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Phosphate materials for lithium batteries and energy storage

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Abstract

The trend to electrification in our societies calls for other sources of energy and storage than carbon materials, especially fossil ones. Lithium batteries have emerged in the last decades as a convenient way to store and deliver the most noble and versatile form of energy: electricity. From cell phones and other portable applications, the technology is now growing fast as a vector to store energy for transportation and use on the grid. Lithium's light weight, its reactivity to form Li₂O and its small ionic radius have led to the development of Li-insertion oxide structures that can act as electrode materials or electrolytes. Phosphate materials have recently been discovered that can make new stable complex oxide structures allowing the design of safer, performing and economically viable large-scale storage batteries, C-LiFePO₄ being the most successful one to date.

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Keywords: phosphates, lithium, battery, insertion electrode, energy storage, LiFePO₄, olivine.

Introduction

Energy and energy storage are becoming key issues for our societies and the XXIth century will see major changes in the development of new forms of energy and consequently new means for its storage.

Until now, most industrialized and emerging countries have benefited from fossil energy sources that were widely and easily available, diversified and at an affordable cost: coal, petroleum and natural gases. With an unprecedented demographic growth, generalization of the industrial development and the consequences of human activities on the generation of gaseous effluents from combustion on pollution and climate change, it is becoming obvious that other forms of energy and means of storage need to be developed in a near future, especially in the ever increasing transportation sector. Such development will trigger new economies and industries linked to energy generation and storage per se but also to natural resources exploitation that must be sustainable and environmentally compatible given the scale of their use for energy generation and storage and for transportation.

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Nuclear fusion, the actual source of all solar activity and external radiation, is in fact the main source of energy on earth and it will remain so unless man succeeds its elusive dream of controlling nuclear fusion locally and for useful applications. At the earth level, energy from the sun is present under different forms:

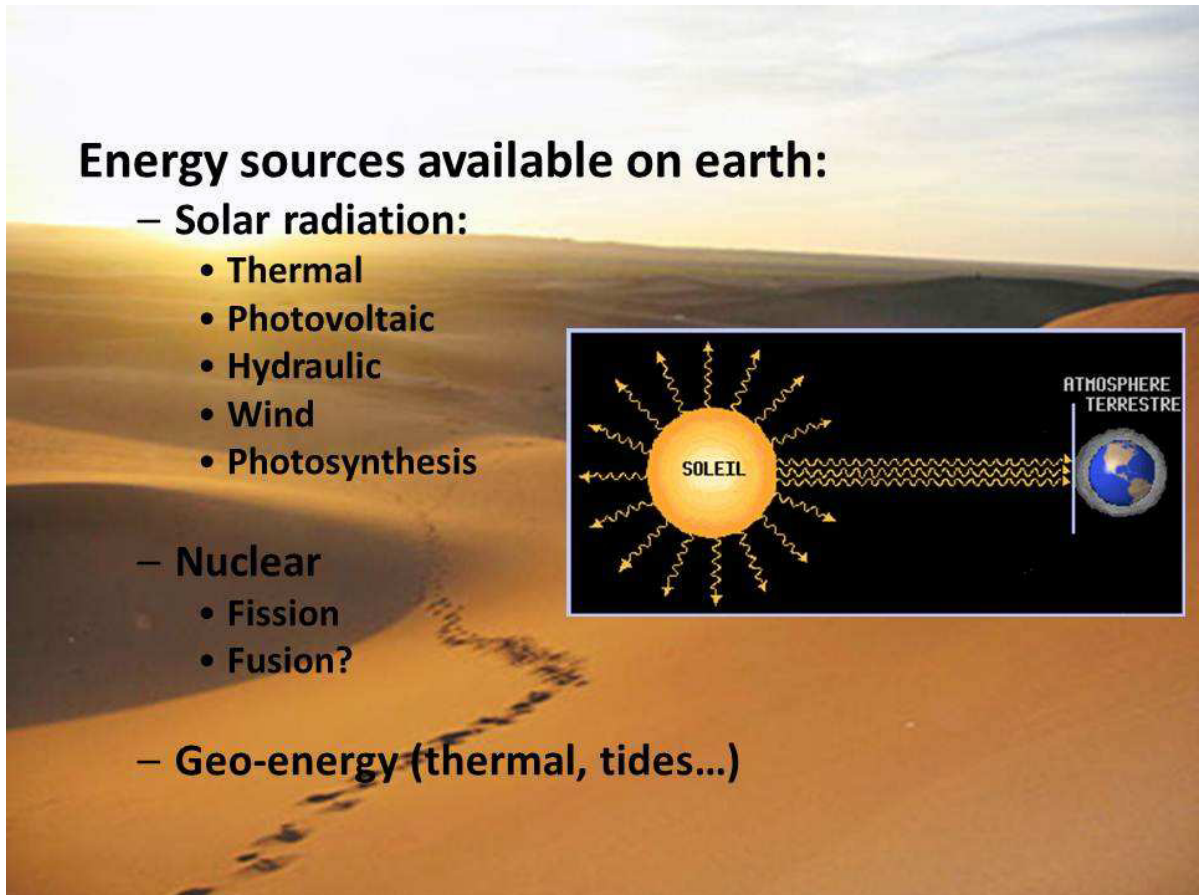
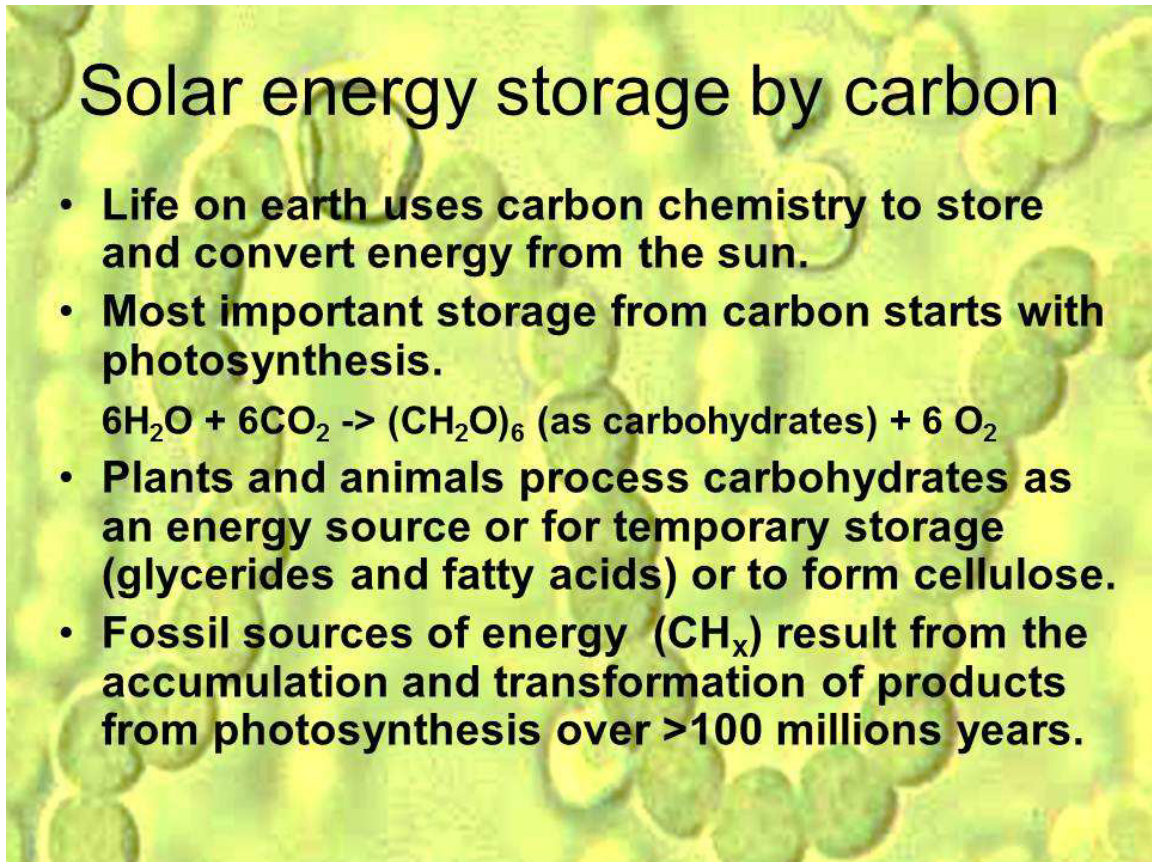


Fig. 1. Energy sources available on earth

Very early on in the earth's geological history, new forms of life have learned to use solar radiation as a source of energy for their growth and to store this energy as carbohydrates from available chemicals: water and gases present in the earth atmosphere: $\text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons (\text{CHO})_x$:



Solar energy storage by carbon

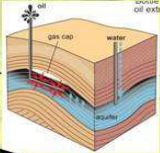



- **Life on earth uses carbon chemistry to store and convert energy from the sun.**
- **Most important storage from carbon starts with photosynthesis.**
$$6\text{H}_2\text{O} + 6\text{CO}_2 \rightarrow (\text{CH}_2\text{O})_6 \text{ (as carbohydrates)} + 6 \text{O}_2$$
- **Plants and animals process carbohydrates as an energy source or for temporary storage (glycerides and fatty acids) or to form cellulose.**
- **Fossil sources of energy (CH_x) result from the accumulation and transformation of products from photosynthesis over >100 millions years.**

Fig. 2. Energy storage with carbon (blue-green algae background)

The extraordinarily diversified chemistry of carbon is at the origin of life on earth but also at the origin of the huge storage mode of solar energy over time, namely the fossil hydrocarbon storage, e.g., coal, petroleum and natural gas; these resulting ultimately from the accumulation over several hundred million years of different living organisms from photosynthetic activity whose sediments have been transformed in the earth crust chemical reactor.

Such a storage mode of solar energy through fossil carbon offers different advantages but also presents drawbacks and limitations when its use becomes widespread. The energy and power available in the gas tank of a car is the perfect example of the success of carbon to store and deliver energy, but also of the capacity of mankind to totally modify its environment and way of life. Taping this finite source of fossil energy is now achieved however at the price of pollution, greenhouse gas accumulation and the disappearance of easily accessible reserves. Furthermore, the inefficiency of conversion of petroleum to the wheel of a car (<5%) or to other forms of non-thermal energy, the raising price of this limited resource and the difficulty to 'recharge' such a fuel, points out to the need to develop other energy storage modes better adapted than carbon to store the different forms of solar energy on earth:

C storage characteristics

- **Advantages:**
 - Presently available: coal, petroleum and natural gas.
 - Energy and Power in a very dense form (Wh,W/kg,L).
 - Partially renewable (if from biomass).
- **Disadvantages:**
 - Inefficient conversion to electricity (~ 30%)
 - Pollution and greenhouse effect from fossil sources (CO₂, SO_x...).
 - ‘Slow recharge’ (vs battery)
 - Petroleum (>100 million years) → 
 - Biomass (one season-25 years) → 
 - Animal (one night or more...)
 - 
 - 




Fig. 3. Advantage and disadvantage of energy storage with carbon chemicals

Thermodynamics teaches that energy is preserved during its transformation but degrades at least partially to a lower form, usually thermal:

Energy conversion and storage

- **Conversion rules:**
 - First law of thermodynamics:
 - Energy can be converted into other forms but is conserved (no gain, no loss)
 - Second law of thermodynamics:
 - Energy nobility is degraded (entropy) at each conversion
 - e.g. electric => mechanic => thermal
- **Chemical means to store solar energy:**
 - Storage by carbon (C, CH_x, CHO_x...)
 - Efficient conversion to thermal energy
 - Electrochemical storage (Li, H₂, redox...)
 - Efficient conversion to and from electricity.

Fig. 4 Energy conversion and storage

However, certain forms of energy, so called 'noble energies', can be transformed more efficiently into other forms. Electrical energy especially can be easily transformed into mechanical, light, chemical, electrochemical or thermal energy with an efficiency close to 100% by opposition to fossil chemical form of energy whose conversion efficiency to electrical energy is about 35% only, the rest being lost as degraded thermal energy. For these reasons, electrical energy storage is quite attractive whether for large scale storage of intermittent sources of energy: solar, wind or waves.... or electrical transportation: EV (Electrical Vehicle), PHEV (Plug-in Hybrid Electrical Vehicle), HEV (Hybrid Electrical Vehicle) or for its day-to-day uses in small mobile applications such as laptops, cell phones, portable tools.... It is a fact that primary cells and batteries have contributed to the acceleration of the electrification of our societies, resulting in an ever increasing need for lighter and more compact storage batteries evolving from initial Volta cell to Leclanché (Zn-MnO₂), to Planté (Pb-PbO₂) and Edison (Fe-Ni) still in use in certain applications, and more recently to lithium systems.

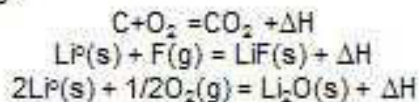
2 – Lithium batteries and their applications

The basic difference between chemical storage and electrochemical storage is illustrated in the following figure:

Electrochemical storage

• Chemical reaction:

Direct combination of atoms with electron exchange and heat release, e.g.:



• Electrochemical reaction:

'Reversible' reaction with ion exchange separated from electron exchange to obtain an electrical work:

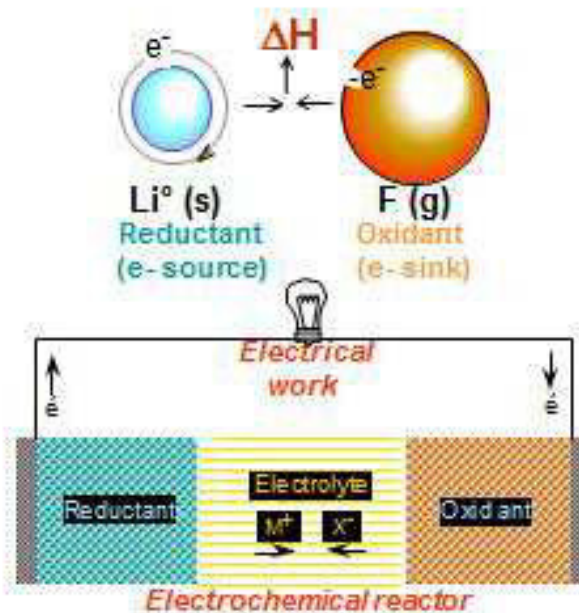
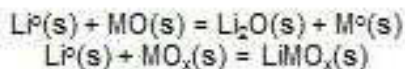
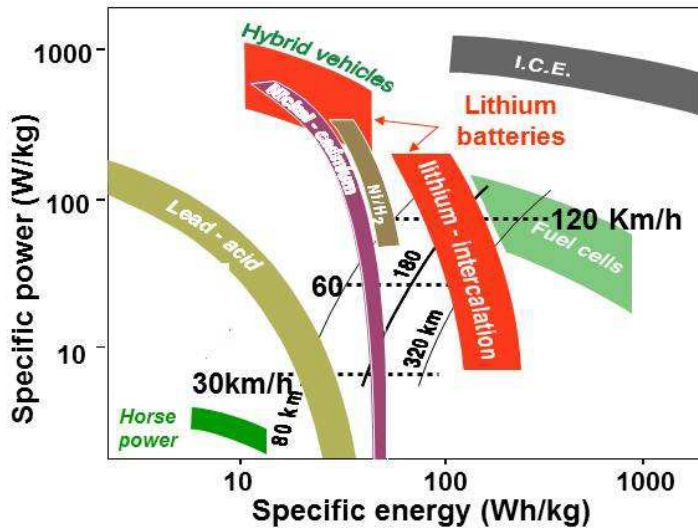


Fig. 5 Electrochemical vs chemical energy storage.

In the first case, the chemical reaction, the reducing agent (electron donor) meets directly with an oxidant (electron acceptor) to combine the two elements together with an electron exchange and energy release (heat). In the second case, the electrochemical reaction, these two exchanges are separated in such a way that the reductant and/or the oxidant will reach each other through an electrolyte (in ionic form) while the electron must go through a metallic circuit in order to produce an electrical work equivalent to the energy (free) of the overall reaction. In a rechargeable battery, these exchanges are reversible whenever the external circuit forces the electron (and the ions) in the reverse direction.

Lead has been (and nickel later on) the main element used in rechargeable batteries since lithium appeared some 50 years ago, first in primary cells followed later by rechargeable cells. Lead's atomic weight and its limited storage and power capability rapidly disqualified the first electric vehicles from significant applications as early as the turn of the XXth century as illustrated by comparing the specific power and energy of lead with different sources of energy including the more recent lithium systems. :

Lithium impact on electrical transportation



Edison and the electric vehicle: no progress from 1913 to ~1970

➔ By its low weight and reactivity, lithium broke the vicious circle inherent to the lead-acid battery!

Fig. 6 Ragone curves used to compare different sources of energy and power for transportation.

Ironically it is the lead-acid battery that finally contributed to the Internal Combustion Engine’s (ICE) success by activating the automatic starter of the gas powered car. This Fig. 6 is useful to compare easily the different modes of chemical and electrochemical energy storage in the case of automotive transportation. Specific energy and power are translated into range and speed of the vehicle for the different storage modes: from lead-acid to lithium batteries, fuel cells, ICE and even for living organisms (e.g., horse) allowing easier comparison; however other parameters such as recharge time, cost and availability are not taken into account.

First criteria to design a high performance battery are found in the periodic table of the elements as shown in the following figure :

Why a lithium battery ?

Energy storage capacity depends on the reaction's free energy (ΔG) and chemical reactant weights:

$\Delta G_{(react.)} = n F E$

Specific energy:
(Wh/kg) = $n F E / \Sigma R_{wt}$

Specific power:
(W/kg) = $V I / \Sigma R_{wt}$

Li (s) + F₂ (g) → LiF

Li

- Light weight (7g/at.) vs Pb (207 g/at.)
- Small ionic radius: 0.068nm => fast ion diffusion in many solids
- (+) Allows high voltage emf, (3-5 Volts), (-) not compatible with water
- Forms useful passivation films (SEI) in many non-aqueous solvents

Fig. 7. Li weight is important but other lithium and lithium-ion characteristics are also uniques.

Thermodynamics teaches that the storage capacity (e.g. Wh/kg) of a battery is directly proportional to the electrochemical reaction free energy (ΔG) and inversely proportional to the reactants' weights. Lithium light weight (7g/at. Vs 207g/at.for lead), its reactivity (as a reductant) (high ΔG), its small ionic radius (0.6Å) favourable to Li⁺-ion insertion in crystal structures and its tendency to form Li⁺-ion conducting passivation layers (SEI, Solid Electrolyte Interface) made this element the material of choice to design high specific energy batteries to store electrical energy. In less that 50 years, lithium cells have evolved from primary button cells to rechargeable cells using lithium-metal, C₆Li or rocking-chair anodes, while using a variety of liquid, solid, polymer Li⁺-ion conducting electrolytes. Their success being due in most part to the development of Li⁺-ion insertion electrodes (cathodes) essential for long cycle life and energy efficiency (energy-out/energy-in).

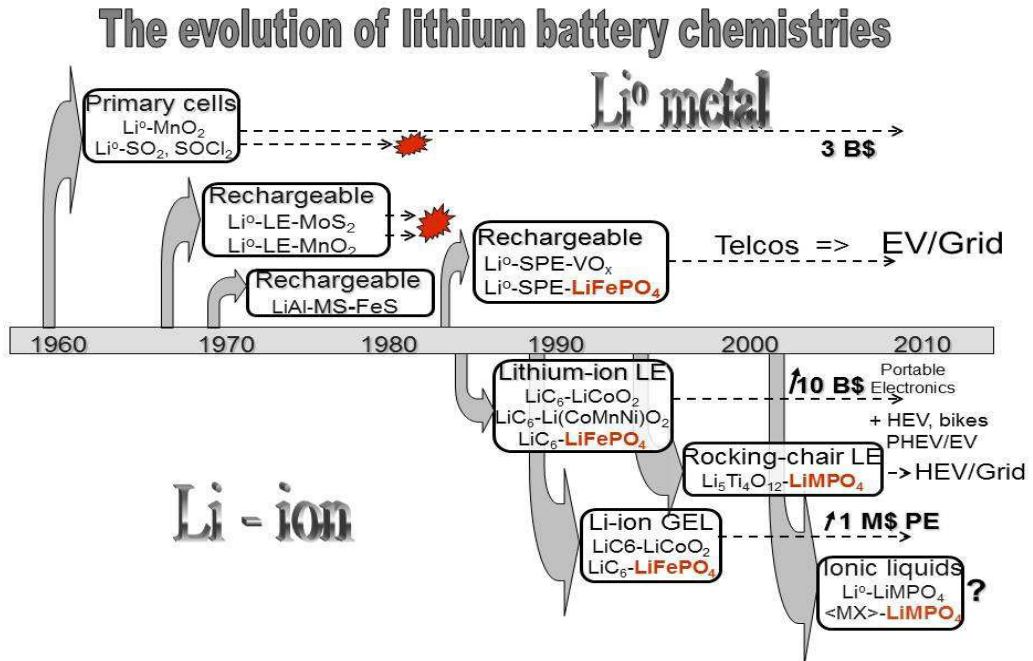


Fig. 8. Lithium battery chemistries evolution over 50 years. LE is for liquid aprotic electrolytes, MS for LiCl-KCl molten salts, SPE for solid ethylene oxide polymer electrolytes and GEL for polymer-liquid gel electrolytes.

The typical lithium rechargeable batteries presently available are illustrated in Fig. 8 and 9 and are: LiC₆/cobalt oxide-based lithium-ion presently used for portable electronics, the lithium iron phosphate systems using LiC₆ anode, the lithium titanate Li₄Ti₅O₁₂ anode or the all-solid lithium metal-polymer anode/electrolyte system.

Main lithium battery technologies

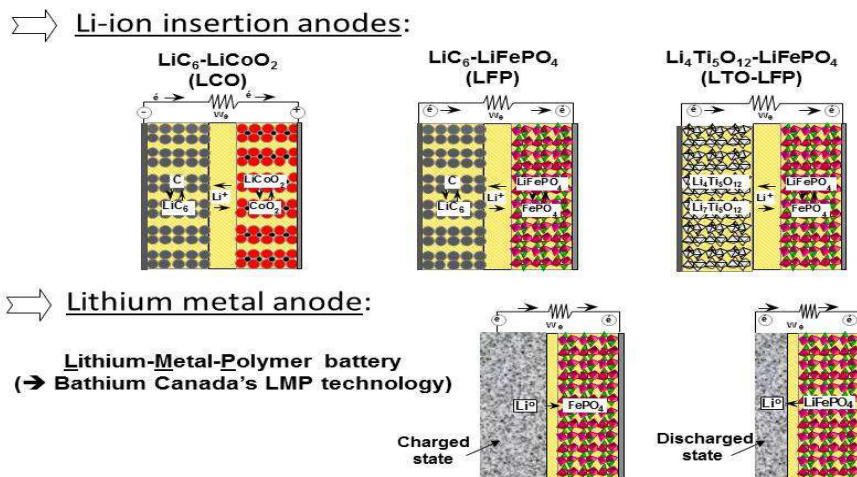


Fig. 9 Two competing technologies for large battery applications: lithium metal (solid polymer) vs lithium-ion (liquid electrolyte).

One scientist has especially influenced the phenomenal growth of lithium rechargeable batteries with his discovery of complex oxide Li^+ -insertion electrodes. As early as 1980, Dr. J.B. Goodenough invented the LiCoO_2 insertion cathode that made possible the lithium-ion battery used in most electronic applications. He was also co-inventor of the manganese oxide spinel cathode under development and more recently was the inventor of the iron phosphate cathodes of the olivine and nasicon structures [1,2].

One conclusion derived from Figure 7 is that the ideal ‘Lithium Battery’ should be the lithium-air system given the light weight of the reactants and the energy of the $\text{Li}^0\text{-O}_2$ couple to form Li_2O ($>5\text{kWh/kg}$). However, the reversibility of the O_2/O^- electrode and the development of an electrolyte compatible with both the oxygen and lithium electrodes solvent are still elusive. Today, the success of lithium batteries rests on the use of multivalent transition metal oxides capable of reduction and of reversible lithium-ion insertion/deinsertion instead of oxygen itself thus reducing the energy storage capacity ($\sim 0.5\text{kWh/kg}$). Despite this success, oxide cathodes, especially cobalt-based ones, have led to safety issues in the charged state (e.g. lamellar CoO_2) due to oxygen release in abusive conditions that have triggered expensive cellular phone or laptop recalls after accidental fires.

By showing that the complex polyoxides such as phosphates, e.g. LiFePO_4 , can reversibly insert lithium ions at a voltage as high as 3.44V vs Li^0 while stabilizing oxygen with the P-O covalent bond [1], Dr. Goodenough allowed the lithium-ion technology to build safe large batteries that can address new markets such as the electric vehicle and grid energy storage. Phosphate chemistry will be discussed in a following section.

Fig.10 illustrates the main present applications in portable electronics and tools and the phenomenal growth of these markets now over 10 billion dollars.

Typical lithium rechargeable markets



Lithium metal primary cells.

Present lithium-ion rechargeable applications

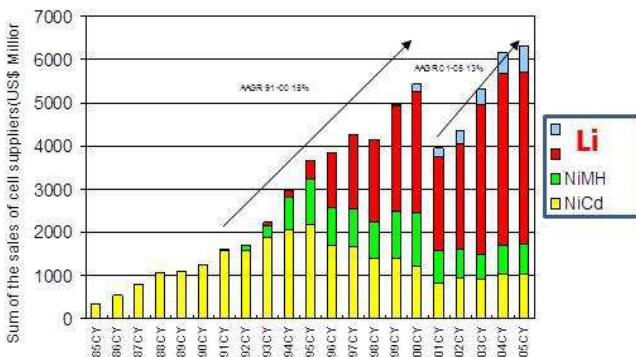


Fig. 10. Present Li-ion battery applications and growth.

Figure 11 illustrates some future and already existing applications for large Li-batteries ranging from energy storage from different intermittent sources of energy as well as for energy storage at the distribution level (smart grid) or at user level for mobile applications of electrical energy. The illustration covers the special case of Québec where solar energy (hydraulic form) could be used for electrical transportation but also the case of Morocco with its large potential for direct solar energy (photovoltaic) not to mention the huge phosphate mineral deposits to support large phosphate-based lithium batteries.

Phostech's vision of the future

(making lithium a partial alternative to carbon fuels!)

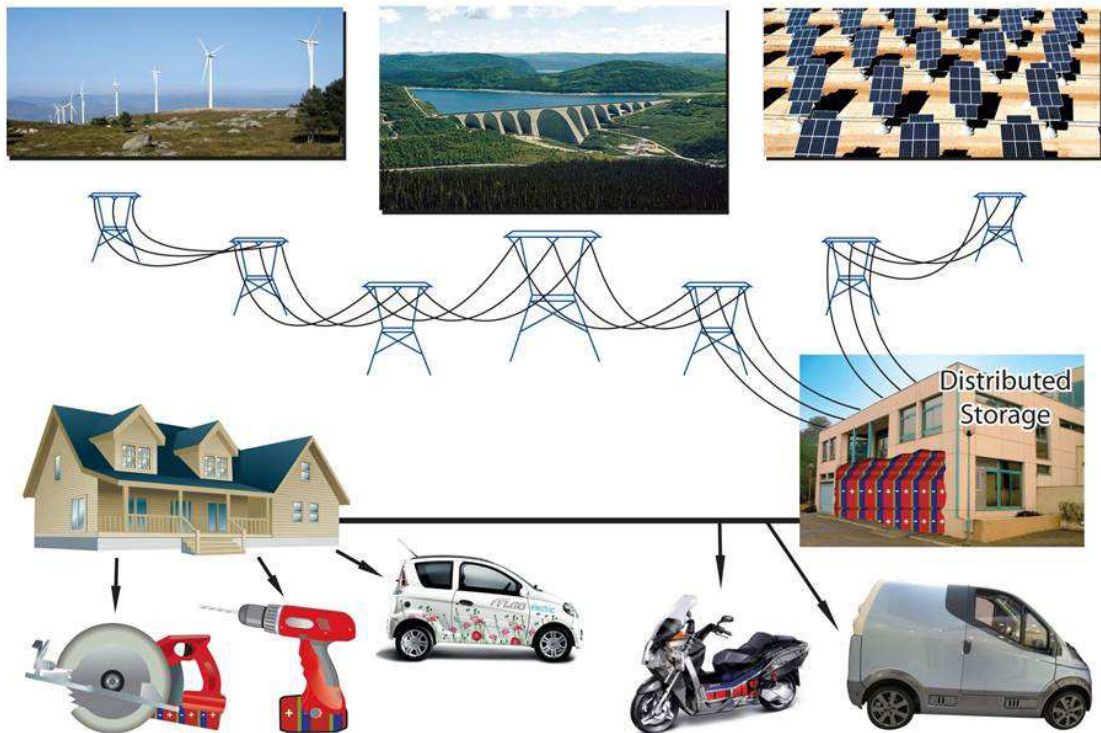


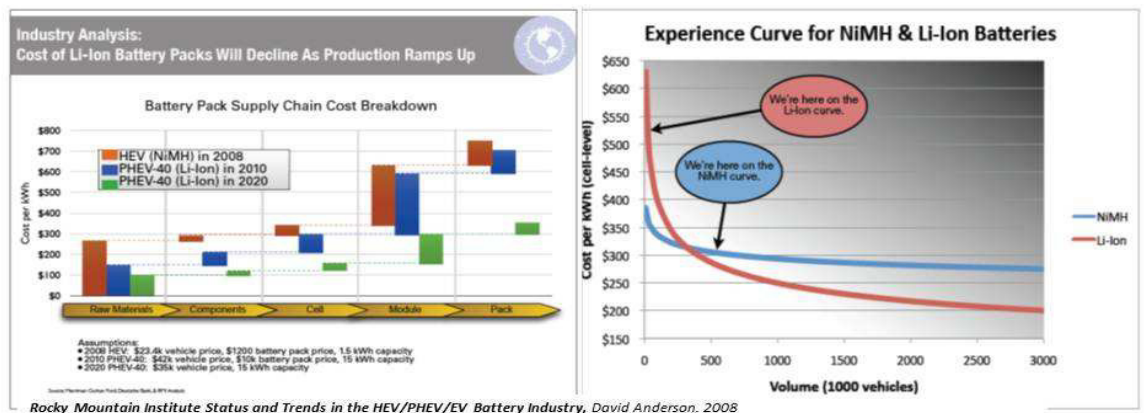
Fig. 11. Illustration of large lithium battery uses on the grid and for electrical transportation.

Now that small lithium batteries have broken the vicious circle of the lead acid battery (with 4 to 5 times the specific energy & power and cycle life) and proven to be a commercial success in the portable electronics and tool markets, new challenges associated with large lithium batteries must be addressed. For example, to meet the electric vehicle challenges further than the existing HEV application and market, large lithium batteries must prove safe, environment compatibility and sustainable (with recycling) and demonstrate 10-15 years of calendar life under harsh environments (high and low temperatures, mechanical shocks...) and most important, must reduce the present fabrication cost (materials, processes, cells and battery management system) by a

factor of 5 to 3, depending on cycle life. Failing to meet these challenges will confine the lithium rechargeable battery to marginal EV and PHEV applications and to smaller systems like e-bikes and HEV where the installed battery source is smaller and remain affordable.

Cost reduction projections required from volume production are illustrated in Figure 12.

Li-ion cost breakdown: the main challenge for PHEV et VE penetration



Rocky Mountain Institute Status and Trends in the HEV/PHEV/EV Battery Industry, David Anderson, 2008

HEV:	1.5 kWh	1200\$ pack in 2008	23.4k\$ per vehicle
PHEV-40:	15 kWh	10,000\$ pack in 2010	42 k\$ per vehicle
PHEV-40:	15 kWh	5 000\$ pack in 2020	35 k\$ per vehicle
EV-200:	48 kWh	12 000\$ pack (250\$/kWh)	

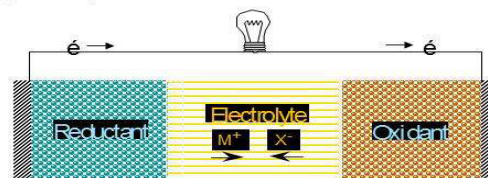
(1000 cycles)

Fig. 12. Cost breakdown of Li-ion battery, trend and impact of installed battery size on the vehicle cost. Figures from: Status and trends in the HEV/PHEV/EV battery industry. Rocky Mountain Institute, David Anderson, 2008.

3 – The rightful place of phosphates (phosphorus) in lithium batteries.

Figure 13 illustrates present and potential uses of phosphates (and phosphorus) in the different electrolytes, anodes and cathodes of lithium batteries:

Applications of phosphates in lithium batteries



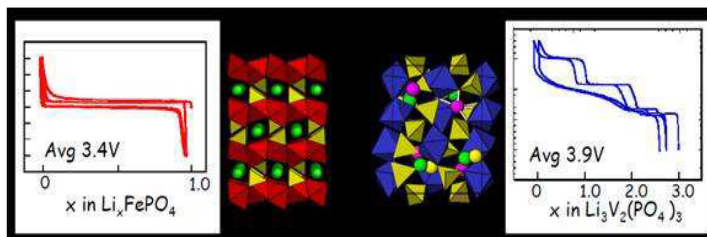
Lithium battery technology	Present or potential applications
Liquid aprotic electrolytes:	Cathodes: LiFePO_4 [1], R&D: LiMPO_4 [1], $\text{Li}_3\text{MM}'(\text{PO}_4)_3$ [2], LiFePO_4F [3] Anode: LiC_2 or $\text{Li}_4\text{Ti}_5\text{O}_{12}$, R&D: FePO_4 [4], $\text{LiTi}_2(\text{PO}_4)_3$ [5], Li-Sn-P [6]... Electrolyte: Organic carbonates+ LiPF_6 , R&D: flame retardant phosphates? Separator: PP or PE, ceramic, R&D: $\text{Li}_{1.3}\text{Ti}_{1.7}\text{Al}_{0.3}(\text{PO}_4)_3$ [7]
Solid polymer electrolyte:	Cathode: LiFePO_4 , R&D: LiPO_3 surface additive or binder[8] Anode: Li^0 Electrolyte-Separator: Polyether copolymer + imide salt (TFSI)
Solid electrolyte (R&D):	Cathodes: LiCoPO_4 [9] Anodes: $\text{LiTi}_2(\text{PO}_4)_3$ [5], $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ [9] Electrolyte-Separator: LiPON [10], LiSiCON , $\text{Li}_{1.3}\text{Ti}_{1.7}\text{Al}_{0.3}(\text{PO}_4)_3$ + Li_3PO_4 [11]

Fig. 13. Present (red) and under development (magenta) uses of phosphates in Li-batteries.

Historically, the use of phosphorus in lithium batteries is as a lithium salt, LiPF_6 , essential to induce Li^+ -ion conductivity in liquid electrolytes but also, until now, essential to condition and make reversible the graphite anode by contributing to the formation of a useful passivation film SEI (Solid Electrolyte Interface). It is interesting to note that the first phosphate crystalline structures (Nasicon and Lisicon) of interest for batteries have been studied first as solid lithium (or sodium)-ion conducting electrolytes. Depending on the transition metal used, these Li-ion conducting solids can also behave as reversible electrodes in which Li^+ -ion can reversibly be inserted or de-inserted coupled with a variation of the oxidation state of the transition metal. It is interesting to note that Dr. J.B. Goodenough worked on Nasicon phosphate structure as electrolyte and electrode material, [1,2], before inventing the LiFePO_4 cathode of the olivine structure. Fig. 14 illustrates applications of phosphate structures as electrolytes and as Li-reversible electrodes:

Phosphates presently used in Li-batteries

- Today, LiPF_6 is the most widely used phosphorous derivative in most rechargeable Li-ion batteries.
- LiFePO_4 and its analogs of the olivine structure is the most recent discovery as a reversible Li-ion cathode material for large batteries.
- More open Nasicon structure materials, e.g., $\text{Li}_x(\text{M}_x\text{M}'_{1-x})_2(\text{PO}_4)_3$ are actively studied both as electrolytes and electrodes:



Nazar IMLB 2004, Nara, Japon ↗

Aono Solid State Ionics, 47 (1991), 257-264 ↗

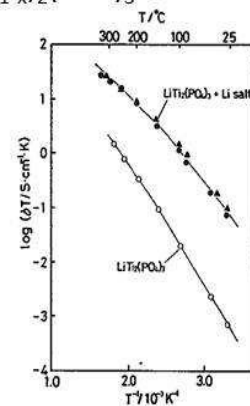


Fig. 3. Temperature dependence of the electrical conductivity: $\text{LiTi}_3(\text{PO}_4)_3$ (O); $\text{LiTi}_3(\text{PO}_4)_3 + 0.2\text{Li}_3\text{PO}_4$ (●)

Fig. 14. Phosphates structures currently used as cathode and electrolyte

Versatility of polyanions Nasicon phosphate structures as electrolytes or as electrodes plus their thermal stability linked to the P-O covalent bond make possible several applications in lithium batteries. However, it is the olivine phosphate structures illustrated in Fig. 15, more compact and favorable to high voltage $\text{M}^{2+}/\text{M}^{3+}$ transition metal couple that enabled the success of the LiFePO_4 cathode in new generations of lithium batteries as proposed by Dr. J.B. Goodenough [1]:

The unique case of the LiFePO_4 olivine structure!

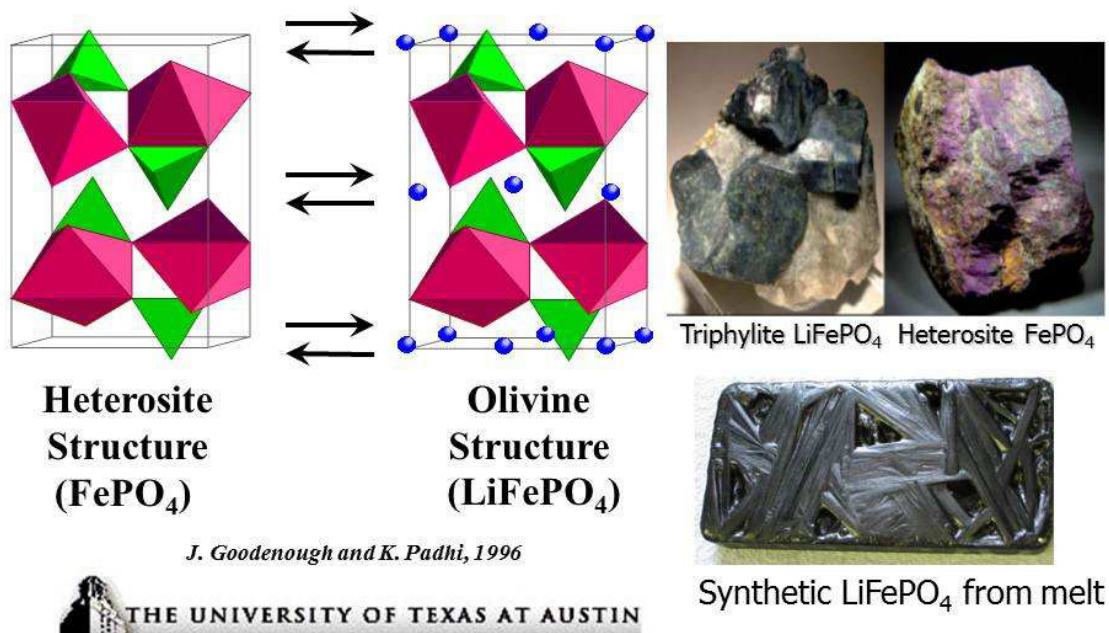


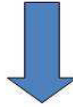
Fig. 15. Natural or synthetic LiFePO_4 as a Li-ion reversible structure

The iron phosphate olivine structure exist in nature both in its lithiated and delithiated form (triphylite and heterosite) that correspond to the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple reversible at 3.45V vs Li° , an unusually high voltage for iron, a non-toxic element widely available in the earth crust. As shown on Fig. 15, thermal stability of triphylite is such that it is possible to melt-synthesize the product at 1000°C .

Despite these attractive features, the LiFePO_4 cathode presented some drawbacks: a density lower than the layered oxides such as LiCoO_2 and more important, limited transport properties. Electronic conductivity is lower than in cobalt or nickel oxides, consequence of the covalent polyanionic phosphate. Li^+ -ion diffusivity is also limited given the tortuous channel structure for Li-ion diffusion in the olivine vs lamellar oxides. Lower density is more important for small portable applications for which volume is a must and might be improved by Fe substitution in $\text{LiFe}_{1-y}(\text{M}_y)\text{PO}_4$, e.g. $\text{M}_y = \text{Mn}$ or Co . Limited Li^+ diffusivity in the olivine structure is solved by technology by using sub-micronic particle size as suggested by Dr. Goodenough [1].

The most important question of the low intrinsic electron conductivity in LiFePO_4 was finally solved based on N. Ravet's observation [12] that the pyrolysis of traces of organic material during or after the LiFePO_4 synthesis generates a conductive nano-pyrolytic carbon deposit on the LiFePO_4 surface. This fortuitous contamination from polypropylene jars made during reactant grinding led to a strategy of carbon nano-painting from different organic precursors based on the observation that inert or reducing condition required to synthesize LiFePO_4 allowed the deposition of pyrolytic carbon without full reduction of iron to metallic state, Figures 16-18, reference [12].

Symbiotic association of C and LiFePO_4
to make high performance C-LiFePO_4



Nanometric Pyrolytic Carbon Deposition (PCD) on LiFePO_4 particles allows rapid electron exchanges and high rates



Pyrolytic Carbon Deposited (PCD) C-LiFePO_4

Specific capacity, uncoated LiFePO_4 :	100-110 mAh/g, [1]
Specific capacity, PCD C-LiFePO_4:	150-165 mAh/g, [12]

Fig. 16. Strategy for LiFePO_4 optimization

Nano-scale pyrolytic carbon deposit illustrated on Fig. 17 is intimately bonded to the LiFePO_4 surface and the symbiotic product represented as C-LiFePO_4 :

Symbiotic association of LiFePO_4 with pyrolytic carbon allows energy, power and cyclability optimization

Organic precursor pyrolysis during or after LiFePO_4 synthesis can form a nanometric conductive C deposit:

The organic precursor can be a solid, a liquid or a gas, including CO.

As illustrated, the pyrolytic carbon deposit (PCD) is intimately linked to the elementary or secondary (agglomerated) particles.

An additional benefit from the carbon deposit is to reduce LiFePO_4 sintering during synthesis, allowing the definition of a final product from its precursor size and shape, e.g. 50nm à 15 μ particles or agglomerates.

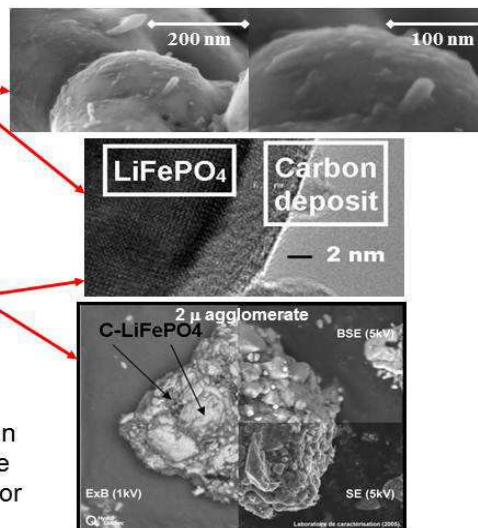


Fig. 17. Illustration of nano carbon deposits (including C nano tubes CNT) on LiFePO_4 elementary or secondary particles.

The symbiosis between LiFePO_4 and pyrolytic carbon deposit is essential to obtain full material capacity, power and cyclability. This is recognized by the fact that carbon is present in most LiFePO_4 described in scientific publications and in most commercial products. Pyrolytic Carbon Deposit (PCD) patents described in Fig. 18 are complementary to Dr. Goodenough's basic composition patents:

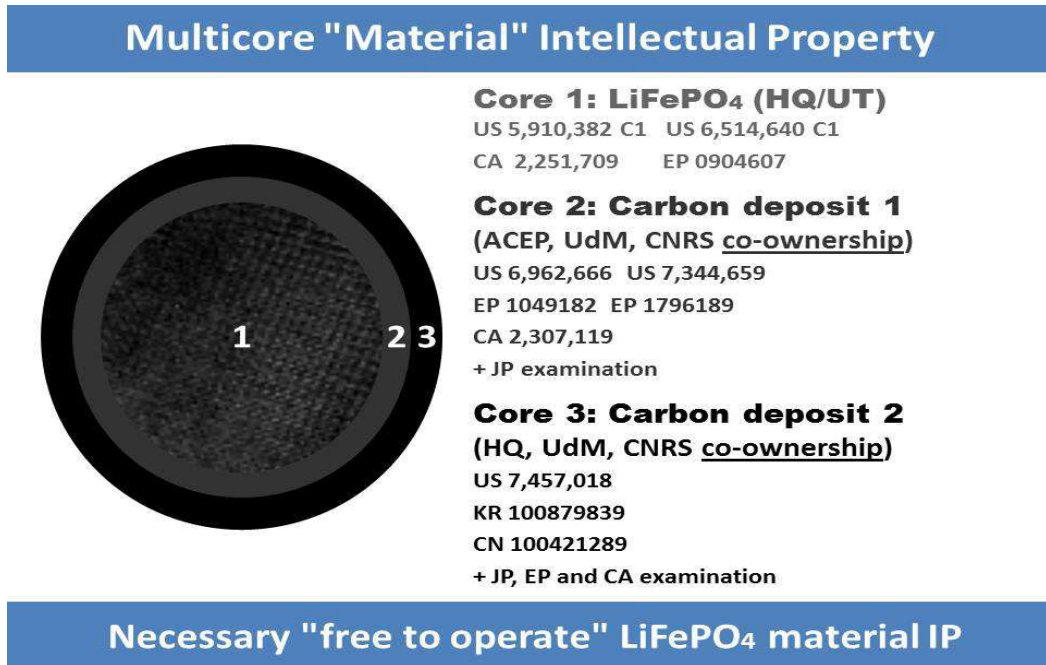


Fig. 18 Carbon coating patents are complementary to Goodenough LiMPO_4 patents.

The regrouping of University of Texas and Université de Montréal patents was decisive in the incorporation of Phostech Lithium inc, in 2001, created to develop and make C-LiFePO_4 available for large battery applications. A brief overview of the society is given in Fig. 19:



Phostech Lithium

Phostech/Süd-Chemie's short history

- 1997, Goodenough (LiMPO_4)
- 1999, Ravet et al, (C-LiFePO_4)
- 2000, Solid-state process to make C-LiFePO_4 , (P1).
- 2001, Phostech inc incorporation as a UdeM startup.
- 2004, Süd-Chemie develops an hydrothermal process in Germany, (P2).
- 2006, First production plant (P1) in St-Bruno, Canada.
- 2008, Süd-Chemie becomes Phostech's sole shareholder with exclusive rights to make and sell C-LiFePO_4 .
- 2011 Second production plant (P2) built in Candiac, Québec, Canada.

LiFeP₄WER
 PERFORMANCE BATTERY MATERIAL

Fig. 19. Phostech's short history

Participation of Süd-Chemie into Phostech (its sole shareholder since 2008) resulted in a second grade (P2), more powerful and obtained by precipitation from a hydrothermal process. The process is complementary to the (P1) solid process implemented by Phostech in its St-Bruno plant. Phostech’s main C-LiFePO₄’s product, characteristics and applications by customers are illustrated in the following figures 20-24:

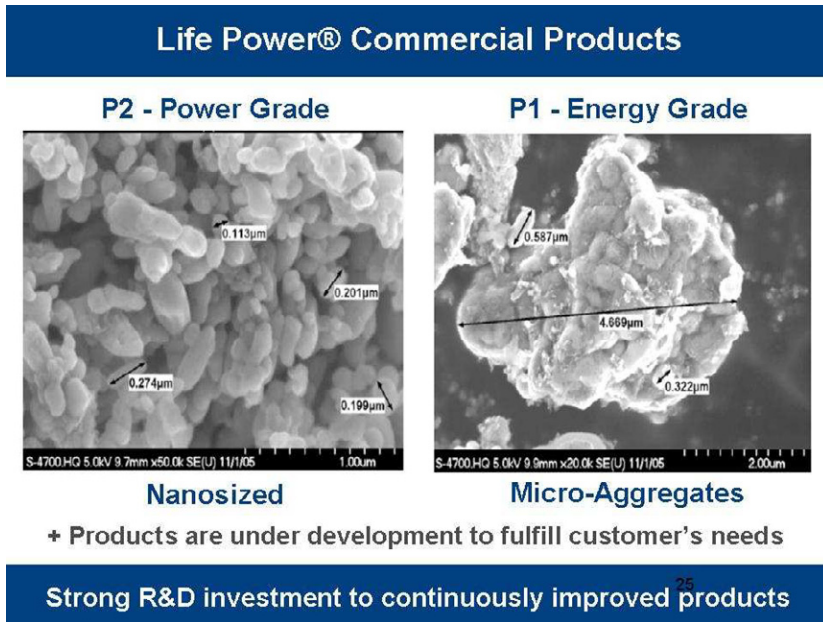


Fig. 20. Phostech Energy grade (P1) and Power Grade (P2)

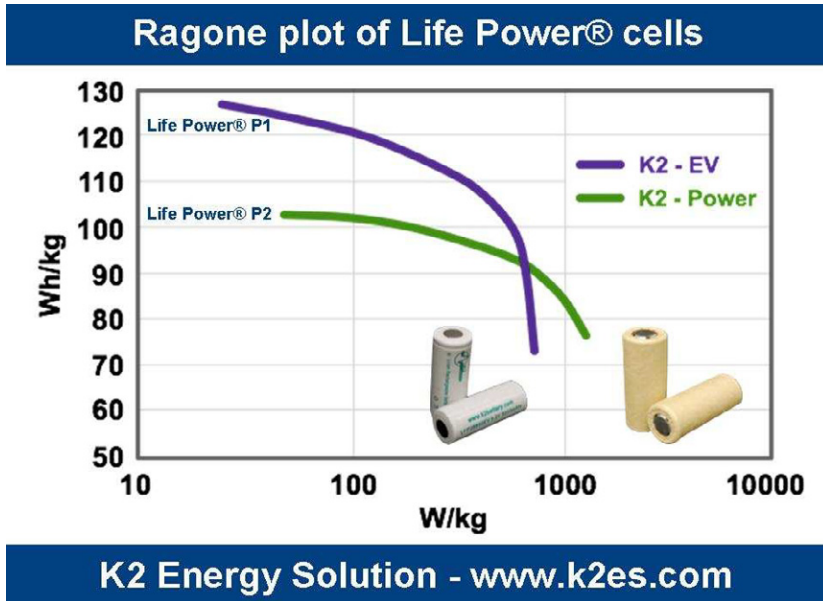


Fig. 21. Phostech’s products in K2 Energy Solution cells.

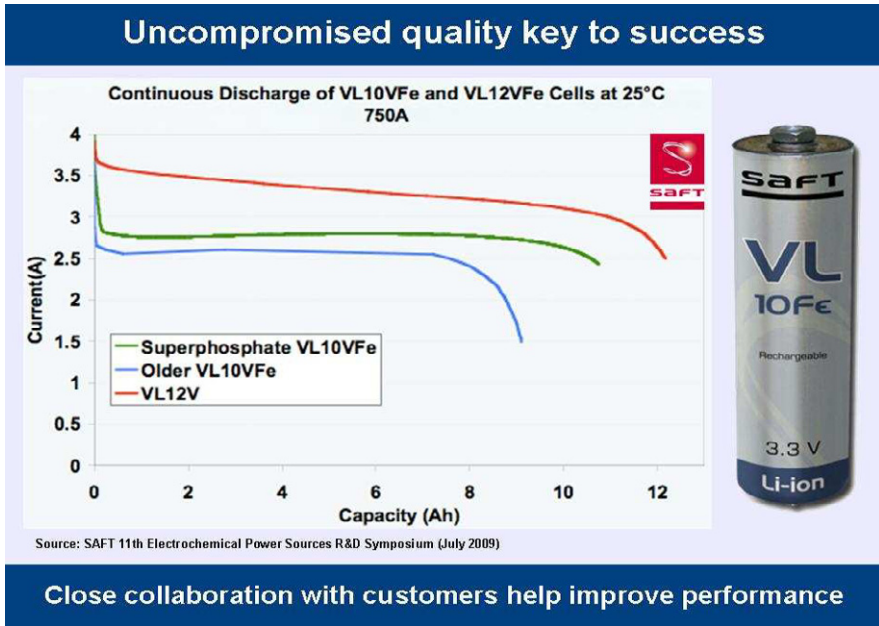


Fig. 22. High power cells made by SAFT from (P2)



Fig. 23. Cells and battery packs made from Phostech grades.

Some Life Powered Applications



Fig. 24. Applications under developments with Phostech's products.

Several processes are known to produce **C-LiFePO₄** as summarized and commented in Figure 25:

C-LiFePO₄ production processes

Simplified representation

Process	Reaction	Characteristics
1- Solid State (examples)	$\text{FePO}_4, \text{Li}_2\text{CO}_3, \text{Copolymer P1}$ $\text{Fe}_2\text{O}_3, \text{Li}_2\text{CO}_3, \text{LiH}_2\text{PO}_4, \text{C}$ $\text{Fe}_2\text{C}_2\text{O}_4, \text{NH}_4\text{H}_2\text{PO}_4, \text{Li}_2\text{CO}_3$ $\text{Fe}_2(\text{PO}_4)_3, \text{Li}_3\text{PO}_4$	+ Simplicity, one step - Reactant cost - Mixing solids? 100%?
2- Liquid Phase (solvent, e.g., H ₂ O)	$(\text{Fe}) + (\text{H}_3\text{PO}_4) + (\text{LiOH}),$ solubles, P2	+ Liquid reactive media + Nano precipitation + Low cost reactants - Capital intensive
3- Liquid Phase (molten)	$(\text{Fe}) + (\text{PO}_4) + (\text{Li}),$ Non specific P3	+ Liquid reactive media + Commodity prices - Powderization

Phostech produces both P1 and P2 commercially and develops P3

Fig. 25. Examples of solid, liquid or molten state processes to make LiFePO₄

Phostech commercially makes C-LiFePO₄ with a solid-state process **P1** and with a solvent-assisted process **P2** and jointly develops with École Polytechnique-Université de Montréal a third process **P3** by melting illustrated in Fig. 25-26 that can form LiFePO₄ from a wide array of commodity reactants.

Melt process to make LiMPO₄



P3 process

A Canadian consortium:

- École Polytechnique-Phostech
- Université de Montréal
- Canmet
- University of Western Ontario
- Bathium Canada (application tests)

Goals:

- To make a new C-LiFePO₄ grade:
 - at low cost (<10\$/kg)
 - high performance and useful life
 - Essential for EV market

Process main steps:

- Mixing-melting-casting
- Submicron comminution
- Pyrolytic C deposition

Recently proposed to Automobile Partnership Canada

Fig. 26. Low cost process development for large lithium battery applications

Other lithium battery components are available from Phostech/Süd-Chemie, namely a phosphate electrolyte (Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃) of the nasicon structure and a new generation of anode (C-Li₄Ti₅O₁₂).

Finally Fig. 27 illustrates the second Phostech commercial plant built in Candiac to produce the P2 grade of C-LiFePO₄:

Candiac (Québec) Life Power® P2 Commercial Plant
60 M€ investment by Süd-Chemie



Feb. 03, 2011



August 07, 2011

2,500 tons/yr Life Power® plant based on wet-process
developed in Germany (Süd-Chemie Moosburg R&D center)

Fig. 27. Phostech P2 plant built in Candiac for production early 2012.

4 – Future evolution of lithium batteries (and phosphates) for large scale storage of energy.

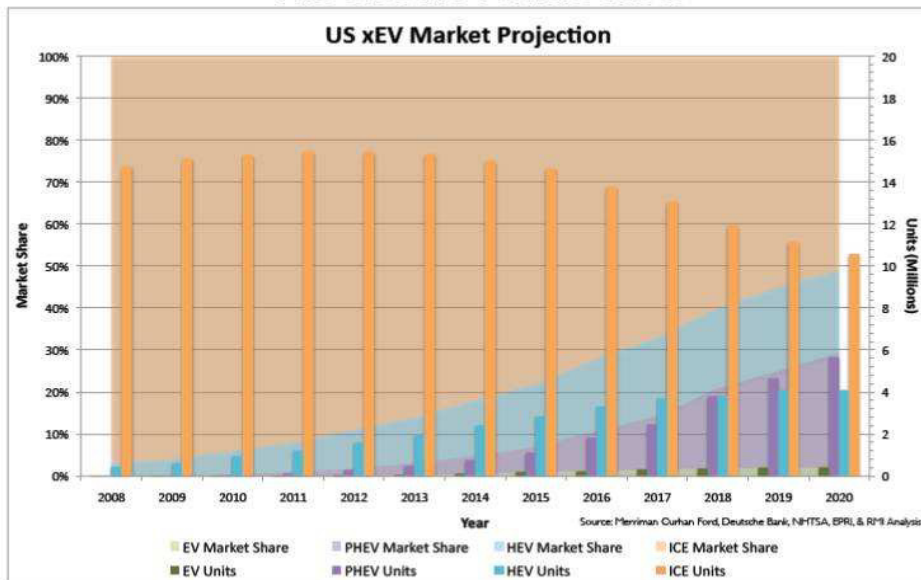
In less than 50 years, lithium primary cells have evolved to high energy rechargeable batteries present in our daily life and have accelerated the trend to an ‘all-electric-society’ with portable electronics and tool omnipresence. The need to diversify our sources of energy away from fossil fuels makes electricity, a noble form of energy, easy and efficient to convert to other forms and distribute, a perfect solution for modern societies including the important transportation sector and the electric vehicle. However, such a strategy calls for an efficient means of storage for this instantaneous form of energy. Large lithium batteries can represent such a solution.

Technically, small rechargeable batteries have met the minimal performances required in terms of energy and power, still, there are formidable challenges to prove the viability of large batteries in terms of safety, environment compatibility (recycling), 10-15 year calendar life and most important, low manufacturing costs including materials, process and designs.

Which Li-cell chemistry will prevail in large lithium batteries? It is too soon to tell. For example, will the success of the graphite anode lithium-ion technology apply to large batteries that have much more stringent safety and long shelf and cycle life requirements? Or will other anodes such as metallic lithium (with solid electrolytes) or titanate anodes age better in those conditions? Nevertheless and whatever the winning anode or new electrolyte formulation, the author believes that in any case phosphates, especially iron-based phosphate olivine cathodes, will be present in large lithium batteries given the availability and price of iron as well as phosphate. Over time, thermal and chemical stability of phosphates will reveal the discriminating factor, as iron already did with the lower, less aggressive voltage (3.4V) of C-LiFePO₄ olivine. Meanwhile one can anticipate that niche markets will develop for each of the Li-C₆, Li⁰ and Li₄Ti₅O₁₂ anodes given their different characteristics as suggested in Figure 8.

One could easily assess, based on the projections in Figure 28, for EV, PHEV and HEV penetration in the US market, the impact of phosphate-based lithium batteries. The quantity of C-LiFePO₄ to be produced annually in such a case, for cumulative EV, PHEV and HEV in 2020, would be about 55 000 tons, using a 2 kg C-LiFePO₄ per kWh ratio:

Potential markets for phosphates in large Li-batteries? The Electric Vehicle case.



Phostech/Süd-Chemie’s production in 2012: 3000 t/y
 Global cathode market for Li-ion batteries in 2010: 30 000 t/y
 (EV + PHEV + HEV) projected cathode market in 2020 translates into 55 000 tons phosphate:
 (estimate based on 2kg C-LiFePO₄ per kWh and 1.5, 15, 48 kWh, per HEV, PHEV et EV)

Fig. 28. Potential phosphate market from electric market projection to 2020. From: Status and trends in the HEV/PHEV/EV battery industry. Rocky Mountain Institute, David Anderson, 2008.

These 'conservative' projections till 2020 do not reveal a large impact of phosphate-based electric vehicles on worldwide annual phosphate consumption, less than a few percent for the US market. However, these are conservative projections limited to electric transportation; more optimistic projections can be found and the reader could use the present conversion ratio to assess higher market penetration data or the impact of another large lithium battery application such as grid energy storage on phosphate consumption.

5 - Conclusion

Electricity, the most noble form of energy, is becoming the energy vector of choice and will continue to develop with the trend toward modern society electrification. Lithium batteries have accelerated this trend with the phenomenal development of portable electronics and tools. Large scale storage of electricity in lithium batteries is becoming a must to support the development of new intermittent sources of energy (e.g., wind, photovoltaic), to optimize present electrical grid operation and reliability and also to help substitute progressively fossil sources of energy in the important transportation sector.

In the past 50 years, lithium has allowed the emergence of high energy, high power rechargeable batteries that have rapidly replaced most lead-acid and nickel-alkaline systems in portable applications. This commercial success has triggered a new interest for electric transportation from existing HEV cars to PHEV and EV, now actively developed. Still, before these applications become reality, large battery safety, calendar life and commercial viability must be demonstrated. As to this last point, the challenge is to reduce the battery cost by a factor of 5 to 3 depending on the calendar and cycle life that will be achieved.

The use of phosphates in the energy sector is thus closely linked but also, like iron, a contributing element, to the success of large lithium batteries because of its availability in the earth crust and its chemical stability; whatever the lithium cell chemistry that will prevail as to the anode and electrolyte. Morocco, with its large potential for solar energy and unique phosphate mineral resources, has every interest in that large lithium batteries meet their technical and economic challenges just like Québec and Canada, that benefit from another form of solar energy (hydraulic) that was instrumental in the development of their expertise in lithium batteries and battery components.

References

- [1] J. B. Goodenough et al, US Pat. 5, 910, 382. Also, J.B. Goodenough et al, J. Electrochem. Soc., 144, (1997), p.1188.
- [2] J. B. Goodenough et al, 36th Power Sources Conférence, 110, June 6, 1994.
- [3] L. Nazar et al, Electrochemical and Solid-State Letters, 13 (4), (2010), A43-A47.
- [4] Son et al, Applied Phys. Letters, 85(24), (2004), p.5875.
- [5] Wessells et al, J. Electrochem. Soc., 158(3), (2011), p.352.
- [6] M. Bichat et al, Chem. and Mat. Science, Ionics, 11(1-2), 66(2005).
- [7] Weppner et al, Solid State Ionics, 118, (1999), p.149.
- [8] Besner et al, US 6,492,061 et US 6,451,487.
- [9] Nagata et al, Journal of Power Sources, 174, (2007), 921
- [10] Bates et al, US Pat. 5,597,660.
- [11] Adachi et al, Solid State Ionics, 47, (1991), p.257.
- [12] Ravet et al., ECS Meeting Abstract, Vol 99-2, Abstract No. 127, Oct. 17-22, 1999, Honolulu. Also, US 6, 926, 666, US 6, 855, 273 and 7,334,659