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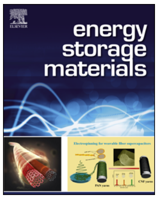

All solid-state polymer electrolytes for high-performance lithium ion batteries

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ABSTRACT

All solid-state polymer electrolytes have been received a huge amount of attention in high-performance lithium ion batteries (LIBs) due to their unique characteristics, such as no leakage, low flammability, excellent processability, good flexibility, wide electrochemical stability window, high safety and superior thermal stability. In this review, we summarized a series of all solid-state polymer electrolytes based on modified poly (ethylene oxide), polycarbonate, polysiloxane, succinonitrile and organic-inorganic hybrid composite. The recent progress on all solid-state polymer electrolytes has been reviewed in term of their potential application in LIBs. It is expected that the high-performance solid-state polymer electrolytes can be used in portable electrochemical devices, electric vehicles and grid energy storage.

Contents

1. Introduction

With the rapid exhaustion of non-renewable fossil fuels and aggravation of environment problems, it will become a main direction to use a variety of alternative energy sources to replace gasoline for the automotive applications, especially for pure electric vehicles (EVs) and hybrid electric vehicles (HEVs) [1–3]. Requirements for LIBs technology with respect to battery-powered electric vehicle market is listed in Table 1. Noteworthy is that both energy density and specific power must be simultaneously attained for plug-in hybrid electric vehicles (PHEVs) [4]. Another issue is the cost, which will be reduced with the increase in production volume of electric vehicles.

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Table 1
Required performance and cost of batteries with respect to battery-powered electric vehicle applications [4].

	Year			
	2010	2015	2020	2030
Application	Advanced HEV	PHEV	Advanced PHEV	Pure EV
Performance	1	× 1.5	× 3	× 7
Energy density (Wh/kg)	70	100	200	700
Specific power (W/kg)	2000	2000	2500	1000
Cost ($/kWh)	1220	370	240	60

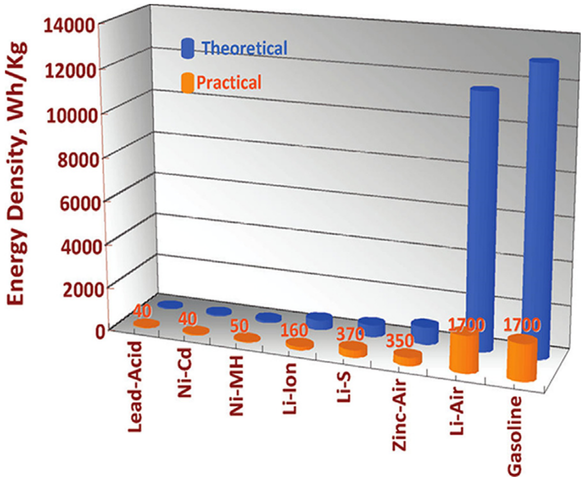

Fig. 1. The gravimetric energy densities (Wh/kg) for various types of rechargeable batteries compared to gasoline. The theoretical density is based strictly on thermodynamics and is shown as the blue bars while the practical achievable density is indicated by the orange bars and numerical values. For Li-air, the practical value is just an estimate. For gasoline, the practical value includes the average tank-to-wheel efficiency of cars [11]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The core technology of electric vehicles is the electrical power, whose propulsion based more intensively on secondary batteries with high energy density and power density [5]. The energy density of gasoline for automotive applications is approximately 1700 Wh/kg as shown in Fig. 1. In comparison to the gasoline, the mature, highly safe and reliable nickel-metal hydride batteries are unsatisfactory for electric vehicles applications due to their relatively low energy density [6]. LIBs are considered as the most probable candidates for large scale electrical power storage systems due to many advantages, such as the high specific energy density, high working voltage, low self-discharge rate, fast charge/discharge, long lifetime and no memory effect [7–9]. However, the energy density of current LIBs is typically between 100 and 200 Wh/kg, which limits the popularization of automotive applications [10,11]. With the acceleration of the automotive commercialization process, it is urgent to increase the energy density of LIBs up to 300 Wh/kg. In this regard, the metallic Li has to be used as anode due to the highest theoretical specific energy density (3860 mAh/g) among all anode materials for rechargeable lithium batteries [12,13]. The LIBs with high security, reliability, long lifetime and low cost are considered as the most promising energy storage systems in the field of portable electrochemical devices, electric vehicles market and grid energy storage [14–18].

Metallic Li anode in LIBs has been developed for a long time. However, due to the safety issue arising from Li dendrite growth in liquid organic electrolyte, the graphite successfully replaced metallic Li in commercial LIBs since 1991. Unfortunately, the low energy density of graphite anode has hindered the development of LIBs. Furthermore, the wide use of volatile and flammable liquid organic solvents as the electrolyte solution in currently commercial LIBs is prone to cause safety problems during cycling [19,20]. Moreover, it is difficult to effectively improve the energy density of LIBs by applying high voltage cathode materials due to the electrochemical instability of liquid organic electrolytes and separators at high voltage [21]. To safely utilize lithium metal in LIBs, the gel polymer electrolyte has been proposed. The gel polymer electrolyte is immobilized by a small amount of liquid organic solvents as plasticizers in a polymer network. However, the liquid components remain in the gel polymer electrolyte and it cannot fundamentally solve the safety issues of LIBs [22,23]. The all solid-state LIBs with much higher energy density than that of the currently available LIBs are the most promising battery systems. In solid-state LIBs, all solid-state electrolyte materials without any liquid components can act as both electrolyte and separator [24]. Basic requirements for the solid-state electrolyte are high Li^+ ion conductivity, suitable mechanical strength, and excellent interface stability with electrodes.

All solid-state electrolyte materials mainly include inorganic solid electrolytes (ISEs), solid polymer electrolytes (SPEs) and organic-inorganic hybrid composite electrolytes. The ISEs are classified into oxide-based, sulfide-based and etc. [25–27]. Since the lithium ion transference number of the ISEs is almost unity, the ionic conductivity is almost comparable to that of organic liquid electrolyte [28]. However, in spite of the presence of highly ion conductive ISEs, there are still many issues that limit the practical application at the present stage, like the large interface impedance between electrode and ISEs and the difficulty of processing [29].

SPEs have been paid much attention for promising materials in many electrochemical applications, especially polymer lithium batteries [30,31]. SPEs are formed by the polymer host as the solid matrix along with alkali metal salt in absence of the addition of organic liquid solvents [32]. SPEs offer outstanding advantages over conventional liquid electrolytes including no leakage of electrolytes, low flammability, good flexibility, safety and stable contact between the electrode and electrolyte [31,33]. More importantly, SPEs possess excellent processability and flexibility as compared to ISEs [34,35]. These properties make SPEs have strong adhesive function on the surface of electrodes and thus decrease the interface impedance between electrolytes and electrodes. The comprehensive requirements for SPEs used in lithium battery includes high mechanical strength, excellent flame retardancy, superior thermal stability, high ionic conductivity at ambient temperature, and wide electrochemical window [36–39]. The minimum requirements on each property of all solid-state polymer electrolyte are summarized in Table 2. Suitable SPEs are mainly aimed in the development of high safety, high energy and power density rechargeable batteries, which can be used in miniature electronic devices, energy conversion units, supercapacitors, electric vehicles and etc. [38,40]. Recently, several types of SPEs have been developed and characterized, such as poly (ethylene oxide) (PEO), polycarbonate, polysiloxane, and plastic crystal.

In addition, the organic-inorganic hybrid composite electrolytes are formed by high surface area inorganic fills in proportion with polymer system [41–43]. Due to the synergistic effect of

Table 2
The minimum requirements for all solid-state polymer electrolytes in LIBs.

Parameter	Requirement
Li^+ ion conductivity	$\geq 10^{-5}$ S/cm at 25 °C
Stable potential window	≥ 4.0 V vs. Li^+/Li
Mechanical property	≥ 30 MPa
Thermal stability	> 150 °C
Limit oxygen index (LOI)	$> 27\%$