO: Lithium-ion Cells

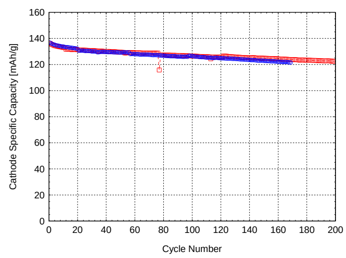


J. Barker et al. Solid State Ionics ***177****, 2635, (2006)*

$LiVPO_4F$ Lithium-ion cells: Cycling



$LiVPO_4F$ Lithium-ion cells: Latest Cycling

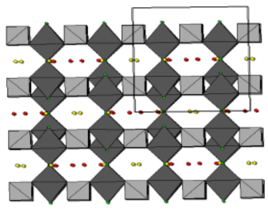


$Na_3V_2(PO_4)_2F_3$

0.5 V_2O_5 + $(NH_4)_2HPO_4$ + C → VPO_4 + 2 NH_3 + H_2O + 0.5 CO

3 NaF + 2 VPO_4 → $Na_3V_2(PO_4)_2F_3$

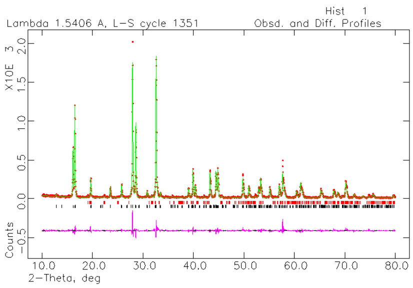
Fluorophosphate – $Na_3V_2(PO_4)_2F_3$



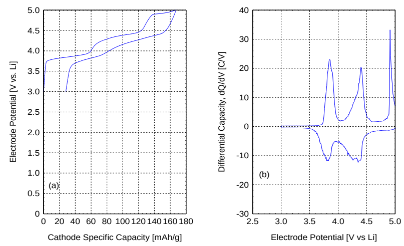
- Framework Tetragonal Structure built up from $[PO_4]$ tetrahedra and $[VO_4F_2]$ bi-octahedra with bridging Fluorine.
- Representation left is shown along the a-axis
- V in the MO_4F_2 octahedra
- Electrochemistry suggests 3 sites for the Na ions

J. Barker et al. Solid State Ionics ***177***, *1495, (2006)*

Refined Structure – $Na_3V_2(PO_4)_2F_3$

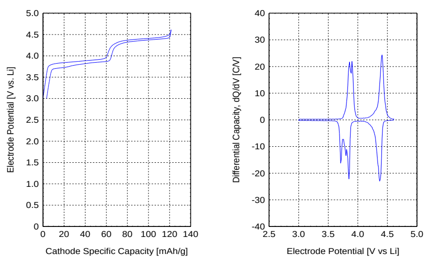


Li//$Na_3V_2(PO_4)_2F_3$



Simple Analytical Tool: weigh the cathode!

Li//$Na_3V_2(PO_4)_2F_3$



Novel Battery Applications

Alternate Cell Configurations

LITHIUM-ION

Graphite / Li electrolyte / Li cathode

SYMMETRICAL LITHIUM-ION

$LiVPO_4F$ / Li electrolyte / $LiVPO_4F$

SODIUM-ION

Hard Carbon / Na electrolyte / Na cathode

HYBRID-ION

Graphite / Li electrolyte / Na Cathode

Symmetrical Lithium-ion Cells

Symmetrical $LiVPO_4F$ Lithium-ion Cells

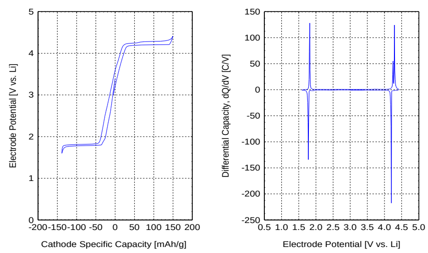
Concept

- Use the same active material as both anode and cathode
- Simplicity of manufacture and use (single electrode coating)
- Intrinsically safe: bullet-proof technology
- Very low cost
- Ideally suited for large format applications
- Bi-polar: Charge in either direction

Anode = Cathode = $LiVPO_4F$: 150 mAh/g

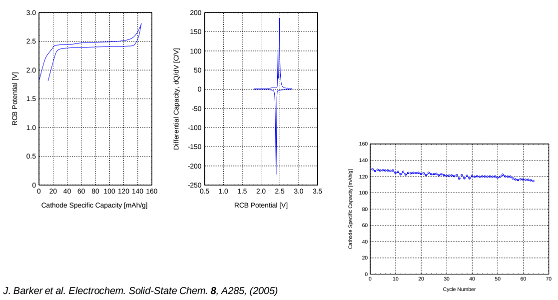
Electrolyte: 1M $LiPF_6$ in EC/DMC

Li//$LiVPO_4F$ – Dual Plateau Behavior



J. Barker et al. Electrochem. Solid-State Chem. **8**, A285, (2005)

$LiVPO_4F$//$LiVPO_4F$ Lithium-ion Cells



J. Barker et al. Electrochem. Solid-State Chem. **8**, A285, (2005)

Sodium-ion Cells

Sodium-ion Batteries

Concept

Sodium-ion: A safer/cheaper alternative to lithium-ion technology?

An enabling technology

Energy Density similar to lithium-ion

Anode: Hard carbon

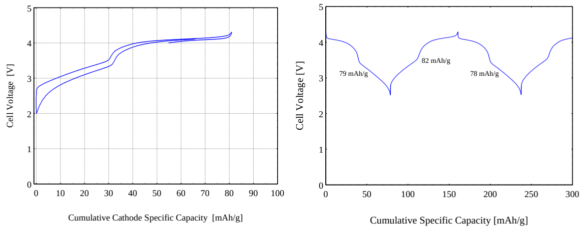
Electrolyte: 1M $NaPF_6$ in EC/DMC

Cathode: Na insertion material

Anode Reaction: Reversible Na^+ insertion

Cathode Reaction: Reversible Na^+ insertion

Sodium-ion: Hard Carbon/Na^+/$Na_3V_2(PO_4)_2F_3$



J. Barker et al. Electrochem. Solid-State Chem. ***6****, A1, (2003)*

Hybrid-ion Cells

Hybrid-ion Batteries

Concept

Hybrid-ion: An enabling technology - many new cell chemistries

Key Feature: Fully lithiated graphite is stable in a Na electrolyte

Anode: Graphite (but can also use e.g. $Li_4Ti_5O_{12}$)

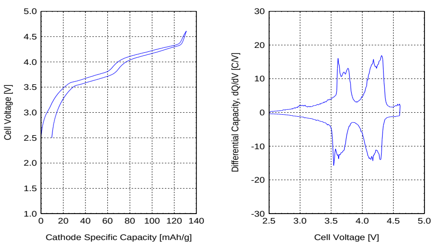
Electrolyte: 1M $LiPF_6$ in EC/DMC

Cathode: Na^+ insertion material

Anode Reaction: Reversible Li^+ insertion

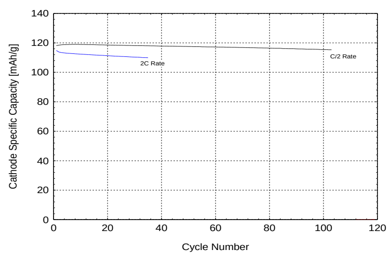
Cathode Reaction: Reversible Na^+ insertion (initially)

Hybrid-ion: Graphite /Li^+/$Na_3V_2(PO_4)_2F_3$



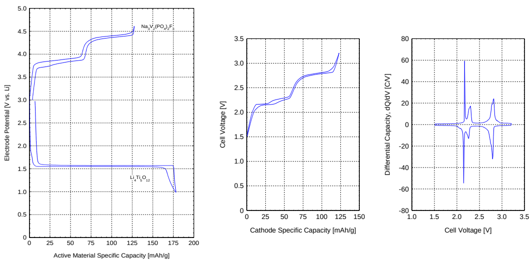
J. Barker et al. Electrochem. Solid-State Chem. 9, A190, (2006)

Hybrid-ion: Graphite /Li^+/$Na_3V_2(PO_4)_2F_3$

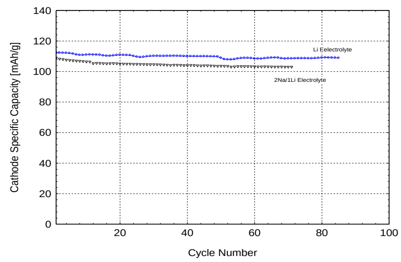


J. Barker et al. Electrochem. Solid-State Chem. 9, A190, (2006)

Hybrid-ion: $Li_4Ti_5O_{12}/Li^+/Na_3V_2(PO_4)_2F_3$



Hybrid-ion: $Li_4Ti_5O_{12}/Li^+/Na_3V_2(PO_4)_2F_3$



Other Phosphates – but no time to mention!!

- **Li_2MPO_4F** (US#6810686 + others)
- **Na_2MPO_4F** (US#6810686 + others)
- **$LiVPO_4$.OH** (US#6777132)
- **$LiVP_2O_7$**
- **β-$LiVOPO_4$**
- **New Active Phosphate Phases** – *ca.*150 mAh/g, 4 V vs. Li average, sloping and flat voltage profiles

Summary: Phosphates for Lithium-ion

✓Both sloping and flat discharge profiles are possible depending on the metal combinations and structure.

✓Carbothermal Reduction – low cost processing, scalable

✓Through the use of preparative methods exceptional life cycling and high rate performance may be attained.

✓Phosphate materials have demonstrated superior safety characteristics.

✓Applicability into new battery chemistries: sodium-ion, hybrid-ion, symmetrical lithium-ion etc.

Thank you for your attention!

www.valence.com
www.jerrybarker.co.uk