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## **COMPARISON OF LITHIUM-ION BATTERY CATHODE MATERIALS AND THE INTERNAL STRESS DEVELOPMENT**

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### **ABSTRACT**

The need for development and deployment of reliable and efficient energy storage devices, such as lithium-ion rechargeable batteries, is becoming increasingly important due to the scarcity of petroleum. Lithium-ion batteries operate via an electrochemical process in which lithium ions are shuttled between cathode and anode while electrons flowing through an external wire to form an electrical circuit. The study showed that the development of lithium-iron-phosphate ( $\text{LiFePO}_4$ ) batteries promises an alternative to conventional lithium-ion batteries, with their potential for high energy capacity and power density, improved safety, and reduced cost. However, current prototype  $\text{LiFePO}_4$  batteries have been reported to lose capacity over ~3000 charge/discharge cycles or degrade rapidly under high discharging rate. In this study, we report that the mechanical and structural failures are attributed to dislocations formations. Analytical models and crystal visualizations provide details to further understand the stress development due to lithium movements during charging or discharging. This study contributes to the fundamental understanding of the mechanisms of capacity loss in lithium-ion battery materials and helps the design of better rechargeable batteries, and thus leads to economic and environmental benefits.

### **INTRODUCTION**

#### **The Need for Rechargeable Batteries**

For over a century, petroleum-derived fuels have been the first choice as an energy source for transportation, and accounted for more than 71.4% of U.S. petroleum use in 2009 [1]. Although the petroleum-based fuel energy resource is convenient and technically matures, researchers started looking for alternative energy sources such as batteries due to the shortage of petroleum and because burning fossil fuels have

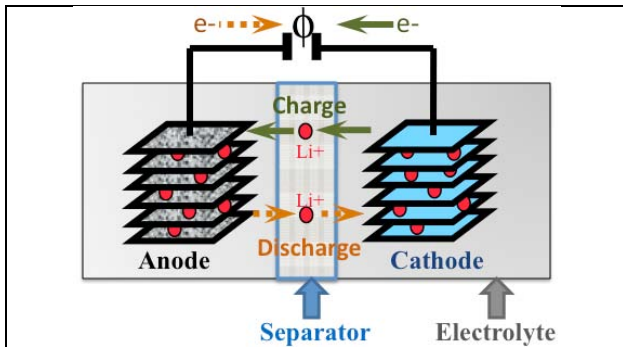
become an environmental issue. It is reported that 98% of carbon dioxide emissions come from petroleum fuels [2]. Since carbon dioxide accounts for the largest share of greenhouse gases, to meet the stated goal of reducing total U.S. greenhouse gas emissions to 83% below 2005 levels by 2050, an alternative energy storage system is required.

One of the most promising energy storage solutions for future automotive technology is the rechargeable battery. Compared with other resources such as flywheels, capacitors, biofuel, solar cells, and fuel cells, rechargeable batteries are more portable and provide quick energy storage and release [3-5]. Moreover, it is more difficult to use these other resources globally than it is to use rechargeable batteries, due to the operating environment limitations for these other energy sources [3]. Compared with capacitors, rechargeable batteries have lower self-discharge rates [3, 5], thus holding their charge for longer periods of time. Therefore, to best serve as a future automotive technology, rechargeable batteries should have both high energy and power densities [4], the ability to output high current for a long period of time, and to be fully charged quickly. The durability and environmental friendliness of rechargeable batteries is also very important. They should work for several years safely under different climatic conditions, and even if involved in an unfortunate car collision.

#### **Fundamental Science in Li-ion Battery Materials**

Among the rechargeable batteries, Li-ion batteries have dominated the field of advanced power sources due to their high gravimetric and volumetric energy density [6]. The most common Li-ion battery applications in the market are for portable electronics, power tools, and transportation. Li-ion battery contains three main parts: cathode, anode, and the electrolyte (Fig. 1). It operates via an electrochemical process

in which lithium ions are shuttled between cathode and anode while electrons flow through an external wire to form an electrical circuit. During discharge, an electrical circuit is formed, and lithium ions move out (extraction) from the anode to the cathode (intercalation) to neutralize these charges (Fig. 1). The reactions occur continuously and while electrons continue to flow, providing electrical energy to the connected device. The electrical energy is then restored to the battery upon recharge.



**Figure 1. Electrochemical processes in lithium-ion batteries during charging and discharging. Lithium ions are shuttled between the anode and the cathode to provide charge neutrality so that the reactions can continue and electrons can keep flowing to provide electrical energy to the connected device.**

Both anode and cathode materials exhibit layered structures, which allow lithium ions to stay in or pass through the structures. In the cathode side, intercalated lithium compound such as  $\text{LiFePO}_4$ ,  $\text{LiMn}_2\text{O}_4$ , and  $\text{LiCoO}_2$  are commonly used. In the anode side, layered carbon materials (graphite or carbon nanotube) [7, 8], titanate materials [9], or silicon nanowires [10] are widely used due to their low electrochemical potential with respect to Li metal [11]. The most common electrolyte is a solution that contains lithium salt in an organic solvent. To avoid unnecessary reactions between electrode materials and  $\text{H}_2$  or  $\text{O}_2/\text{H}_2\text{O}$  in electrolyte, organic solvent or organic solid are adopted to replace aqueous solvent [11]. The current collectors, connecting to anode and cathode, carry electrons and transit the current to the external circuit. The separator is a membrane that lies between anode and cathode to avoid a possibility of short circuit (Fig.1).

### **The Prospective Cathode Materials**

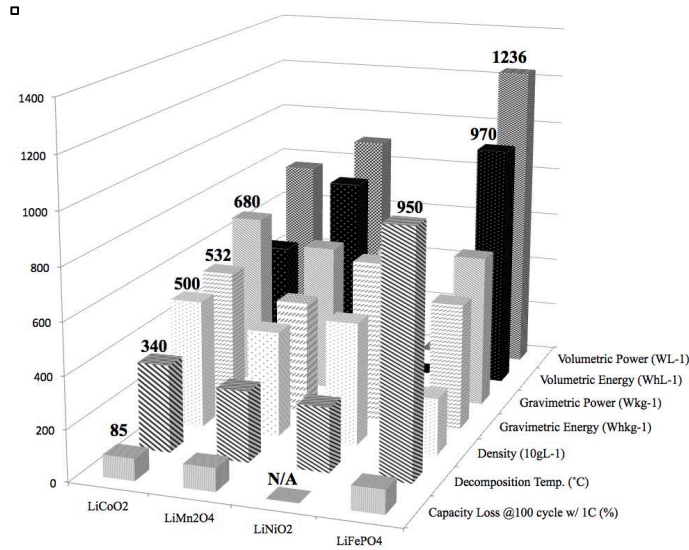
In this study, we provide an overall comparison of commonly used cathode materials for Li-ion batteries. There are four mainstream cathode materials in the present market:  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiNiO}_2$ , and  $\text{LiFePO}_4$ .  $\text{LiCoO}_2$  is the most commonly used in portable electronic devices due to its excellent charging/discharging rate and power/energy density [12]. However, a battery with  $\text{LiCoO}_2$  as its cathode material does not have good thermal stability [13]. Moreover, Co is toxic and expensive, which makes  $\text{LiCoO}_2$  an imperfect choice for a cathode material for electric vehicles (EVs), hybrid

electric vehicles (HEVs), and plug-in hybrid electric vehicles (PHEVs).  $\text{LiMn}_2\text{O}_4$  is able to provide higher voltage, but it does not have a good power/energy density [14]. Its relatively short cycle life and high capacity loss [15] indicate that it is not an ideal cathode material for Li-ion batteries for EV/HEV/PHEV applications. The  $\text{LiNiO}_2$  material, with the same structure as  $\text{LiCoO}_2$ , provides good power and energy densities [16]. However, since it is very difficult to prepare pure  $\text{LiNiO}_2$  composite, Co-doped  $\text{LiNiO}_2$ ,  $\text{Li}_{1-x}(\text{Ni}_{0.8}\text{Co}_{0.2})_{1+x}\text{O}$ , is usually considered as an alternative material in research and applications [17]. With the demand for Li-ion batteries increasing worldwide, a new Li-ion battery cathode material,  $\text{LiFePO}_4$ , was developed by Goodenough in 1996 [18]. He and his group discovered that  $\text{LiFePO}_4$  is a good candidate for a cathode material due to its low price and high thermal stability. However,  $\text{LiFePO}_4$  suffers from low intrinsic electronic conductivity ( $10^{-10}$ – $10^{-9} \text{ Scm}^{-1}$ ) [19]. Based on the study by Chung and Chiang [20], the low electronic conductivity of  $\text{LiFePO}_4$  could be significantly enhanced by doping other metal elements such as zirconium, niobium, and magnesium [20]. In the following section, characteristics and specifications of aforementioned cathode materials were collected and compared for Li-ion batteries. Specifically, we focus on (1) volumetric power and energy densities, (2) gravimetric power and energy densities, (3) stability, safety and environmental factors, and (4) capacity and rate-capacity.

### **Characteristics of Cathode Materials**

**1. Volumetric Power and Energy Densities:** Power and energy densities are important properties for cathode materials. They determine the energy release rate and energy storage capacity per unit weight or volume. For electric vehicles, the volumetric power density and energy density are very important, because with the same energy capacity, a smaller battery is easier to fit into a car. For battery cathode materials: it is observed that  $\text{LiFePO}_4$  has the highest volumetric power density and energy density ( $1236 \text{ WL}^{-1}$ ,  $970 \text{ WhL}^{-1}$ , respectively) among the four mainstream cathode materials [21, 22] (Fig. 2).  $\text{LiCoO}_2$  has a volumetric power density of around  $767 \text{ WL}^{-1}$  and an energy density of around  $483 \text{ Wh/L}$ . These values are roughly half that of  $\text{LiFePO}_4$  [21, 22] (Fig. 2).  $\text{LiMn}_2\text{O}_4$  has a volumetric power density and energy density ( $900 \text{ WL}^{-1}$ ,  $785 \text{ WhL}^{-1}$ ) higher than those of  $\text{LiCoO}_2$ . However,  $\text{LiMn}_2\text{O}_4$  has a slightly lower volumetric power density and energy density than that of  $\text{LiFePO}_4$  [21, 22] (Fig. 2). The volumetric power and energy density data of  $\text{LiNiO}_2$  were not available since pure  $\text{LiNiO}_2$  is difficult to prepare. In addition, the United States Advanced Battery Consortium (USABC) listed goals for advanced batteries for EVs where volumetric power density should at least be  $600 \text{ WL}^{-1}$  and the volumetric energy density should at least be  $300 \text{ WhL}^{-1}$  [23] (Table 1). Considering batteries as a whole (including cathode, anode, and electrolyte), current battery technologies, however, are only able to deliver  $250$ – $360 \text{ WhL}^{-1}$  for  $\text{LiCoO}_2$  batteries,  $330 \text{ WhL}^{-1}$  for  $\text{LiMn}_2\text{O}_4$  batteries,  $450 \text{ WhL}^{-1}$  for  $\text{LiNiO}_2$  batteries, and  $220 \text{ WhL}^{-1}$  for  $\text{LiFePO}_4$  batteries. Therefore, the performance of advanced batteries still

falls short of the EV goals set forth in 2006 by USABC [23]. Note that the values reported in Fig. 2 are based on raw materials and the values reported in Table 1 are batteries as a whole (including cathode, anode, and electrolyte) with the said cathode materials.



**Figure 2: Comparison of various cathode materials, LiCoO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>, LiNiO<sub>2</sub>, and LiFePO<sub>4</sub>, looking at the volumetric power/energy, gravimetric power/energy, density, decomposition temperature, and capacity loss. The capacity is measured as the hourly (dis)charge rate for 100 cycles. Among these materials, LiFePO<sub>4</sub> provides high volumetric power/energy, gravimetric energy, low density, high decomposition temperature, and comparable capacity loss. This suggests that LiFePO<sub>4</sub> is the choice for compact and lightweight energy materials.**

**2. Gravimetric Power and Energy Densities:** The gravimetric power and energy densities are very important for portable devices. That is, with the same power and energy capacity, a lighter battery is easier to carry [22, 24, 25]. It is observed that LiNiO<sub>2</sub> has high gravimetric power and energy densities of 600 Wkg<sup>-1</sup> and 629 Whkg<sup>-1</sup>, respectively (Fig. 2). The gravimetric power density of LiFePO<sub>4</sub> is reported around 600 Wkg<sup>-1</sup> whereas its gravimetric energy density (495 Whkg<sup>-1</sup>) is lower than that of LiNiO<sub>2</sub>. LiCoO<sub>2</sub> has a gravimetric power density of around 680 Wkg<sup>-1</sup> and an energy density of around 532 Whkg<sup>-1</sup>. These values are slightly higher than that of LiFePO<sub>4</sub> [22, 24, 25] (Fig. 2). Finally, LiMn<sub>2</sub>O<sub>4</sub> has a gravimetric power density of around 584 Wkg<sup>-1</sup> and an energy density of around 440 Whkg<sup>-1</sup>. These values are comparable to that of LiFePO<sub>4</sub> [22, 24, 25] (Fig. 2). The density of each cathode material was also listed in Figure 2. LiFePO<sub>4</sub> has the lowest density (2.2 kgL<sup>-1</sup>) and LiCoO<sub>2</sub> has the highest (5 kgL<sup>-1</sup>), which is more than twice of that of LiFePO<sub>4</sub>. Gravimetric power/energy densities should not be directly converted to volumetric power/energy densities based on the provided density values. This is due to the different synthetic methods that were chosen

based on different demands, and the weight of electrolytes was sometimes included in the collected data when the gravimetric power and energy densities were calculated. According to the USABC, gravimetric power density should at least be 400 Wkg<sup>-1</sup> and the gravimetric energy density should at least be 200 Whkg<sup>-1</sup> [23] (Table 1). However, considering batteries as a whole (including cathode, anode, and electrolyte), current battery technologies are only able to deliver 106-250 Whkg<sup>-1</sup> for LiCoO<sub>2</sub> batteries, 100 Whkg<sup>-1</sup> for LiMn<sub>2</sub>O<sub>4</sub> batteries, 192 Whkg<sup>-1</sup> for LiNiO<sub>2</sub> batteries, and 90-110 Whkg<sup>-1</sup> for LiFePO<sub>4</sub> batteries. Therefore, the performance of advanced batteries falls short of EV goals set forth in 2006 by the USABC [23].

**Table I. Volumetric and gravimetric energy density for 4 different types of Li-ion batteries and the comparison to USABC requirements.**

Energy Density	LiCoO <sub>2</sub>	LiMn <sub>2</sub> O <sub>4</sub>	LiNiO <sub>2</sub>	LiFePO <sub>4</sub>	USABC
Volumetric (WhL <sup>-1</sup> )	305	330	450	220	300
Gravimetric (Whkg <sup>-1</sup> )	180	100	170	130	200

**3. Stability, Safety, and Environmental Factors:** The safety issue for Li-ion batteries is an important factor that determines potential applications, especially for EV/HEV/PHEV and other electronic devices. Battery safety is attributed primarily to the material's thermal stability, and the reported overheating and explosion of Li-ion batteries is mainly due to a battery's thermal instability [26]. The differential scanning calorimetry (DSC) test is widely used to investigate the exothermic or endothermic reaction for composite explosives. It determines the ability of a material to absorb or release heat during electrochemical reactions such as lithium insertion or extraction in Li-ion batteries. By using DSC testing, Xia et al. [27] collected the thermal activity and predicted the resultant thermal stability for different cathode materials. They observed that LiFePO<sub>4</sub> has the lowest exothermic peak temperature (289°C) and exhibited endothermic heat flow (-6 Wg<sup>-1</sup>). That is, during electrochemical reactions, LiFePO<sub>4</sub> will see smaller temperature increases than with the other three cathode materials. Moreover, it is observed that LiMn<sub>2</sub>O<sub>4</sub> has an exothermic peak at 302°C, which can easily be reached during a car accident. LiCoO<sub>2</sub> and LiNiO<sub>2</sub> also release heat and cause overheating or even explosion at higher temperatures of around 300-400°C, suggesting that LiCoO<sub>2</sub> and LiNiO<sub>2</sub> as cathode materials are an undesirable choice for energy storage systems for EV/HEV/PHEV applications. In contrast, the electrochemical reaction of LiFePO<sub>4</sub> is endothermic, suggesting that LiFePO<sub>4</sub> is a safer battery material. In general, exothermic peak temperature can be used as a description of self-reaction temperature. The lower the peak temperature, the safer a material is. The decomposition temperature also indicates that LiFePO<sub>4</sub> (950°C) has much higher thermal stability than any other material (Fig. 2). The decomposition temperatures for

LiCoO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>, and LiNiO<sub>2</sub> are 340°C, 275°C, and 250°C, respectively (Fig. 2) [27].

In addition to the safety issue, we also compare the cost of cathode materials and environmentally-related factors (Table 2). We note that Co is toxic and Ni has the potential to cause heavy metal pollution. LiFePO<sub>4</sub> is made from non-toxic materials and the transition metal is abundant (160 billion tons in the Earth). As a result, batteries made from this type of cathode material could be relatively cheaper than that of LiCoO<sub>2</sub> since the transition metal storage of LiCoO<sub>2</sub> is approximately 8.3 million tons (0.005% of LiFePO<sub>4</sub>). The transition metal storage of LiMn<sub>2</sub>O<sub>4</sub> and LiNiO<sub>2</sub> are 99.7 million and 48 billion tons, respectively. It is suggested that LiFePO<sub>4</sub> as a cathode material for rechargeable batteries is more environmental friendly and cost effective than the other three cathode materials (Table 2).

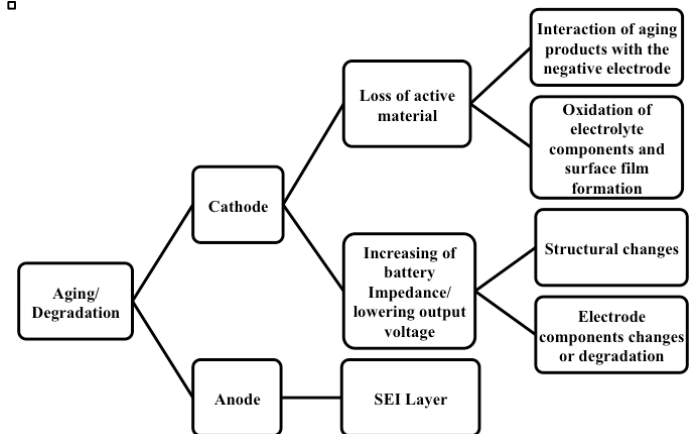
**Table II. Thermal stability characteristics and other factors in cost and environmental issues for battery materials.**

	LiCoO <sub>2</sub>	LiMn <sub>2</sub> O <sub>4</sub>	LiNiO <sub>2</sub>	LiFePO <sub>4</sub>
Exothermic peak temperature (C°)	367	302	348	289
Exothermic heat flow (Wg <sup>-1</sup> )	20	7	33	-6
Environmental pollution	toxic Co	good	heavy metal Ni	good
Battery cost	expensive	moderate	cheap	cheap
Storage of transition metal (×10 <sup>6</sup> ton)	8.3	99.7	48,000	160,000

**4. Capacity and Rate-capacity:** The capacity of a battery is the amount of charge available expressed in milliampere-hours (mAh), and it depends on discharge conditions such as the magnitude of the current, the voltage of the battery, temperature, and other factors. Rate-capacity loss after thousands cycling is one of the biggest obstacles for advanced rechargeable battery technology. To better examine the rate-capacity, four mainstream cathode materials were compared for their retained capacity. The retained capacity of cathode materials is measured after a certain amount of cycles at an nC discharge rate, where a rate nC corresponds to a full discharge in 1/n hours. For example, 0.25C is the rate in which a battery is totally discharged in 4 hours. The higher the value of the rate nC, the better the energy output ability of the battery material is. Studies showed that after 100 cycles at 1C-rate discharging, LiFePO<sub>4</sub> processes 92% capacity retention, LiMn<sub>2</sub>O<sub>4</sub> processes 90% and LiCoO<sub>2</sub> processes 85% capacity retention, respectively [28] (Fig. 2). By extrapolation, if the capacity retention is measured under a higher rate (n>1), LiFePO<sub>4</sub> has a better capability to maintain rate-capacity than that of other cathode materials. Since the preparation and synthetic methods for LiNiO<sub>2</sub> are extremely difficult, its capacity retention data is unavailable. Nevertheless, the rate-capacity loss of LiFePO<sub>4</sub> is reported after thousand-cycles high-rate discharging [29, 30]. It is observed that under a high discharge rate, the capacity retention rate of LiFePO<sub>4</sub> batteries is not as good as that of other batteries.

## FACTORS OF ELECTRODE FAILURE

Electrode failures of Li-ion batteries are usually a result of the accumulation of aging or degradation, which affect electrodes' ability to hold charge and result in capacity loss of Li-ion batteries, and the mechanism could be categorized based on storage/cycling or chemical/mechanical activities. For anode materials, the aging/degradation mechanism is primarily determined by the development of solid-electrolyte interphase (SEI) film [31]; it is a chemical reaction. For cathode materials, the aging/degradation mechanisms could be categorized into 2 groups: (1) ones would cause the loss of active material via storage and cycling, such as chemical interaction of aging products with anodes, oxidation of electrolyte components, and surface film formation [29-35], (2) ones would increase the battery impedance or decrease the output voltage, such as structural changes, electrode components changes, or materials degradation [36-38] (Fig. 3). In general, the aforementioned four phenomena do not happen alone and mechanism of electrode failure is caused by several factors taking place at the same time, which makes it more complicated.



**Figure 3: Electrode aging/degradation categories based on different causes and influences. The proposed work focuses on understanding the interplay between structural changes and deterioration in LiFePO<sub>4</sub> cathode material.**

Cathode materials are considered as the vital part of Li-ion batteries since cathode materials affect both performance and cycling life of Li-ion batteries. Since aging/degradation mechanism of cathode materials is much more complicated than that of anode materials, and since there are varieties of electrode materials, it is difficult to provide a general explanation for cathode aging/degradation mechanisms in all Li-ion systems. In this article, the authors focus on basic factors such as storage, state of charge, and Jahn-Teller effect.

While storing electrode materials, aging/degradation usually occurs because of the side reactions due to thermodynamic instability of materials [39-42]. Moreover, the state of charge, cycling conditions, and temperature are three main factors that cause materials age/degrade. Finally, cycling

with kinetically induced effects, such as volume variations and concentration gradients, could potentially result in the capacity loss of Li-ion batteries.

### Storage

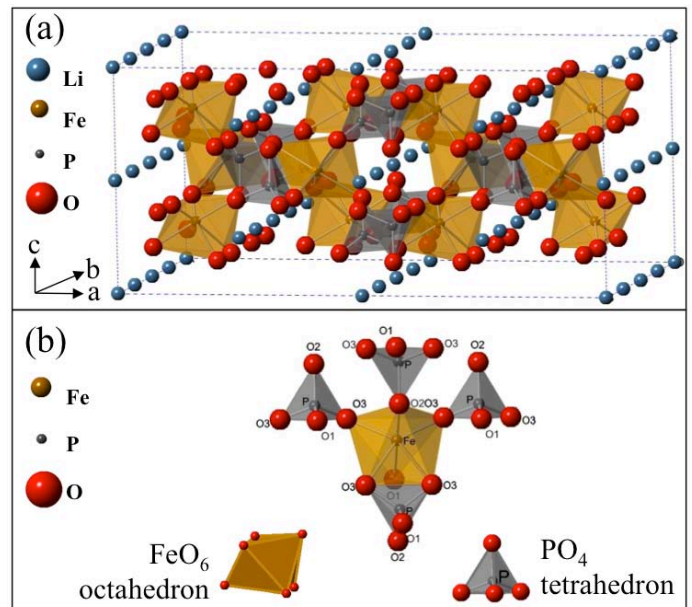
As the cathode material of Li-ion batteries, LiFePO<sub>4</sub> is the promising green material at present for its low cost, non-toxicity, rich source of raw materials and great electrochemical performance [43]. Yet, although commonly considered as highly stable toward air and H<sub>2</sub>O, aging/degradation of the electrochemical performance of LiFePO<sub>4</sub> was shown after being exposed to air for a few weeks at ambient temperature [44]. To observe the side reaction and side phase of LiFePO<sub>4</sub> materials in the atmosphere of humid-hot air, a nano-scaled sample of LiFePO<sub>4</sub> material (70 nm) in 120°C hot air was stored for 30 days. By comparing it with a pristine sample under the X-ray Diffraction (XRD) test, the decreasing unit-cell volume after storing in high temperature was observed, suggesting that the delithiation occurred during hot-air [45]. In the parallel study to the XRD test, the decreased unit-cell volume is calculated based on Vegard's Law, which equivalents to 11% lithium missing during the high temperature storage. Moreover, the amount of Fe<sup>3+</sup> determined by the Mossbauer spectroscopy accounts for 45% of total iron, which is far more than 11% loss of lithium. This phenomenon indicates that while storing, in addition to the trivalent Fe from delithiation, an amorphous ferric phosphate side-phase grows detrimentally to olivine LiFePO<sub>4</sub> upon air exposure. Therefore, this loss of active materials in LiFePO<sub>4</sub> cathode materials could potentially lead to the capacity loss for Li-ion batteries.

### State of Charge

In current EV/HEV/PHEV markets, LiMn<sub>2</sub>O<sub>4</sub> is adopted as cathode materials for Li-ion batteries [46]. LiMn<sub>2</sub>O<sub>4</sub> cathode materials provide higher voltage than other materials, but its usage is limited by its short cycle life [15, 47, 48]. It is observed that the accelerated aging/degradation of LiMn<sub>2</sub>O<sub>4</sub> cathode materials is due to the dissolution of Mn in electrolyte under various charging voltage: with a higher charging voltage than 4.2V or nearly fully discharged. During very low state of charge or a high temperature (55°C), a disproportionation reaction will occur, which consumes two Mn<sup>3+</sup> at two Mn sites in LiMn<sub>2</sub>O<sub>4</sub> cathode materials while Mn<sup>3+</sup> is converting to Mn<sup>2+</sup> and Mn<sup>4+</sup> [15, 31, 48]. The Mn<sup>4+</sup> stays in one of the two Mn sites and takes the place of Mn<sup>3+</sup>. Mn<sup>2+</sup> ions, on the other hand, escape from LiMn<sub>2</sub>O<sub>4</sub> and dissolve in the electrolyte. The empty Mn site caused by the Mn<sup>2+</sup> dissolution is then replaced by a lithium ion. Therefore, new composite materials Li[LixMn<sub>2-x</sub>]O<sub>4</sub> is produced. Due to the element change on Mn sites in spinel structure, structural change happens during the dissolution. Moreover, the LiPF<sub>6</sub>, which solute in electrolyte as conductive salt, turns to HF acid at times. HF acid could then react with Li[LixMn<sub>2-x</sub>]O<sub>4</sub> material and make it soluble in electrolyte. After Mn<sup>2+</sup> ions getting into the electrolyte, many side reactions could be activated [49-51].

### Structure and Jahn-Teller Effects

Structure failure of cathode materials caused by phase transformations during the insertion and desertion of lithium ion is a main factor that influences the aging/degradation mechanisms. A perfect eight-unit cell crystal LiFePO<sub>4</sub> model without dislocations is shown in Fig. 4-(a) and lithium ions lay in the spaces along the b(y)-direction in the crystal. The crystal structure is made up by FeO<sub>6</sub> octahedras, PO<sub>4</sub> tetrahedras and lithium ions (Fig. 4-b). During discharging and charging, lithium ions shuttle in and out of the crystal through the spaces along the b(y)-axis and potentially lead to structural distortions or failures.



**Figure 4. (a) Eight LiFePO<sub>4</sub> unit cells without dislocations where lithium ions lay in the spaces along the b(y)-direction. (b) A FeO<sub>6</sub> octahedra and five PO<sub>4</sub> tetrahedras connect each other by sharing one edge and three corners.**

The olivine-type crystal structure of LiFePO<sub>4</sub> belongs to space group Pnma, in which Li, Fe and P atoms occupy octahedral 4a (0, 0, 0), octahedral 4c (x, 1/4, z) and tetrahedral 4c (x,y,z) sites, respectively (Fig. 4-a). A FeO<sub>6</sub> octahedra lies in the middle and is surrounded by five PO<sub>4</sub> tetrahedras (Fig. 4-b). One of the PO<sub>4</sub> tetrahedras shares an edge (O-O bond) with the FeO<sub>6</sub> octahedra, and the other four share four corners respectively. The structures of LiFePO<sub>4</sub> and FePO<sub>4</sub> have similar crystal structures except for the lattice parameter of FePO<sub>4</sub> is smaller than that of LiFePO<sub>4</sub>, due to differences in lattice parameters of LiFePO<sub>4</sub> (a=10.334Å, b=6.002Å, c=4.695Å) and FePO<sub>4</sub> (a=9.826Å, b=5.794Å, c=4.784Å); mismatch occurs during the phase transformation. The differences in lattice parameters could also be attributed to the different valences of Fe: the valence of Fe is +2 for LiFePO<sub>4</sub>, and the valence of Fe is +3 for FePO<sub>4</sub> [52, 53]. The difference in lattice parameter could be related to the Jahn-Teller effect. It states the relationship between metal valences and lattice

parameters, which could be used to justify lattice parameter changes of  $\text{LiFePO}_4$  and  $\text{FePO}_4$  [54]. In short, the outer shell electrons of an atom have strong shielding effect causing by charge neutralization between outer shell electrons and atomic nucleus. The shielding effect would cancel out parts of the electrostatic forces between the atomic nucleus and atoms around it. Changing the valence of an atom will lead to different electron configuration and that in outer shell will have different intensity of shielding effect in each direction. Therefore, when Li-ions move out from  $\text{LiFePO}_4$ , the valence of Fe-ions changes, and then the shielding effect in different directions around Fe-ions change; this phenomenon may cause the structure of Fe octahedra to change.

## A DISLOCATION BASED STRESS DEVELOPMENT

Based on studies of aging/degradation mechanisms of electrode materials, several methods to improve the stability of Li-ion battery have been developed. Such as: (1) decreasing electrolyte decomposition by surface modification and reducing specific surface area [31, 55, 56, 57, 58], (2) neutralizing acid by adding proper additives into electrolyte [31, 59], and (3) stabilizing the structure by doping anions and cations [60, 61]. However, among the aforementioned methods, almost no one could predict and prevent degradations caused by cathodes structural failures due to delithiation. Therefore, a better understanding of the mechanism and plausible models to depict cathode materials structural failures due to delithiation are required.

In this article, previous works on dislocation based stress field are discussed and stress distributions in  $\text{LiFePO}_4$  cathode materials are provided. We choose  $\text{LiFePO}_4$  as our model system due to: (i) It is recognized that  $\text{LiFePO}_4$  is a promising cathode material for Li-ion batteries, thus understanding stress accumulations inside the material is important for developing longer-lasting Li-ion battery materials. (ii)  $\text{LiFePO}_4$  has a 3D matrix structure with anisotropic elastic materials property. Once we successfully build up a model system for this sophisticated material, we are then able to provide a general mathematical framework for other Li-battery cathode materials, such as  $\text{LiCoO}_2$ ,  $\text{LiMnO}_2$ , and  $\text{LiNiO}_2$ .

Chen et al. observed cracks in  $\text{LiFePO}_4$  particles from SEM images, suggesting accumulation of dislocations [62]; the cracks along c(z)-direction was also observed. With  $\text{Li}_{0.5}\text{FePO}_4$  samples, a slight rotation around b(y)-direction of the two phases was observed, indicating the deformation and dislocation associated with delithiation. Therefore, the distortion zones and dislocations could potentially form via phase transformations during the insertion and desertion of lithium ions and potentially leads to structural failures [63, 64]. Moreover, it is observed that the lithium ion insertion and extraction process leads  $\sim 7\%$  volume change between  $\text{LiFePO}_4$  and  $\text{FePO}_4$  phase crystals. It is due to internal stress and strain accommodations occur in  $\text{LiFePO}_4$  crystals because of the coherent interface between phase boundaries [65]. The internal strains initiate dislocations that form after several intercalation-

extraction cycles inside cathode materials, and these dislocations potentially lead the growth of minor cracks.

In 1953, J. D. Eshelby et al. developed general solutions for evaluating dislocation stresses for an arbitrary homogeneous anisotropic solid material [66]. Elastic equations for pure screw dislocation lines with infinite length in monoclinic crystal system materials and for pure edge dislocation lines with infinite length in orthorhombic crystals were developed. However, limited by computational methods at that time, only few equations for simple cases were fully solved. With the developments of computers, stress distribution around dislocations with anisotropic materials properties were illustrated [67]. Recently, solutions for stress fields of dislocation loops have been developed [68]. In 1975, H. L. Heinisch et al. calculated the elastic stress field, self-energies, and energy factors of straight edge and screw dislocations in olivine materials [67]; stress distributions were provided for different directions of dislocations. From their results, Heinisch et al. concluded that orthorhombic olivine materials have moderate elastic anisotropy, though the effects of anisotropy seem to be relatively small. According to their model, they did not successfully predict the slip directions and glide plane preference of dislocations for orthorhombic anisotropic materials based on the elasticity theory.

In this article, we provide dislocation stress distributions for  $\text{LiFePO}_4$  crystals (Fig. 5). Based on the lattice parameters of  $\text{LiFePO}_4$ , we set the dimension as  $100L \times 100L$  on the a(x)-b(y) plane, where  $L=10\text{\AA}$ . It is a plausible model size due to: (i) the reported  $\text{LiFePO}_4$  particle size is among several hundred nanometers [69], which could be correctly represented by  $100L \times 100L$  in our model system, (ii) our model size of  $100L \times 100L$  is sufficient to avoid  $4L \times 4L$  dislocation core regions, the region within which the elastic solutions would not be valid [70], and (iii) our model size of  $100L \times 100L$  is sufficient to depict overall stress distributions without any boundary effects. Classical [70] and generalized [71] stress field for a single edge dislocation (with Burger's Vector,  $b_x=1$ ) with isotropic materials property [72] were compared in Figure 5(a) and (b). Similarly, classical and generalized stress field for a screw dislocation (with Burger's Vector,  $b_z=1$ ) with isotropic materials property [72] were compared in Figure 5(f) and (g). The results suggest generalized stress field are equivalent to classical ones, which provide us a solid basis to vary materials properties on the said generalized solutions. By incorporating anisotropic material property of  $\text{LiFePO}_4$  [72] into our model systems, the results reveal that the stress field are comparable to ones with isotropic materials property (Fig. 5(c) and (h)), which is in the agreement of Heinisch et al.: the effects of anisotropy for orthorhombic olivine materials is insignificant [67].

In most cases, Burger's vectors are not perfectly parallel to one specific axis. Therefore, we expand our model system to exam stress variations for arbitrary Burger's vector's directions. Interesting stress fields are observed for  $b_x=1, b_y=1$  in Fig. 5(d) (for Burger's vectors align with  $45^\circ$  from the +x direction) and  $b_x=0, b_y=1$  in Fig. 5(e) (for Burger's vectors align with  $90^\circ$  from the +x direction). Comparing with stress field in Fig. 5-a

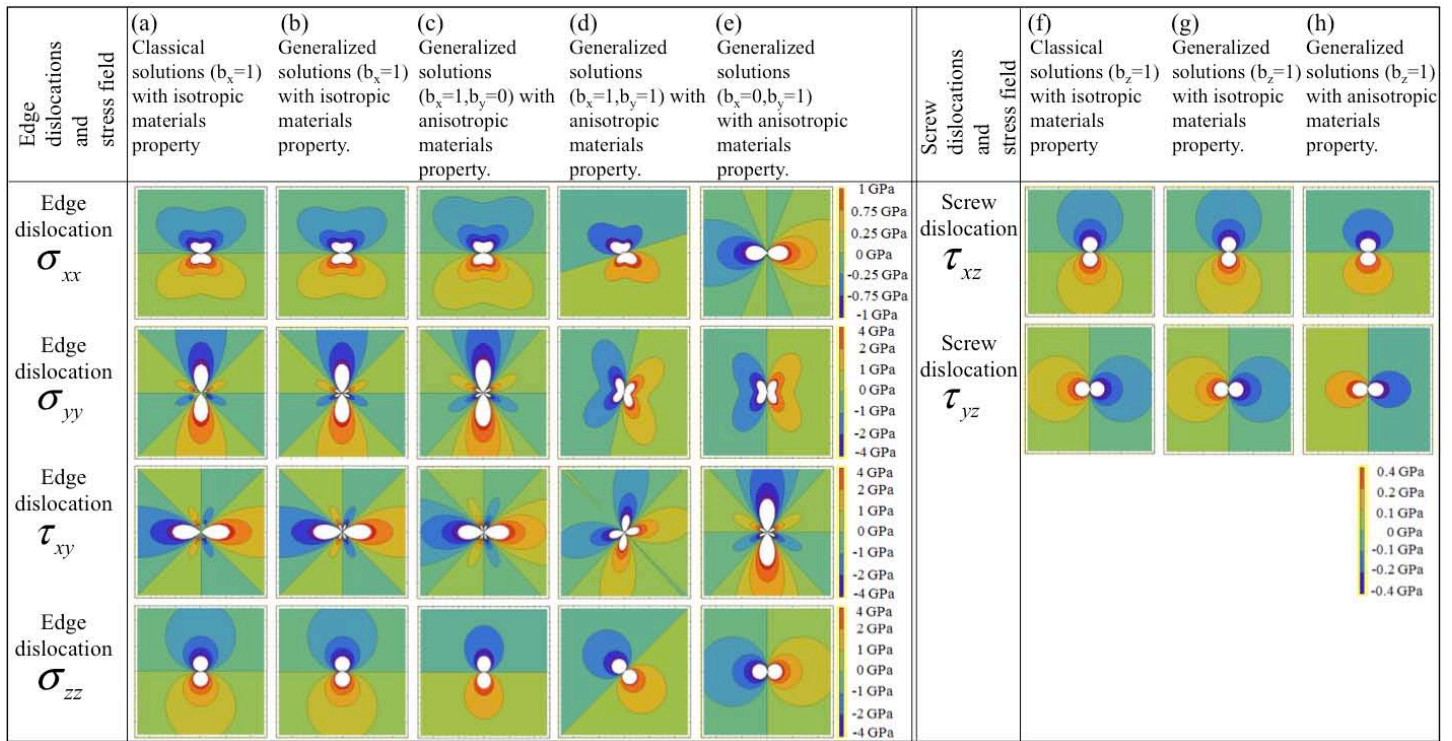
and the one in Fig. 5-e, it is suggested that stress values for arbitrary Burger's vector's directions could be simply calculated by utilizing linear transformations. Moreover, the stress field for the screw dislocation is derived via the displacement in the c(z)-direction, therefore Burger's Vectors in x and y directions are unavailable.

### CONCLUSION

This study provides an overview of four mainstream lithium-ion battery cathode materials. Characteristics of LiCoO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>, LiNiO<sub>2</sub>, and LiFePO<sub>4</sub> were collected and compared. Specifically, we focused on specifications for (1) volumetric power and energy densities, (2) gravimetric power and energy densities, (3) stability, safety and environmental factors, and (4) capacity and rate-capacity. Since synthetic methods are different for the four different cathode materials, only the representative data that appeared most frequently within the past five years were chosen to ensure that data from different literature sources are comparable. Current electrochemical technology is still limited to developing cathode materials to achieve EV goals set by the USABC. The

main obstacle for advanced rechargeable batteries is found in the rate-capacity loss at high C-rate discharging. It is currently one of the most challenging issues in developing energy storage systems for EV/HEV/PHEV, and the enhancement of rate-capacity retention is the primary design goal of battery chemistry in the electrochemical community.

Moreover, we report stress fields caused by a single dislocation inside LiFePO<sub>4</sub> particles. Different dislocations with different Burgers vectors directions have significant influences in the stress developments. With multiple dislocations accumulations and interactions (will be published somewhere else), fractures of LiFePO<sub>4</sub> are formed and observed experimentally. It is believed that fractures inside LiFePO<sub>4</sub> are potential failure mechanisms responsible for the rate-capacity loss in Li-ion batteries. This study contributes to the fundamental understanding of the stress development in cathode materials and it is related to the capacity loss in lithium-ion battery. This study helps the design of better rechargeable batteries, and thus advances technology in energy storage systems for future transportation.



**Figure 5. Stress field for edge and screw dislocations. (a) Stress distribution calculated via classical solutions [70] for a single edge dislocation with isotropic materials property. (b) & (c) Stress distribution calculated via generalized solutions [71] for a single edge dislocation with isotropic and anisotropic materials property, respectively. (d)&(e) Stress distribution for varied Burger's vectors directions; generalized solutions for a single edge dislocation with anisotropic materials property are adapted. (f) Stress distribution calculated via classical solutions [70] for a single screw dislocation with isotropic materials property. (g) & (h) Stress distribution calculated via generalized solutions [71] for a single screw dislocation with isotropic and anisotropic materials property, respectively.**

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