Supporting Information

Mechanistic Insight into the Improved Li Ion Conductivity of Solid Polymer Electrolytes

Sudeshna Patra,[1,#] Pallavi Thakur, [1, #] Bhaskar Soman,[1,#] Anand B. Puthirath,[1,2] Pulickel M. Ajayan,[2] Santosh Mogurampelly,[3,£*] Karthik Chethan V. ,[4*] and Tharangattu N. Narayanan[1*]

[1]Tata Institute of Fundamental Research - Hyderabad, Sy. No. 36/P, Gopanapally Village, Serilingampally Mandal, Hyderabad - 500107, India.

[2]Department of Materials Science and Nanoengineering , Rice University, Houston, TX 77005, USA.

[3] Institute for Computational Molecular Science, Temple University, Philadelphia, PA 19122, USA.

[4]Department of Chemical Engineering, BITS Pilani Hyderabad Campus, Jawahar Nagar, Shameerpet, Hyderabad - 500078, India.

[£]Department of Physics, Indian Institute of Technology Jodhpur, Rajasthan 342037 INDIA.

([#] Equally Contributing Authors. *Corresponding Authors: tnn@tifrh.res.in or tn_narayanan@yahoo.com (T. N. N.), kvenk@hyderabad.bits-pilani.ac.in (K.C.V.), and santosh@iitj.ac.in (S. M.). [£] Present Address)

Figure S1. Photographs of LiPEOP SEs.

Sample	Amount of LiClO4(g)	Amount of PEO(g)	Amount of PDMS(mL)	Amount of cross-linker(uL)
10% LiPEOP	**0.01**	**0.1**	**0.5**	**100**
20% LiPEOP	**0.02**	**0.1**	**0.5**	**100**
30% LiPEOP	**0.03**	**0.1**	**0.5**	**100**

Table S1: Detailed composition of each precursor of the solid polymer electrolyte membrane.

The Sylgard 184 Silicone Elastomer from Dow Corning is supplied as two part liquid component kit (1:1 ratio of base and curing agent)

The Base (part A) contains the followings:

1. Dimethyl siloxane, dimethylivinyl terminated
2. Dimethylvinylated & trimethylated silica
3. Tetra (trimethoxysiloxy) silane
4. Ethyl benzene

Volatile Organic Compound (VOC) content: 8 grams/liter

The Curing Agent (part B) contains the followings:

1. Dimethyl methylhydrogen siloxane
2. Dimethyl siloxane, dimethylvinyl terminated
3. Dimethylvinylated and trimethylated silica
4. Tetramethyl tetravinyl cyclotetra siloxane
5. Ethyl benzene

Maximum VOC content including water: 85 grams/liter

Section I. Conversion of Buckingham potential parameters to Lennard-Jones parameters for PDMS.

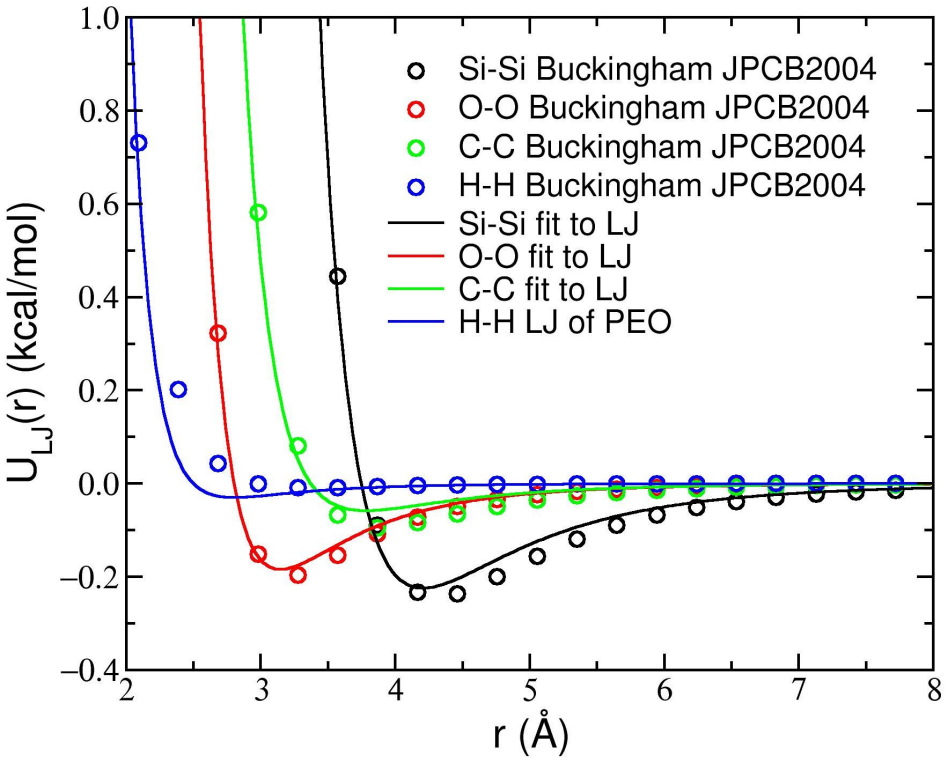

Figure S2. Fitting the Buckingham potential parameters of Borodin and Smith[1] with the Lennard-Jones model. The fitted LJ parameters are shown in the full list of FF parameters in this SI.

Section II. Mean squared displacement of ions

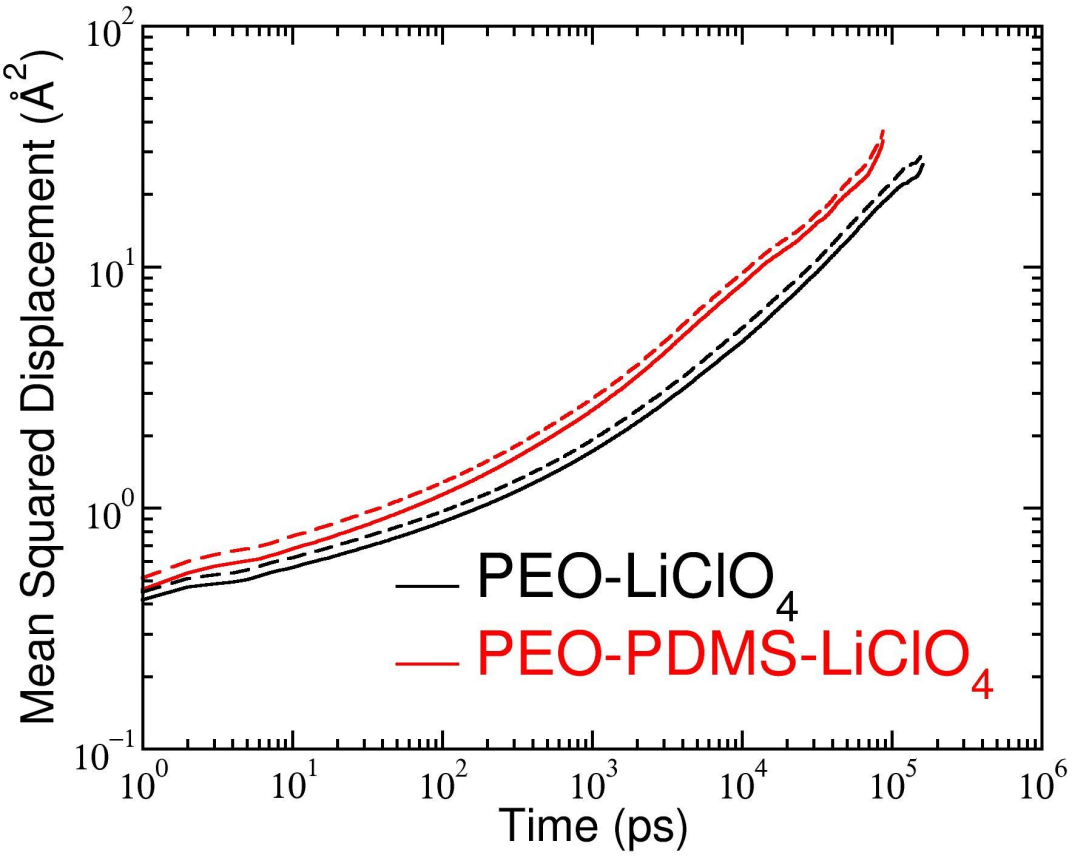

Figure S3. Mean squared displacement of ionic species in the PDMS loaded and unloaded electrolytes. The PDMS is seen to increase the diffusion of ions in the electrolytes.

Section III. Radial distribution functions

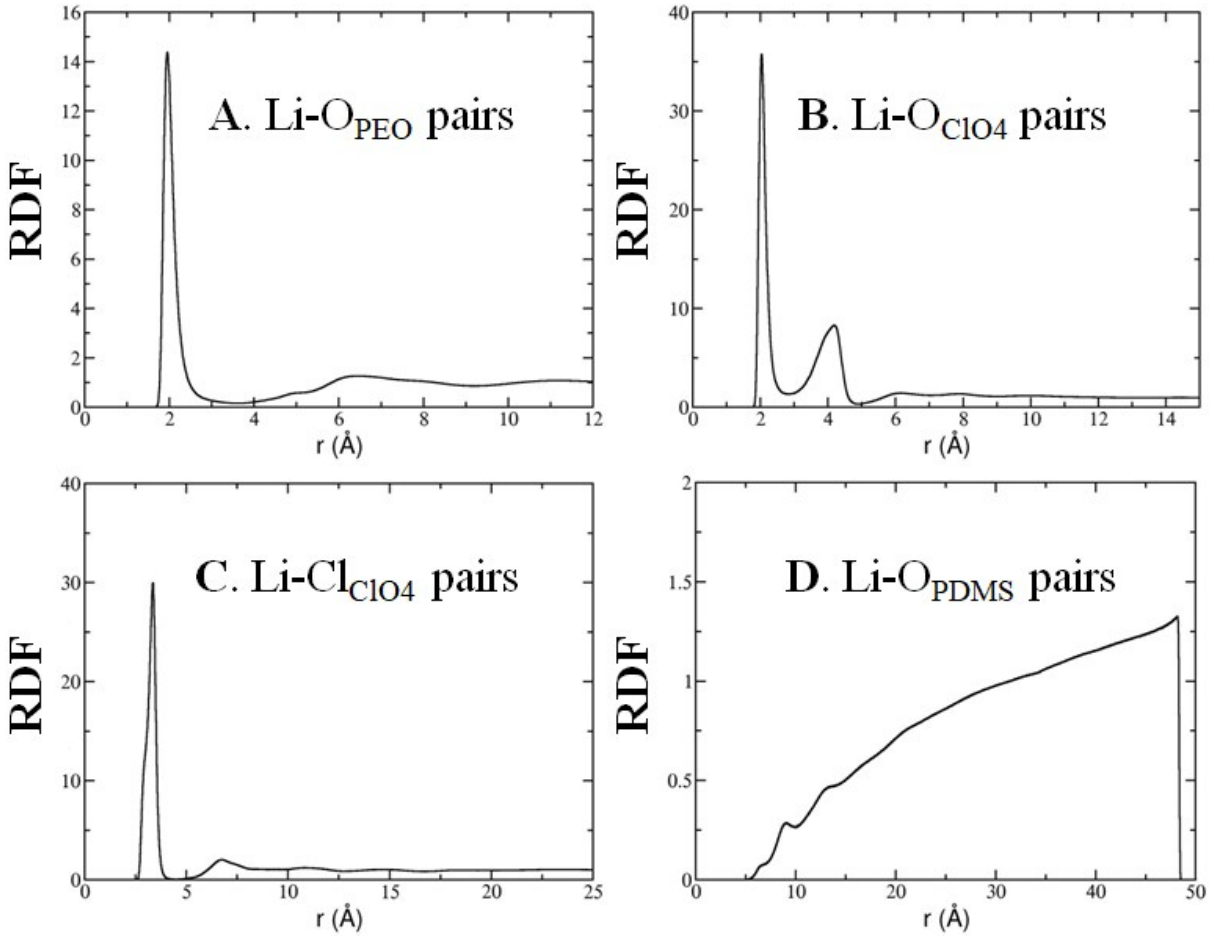

Figure S4. Radial distribution functions (RDF) in LiPEOP electrolyte depicting the lithium ion interaction with the polymer, anions and PDMS.

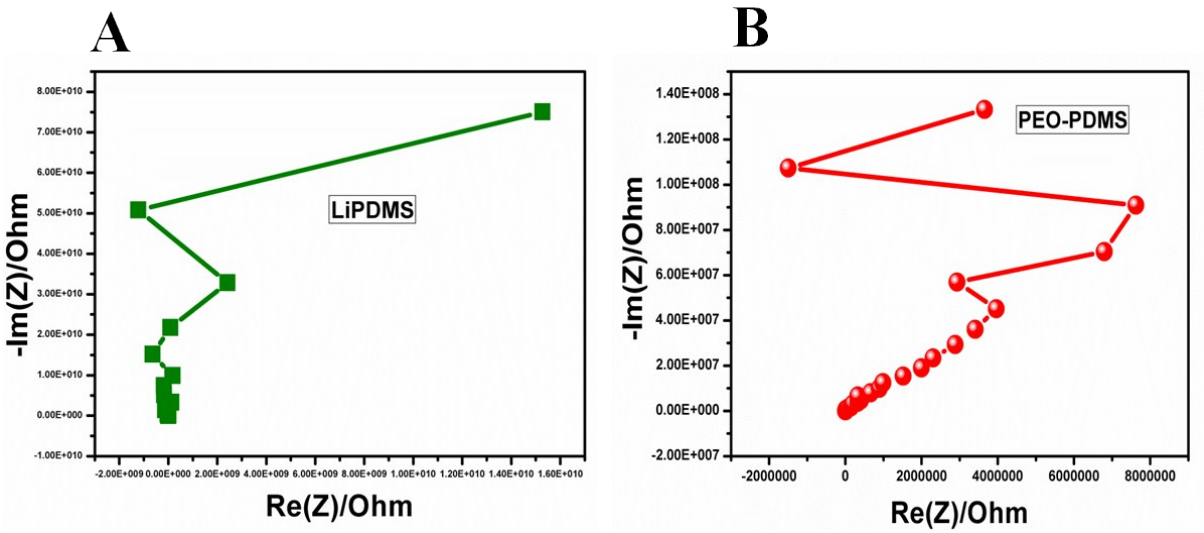

Figure S5. The EIS studies (Nyquist plots) on PEO-PDMS (without salt) and LiPDMS (without PEO) membranes - indicating the absence of any ionic conductivity in these membranes.

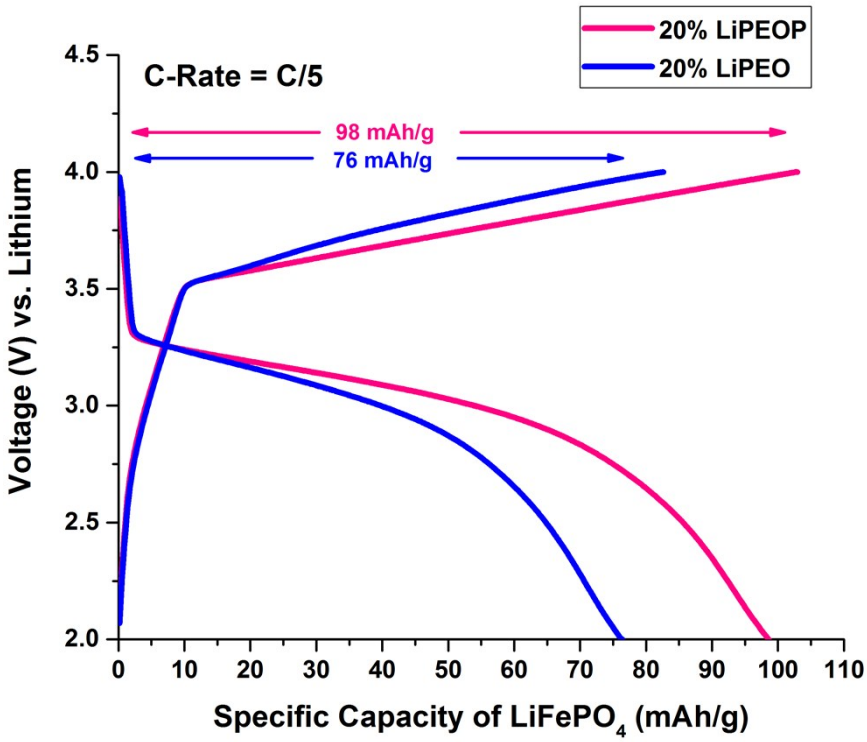

Figure S6. Charge-discharge cycles showing the effect of addition of PDMS in 20% PEO electrolyte on the 2nd cycle of charge- discharge of $LiFePO_4$ half cells at C/5 rate (0.2C).

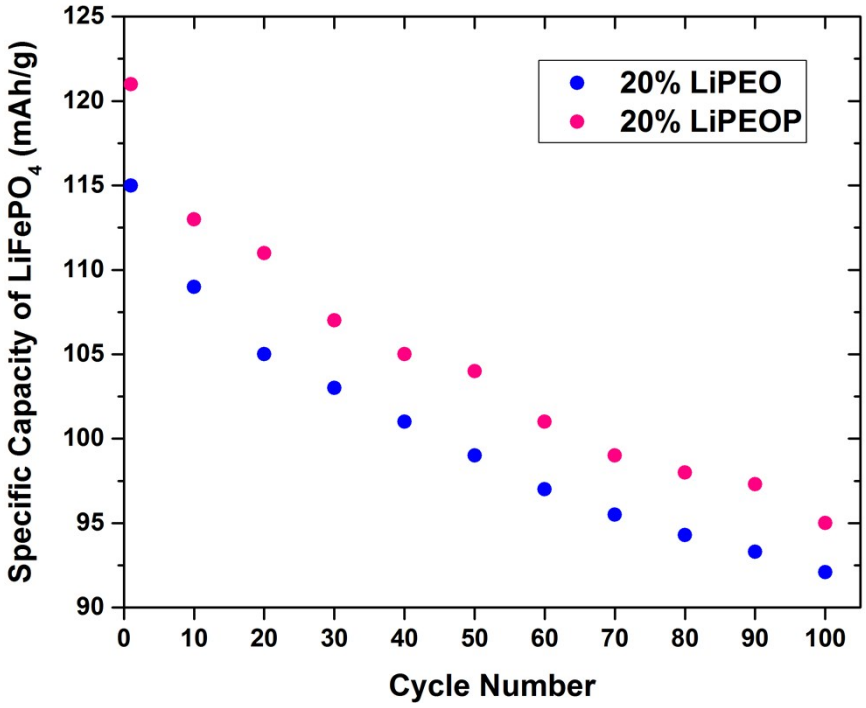

Figure S7. The specific (discharge) capacity *vs* number of cycles (charge-discharge) for both 20% LiPEO and LiPEOP indicating the performance stability under 0.02C.

Section IV. Full list of force field parameters in LAMMPS format:

Generated by Santosh Mogurampelly
Contact: santosh@iitj.ac.in
#
#ref2: santosh2017 for PEOLIPF6
(adapted from original reference to be cited is OPLS: W. Jorgensen, D. Maxwell, and J. #TiradoRives, J. Am. Chem. Soc. 118,11225 (1996).)
Santosh Mogurampelly and Venkat Ganesan "Structure and mechanisms underlying ion #transport in ternary polymer electrolytes containing ionic liquids" J. Chem. Phys. 146, #074902 (2017) https://aip.scitation.org/doi/pdf/10.1063/1.4976131
#ref3: OPLS1996: W. Jorgensen, D. Maxwell, and J. TiradoRives, J. Am. Chem. Soc. #118,11225 (1996)
#JPCB2008: Klähn, M.; Seduraman, A.; Wu, P., A Force Field for Guanidinium-Based Ionic #Liquids That Utilizes the Electron Charge Distribution of the Actual Liquid: A Molecular #Simulation Study. J. Phys. Chem. B 2008, 112,10989-11004.
#OPLSJCTC2009: S.V. Sambasivarao, O. Acevedo, Development of OPLS-AA Force Field #Parameters for 68 Unique Ionic Liquids; J. Chem. Theory Comput., 2009, 5, 1038-1050.
#OPLSJCTC2017: B. Doherty, X. Zhong, S. Gathiaka, B. Li, O. Acevedo, Revisiting OPLS #Force Field Parameters for Ionic Liquid Simulations; J. Chem. Theory Comput., 2017, 13, #6131-6145
#PDMSJPCB2004: James S. Smith, Oleg Borodin, and Grant D. Smith, "A Quantum #Chemistry Based Force Field for Poly(dimethylsiloxane)", J. Phys. Chem. B, Vol. 108, No. #52, 2004
#UFF Balbuena1999: Tao Li and Perla B. Balbuena, "Theoretical Studies of Lithium #Perchlorate in Ethylene Carbonate,
#Propylene Carbonate, and Their Mixtures", J. Electrochem. Soc. 146 (10) 3613-3622 (1999
#
#WICKJPCB2012: Hui Wu, Oneka T. Cummings, and Collin D. Wick, J. Phys. Chem. B #2012, 116, 14922−14932, "Computational Investigation on the Effect of Alumina Hydration #on Lithium Ion Mobility in Poly(ethylene oxide) LiClO4 Electrolytes" #https://pubs.acs.org/doi/pdf/10.1021/jp307794r
#CLO4- from BAADEN2000: M. Baaden, F. Berny, C. Madic, and G. Wipff, "M3+ #Lanthanide Cation Solvation by Acetonitrile: The Role of Cation Size, Counterions, and #Polarization Effects Investigated by Molecular Dynamics and Quantum Mechanical #Simulations", J. Phys. Chem. A, 2000, 104 (32), pp 7659–7671 #https://pubs.acs.org/doi/pdf/10.1021/jp001352v
#AMBER for CLO4 by Baaden at https://personalpages.manchester.ac.uk/staff/Richard.Bryce/amber/org/ORG1.frcmod
#
#LUCK1987: G. Heinje, W. A. P. Luck, and K. Heinzinger, J. Phys. Chem. 1987, 91, 331-338, "Molecular Dynamics Simulation of an Aqueous NaClO4 Solution", https://pubs.acs.org/doi/pdf/10.1021/j100286a020

#Structures:
#
PEO: H-[CH2-O-CH2]-H (note: the terminus carbon has different charge than normal C)
PDMS: C3H9-Si-[C2H6OSi]-O-Si-C3H9 (note: the terminus is methyl; structure was built using Materials Studio)
PDMS: note: the terminus silicon has different charge than normal Si

```
#recommended settings in lammps input script
#units          real
#atom_style     full
#pair_modify    tail yes mix arithmetic
#special_bonds  lj/coul 0.0 0.0 0.5
#kspace_style   pppm 1e-5

mass    1 15.99940 # AO
mass    2 12.01120 # BC
mass    3 1.007970 # CH
mass    4 12.01120 # CPD
mass    5 35.45299 # Cl
mass    6 1.007970 # HPD
mass    7 6.941000 # Li
mass    8 15.99940 # OCl
mass    9 15.99940 # OPD
mass    10 28.0855 # SiP

#pair_style     lj/cut/coul/long/gpu    12.0
pair_coeff     1  1  0.1400       2.90   #AO : oxygen in PEO; santoshjcp2017
pair_coeff     2  2  0.0660       3.50   #BC : Carbon in PEO and Terminus Carbon in methyl in PEO
pair_coeff     3  3  0.0300       2.50   #CH : Hydrogen in PEO
pair_coeff     4  4  0.0580       3.37   #CPD: C atom in PDMS; JPCB2004 Buckingham to LJ
pair_coeff     5  5  0.3000       3.469  #Cl : Cl atom in ClO4 anion; BAADEN2000 sigma=1.947*2/2^(1/6) (AMBER TYPE LZ Rmin--> OPLS sigma)
pair_coeff     6  6  0.0300       2.50   #HPD: H atom in PDMS; took as same as Hydrogen in PEO
pair_coeff     7  7  0.1910       1.46   #ELi: Li ion UFF Balbuena1999
pair_coeff     8  8  0.2100       2.96   #OCl: O atom in ClO4 anion; BAADEN2000 sigma=1.6612*2/2^(1/6) (AMBER TYPE O Rmin--> OPLS sigma
pair_coeff     9  9  0.1840       2.80   #OPD: O atom in PDMS; JPCB2004 Buckingham to LJ
pair_coeff     10 10 0.2240       3.75   #SiP: Si atom in PDMS; JPCB2004 Buckingham to LJ
pair_coeff     5  7  0.3500       3.05   #Cl-ELi: This work DFT b3lyp/631g++
pair_coeff     7  8  0.2500       2.25   #ELi-OCl: This work DFT b3lyp/631g++

#bond_style     harmonic
bond_coeff     1       320.00  1.410   #AO-BC; santoshjcp2017
bond_coeff     2       268.00  1.529   #BC-BC
bond_coeff     3       340.00  1.090   #BC-CH
bond_coeff     4       340.62  1.105   #CPD-HPD CVFF
bond_coeff     5       238.00  1.809   #CPD-SiP CVFF
bond_coeff     6       250.00  1.440   #Cl-OCl: LUCK1987
bond_coeff     7       392.80  1.665   #OPD-SiP CVFF

#angle_style    harmonic
angle_coeff    1       50.0  109.5   #AO-BC-BC   ; santoshjcp2017
angle_coeff    2       35.0  109.5   #AO-BC-CH
```

```
angle_coeff    3      60.0  109.5   #BC-AO-BC
angle_coeff    4      37.5  110.7   #BC-BC-CH
angle_coeff    5      33.0  107.8   #CH-BC-CH
angle_coeff    6      44.4  113.5   #CPD-SiP-CPD CVFF
angle_coeff    7      44.1  117.3   #CPD-SiP-OPD CVFF
angle_coeff    8      39.5  106.4   #HPD-CPD-HPD CVFF
angle_coeff    9      34.6  112.3   #HPD-CPD-SiP CVFF
angle_coeff    10     75.0  109.5   #OCl-Cl-OCl  LUCK1987
angle_coeff    11     42.3  113.1   #OPD-SiP-OPD CVFF
angle_coeff    12     31.1  149.8   #SiP-OPD-SiP CVFF

#dihedral_style     opls
dihedral_coeff  1      2.81980 -2.56060  0.82160 -0.92030 #AO-BC-BC-AO
dihedral_coeff  2      0.00000  0.00000  0.46800  0.00000 #AO-BC-BC-CH
dihedral_coeff  3      1.66780 -0.56530 -0.00330 -0.29310 #BC-AO-BC-BC
dihedral_coeff  4      0.00000  0.00000  0.76000  0.00000 #BC-AO-BC-CH
dihedral_coeff  5      0.00000  0.00000  0.30000  0.00000 #CH-BC-BC-CH
dihedral_coeff  6      0.00000  0.00000  0.80000  0.00000 #HPD-CPD-SiP-CPD CVFF
dihedral_coeff  7      0.00000  0.00000 -0.20000  0.00000 #HPD-CPD-SiP-OPD CVFF
dihedral_coeff  8      0.00000  0.00000  0.80000  0.00000 #SiP-OPD-SiP-CPD CVFF
dihedral_coeff  9      0.00000  0.00000  0.60000  0.00000 #SiP-OPD-SiP-OPD CVFF
```

Section V. Contents of the LAMMPS input file for the MD production runs

```
#lammps input file
print                    .
print
==========================================================================
print "Beginning of lammps input file"
print
==========================================================================
print                    .

echo both
units          real
timer          loop
processors      * * *
atom_style     full

boundary       p p p
#package              gpu 1
#pair_style     lj/cut/coul/long/gpu     12.0
pair_style     lj/cut/coul/long     9.0
kspace_style    pppm 1e-5
bond_style     harmonic
angle_style    harmonic
dihedral_style  opls
special_bonds   lj/coul 0.0 0.0 0.5
pair_modify     tail yes mix arithmetic
variable       molname  string  peowt50_pdmswt50_liclo4_15to1

variable       numsteps  index   10000000
variable       nanosec   index   60ns
variable       Tstep     index   2.0
variable       itemp     index   350.0
variable       ftemp     index   350.0
variable       pressure  index   1.0
variable       restfreq  index   500
variable       dcdfreq   index   500
variable       ensemble  index   min_equil
variable       ensemble1 index   heat
variable       ensemble2 index   npt
#read_data     ./data.${molname}
#read_data
/gpfs/projects/arl/tug88733/tnn/peoliclo4/400K_BUCKINGHAM/data.peowt50_pdmswt50_l
iclo4_15to1_npt_40ns_for_BAADEN2000
read_restart    ./peowt50_pdmswt50_liclo4_15to1_npt_40ns.rst2
pair_style     lj/cut/coul/long     9.0
pair_modify     tail yes mix arithmetic
include        ./param.lammps_BAADEN2000
```

```
neighbor        2.0 bin
neigh_modify    delay 1 every 1 check yes
#velocity       all create ${itemp} 11111111 mom yes rot yes dist gaussian

variable        nevery    index 1
variable        nrepeat   index 1000000
variable        nfreq     index 1000000

group           peo type 1 2 3
group           liclo4 type 7 5 8
group           peoliclo4 type 1 2 3 7 5 8
group           pdms type 4 6 9 10
group           pdmsliclo4 type 4 6 9 10 7 5 8

#delete_atoms    group pdms

set             type 5 charge 0.58000 #BAADEN2000
set             type 8 charge -0.3950 #BAADEN2000

print                   .
print
==========================================================================
print "${ensemble2} simulation for ${nanosec} production: ${molname} system"
print
==========================================================================
print                   .

reset_timestep  0
timestep        ${Tstep}
fix             fixshake all shake 0.0001 20 0 b 3 4
fix                     fix${ensemble2} all npt temp ${ftemp} ${ftemp} 100.0 iso ${pressure}
${pressure} 1000.0
fix             fixmomentum all momentum 1000 linear 1 1 1
dump            dumptrj all dcd ${dcdfreq} ${molname}_${ensemble2}_${nanosec}.dcd
dump_modify     dumptrj unwrap yes
thermo          500
variable        avga equal lx
variable        avgb equal ly
variable        avgc equal lz
variable        avgdensity equal density
fix             fixavgdensity all ave/time ${nevery} ${nrepeat} ${nfreq} v_avga v_avgb v_avgc
v_avgdensity file avg_a_b_c_density_${ensemble2}.dat
thermo_style    custom time temp pe etotal press lx ly lz density ebond eangle edihed
restart                                         1000      ${molname}_${ensemble2}_${nanosec}.rst1
${molname}_${ensemble2}_${nanosec}.rst2
restart         500000 ${molname}_${ensemble2}_${nanosec}.rst*
run             ${numsteps} #5 ns
write_data      data.${molname}_${ensemble2}_${nanosec}
log             log.${molname}_${ensemble2}_${nanosec}
```

```
unfix           fix${ensemble2}
unfix           fixmomentum
unfix           fixshake
undump          dumptrj
unfix           fixavgdensity

print                   .
print
==========================================================================
print "DONE"
print
==========================================================================
print                   .
```

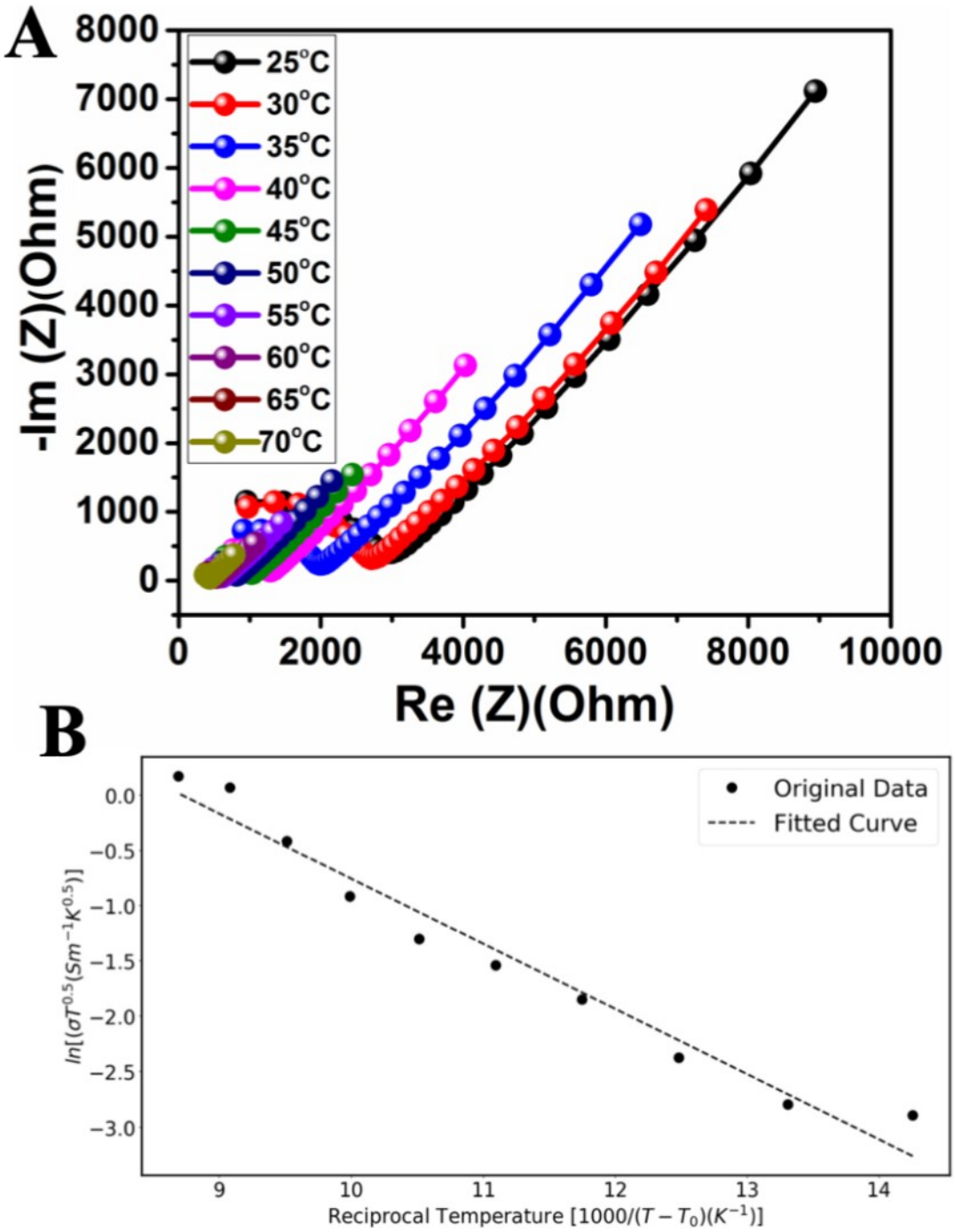

Figure S8. (A): Temperature dependent Nyquist plots for 20% LiPEOP. (B): The temperature dependent ionic conductivity of 20%LiPEOP plot, where it has been fitted using Vogel- Tammann- Fulcher (VTF) model.

Reference:

1. J. S. Smith, O. Borodin, G. D. Smith, *J. Phys. Chem. B*, 2004**, 108**, 20340- 20350.