Journal of Power Sources 389 (2018) 120–134

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Challenges and perspectives of garnet solid electrolytes for all solid-state lithium batteries

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HIGHLIGHTS

- Main issues of LLZO-based solid electrolytes are comprehensively discussed.
- Advanced synthesis methods of LLZO are summarized.
- Strategies developed to improve the ionic conductivity of LLZO are covered.
- Interface properties between LLZO and electrodes are reviewed.
- Solid-state batteries based on LLZO are highlighted.

ARTICLE INFO

Keywords:
$Li_7La_3Zr_2O_{12}$
Garnet solid electrolyte
Solid-state lithium battery
Ionic conductivity
Interfacial property

ABSTRACT

Garnet $Li_7La_3Zr_2O_{12}$ (LLZO) solid electrolytes recently have attracted tremendous interest as they have the potential to enable all solid-state lithium batteries (ASSLBs) owing to high ionic conductivity (10^{-3} to 10^{-4} S cm^{-1}), negligible electronic transport, wide potential window (up to 9 V), and good chemical stability. Here we present the key issues and challenges of LLZO in the aspects of ion conduction property, interfacial compatibility, and stability in air. First, different preparation methods of LLZO are reviewed. Then, recent progress about the improvement of ionic conductivity and interfacial property between LLZO and electrodes are presented. Finally, we list some emerging LLZO-based solid-state batteries and provide perspectives for further research. The aim of this review is to summarize the up-to-date developments of LLZO and lead the direction for future development which could enable LLZO-based ASSLBs.

1. Introduction

With the rapid development of portable electronics, electric vehicles and grid energy storage, lithium-ion batteries (LIBs) with high energy densities have become the dominant power supplies [1–5]. Organic electrolytes are used in most commercial LIBs. The high ionic conductivity (up to 10^{-2} S cm^{-1}) [6] in a liquid medium ensures rapid ion movements, good battery performance, and decent rate performance. However, current LIBs are suffering from safety problems due to the inherent flammability and easy leakage of liquid electrolytes. In addition, the limited energy and power densities (theoretical specific energy: ~390 Wh kg^{-1} [7]) are also obstacles for widespread adoption in electric vehicles (Fig. 1a).

To advance LIBs to the next generation, many efforts are focused on Li metal as anode because of its high theoretical specific capacity of 3860 mAh g^{-1} and the lowest electrochemical potential of −3.04 V vs. SHE [8–22]. However, critical issues still exist for Li metal anode in organic electrolytes. First, the formed solid electrolyte interphase (SEI) on Li metal is unstable due to the intrinsic high-reactivity of Li metal with organic electrolytes, resulting in decline of capacity and low Coulombic efficiency. Second, almost infinite volume change occurs during charge/discharge cycles, which is more severe than that of

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https://doi.org/10.1016/j.jpowsour.2018.04.019
Received 31 January 2018; Received in revised form 31 March 2018; Accepted 5 April 2018

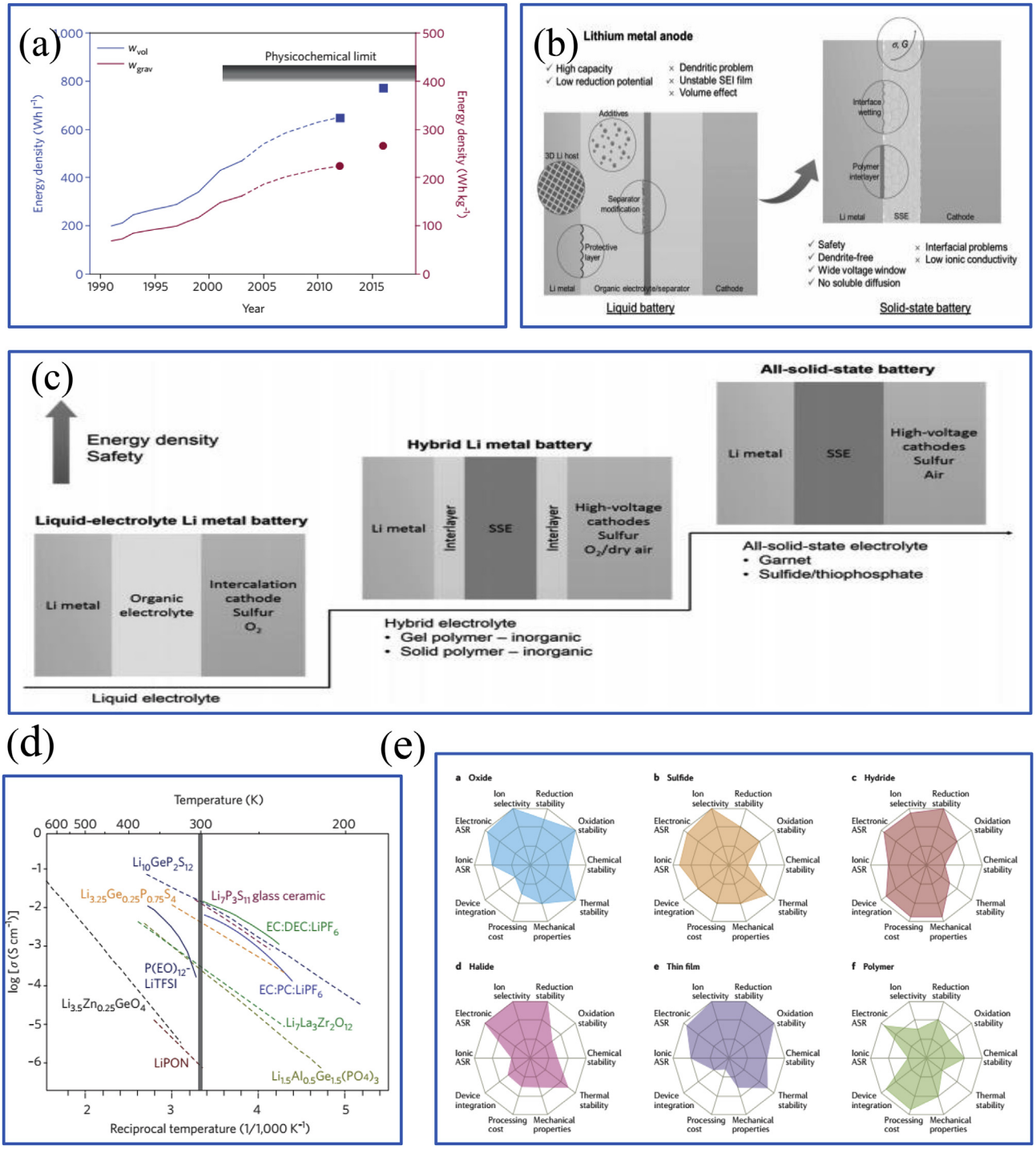

Fig. 1. (a) Energy densities of the standard cylindrical 18650 LIB cells (with a volume of approximately 16 cm^3 and a mass of 48 g) over the past 25 years. Reproduced with permission [7]. Copyright 2016, Springe Nature. (b) Advantages, existing problems and schematic of recent solutions for the Li-metal anode in organic liquid electrolytes (left). Advantages, problems, and current strategies to address the problems of Li-metal anode using solid electrolytes (right); (c) Development of Li-metal batteries from the liquid electrolyte battery to the polymer–inorganic hybrid battery, and finally all-solid-state battery. Reproduced with permission [24]. Copyright 2017, John Wiley and Sons. (d) Ionic conductivities of solid electrolytes are shown in comparison to those of liquid electrolytes and polymers. Reproduced with permission [7]. Copyright 2016, Springe Nature. (e) Performance of different solid electrolyte materials. Radar plots of the performance properties of oxide solid electrolytes (panel a), sulfide solid electrolytes (panel b), hydride solid electrolytes (panel c), halide solid electrolytes (panel d), thin-film electrolytes (panel e) and polymer solid electrolytes (panel f). ASR, area-specific resistance. Reproduced with permission [32]. Copyright 2017, Springer Nature.

silicon anode (300–400% volume change) [23]. Third, uneven deposition of Li metal can result in dendrite formation which can penetrate separators and short batteries. Moreover, “dead Li” (Li dendrites wrapped by the reaction products of SEI films and out of accessibility to current collectors and electrons, converting Li dendrites to electrochemically inert dead Li) [23] would form upon cycling, which results in loss of active material and increasing impedance. Although some strategies have been developed to solve these issues, the instability nature of Li metal in liquid electrolytes still exists (Fig. 1b) [24].