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An Overview of Lithium-Ion Battery Cathode Materials

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ABSTRACT

The need for the 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. In this work, we provide an overview of commercially available cathode materials for Li-ion rechargeable batteries and focus on characteristics that give rise to optimal energy storage systems for future transportation modes. The study shows that the development of lithium-iron-phosphate ($LiFePO_4$) batteries promises an alternative to conventional lithium-ion batteries, with their potential for high energy capacity and power density, improved safety, and reduced cost. This work contributes to the fundamental knowledge of lithium-ion battery cathode materials and helps with the design of better rechargeable batteries, and thus leads to economic and environmental benefits.

INTRODUCTION

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 mature, researchers started looking for alternative energy sources such as batteries due to the shortage of petroleum and because burning fossil fuels has 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.

THE PROSPECTIVE CATHODE MATERIALS

Among the rechargeable batteries, Li-ion batteries have dominated the field of advanced power sources due to their high gravimetric and volumetric energy densities [6]. 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: $LiCoO_2$, $LiMn_2O_4$, $LiNiO_2$, and $LiFePO_4$. $LiCoO_2$ is the most commonly used in portable electronic devices due to its excellent charging/discharging rate and power/energy density [7]. However, a battery with $LiCoO_2$ as its cathode material does not have good thermal stability [8]. Moreover, Co is toxic and expensive, which makes $LiCoO_2$ an imperfect choice for a cathode material for electric vehicles (EVs), hybrid electric vehicles (HEVs), and plug-in hybrid electric vehicles (PHEVs). $LiMn_2O_4$ is able to provide higher voltage, but it does not have a good power/energy density [9]. Its relatively short cycle life and high capacity loss [10] indicate that it is not an ideal cathode material for Li-ion batteries for EV/HEV/PHEV applications. The $LiNiO_2$ material, with the same structure as $LiCoO_2$, provides good power and energy densities [11]. However, since it is very difficult to prepare pure $LiNiO_2$ composite, Co-doped $LiNiO_2$, $Li_{1-x}(Ni_{0.8}Co_{0.2})_{1+x}O$, is usually considered as an alternative material in research and applications [12]. With the demand for Li-ion batteries increasing worldwide, a new Li-ion battery cathode material, $LiFePO_4$, was developed by Goodenough in 1996 [13]. He and his group discovered that $LiFePO_4$ is a good candidate for a cathode material due to its low price and high thermal stability. However, $LiFePO_4$ suffers from low intrinsic electronic conductivity (10^{-10}–10^{-9} Scm^{-1}) [14-18] and many efforts have contributed toward improving this material property. For example, Chung and Chiang desmonstrated that the low electronic conductivity of $LiFePO_4$ could be significantly enhanced by doping other metal elements such as zirconium, niobium, and magnesium [20]; the low-level doping with these aliovalent ions was attempted to achieve the better electronic conductivity and it was increased by a factor of $\sim 10^8$ [20]. In addition, several studies focused on examining the phase change of $LiFePO_4$ [19]. It is observed that factors like temperature particle sizes, and non-equilibrium state under the over-potential could also influence $LiFePO_4$ kinetics. Moreover, Malik et al. [21] have reported that an alternative single-phase transformation path exhibited in $LiFePO_4$ at low potential might be the key reason that LiFePo4 exhibit remarkable high-rate capability.

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 $LiFePO_4$ has the highest volumetric power density and energy density (1236 WL^{-1}, 970 WhL^{-1}, respectively) among the four mainstream cathode materials [22, 23] (Figure 1). $LiCoO_2$ has a volumetric power density of around 767 WL^{-1} and an energy density of around 483 WhL^{-1}. These values are roughly half that of $LiFePO_4$ [22, 23] (Figure 1). $LiMn_2O_4$ has a volumetric power density and energy density (900 WL^{-1}, 785 WhL^{-1}) higher than those of $LiCoO_2$. However, $LiMn_2O_4$ has a slightly lower volumetric power density and energy density than that of $LiFePO_4$ [22, 23] (Figure 1). The volumetric power and energy density data of $LiNiO_2$ were not available since pure $LiNiO_2$ 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 WL^{-1} and the volumetric energy density should at least be 300 WhL^{-1} [24]. Considering batteries as a whole (including cathode, anode, and electrolyte), current battery technologies, however, are only able to deliver 250-360 WhL^{-1} for $LiCoO_2$ batteries, 330 WhL^{-1} for $LiMn_2O_4$ batteries, 450 WhL^{-1} for $LiNiO_2$ batteries, and 220 WhL^{-1} for $LiFePO_4$ batteries. Therefore, the performance of advanced batteries still falls short of the EV goals set forth in 2006 by USABC [24].

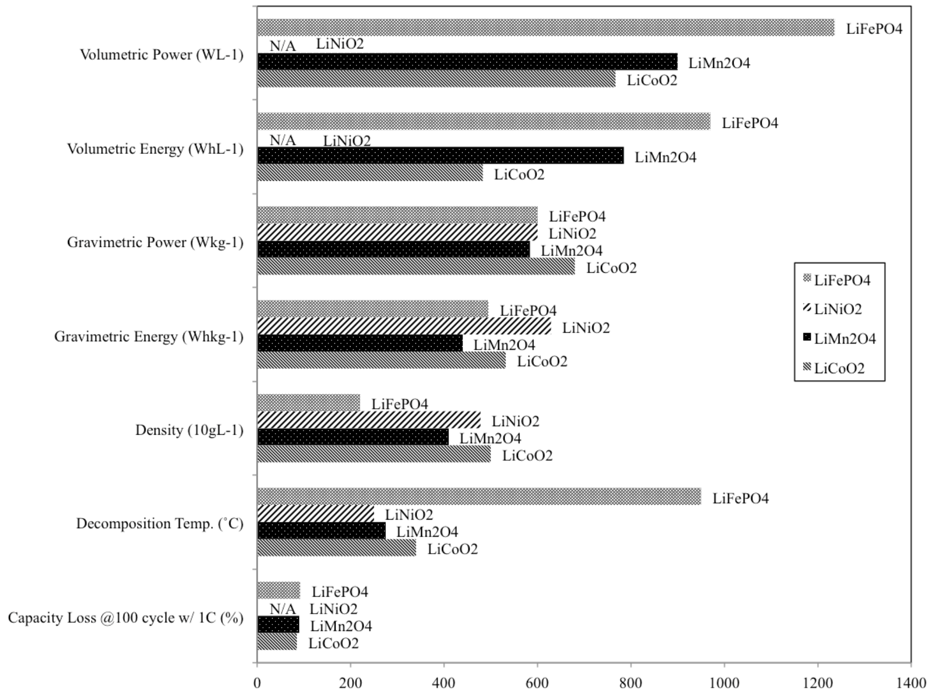

Figure 1. A comparison of $LiCoO_2$, $LiMn_2O_4$, $LiNiO_2$, and $LiFePO_4$ cathode materials by important properties (from rear to front): Volumetric power/energy density, gravimetric power/energy density, material density, decomposition temperature, and capacity retention after 100 cycles at 1C-rate.

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 [23, 25, 26]. It is observed that $LiNiO_2$ has high gravimetric power and energy densities of 600 Wkg^{-1} and 629 $Whkg^{-1}$, respectively (Figure 1). The gravimetric power density of $LiFePO_4$ is reported around 600 Wkg^{-1} whereas its gravimetric energy density (495 $Whkg^{-1}$) is lower than that of $LiNiO_2$. $LiCoO_2$ has a gravimetric power density of around 680 Wkg^{-1} and an energy density of around 532 $Whkg^{-1}$. These values are slightly higher than that of $LiFePO_4$ [23, 25, 26] (Figure 1). Finally, $LiMn_2O_4$ has a gravimetric power density of around 584 Wkg^{-1} and an energy density of around 440 $Whkg^{-1}$. These values are comparable to that of $LiFePO_4$ [23, 25, 26] (Figure 1).

The density of each cathode material was also listed in Figure 1. $LiFePO_4$ has the lowest density (2.2 kgL^{-1}) and $LiCoO_2$ has the highest (5 kgL^{-1}), which is more than twice of that of $LiFePO_4$. 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^{-1} and the gravimetric energy density should at least be 200 $Whkg^{-1}$ [24]. However, considering batteries as a whole (including cathode, anode, and electrolyte), current battery technologies are only able to deliver 106-250 $Whkg^{-1}$ for $LiCoO_2$ batteries, 100 $Whkg^{-1}$ for $LiMn_2O_4$ batteries, 192 $Whkg^{-1}$ for $LiNiO_2$ batteries, and 90-110 $Whkg^{-1}$ for $LiFePO_4$ batteries. Therefore, the performance of advanced batteries falls short of EV goals set forth in 2006 by the USABC [24].

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 [27]. 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. [28] collected the thermal activity and predicted the resultant thermal stability for different cathode materials. They observed that $LiFePO_4$ has the lowest exothermic peak temperature (289^oC) and exhibited endothermic heat flow (-6 Wg^{-1}). That is, during electrochemical reactions, $LiFePO_4$ will see smaller temperature increases than with the other three cathode materials. Moreover, it is observed that $LiMn_2O_4$ has an exothermic peak at 302^oC, which can easily be reached during a car accident. $LiCoO_2$ and $LiNiO_2$ also release heat and cause overheating or even explosion at higher temperatures of around 300-400^oC, suggesting that $LiCoO_2$ and $LiNiO_2$ as cathode materials are an undesirable choice for energy storage systems for EV/HEV/PHEV applications. In contrast, the electrochemical reaction of $LiFePO_4$ is endothermic, suggesting that $LiFePO_4$ 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 $LiFePO_4$ (950^oC) has much higher thermal stability than any other material (Figure 1). The decomposition temperatures for $LiCoO_2$, $LiMn_2O_4$, and $LiNiO_2$ are 340^oC, 275^oC, and 250^oC, respectively (Figure 1) [28].

In addition to the safety issue, we also compared the cost of cathode materials and environmentally-related factors. We note that Co is toxic and Ni has the potential to cause heavy metal pollution. $LiFePO_4$ 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 $LiCoO_2$ since the transition metal storage of $LiCoO_2$ is approximately 8.3 million tons (0.005% of $LiFePO_4$). The transition metal storage of $LiMn_2O_4$ and $LiNiO_2$ are 99.7 million and 48 billion tons, respectively. It is suggested that $LiFePO_4$ as a cathode material for rechargeable batteries is more environmental friendly and cost effective than the other three cathode materials.

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, $LiFePO_4$ processes 92% capacity retention, $LiMn_2O_4$ processes 90% and $LiCoO_2$ processes 85% capacity retention, respectively [29] (Figure 1). By extrapolation, if the capacity retention is measured under a higher rate (n>1), $LiFePO_4$ has a better capability to maintain rate-capacity than that of other cathode materials. Since the preparation and synthetic methods for $LiNiO_2$ are extremely difficult, its capacity retention data is unavailable. Nevertheless, the rate-capacity loss of $LiFePO_4$ is reported after thousand-cycles high-rate discharging [30, 31]. It is observed that under a high discharge rate, the capacity retention rate of $LiFePO_4$ batteries is not as good as that of other batteries.

CONCLUSIONS

This study provides an overview of four mainstream lithium-ion battery cathode materials. Characteristics of $LiCoO_2$, $LiMn_2O_4$, $LiNiO_2$, and $LiFePO_4$ 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. In conclusion, 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.

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