ppc@12.5

Free Volume Characteristics and Ionic Conductivity in PEO-Based Solid Polymer Electrolytes: a Positron Annihilation Spectroscopy Study

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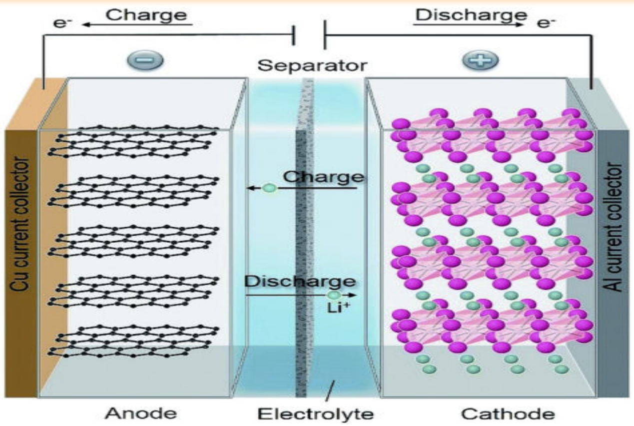
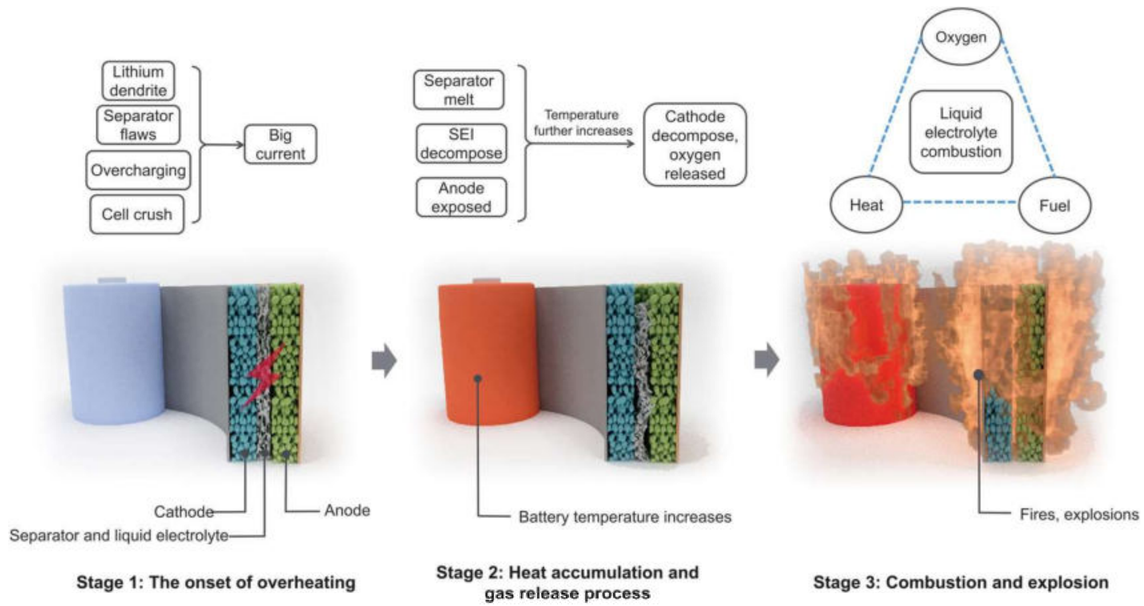
Talk plan

- **Li-ion battery: paradigm shift to solid polymer electrolyte**
- **Solid Polymer Electrolyte: contemporary issues and mitigation**
- **Ionic conductivity in SPE**
- **Effect of filler shape: anisotropic *vs*. spherical nanofiller**
- **Alumina nanorod *vs*. nanoparticle SPE: synthesis, characterization, free volume and conductivity study**
- **Summary & Conclusion**
- **Future studies**

Li-ion battery: paradigm shift to solid polymer electrolyte





K. Liu et al, Sci. Adv. 4 (2018) eaas9820

ALL-SOLID-STATE Li BATTERY

Thermo-mechanical & chemical stability

High flexibility

STATE-OF-THE-ART TECH.

Li salt in organic carbonate (EC, DMC, DEC) liquid

ISSUES OF CURRENT TECH.

Leakage issue, FIRE, Li dendrite growth

IONIC SOLID ELECTROLYTE

High safety

Poor cycle performance

Unstable interface

SOLID POLYMER ELECTROLYTE

fire retardant, suppressed Li dendrite growth, light weight & flexible, easy processing, cost effective

Global Energy Demands: Li-ion Battery at Forefront of Research

<u>Proposition:</u> All-solid-state Li-ion battery

SPE in Li-ion battery: contemporary issues & mitigation

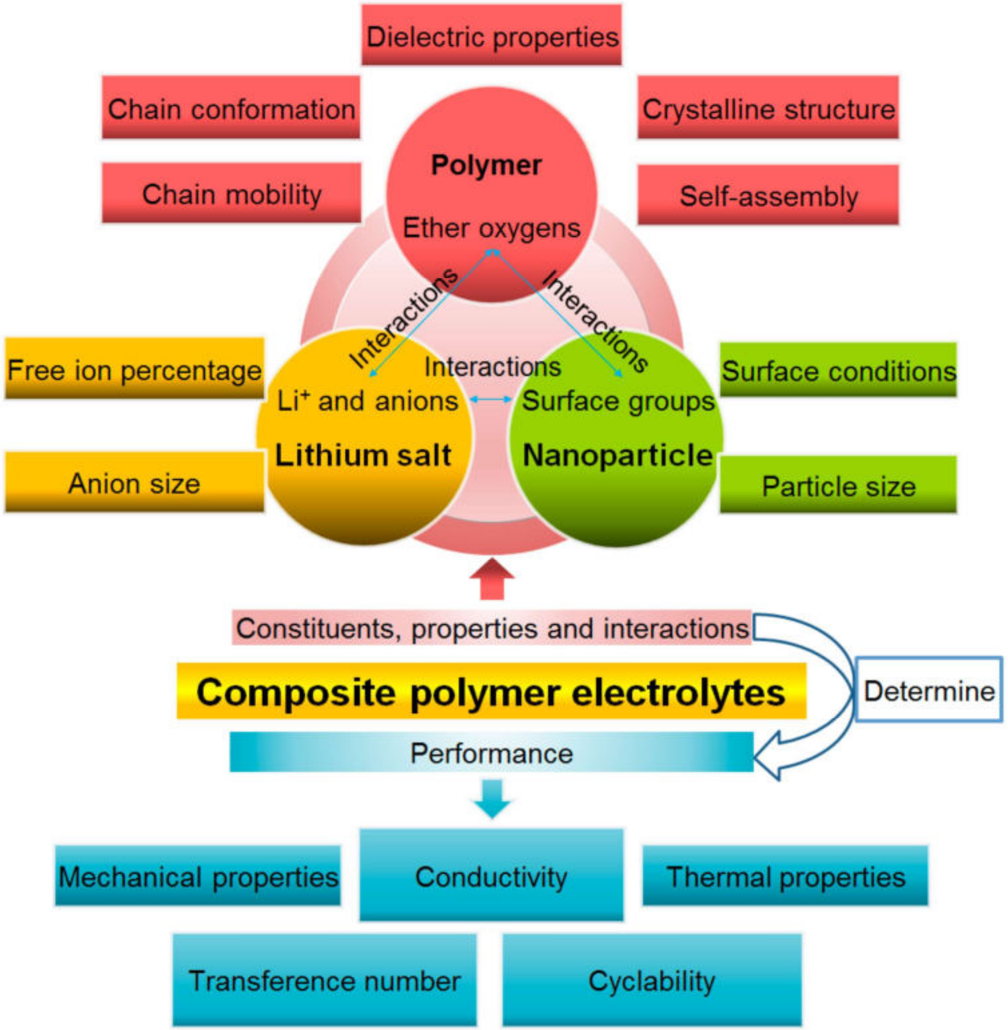
Solid electrolyte desired σ > 10^{-4} Scm^{-1} (for industrial application)

SPE limitation

- Narrow electrochemical window
- Less r.t. conductivity
- Unstable electrode-electrolyte contact
- Dual ion conduction

SPE mitigation

- Ceramic oxide, MOF, ionic liquid as fillers
- Li conducting channels
- Quasi-solid-state electrolyte
- Single Li ion conductor

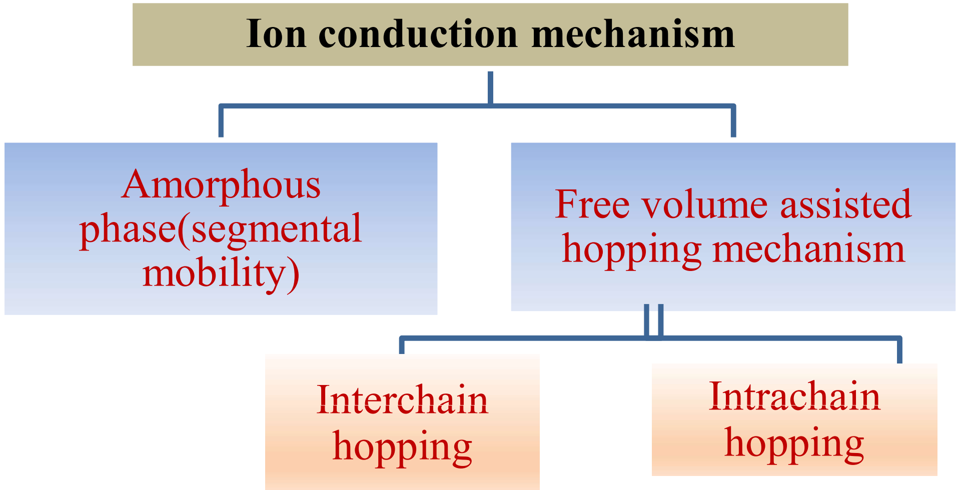


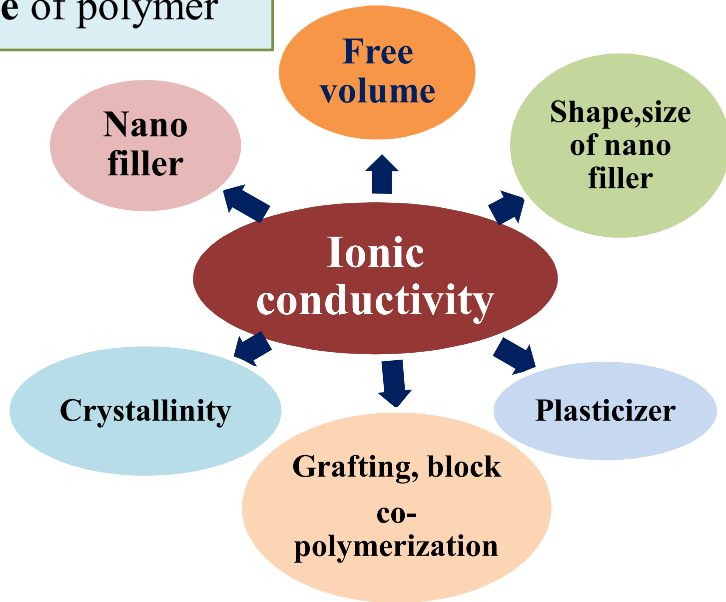
W. Wang et al, Polymers 8 (2016) 387

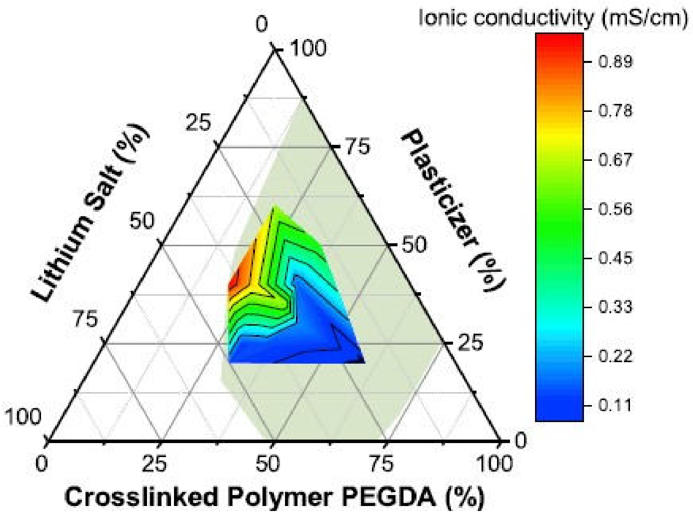
Ionic Conductivity in SPE: Factors and Mechanisms

❖ **Ionic conductivity = (charge carrier concentration)×(mobility)**

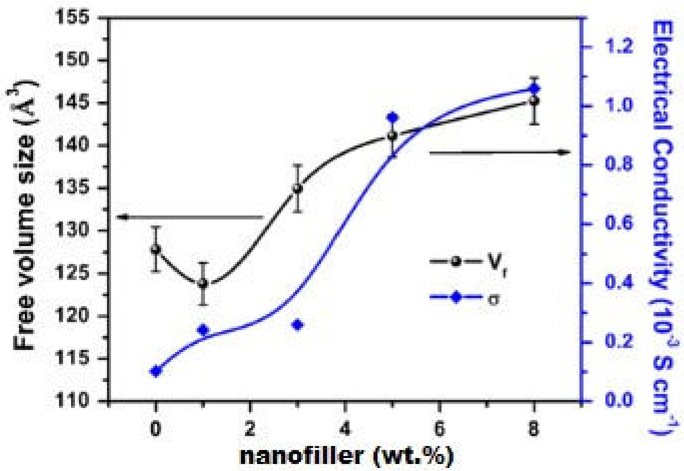
associated with **Segmental Dynamics** & **Free Volume** of polymer





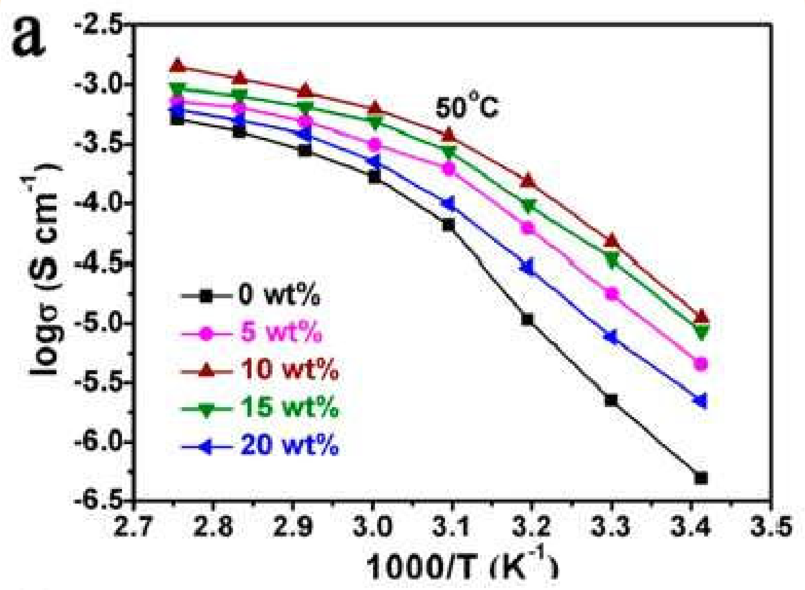


S. Li et al, Joule 2 (2018) 1838–1856

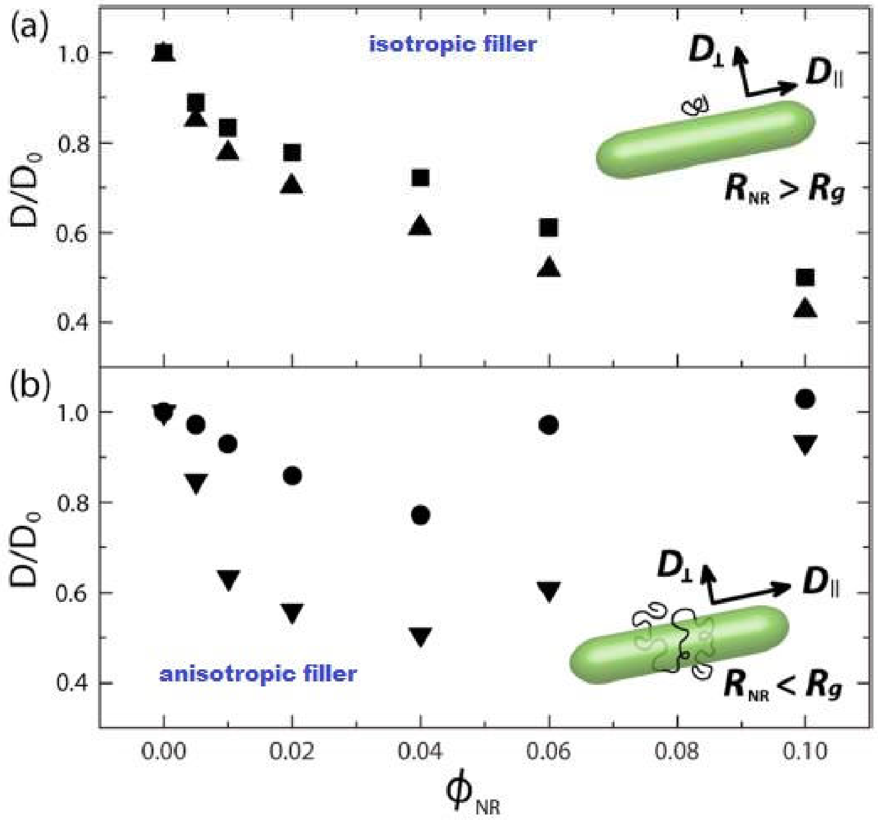


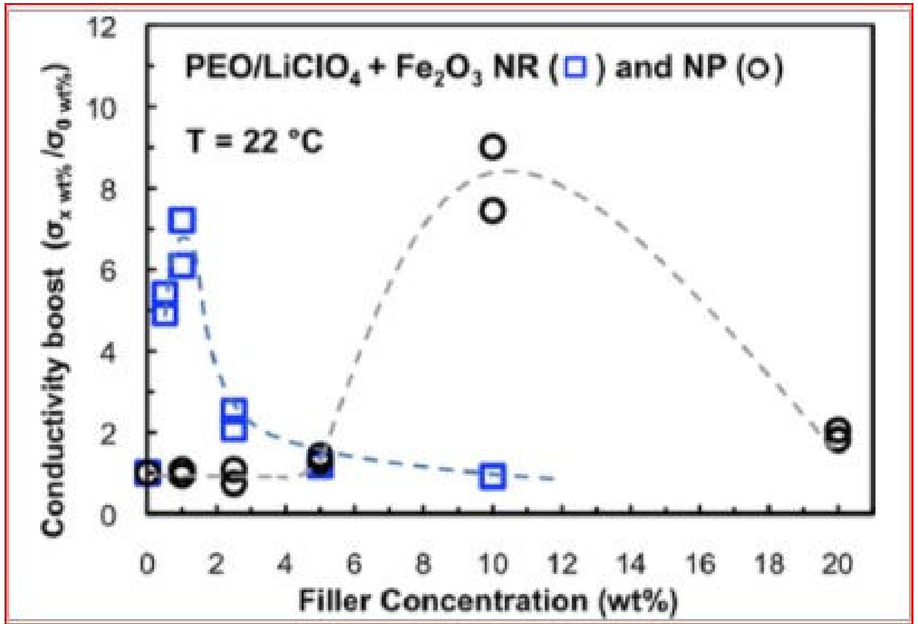
DOI:10.1007/512648-018-1280-7

Effect of filler shape in SPE: Literature survey



O. Sheng et al, Nano Lett. 18 (2018)3104–3112





J. Choi et al, ACS Macro Lett. 3 (2014) 886−891

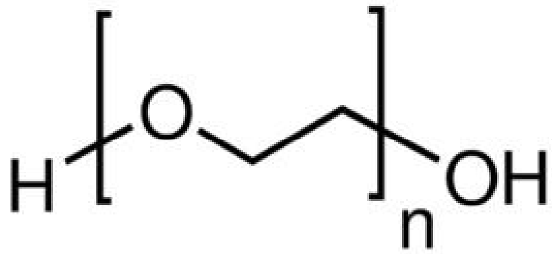
N. Suong et al, J. Phys. Chem. C 116 (2012) 21216–21223

Solid Polymer Electrolyte (SPE) in Li-ion Battery

Polymer: **PEO**, PPO, PVAc, PVDF, PVDF-HFP, PMMA *etc*.

Salt: $LiClO_4$, $LiPF_6$, $LiAsF_6$, **LiTFSI**, LiTf *etc*.

Filler: SiO_2, Al_2O_3, TiO_2 , garnet, IL, MOF *etc*.

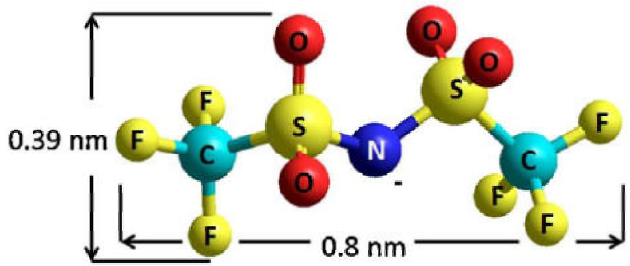


PEO

PEO

- Semicrystalline polymer: flexible backbone
- Excellent Li ion solvation (ion-ether 'O' linkage)
- Low glass transition temperature (~220K)
- High Li^+ donor number

TFSI- Anion



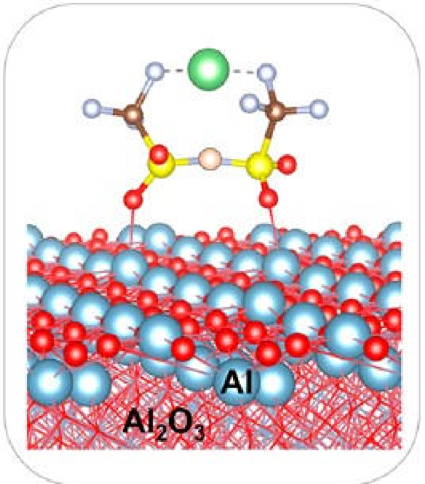
P. Meister et al, Electrochim. Acta 130 (2014) 625–633

❖**LiTFSI advantages**

Easy Dissociation

Big size anion---Less mobility

Single Li ion conductor (SLIC)



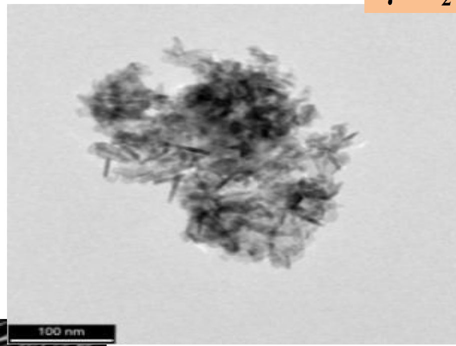
S. J. Kwon et al, Macromolecules 51 (2018) 10194−10201

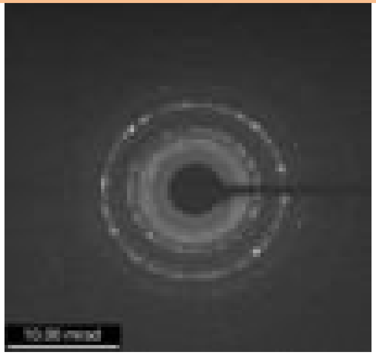
PEO-Al_2O_3 Nanorods Based SPE: Effect of Anisotropic Filler

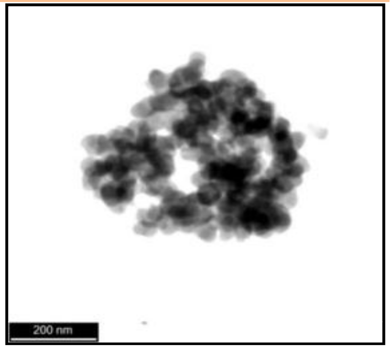
<u>Electrolyte:</u> PEO-5wt% LiTFSI-*x* Alumina nanorod/nanoparticle

<u>SPE preparation:</u> Solvent casting technique in acetonitrile

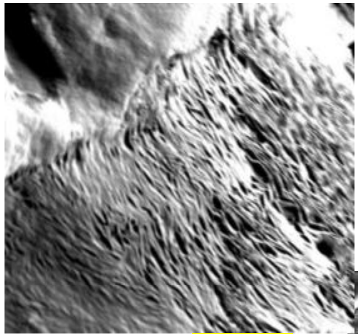
Material	Details
PEO	Mw=300000 Da, Sigma Aldrich
LiTFSI	Sigma Aldrich
Al_2O_3 nanorod	Sigma Aldrich
γ-Al_2O_3 nanoparticle	Otto Chemicals







Nanorods~50-80 nm (length) ~5-8 nm (dia)
Nanoparticles ~ 20-30 nm



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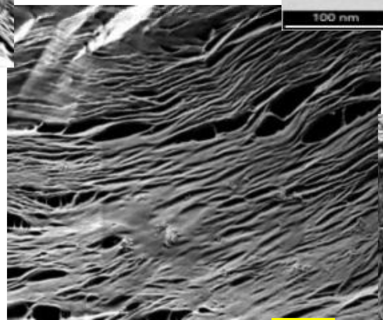

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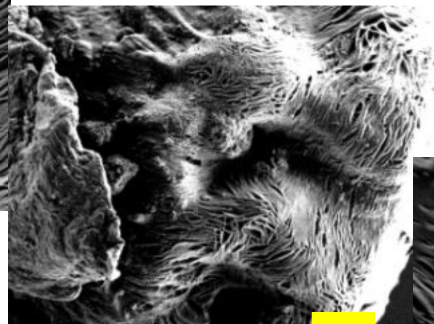

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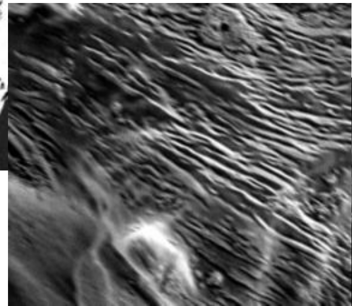

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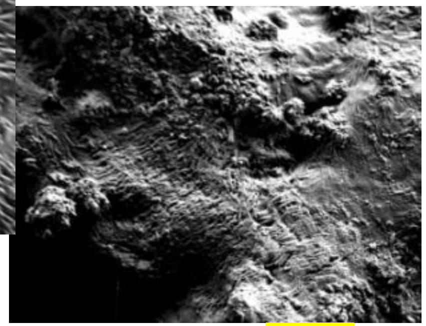

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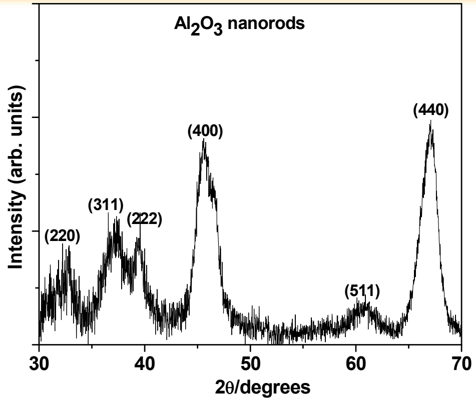
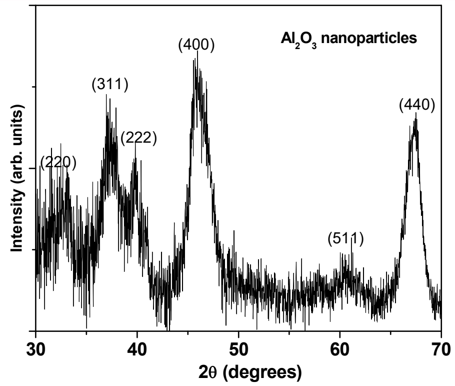
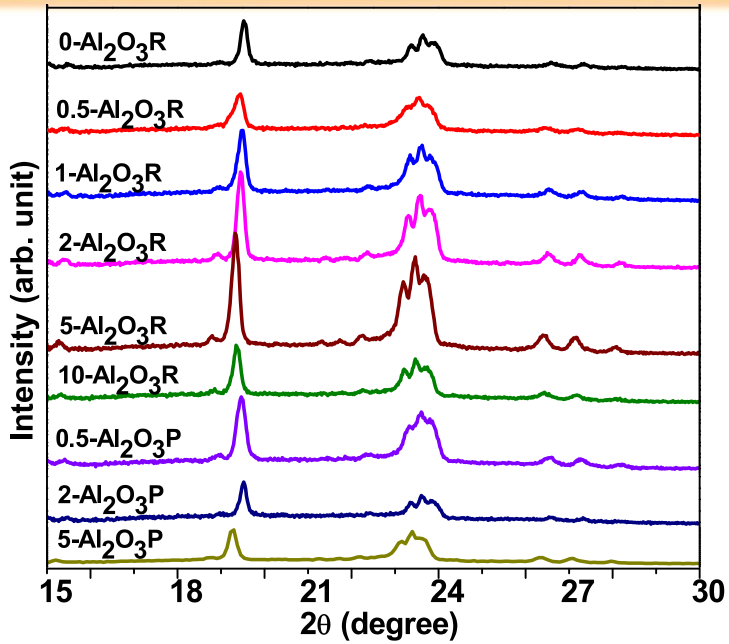
SEM: fractured surface of SPE

- Mechanical strength of the films not hampered due to Al_2O_3 nanorods loading
- Different morphology at highest loading : Aggregation effect

PEO-Al_2O_3 Nanorods Based SPE: Characterization

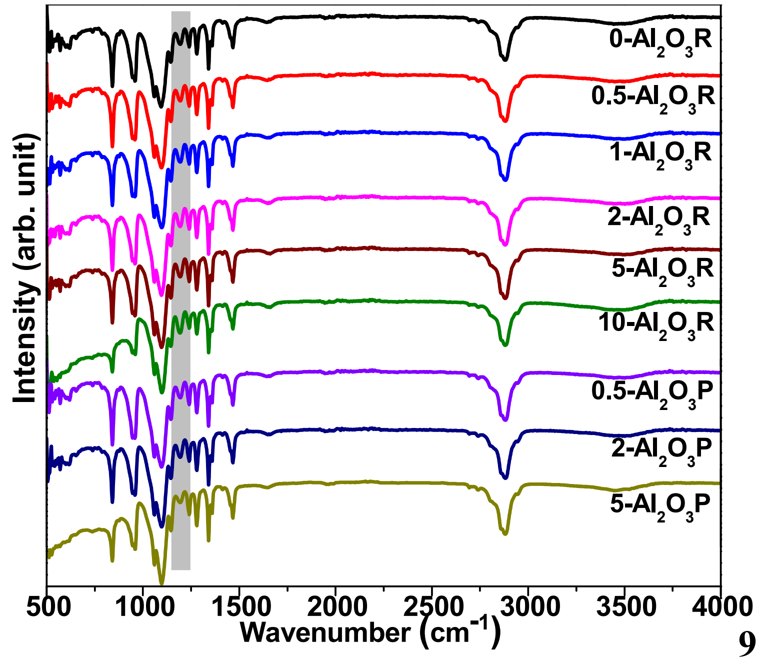




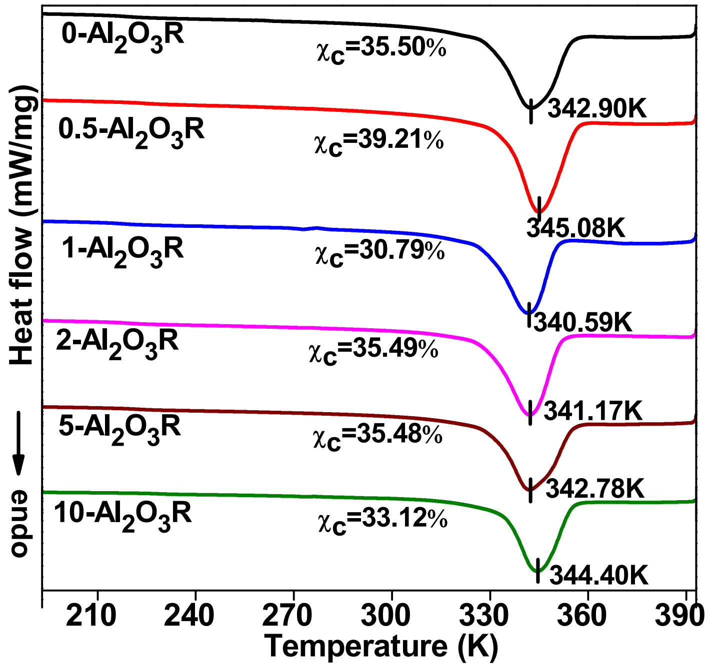


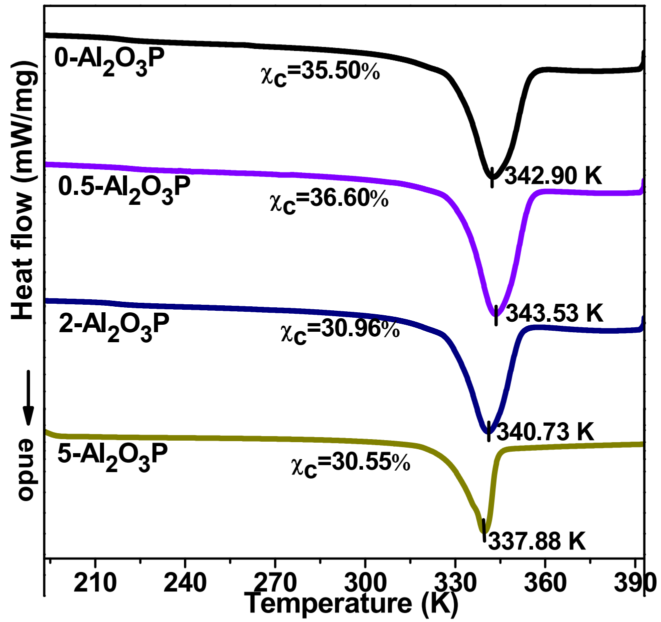
- ❑ Characteristics peaks of Al_2O_3 nanorods and nanoparticles
- ❑ XRD of SPE: characteristic peaks of PEO
  - **2θ~19.0º —interchain distance, 4.67 Å**
  - **2θ~ 23.2º—intrachain fold distance, 3.83 Ǻ**
- ❑ No new peaks in SPE**: fine dispersion of nanofiller**
- ❑ Peak intensity decrease—change in crystallinity

Wavenumber (cm^{-1})	Group
850	C-O-C stretch
1104	Asymm. CH_2 stretch
1190	Li^+—O complex
1460	Symm. C-H stretch
2900	Asymm. C-H stretch
3400	Surface -OH of alumina
Shaded region	TFSI anion



PEO-Al_2O_3 Nanorods Based SPE: Thermal Analysis Using DSC



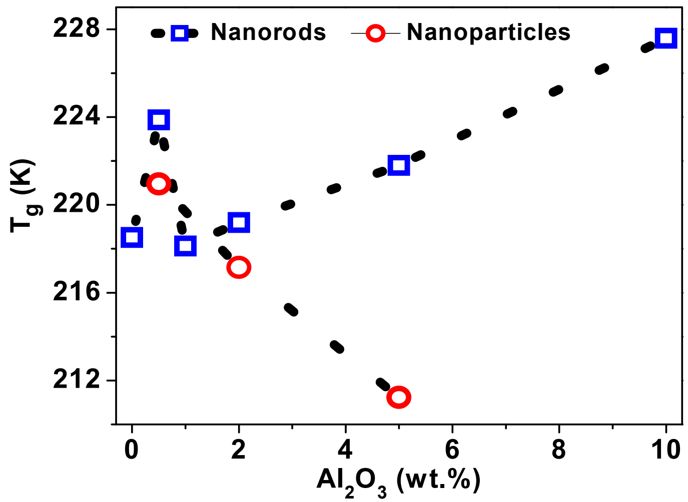


- ❑ Melting point similar**:** crystallite size of PEO in the SPE samples similar
- ❑ **Change in crystallinity**

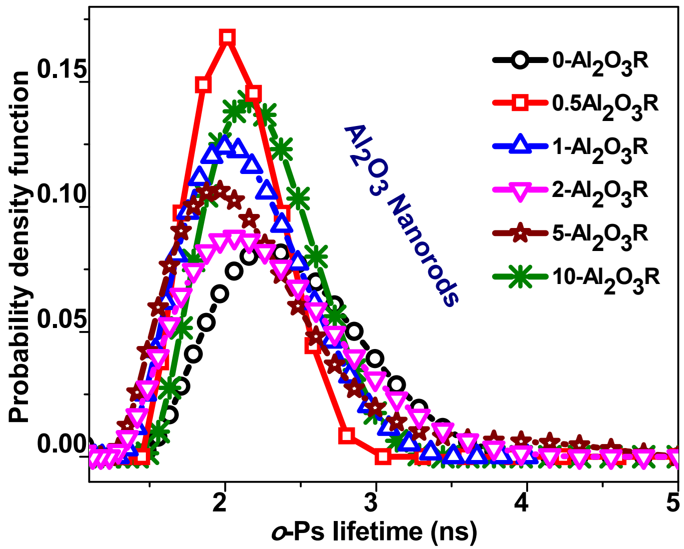
  increases for lowest loading**:** “**anti-plasticization effect**”

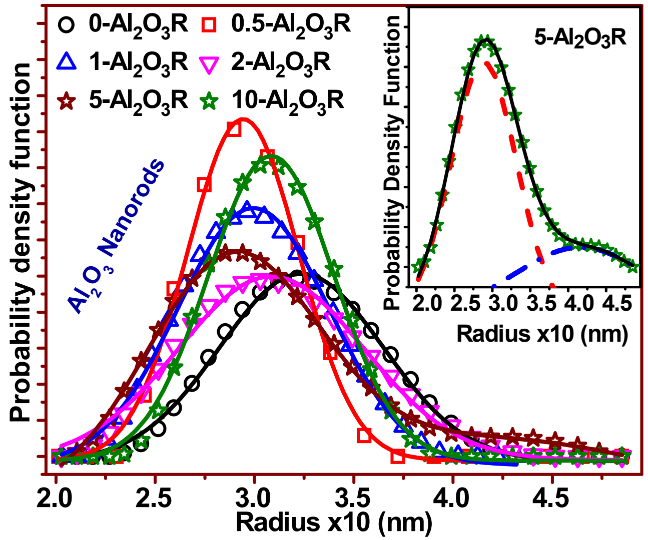
  decrease at higher concentration**: aggregation effect**

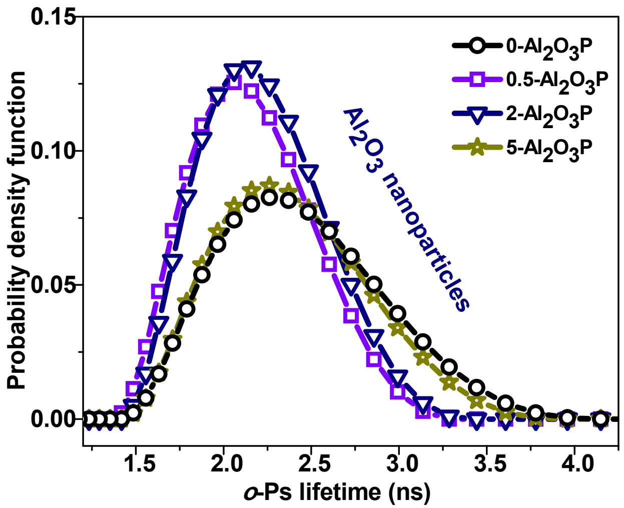
  Crystallinity further lowers for nanoparticles
- ❑ Increase in T_g—slowing chain dynamics due to **interphase formation in nanorods**
- ❑ T_g decrease for nanoparticles—increase in amorphous fraction



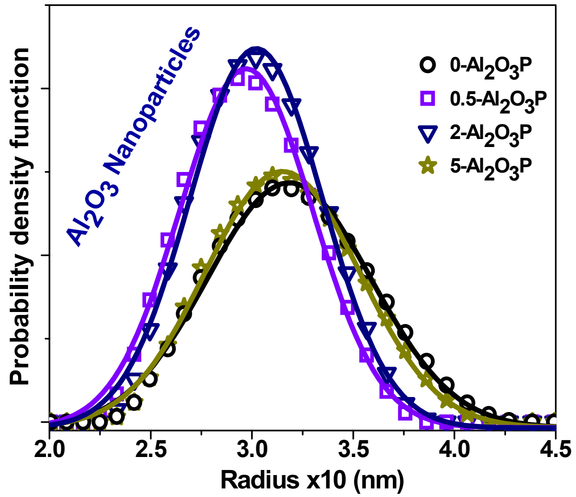
PEO-Al_2O_3 Nanorods Based SPE: PALS Study







$$n(R) = \frac{2\Delta R}{(R+\Delta R)^2}\left[\cos\left(\frac{2\pi R}{R+\Delta R}\right)-1\right]\alpha_3(\lambda)$$



- Segmental dynamics: size distribution of Fv holes in polymer
- F_v size distribution---CONTIN
- *o*-Ps lifetime distributions transformed to free volume size distribution

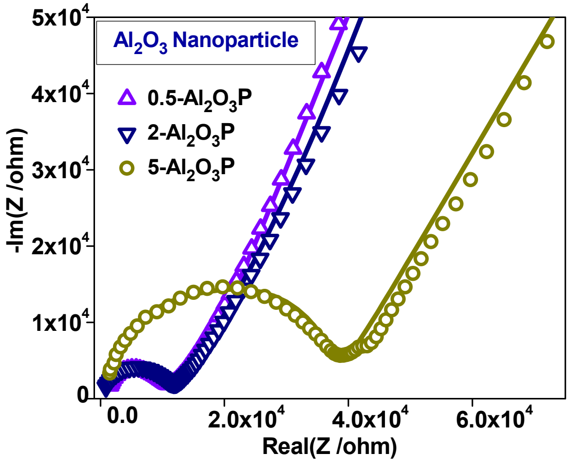
PALS Study (contd...)

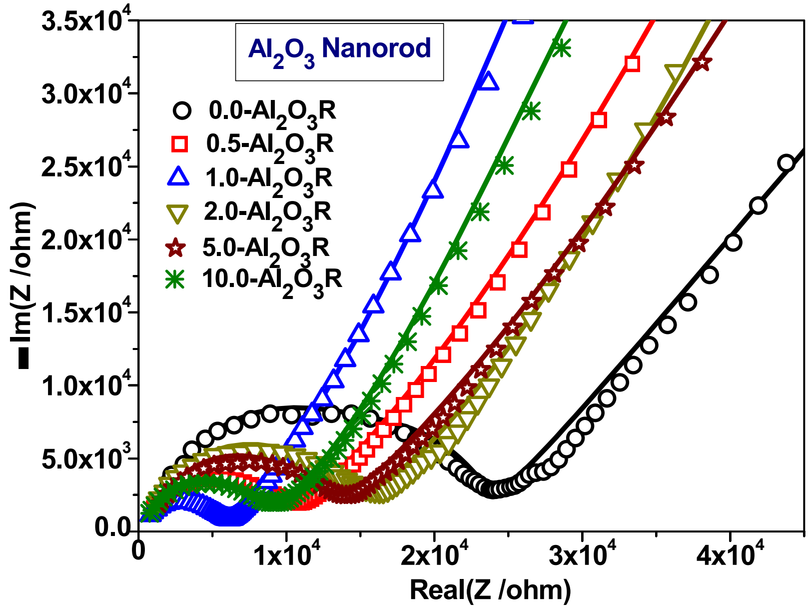
SPE	τ_{avg} *o*-Ps (ns)	Intensity (%)	R×10 (nm) ±0.005	FWHM ×10 (nm)
0-Al_2O_3R	2.44±0.09	10.11±0.61	3.236	0.971
0.5-Al_2O_3R	2.08±0.03	13.14±0.36	2.942	0.663
1-Al_2O_3R	2.15±0.03	12.70±0.46	2.994	0.900
2-Al_2O_3R	2.29±0.04	11.55±0.79	3.084	1.100
5-Al_2O_3R	2.24±0.01	8.28±0.90	2.886	0.861
	3.85±0.04	4.47±1.02	4.160	1.713
10-Al_2O_3R	2.24±0.04	12.58±0.40	4.160	2.004
0.5-Al_2O_3P	2.16±0.06	11.89±0.58	2.971	0.772
2-Al_2O_3P	2.22±0.05	12.22±0.51	3.021	0.768
5-Al_2O_3P	2.39±0.02	9.26±1.01	3.150	0.898

- ❑ Avg. F_v size less than PEO at lower loading: **anti-plasticization effect of Al_2O_3 nanofiller**
- ❑ F_v size increases with filler loading
- ❑ Increase in F_v levels-off at highest loading: **Aggregation effect**
- ❑ FWHM follows F_v size trend

- ❑ **Nanorods shows bimodal distribution; Nanoparticle shows single distribution of F_v holes**
- ❑ **Bimodality---Two different spatial zones in nanorods**
- ▪ **Bulk F_v holes (smaller) and F_v at interphases (larger)**
- ❑ **Bimodal distribution not discernible till 2% loading**

PEO-Al_2O_3 Nanorods Based SPE: Electrochemical Impedance Spectroscopy (EIS) Study

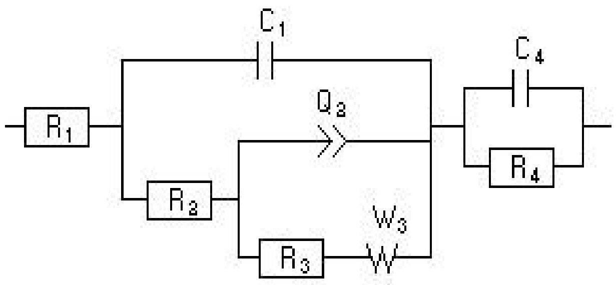




- Linear region: Warburg impedance (**ion diffusion**)
- Depressed semicircle: **Non-Debye relaxation**

  Distribution of relaxation time
- Bulk conductivity calculation– **model circuit**

σ = thickness/ (resistance×area)



Model circuit components

R_1—wires-electrodes contact resistance

(R_2, C_1)—bulk conduction

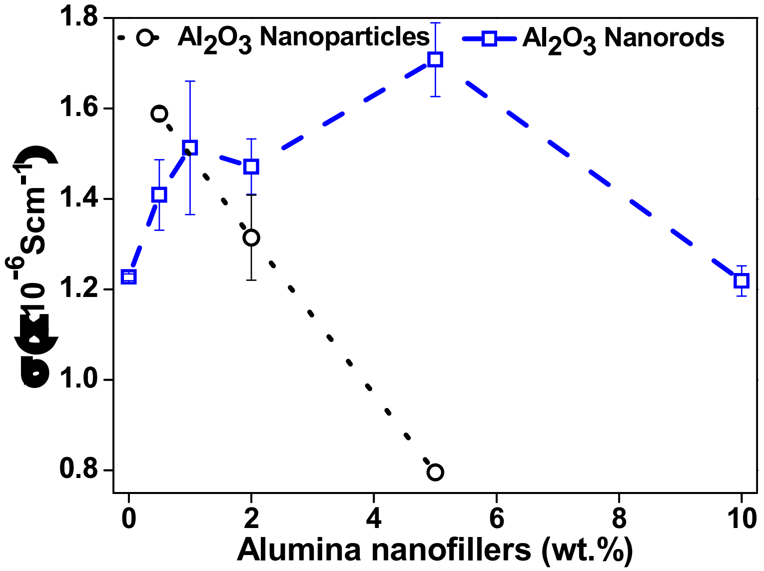
R_3— charge transfer resistance due to polarization at nanorods interface

Q_2—double layer formation along the nanorods interface

W_3—Warburg impedance corresponding to ion diffusion. Presence of slant line in Nyquist plot due to unevenness of electrode-electrolyte interface

(R_4, C_4) —time constant corresponding to electrode-electrolyte interfacial polarization

Comparison of Al_2O_3 Nanorod *vs.* Nanoparticle Laden SPE



❖Conductivity increases with nanorod loading followed by decrease at higher concentration (**aggregation**)

❖Conductivity decreases monotonically for nanoaparticles

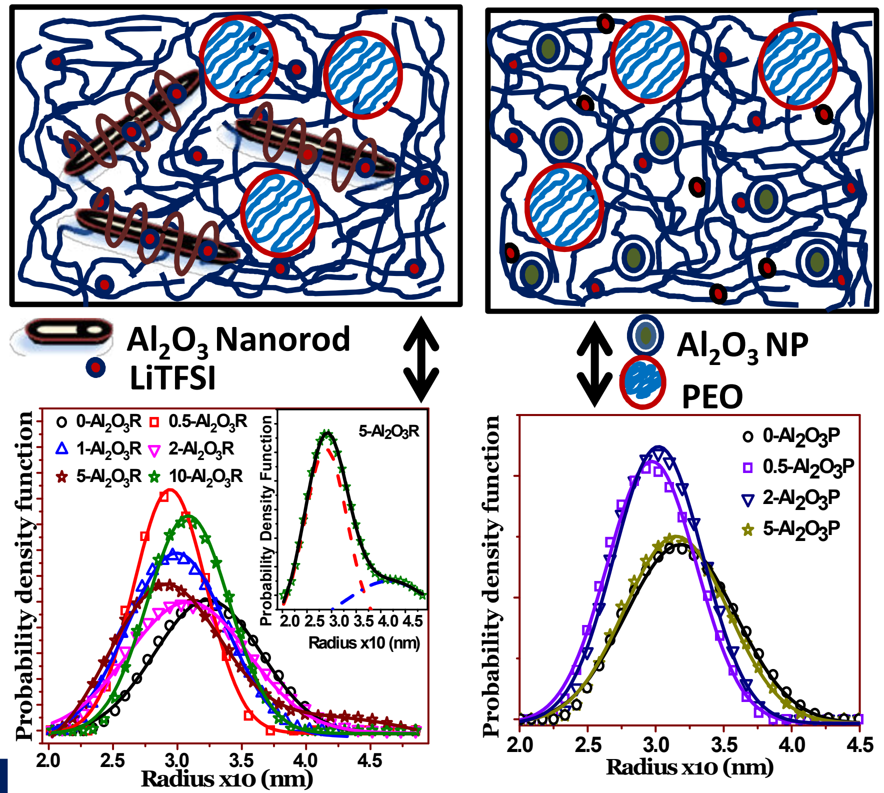
❖Amorphous fraction either similar or less than nanorod SPEs

❖Semi-crystalline morphology similar for both types of filler

❖Bimodal distribution of F_v holes in nanowire (not so in nanoparticles case)

❖Large size interphase in nanorod

❖Role of interphase region in enhancement of conductivity



P. Utpalla et al, Solid State Ionics (under review)

Summary and Conclusion

- SPE can possibly replace liquid electrolyte circumventing major issues associated with these electrolytes
- PEO based solid polymer electrolyte: suitable for battery application
- Optimum concentration/ratio of all constituents & appropriate selection of nanofillers in SPE may yield good ionic conductivity
- Positron annihilation spectroscopy (PAS), Electrochemical impedance spectroscopy (EIS) and Differential Scanning Calorimetry (DSC) suitably employed for understanding the change in semi-crystalline morphology and free volume characteristics of polymer and its impact on ionic conductivity in PEO based SPEs
- Use of salt as plasticizer, fillers forming large interphase free volume (viz. anisotropic filler), **S**ingle **L**i **I**on **C**onducting **(SLIC)** electrolytes are some strategies to enhance conductivity in PEO based SPEs

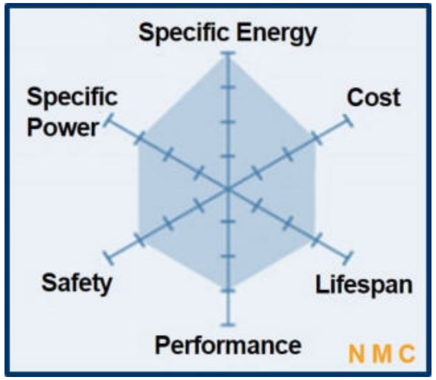
Future Studies

❖Well-aligned nanowire as filler for getting enhanced conductivity in PEO based SPEs

❖Using metal organic framework with interconnected pore networks as filler for enhanced conductivity

❖ Design & testing of prototype Li cell based on these electrolytes

- cell cycle stability, electrochemical window,
- electrode-electrolyte compatibility
- Li symmetric cell performance testing
- Li cells using new cathode viz. NMC, MoS_2



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- Jaideep Mor

and all collaborators…

Thank you for listening

- Any comments/questions?