

ABSTRACT

KHAN, IMON. Molecular Dynamics Simulations of Nanoparticle Dispersed PEO Polymer Electrolytes for Lithium-Ion Batteries. (Under the direction of Dr. Melissa A. Pasquini).

Lithium-ion secondary cells are considered as one of the most effective solutions to meet the increasing demand for electrochemical power sources. The development of solid-state lithium-ion conducting materials are strongly needed for lithium-ion secondary cells due to their high safety and reliability. Solid polymer electrolytes based on high molecular weight dielectric polymer matrix, generally polyethylene oxide (PEO), seem the most suitable and commonly studied electrolytes. However, the ionic conductivity of PEO-lithium salt (LiX) electrolytes only reach practically useful values at high temperatures. Recently, the addition of inorganic particle fillers dispersed in host polymer such as TiO_2 , Al_2O_3 or SiO_2 to PEO-LiX to form a composite solid polymer electrolyte (CSPE) has been reported. Such nanoparticles are believed to increase ionic conductivity as they kinetically inhibit crystallization from the amorphous state. Although a lot of research is being done to develop the most suitable electrolyte systems that meet all of the requirements, it is challenging to reach to an optimized composition as there are several parameters influencing the electrochemical properties in a CSPE.

Computational tools can be used to predict and recognize these parametric effects which are hard to achieve from experimentation only. Therefore, the goal of this work is focused on molecular dynamics simulations of PEO-LiCl-nanoparticle systems. Li-ion mobility has been observed by controlling the sizes and types of SiO_2 nanoparticles. These observations provide insights into the various changes in lithium-ion conductivity due to the sizes and types of nanoparticles and can take steps to control them. This knowledge can enable the molecular level design for the efficient incorporation of nanoparticles into solid polymer electrolytes for use in Li-ion batteries.

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Molecular Dynamics Simulations of Nanoparticle Dispersed PEO Polymer Electrolytes for
Lithium-Ion Batteries

by
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DEDICATION

This work is dedicated to my mother, Shirin Khan who has raised me to be a strong person, showed me the true meaning of perseverance, and taught me how to be positive in every stage of life. I would also like to dedicate it to those people who inspired me in different stages of my life: my wife, teachers and my friends.

BIOGRAPHY

Imon was born and raised in Tangail, Bangladesh. Imon completed his Bachelor degree in Textile Technology from University of Dhaka with a specialization in Wet Processing Technology. He worked for the textile industries for five years in diverse positions in several internationally recognized companies. He started his journey with COATS dye house production, worked in BASF as a textile finishing and sizing expert, and also worked in DECATHLON as a component leader where he was engaged in development of innovative fabric for sportswear. He had the opportunity to experience the complete value chain of textile industries from manufacturing to retail through his industrial journeys. The passion for learning new things made Imon take the decision to pursue his Masters degree in Textile Engineering at NC State University. He plans on continuing on into the PhD program, here in the College of Textiles to attain a degree in Fiber and Polymer Science focusing on polymer blend compatibility and nonwovens.

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CHAPTER 1

Overview

1.1. Motivation

Human civilization is largely dependent on the usage of energy at its various forms such as heat, light, electrical, mechanical and so on. In the last few decades, energy use and electricity consumption have been increased due to the rapid increase in the world population and diverse consumer behavior. A large portion of the total energy is consumed by the industry, transportation, and construction sectors. The demand of world energy is growing rapidly with a projection of more than double by 2050 and more than triple by the end of the century. A straightforward incremental growth in existing energy networks with the conventional ways will neither be sufficient to meet this growing demand nor be a sustainable solution¹. The use of renewable energies such as solar, wind, tidal, wave, hydrokinetic (marine and river current), biomass and so on to cover the increasing energy deficit has become popular in recent days. However, there are limitations to utilize these energy sources. Most of the times, there is a far distance between the electricity generation places and the locations where it is consumed⁴¹. Long transmission lines are used to ensure the power supply that increase the investment cost and energy lost. On the contrary, renewable energy sources sometimes make this situation more complicated due to their daily and seasonal fluctuations. To overcome these difficulties, short and long-term energy storage is considered as one of the remarkable solutions. A growth in production of energy storage systems is much required to ensure the low cost, high efficiency and stability of power supply as well as the large scale implementation of renewable energy sources.

Battery is considered as one of the most suitable forms of energy storage which is actually a device that can store the electricity in the form of chemical energy. Battery technology is more preferable compared to many other renewable energy technologies due to their wide range of applications from personal electronic devices to large-scale electric grids. Batteries are the major source of electrochemical energy which have an essential role in our daily life. Since the invention of batteries, researchers are continuously trying to develop advanced battery materials to enhance the performance of batteries and minimize their safety concerns as well. Among different types of batteries developed so far, Li-ion batteries possess a great interest due to their high energy and power density, good rate capability, no memory effect, and so on. However, Li- ion batteries have some safety issues and high cost. Researches are going on to overcome the safety issues of Li- ion batteries as well as increase the battery efficiency keeping them cost effective at the same time. Development of solid state electrolyte system for batteries instead of the conventional liquid electrolyte is an example of such continuous research effort. Incorporating nanoparticles in polymer matrix to form composite solid polymer electrolyte system for lithium ion battery has drawn a great research interest in recent days. Some experiments demonstrated that the addition of nano-sized inert ceramic filler like TiO_2 , Al_2O_3 or SiO_2 to polymer electrolytes, may increase the conductivity of the electrolyte system³⁴⁻³⁶. On the other hand, some experiments demonstrated lower conductivity upon the addition of nanoparticles⁵⁸. These results have initiated research interest in developing a fundamental understanding of what happens inside the composite polymer electrolytes during charging and discharging of the Li-ion batteries. Molecular dynamics (MD) simulations can describe the ion transport mechanism within the polymer nanocomposites by providing atomic-level details about

the structure, dynamics, and energetics of such interactions which can be further compared with experimental data.

The goal of the present study is to explore the parametric effects in a composite solid polymer electrolyte system by using molecular dynamics simulation which is hard to achieve from experiments. Specifically, plan is to compare the Li-ion diffusivity for different electrolyte systems by varying the size and types of nanoparticles in the systems which may help designing a suitable polymer electrolyte system to meet the increasing demand for electrochemical power sources.

1.2. Background Information

Nanoparticles when incorporated in polymer matrix to form composite solid polymer electrolyte system for lithium ion battery, shows enhanced performance in terms of ion transportation and mechanical properties. Development of advanced battery materials can open an attractive horizon of future applications to ease our daily life. However, there is still a long way to master the efficient composition of such solid state battery materials since there are so many components in such electrolyte system.

1.2.1. Batteries

A battery is a device used for the storage of electrical energy which plays an important role in our daily life. Electrical energy is easy to apply and convert into heat, light and mechanical energy but it is hard to store directly. Though capacitors or superconducting coils allow its direct storage, the quantities compared to the huge demand of applications is so small. Due to this limitation, the storage of electrical energy requires to get converted into another form

of energy and the concept of battery came into scenario in which the energy of chemical compounds act as storage medium and converts into electrical energy during discharge^{2, 3}. In general, batteries are two or more electrochemical cells, electrically interconnected, each of which contains two electrodes and an electrolyte. The redox (oxidation-reduction) reaction occurs at the electrodes and electrochemical energy is converted into electrical energy.

Depending on the conversion of energies, two different battery systems exist:

1. *Primary battery*: Non reversible electrochemical reaction takes place in this battery system. Chemical compounds are permanently changed and electrical energy is released until the original compounds are completely exhausted during discharge. These batteries can be used for once.
2. *Secondary battery*: Reversible electrochemical reaction takes place in this battery system. This battery is also known 'Rechargeable batteries' that can be discharged and recharged many times. Original chemical compounds used in this battery system can be reconstituted within the battery when by electrical energy is injected that is the battery is recharged.

Secondary batteries are treated as genuine electrochemical storage systems.

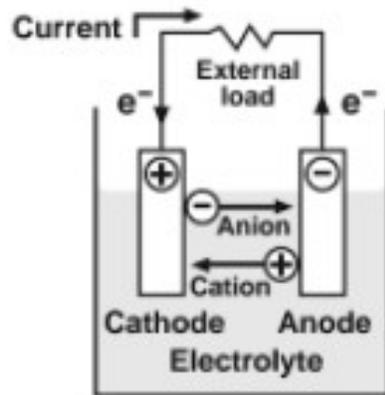


FIGURE 1.1 Schematic of an electrochemical cell (image taken from Research studies Press Ltd.)

FIGURE 1.1 represents the schematic of an electrochemical cell that consists of the below essential components:

- A negative electrode, Anode - donates electrons to external circuit
- A positive electrode, Cathode - to which cations migrate
- Electrolyte - enables ion transfer between two electrodes
- A separator - electrically isolates the positive and negative electrodes.

Batteries are in many sizes and shapes, from miniature cells in hearing aids and wristwatches to small, thin cells used in smartphones, to large batteries used in cars and trucks. The market size of the battery industry is quite large and growing faster. According to a report by Grand View Research, Inc., the global battery market is expected to reach USD 132.55 billion by 2024³.

Researchers have been working on developing various battery materials since its invention to find an efficient battery system. The chronological development since the very first copper-zinc battery to nickel-cadmium battery and then lead-acid battery to latest lithium and lithium ion batteries illustrates that trend of much needed development to meet its increasing demand⁴. In recent days, lithium based batteries have become popular which are of two types: 1) lithium battery, and 2) lithium ion battery. Initially, lithium battery was developed in which pure lithium metal was used as anode since lithium has the greatest electrochemical potential, lightest weight of all metals. But it has potential security risk of flammability and explosion since lithium metal is explosive in nature. For a better solution, lithium ion battery came into market where lithium compounds are used as anode. Lithium ion batteries are rechargeable and have become components in most portable electronics because of their high energy and power density^{5, 6}.

FIGURE 1.2 represents several rechargeable batteries and their volumetric and gravimetric energy densities. The FIGURE illustrates that the gravimetric energy density of Li-ion batteries is two times higher than Ni-Cd batteries and one time higher than Ni-MH batteries. When compared with lead-acid batteries, the gravimetric energy density of Li-ion batteries is almost five times higher than that of lead-acid batteries.

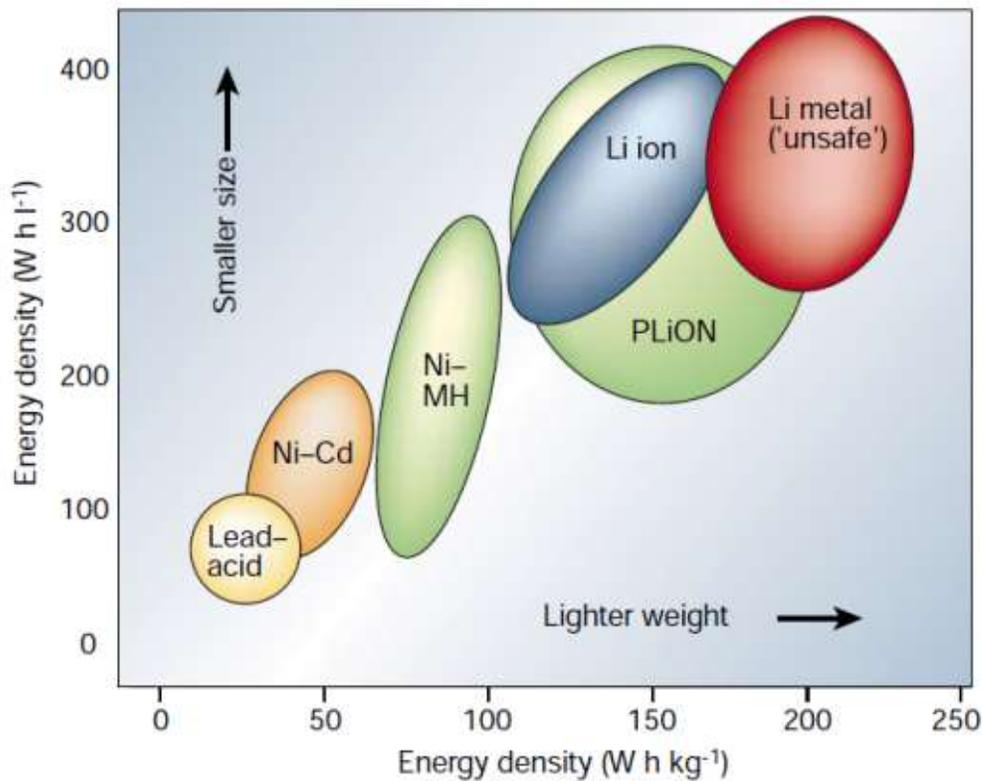


FIGURE 1.2 Comparison of different battery technologies in terms of volumetric and gravimetric energy densities (image taken from Ref. 36)

Li-ion batteries provide higher volumetric energy densities as well compared to any other battery technologies shown in the FIGURE. Lead-acid batteries and Ni-Cd batteries have restriction to automobiles and power tools application. Table 1 below represents some additional advantages of Li-ion batteries compared to lead acid and nickel cadmium or nickel metal hydride batteries (NiMH) such as high-energy efficiency, a relatively long cycle life along with no memory effects.

Table 1. Comparison between different battery technologies (table taken from Ref. 50).

Specifications	Lead acid	NiCd	NiMH	Li-ion		
				Cobalt	Manganese	Phosphate
Specific energy density (Wh/kg)	30–50	45–80	60–120	150–190	100–135	90–120
Internal resistance (mΩ)	<100	100–300	200–300	150–300	25–75	25–50
	12 V pack	6 V pack	6 V pack	7.2 V	per cell	per cell
Cycle life (80% discharge)	200–300	1000	300–500	500–1000	500–1000	1000–2000
Fast charge time	8–16 h	1 h typical	2–4 h	2–4 h	1 h or less	1 h or less
Overcharge tolerance	High	Moderate	Low	Low. Cannot tolerate trickle charge		
Self-discharge/month (room temp.)	5%	20%	30%	<10%		
Cell voltage (nominal)	2 V	1.2 V	1.2 V	3.6 V	3.8 V	3.3 V
Charge cutoff voltage (V/cell)	2.40	Full charge detection by voltage signature		4.20		3.60
	Float 2.25					
Discharge cutoff voltage (V/cell, 1C)	1.75	1.00		2.50–3.00		2.80
Peak load current	5C	20C	5C	>3C	>30C	>30C
Best result	0.2C	1C	0.5C	>1C	<10C	<10C
Charge temperature	–20 to 50 °C	0 to 45 °C		0 to 45 °C		
	(–4 to 122 °F)	(32 to 113 °F)		(32 to 113 °F)		
Discharge temperature	–20 to 50 °C	–20 to 65 °C		–20 to 60 °C		
	(–4 to 122 °F)	(–4 to 49 °F)		(–4 to 140 °F)		
Maintenance requirement	3–6 months	30–60 days	60–90 days	Not required		
	(topping charge)	(discharge)	(discharge)			
Safety requirements	Thermally stable	Thermally stable, fuse protection common		Protection circuit mandatory		
In use since	Late 1800s	1950	1990	1991	1996	1999
Toxicity	Very high	Very high	Low	Low		

1.2.1.1. Li-ion Batteries

Lithium is the most reducing element and the lightest metal in the periodic table. So, it is easy to understand the appeal of Li as a battery material since it promises high operating voltage, low weight, and high energy-storage density. Due to these appealing features of Li, there have been many discussions for its use in primary (nonrechargeable) and secondary (rechargeable) batteries since 1950s³⁹⁻⁴⁵. Lithium primary battery was first proposed by M. Stanley Whittingham in 1970s⁴² in which Li metal was used as anode material. The light weight property of Li metal facilitates easy fabrication in developing high energy devices. One of the drawbacks of Li primary battery is that these are not rechargeable rather disposable batteries. Apart from this, the major issue of Li primary battery is the safety problem which is high flammability of the

battery caused by the lithium dendrite. Many efforts had been made to substitute lithium metal with other compounds to resolve this problem. For example, Exxon used a lithium–aluminum alloy instead of pure Li as the anode to avoid dendrite growth⁴⁶. Several other demonstrations took place in between late 1980s and early 1990s in order to commercialize Li-ion battery. In 1991, Sony commercialized the first successful Li-ion batteries in which they used a carbon host structure containing lithium at the anode instead of metallic lithium⁴⁷. Research and commercialization of Li-ion batteries became a prominent trend since then which is still continuing and offering many new possible solutions to us^{48, 49}.

At present, Li-ion batteries are leading the rechargeable batteries industries and the market is continuously increasing due to the higher demand of portable information technology (IT) devices⁵¹. FIGURE 1.3 illustrates the Li-ion battery market demands of portable IT devices. Apart from the portable IT devices, electric vehicles are drawing huge attention due to their potential reduction in greenhouse gases and eliminate the dependence on gasoline. Li-ion battery technology for electric vehicles (EVs) and hybrid electric vehicles (HEVs) was started in 2009^{52, 53} since Li-ion batteries are considered the most suitable for electric vehicles⁵⁴ because of the higher power output and capacity for higher energy. A Li-ion battery is comparatively lighter and smaller than other rechargeable batteries of the same storage capacity⁵⁵. However, further studies on new materials and structures are being carried out to match enough energy and power densities for the electric vehicle.

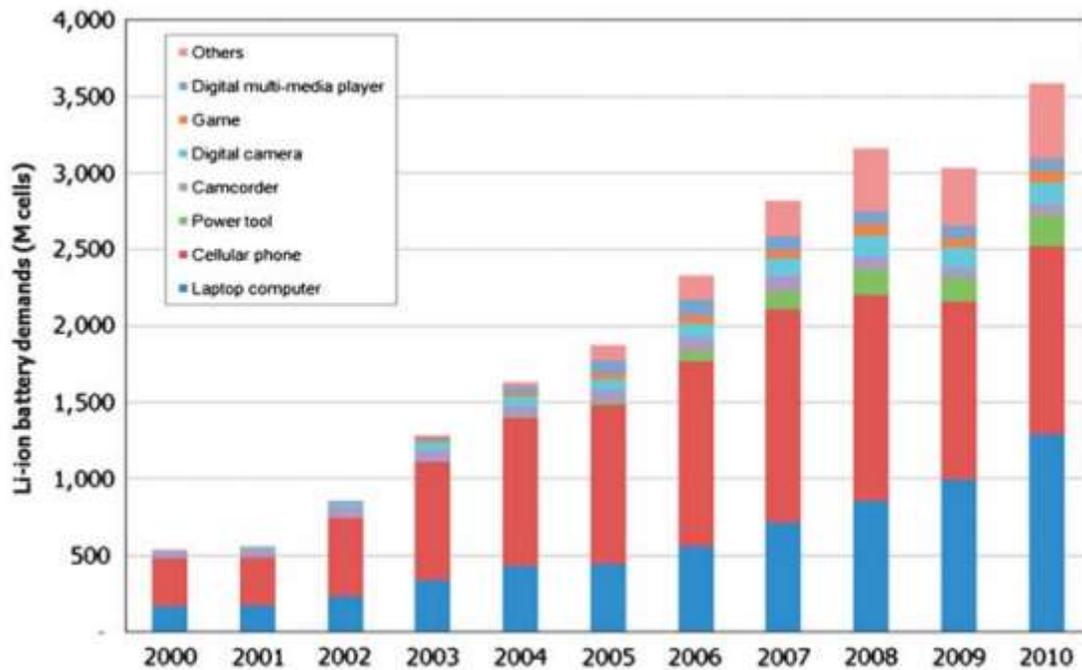


FIGURE 1.3 Li-ion market demands due to mobile IT devices (image taken from Ref. 51).

Li-ion batteries are of various sizes and configurations that can be categorized as cylindrical, coin, prismatic, thin and flat Li-ion batteries. Cylindrical and prismatic batteries are mostly seen in our daily personalized items which are almost similar in structure typically constructed with anode, cathode, separator, copper/aluminum current collectors and liquid electrolyte. For cylindrical and prismatic batteries, all the components are wrapped together and then packed compactly inside a cylindrical steel case or a semi-hard plastic case. Coin-type Li-ion batteries are in more compact configuration often seen in laboratories for research and development purposes. Thin and flat Li-ion battery was invented by Bellcore researchers to introduce polymeric electrolytes into a liquid Li-ion system⁵⁶. This type of Li-ion battery possess

unique flexibility due to not containing liquid electrolyte like other three types. FIGURE 1.4 represents the schematics of shapes and components of various Li-ion battery configurations.

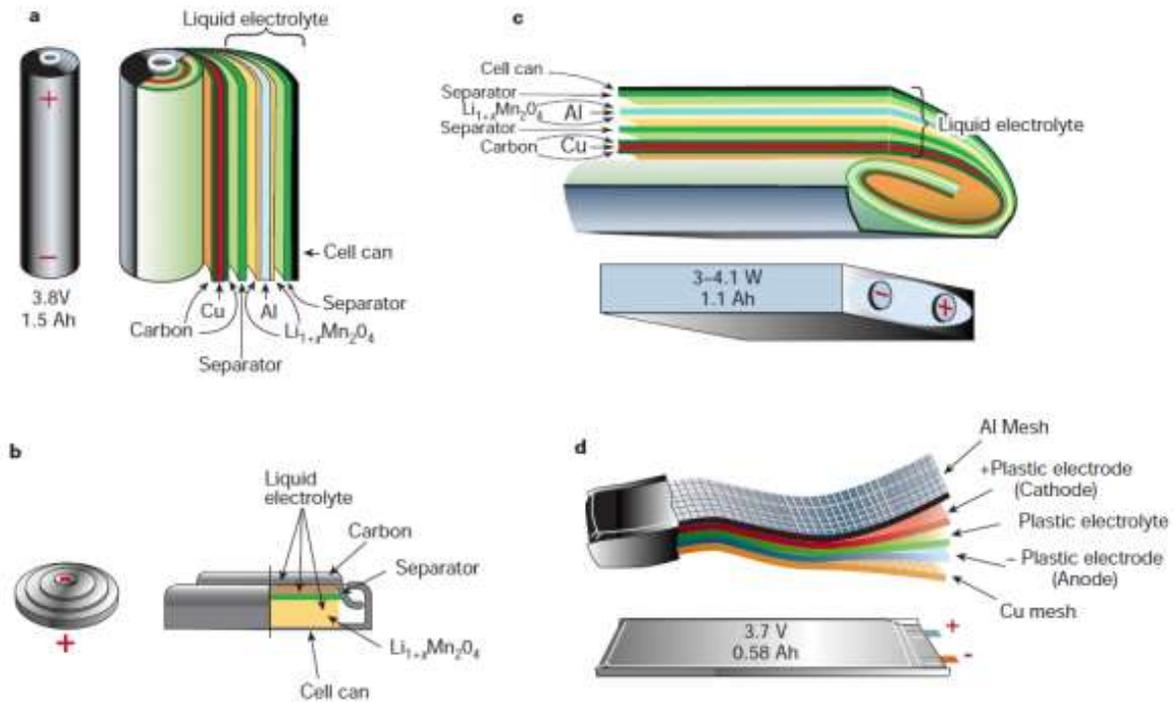


FIGURE 1.4 Schematic of the shapes and components of various Li-ion battery configurations: (a) cylindrical, (b) coin, (c) prismatic, and (d) thin and flat (adapted from Ref. 36)

In general the constituents and basic working principle of a Li-ion battery is the same in all the different shapes and configurations. In a lithium ion battery, lithium dissolved as ions into a carbon is used as anode, cathodes are lithium liberating compounds, typically electro-active oxide materials that is

Lithium Cobalt-oxide (LiCoO_2)

Lithium Manganese-oxide (LiMn_2O_4)

Lithium Nickel-oxide (LiNiO_2)

Electrolyte is usually a lithium salt in an organic solvent and fine porous polymer film is used as separator. During charging and discharging the battery, Li-ions are inserted or extracted from interstitial space between atomic layers within the active material. Li-ions are transferred between anode and cathode through lithium electrolyte. FIGURE 1.5 illustrates the mechanism of lithium ion battery during discharging and charging.

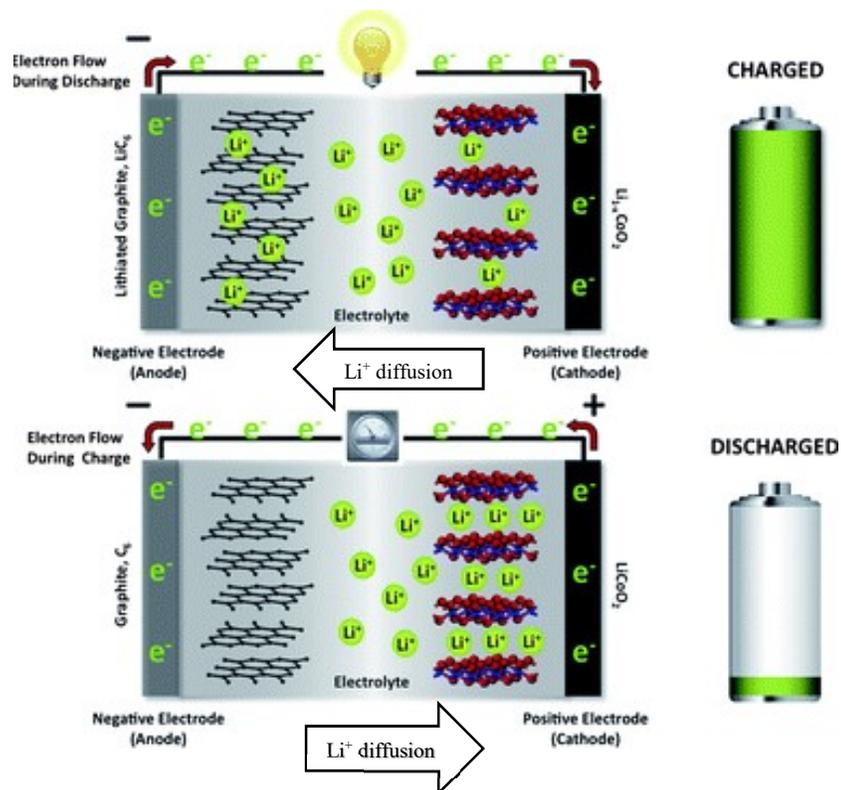
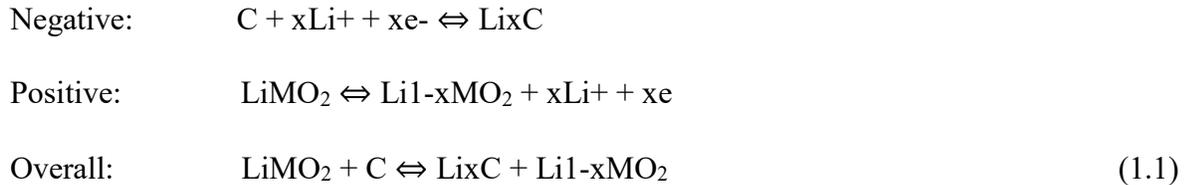


FIGURE 1.5 Schematic of a lithium ion battery (adapted from steemit.com)

The chemical reaction that takes place at anode and cathode inside a commercial battery can be described as below⁵⁷:



In this study, we have focused on the electrolyte materials for lithium ion battery that plays a vital role in battery efficiency by ensuring smooth ion conductivity through its pathway.

1.2.2. Electrolytes

Electrolyte is one of the essential components for a battery system that facilitates the effective ions transport through it and thus imparts a vital role in the performance of battery. In conventional lithium ion rechargeable batteries, solid electrodes and liquid electrolytes have been used that possess potential risks concerning volatilization, flammability and explosion^{7, 8}. So, electrolytes selection is very important for lithium ion batteries not only for the effective transport of Li-ion but also to meet the safety requirement.

Solid-state electrolytes could overcome most of the safety concerns with liquid electrolytes because of their intrinsic solid character⁹. Solid-state electrolytes are better than conventional liquid electrolyte as they do not corrode, combust, leak or cause internal shorting. Moreover, solid electrolytes help resisting the dendrite growth in battery system by their inert nature toward metallic lithium^{10, 11}. A solid-state battery should possess some important functional properties

that is chemical stability in the presence of an anode or high-voltage cathode material, thermal stability during charging and discharging, wide range of electrochemical stability against irreversible reaction along with high total Li ionic conductivity^{12, 13}. Solid state electrolytes have attractive and wide range of potential applications some of which have been depicted in FIGURE 1.6 (b). However, there is still a long way to develop the right solid state electrolyte materials that meets all the requirements.

The solid state electrolytes can be classified into three categories as illustrated in FIGURE 1.6

(a):

(i) *Inorganic solid electrolytes (ISEs)*,

(ii) *Solid polymer electrolytes (SPEs)*,

(iii) *Composite solid electrolytes (CSEs)*

Inorganic solid electrolytes (ISEs) are mostly oxides, sulfides and nitrides of lithium containing compounds which have intrinsic high ionic conductivity. Most of these materials possess crystalline structures with a specific framework that exhibit anisotropic conductivity for faster ion transportation through the vacant and interstitial sites within their framework structure.

Solid polymer electrolytes (SPEs) are usually composed of a lithium salt dissolved in a high molecular weight polymer matrix¹⁴ that form a macromolecular architecture, and can serve as a barrier for dendrite suppression due to their comparatively high mechanical strength. The usage of ether based polymers as electrolytes was initiated after the discovery by Wright in 1975 showing conductivity in salt solutions of poly (ethylene oxide) (PEO) which opened up a new horizon for solid-state electrochemistry¹⁵. Later on, the potential use of PEO in lithium batteries

was explored by Armand and others¹⁶ and since then it stands out as very attractive candidate for use in lithium batteries.

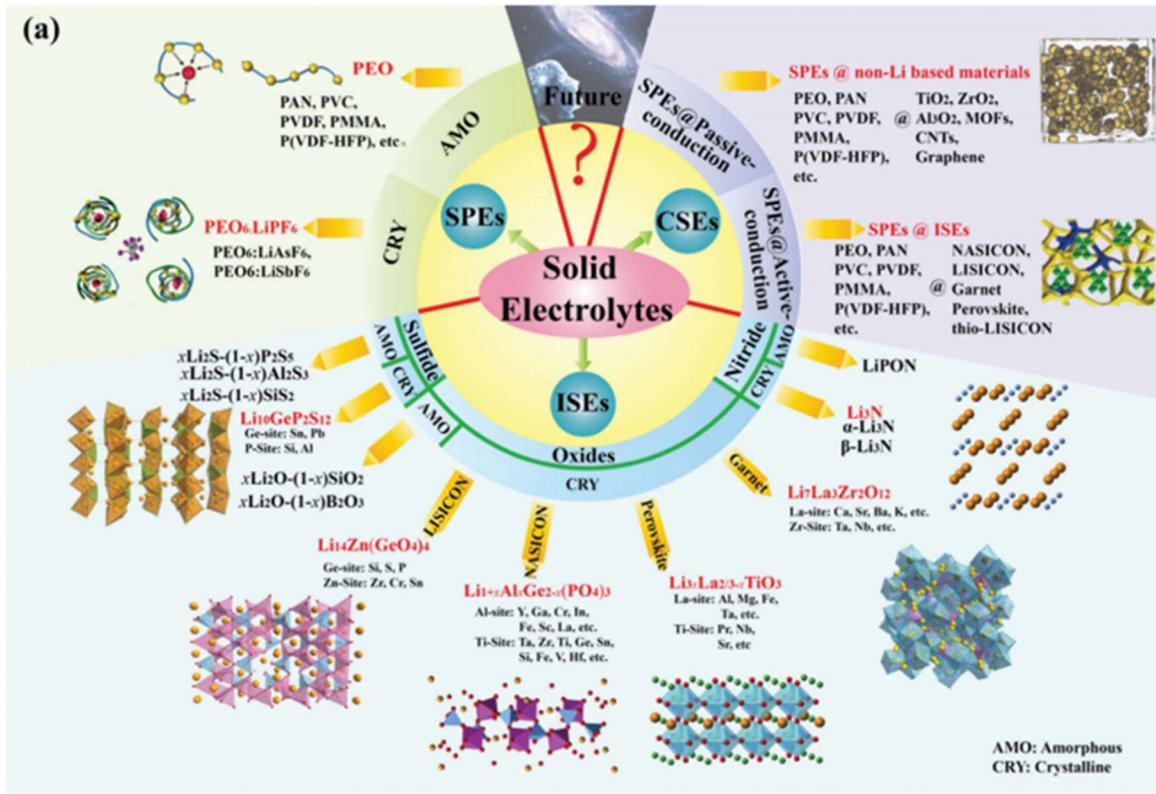


FIGURE 1.6 (a) Categories of solid electrolytes.

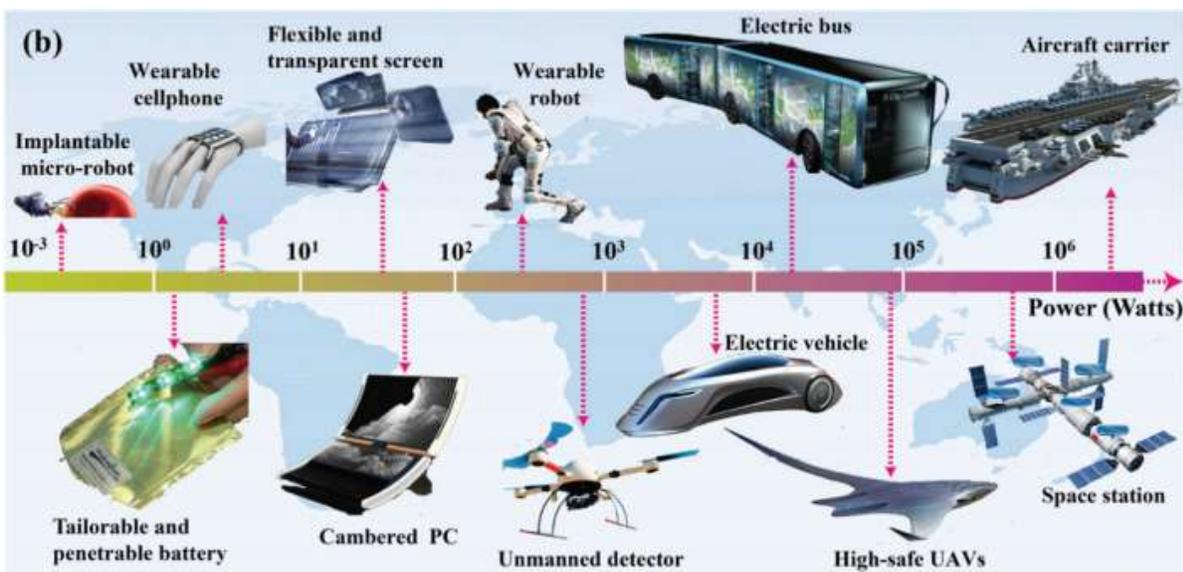


FIGURE 1.6 (b) Potential applications and technologies with solid electrolytes in the future (image taken from the work of Renjie Chen and others, Materials Horizon, The Royal Society of Chemistry, 2016)

In general, a SPE system contains a salt (for instance LiPF_6 , LiCl_2) with a low lattice energy and host polymer (for example PEO) with a high dielectric constant to facilitate dissociation and transport of ions¹⁷. The system is chemically stable as it contains only C-O, C-C and C-H bonds and local relaxation and segmental motion of the PEO polymer chains facilitates the ionic conductivity of the electrolyte. The polymer forms a rubbery solid electrolyte with the addition of a Li salt^{18,19} which possesses zero risk of leakage of electrolyte, lightweight and high flexibility. However, at ambient temperature, PEO does not provide a high lithium-ion conductivity as a result of its high degree of crystallinity¹⁵.

Composite solid electrolytes (CSEs) are composed by adding inorganic solid particles or fillers into conventional polymer electrolytes. In this electrolyte system, TiO_2 , Al_2O_3 or SiO_2

inorganic particle fillers are mostly dispersed in host polymer that is PEO which increases the ionic conductivity, supports polymer matrix to improve mechanical properties and restricts the recrystallization of polymer chains. This happens due to nanoparticles' surface groups with Lewis acid character and large surface area, which increase the size of local amorphous regions and thus promote Li^+ transport through preferential ion conduction pathways²⁰⁻²².

In this study, we have focused on the composite solid electrolytes since it's a strongly demanded area of development needed.

1.2.3. Characteristics of Polymers

Polymers are substances composed of molecules that have long sequences of one or more species or groups of atoms linked to each other by covalent bond primarily. In simple words, polymers are long chain molecules made up of small building blocks or monomers. Mainly carbon atoms continuously linked to each other form the backbone of a polymer. Due to polymer microstructure and morphology, polymers exhibit special chemical, mechanical, rheological, optical and transport properties. The key structural features of polymers is a consequence of their physical properties that result from their long chain structures and high molecular weight. Many conformations are possible for polymers because of their bond rotation from completely folded to fully extended phases. Polymer chains have an internal degree of freedom and they are able to exhibit elastic properties as a result of this. In general, different polymers that is PEO, PAN, PVC, PVDF, PMMA have been used as polymer matrix for solid state polymer electrolyte systems.

Poly (ethylene oxide) (PEO)

PEO is a polyether compound which has C-O-C groups in its structure. It is also known as Polyethylene glycol (PEG) depending on its molecular weight. PEO, or PEG is synthesized by suspension polymerization. PEO is very popular for its attractiveness to be used as the polymer matrix for both solid state polymer electrolyte and polymer composite electrolyte. It also used for various medical, chemical and biological applications along with its commercial and industrial uses.

Poly (acrylonitrile) (PAN)

PAN is a synthetic, semi crystalline polymer which is thermoplastic in nature. It does not melt under normal conditions and degrades before melting. PAN is synthesized by free radical polymerization of acrylonitrile. It is a versatile polymer used for various products including ultrafiltration membranes, hollow fibers for reverse osmosis, fibers for textiles, etc. PAN fibers are the chemical precursor of high-quality carbon fiber.

Poly (vinyl chloride) (PVC)

PVC is produced from vinyl chloride monomer (VCM) mostly by suspension polymerization. It is a thermoplastic polymer and has high mechanical and chemical properties. It is vastly used for construction pipe, doors and windows. It is also used for bottles, other non-food packaging, bank cards, electric cables, floorings, etc.

Poly (vinylidene fluoride) (PVDF)

PVDF is a highly non-reactive thermoplastic polymer produced by the polymerization of vinylidene difluoride. PVDF has a relatively low melting point of around 177 °C. It used in piping products, sheet, tubing, films, and an insulator for wire. It is popular for lithium-ion batteries application and commonly used in chemical, semiconductor, medical and defense industries as well.

Poly (methyl methacrylate) (PMMA)

PMMA is a transparent thermoplastic often used in sheet form as a lightweight alternative to glass. PMMA can be produced by emulsion polymerization, bulk polymerization and solution polymerization. Commercial PMMA is atactic and completely amorphous. It has wide range of application in transparent glass substitute, medical technologies and implants, artistic and aesthetic uses.

1.2.4. Characteristics of Nanoparticles

A nanoparticle is a microscopic particle between 1 and 100 nanometres (nm) in size typically that behaves as a whole unit with respect to its transport and properties. Nanoparticles work as a bridge between bulk materials and atomic or molecular structures and show size-dependent properties whereas bulk materials have constant physical properties regardless of its size. The properties of materials change as their size approaches the nanoscale. As a result, a number of special properties are exhibited by nanoparticles relative to bulk materials. A very high surface area to volume ratio of nanoparticles leads to a huge driving force for diffusion. Inorganic nanoparticles including SiO_2 ^{23, 24}, Al_2O_3 ²⁵, TiO_2 ^{26, 27} are incorporated with solid polymer electrolytes to form composite solid polymer electrolytes that can display the advantages of their respective components. They compensate each other regarding their drawbacks and enhance the overall performance of solid electrolytes in terms of ionic conductivity, mechanical strength, electrochemical window and transference number. Based on the contribution of the fillers to ionic conductivity, we can divide them into two categories i.e i) passive fillers and ii) active fillers. Passive fillers like SiO_2 , TiO_2 do not directly participate in

the conduction process whereas, active fillers, such as Li_3N , LAGP, participate in the Li transport process.

In this study we have used SiO_2 nanoparticles which is also known as silica. It is most commonly found in nature as quartz²⁸ and has the ability to be functionalized with a range of molecules and polymers. Silica is one of the most complex and abundant families of materials, available as a compound of several minerals. It has a higher melting point of 1,713 °C and shows very good electrical and insulating properties. In most of the cases, silicates are in tetrahedral coordination where a Si atom is surrounded by four oxygen atoms. SiO_2 exists in many crystalline forms known as polymorphs such as α -quartz, β -quartz, α -tridymite, β -tridymite, β -cristobalite, seifertite, 2D silica etc. For our study we have specifically used two-dimensional silica (2D silica) which is a layered crystalline form of silicon dioxide. There are two types of 2D silica: one is based on SiO_4 tetrahedra, covalently bonded to the substrate and the other is graphene-like fully saturated sheets that interact with substrate by weak van der Waals bonds²⁹. Both the types represent hexagonal crystal symmetry. 2D silica has great potential for applications in electronics as the thinnest gate dielectric. Most of the time, SiO_2 is obtained by sand mining and purification of quartz which goes through further chemical processing to make a purer or more reactive or fine-grained product.

1.2.5. Molecular Dynamics (MD) Simulations

MD is one of the computational simulation techniques for studying the molecular level details for a system of interacting particles. MD simulations is widely used in computational materials science, biochemistry and biophysics to calculate properties at molecular scale. This method allows the atoms and molecules to interact for a fixed period of time, providing a view of

the dynamic evolution of the system. The trajectories of atoms and molecules are determined by numerically solving Newtonian equations of motion at regular intervals of time known as time steps. Interatomic potentials or molecular mechanics force fields are used to calculate the forces between the particles and their potential energies. MD simulations of the molecular model can be used to extract structural information and dynamic features by solving the total energy (E_{total}) for all the particles in the system³⁰ given as,

$$E_{total} = E_{kin} + E_{pot}$$
$$E_{pot} = E_{bonded} + E_{non-bonded} = E_{bonded} + E_{vdW} + E_{es} \quad (1.2)$$

Where E_{kin} is the total kinetic energy and E_{pot} is the total potential energy of the system. E_{pot} is comprised of E_{bonded} and $E_{non-bonded}$ terms. $E_{non-bonded}$ is consisting of the van der Waals (E_{vdW}) and electrostatic (E_{es}) energies. The set of bonded and non-bonded parameters is known as “force field”. The parameters of individual atoms in a system, can be described by all-atom force fields, whereas united-atom force fields treat groups of atoms as particles. Force fields are usually parameterized by using experimental data or from ab-initio quantum mechanics calculations. A specific force field is applicable to the chemical classes which were used to define the parameters. Force fields parameterized for organic molecules contain all the information about the bond order and hybridization of each atoms, listed by specific atom types. COMPASS³¹, DREIDING³², and CHARMM³³ are some examples of force fields commonly used. Different other force fields have been approached in recent days for modelling amorphous linear and branched PEO of different molecular weights with various lithium salts and concentrations which are more detailed and complex.

CHAPTER 2

Simulations of Nanoparticle Dispersed PEO Polymer Electrolytes

2.1 Introduction

The design of polymer electrolytes is an important research area to meet the high demand of electrochemical energy storage system and their applications. The development of such solid polymer electrolytes requires the goal of achieving enhanced conductivities and mechanical strengths in the same material. The presence of nanoparticles in polymer electrolytes may enhance the ionic conductivity for the electrolyte system in lithium ion batteries. Some experiments have been demonstrated which shows that the addition of chemically inert ceramic particles or nanoparticle such as TiO_2 , SiO_2 , Al_2O_3 to polymer electrolytes, enhance the conductivity of the polymer matrix³⁴⁻³⁶.

Computational modelling of polymer electrolytes may at first seem an intriguing approach since the materials used in the system are complex with multiple phases co-existing. There is interest in developing polymer electrolytes for a variety of applications and address the fundamental phenomena by choosing methods that meet the requirements of an efficient battery. MD simulations have become a widely used computational technique to study solid polymer electrolyte systems since dynamic properties like ion mobility can be correlated to the molecular level structure of the system and can also be compared with experimental results³⁷. Several MD simulations have been done to study the effect of nanoparticles on polymer electrolytes. For instance, the study on the transport mechanisms of ions in CSPEs consisting of TiO_2

nanoparticles depicted the influence of nanoparticles upon the polymer mobility and conformations as the main mechanism underlying the changes in ion mobilities³⁸.

In the current study, a MD simulations are done for a composite polymer electrolyte system in which SiO₂ nanoparticles are dispersed on the host polymer matrix that is Poly(ethylene oxide) (PEO). We have chosen PEO as the host polymer matrix since PEO-based polymer electrolyte system is the most extensively researched system as 1) PEO can complex with lithium salts (Li⁺) to form polymer electrolytes, and 2) The ethylene oxide (EO) units have a high donor number for Li⁺ and provide high chain flexibility, which are very important factors for promoting ion transport. PEO possesses a high dielectric constant and strong ability of solvating Li⁺ as well⁵⁹. Experimental demonstrations are available where TiO₂, SiO₂, Al₂O₃ nanoparticles have been used³⁴⁻³⁶. We have chosen SiO₂ for our work because we found MD simulations for electrolyte systems containing Al₂O₃⁶⁰ and TiO₂³⁸ nanoparticles but we haven't found sufficient MD simulations for electrolyte systems that contains SiO₂ nanoparticles. LiCl salt has been used in the systems that generates Li⁺ cations and Cl⁻ anions in the electrolytes. MD simulations have been done for various electrolyte systems built where we kept the polymer and ions fixed and changed the size and quantity of silicate nanoparticles. These MD simulations investigate how the nanoparticles impact the ionic diffusivity in a polymer electrolyte system when there is a change in nanoparticle size and/or quantity.

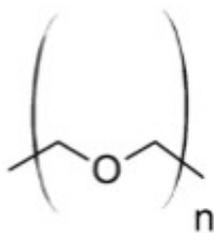


FIGURE 2.1 The repeat unit for the flexible backbone polymer used in this study: PEO

2.2 Methodology

We have used Accelrys Materials Studio software version 5.5⁶¹ for all of our modelling and calculations. We have used the ‘TEX-DRAGONAGE’ computer in the Pasquinelli lab which has an Intel(R) Core(TM) i7 CPU 860 @ 2.80GHz 2.79 GHz processor with 8.00 GB RAM and 64-bit Operating System.

2.2.1 Molecular Model of the PEO Chains

A flexible backbone polymer was chosen for this study. The polymer used in the simulations is Poly (ethylene oxide) which is used as polymer electrolyte in lithium ion batteries. The length is the approximate end-to-end length, MW is the molecular weight, and RU is the number of repeat units for the initial PEO chain.

Abbreviation	Name	Length (Å)	MW(a.m.u.)	RU
PEO	Poly(ethylene oxide)	150	2645	60

The repeat unit of polymer is depicted in FIGURE 2.1. The number of repeat units is set to 60 resulting the molecular weight about 2645 a.m.u. With this molecular weight, the polymer used in this study is long enough to study the impact of nanoparticles on polymer electrolyte. The structure of PEO was built using the polymer builder module. The polymer is built in head-to-tail configuration and in isotactic conformation. The end groups were set as CH₃ groups to avoid end group interaction with each other and nanoparticle. All of the polymers were minimized with a

geometry optimization for 2000 steps by using molecular mechanics methods in the conjugate gradient algorithm by using modified PCFF force field for polymer-inorganic hybrid materials by Heinz group⁴⁰ called Interface force field. Atom based method with 12.5 Angstrom cut-off distance was used to calculate van der Waals interactions. Fine level Ewald summation algorithm was used to calculate electrostatic coulomb type interactions.

2.2.2 Molecular Model of the Nanoparticles

The silicate nanoparticles were built by using Materials Studio. We chose the SiO₂ _21A_3d structure from the structures in Materials Studio server and cut that into pieces to shape the structure to create a roughly spherical nanoparticle. We built four different types of SiO₂ of various diameters. After building the nanoparticles of desired sizes, free surface oxygens of silicate nanoparticles were saturated by –H groups. Silicate nanoparticles were optimized for 2000 steps by using same the method utilized for PEO chains mentioned above.

Table 2. The series of nanoparticles used in the simulations. The diameter is the approximate diameter of the nearly spherical shaped silicates

SiO ₂ nanoparticles	Diameter (Å)
Si ₃₂ O ₆₄ (H ₂ O) ₁₈	18.40
Si ₆₄ O ₁₂₈ (H ₂ O) ₃₂	20.05
Si ₉₆ O ₁₉₂ (H ₂ O) ₄₁	23.96
Si ₁₂₈ O ₂₅₆ (H ₂ O) ₄₈	24.69

2.2.3 Construction of Periodic PEO-silicate Cells

The cells were prepared by using the Amorphous Cell builder module. Each cell was constructed with 10 chains of PEO each consisting of 60 monomers. All cells have 20 Li⁺ and 20 Cl⁻ ions.

<u>Molecule</u>	<u>Number</u>
PEO ₆₀	10
Li ⁺	20
Cl ⁻	20

We built the first electrolyte system with PEO chains and ions only. For the second electrolyte system, we added 1 silicate nanoparticle into the first system. Similarly, we built the third and fourth electrolyte systems by adding 2 and 3 silicate nanoparticles respectively. For each electrolyte system with nanoparticles, we have got 4 different cells since we have modelled 4 types of silicate nanoparticles. So, we have got 12 electrolyte systems for the second, third and fourth electrolyte systems with nanoparticles. Counting the first electrolyte system (without nanoparticle), the total number of electrolyte systems became 13. Each of these 13 cell models was further prepared 3 times with different coordinates by using Monte Carlo Algorithm of Amorphous Cell Construction Module resulting 39 different models in total. The cell density was fixed at 1 g/cm³ for all models. Each cell was optimized by using Smart molecular mechanic minimizer algorithm installed in Forcite Module which can choose optimization method based on the system. 1000 step molecular mechanics minimization were applied for each cell.

2.2.4 Molecular Dynamics (MD) Simulations

MD simulations were performed by using the Forcite Module. We used a constant number of molecules, constant volume, and constant temperature canonical (NVT) ensemble at 300 K with no applied pressure and using the Interface⁴¹ force field. We used a time step of 0.5 fs, an equilibration time of 30 ps, and a production run time of 70 ps with 100 ps total simulation time. Although the simulation time is very short, the system equilibrated very fast due to the high density and previously optimized solid nanoparticles. All cutoff radii were set to 12.5 Å for non-bond van der Waals interactions and Ewald summation method to calculate Coulomb type electrostatic non-bond interactions.

2.2.5 Data Analysis Tools

In MD simulations, the mobility of atoms can be described through the mean square displacement (MSD), which is defined from the particle displacement $[x(t),y(t),z(t)]$ as a function of each time interval (Δt) by using:

$$MSD(n\Delta t) = \frac{\sum_{m=1}^{N-n} [x(m\Delta t + n\Delta t) - x(m\Delta t)]^2 + [y(m\Delta t + n\Delta t) - y(m\Delta t)]^2 + [z(m\Delta t + n\Delta t) - z(m\Delta t)]^2}{N - n} \quad (2.1)$$

where (N) is the total number of time samples and (N-n) is the number of intervals per $n\Delta t$ ³⁹.

MSD analyses can be made more specific by limiting them to a particular set of atoms in the system. For example, in a determination of the diffusion coefficient of a gas through a porous

material, it is the movement of the gas molecules that is of interest. Hence, MSD calculation can be carried out on a set composed of gas molecules⁶¹. For our case, we are interested in the MSD of Li⁺ ions in the PEO in absence and presence of silicate nanoparticles. Our other variables are the silicate nanoparticle size and the number of nanoparticles; thus, we are also analyzing the system for nanoparticle concentrations for the same size of nanoparticle. MSD are analyzed for Li⁺ ions for all 3 different models of 13 different systems.

Next, time dependent diffusion coefficient (D) was calculated by using

$$D(n\Delta t) = \frac{MSD(n\Delta t)}{6n\Delta t} \quad (2.2)$$

This expression is called the Einstein relation since it was first derived by Albert Einstein in his Ph.D. thesis in 1905. The factor of 6 in EQUATION 2.2 becomes 4 for a two-dimensional system and 2 for a one dimensional system. For our case, we used six for three dimensional periodic cell.

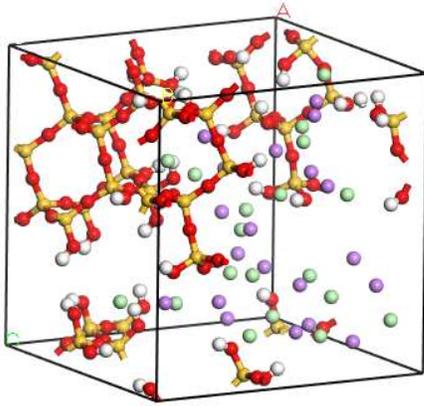
2.3 Results and Discussions

MD simulations were performed for all 3 different initial structures of 13 different systems of PEO-silicate composite cells. After a system equilibration time of 30 ps, the dynamics of the system were recorded for 100 ps. All results below are extracted from these 100 ps simulations.

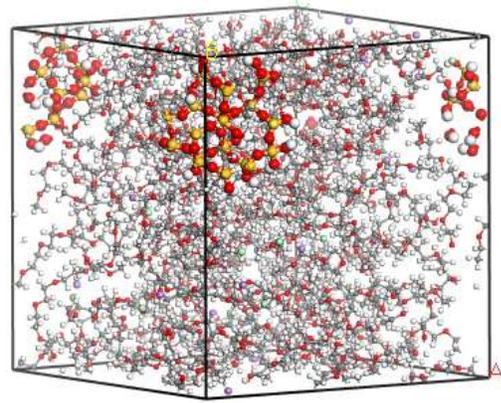
2.3.1 Time Trajectory of PEO Interaction with Nanoparticles

Snapshots taken from the MD simulation trajectories of the PEO electrolyte cells are given in FIGURE 2.2. These snapshots depict the interaction between PEO chains and nanoparticle in the modelled cells. From the initial time steps to the end of the simulations, the conformations of the PEO polymer chains have been observed in the cells when there is A) only one silicate nanoparticle with ions, B) one silicate nanoparticle with PEO chains and ions in the system, C) two silicate nanoparticles with ions, D) two silicate nanoparticles with PEO chains and ions in the system, E) three silicate nanoparticles with ions, and F) three silicate nanoparticles with PEO chains and ions in the system. No wrapping of the PEO polymer chains around the nanoparticle or any of adsorption have been observed from the visuals of the trajectories. No significant gaps in the polymer density or no breakage of the polymer chains have been observed from the visuals of the trajectories.

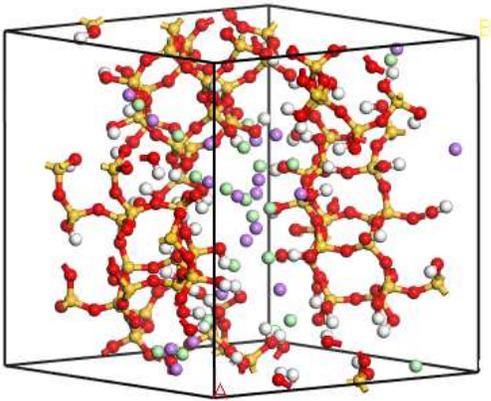
A)



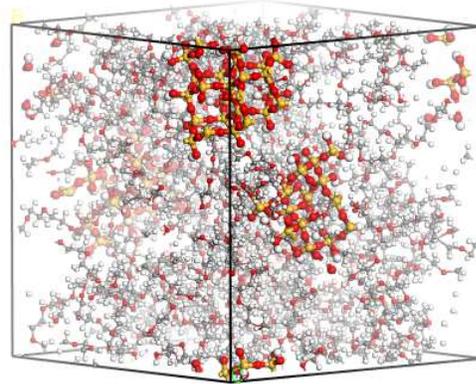
One nanoparticle with ions only



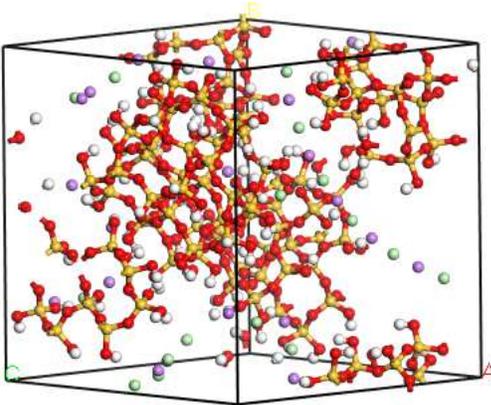
B) One nanoparticle, PEO chains and ions



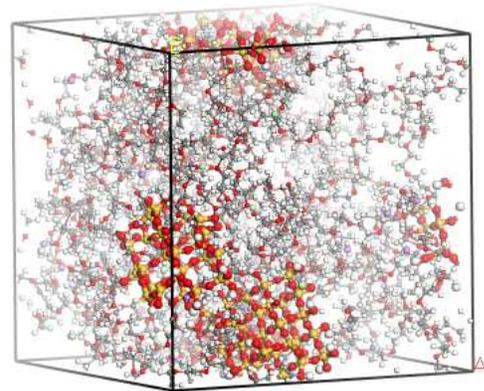
C) Two nanoparticles with ions only



D) Two nanoparticles, PEO chains and ions



E) Three nanoparticles with ions only



F) Three nanoparticles, PEO chains and ions

FIGURE 2.2 MD snapshots of cells when there is A) one nanoparticle with ions only, B) one nanoparticle, PEO chains and ions, C) two nanoparticles with ions only, D) two nanoparticles, PEO chains and ions, E) three nanoparticles with ions only, F) three nanoparticles, PEO chains and ions, The colors used for the polymer represent the following atoms: carbon is grey, hydrogen is white, oxygen is red, silicon is yellow, lithium ion is violet and chloride ion is green.

2.3.2 MSD Analysis of Lithium-ion

MSD have been calculated for Li^+ ions for all 3 different models of 13 different systems. Average MSD of Li^+ as a function of number of silicate nanoparticles have been calculated and plotted in FIGURE 2.3. FIGURE 2.3 depicts that MSD of Li^+ is higher for a system that has nanoparticles than the system without any nanoparticles. The addition of one nanoparticle and two nanoparticles in the system increased the MSD of Li^+ by up to 285% to 425% respectively.

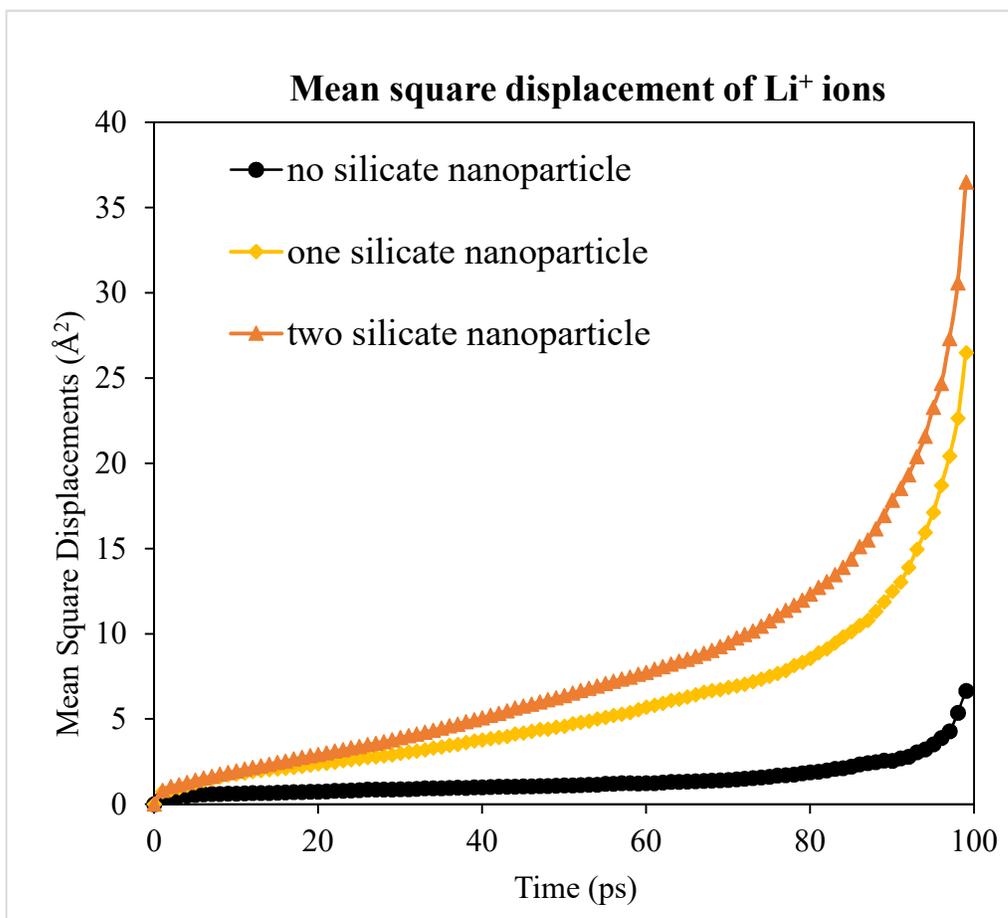


FIGURE 2.3 MSD of Li⁺ as a function of number of silicate nanoparticles

MSD of Li⁺ as a function of type of silicate nanoparticles has been plotted in FIGURE 2.4. FIGURE 2.4 illustrates a random pattern in Li⁺ MSD due to the change of type of silicate nanoparticle. Using the MSD values, we have calculated the time dependent diffusion coefficient, D (refer to EQUATION 2.2) in the next section which better represents the ionic conductivity in an electrolyte cell.

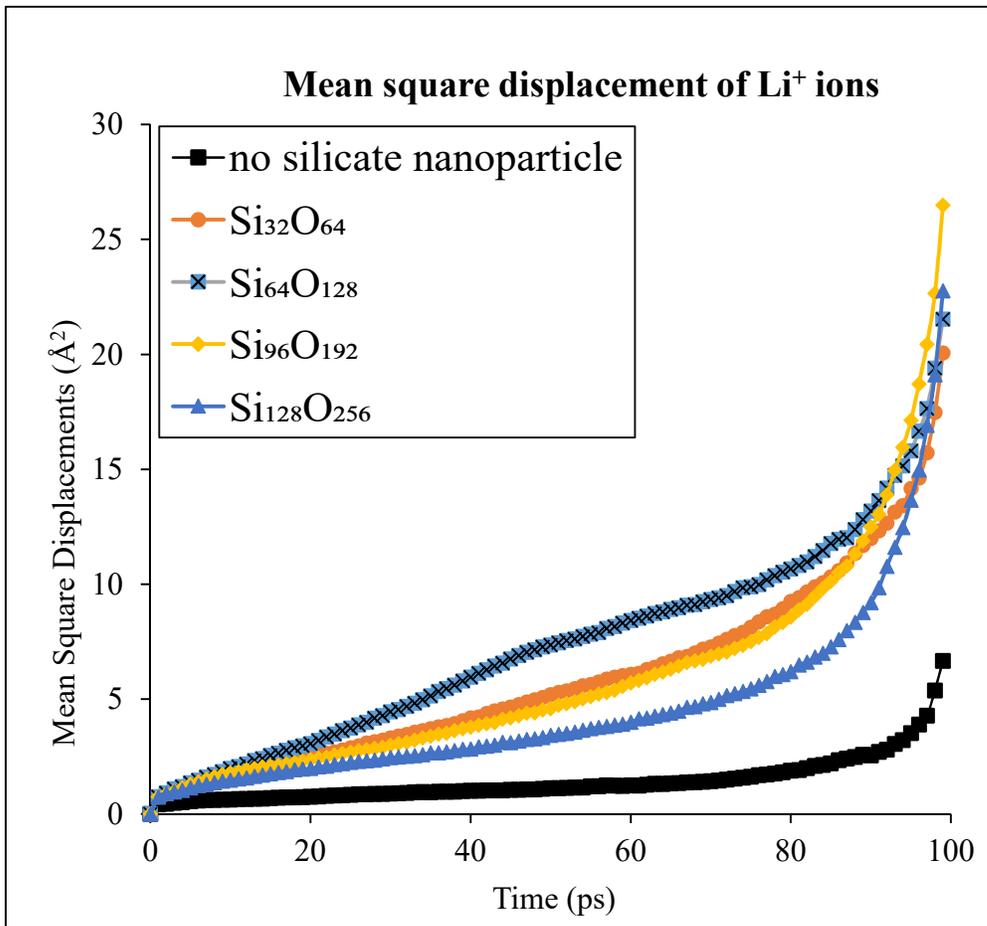


FIGURE 2.4 MSD of Li⁺ as a function of type of silicate nanoparticles

2.3.3 Time Dependent Diffusion Coefficient, D

Time dependent diffusion coefficient, D was calculated from the calculated average MSD of Li⁺ for all the systems. D as a function of number of silicate nanoparticles has been plotted in FIGURE 2.5 that represents the effect of number of silicate nanoparticles on Li⁺ diffusivity in electrolyte cell. FIGURE 2.5 depicts that D increases with the increase of number of nanoparticles in the electrolyte system. For almost all of the models, the increase in D is more for

3 nanoparticles including system as compared to having only 0, 1 and 2 nanoparticles in the system.

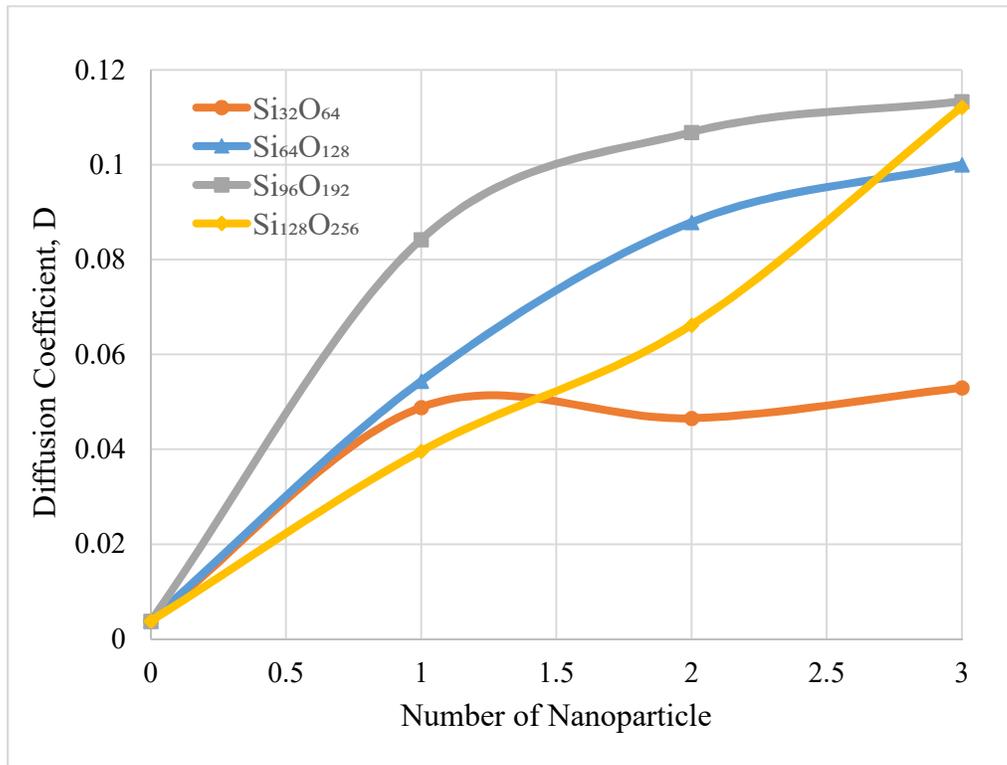


FIGURE 2.5 Diffusion Coefficient (D) as a function of number of silicate nanoparticles

Relatively smaller Si₃₂O₆₄ nanoparticle did not increase the D value as much as larger nanoparticles. In addition, Si₁₂₈O₂₅₆ nanoparticle have different trend for D values than other nanoparticle.

We also can observe the effect of silicate nanoparticle size on Li⁺ diffusivity in electrolyte system from FIGURE 2.5. FIGURE 2.5 represents that the bigger the size of the

nanoparticle, the higher the diffusion coefficient. For 1 silicate nanoparticle systems, the diffusion coefficient for the model with $\text{Si}_{128}\text{O}_{256}$ is much higher than that of $\text{Si}_{96}\text{O}_{192}$, $\text{Si}_{64}\text{O}_{128}$ and $\text{Si}_{32}\text{O}_{64}$ based models. In general, the pattern is the same for 2 silicate and 3 silicate nanoparticle systems. However, the diffusion coefficient value is almost similar for 3 silicate nanoparticle systems based on $\text{Si}_{128}\text{O}_{256}$ and $\text{Si}_{96}\text{O}_{192}$. The reason might be the very small size difference between these two nanoparticles (refer to chapter 2.3.2). We think that the cell size constructed for this study is small for 2 and 3 nanoparticle as large as $\text{Si}_{128}\text{O}_{256}$ nanoparticle. For other three silicate nanoparticle with $\text{Si}_{32}\text{O}_{64}$, $\text{Si}_{64}\text{O}_{128}$ and $\text{Si}_{96}\text{O}_{192}$ structures, diffusion coefficients are increasing both with particle size and number.

2.3.4 Radial Distribution Function, RDF

To compare the structural properties of the solid polymer electrolyte interacting with the Li ions in the systems, radial distribution functions (RDF) have been calculated and illustrated in FIGURE 2.6. RDF plot for Li^+ - oxygen in PEO depicts the highest peak which indicates the strongest interaction is between oxygen in PEO and Li^+ in the system. Second strongest interaction is between oxygens in PEO and surface hydrogens of silicate and the weakest interaction is between Li^+ and silicate oxygens.

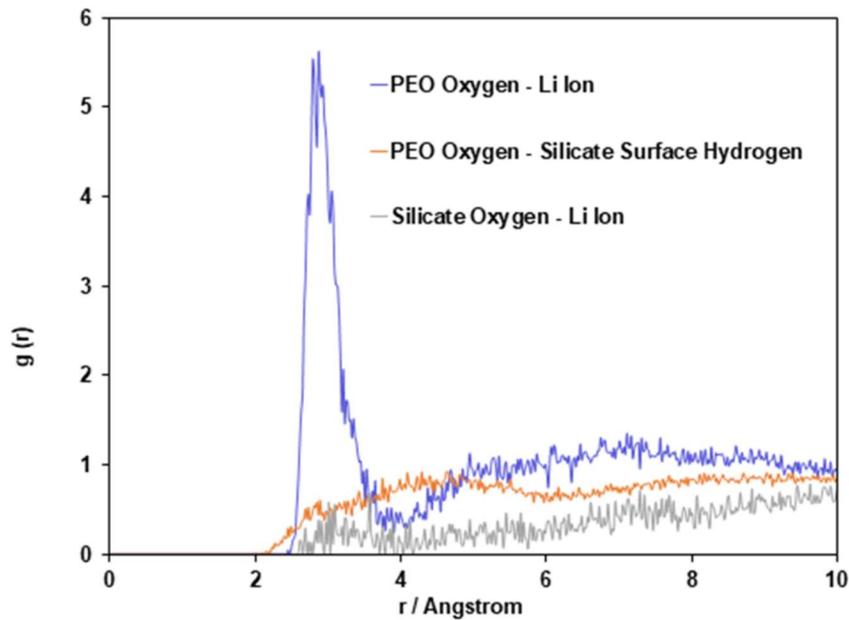


FIGURE 2.6. Radial distribution functions for Li^+ - Oxygen in PEO, Surface Hydrogen in SiO_2 - Oxygen in PEO, and Li^+ - Oxygen in SiO_2 for electrolyte system with two $\text{Si}_{32}\text{O}_{64}$ nanoparticles.

2.4 Conclusion

The MD simulations indicate that Li^+ diffusivity is increased significantly when silicate nanoparticles are included in the PEO matrix. The simulations also provide an indication of the increase in Li^+ diffusivity with the increase in silicate nanoparticle sizes. Further studies on the ionic conductivity calculation might provide a direct guideline on utilizing these materials for experimental applications. Cell sizes should be larger to get better results for larger nanoparticles. Otherwise high weight ratio of large nanoparticles change the mobility and

moving trajectory of Li^+ ions inconsistently. Even nanoparticles can increase the mobility of Li^+ ions, the major component of polyelectrolyte should still be polymer.

CHAPTER 3

Concluding Remarks

3.1 Overview

Solid state electrolyte science for Li^+ ion batteries are active fields of research but there is still an immense scope of further work necessary to fully understand how to control their properties in distinct environments. Composite solid electrolytes have proven to be more efficient materials, but the large scale and commercial production along with usage is yet to be mastered. Some of the future work proposed below may help in expanding the dimensions towards more efficient composition for Li^+ battery, or may lead to the characterization and production methods for the composite solid electrolytes.

3.2 Toward More Accurate Models

The work presented in the previous chapters is insightful on understanding the underlying chemistry for Li^+ diffusivity in silicate nanoparticle dispersed PEO polymer electrolyte system. But these models have been constructed with many approximations, such as modeling very small size nanoparticle. The extensions to the work suggested here in this section might help correlate atomic-level composition details to the real-world experimental systems.

3.2.1 Effects of Simulation Time

These simulations have been run for a very short time. Even though the result investigated in this study is pretty significant, the simulations should be run for prolonged time to better correlate these results to real systems. Since the system density is high, nanoparticle

mobility is slow and system equilibrated very fast we could get good results even for short time period.

3.2.2 Effects of Nanoparticle Types

In this study, we have modelled solid composite electrolyte using only one type of nanoparticle which is silicate. However, further studies should be carried on for other nanoparticle systems like TiO_2 and Al_2O_3 which are also used as fillers in experiments. Since the objective of this study is to predict and recognize the parametric effects in a polymer composite electrolyte system which is hard to achieve from experiments, studying other nanoparticle based system is very essential to help design a suitable polymer electrolyte system that will meet the increasing demand for electrochemical power sources.

3.2.3 Mechanical Properties

Along with the ionic conductivity in such solid composite electrolyte, mechanical properties like modulus, breaking strains and stiffness of the electrolyte materials are also relevant and important. It is well known that silicate nanoparticles, clays, zeolites and POSS structures can increase the mechanical properties of soft materials such as PEO polyelectrolytes^{35,36}. Further studies can be done to measure the mechanical properties of such solid composite electrolyte system to better understand the shelf life and flexibility of this electrolyte material.

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