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Screening polyethylene oxide-based composite polymer electrolytes via combining effective medium theory and Halpin-Tsai model

Yuanji Li [a,d], Yu Zhao [b], Yanhua Cui [b,*], Zheyi Zou [c], Da Wang [c,*], Siqi Shi [c,d]

[a] Qianweichang College, Shanghai University, Shanghai 200444, China
[b] Institute of Electronic Engineering, China Academy of Engineering Physics, Mianyang 621000, China
[c] School of Materials Science and Engineering, Shanghai University, Shanghai 200444, China
[d] Materials Genome Institute, Shanghai University, Shanghai 200444, China

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ABSTRACT

Polyethylene oxide (PEO) based materials are promising candidates for the matrices in composite solid polymer electrolytes (CSPEs) for high-energy density lithium ion batteries. Experimental screening of high-performance CSPEs with high efficiency still appears to be challenging for the moment, due to the complications of the compositions involved. Here, we propose and test the joint application of effective medium theory (EMT) and Halpin-Tsai model that can predict with satisfactory accuracy the effects of the filler volume fractions and of the particle sizes on the conductivities and Young's moduli of CSPEs. The application of this theoretical framework can be extended to other polymer based CSPEs and potentially enables us to build a CSPEs database for data mining to accelerate the screening process.

1. Introduction

Nowadays, there is an urgent need, driven by portable devices and electric vehicles, for developing more capacitive lithium ion batteries [1]. Besides anode and cathode materials, electrolytes are also of great importance in the operation of Li-ion batteries. Liquid electrolytes are extensively used in lithium ion batteries due to their high ionic conductivities. Nevertheless, safety problems such as leakage and corrosion have encumbered the improvement of commercial lithium ion batteries. In comparison, solid-state electrolytes have been proven to be reliable in safety [2]. It will be a giant technological leap once a solid-state electrolyte with a performance comparable to that of a typical liquid electrolyte is found. Hence, much attention has been paid to screening high-performance solid-state electrolytes these years. The fast ionic conduction of solid polymers, when combined with alkali metal salts, was first suggested by Wright [3]. Solid polymer electrolytes also show flexible structure without leaks and are available in different geometries [4]. In this way, their applications in batteries served for wearable smart textile are promising. Among the solid polymer electrolytes, polyethylene oxide (PEO) based electrolytes have been mostly studied because of their excellent solubility for lithium salts. Nonetheless, little progress has been made in the commercialization of lithium ion batteries containing PEO-based electrolytes due to their low ionic conductivities (usually $\sim 10^{-8}$ S cm^{-1} at room temperature) [5]. A variety of methods have been utilized to deal with this problem [6–8]. Inspired by Liang [9] who first added inert fillers into inorganic electrolytes in order to improve their ionic conductivities, Weston et al. [10,11] combined $(PEO)_8$-$LiClO_4$ with α-Al_2O_3. A large amounts of work has then focused on the effect of adding non-conducting oxides into polymer based electrolytes. Croce et al. [12] considered the incorporation of doped β^{Prime}-Al_2O_3 powders and $(PEO)_8$-NaI, which exhibits positive mechanical properties as well as ionic conductivities. Wieczorek et al. [13] mingled $(PEO)_{10}$-NaI with 10 vol.% θ-Al_2O_3 and 10 vol.% α-Al_2O_3 respectively and an increase of ionic conductivity exceeding 10^{-5} S cm^{-1} at room temperature (RT) was observed for both situations. In the case of $(PEO)_8$-$LiClO_4$ mixed with a stable ceramic material (γ-$LiAlO_2$), the ionic conductivity surpassing 10^{-6} S cm^{-1} was obtained at RT by Scrosati et al. [14]. Studies aimed at ameliorating the electrical properties of CSPEs for other systems are also available [15–24]. Therefore, combining inert oxide fillers with PEO-based electrolytes has been proved to be a feasible method of enhancing the ionic conductivities of CSPEs.

Although this has been an effective means, the test of a huge amount of materials and their combinations remains a formidable task. It will be more convenient and efficient if we can do a fast but

* Corresponding authors.
E-mail addresses: cuiyanhua@caep.cn (Y. Cui), wander0826@hotmail.com (D. Wang).

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reliable pre-screening of the candidate CSPEs by means of simple theories before they are synthesized and tested. It was reported that besides ionic conductivities, mechanical stability is also a significant aspect of a candidate CSPE, given the relatively poor mechanical properties of polymer materials [8,25,26]. For the simulation of ionic conductivity, the effective medium theory (EMT) has been widely used [27–35]. The mechanical stability can be roughly characterized by the Young's modulus of the material. Since the Halpin-Tsai model has been extensively employed to evaluate the Young's modulus of micro and nano composites in terms of simplicity and accuracy, it is considered to be suitable for predicting the Young's modulus of polymer composites [36–39].

In this paper, we propose the combined usage of EMT and Halpin-Tsai model to screen the composite solid polymer electrolytes according to their electrical and mechanical properties. Different from the materials scale of screening process introduced by Gao et al. [40], this method is specifically designed and tested for nano and micro-scaled particle sizes. We first use EMT to make predictions on the ionic conductivities of various types of PEO-LiX based electrolytes when different inorganic fillers are added and the size of their particles changed. The selected CSPEs are then tested via Halpin-Tsai model for their mechanical stability. If a material passes these two tests, one can consider it to be a promising candidate. Finally, we propose that this screening process can be accelerated via the combination of data mining and the mathematical assessment [41] and thus could even be automated in the near future.

2. Introduction of mathematical models

The EMT and Halpin-Tsai models are used for evaluating the ionic conductivities and Young's modulus of CSPEs, respectively. The similarity between them is that they can analyze the influence of grain volume fractions as well as particle size on the properties of CSPEs, which means that they share two identical parameters in the respective equation. In this section, we introduce the elementary idea of effective medium theory and Halpin-Tsai equations.

2.1. The development of EMT equation

2.1.1. The basic idea of EMT

The effective medium theory (EMT) has been successfully utilized to analyze the conductivity of composite materials which mainly serve as solid electrolytes in batteries for decades. Bruggeman first proposed the effective medium theory in 1935 [42] and then Landauer clarified the effective medium theory with an example in 1952 [43]. For the mixture including materials 1 and 2 in Fig. 1, the area, which surrounds the shaded region, is treated as a homogeneous medium with the conductivity equal to the one of mixtures (material 1 and material 2), namely the effective conductivity. Further mathematical explanation using Green function was provided by Nan in 1993 [44]. In this way, the original effective medium equation is given by Landauer as follows:

$$\frac{f_1(\sigma_1-\sigma^*)}{\sigma_1+2\sigma^*}+\frac{f_2(\sigma_2-\sigma^*)}{\sigma_2+2\sigma^*}=0 \tag{1}$$

where f_1 and f_2 are the fractions of total volume occupied by material 1 and 2; σ_1 and σ_2 are the conductivities of material 1 and 2; σ^* is the effective conductivity. The conductivity of the mixture can be obtained by solving this quadratic equation.

2.1.2. Improvement of EMT equation based on the percolation theory

In 1973, Kirkpatrick [45] improved the EMT Eq. (1) according to the percolation theory:

$$\frac{f_1(\sigma_1-\sigma^*)}{\sigma_1+(\frac{1}{f^*}-1)\sigma^*}+\frac{f_2(\sigma_2-\sigma^*)}{\sigma_2+(\frac{1}{f^*}-1)\sigma^*}=0 \tag{2}$$

where f^* is the percolation threshold and according to Sher-Zallen invariant proposed by Sher and Zallen [46], if the radii of the major phase and the minor phase grains are nearly equal, f^* tends to be in the region of 0.16.

2.1.3. Improvement of EMT equation by considering dipole–dipole interaction

In 1978, Granqvist and Hunderi [47] noticed that one of the weaknesses of the primary EMT equation is to neglect the situation where the volume fraction of either component in the mixture gradually increases and thus the simple EMT equation is not suitable for dealing with it because of the local-field effect. To cope with this problem, they introduced the effective depolarization factors L_i^* appropriate for each geometrical configuration.

$$\frac{f_1(\sigma_1-\sigma^*)}{\sigma^*+L_i^*(\sigma_1-\sigma^*)}+\frac{f_2(\sigma_2-\sigma^*)}{\sigma^*+L_i^*(\sigma_2-\sigma^*)}=0 \tag{3}$$

2.1.4. Improvement of EMT equation by meliorating σ_1 and σ_2

Nakamura [48] improved the EMT equation proposed by Kirkpatrick through replacing σ_1 and σ_2 with σ_1^a and σ_2^a according to the Maxwell-Garnett rule [49]. R is the radius of the filler particles.

$$\frac{f_1(\sigma_1^a-\sigma^*)}{\sigma_1^a+(\frac{1}{f^*}-1)\sigma^*}+\frac{f_2(\sigma_2^a-\sigma^*)}{\sigma_2^a+(\frac{1}{f^*}-1)\sigma^*}=0 \tag{4}$$

$$\sigma_1^a=\sigma_1+\frac{Rf_2\sigma_1(\sigma_2-\sigma_1)}{R\sigma_1+f_1(\sigma_2-\sigma_1)} \tag{5}$$

$$\sigma_2^a=\sigma_2+\frac{Rf_1\sigma_2(\sigma_1-\sigma_2)}{R\sigma_2+f_2(\sigma_1-\sigma_2)} \tag{6}$$

Based on the idea of Nakamura, Nan and Smith [50] improved the EMT equation by considering the system of three phases which consists of the matrix, the inserted grains and the highly conducting interface layer covered on the grain surface. Furthermore, by treating the last two phases as an integrity and employing Maxwell-Garnett mixture rule, the equivalent conductivity σ_c can be expressed as:

$$\sigma_c=\sigma_1\frac{2\sigma_1+\sigma_2+2K_1^3(\sigma_2-\sigma_1)}{2\sigma_1+\sigma_2-K_1^3(\sigma_2-\sigma_1)} \tag{7}$$

$$K_1=1/(1+2t/R) \tag{8}$$

where σ_1 and σ_2 are the conductivities of the interface layer and the inserted grains; t is the thickness of interface layer and R is the

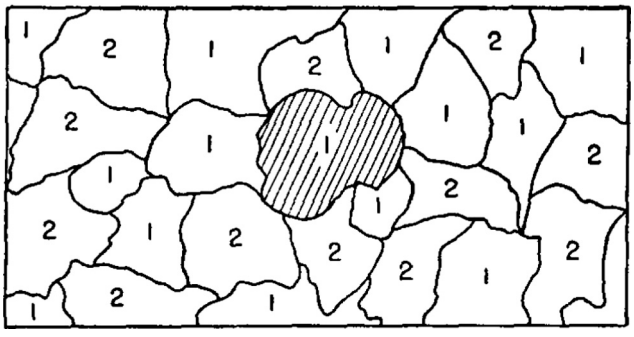

Fig. 1. The shaded area is surrounded by the mixture of material 1 and material 2.