Atomistic investigation of the nanoparticle size and shape effects on ionic conductivity of solid polymer electrolytes

CrossMark

Qin Li, Haleh Ardebili *

Mechanical Engineering Department, University of Houston, Houston, TX 77004, USA

ARTICLE INFO

ABSTRACT

Adding nanoparticle fillers is a potential route to enhance room temperature ionic conductivity of solid polymer electrolytes. In this work, we use molecular dynamics simulation to elucidate the role of nano-scale filler size and shape on ionic conductivity. Our key conclusions are that the addition of nanofillers can affect the salt dissociation, lithium-ion mobility, and the dynamics of polymer chains. The repulsive nanofillers of different sizes appear to suppress ion-cluster formation and enhance lithium ion mobility. Smaller size nanofillers are found to be comparatively more effective in increasing the mobility of lithium ions while shape effects appear to be insignificant.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Solid polymer electrolytes (SPEs) and polymer gel electrolytes (PGEs) have attracted intensive studies during the past decades due to their potential applications in various advanced devices including lithium ion batteries [1–3], supercapacitors [4], and stretchable actuators [5]. Compared to the traditional organic liquid electrolytes used in Li ion batteries, SPEs offer enhanced safety, stability and thin film manufacturability but their low ionic conductivity especially at room temperature has suppressed their development [6,7]. One effective method to improve the ionic conductivity introduced by Croce et al. [8] is adding nanosized fillers into SPE to form the polymer nanocomposite electrolyte (PNCE) which can produce up to three orders of magnitude enhancement. Beside the common spherical shape, nanofillers with other shapes like rod [9], sheet [10], and hybrid [11], have also been utilized to obtain higher ionic conductivities. The reasons for the nanofiller induced increase in the ionic conductivity of polymer electrolyte are still not fully understood. Ionic conductivity generally depends on the concentration and mobility of the conductive ions. Recent experiments have demonstrated that nanofillers can facilitate the Li salt dissociation [12–14] and therefore, increase Li ion concentration. Furthermore, experiments have shown that nanofillers disrupt the recrystallization of polymer matrix and consequently, increase the amorphous regions in the polymer matrix where the Li ion mobility is relatively higher [15,16]. However, at higher filler concentrations, adverse effects of nanofillers can dominate including aggregation, ion trapping, increased crystallinity, and constriction of polymer mobility [17–19] leading to the decline in ion conductivity.

Although a few studies have proposed models that provide interesting insights into the mechanisms of conductivity improvement in PNCEs [19,20], the effects of nanofiller's shape and size however remain unclear.

Molecular dynamics (MD) simulation is a powerful tool that can provide us insights at the molecular level on the phenomena of interest. MD simulations of polymer composites have traditionally focused on mechanical properties [21–27]. For example, some of the aforementioned works have shown that the nature of filler surface (attractive, repulsive or neutral) can play an important role in the composite mechanical properties. Also, the perturbed confinement of polymer chains near the solid surface has been investigated in the past. [28–30] Our interest is in the atomistic investigation of ionic conductivity in polymer electrolytes—which generally are comprised of the polymer host and the alkali metal salt. For example, Siqueira and Ribeiro performed united atom MD simulations of polyethylene oxide (PEO)/LiClO$_4$ system [31,32] to reveal the temperature and salt concentration effects on both static and dynamic properties. Other works have targeted the same system but focused on ion pairing and lithium ion hopping process [33,34]. PEO hosts doped with different salts have also been investigated [35–49]. MD simulations have also been used to analyze polymer nanocomposite electrolytes. These works concluded that incorporation of titania and alumina fillers did not show direct evidence of ionic conductivity enhancement. In fact, the dynamics of the PEO chains and the charge carriers were found to be slowed down by the nanofillers [50–54]. There are also other polymer-based electrolytes [55–61] like the polymer/ionic liquid mixture [59,60] and copolymer single ion conductor [61] that have been investigated by MD simulations.

In this work, we focus on using molecular dynamics simulation to understand the shape and size effects of nanofillers on the ionic conductivity of solid polymer electrolytes. Specifically, we consider PEO/LiClO$_4$ solid electrolyte with EO:Li ratio of 10:1, with and without TiO$_2$ nanofillers.

---

* Corresponding author.
    E-mail address: hardebil@central.uh.edu (H. Ardebili).

2. Simulation details

We created a relatively long PEO chain with 200 CH_2CH_2O repeat units capped by methyl groups in both ends. 200 $LiClO_4$ molecules are doped into 10 such PEO chains in the form of disassociated ions corresponding to the ratio between ether oxygen (EO) atoms and lithium ions (EO:Li) at 10:1. All atoms were wrapped into a periodic simulation cell with the side length of about 50 Å. That was the case without nanofiller denoted by PEL. Based on the PEL case, we made a void in the center of the simulation box by pushing PEO and $LiClO_4$ atoms in the central region away and placed the TiO_2 nanofiller inside to form our desired nanocomposite. The position of the nanofiller was fixed during the simulations to approximate the behavior of solid polymer nanocomposites.

In order to investigate the influence of nanofiller's shape and size we created 3 nanofillers. Two spherical TiO_2 nanofillers with diameters of about 2.4 nm and 1.2 nm and a rod-like nanofiller with a diameter of 1.5 nm and height of 4 nm were cut from a bulk TiO_2 crystal (rutile). The dimensions of the rod-like nanofiller are chosen to ensure the same volume as that of the larger spherical nanofiller. Some surface atoms were removed to make the ratio of Ti:O = 1:2. For convenience, hereafter we name the simulation case with the larger spherical nanofiller PNC1(2.4), the simulation case with the smaller spherical nanofiller PNC2(1.2) and the one with the rod-like filler PNC3(rod). In addition, we created two other simulation cases by modifying the Li ion-nanofiller and PEO-nanofiller interactions in PNC1(2.4) and

PNC2(1.2) to purely repulsive by setting the attraction terms in the force field to zero (in experiments this could be done by chemical functionalization of the nanofiller's surface) and we call these new cases PNC1-SR and PNC2-SR, respectively. Such artificial filler surfaces have been used in a previous MD study [50].

Fig. 1 shows three of our simulation cases PNC1(2.4) (a), PNC2(1.2) (b), and PNC3(rod) (c). The simulation cases are visualized using the Visual Molecular Dynamics (VMD) [62]. Due to the complexity of the
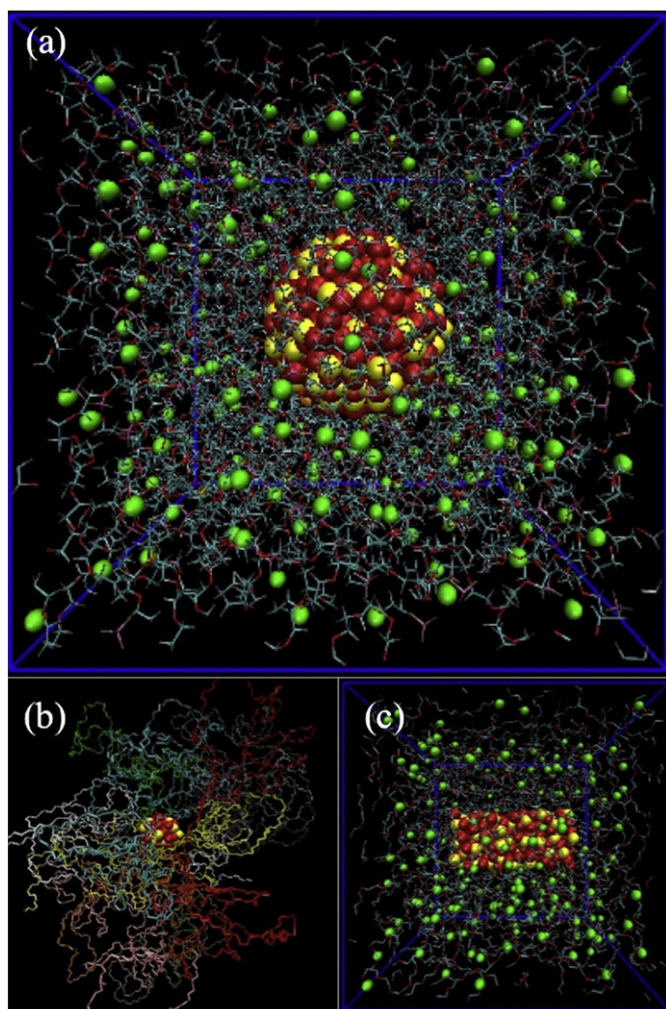

Fig. 1. Simulation cases of PNC1(2.4) (a), PNC2(1.2) (b), and PNC3(rod) (c) visualized by VMD. Lithium ions and nanofiller atoms are shown in solid spheres. PEO chains (different chains are classified by different colors) are shown in their original configurations in (b).

Table 1
The force field parameters used in this study.

Bonds	K_{ij} (kcal mol^{-1} Å^{-2})	r_0 (Å)	
C–C	309.194	1.513	
C–O	369.733	1.390	
C–H	327.717	1.090	
Cl–O	350.000	1.440	

Angles	K_{ijk} (kcal mol^{-1} rad^{-2})	Θ_0 (deg)	
C–C–H	42.924	98.400	
H–C–H	38.551	93.400	
O–C–C	59.535	96.500	
O–C–H	56.034	100.800	
C–O–C	74.544	107.100	
O–Cl–O	100.000	109.500	

Dihedrals	K_1 (kcal mol^{-1})	K_2 (kcal mol^{-1})	K_3 (kcal mol^{-1})	K_4 (kcal mol^{-1})
O–C–C–H	0.278	0.000	0.000	−0.278
H–C–C–H	0.278	0.000	0.000	−0.278
C–O–C–H	0.808	0.000	0.000	−0.808
O–C–C–O	2.602	0.050	−2.552	0.000
C–O–C–C	2.021	−1.001	−0.701	−0.320

Non-bonded	A_{ij} (kcal mol^{-1}) or A'_{ij} (kcal mol^{-1} Å^{12})	B_{ij} (Å^{-1})	C_{ij} (kcal mol^{-1} Å^6)
H–H	2651.299	0.267	27.389
H–C	4322.793	0.293	138.332
H–O_{PEO}	14,185.128	0.256	104.539
H–Li	5002.437	0.192	0.000
H–Cl	5284.667	0.297	207.110
H–O_{LiClO4}	5284.928	0.276	86.977
H–Ti	88,630.000[a]	N/A	32.000
H–O_{TiO2}	14,175.980	0.256	103.950
C–C	14,985.539	0.324	641.213
C–O_{PEO}	33,724.143	0.280	505.891
C–Li	22,380.760	0.211	0.000
C–Cl	29,407.119	0.327	1002.098
C–O_{LiClO4}	29,415.215	0.304	420.836
C–Ti	125,000.000[a]	N/A	496.000
C–O_{TiO2}	33,702.400	0.280	503.040
O_{PEO}–O_{PEO}	75,893.733	0.246	399.130
O_{PEO}–Li	55,853.769	0.184	0.000
O_{PEO}–Cl	138,350.274	0.285	790.617
O_{PEO}–O_{LiClO4}	138,529.656	0.265	332.024
O_{PEO}–Ti	97,622.000[a]	N/A	32.000
O_{PEO}–O_{TiO2}	75,844.800	0.246	396.890
Li–Li	44,186.257	0.137	0.000
Li–Cl	83,642.765	0.213	0.000
Li–O_{LiClO4}	83,708.296	0.198	0.000
Li–Ti	83,247.274	0.145	0.000
Li–O_{TiO2}	76,010.943	0.179	0.000
Cl–Cl	781,407.189	0.330	1566.093
Cl–O_{LiClO4}	787,164.229	0.307	657.689
Cl–Ti	748,199.920	0.225	435.313
Cl–O_{TiO2}	403,203.654	0.278	1044.706
O_{LiClO4}–O_{LiClO4}	793,006.730	0.285	276.200
O_{LiClO4}–Ti	753,476.394	0.210	182.812
O_{LiClO4}–O_{TiO2}	404,731.035	0.258	438.730
Ti–Ti	717,700.000	0.154	121.000
Ti–O_{TiO2}	394,176.450	0.190	290.387
O_{TiO2}–O_{TiO2}	271,700.000	0.234	696.900

[a] The value is for the parameter A'_{ij}.