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Revisiting Olivine Phosphate and Blend Cathodes in Lithium Ion Batteries for Electric Vehicles

Yujing Bi and Deyu Wang

Abstract

As electric vehicle market growing fast, lithium ion batteries demand is increasing rapidly. Sufficient battery materials supplies including cathode, anode, electrolyte, additives, et al. are required accordingly. Although layered cathode is welcome in high energy density batteries, it is challenging to balance the high energy density and safety beside cost. As consequence, olivine phosphate cathode is coming to the stage center again along with battery technology development. It is important and necessary to revisit the olivine phosphate cathode to understand and support the development of electric vehicles utilized lithium ion batteries. In addition, blend cathode is a good strategy to tailor and balance cathode property and performance. In this chapter, blend cathode using olivine phosphate cathode will be discussed as well as olivine phosphate cathode.

Keywords: phosphate, phosphate composite, blend cathode, lithium ion battery, electric vehicles, stability, rate capability, safety

1. Introduction

Batteries are used as the power source in electric vehicles and take the critical role for driving mileage improvement and transportation safety as well as cost control. Battery energy density is the important parameter related with the driving mileage. As battery material and technology development, energy density of lithium ion battery for electric vehicle has been increased to 300 Wh/kg at cell level, [1, 2] it has big progress compared with the lead acid battery at beginning period. Lithium ion battery is basically composed by cathode, anode, separator and electrolyte. Lithium ions move between cathode and anode to store and output energy through reversible chemical reaction. In present commercial lithium ion batteries, lithium ions are reserved in cathode side and the reversible lithium concentration in cathode mainly determine the battery energy density. Three type of cathodes have been widely utilized in commercial lithium ion batteries, layered oxide which has two-dimensional lithium ion diffusion pathway, spinel oxide that provides three-dimensional lithium ion transportation space, and olivine phosphate with one-dimensional lithium ion diffusion channels. Each of them has their merit and are servicing the specialized portable power source market.

Lithium ion battery utilized on electrical vehicles has high requirement on safety, long lifespan, high energy density, high power density as well as low cost.

Olivine phosphate cathode has stable crystal structure and present advantage on safety, long cycling stability and cost effective. In this chapter, lithium iron phosphate, lithium manganese phosphate and related composite cathodes are reviewed to understand material technology development. Blend cathode demonstrates the possibility to tailor and balance the cathode property and performance. Binary and ternary blend cathodes using olivine phosphate are summarized and discussed.

2. Olivine phosphate cathode

Iron source is abundant in earth, it is inexpensive and less toxic than cobalt and nickel, using iron redox in cathode is promising to reduce cathode material cost. Inspired and encouraged by the successful development of LiCoO_2 cathode, layered LiFeO_2 prepared by ion-exchange from $\alpha\text{-NaFeO}_2$ presents iron redox activity [3]. But it is metastable and the performance was not attractive due to anion issues [4]. Comparing with other iron compounds, $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox energy and potential can be adjusted by different anion groups. As consequence, polyanions were considered to build stable framework structure and improve redox stability. Due to $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox potential is influenced by the corresponding anion group. A series of iron polyanion compounds were screened to search stable cathodes for lithium ion batteries [5]. In **Figure 1a**, $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox energy is compared in different phosphates. The lower redox energy below Fermi level can achieve higher voltage compared with lithium. $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple demonstrates the lower redox energy in LiFePO_4 and higher redox potential at 3.5 V (*vs.* Li^+/Li). This voltage matches with stable window of carbonate electrolytes very well and accelerate the development of lithium iron phosphate. It delivered 110 mAh/g capacity firstly reported by Nobel laureate J. B. Goodenough at 1997 and has been successfully commercialized with decades of research and development.

2.1 Lithium iron phosphate

The ordered olivine structure of LiFePO_4 is constructed by P-O framework with space group Pnma . Oxygen atoms are hexagonal-close-packed stacking order. Phosphorus atoms occupy tetrahedral sites, iron and lithium atoms locate at octahedral 4a and 4c position in Pnma space group. PO_4 tetrahedral share one edge with FeO_6 octahedron and two edges are shared with LiO_6 octahedron. The FeO_6

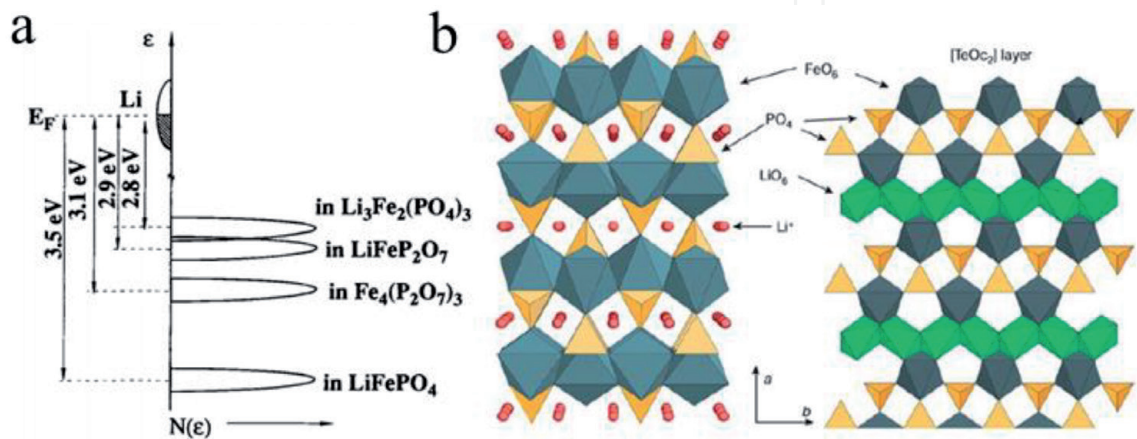


Figure 1. (a) Iron redox energy and potential can be adjusted by polyanion groups [5]. (b) LiFePO_4 crystal structure [6].

octahedra are linked through corner in bc-plane and LiO6 octahedra form edge-sharing chains in b direction [6]. Li resides in chains of edge-shared octahedra and connecting as the Li diffusion channel. PO₄ polyanion framework is very stable in thermal dynamics as P-O bonding energy is high. During heating up to 350°C in N₂ or O₂ atmosphere [7], LiFePO₄ and delithiated FePO₄ structure were not changed which contributes to the high safety performance.

Li diffusion pathway in olivine LiFePO₄ is one dimensional channel along [010] direction due to LiO6 octahedra is only continuous along b-axis. Although theoretical intrinsic ionic diffusion coefficient is 10^{-8} – 10^{-7} cm²/s for both LiFePO₄ and FePO₄ [8, 9] the tested lithium ion diffusion coefficient is lower than 10^{-12} cm²/s. As structure defects existing, such as Li/Fe anti-site defect, stacking fault and impurities, one-dimensional channels would be block and the ionic diffusion coefficient will be dramatically decreased [10]. In ordered olivine structure, corner-shared FeO6 does not form a continuous 3D network, and transition metal-d-oxygen-p hybridization in phosphate is weak [11]. Accordingly, the electronic conductivity of LiFePO₄ at room temperature is only $\sim 10^{-10}$ S/cm [12], which is usually thought as semiconductor [13]. Slow kinetics of lithium ion diffusion and low electronic conductivity lead to the poor rate capability of LiFePO₄. Thus, numerous works have been devoted to overcome this drawback. Such as reducing particle size, element substitution, surface coating et al.

2.2 Reaction mechanism

Phase transformation mechanism in cathode during delithiation and lithiation is critical for electrochemical performance in lithium ion battery. When lithium ion extracting from LiFePO₄, olivine LiFePO₄ host will transform to FePO₄ which have same structure. Even all active lithium ions are extracted out from LiFePO₄, lattice volume only vary 6.5–6.8%, which demonstrate high crystal structure stability. Although the two phases reaction mechanism in lithiation/delithiation is widely accepted, the specific transformation route is reported as several models, which are highly related with material morphology, particle size, even experimental conditions [14, 15].

Core-shell (shrinking-core) model was proposed when LiFePO₄ was initial reported by J. B. Goodenough at 1997 [7]. In lithiation process, lithium ions will be reserved from surface to particle core in FePO₄ phase, two-phase boundary moves accordingly. In delithiation process, phase boundary will move reversibly from core to surface. In order to have deep and clear understanding on reaction mechanism, advanced operando/ex-situ characterization technologies are involved to study the structure changes furtherly. Beside two phases coexistence phenomenon (two phases distribution may be different), lithium deficient Li_{1-x}FePO₄ was seizing especially in nano size particle and high rate tests. Solid solution mechanism is reported to support the fast lithium transportation [16].

No matter phase transformation would undergo which mechanism in detail, the rigid P-O tetrahedral in structure provides rigid framework and contributes to highly reversible and stable delithiation/lithiation.

2.3 Carbon coating

Limited by the intrinsic low electronic conductivity, lithium utilization ratio in LiFePO₄ is low (~ 0.6) and decays fast. Carbon coating was developed to improve material conductivity. This approach can be achieved through simple process by mixing carbon precursors with active materials followed by calcination. However, the electrochemical performance is influenced by the carbon coating quality.

Numerous works were reported to study and optimize carbon coating for LiFePO_4 from different carbon sources, coating methods, carbon structure and carbon composite [17]. Beside enhancement of electronic conductivity, carbon coating can also be used to control LiFePO_4 particle growth in calcination.

Beside conventional carbon coating, advanced carbon materials such as carbon nanotube, graphene and carbon fibers are introduced to form composite for pursuing high performance. Benefitting by excellent electronic conductivity from carbon coating layer and carbon composite, LiFePO_4 material can be prepared into thick electrode without sacrifice performance [18].

2.4 Lithium manganese phosphate

Encouraged by well development of LiFePO_4 , pure phase of lithium manganese olivine is expected to improve energy density due to the high redox potential (4.1 V *vs.* Li^+/Li) of $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple. However, lithium ion diffusion kinetics and electronic conductivity in LiMnPO_4 is even worse than LiFePO_4 and hard to prepare the pure phase with high performance [19, 20]. Morphology control and particle size reduction are effective solutions to improve the sluggish kinetics property referencing from LiFePO_4 development [21]. A facile polyol synthesis approach is developed to prepare well-crystallized LiMnPO_4 with ~30 nm thick nanoplates (as shown in **Figure 2**) [22]. High ratio of (020) plane which orientated in a-c plane and has short length along b-axis provides morphology to optimize kinetics property. Pure phase LiMnPO_4 prepared by polyol method can deliver 159 mAh/g reversible capacity at 50°C, and retained 95% over 200 cycles. Elemental substitution was applied on LiMnPO_4 to modify the olivine structure. Fe, Ni and Mg substitution made contribution to improve electronic conductivity, but only Fe substitution presents the positive function on electrochemical performance enhancement [24]. Poly synthesis method was further developed and cheap solvent DMSO was used to replace polyhydric alcohols in co-precipitation reaction. 50–100 nm Fe substituted $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ presents promising capability and cycling stability as presented in **Figure 2** [23, 25]. Considering kinetics of LiFePO_4 is better than LiMnPO_4 , a core-shell structure of $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/\text{C}$ which has Fe rich on surface is prepared by adjusting co-precipitation process. LiFePO_4 is controlled to grow on LiMnPO_4 shell [26]. Comparing with $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ solid solution cathode, lithium ion diffusion kinetics is further enhanced due to the lower charge transfer resistance is achieved in this structure modification.

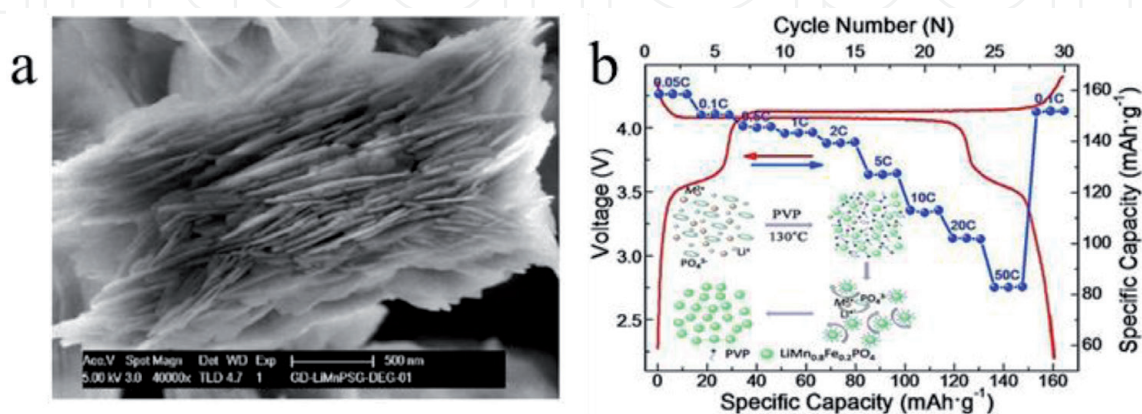


Figure 2. (a) (020) Oriented LiMnPO_4 prepared by polyhydric alcohols approach [22]. (b) Developed co-precipitation method for synthesis of Fe substituted LiMnPO_4 [23].

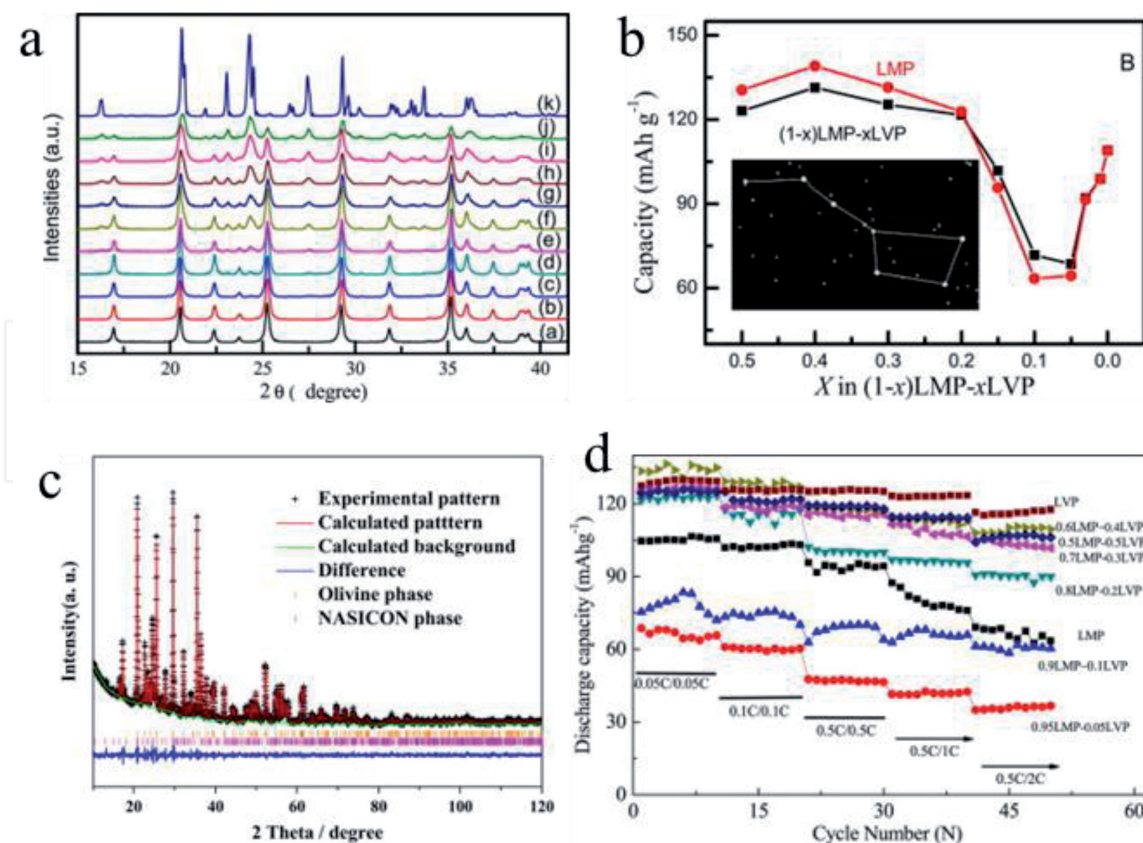


Figure 3.
(a) XRD patterns of the LMP and LVP sample prepared by different ratios. (b) Influence of LVP amount on reversible capacity of LMP-LVP composite [29]. (c) XRD pattern of LMFP and LVP composite cathode [30]. (d) Rate capability of LMP and LVP composite cathodes [29].

2.5 Composite cathode

Although the Mn doped $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ can deliver higher energy density contributed by the higher redox potential of $\text{Mn}^{3+}/\text{Mn}^{2+}$, rate performance is geared down when increasing manganese ratio. NASICON structured phosphate $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ has open lattice framework which guarantee the fast Li ion transportation in cathode bulk phase [27]. As consequence, high rate NASICON cathode is integrated with olivine phosphate to improve Li diffusion kinetics [28]. In LiMnPO_4 -LVP composite cathode prepared by solid state approach, both the NASICON and olivine phase diffraction peaks and plateau character could be identified even LVP ratio is below 3% [29]. As the composite LVP ratio is higher than 20%, the capacity contributed from $\text{Mn}^{2+}/\text{Mn}^{3+}$ plateau is increased and indicates that LVP composite can improve activity of Mn redox in olivine phase. Checking the lattice parameters, olivine phase LiMnPO_4 is substituted by a small amount of vanadium [30]. The composite cathode presents enhanced rate capacity (Figure 3).

3. Blend cathodes

The present commercial cathode layered oxide, spinel oxide and olivine phosphate have their own advantage and have already been successfully utilized in different lithium ion battery designs according to the application scenarios. The blend of different cathode is a facile method to tailor the properties and performance of electrodes for lithium ion batteries.

3.1 Blend cathode – olivine phosphate and layered oxide

Layered structure oxide contained nickel cobalt manganese (NMC) has much higher theoretical capacity (~ 270 mAh/g) than olivine phosphate cathodes (~ 170 mAh/g). Limited by the delithiated structure stability at high voltage and electrolyte decomposition window [31, 32], only <0.8 Li in layered oxide cathode will participate in charge–discharge process. Although NMC cathode can be used to prepare high energy density lithium ion batteries for electric vehicles, the safety concerns arise comparing with the one using olivine phosphate cathodes [33, 34]. Blend cathode including both olivine and layered oxide cathode would a moderate strategy to integrate.

$\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/\text{C}$ was mixed directly with $\text{LiNi}_{0.88}\text{Co}_{0.09}\text{Al}_{0.03}\text{O}_2$ (NCA) to improve the comprehensive performance. The reasonable ratio of $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/\text{C}$ can extend cycling life of Ni rich cathode without sacrificing capacity at electrode level [35]. Adding 1% and 2% $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/\text{C}$, electrodes present similar discharge capacity. But the capacity retention ratio is increased from 77% using pristine NCA to 88% using 2% olivine addition. Using $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ (NMC532) and $\text{LiFe}_{0.15}\text{Mn}_{0.85}\text{PO}_4$ blend cathode, cycling stability is enhanced when LFMP/C ratio in blend cathode is less than 10% [36].

LiCoO_2 presents more stable structure stability with adding LiFePO_4 , both the particle cracking and irreversible phase transformation are inhabited even cycling at high cutoff voltage. Mixing with 12 wt% LiFePO_4 , discharge capacity of blend cathode is decreased to 177.9 mAh/g at 0.2C charging to 4.5 V (*vs.* Li^+/Li). However, overpotential of cobalt redox is reduced and presents enhanced cycling stability [37].

Redox dynamics in LiFePO_4 and LiCoO_2 blend cathode is different with individual component. At low C-rate, each components of the blend cathode can independently present their redox reaction. When working at high C-rate, the effective C-rate for each constituent is higher than nominal value. However, the rate performance of blend cathode is significantly improved [38]. Buffer effect is proposed that the internal pathway would be constructed by component with fast reaction kinetics as shown in **Figure 4**. Lithium is redistributed among the constituents to reach an equilibrium potential during relaxation.

Despite electrochemical performance is improved by blending, LiFePO_4 and layered oxide cathode blend cathode may have heterogeneity issue as material property such as particle size and density are different. 3D X-ray tomography technology is

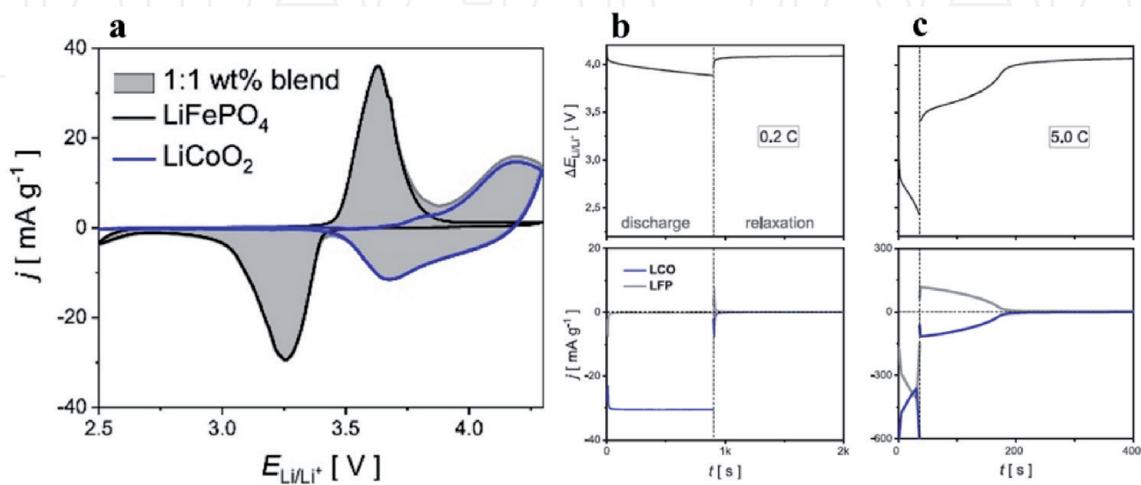


Figure 4.

a) Cyclic voltammetry of a blend electrode illustrating the contributions of LiFePO_4 and LiCoO_2 . (scanning rate 25 $\mu\text{V/s}$). *b)* and *c)* potential profile and specific current during discharge and subsequent relaxation of a LiFePO_4 and LiCoO_2 blend at 0.2C and 5C [38].

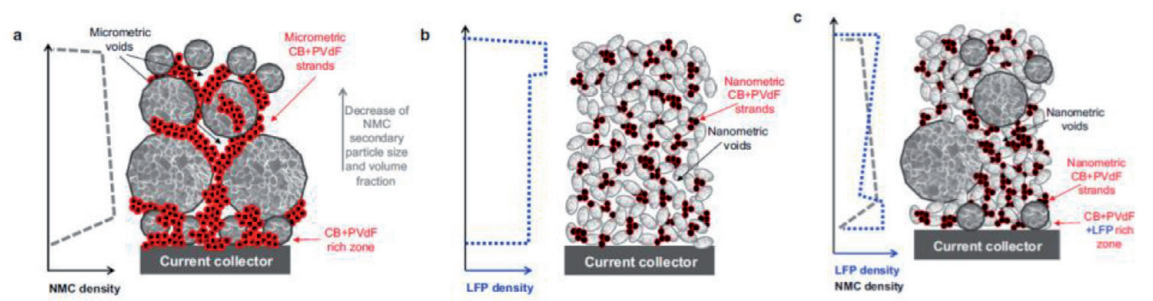


Figure 5.
Schematic figure of typical features in a) NMC, b) LFP, and c) NMC/LFP blend electrodes [39].

used to check the composition distribution in prepared blend electrodes [39, 40]. Small NMC, nano sized LiFePO_4 and carbon additives are enriched in layer close to current collector and large particle NMC is depleted in this region. Although electrode composition is close to design value above the NMC depleted layer, the mean NMC particle size presents gradient distribution toward top surface, as demonstrated in **Figure 5**. Beside local morphology heterogeneities, LiFePO_4 agglomeration and cavities are observed in NMC rich zones. The heterogeneity issue may can be resolved by technique and equipment optimization, but the reported results reveal that materials properties differences should be considered to prepare uniform electrodes with high quality especially for blend cathodes.

3.2 Blend cathode – olivine phosphate and spinel oxide

Spinel oxide cathode has advantage of low cost, high thermal stability and high rate capability. However, spinel oxide suffers from fast capacity fading in long cycling test, especially at high temperature. Olivine phosphate has excellent cycling stability and could blend with spinel to pursue the comprehensive performance.

$\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$ (LFMP) and spinel oxide blend cathode demonstrates linear changing on tap density, reversible capacity, energy density and power density at low C-rate by adjusting blend ratio between two components. However, synergetic effect was observed in blend cathode at high C-rate [41]. Discharge curves of blend cathode at 3C presents lower polarization for $\text{Mn}^{3+}/\text{Mn}^{2+}$ plateau as shown in **Figure 6**. Structure change was studied by in-situ XRD characterization during 3C pulse discharge and the following relaxation. (004) diffraction peak of spinel cathode shifts toward lower angle during discharge and moves to high angle in relaxation period. This result indicates that spinel component is reoxidized in relaxation step. As lithium diffusion in LFMP is slower than spinel LiMn_2O_4 , the higher delithiated state LFMP will provide lithium ions to spinel for reaching a common

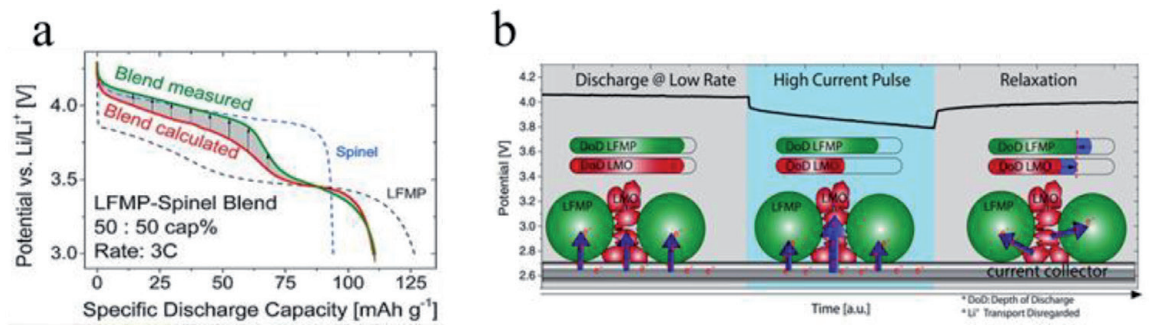


Figure 6.
(a) Discharge curve comparison of blend cathode and individual component [42]. (b) Schematic illustration of buffer effect in blend cathode during pulse power test [41].

Label	NMC/LMFP/LMO [wt%]	Areal capacity [mAh cm ⁻²]	Mass loading [mg cm ⁻²]	Specific capacity [mAh g _{AM} ⁻¹]	Porosity [%]	Density [g cm ⁻³]	Conductivity [S cm ⁻²]
100%NMC	100:0:0	2.51 ± 0.02	15.86 ± 0.07	170.14 ± 0.67	33 ± 2	2.83 ± 0.05	0.68 ± 0.11
100%LMFP	0:100:0	2.53 ± 0.04	17.89 ± 0.25	151.27 ± 0.30	32 ± 2	2.13 ± 0.03	1.16 ± 0.03
100%LMO	0:0:100	2.58 ± 0.02	26.25 ± 0.01	105.41 ± 0.08	31 ± 1	2.73 ± 0.02	0.39 ± 0.20
75%NMC	75:12.5:12.5	2.48 ± 0.01	16.07 ± 0.02	165.57 ± 0.12	32 ± 2	2.72 ± 0.04	1.84 ± 0.19
75%LFMP	12.5:75:12.5	2.46 ± 0.08	17.70 ± 0.55	149.25 ± 0.29	32 ± 2	2.27 ± 0.03	1.89 ± 0.19
75%LMO	12.5:12.5:75	2.59 ± 0.07	23.20 ± 0.28	118.49 ± 3.72	30 ± 2	2.70 ± 0.03	1.52 ± 0.19
33%each	33.3:33.3:33.3	2.41 ± 0.2	18.79 ± 0.65	136.45 ± 11.95	32 ± 2	2.54 ± 0.04	2.04 ± 0.20

Table 1.
Characteristic properties of electrodes with an aerial capacity of approximately 2.5 mAh cm⁻² and a porosity of 30% calculated from the electrodes' thickness. Mass loading includes active materials, binder, and conductive carbon. Specific capacity is based on 93% active material (AM) content. The proportions indicated in the second column are based on the total AM [45].

equilibrium potential state (demonstrated in **Figure 6**). This buffer effect reduces the electrode polarization and improves the power pulse capability. Energy density and power density at high C-rate are enhanced contributed by the reduction of electrode polarization by blend ratio optimization [42].

Manganese dissolution is notorious for lithium ion batteries using spinel LiMn_2O_4 cathodes [43]. Dissolution mechanism is generally ascribed to the presence of HF generated by the reaction between hexafluorophosphate anion and water impurity. Dissolved manganese will be reduced/deposited on anode side and involved in SEI formation in graphite surface. Spinel cathode will lose reversible capacity by manganese dissolution and anode impedance will be dramatically increased by manganese migration and deposition, as a result spinel cathode performance in lithium ion battery is poor, especially calendar life and cycling stability at high temperature. This issue can be alleviated by using blend cathode design. Layered structure cathodes such as LiCoO_2 and NMC reported that can work as proton scavenger through Li ion and proton exchanging in blend cathodes [44]. In LFMP and spinel oxide cathodes, dissolved manganese may be precipitation on LFMP particle surface instead of migrating to anode side. This result is also approved in $\text{LiFe}_{0.3}\text{Mn}_{0.7}\text{PO}_4$ and $\text{LiMn}_{1.9}\text{Al}_{0.1}\text{O}_4$ blend cathode that manganese dissolution from spinel cathode is dramatically reduced [42].

3.3 Ternary blend cathodes

Based on the development of binary blend cathode, ternary blend cathode composed by olivine phosphate, layered oxide and spinel oxide are proposed to study. Mixing three components at even ratio (33% for each), the ternary blend electrode presents highest electronic conductivity when all the other electrode parameters are controlled at same level (as list in **Table 1**) [45]. Redox activities studies reveal that each component in blend cathode can work independently and contributes to reduce the over-potential [46]. This is consistent with other reports.

4. Safety

Along with energy density of lithium ion battery increasing, safety concerns are seriously raised. Safety performance and evaluation is one of the critical criteria for the practical utilization of novel battery materials/technologies. Although battery management systems (BMS) are equipped on electrical vehicles to monitor all the cells and ensure the safety operation, battery still has thermal runaway risk and would cause disaster results. Many countries published the strict compulsory standards for battery safety tests before releasing to commercial utilization on EVs [47]. Therefore, it is important to pay attention on safety development as well as energy/power density improvement.

Lithium ion battery is a comprehensive system and sensitive to temperature. When battery temperature rising to the cathode decomposition triggering point, the exothermic reaction will abruptly release heat and accelerate thermal runaway which is the detrimental safety issue. Thermal studies of materials components in lithium ion batteries can be investigated by differential scanning calorimetry (DSC) or accelerating rate calorimetry (ARC) [48]. As cathode material property are different, the onset reaction temperature and released heat are varied. In brief, the onset temperature for cathodes follow the order: $\text{LiFePO}_4 > \text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2 > \text{LiCoO}_2$ as compared in **Figure 7** [47]. Polyanionic phosphate cathodes have robust P-O covalent constructing stable three-dimensional framework, it reduces the reactivity between cathode and electrolyte.

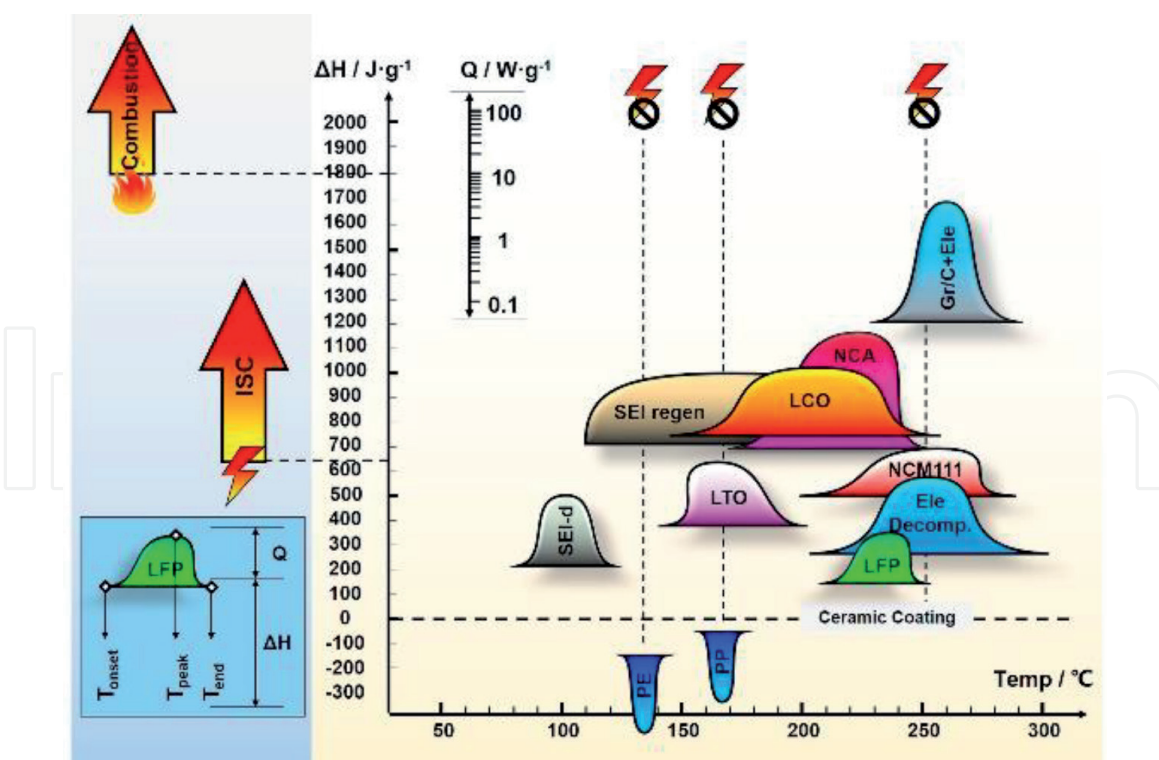


Figure 7.
The energy release diagram of different cathode in lithium ion batteries [47].

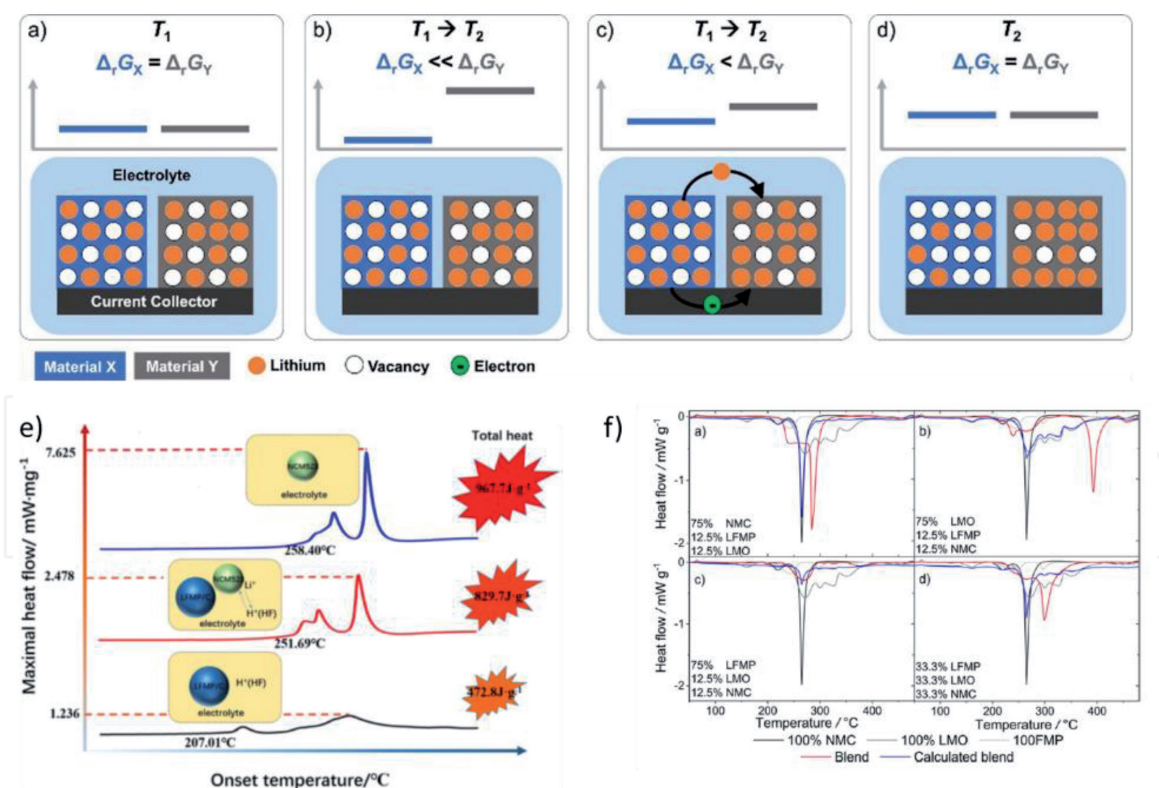


Figure 8. (a–d) Schematic description of Li redistribution among the components induced by a temperature change [38]. (e) Thermal performance comparison in LFMP/C and NMC₅₂₃ blend cathode [36]. (f) Differential scanning calorimetry of fully charged blend electrodes (red) comparing with individual cathode at different ratios [45].

Although spinel is reported that onset temperature is little higher than LiFePO_4 [49], but the exothermic reaction enthalpy is higher than LiFePO_4 and the peak shape is more sharp which means more heat will be generated in shorter time.

Although electrochemical performance of layered oxide cathodes have been improved a lot by material modification [33, 50, 51], they are still hard to compete with LiFePO_4 on safety performance evaluation. Blend cathode is a reasonable method to balance the comprehensive performance. By adding olivine phosphate cathode $\text{LiFe}_{0.15}\text{Mn}_{0.85}\text{PO}_4/\text{C}$ in NMC523 cathode, the exothermic reaction enthalpy is significantly decreased [36]. But there is no linearly relationship between LFMP adding ratio and thermal performance (**Figure 8**).

5. Summary

Olivine phosphate has been successfully commercialized and used in lithium ion batteries to equip on electrical vehicles. Although energy density is not competitive comparing with using layered oxide cathode especially Ni rich cathode, olivine phosphate present excellent safety performance. Manganese substitution and composited with lithium vanadium phosphate is carried out to improve energy density and power density. Beside this, blend cathode is an effective strategy to improve energy density without sacrificing safety advantage. Binary and ternary blend cathode present the possibility to tailor cathode property and performance. Blend cathodes show synergetic effect on rate capability and thermal stability tests which is higher than nominal value. Structure and electrochemistry studies reveal that buffer effect in blended components is contributed to the improvement. This chapter provides opinions from material science and electrochemistry viewpoints to understand the requirement of lithium ion battery on cathode materials development.

Conflict of interest

The authors declare no conflict of interest.

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