

Investigation on the effect of LiTFSI salt on PVDF-based Solid Polymer Electrolyte Membranes for Lithium-Ion Batteries

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Abstract

Solid polymer electrolytes provide an alternative approach to providing improved safety whilst concurrently acting as a performance enhanced separator within Lithium-ion batteries (LIBs). We study the effects of Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salts in a polymer blend with Polyvinylidene fluoride (PVDF) and Poly(vinylpyrrolidone) (PvP) or Poly(4-vinylpyridine) (P4VP) on the performance of SPE membranes. Characterization by XRD & FT-IR highlights the changes due to LiTFSI. Improved thermal stability, strength and dielectric performance are also seen.

Background

- The electrolyte component in LIBs is a critical variable that acts as a medium for the movement of ions across the battery and is a facilitating location for reactions and side reactions.
- Liquid electrolytes have questionable drawbacks such as the combustible and toxic properties of organic solvents, whilst aqueous solvents tend to decompose at high working voltages thereby restricting the energy density of the battery.
- SPEs provides higher value for safety and mechanical stability within LIBs however are limited by their relatively weaker ionic conductivity and smaller energy density.

Experimental

Material Synthesis

- The membranes were prepared by the mixing of two solutions, **A with DMF** and **B with acetone**. Solution A was composed of a consistent 1.2 g worth of PVDF and 0.2 g of the copolymer, **PvP** or **P4VP**, to make the polymer backbone within 20 mL of DMF. Solution B was used for the LiTFSI content at two masses, 1.2 g or 1.6 g dissolved within 20 mL of acetone. Solutions were mixed for 2.5 hours under magnetized stirring at 125°C until gel formation. Samples were heated at 180°C overnight. Another set of samples involved the incorporation of metal fillers **Al₂O₃**, **ZrO₂** and **SiO₂**.

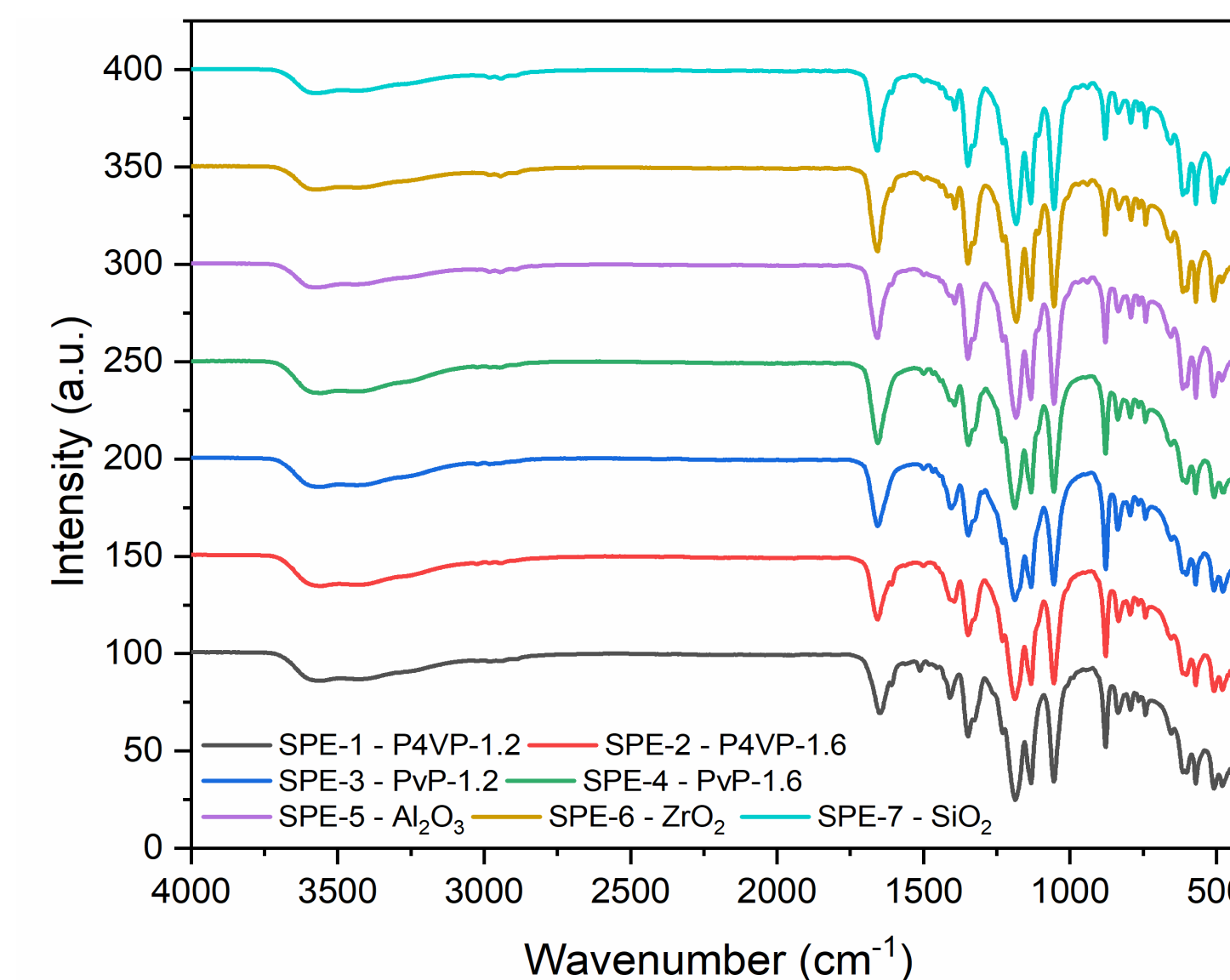
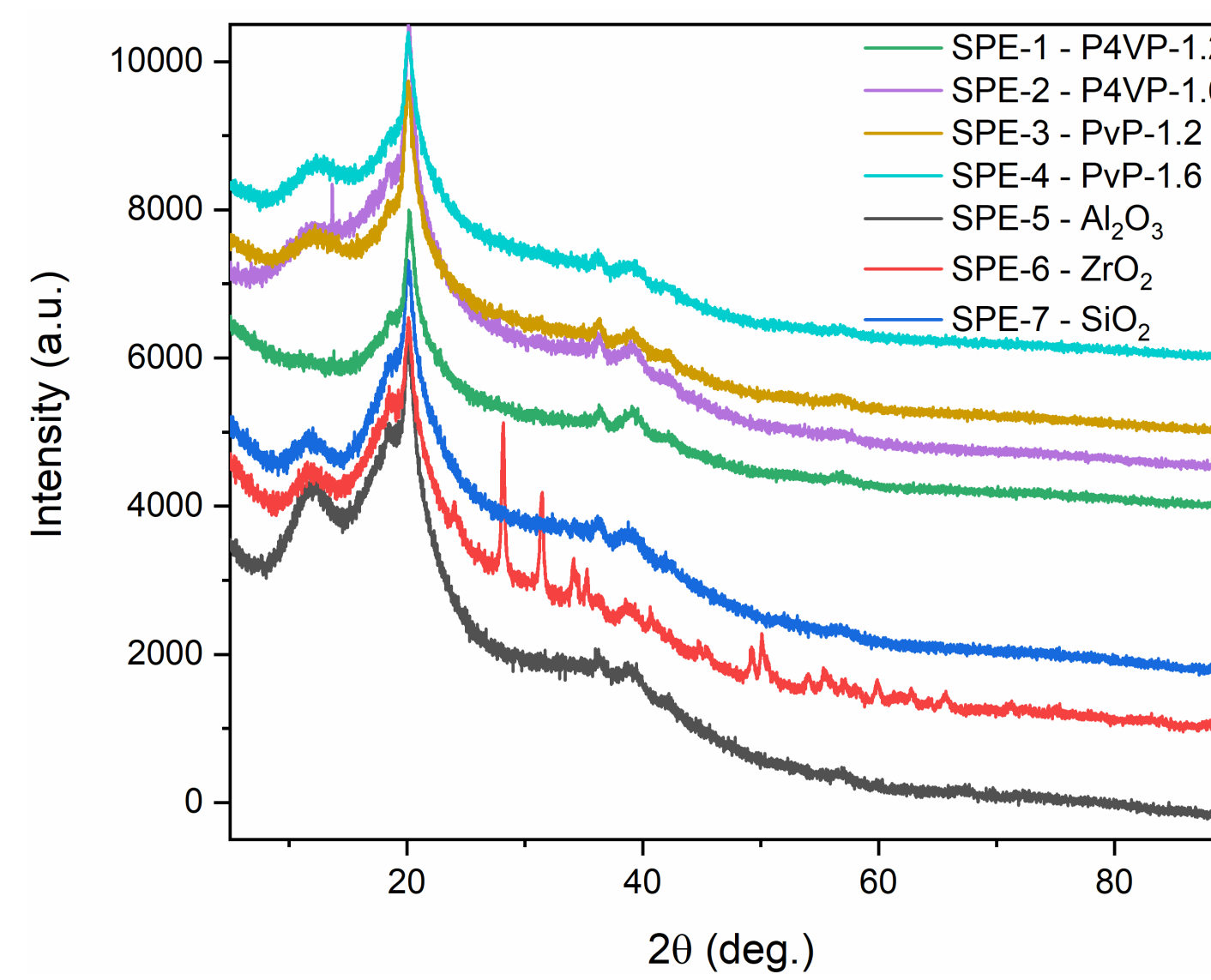
Characterization and Performance Testing

- SPE samples were dissected into 15 mm segments with thickness between 0.15-0.30 mm and were for XRD, FT-IR, Raman and SEM analysis.
- Tensile capacity of the SPE samples were studied with specifications of 25 mm for gauge length, width of 13.1 mm and a process speed of 5 mm/min.
- The dielectric performance such as the dielectric constants was evaluated and finally TGA to investigate changes in thermal stability.
- Full-cell configurations were made inside CR-2032 coin-cells with the SPE samples placed between two reference Li foils and were fabricated within a glovebox chamber for LSV testing at 0.5-5 V vs. Li+/Li and a scan rate of 2 mV/s.

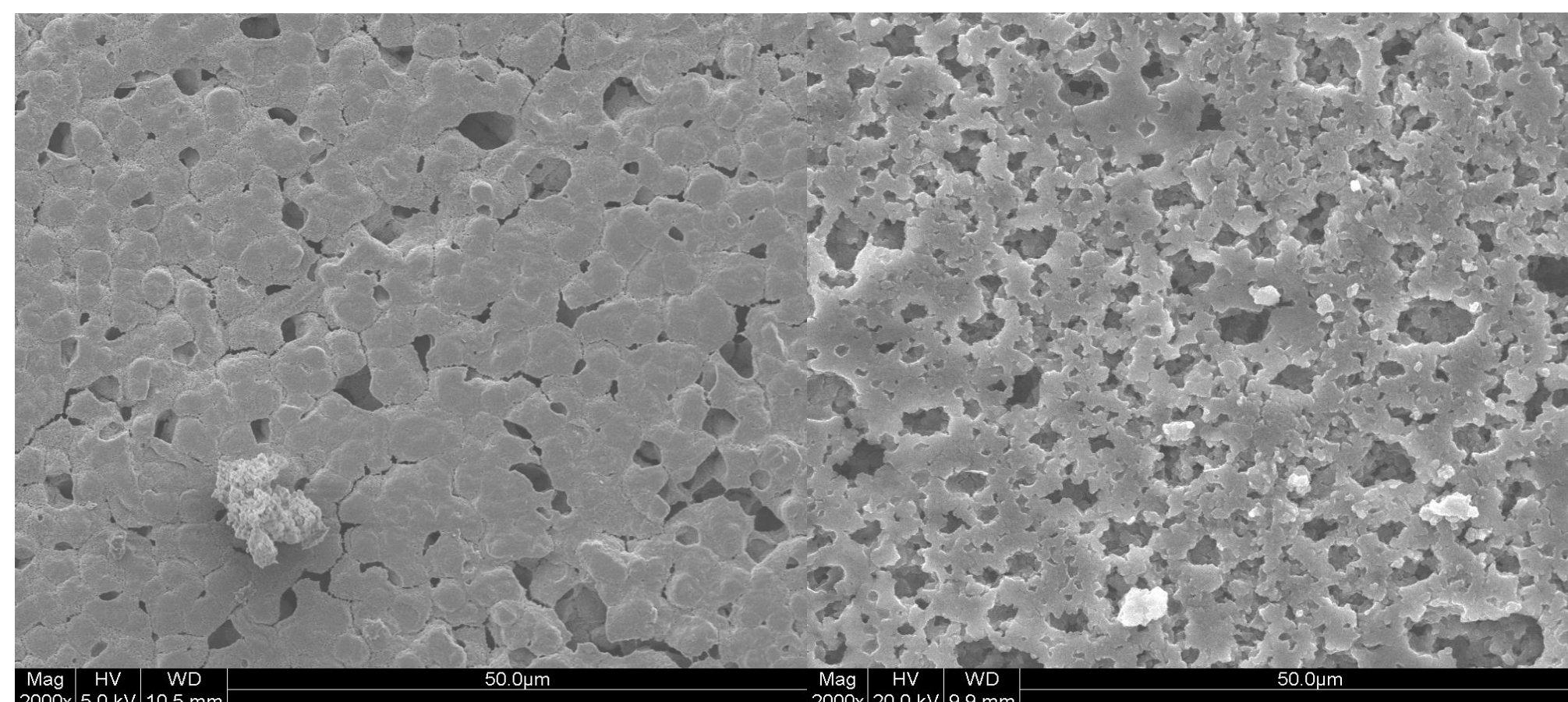
SPE sample grown on petri dish. Uneven curling is present with non-uniform thickness.



Results & Discussion



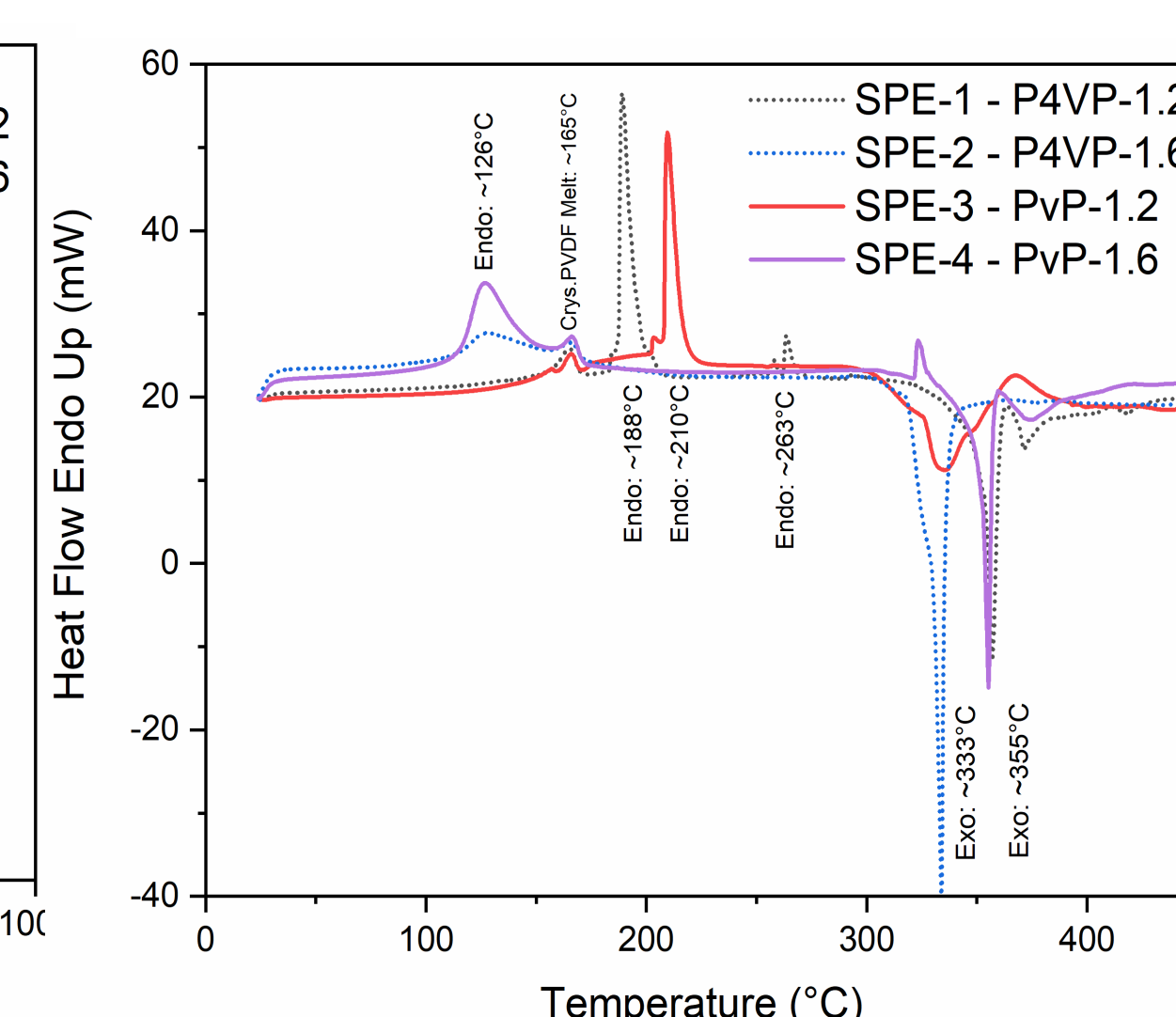
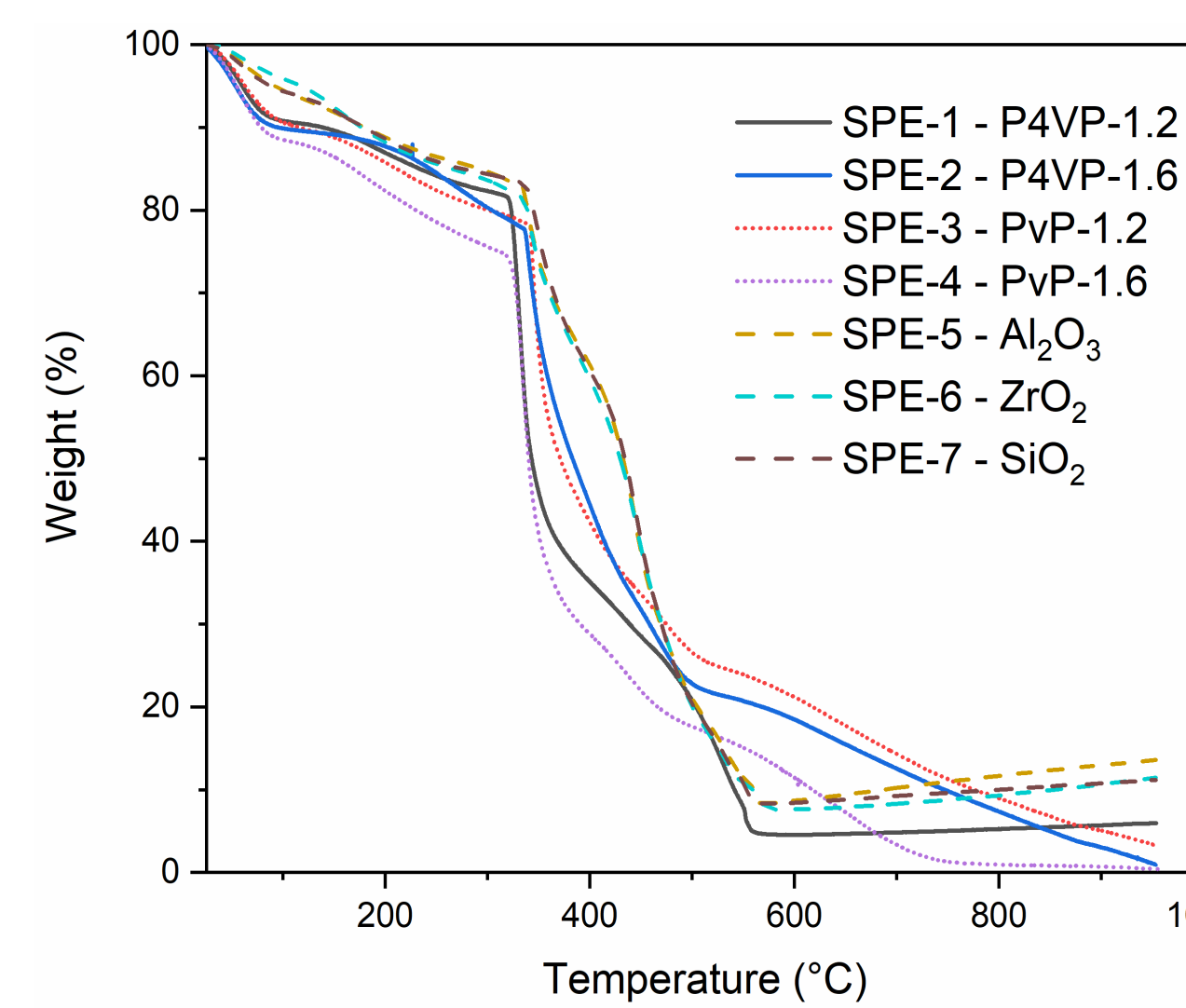
XRD analysis depicted an increase in the amorphization of the SPE samples with increasing LiTFSI content, whilst FTIR highlights the important functional groups present between the SPE samples as well as a slight change in LiTFSI signal.



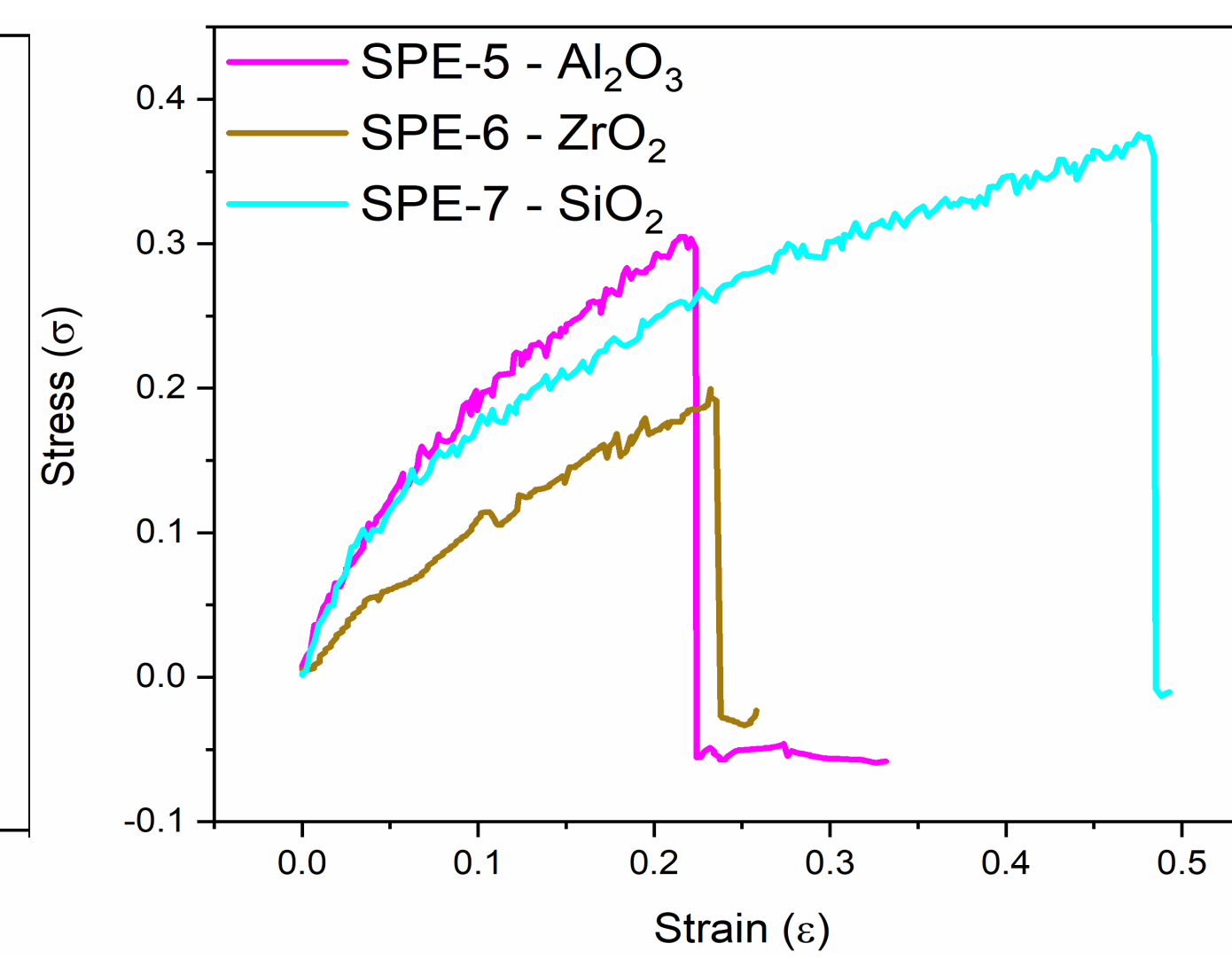
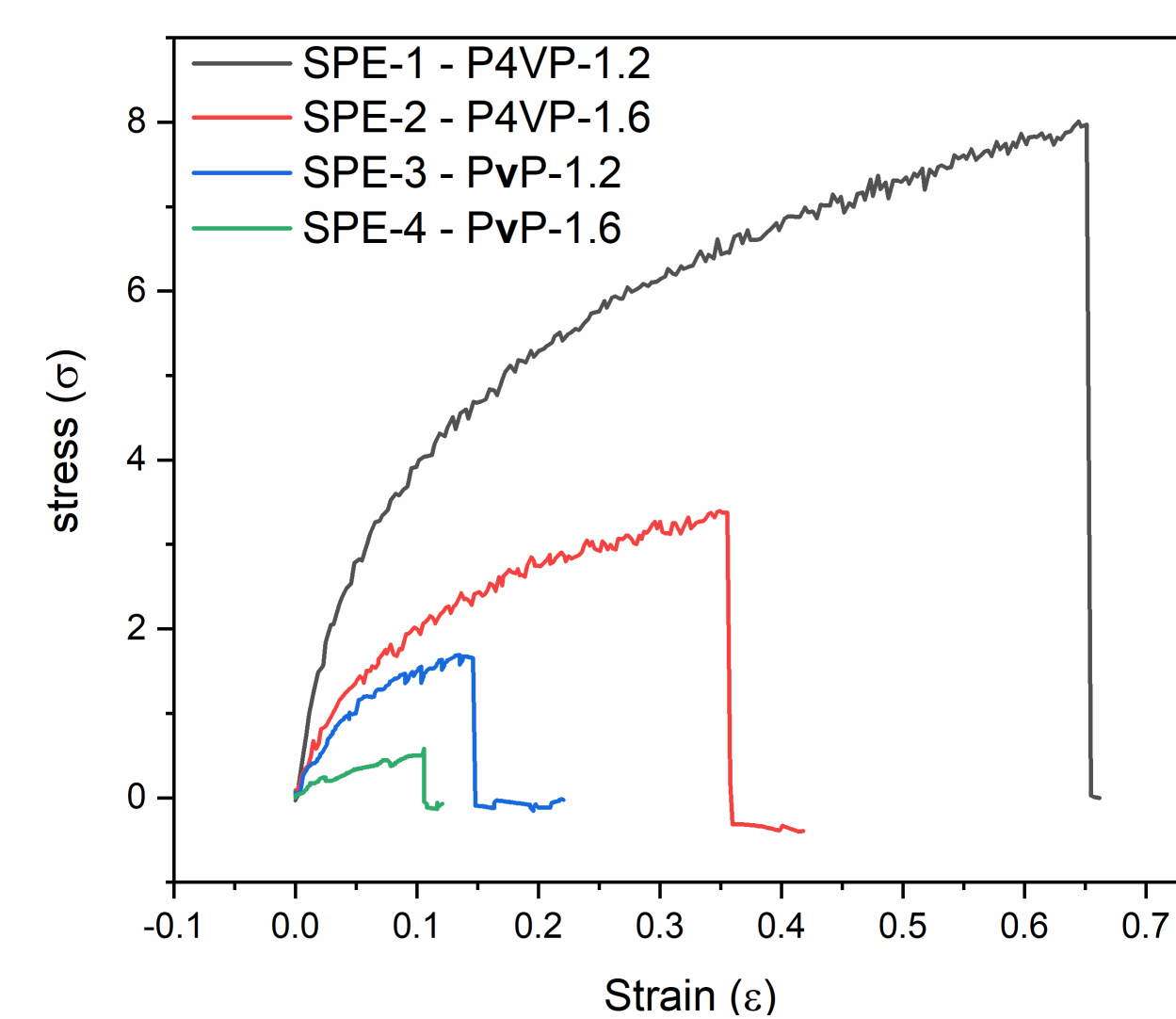
SEM micrographs at scale of 50 μm demonstrated increase in porosity at the effect of increased LiTFSI concentration.

Porosity texture changed into a "Punch-out" chunks description after metal-filler incorporation

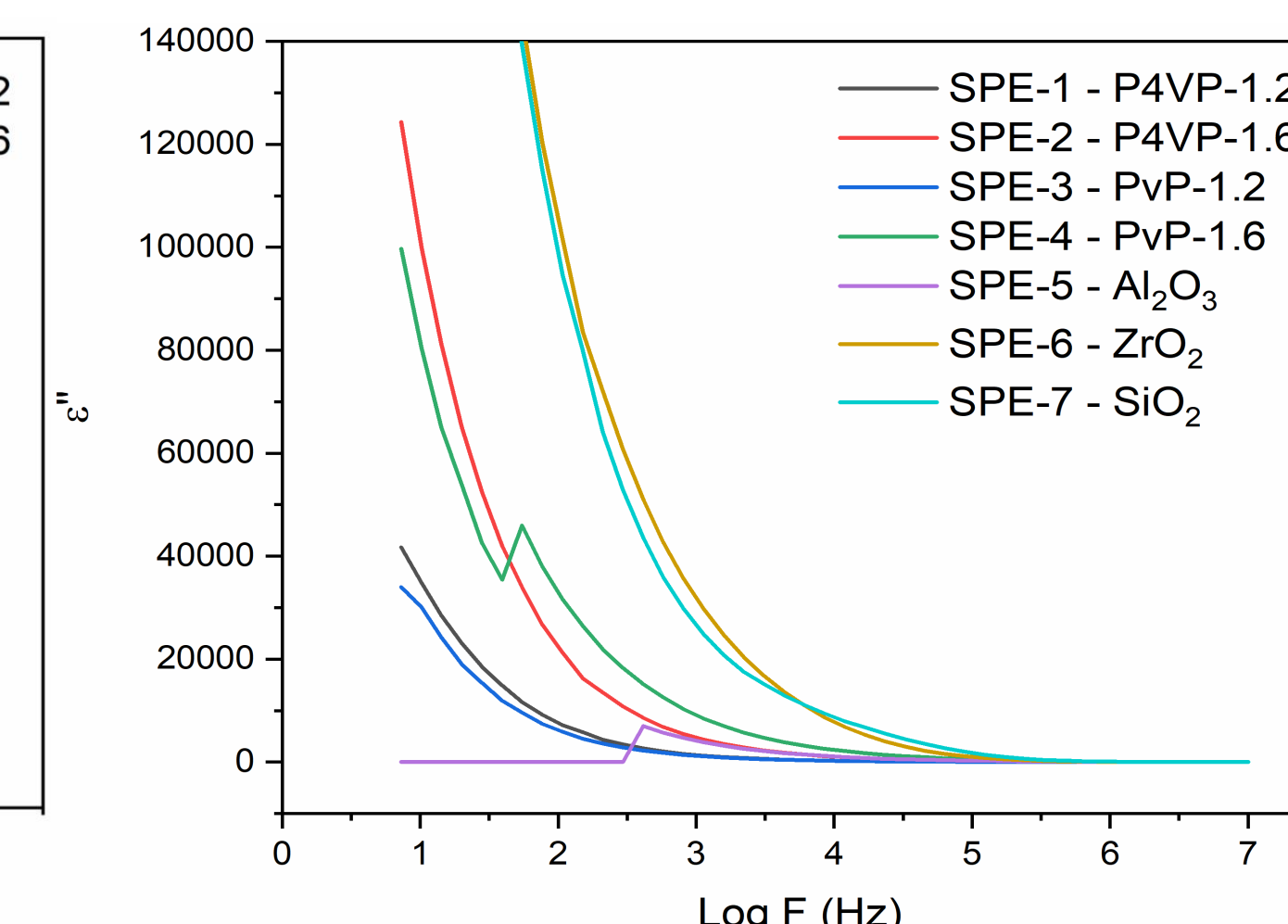
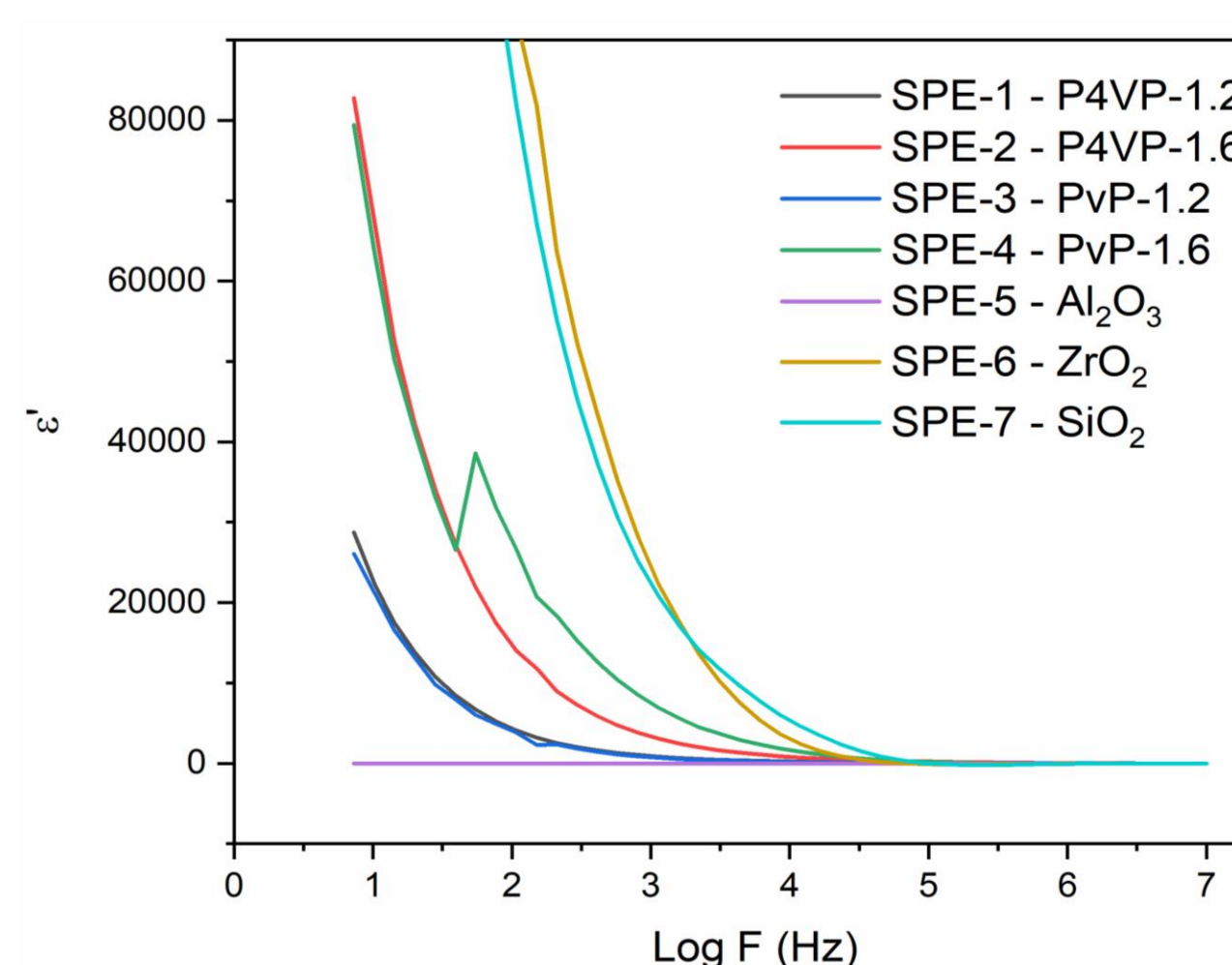
The addition of a copolymer improved thermal stability with a higher temp. threshold before polymer blend degradation and DSC shows the inhibition of endotherms pertaining to crystalline PVDF.



Further increase to 1.6 g of co-polymer resulted in a deterioration of mechanical limits. Further limits are imposed with addition of metal-fillers.



Dielectric constant ε' and dielectric loss ε'' showed greater values with increased LiTFSI content.



References

- M. Unge, H. Gudla, C. Zhang, D. Brandell, Electronic conductivity of polymer electrolytes: Electronic charge transport properties of LiTFSI-doped PEO, Phys. Chem. Chem. Phys. 22 (2020) 7680–7684. <https://doi.org/10.1039/d0cp01130d>.
- F. Wang, L. Li, X. Yang, J. You, Y. Xu, H. Wang, Y. Ma, G. Gao, Influence of additives in a PVDF-based solid polymer electrolyte on conductivity and Li-ion battery performance, Sustain. Energy Fuels. 2 (2018) 492–498. <https://doi.org/10.1039/c7se00441a>.
- S. Rajendran, P. Sivakumar, R.S. Babu, Studies on the salt concentration of a PVDF-PVC based polymer blend electrolyte, J. Power Sources. 164 (2007) 815–821. <https://doi.org/10.1016/j.jpowsour.2006.09.011>.