

# A Novel Approach Enabling Atomic Scale Characterization for Li-on Battery Components probed by Positron Annihilation Lifetime Spectroscopy (PALS)

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Positron annihilation lifetime spectroscopy (PALS), displayed in Figure 1, is a well-established and very sensitive nondestructive spectroscopy technique that allows studying nanodefects in materials such as free volume and its fraction. The PALS spectra were fitted into 3 or 4 parameters, including  $\tau_3$  with  $I_3$  and  $\tau_4$  with  $I_4$ , associated with the pick-off annihilation of ortho-positronium (o-Ps within the crystalline and amorphous regions of the polymers).

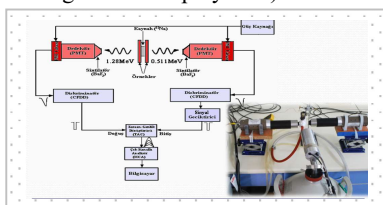


Figure 1. Positron Annihilation Lifetime Spectroscopy

Polymers and their blends have been widely applied in various industries, including energy storage devices. Lithium-ion batteries play a significant role in which electrolytes are critical for transporting positive lithium ions between electrodes. Liquid electrolytes that are currently in use are often flammable, volatile, toxic, and more prone to short circuit and leakage, leading to environmental and safety concerns. To overcome these disadvantages, solid polymer electrolytes (SPEs) have emerged as alternative systems. While SPEs provide decent mechanical stability, deformability and biocompatibility, their low ionic conductivity at room temperature compared to liquid electrolytes remains a major challenge for their commercial use.

Linear poly(ethylene oxide) (PEO) has gained significant attention as an SPE due to its excellent characteristics, including fast segmental dynamics and the ability to dissolve different lithium salts. At room temperature, however, PEO is a semicrystalline polymer with an ionic conductivity ranging between  $10^{-6} - 10^{-8}$  S/cm, in which crystalline regions impede ion transport. The ionic conductivity increases up to  $10^{-3}$  S/cm above its melting temperature ( $T_m = 60^\circ\text{C}$ ), yet with a severe reduction in mechanical strength, which limits its application in a solid-state battery. To overcome these drawbacks, one method is to use PEO with another polymer that can provide mechanical rigidity and eliminate crystallinity. In this sense, the high glass transition temperature ( $T_g$ ) polymer poly(methyl methacrylate) (PMMA) is commonly used. Incorporation of PMMA into PEO significantly increased the mechanical

properties, such as the storage modulus, making the liquid-like behavior of PEO more solid-like. Additionally, the effect of free volume on ionic conductivity was investigated by various studies in PEO-based SPEs. The increase in free volume in the polymer matrix resulted in assisted ion migration, enhancing the ionic conductivity in these SPEs. Here, we take advantage of the enhanced free volume due to the increased number of free end groups in nonlinear PEOs and suppressed crystallization arising from branching as well as PMMA addition to facilitate the transportation of  $\text{Li}^+$  ions in PEO/PMMA-based copolymer electrolytes. Therefore, to relate the free volume of branched PEOs with the ionic conductivity of PEO-grafted PMMA copolymers with varying molecular weights (PEO (1.5 kDa & 20 kDa)) for the temperature range from 30 to  $90^\circ\text{C}$ , we employed PALS.

Furthermore, the obtained results from PALS and EIS are displayed in Figure 2 for the free volume estimations as a function of temperature for PEO with increasing branching. In addition, it is evident that there were two different clear trends for the free volume above and below a certain temperature, which turns out to be the melting temperature for PEOs, and this temperature agrees well with the estimations from the differential scanning calorimetry experiments. This changing trend could be well related to the melting crystals and higher branched arms in the PEO matrix, producing significant additional free volume. It is also evident that the enhanced free volume probed by PALS resulted in an increase in ionic conductivity in branched PEO/PMMA systems when compared to the blend PEO/PMMA electrolytes. Eventually, the PALS is planned to be used for structural changes observed in electrodes due to possible reasons such as doping, aging, and cycling.

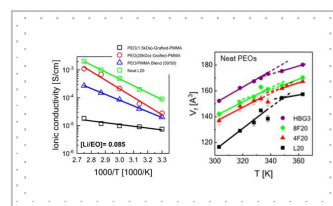


Figure 2. Temperature-dependent ionic conductivity measurements with free volume measurements probed by PALS.

## References

[1] Bakar, R. Developing Various Design Strategies for Poly (ethylene oxide) (PEO) Based Dry Polymer Electrolytes (SPEs). PhD Thesis. Koç University.



I specialized in lithium-ion batteries, solid polymer electrolytes (SPEs) polymer physics, rheology, morphology, polymer blends and additives within depth understanding of structure-property relationships of polymers as new functional and smart materials for polymer electrolytes. Currently working as a Cell development R&D engineer at SIRO, focusing on developing novel lithium-ion batteries.

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