Warsaw University of Technology
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Polyacetals with oxymethylene and oxyethylene units as alternatives to PEO in lithium-ion batteries

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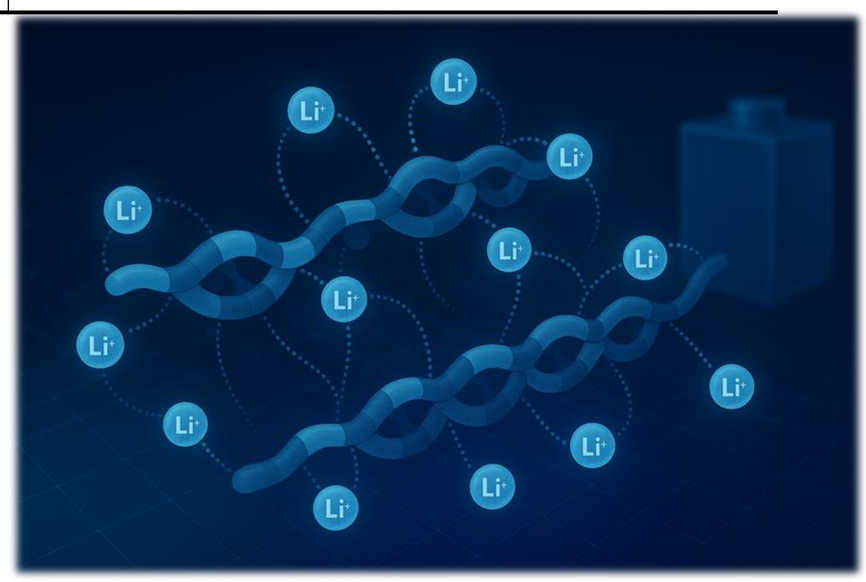
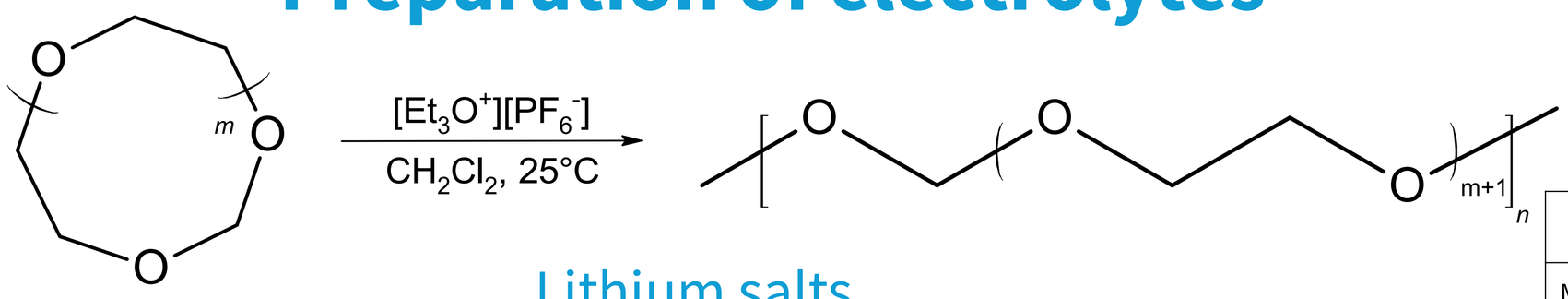
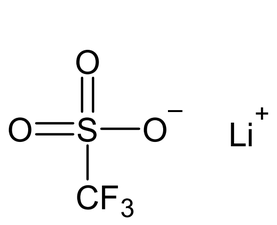
Polyethylene oxide (PEO) is the most common polymer in lithium-ion cell electrolytes, but its tendency to crystallize limits ionic conductivity. Our goal was to replace PEO with polyacetals containing alternating oxymethylene (MO) and several oxyethylene (EO) units. The introduction of oxymethylene units disrupts the regular structure of oxyethylene chains, which can inhibit crystallization and thus lead to higher ionic conductivity compared to PEO-based electrolytes. Ionic conductivity is slightly affected by the length, architecture, and end groups of the tested polymer matrices, as well as the use of ceramic additives such as nanosilica. However, replacing the lithium salt with 2-trifluoromethyl-4,5-dicyanoimidazole lithium salt (LiTDI) can increase the conductivity by up to half an order of magnitude. This enables the formulation of a polymer electrolyte that does **not** require a low-molecular-weight organic solvent additive, while still achieving a conductivity on the order of **10^{-4} S cm^{-1}** at 40 °C.

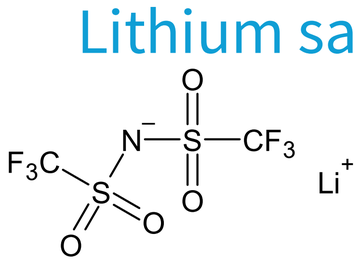


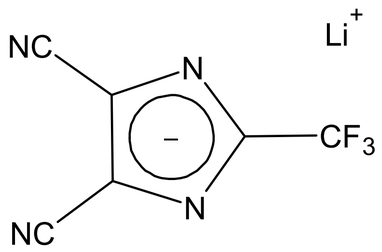
Preparation of electrolytes



Lithium salts

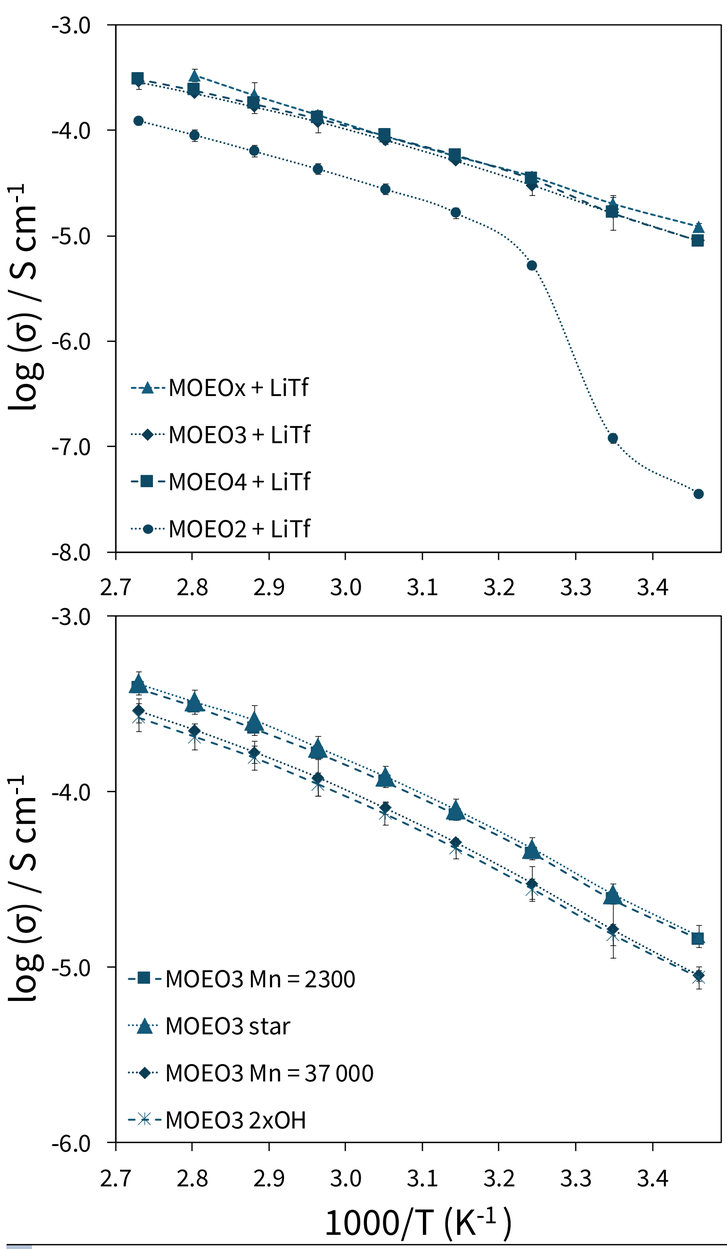


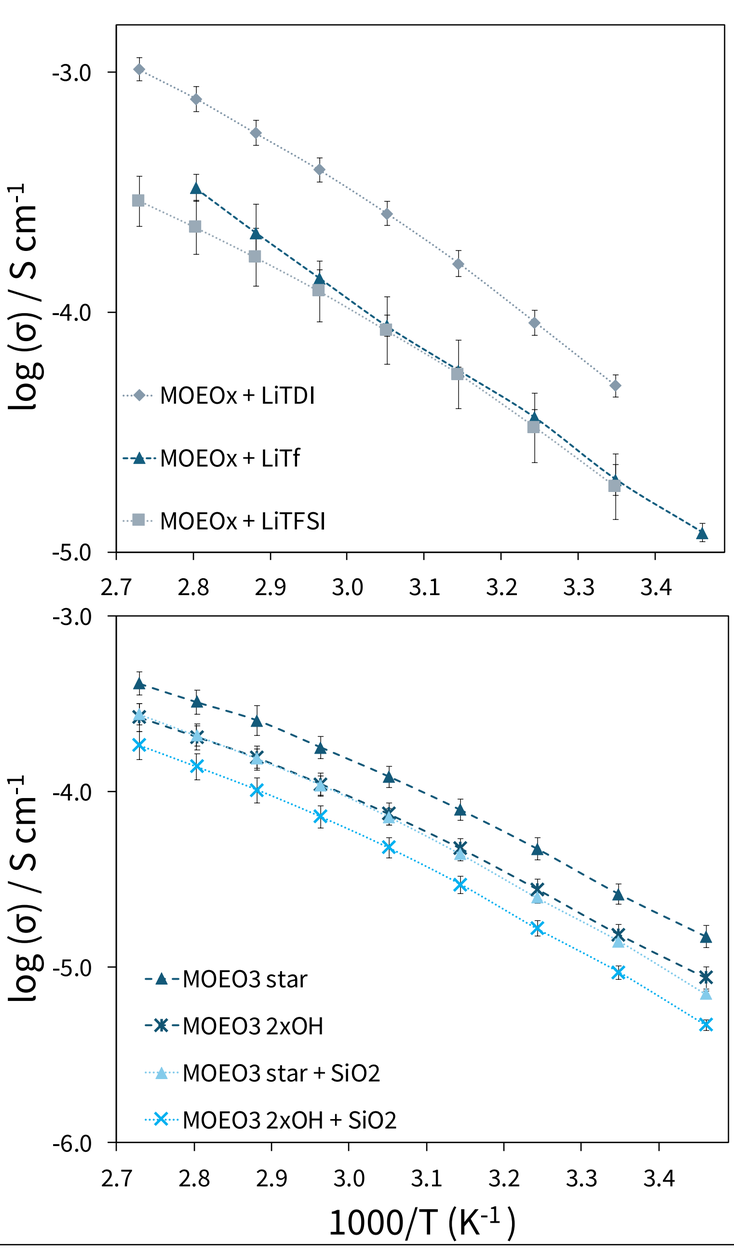




	M_n/g mol^{-1}	T_g/°C	T_m/°C
MOEO2	36 000	-63	40
MOEO3	37 000	-67	-
MOEO4	32 800	-63	27 35
MOEOx	30 000	-72	-

Electrochemical properties





Summary

- Using cationic polymerization under mild conditions, both linear and star-shaped polymers with varying molar masses, end groups, and different ratios of oxyethylene (EO) to oxymethylene (MO) units were successfully synthesized.
- The polymer's molar mass, architecture, and end-group structure (which is present in low concentration) have only a minor influence on ionic conductivity. In contrast, the choice of lithium salt has a significant impact on conductivity.
- Polymers with a 2:1 ratio of oxyethylene to oxymethylene units are insufficient for effective ion coordination. Moreover, their tendency to crystallize easily leads to a sharp decrease in conductivity below the melting point.
- Introducing MO units of varying lengths along the macromolecular backbone can disrupt the regular polymer structure, suppress crystallinity, and thereby improve ionic conductivity.
- The highest conductivity achieved for electrolytes based on linear poly(oxymethylene-co-oxyethylene) with LiTDI salt was approximately 10^{-4} S cm^{-1} at 40°C.