

The Safety Advantages of Valence's Saphion[®] Technology

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Summary:

Among lithium transition metal oxides, LiCoO_2 has long been the chemistry of choice in current commercially available lithium ion batteries. This was a natural outcome due to a demonstrated electrical performance in many of today's electronic consumer products. A primary challenge in designing larger format lithium ion batteries has been achieving safe behavior under normal or abusive conditions. The choice of cathode materials used in these batteries has been found to have a profound effect on this safety behavior and LiCoO_2 , in particular, demonstrates very poor thermal stability. This instability is directly related to the ease of oxygen liberation from the LiCoO_2 structure. To address these limitations, Valence Technology has spent several years developing an intrinsically safe cathode material, recently introduced as a novel phosphate, $\text{LiFe}_{1-x}\text{Mg}_x\text{PO}_4$ – the core of the proprietary Saphion[®] technology. Even under severe abusive conditions this material will not liberate oxygen and therefore does not pose any significant safety hazard. In the attached document, an in-depth discussion focusing on the fundamental safety of the phosphate material is presented. This safety behavior is compared with that of LiCoO_2 .

Introduction:

During the last few years, rechargeable lithium ion batteries have reached an established commercial status with a production rate of several million units per month. Research on cathode materials has primarily focused on lithium transition metal oxides. Currently LiNiO_2 , LiMn_2O_4 , and LiCoO_2 have successfully been incorporated in lithium ion cells. LiCoO_2 is by far the most commercially available, particularly in small portable electronics applications because of its higher energy density, ease of synthesis and reasonable rate capability. Thermal stability studies of LiNiO_2 , LiMn_2O_4 , and LiCoO_2 have shown LiMn_2O_4 spinel to be the most stable of these.^{1,2} However, poor electrochemical performance of the spinel has prevented this material from being the material of choice in full prototype batteries. In spite of the fact that LiCoO_2 is widely accepted commercially, its cost, low abundance of Co in the earth's crust and environmental concern remain a severe problem.

An iron-based cathode would be ideal and would alleviate both the economic and environmental concerns with LiCoO_2 , as well as open the long-awaited window for large platform applications. In fact, in the last few years, researchers have put significant effort towards developing an iron-based cathode. Most of the focus has been dedicated to developing an Fe analog to layered LiCoO_2 system in order to alleviate the safety and thermal stability concerns associated with the latter. However, this concerted effort has not met the desirable electrochemical performance required in a viable cathode material.^{3,4}

Recently, a series of materials incorporating large poly-anions, such as $(\text{PO}_4)^{3-}$, have been investigated. Most notable of these is the rhombohedral modification of lithium iron phosphate, LiFePO_4 .^{5,6} LiFePO_4 , with its high available capacity of 170 mAh/g compared to 148 and 150 mAh/g for LiMn_2O_4 and LiCoO_2 , respectively, is currently regarded as the most promising cathode material for small low-power and large platform applications. Its low cost, non-toxicity, composition based on relatively abundant Fe, excellent thermal stability, good

safety characteristics, and very good electrochemical performance add to an already long list of desirable criteria required for a viable cathode material. Furthermore, the safety properties of the Mg-substituted material (Saphion[®] technology) have been demonstrated to be very similar to those described for the LiFePO₄ (Mg being inert). Therefore, the discussion will be limited to the pure iron phosphate compound.

The structural advantage:

In the LiFePO₄ structure, the oxide ions form a hexagonal close-packed (hcp) arrangement. The metal (Fe) ions form zigzag chains of octahedra in alternate basal planes bridged by the tetrahedral phosphate groups (PO₄)³⁻. The lithium ions occupy octahedral sites, located in the remaining basal planes. The strong covalent bonding between the oxygen and P⁵⁺ to form (PO₄)³⁻ units allows for greater stabilization of the structure compared to layered oxides, e.g., LiCoO₂ where the oxide layers are more weakly bound. This strong covalency stabilizes the anti-bonding Fe³⁺/Fe²⁺ state through an Fe-O-P inductive effect. Consequently, oxygen atoms are more difficult to extract (see Fig. 1).

Under typical abuse conditions there is no likelihood for phosphate decomposition and therefore no chance for oxygen liberation from the structure. Only under extended duration and extensive heating (typically > 800°C) can condensation (with oxygen release) of the monophosphate moiety occur, this process allowing production of condensed phases such as the diphosphates and triphosphates.

Furthermore, upon removal of lithium, Li_xCoO₂ undergoes an anisotropic (non uniform) expansion of the unit cell (for x > 0.5), whereas in LiFePO₄, the expansion of the unit cell is isotropic,⁷ This particular anisotropic behavior for LiCoO₂ is particularly important for the battery safety in that it affects the structural integrity of the material and hence its safety. Removal of all the lithium available in LiFePO₄ does not result in any structural modification of the material.

This stability applies for all states of charge, i.e., it does not depend on the amount of lithium extracted from the structure. Certainly the thermal stability of Saphion[®] chemistry, i.e., $\text{LiFe}_{1-x}\text{Mg}_x\text{PO}_4$, is far better than for partially de-lithiated LiCoO_2 . The composition of $\text{LiFe}_{1-x}\text{Mg}_x\text{PO}_4$, by design, limits the amount of lithium extracted. Furthermore, it is also generally understood that the transition metal mono-phosphates are close to refractory in nature with melting points often far in excess of 1000 °C, thereby adding to their safety characteristics under thermal abuse conditions.

Using DFT^{8,9} (see *Appendix A*), we have attempted to model the stability of phosphate materials through their propensity to lose oxygen. It is this oxygen that would assist any reactions ensuing from battery operation under certain abuse conditions. Therefore, one way to evaluate materials safety would be to model their resilience towards oxygen loss and verify the findings experimentally.

Oxygen Defect Energies:

Oxygen defect energy is the energy associated with removing oxygen from the structure and converting it to oxygen gas. This is achieved by treating O_2 as an ideal gas and calculating the oxygen chemical potential, assuming the defect energy is a linear function of composition.

Table 1: Oxygen defect energies for olivine phosphates and layered oxide cathode materials

Compound	$E_{\text{defect}}(x=0)$	$E_{\text{defect}}(x=1)$
<i>Olivine Phosphates</i>		
Li_xFePO_4	1.6	1.8
Li_xCoPO_4	0.3	1.8
<i>Layered Oxides</i>		
Li_xCoO_2	0.2	1.6
Li_xNiO_2	0	???

These data are in accordance with the electro-negativity of the metals involved. When oxygen is pulled out from the structure, the available electrons will go to the most electro-negative ion, Co^{3+} in this case. Defect electrons generally go to P, yielding similar (and high) defect energies. Because Co^{3+} is so highly electronegative, defect electrons reduce Co, creating a low defect energy. It is clear that for $x=0$ (i.e., the charged state), iron phosphate is the most stable of all the chemistries currently used in lithium ion batteries with LiCoO_2 and LiNiO_2 having the highest propensity of losing oxygen in the charged state.

Electron Density Maps:

An electron density map is an elegant way of looking at the distribution of negative charge donated by the removed oxygen, depicted as blue color in Figs. 2a and 2b. When a metal is less electro-negative, there is less hybridization between the metal ion and the oxygen orbitals as clearly illustrated in the case of LiFePO_4 (Fig. 2a). In contrast, there is a strong orbital overlap or hybridization when the Co^{3+} ion is involved (Fig. 2b). Direct estimates of the magnetic moments for Fe^{3+} and Co^{3+} change accordingly (i.e., no change for LiFePO_4). The redox couple is further corroborating evidence since it is a measure on how energies change when electrons are added to a metal, whereby the higher the redox couple, the easier it is to create oxygen defects.

$$E_{\text{Fe}^{3+/2+}} = 3.5 \text{ V vs. Li/Li}^+ \text{ (in LiFePO}_4\text{)}$$

$$E_{\text{Co}^{3+/2+}} = 4.0 \text{ V vs. Li/Li}^+ \text{ (in LiCoO}_2\text{)}$$

$$E_{\text{Co}^{3+/2+}} = 4.8 \text{ V vs. Li/Li}^+ \text{ (in LiCoPO}_4\text{)}$$

Oxygen Defect Concentration:

Fig. 3 shows the calculated O defect concentration for layered LiCoO_2 and the Olivine LiFePO_4 as a function of lithium composition. Because of the extreme sensitivity of the exponential dependences involved, these graphs are only

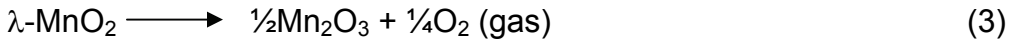
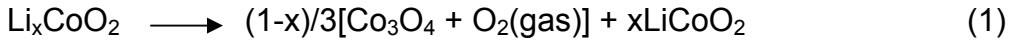
qualitative. However, we believe that the difference is clear. When fully discharged, the two materials have comparable O defect concentrations. However, upon charging (removal of lithium), the lithium cobalt oxide becomes more unstable faster than the phosphate. Upon full charge, the O defect concentration differs by several orders of magnitude. This is further discussed experimentally below.

Thermal Stability:

With higher energy density batteries available, safety is the paramount concern for consumer batteries, and more advanced safety technology is required. The behavior and thermal stability of the cathode in the charged state is essential in determining the safety of the final cell. There are various approaches in evaluating the safety of cells under abuse conditions. The over-charge conditions, for example, may lead to thermal runaway. It is therefore important to understand the cause of this heat generation since it is closely related to the temperature rise in the cell. Previous work has shown that the electrolyte decomposition becomes significant when voltages exceed 4.5 V, and that the reaction of the cathode material with the electrolyte decomposition products happens with large heat generation resulting in cell failure and possible hazardous cell rupture.¹⁰

Over-charging the cathode materials in lithium ion batteries can lead to a variety of electrochemical reactions depending on the specifics of the system's chemistry. For example, solvent oxidation due to the abnormally higher cathode voltage and formation of inert material may result. Thermal abuse of the cathode will lead, as in the case of LiCoO_2 , to oxygen loss from the oxide structure. Build up of oxygen gas will increase the pressure in the cell and assist any combustion reaction because of the accumulation of flammable gas mixtures in the cell. This results in a serious safety concern. It has been established that for the most common cathodes used today, LiCoO_2 , LiNiO_2 , and LiMn_2O_4 , the following

decomposition reactions occur for the charged cathodes under abuse conditions.¹



Therefore, for all the lithium transition metal oxides used today in lithium ion batteries, oxygen loss is a result of the material decomposition. The exothermic behavior and related oxygen liberation reaction for the cobalt system is a particular problem. This reaction is particularly severe when the cathode is in a charged (de-lithiated) condition.¹¹⁻¹³

Differential Scanning Calorimetry (DSC) offers a convenient way of studying the thermal stability of charged cathodes under controlled conditions whereby the rate of temperature rise is controlled and the heat generated is estimated. During DSC scans in the temperature range 23-400 °C, the exothermic heat flow for LiFe(Mg)PO₄ (Saphion®) is observed around 270 °C and the total equivalent heat generated is 124 J/g (Joules per gram of material). In contrast, the total heat generated for the equivalently charged LiMn₂O₄, LiCoO₂ and LiNiO₂ are 240, 570 and 890 J/g, respectively. The event onset occurs earlier for the oxide materials than for the phosphate-based cathode. The same amount of lithium or mAh/g-eq was removed electrochemically from all the cathodes and the same electrolyte EC:DMC (2:1) was used for all the tests in Fig. 4. The remarkable thermal stability of LiFe(Mg)PO₄ is reflected in its very small exotherm compared to the currently commercially used LiCoO₂. The phosphate material will therefore produce batteries with a higher tolerance to very high temperatures.

Conclusions:

Fundamental properties of lithium iron phosphate, the core of Valence's Saphion[®] technology, make for an intrinsically safe cathode material for lithium ion applications currently available. When fully charged, no excess lithium is left in the cathode (unlike LiCoO_2 where 50% still remains). The redox voltage is low enough to ensure no electrolyte decomposition occurs. We have also demonstrated that this material has a high resistance to oxygen loss, which would otherwise result in a significant exothermic event upon heating.

Appendix A:

All calculations are performed in the Local Density Approximation (LDA) or Generalized Gradient Approximation (GGA) to Density Functional Theory (DFT) as implemented in the Vienna Ab Initio Simulation Package (VASP).^{8,9} The nuclei and core electrons are represented with ultra-soft pseudopotentials and all structures are fully relaxed with respect to internal and external cell parameters unless explicitly stated. The wave functions are expanded in plane waves with kinetic energy below 405 eV. Brillouin zone integration of the band structure is performed with a Monkhorst-Pac mesh of k-points large enough to give adequate convergence. Unless otherwise stated, the charge density is ferromagnetically spin-polarized. This is an approximation, since most oxide systems are anti-ferromagnetic, but the effect of the approximation on such quantities as oxygen defect energies and Li activation barriers is unlikely to be significant.

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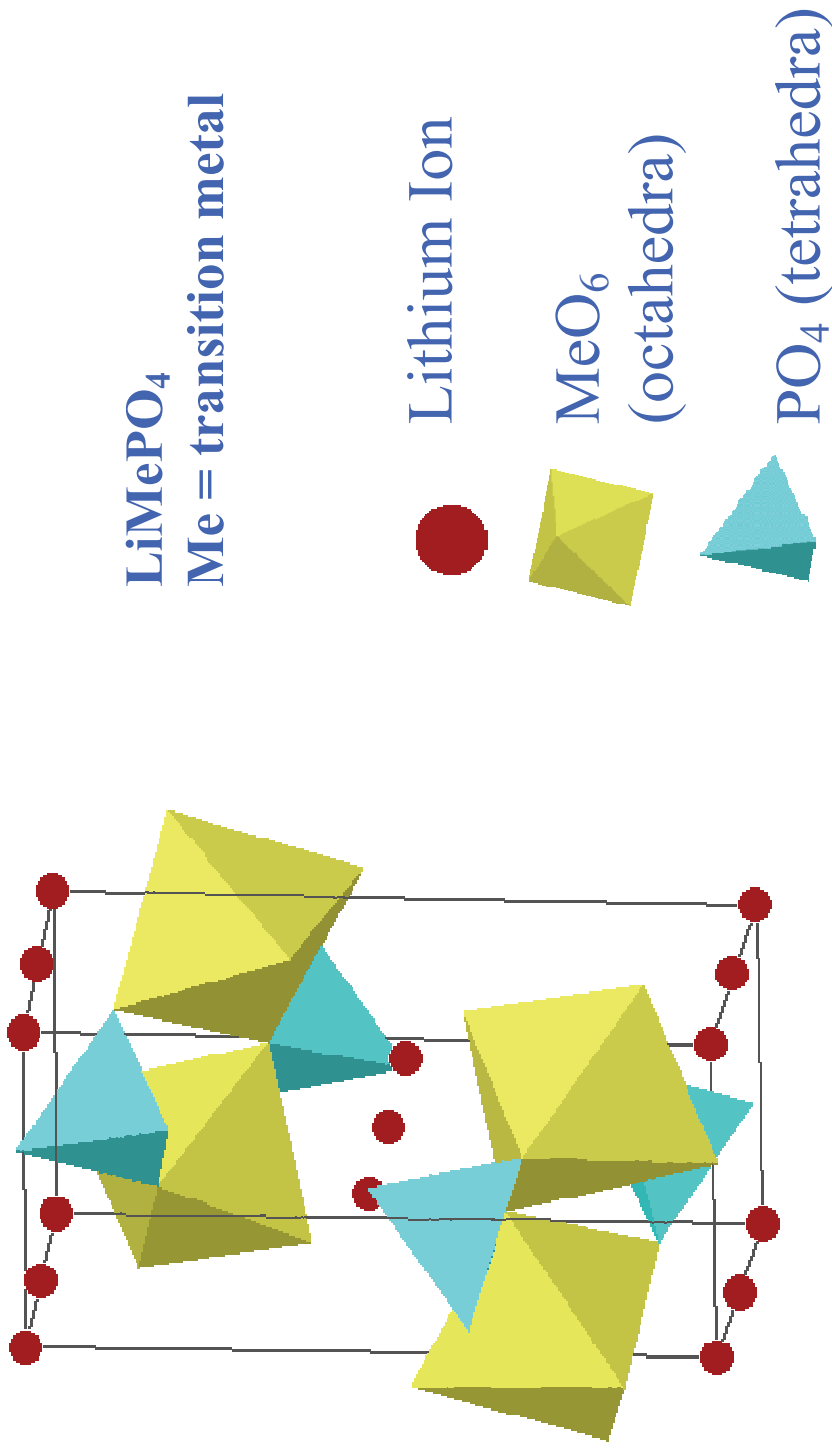


Fig. 1: LiMePO₄ unit cell representation (shown is corner sharing of oxygen by PO₄ and MeO₆)

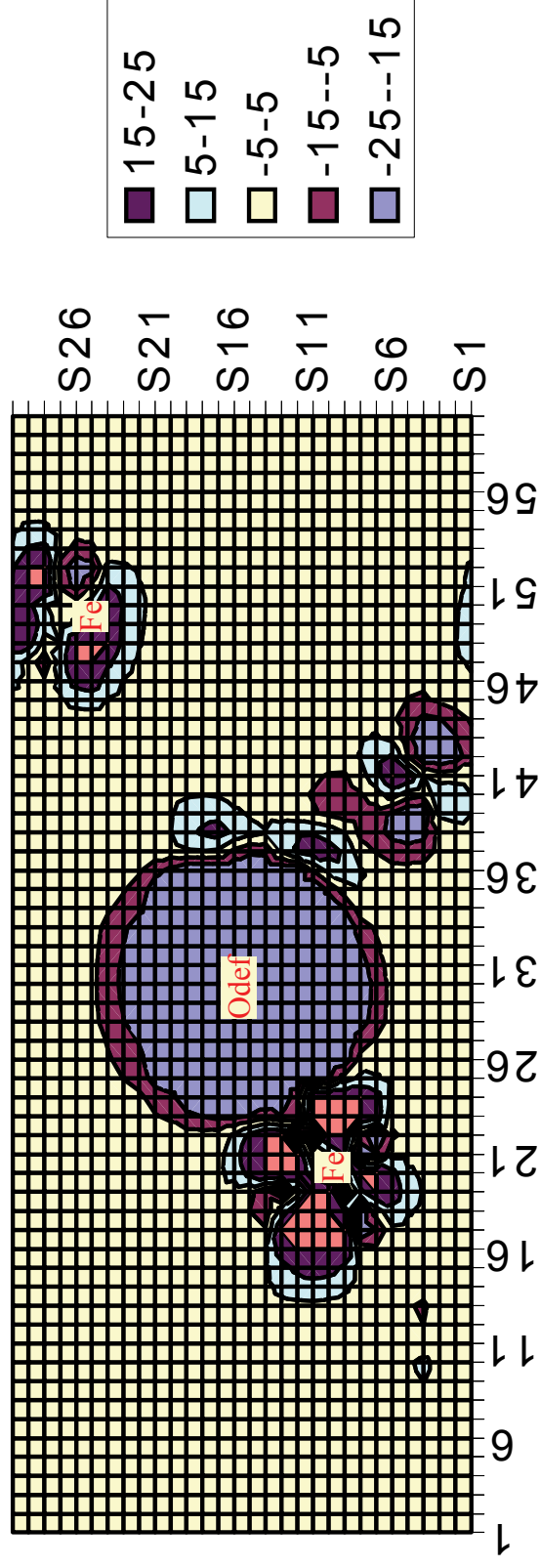


Fig.2a: Electron-density map for LiFePO₄

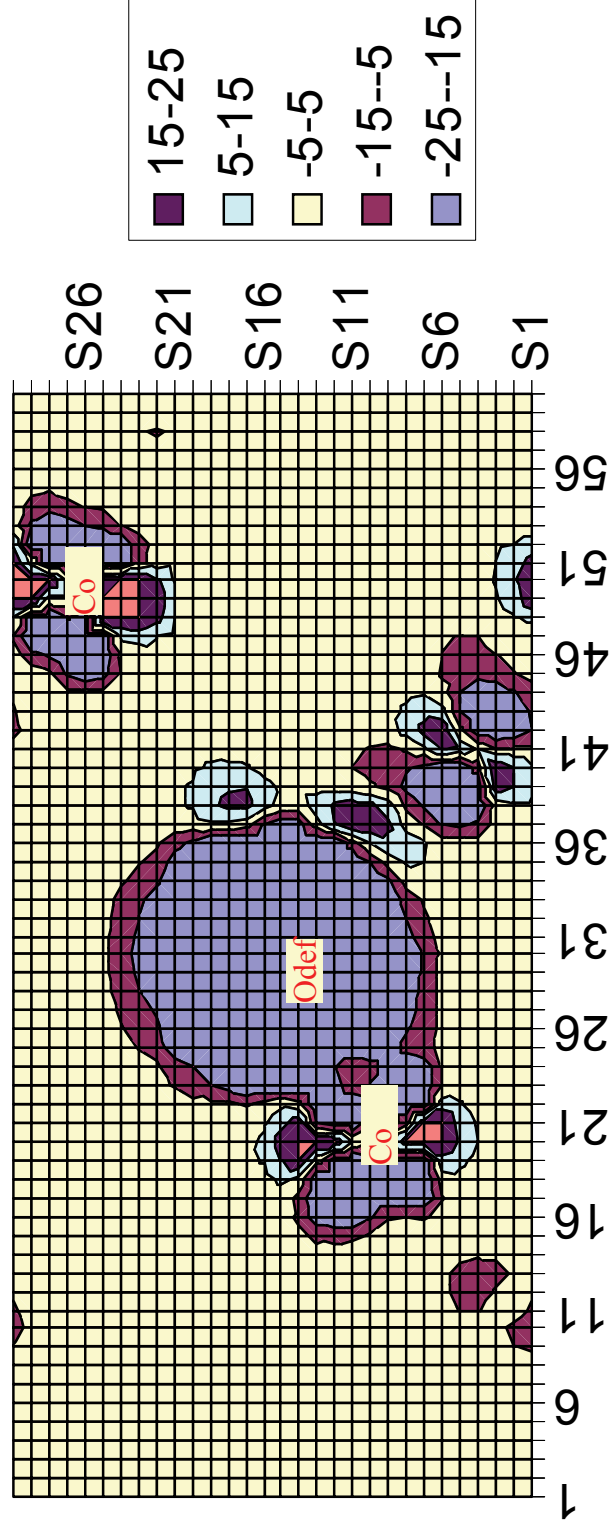


Fig. 2b: Electron density map for LiCoPO_4

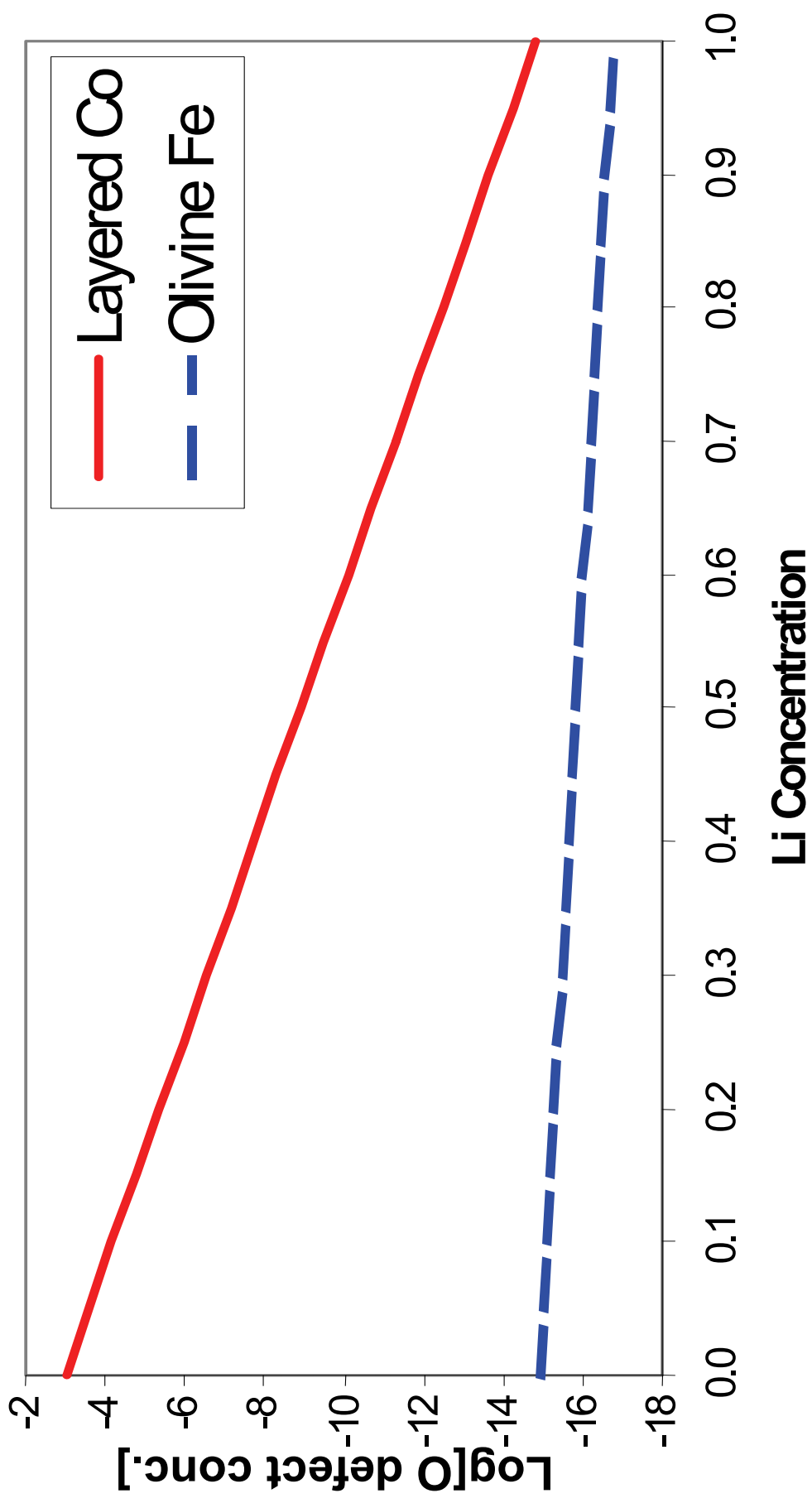


Fig. 3: Layered Li_xCoO_2 vs. Olivine Li_xFePO_4 ($T=600\text{ }^\circ\text{C}$) O^{2-} Defect Concentration vs. Li Concentration

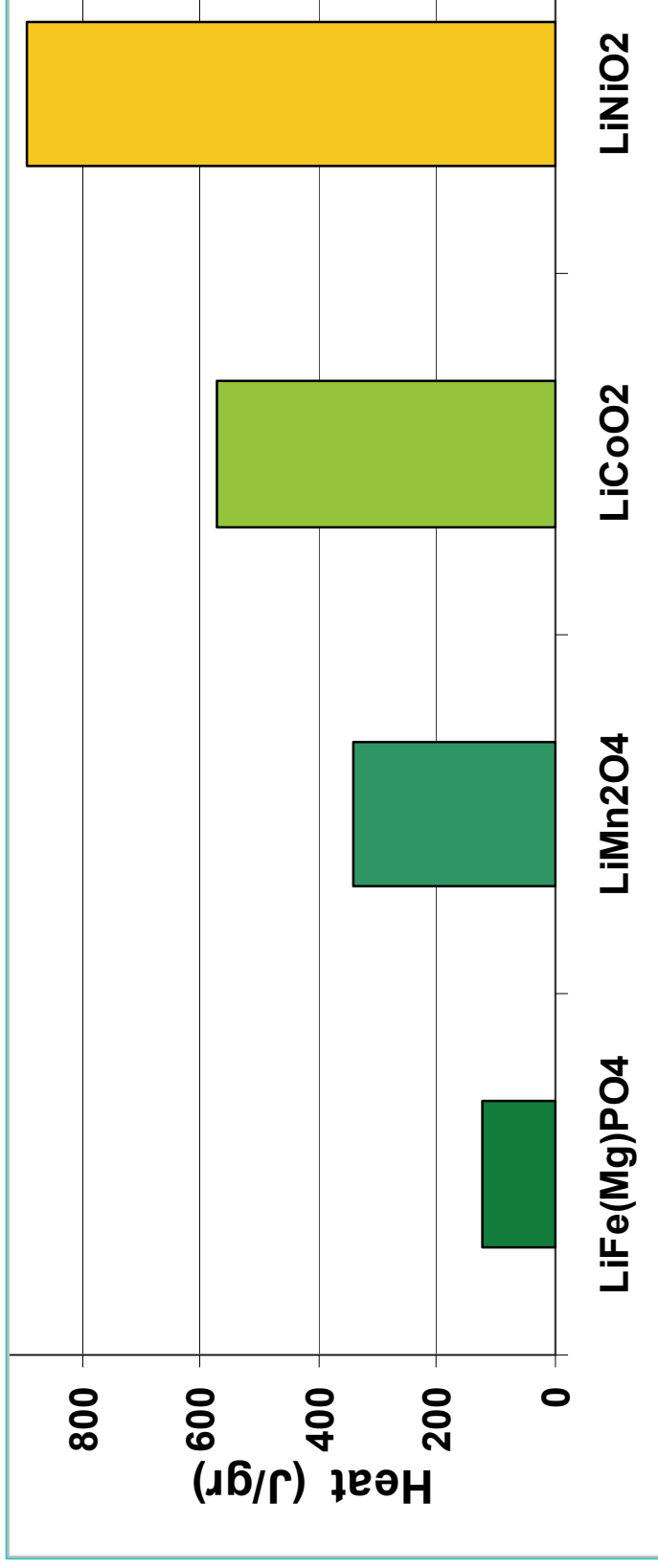


Fig. 4: Comparison of released heat calculated from DSC profiles of various charged cathodes heated from 23 °C to 400 °C at a rate of 5 °C/min. Comparison shows greater thermal stability of Saphion® lithium phosphate-based chemistry.