The Electrochemical Performance and Applications of Several Popular Lithium-ion Batteries for Electric Vehicles - A Review

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Abstract. The Lithium-ion battery is one of the most common batteries used in Electric Vehicles (EVs) due to the specific features of high energy density, power density, long life span and environment friendly. With the development of lithium-ion battery technology, different materials have been adopted in the design of the cathodes and anodes in order to gain a better performance. $LiMn_2O_4$, $LiNiMnCoO_2$, $LiNiCoAlO_2$, $LiFePO_4$ and $Li_4Ti_5O_{12}$ are five common lithium-ion batteries adopted in commercial EVs nowadays. The characteristics of these five lithium-ion batteries are reviewed and compared in the aspects of electrochemical performance and their practical applications.

Keywords: LMO · NMC · NCA · LFP · LTO · Lithium-ion battery
Electrochemical performance

1 Introduction

Due to the concerns on the pollutant emissions and the climate change due to large consumption of fossil fuels to support a variety of anthropogenic activities, electrification of the transport sector has been included as one of the national strategies by many countries. As an alternative to the internal combustion engine (ICE) vehicle, Electric Vehicle (EV) has become increasingly popular in recent years due to the improvement of performance in acceleration and endurance. Comparing to the ICE vehicles, the advantages of EVs can be summarised as following aspects:

(1) Higher efficiency: Generally, the average Tank-to-wheel efficiency of ICE cars are around 30% and even lower than 15% if stop-and-start behaviour occurs frequently [1,2]. However, ICEs do not work in high-efficiency region in most cases, especially when the vehicles are running at a low speed in urban areas. In contrast, the average battery-to-wheel efficiency of EVs can be up to 87% which is much higher than ICE based vehicles [1].

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(2) Environmentally friendly: A Battery Electric Vehicle (BEV) is fully powered by the batteries, thus there is no emission produced when an EV is running on the road. Moreover, the emissions of a gasoline Hybrid Electric Vehicle (HEV) is around 30% less than an gasoline ICE based vehicle due to the high efficiency benefit [2].
(3) Less noise pollution: EVs produce less noise pollution (especially at low speed driving mode) due to the result of using electric motors to replace ICEs [3]. An EV eliminates at least 25% and 10% of noise compared to an ICE vehicle at operation speed of 10 km/h and 5 km/h respectively [3,4].
(4) Government support: The promotion of EVs has become a national strategy for many countries today, sales of new petrol and diesel vehicles will be banned for the coming decades in many countries. Many government policies have been proposed in order to increase the competitiveness of EVs in the automotive market, such as lower taxes, free charging facilities and free parking, etc.

As the power source of the electric motor and other electric systems, battery plays an very important role to ensure the EVs can operate effectively and reliably. Several popular types of batteries are used in EVs, such as lead acid, nickel-cadmium, nickel-metal hybrid and Lithium-ion battery. Table 1 presents the key characteristics of these batteries [5–9].

Table 1. Comparison of different types of EV batteries

Characteristic	Lead-acid	Ni-Cd	NiMH	Li-ion
Nominal voltage (V)	2	1.2	1.2	3.2–3.7
Energy density (Wh/kg)	30–50	45–80	60–120	100–265
Power density (W/kg)	180	150	250–1000	250–676
Charging efficiency	50–95%	70–90%	66%	80–90%
Self-discharge rate (per month)	5–20%	20–30%	30–35%	3–10%
Charging temperature (°C)	−20–50	0–45	0–45	0–45
Discharging temperature (°C)	−20–50	−20–65	−20–65	−20–60
Cycle life	200–400	500–1000	300–500	600–3000
Memory effect	No	Yes	Yes	No
Green product	No	No	Yes	Yes

Lithium-ion battery is one of the most popular rechargeable batteries which is widely adopted in EVs and HEVs nowadays due to its noticeable advantages, such as high energy and power density, low self discharge rate, no memory effect, low self-discharge rate and longer life span, etc. [10,11].

Due to the different materials used in the design of the cathodes and anodes, lithium-ion batteries can be subdivided into different categories. Some lithium-ion batteries have been applied in EVs successfully, such as $LiMn_2O_4$ (LMO) battery, $LiNiMnCoO_2$ (NMC) battery, $LiNiCoAlO_2$ (NCA) battery, $LiFePO_4$ (LFP) battery and $Li_4Ti_5O_{12}$ (LTO) battery. These five types of lithium-ion battery have their unique advantages. As the power source of EVs, the battery must meet the specific safety and performance requirements with an appropriate cost. This paper presents a review and comparisons of these five lithium ion batteries over two aspects, namely the electrochemical performance and their applications in EVs.

2 Electrochemical Performance

These five types of lithium-ion battery have various electrochemical performances due to the adoption of different chemical materials. In this section, the comparisons of their structure, nominal voltage, energy density, high current rate capability, thermal stability, cyclabilty and safety performance are presented.

2.1 Structure

LMO has a three dimensional spinel structure which improves the diffusion of lithium ions [12–14]. The electrochemical reactions are associated with the insertion and extraction of lithium ions between the cathode ($LiMn_2O_4$) and the anode (lithium) [15–17]. NMC battery is one of the most successful lithium-ion batteries which balances the specific features of Lithium Cobalt Oxide (LCO) battery and LMO battery. NMC contains a layered structure and the battery cathode is compounded by three chemical elements (Nickel, Manganese and Cobalt) with a certain ratio. The difference ratios of these three chemical elements lead to variant battery performances [18–21]. In order to balance the electrochemical performance, stability and cost, NMC-111 (the ratio of Nickel:Manganese:Cobalt equals to 1:1:1) battery has been developed and widely adopted in EVs. NCA battery has similarities with NMC battery, which replaces manganese with aluminium in order to improve specific energy and life span [22,23]. LFP battery has an ordered olivine structure, the FeO_6 octahedras share the common corners [24]. Unlike the lithium-ion batteries with graphite anode, LTO battery adopts Li-titanate as the anode to offer a zero-strain spinel structure [25].

2.2 Specific Energy and Capability at High Current Rate

In order to increase the mileage of EVs after one charge, the battery of the EVs should offer high energy at a safety level. Increasing the operational voltage is one of the methods that can be applied to enhance battery specific energy. A typical $LiMn_2O_4$ battery offers an average working voltage of 3.7 V, the theoretical gravimetric capacity and energy density are 148 mAh/g [12,26,27]. Unfortunately, the highest gravimetric capacity of $LiMn_2O_4$ battery has been attained is around 130 mAh/g (at the small current rate) [27,28]. A LMO battery has no reversible capacity change when operates at 1 C charge or discharge current rate;

when the charge current remains 1 C and discharge current increases to 50 C, the reversible capacity decreases to 78% of its initial capacity; when the charge and discharge current both change to 20 C, the reversible capacity still remains 58% of its initial capacity [29]. These experimental results strongly suggest that LMO battery has low cell resistance and excellent capability at high current rate.

In order to improve the energy density, some researchers doped other chemical materials, such as Ni in LMO battery cathode to form a doped spinel, and the doped spinel battery can provide a higher theoretical gravimetric capacity of 150–160 mAh/g [30–34]. However, some high energy derivatives of $LiMn_2O_4$ have not been adopted in large-scale in EVs yet due to the limitation of thermal stability and cyclability.

As a possible alternative of $LiCoO_2$ battery, NMC battery offers an average working voltage of 3.6 V and a theoretical gravimetric capacity of 280 mAh/g [35]. However, the actual commercial gravimetric capacity in commercial cells is around 170 mAh/g [35]. The reversible capacity of a NMC-111 battery decreases to 78–80% of initial capacity at 4 C discharge current rate [36,37] and the capacity decreases to 73–74% of initial capacity at 8 C discharge current rate [38,39]. This indicates that NMC battery contains high specific energy and good capability at high current rate.

NCA battery and NMC battery have relatively similar electrochemical performance. A typical NCA ($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$) battery offers an average operation voltage of 3.7 V, and theoretical gravimetric capacity of 279 mAh/g [35]. The actual gravimetric capacity in commercial cells is around 200 mAh/g [35]. The capacity of a NCA battery decreases to 93.3% of the initial capacity at the discharge current rate at 0.5 C, and there is no extra capacity loss when the discharge current rate increases to 3 C [40]. It obviously can be found that both NCA and MNC batteries have high specific energy and can provide satisfactory performance at high current rate.

LFP has low electrical conductivity (10^{-9} to 10^{-10} S/cm) due to its ordered olivine structure [24,41–44]. A typical LFP battery offers an average operational voltage of 3.3 V [9] and a theoretical gravimetric capacity of 170 mAh/g [24]. The capacity of a LFP battery decreases to 96% of its initial capacity at a discharge current rate of 1 C; the capacity decreases to 82% and 76% at discharge current rate of 3 C and 5 C respectively [45]. The specific energy of LFP battery is lower than the above three lithium-ion batteries. The capacity fades significantly at high current rate.

Unlike the four types of lithium-ion batteries above, LTO battery replaces the graphite in the anode with $Li_4Ti_5O_{12}$ to form a zero-strain spinel structure [25]. As an anode, the operation voltage is 1.5 V for Li/$Li_4Ti_5O_{12}$ battery cell [46]. When the $Li_4Ti_5O_{12}$ anode couples with cathodes like LMO, NMC, NCA, the operating voltage is 2.1–2.5 V [47]. The theoretical gravimetric capacity of $Li_4Ti_5O_{12}$ anode battery is 175 mAh/g [25]. Although the specific energy of LTO battery is low, it has an excellent capability when operates at high current rate, the capacity decreases to 87% of the initial capacity at 11.4 C charge/discharge current rate [48].

However, it should be noted that in the production process of commercial batteries, the theoretical energy densities are very difficult to achieve due to safety, cost and technology limitation reasons. Table 2 shows the average energy densities for commercial products of these five types of lithium-ion battery [49].

Table 2. Nominal voltage and energy density of commercial products

Cathode	Nominal voltage	Energy density in commercial products
LMO	3.7–3.75	100–240 Wh/kg
NMC	3.6–3.7	150–220 Wh/kg
NCA	3.65	200–260 Wh/kg
LFP	3.2	100–140 Wh/kg
LTO	2.2–2.4	50–80 Wh/kg

Comparing the operational voltage and energy density of these five lithium ion batteries, it can be found that LMO, NMC and NCA batteries enable the EVs to gain a longer mileage on single charge due to the higher energy density. LFP and LTO batteries have low energy density which means the EVs need to bring more battery cells to achieve the energy requirement. However, this results the increasing of vehicle weight, the mileage one a single charge still cannot be improved in essence. On the other hand, more batteries are adopted in EVs leads the Battery Management System (BMS) to face greater challenges.

2.3 Thermal Stability and Safety

Apart to the energy and power requirements, safety is another important issue in EV management. Many factors may cause battery failures, such as over voltage, under voltage, short circuit, over charge/discharge, overheat and collision, etc., and a few accidents due to battery failures have been reported in the public media. However, the most common factor is the generation of heat and gas [5,10,50]. Thus, to have desirable thermal stability is another important aspect in assessing the battery quality. Good thermal stability of a battery enables an EV to operate in a wider temperature range, and reduces the difficulty of the thermal management in an EV.

Thermal stability is a key that directly determines the safety of the battery operation. A typical LMO battery can operate safely at 55 °C, but the capacity decreases to 75% of its initial capacity [26]. The main reason of the capacity fading of a LMO battery during cycling is the Mn dissolution into the electrolyte [51]. The Solid Electrolyte Interphase (SEI) breaks at 90.5 °C and the thermal runaway occurs at 250 °C, then O_2 is released due to the decomposition of $LiMn_2O_4$ [52].

A typical NMC battery loses 7.5% capacity at 85 °C after 26 cycles (0.29% capacity loss per cycle) and loses 22% capacity at 120 °C after 29 cycles [53]. At

80 °C, the SEI has no obvious change but it becomes thicker and forms spherical particles at 120 °C [53]. Flammable and toxic gas (H_2 and CO) are released when the temperature reaches 170 °C and the thermal runaway occurs at 220 °C [54].

For a typical NCA battery, the anodic reactions occur at 90 °C and the SEI film breaks at 120 °C; the cathodic reactions occur at 140 °C and the thermal runaway occurs when the temperature reaches 180 °C [55]. Moreover, thermal runaway could occur at 65 °C if the NCA battery is overcharged. [56]. NCA battery has a drastic behaviour when the temperature reaches thermal runaway, a large amount of gas (317mmol) are released [56]. Oxygen gas is released when Ni^{4+} is reduced to Ni^{2+}, and the thermal runaway may be caused by the reaction of oxygen and flammable electrolyte [57,58]. As a Ni-rich cathode, NCA battery has higher specific energy than NMC-111 battery but lower thermal stability [59].

A typical LFP battery reaches its maximum capacity in a temperature range of 20 °C–30 °C and the capacity decreases to 95% when the temperature reduces from 20 °C to 10 °C [60]. The discharge capacity measured at −10 °C shows that 25.8% loss after 600 cycles but 1.9% gain after 300 cycles from the initial capacity [61]. When the temperature reaches 45 °C, the capacity decreases to 92.7% after 300 cycles and decreases to 85.7% after 600 cycles [61]. When the temperature reaches to 60 °C, 37% of the initial capacity loss after 100 cycles and 45% of initial capacity loss after 110 cycles [62]. The thermal runaway occurs at 260 °C [63] and the thermal runaway occurs at 140 °C for an overcharged LFP battery [56]. The amount of gas is released of a LFP battery at thermal runaway temperature is 61mmol, which is much less than NCA battery [56].

The capacity of a typical LTO battery decreases to 91.3% after 280 cycles (0.25% capacity loss per cycle) at 60 °C, the thermal runaway occurs when the temperature exceeds 260 °C [64]. The research [47] shows that graphite anode produces large amount of C_2H_6 and C_2H_4 at 100 °C, but there is no generation of gaseous decomposition products of LTO anode.

Therefore, the thermal stability and safety level of these five types lithium-ion batteries can be summarised in Table 3.

Table 3. Comparisons of thermal stability and safety level

Type of Lithium-ion battery	Thermal stability	Safety level
$LiMn_2O_4$	Low	Moderate
$LiNiMnCoO_2$	Moderate	Moderate
$LiNiCoAlO_2$	Low	Low
$LiFePO_4$	High	High
$Li_4Ti_5O_{12}$	Very high	Very high

3 Applications

All of these five types of lithium-ion battery have been widely adopted in EVs due to their own specific advantages. The application examples of these five types of lithium-ion battery in EVs are provided in Table 4 based on the information available in the public domain.

Table 4. The applications of various lithium-ion batteries in EVs.

Product model	Battery type	Battery weight (kg)	Nominal driving distance (km)	Top speed (km/h)	Charge time (h)	Release year
Nissan leaf	LMO (with LiNiO2)	294	117–200	150	0.5–20	2010
BMW i3	NMC	230	130–160	150	0.5–9	2013
Tesla model S	NCA	535–556	370–426	193–214	0.5–1.25	2012
BYD e6	LFP	500	330	140	2–10	2010
citron C-zero	LTO	165	127	130	0.25–6	2010

Apart from the electrochemical performance of the batteries, cost and market trend are another two important factors which determine the battery application capability in EVs. In this section, the application capability of these five types of lithium-ion battery are reviewed and compared from the aspects of cost and market trend.

3.1 Cost

The cost of a lithium-ion battery contains the following components: materials of cathode and anode, electrolyte, separator, assembly of cell and module, labour, etc. [65]. Due to the different raw materials adopted and the manufacturing processes, the cost of the mentioned five types of Li-ion battery are also different. Table 5 compares the key properties and cost of the several popular types of lithium-ion used in EVs. [65–68].

Due to the high cost of Co and Ti raw materials and the complex process of manufacturing, the cost of NMC, NCA and LTO batteries are much higher than LMO and LFP batteries. It also should be noted that when LTO is selected as the anode material, the cathode material may be chosen from NMC or NCA, the cost of NMC/LTO or NCA/LTO battery will be much higher. Even though the cost of LTO battery is high, the battery replacement frequency can be reduced for the EVs which require to be recharged often. In contrast, although LMO

Table 5. The key properties and cost comparison of the lithium-ion batteries

Battery type	Energy density	Life span	Cost
LMO	Medium	Low	Low
NMC	High	High	High
NCA	High	Medium	High
LFP	Low	High	Low
LTO	Very low	Very high	Very high

battery has a lower cost, the drawback of poor cyclability and thermal stability, the total operation cost may increase for the EVs to be recharged frequently. Sometimes LMO battery and NMC battery are combined to power an EV in order to enhance the performance and also decreases the battery cost. LMO can be used to improve the acceleration performance with the benefit of high current boost, and the NMC brings good cyclability and thermal stability to the entire power system. LTO battery is generally applied to the price-insensitive and low energy requirement vehicles. Due to the properties of high safety, long life and fast-charge, LTO batteries are favoured by electric buses.

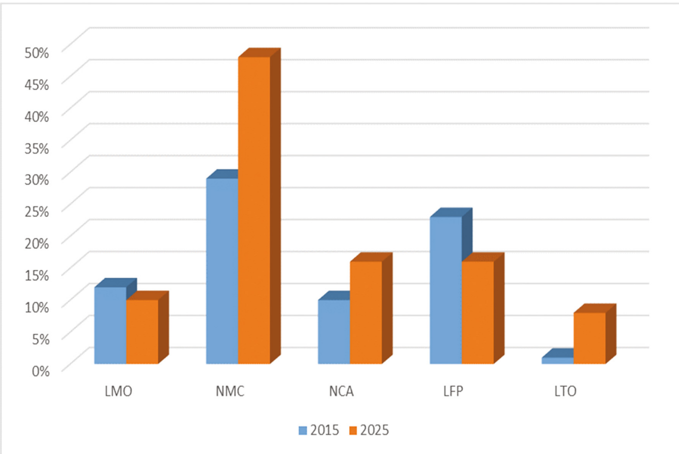

Fig. 1. The market share of different lithium-ion batteries in 2015 and 2025

3.2 Market Trend

According to the estimation results in [69], the market share of NMC, NCA and LTO batteries in 2025 will increase substantially, the expected market growth (from 2015 to 2025) are 4.8 times, 2.9 times and 26.7 times respectively [70].

Figure 1 summarises the market share of lithium-ion battery in 2015 and 2025 respectively [70]. It indicates that NMC, NCA and LTO batteries have a huge potential market in the next few years. Moreover, although the market share of LFP and LMO may decrease, the total market volume is showing a climbing trend [70].

4 Conclusion

$LiMn_2O_4$, $LiNiMnCoO_2$, $LiNiCoAlO_2$, $LiFePO_4$ and $Li_4Ti_5O_{12}$ batteries have been adopted in EVs successfully with their specific features. $LiMn_2O_4$ battery has low resistance due to the spinel structure, this allows $LiMn_2O_4$ battery to offer an excellent performance at high current rate in applications. The extremely low cost makes it highly favoured by the market. Poor performance at high temperature and limited cyclability are the downsides. $LiNiMnCoO_2$ battery has a satisfactory overall performance especially for the high specific energy. A variety of derivatives of $LiNiMnCoO_2$ enable this type lithium-ion battery to face different applications. The extremely high specific energy and moderate life span allows $LiNiCoAlO_2$ to be a good candidate for EVs. High cost and low level of safety are the negatives. The key benefits of $LiFePO_4$ battery are the long life span and low cost. It has good thermal stability when it operates at high temperature but the capacity is greatly attenuated at low temperature. Low specific energy and elevated self-discharge are the main disadvantages. $Li_4Ti_5O_{12}$ battery has the best thermal stability, cyclability and safety performance among these five lithium-ion batteries. No lithium plating at high current rate supports $Li_4Ti_5O_{12}$ battery for fast charging. However, the low specific energy and extremely high cost are the major disadvantages.

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