Phosphates for Lithium-ion Batteries: Materials, Synthesis and Future Opportunities

Valence Technology Inc.

Jerry Barker Consultants

Specialists in Electrochemical and Solid-State Chemistry

www.jerrybarker.co.uk

Overview of Presentation

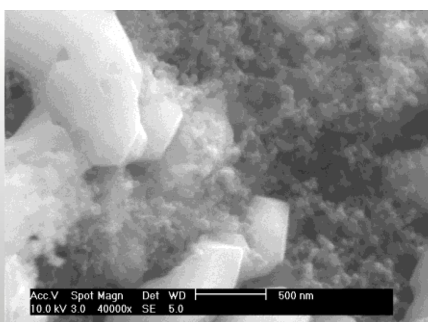
Introduction

- Valence Technology 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 making these active materials at a commercial scale. Developed the Carbothermal Reduction (CTR) Method.
- Today, Valence makes active materials using the CTR approach – up to Metric Tonne/day scale.

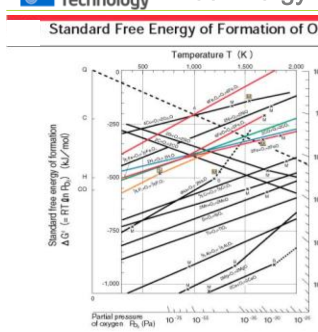
Carbothermal Reduction

- The Carbothermal Reduction (CTR) method utilizes a high surface area carbon as a selective reducing agent
- $2C + O_2 \rightarrow 2\ CO$ = 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)
- By design, the CTR technique leaves behind an embedded conductive network.
- Carbon monoxide formed during the synthesis both promotes further reduction and deposits carbon "nanoparticles"
- Net result: precursor carbon is finely distributed throughout and on surface of final product.

SEM of Carbothermal Material



Free Energy or Ellingham Diagrams



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

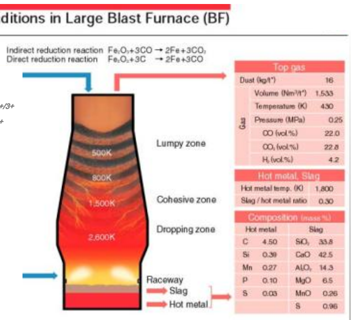
Iron Blast Furnace

Reaction Mechanisms:

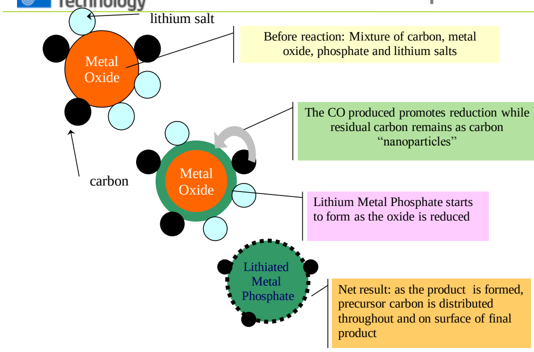
$3 Fe_2O_3 + CO \rightarrow 2 Fe_3O_4 + CO_2$ $Fe^{2+/3+}$
$Fe_3O_4 + CO \rightarrow 3 FeO + CO_2$ Fe^{2+}
$FeO + CO \rightarrow Fe + CO_2$ Fe^{0}

Intermediate Oxidation States:

$Fe^{3+} \rightarrow Fe^{2+}$
$Mn^{3+} \rightarrow Mn^{2+}$
$V^{5+} \rightarrow V^{3+}$
$Mo^{6+} \rightarrow Mo^{4+}$ etc.



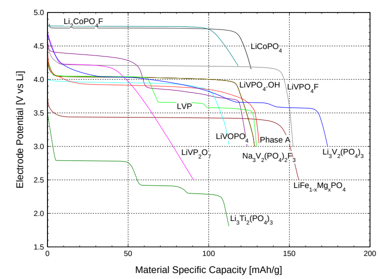
CTR: Schematic Representation



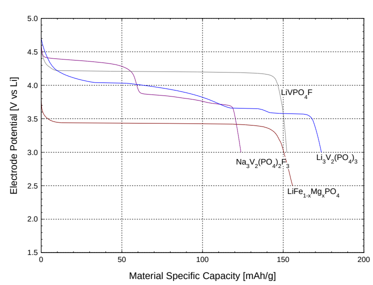
Valence Studied Phosphates

Material	Nominal Voltage vs. Li	Specific Capacity mAh/g	Inventor	US Patent#	Comments
$LiFePO_4$	3.45	140-160	J. Goodenough	US 5910382 and others	Olivine
$LiFe_{1-x}M_xPO_4$	3.45	140-160	J.Barker *et al*	US 6884544 and others	M = Mg, Ca, Zn
$Li_3V_2(PO_4)_3$	3.6-4.7	197	J.Barker *et al*	US 5871866 and others	Nasicon
$LiVPO_4F$	4.2	155	J.Barker *et al*	US 6387568 and others	Triclinic
$LiVPO_4.OH$	4.1	158	J.Barker *et al*	US 6777132 and others	Triclinic
$LiVP_2O_7$	4.1	116	---	---	Diphosphate
Li_2MPO_4F	4.7	143	J.Barker *et al*	US 6964827 and others	M = Co, Ni etc.
Na_2MPO_4F	4.7	122	J.Barker *et al*	US 6872492 and others	M = Co, Ni etc.
$Li_4V_2(SiO_4)(PO_4)_2$	3.6-4.7	260	J.Barker *et al*	US 6136472 and others	Silicophosphate
$Li_3V_{1.5}Al_{0.5}(PO_4)_3$	3.6-4.7	203	J.Barker *et al*	US 5871866 and others	Nasicon
β-$LiVOPO_4$	4.0	159	J.Barker *et al*	US 6645452 (CTR)	Prepared by CTR
$NaVPO_4F$	3.7	143	J.Barker *et al*	US 6872492 and others	Sodium Ion
$Na_3V_2(PO_4)_2F_3$	3.7	192	J.Barker *et al*	US 6872492 and others	Sodium Ion
Novel Phase A	3.8	*ca.* 150	J.Barker *et al*	Pending	Application Pending
Novel Phase B	3.9	*ca.* 140	J.Barker *et al*	Pending	Application Pending
Novel Phase C	3.5	*ca.* 145	J.Barker *et al*	Pending	Application Pending

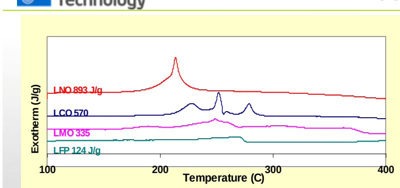
Phosphate Chemistry

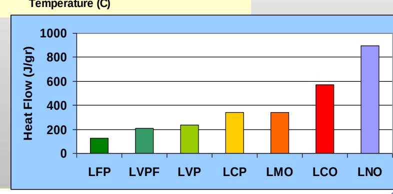


Phosphate Chemistry (cont..)

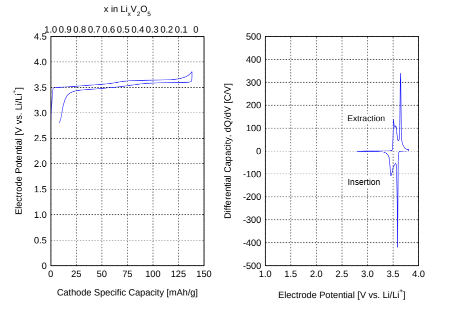


Phosphate Safety

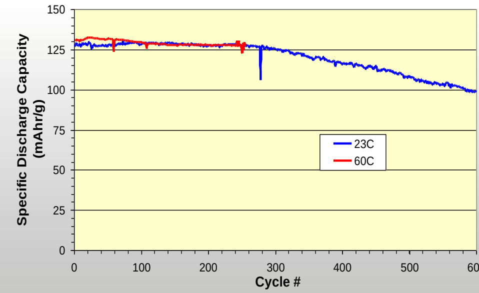




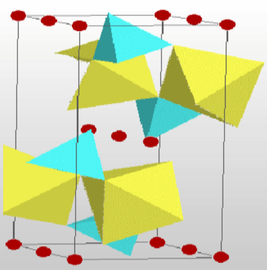
Valence Technology — $Li//\gamma\text{-}LiV_2O_5$



Valence Technology — Cycling of Graphite//$\gamma\text{-}LiV_2O_5$ Prototypes

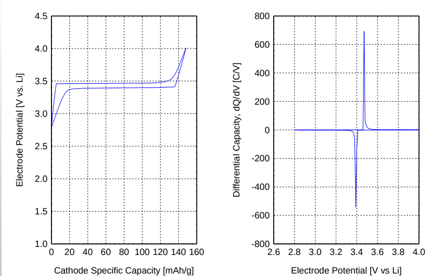


Valence Technology — $LiFe_{1-x}Mg_xPO_4$



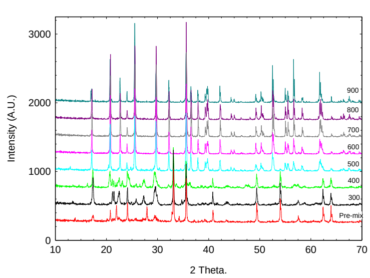
- 3-Dimensional Framework Structure
- Framework comprises PO_4 tetrahedra and MO_6 octahedra
- Fe and Mg occupy the same crystallographic position
- Controlled morphology and particle size give rise to fast electrode kinetics
- 150-170 mAh/g @ 3.45 V vs. Li
- Metric Tonne production

Valence Technology — $Li//LiFe_{1-x}Mg_xPO_4$



Valence Technology — $LiFePO_4$: *ex-situ* XRD study of CTR

$LiH_2PO_4 + ½ Fe_2O_3 + ½ C \rightarrow LiFePO_4 + H_2O + ½ CO$

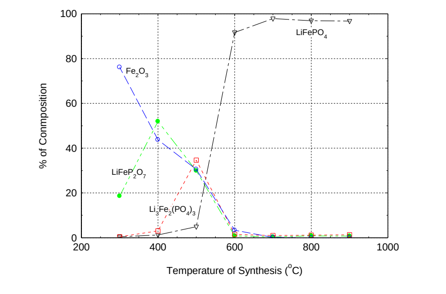


Valence Technology — $LiFePO_4$: *ex-situ* XRD study of CTR

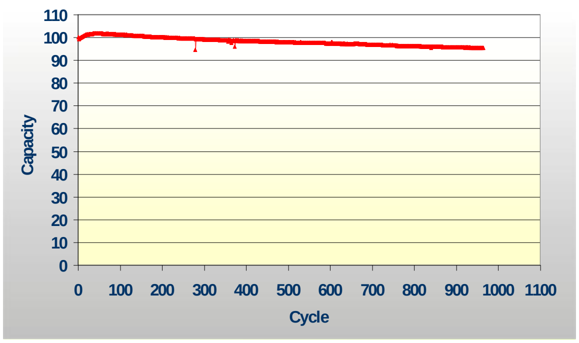
Filename	Temp(°C)	LiH_2PO_4 %	Fe_2O_3 %	$Li_3Fe_2(PO_4)_3$ %	$LiFePO_4$ %	$Li_4P_2O_7$ %	$LiFeP_2O_7$ %	$FePO_4$ %	$Fe_2P_2O_7$ %
S3245	300	2.92	76.15	0.40	0.38	0.74	18.59	0	0
S3245_1	400	0	43.74	3.06	1.24	0	51.959	0	0
S3245_2	500	0	30.54	34.62	4.92	0	29.92	0	0
S3245_3	600	0	3.32	1.50	91.65	0	0.84	0.46	2.24
S3245_4	700	0	0.18	0.96	97.84	0	0.33	0.33	0.36
S3245_5	800	0	0	1.16	96.89	0	0.84	0.32	0.79
S3245_6	900	0	0	1.32	96.73	0	0.73	0.53	0.69

$LiFePO_4$: *ex-situ* XRD study of CTR

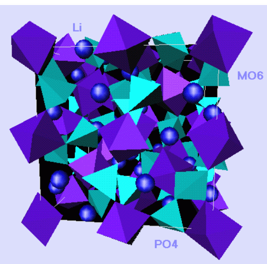
Message: $LiFePO_4$ starts to forms at <400°C under CTR conditions



Cycling of Graphite//$LiFe_{1-x}Mg_xPO_4$ 18650



$Li_3V_2(PO_4)_3$



3-Dimensional Framework Structure

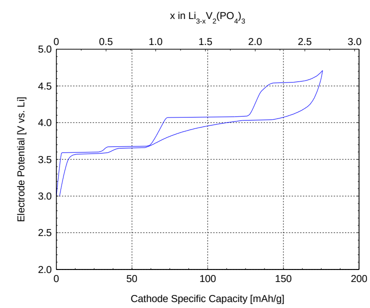
Framework comprises PO_4 tetrahedra and slightly distorted MO_6 octahedra

Three distinct crystallographic sites for Li^+

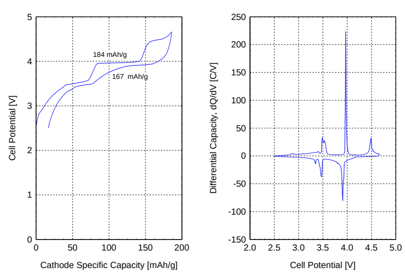
High Li ion mobility gives rise to fast insertion kinetics

All 3 Li ions extractable generating a specific capacity close to theoretical (197 mAh/g)

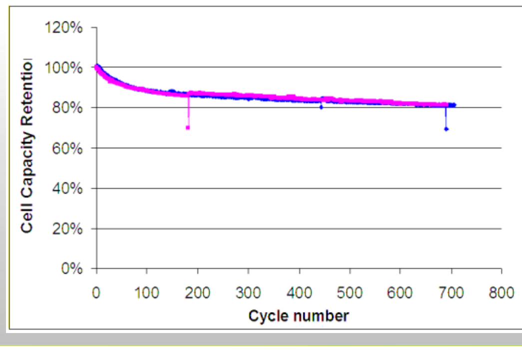
$Li//Li_3V_2(PO_4)_3$



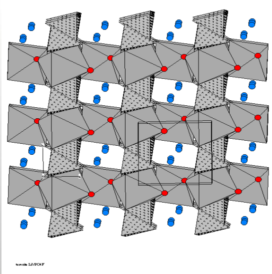
Graphite//$Li_3V_2(PO_4)_3$



Cycling Graphite//LVP Prototypes

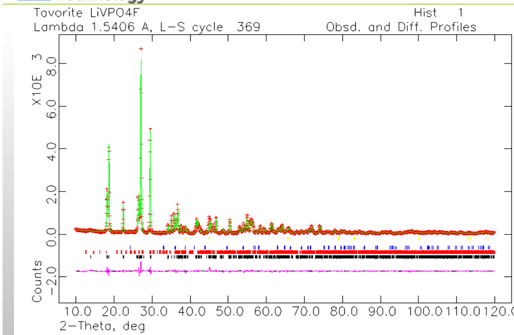


LiVPO$_4$F



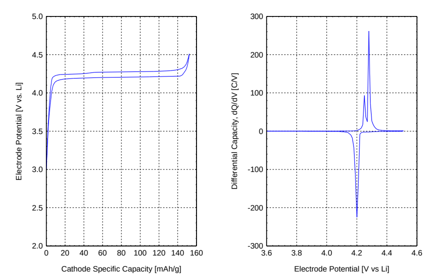
- Framework Triclinic Structure related to the minerals, Amblygonite LiAlPO$_4$F and Tavorite LiFePO$_4$OH
- Structure comprises a 3D framework built up from PO$_4$ tetrahedra and MO$_4$F$_2$ octahedra
- Representation left is shown along the c-axis
- V located in the MO$_4$F$_2$ octahedra
- Electrochemistry suggests 2 sites for the Li ions

Refined XRD for LiVPO$_4$F

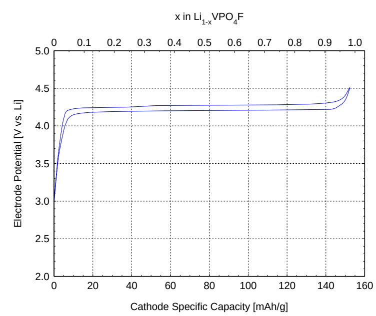


Li//LiVPO$_4$F

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

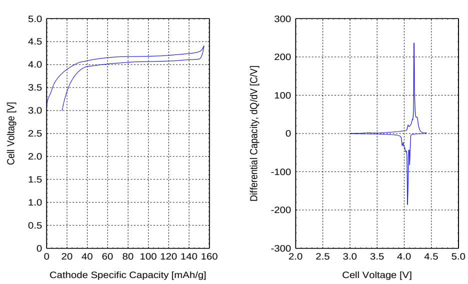


Li//LiVPO$_4$F



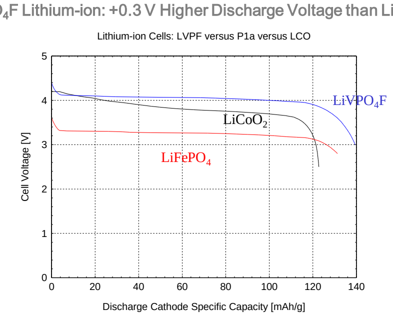
Graphite//LiVPO$_4$F

140 mAh/g Reversible Specific Capacity!!

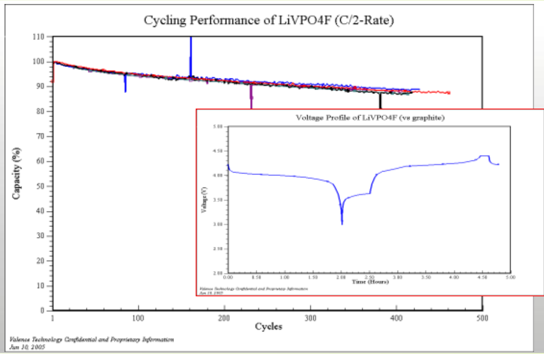


LiFePO$_4$ vs. LiVPO$_4$F vs. LiCoO$_2$

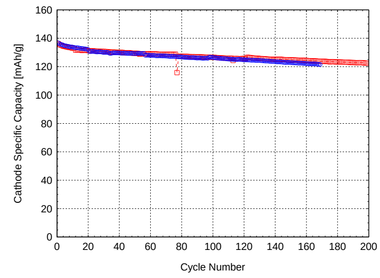
LiVPO$_4$F Lithium-ion: +0.3 V Higher Discharge Voltage than LiCoO$_2$



Valence Technology — Cycling Graphite//$LiVPO_4F$ Prototypes



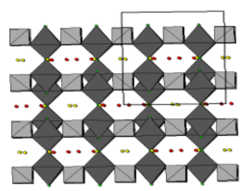
Valence Technology — Latest: Cycling Graphite//$LiVPO_4F$ Cells



Valence Technology — Lithium-ion: $LiFePO_4$ *vs.* $LiVPO_4F$

	$LiFePO_4$	$LiVPO_4F$
Safety	**Excellent**	**Excellent**
Cycle Life	**Excellent**	**Good**
Cost (CTR)	**Good**	**Good**
Energy Density	**Moderate**	**Excellent**
Power	**Excellent**	**Excellent**
Large Format	**Yes**	**Yes**
Float	**Excellent**	**Good**
Temp. Performance	**Excellent**	**Excellent**

Valence Technology — $Na_3V_2(PO_4)_2F_3$



Framework Tetragonal Structure built up from $[PO_4]$ tetrahedra and $[VO_4F_2]$ bi-octahedra with bridging Fluorine.

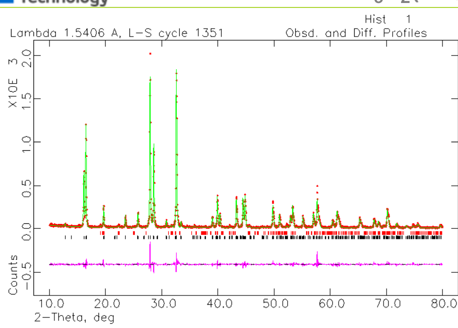
Representation left is shown along the a-axis

V in the MO_4F_2 octahedra

Electrochemistry suggests 3 sites for the Na ions

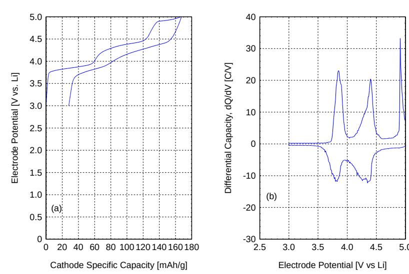
Possibility of Li/Na ion exchange

Valence Technology — Refined XRD for $Na_3V_2(PO_4)_2F_3$



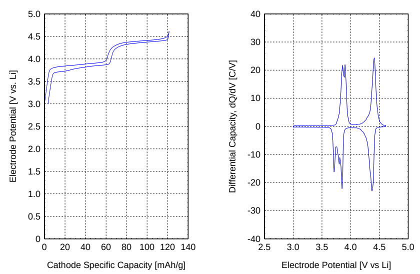
Valence Technology — $Li//Na_3V_2(PO_4)_2F_3$

Simple Analytical Tool: weigh the cathode! Δmass = 16.5 %



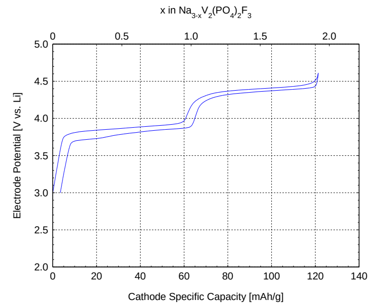
Li//$Na_3V_2(PO_4)_2F_3$

Valence Technology



Li//$Na_3V_2(PO_4)_2F_3$

Valence Technology



Alternate Cell Configurations

Valence Technology

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

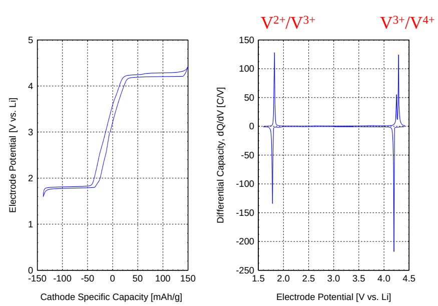
Symmetrical Lithium-ion Cells

Valence Technology

- Concept: Use the same active material as both anode and cathode – for example: $LiVPO_4F$
- Single Electrode Coating gives simplicity of manufacture, cost and use (single electrode coating)
- Intrinsically safe: a 'bullet-proof 'technology
- Ideally suited for large format applications
- Moderate Energy Density but High Rate
- Bi-polar: Charge in either direction
- Improvement over $Li_4Ti_5O_{12}$ Anode Technology

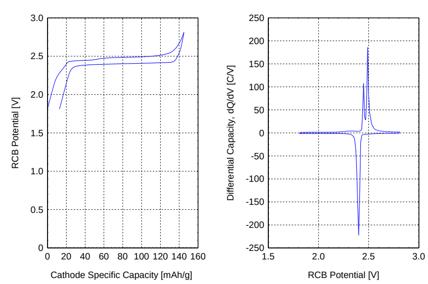
Two Plateaus: Li//$LiVPO_4F$

Valence Technology

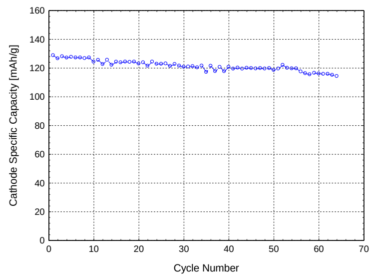


$LiVPO_4F$//$LiVPO_4F$

Valence Technology



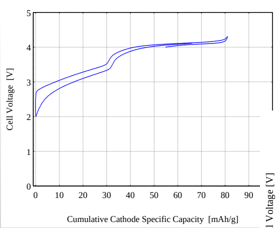
Valence Technology — $LiVPO_4F//LiVPO_4F$

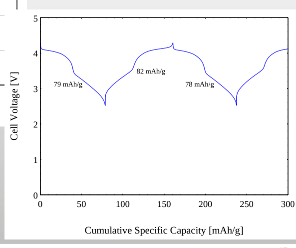


Valence Technology — Sodium-ion Cells

- Sodium-ion: A viable alternative to lithium-ion technology
- Non-graphitic Negative Electrode Material (typically Hard Carbon)
- Energy Density should be similar to lithium-ion
- Possibility of Inexpensive Active Materials
- The field is relatively un-chartered
- Safer Technology?

Valence Technology — Sodium Ion: Hard Carbon/Na^+/$Na_3V_2(PO_4)_2F_3$

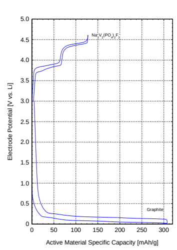


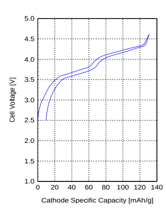


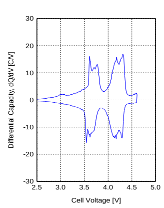
Valence Technology — Hybrid-ion Cells

- Concept: Use Sodium based positive electrodes with Li insertion negatives electrodes - for example: Graphite//$Na_3V_2(PO_4)_2F_3$
- All the Li for the negative electrode reaction originates from the electrolyte
- An enabling technology - many new cell chemistries
- Key Feature: Fully lithiated graphite is stable in a Na^+ electrolyte
- Negative Electrode Reaction: Reversible Li^+ insertion
- Positive Electrode Reaction: Reversible Na^+ insertion (initially)

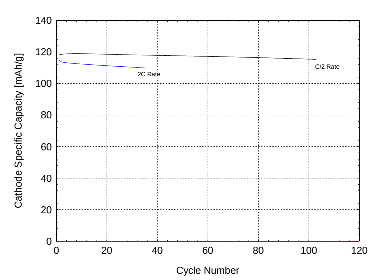
Valence Technology — Hybrid-ion Cell: Graphite/Li^+/$Na_3V_2(PO_4)_2F_3$



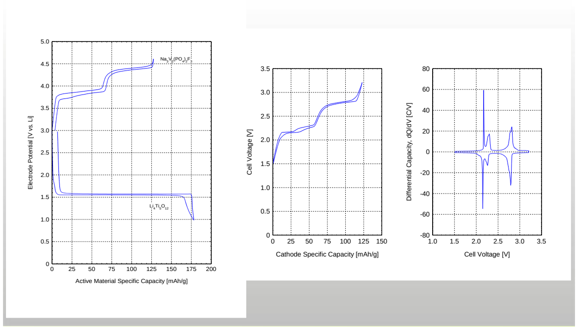




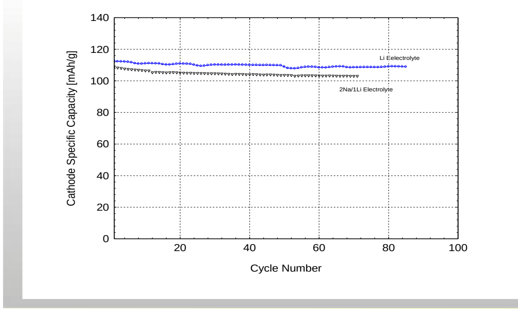
Valence Technology — Hybrid-ion Cell: Graphite/Li^+/$Na_3V_2(PO_4)_2F_3$



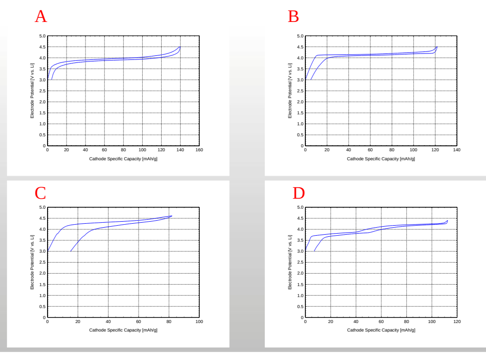
Hybrid-ion Cell: $Li_4Ti_5O_{12}/Li^+/Na_3V_2(PO_4)_2F_3$



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



Novel Phosphate Phases: Not Published



Conclusions

- Both sloping and flat discharge profiles are possible depending on the metal combinations and structure.
- Carbothermal Reduction – low cost processing, scalable
- General attributes include: exceptional life cycling, good rate performance, outstanding safety characteristics.
- Phosphate materials are particularly suitable for large format applications – EV/HEV etc
- Applicability into new battery configurations: sodium-ion, hybrid-ion, symmetrical lithium-ion etc.
- There are still many new active phases to discover – just do not look in the normal places!!

Electric Vehicles

Hybrid Electric Vehicles

Personal Transportation Devices

Defense

Thank you for your attention

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