

Review

Lithium manganese spinel materials for high-rate electrochemical applications

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Abstract

In order to successively compete with supercapacitors, an ability of fast discharge is a must for lithium-ion batteries. From this point of view, stoichiometric and substituted lithium manganese spinels as cathode materials are one of the most prospective candidates, especially in their nanosized form. In this article, an overview of the most recent data regarding physico-chemical and electrochemical properties of lithium manganese spinels, especially, LiMn_2O_4 and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, synthesized by means of various methods is presented, with special emphasis of their use in high-rate electrochemical applications. In particular, specific capacities and rate capabilities of spinel materials are analyzed. It is suggested that reduced specific capacity is determined primarily by the aggregation of material particles, whereas good high-rate capability is governed not only by the size of crystallites but also by the perfectness of crystals. The most technologically advantageous solutions are described, existing gaps in the knowledge of spinel materials are outlined, and the ways of their filling are suggested, in a hope to be helpful in keeping lithium batteries afloat in the struggle for a worthy place among electrochemical energy systems of the 21st century.

Key words

lithium-ion batteries; high-rate applications; cathode materials; spinels



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1. Introduction

According to the forecasts of analytics, the world market is approaching a moment when the prices for electricity produced by lead acid or nickel metal hydride batteries and their rivals, lithium-ion batteries, will become equal [1]. Such an achievement is driven by accelerating demand from the electric and hybrid automobile market arisen from depletion of fossil fuel and turning scientists and engineers to the search of new, non-traditional sources of renewable energy manufactured and stored in a safe and viable fashion. Furthermore, clean energy generated by lithium-ion batteries is of indispensable value for solving the problem of green-house gases, which is increasingly evident in climate change. The latest

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reports anticipate global lithium-ion battery market revenue to surge from \$19.9 billion in 2012 to \$60.5 billion by 2020, with batteries fabricated specifically for electric vehicles and plug-in hybrid electric vehicles accounting for 73% of the total [2]. At the same time, the cost for lithium-ion batteries is predicted to decrease by more than 30 percent, and lithium-ion will emerge as the world's leading rechargeable battery technology. Currently, apart from automotive and energy storage applications, this kind of batteries is almost exclusively used in mobile phones and laptops, home appliances, power tools, etc. Advances in this technology are extensively reviewed, to mention just a few of the most cited ones, see Refs. [3–7].

Like any other battery, the lithium-ion battery consists of a negative electrode (anode), a positive electrode (cathode) and an electrolyte. Both electrodes are able to insert/deinsert lithium ions. During electrochemical reaction, the negative electrode is oxidized, supplying electrons to the circuit and deinserting lithium ions. Passing through the electrolyte, which is the solution of a lithium salt in an organic solvent, these ions insert into the positive electrode. The charge balance is kept by the reduction of the positive electrode by electrons from the circuit. As lithium is the lightest metal, lithium-ion batteries can store more than twice the energy of other cells of the same mass and size.

The main parameters of the lithium-ion batteries are their open-circuit voltage, specific capacity, gravimetric (or volumetric) energy density, and specific rate (power density). The open-circuit voltage V_0 is determined by the Nernst equation, but due to limitations caused by sometimes unknown values of standard electrode potentials in non-aqueous media and thermodynamic properties of electrode materials it is usually a measured quantity. The specific capacity (the quantity of electricity stored) is determined in $\text{mAh}\cdot\text{g}^{-1}$ ($1 \text{ Ah} = 3600 \text{ C}$) by Faraday law as

$$Q = nF/3.6M \quad (1)$$

where n is the number of moles of lithium ions (or electrons) involved in the electrochemical process, $F = 96500 \text{ C}\cdot\text{mol}^{-1}$ is the Faraday constant, and M is the molecular mass of the electrode material. The gravimetric energy density is determined in $\text{Wh}\cdot\text{kg}^{-1}$ ($1 \text{ Wh}\cdot\text{kg}^{-1} = 3600 \text{ J}\cdot\text{kg}^{-1}$) as

$$E = V_0Q \quad (2)$$

If V_0 , Q , and E are determined by thermodynamics and electricity laws, the power density P is governed by kinetics, namely, by the diffusion of lithium ions into (and within) the grains of electrode material, and is a measured quantity. It is determined in $\text{W}\cdot\text{kg}^{-1}$ and defined as the gravimetric energy density divided by the discharge time t ,

$$P = E/t \quad (3)$$

It is accustomed to characterize the power density in the specific current rate units C (not to be confused with coulombs mentioned in the definitions of Q and F), $[C] = \text{A}\cdot\text{kg}^{-1}$. 1 C is a number which indicates the amount of current when the specific capacity Q of a cell is discharged in one hour, and x C is the amount of current that discharges Q in $1/x$ h. For one

and the same cell the C units are proportional to the power density if the rated voltages upon different current loads are considered the same.

Plotting energy densities vs. power densities in bi-logarithmic coordinates obtains the so-called Ragone plot, which demonstrates that lithium-ion batteries offer better properties than lead acid or nickel metal hydride batteries (Figure 1). Clearly, high power densities are of great value in automotive applications enabling one to ensure the starting acceleration of a vehicle. However, another type of devices exists, viz., supercapacitors (shown in Ref. [10]), which offer greater discharge currents than batteries and are their natural competitors. Due to this fact, significant efforts have been undertaken towards improvements of high-rate performance of electrode materials for lithium-ion batteries.

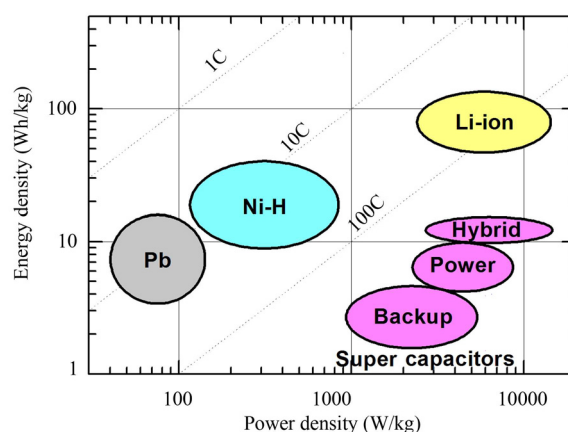


Figure 1. Performance comparison of lithium-ion batteries and their rivals. The data for lead-acid, nickel-hydride batteries, and supercapacitors from Ref. [8], and for lithium-ion batteries from Ref. [9]. Thin diagonal lines signify current rates

It has been already noticed that the power density is significantly governed by the diffusion of lithium ions into (and within) the grains of electrode material. This circumstance has been especially stressed in Ref. [4]. Subdivision leads to great increasing in the area of contact between electrode and electrolyte and decreasing of distances passed by electrons and lithium ions upon diffusion in the electrode material. This means that obtaining electrode materials in a nanosized form may allow for attaining greater charge/discharge rates than in the case of the electrode materials of a large particle size. However, in spite of the exponential growth of the number of followers of this idea (Figure 2a) the dependence of the power density on the particle size is convincingly justified for surprisingly few types of electrode materials, e.g., TiO_2 (shown in Refs. [11,12] and references therein) and MnO_2 [13].

The number of electrode materials employed in commercialized lithium-ion batteries is quite limited (Table 1). Since the time when Sony released the first commercial lithium-ion battery in 1991, LiCoO_2 remains the most popular cathode material. It offers quite high energy density, but presents safety risks due to high toxicity of cobalt compounds.

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