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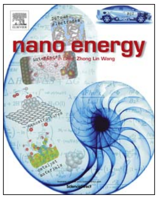

Review

Recent advances in all-solid-state rechargeable lithium batteries

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ABSTRACT

The all-solid-state lithium batteries using solid electrolytes are considered to be the new generation of devices for energy storage. Recent advances in this kind of rechargeable batteries have brought them much closer to a commercial reality. However, several challenges such as insufficient room temperature ionic conductivity (10^{-5}~10^{-3} S cm^{-1}) when compared to those of conventional organic liquid electrolytes (10^{-2} S cm^{-1}), the difficulty in informing an effective electrode-electrolyte interface and insufficient fundamental understanding of the interfacial process after charge/discharge, hindering the reality of such devices. To accelerate the research and development, the overall picture about the current state of all solid-state lithium batteries was reviewed in this article with major focus on the material aspects, including inorganic ceramic and organic solid polymer electrolyte materials. In particular, the importance of the electrolytes and their associated interfaces with electrodes as well as their effects on the battery performance are emphasized by in-depth discussion and data analysis. To overcome the challenges, several possible research directions are also suggested for facilitating further improvement on the battery performance.

1. Introduction

Chemical batteries have played important roles in energy storage and conversion [1,2]. Among currently available battery technologies, lithium-based batteries, such as Li-ion batteries (LIBs), are considered the most promising ones due to their relatively higher energy density [1,3]. Normally, the conventional Li batteries use organic liquid electrolytes, which have relatively low ionic resistance, leading to some drawbacks such as safety issue, insufficient lifetime, high cost, and low power density. However, all-solid-state Li batteries with nonflammable solid electrolytes can avoid some of the issues, in particular, the safety one. Relatively speaking, when compared to liquid-electrolyte Li batteries, all-solid-state ones are believed to be safer, and to have longer cycle life, higher energy density, less requirements on packaging and state-of-charge monitoring circuits [4]. With respect to this, there is a growing interest in all-solid-state batteries. However, inferior cycle performance induced by the continuous development of interfacial resistance layer between cathode and electrolyte materials is one of the major drawbacks that needs to be overcome for the successful commercialization of secondary Li batteries [5,6]. It is expected that all-solid-state batteries should be used widely in large electrical power storage systems such as electrical vehicles as well as electronic devices due to their high energy density and safety. Thus, there are intensive researches on Li-ion-conducting inorganic materials used as solid-state electrolyte for all-solid-state Li batteries in recent years.

In the most recent years, a significant progress has been made for all-solid-state Li batteries by experimentally developing and optimizing solid electrolytes. Moreover, an in-depth fundamental understanding of the potential profile and its distribution across the electrode/electrolyte interface has gained by employing advanced characterization approaches [7]. Regarding commercialization efforts, some companies have been devoted to promote the application of all-solid-state Li batteries in electronic devices and electric vehicles, including Toyota, Solid Energy, Infinite Power Solution, Seeo, Sakti3, Front Edge Technology Inc., Quantum Scape, Bolloré, etc. Overall, in this review we describe the advances in all-solid-state Li batteries and the remaining challenges, and also propose several possible research directions for circumventing the challenges.

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2. Fundamentals of solid electrolytes in all-solid-state Li batteries

2.1. Theory of Li-ion conduction in solid-state electrolytes

Defects widely exist in real crystals, and they play an important role in the properties of solids. Point defects are atomic defects whose effects are limited only to their immediate surroundings [8]. Examples are ionic vacancies in the regular crystal lattice, or interstitial atoms or ions. Ionic conduction in ceramics can be induced by either mobile cations or anions. Ionic conduction can be derived from the motion of vacancies or interstitial ions. These point defects can be intrinsic and stoichiometric defects, such as Frenkel defects (the defects are vacancies accompanied by an interstitial ion), and Schottky defects (the defects are anion vacancies accompanied by a cation vacancy) [9]. A transition-metal cation can have a mixed valence state and thus the intrinsic defects are not necessarily limited to a stoichiometric composition in transition-metal oxides. Electroneutrality can be maintained by the oxidation or reduction of a cation [10]. The formation of intrinsic defects is driven by thermal energy, and the number of defects obeys an Arrhenius-type equation:

$$N_D = N\exp[-\frac{E_F}{2kT}] \tag{1}$$

where N_D is the number of defects, N is the number of ion pairs, E_F is the energy of formation, k is the Boltzmann constant and T is the temperature. The point defects can also be extrinsic, introduced by impurities or dopants substituted in the lattice.

The conductivity of a material with multiple conducting species is given by

$$\sigma = \sum n_j q_j \mu_j \tag{2}$$

Where σ_j is the total conductivity, n_j is the density, q_j is the charge and μ_j is the mobility of the conducting species.

The total conductivity of a mixed conducting material is the sum of the ionic and electric conductivities:

$$\sigma = \sigma_i + \sigma_e \tag{3}$$

The transference numbers are parameters defined to characterize the ionic and electronic contributions to the total conductivity:

$$t_i = \frac{\sigma_i}{\sigma} t_e = \frac{\sigma_e}{\sigma} \tag{4}$$

where t_i and t_e are ionic and electronic transference numbers, respectively. The sum of t_i and t_e is unity [8].

Ionic conduction also obeys an Arrhenius temperature dependence:

$$\sigma_i = \frac{A}{T}\exp\left[-\frac{E_a}{kT}\right] \tag{5}$$

The mobility of charge carrier is

$$\mu = \frac{qD}{kT} \tag{6}$$

where D is the diffusion coefficient [11]. The motion of a single particle jumping from an occupied site to an energetically equivalent unoccupied site may be described by a random-walk theory [12], and its diffusion coefficient is expressed as Eq. (7):

$$D = \left[\frac{z}{2d}\right] l^2(1-c)\upsilon_h \tag{7}$$

where d is 1, 2 or 3 for one-, two-, or three-dimensional motion, l is the jumping distance, c is the concentration of mobile ions, and z is the number of like nearest neighbors. The jump frequency (υ_h) is defined to be Eq. (8):

$$\upsilon_h = \nu_o \exp\left[\frac{-\Delta G_m}{kT}\right] \tag{8}$$

where ν_0 is the attempt frequency, and (ΔG_m) is the migrational free energy, which can be expressed as Eq. (9):

$$\Delta G_m = \Delta H_m - T\Delta S_m \tag{9}$$

Substitution of Eq. (6) into Eq. (2) yields the Nernest-Einstein relation [10]:

$$\sigma_i = \frac{N_c q^2 D}{kT} \tag{10}$$

where N_c is the number of mobile ions. It can be seen that the ionic conductivity is proportional to the N_c and D.

A comprehensive physical description of ion transport in polymer electrolytes is actually not easy because the systems are complex and the lack of simple structure-properties correlations. In this regard, the ionic conductivity of these systems is usually modeled by the Arrhenius or Vogel-Tammann-Fulcher (VTF) equations or both of them together [13–15].

As described, the VTF behavior seemed more suitable for the solid polymer electrolytes [13], which could be described by Eq. (11)

$$\sigma_i = \sigma_0 T^{-\frac{1}{2}}\exp\left[-\frac{B}{T-T_0}\right] \tag{11}$$

where B is the pseudo-activation energy of the conductivity (expressed in units of E_a/k), and T_0 is the reference temperature which normally falls 10–50 K below the experimental (kinetic) glass transition temperature, T_g. The VTF parameters can be obtained by fitting the conductivity data with the linear Eq. (12)

$$\log_{10}(\sigma T^{\frac{1}{2}}) = \log_{10}\sigma_0 - 0.43\frac{E_a}{k(T-T_0)} \tag{12}$$

The VTF equation could be derived by the quasi-thermodynamic models with free volume [16] and configurational entropy [17], and its behavior could be related to ion motion coupled with long range motions of the polymer segments.

As for the composite electrolyte materials consisting of a conducting and an insulating phase, its conductivity could be described by the effective media theories [18].

2.2. Structures and electrochemical processes of all-solid-state Li batteries

Fig. 1 is a schematic diagram showing the structure of an all-solid-state lithium battery, consisting of cathode, electrolyte, anode and current collectors. As identified, the electrolyte plays a critical role in the all-solid-state Li batteries. It functions as both an ionic conductor and separator. It can be seen that the electrodes are attached to both sides of the electrolyte. This structure is actually simpler than the conventional Li-ion batteries with liquid electrolytes. All-solid-state Li batteries need fewer requirements on packaging and thus may significantly reduce the fabrication cost. As for the working principle of an all-solid-state Li battery, it is similar to the Li-ion batteries with liquid electrolytes. During charging, Li-ions de-intercalate from the crystal lattice of the cathode and transfer to the anode via the ionic conductive

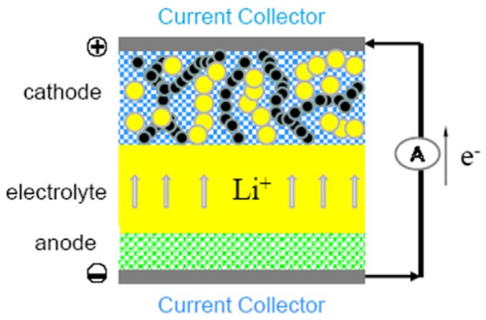

Fig. 1. Schematic illustration of an all-solid-state lithium battery based on Li-ion conduction.