Lithium salt catalyzed episulfide ring opening polymer electrolyte for Li ion Batteries.

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As the need for lithium-ion batteries increases day by day, the demand for high-efficiency and high-capacity batteries is also increasing. Among them, with the progress of research in electrolytes, polymer electrolytes based on polyethylene oxide (PEO), oligomers and lithium salts have attracted great interest in developing the most modern lithium secondary batteries. [1] However, due to the strong interaction of lithium and oxygen in the pure polymer electrolyte, there is a problem of a low lithium transition number, and in the case of an epoxy resin, it takes a lot of time to cure at low temperature. Therefore, the structure of episulfide, a material in which the oxygen of epoxy is replaced by sulfur, was utilized. Herein, LiFSI was used as an initiator and an episulfide structure in which the oxygen of the epoxy was replaced by sulfur was used to analyze the structural properties using FT-IR and ^{1}H-NMR. The sulfur including rings of the material must have a higher energy level, which allows for low-energy release and rapid curing applications at low temperatures.[2] We also show that sulfur's larger atomic size than oxygen atoms and lower competitive strength for lithium ions may result in improved conductivity of PES over PEO.[3,4] The physicochemical properties and electrochemical performance of the cured material were investigated by EIS, DSC, and TGA, and the ionic conductivity of PES-2M at 30°C (>0.2 mS/cm) was shown and thermal stability up to 153°C.

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Lithium Salt Catalyzed Crosslinked Solid Polymer Electrolyte with high Conductivity and Enhancing Anode Interfacial Compatibility for Li-ion Battery

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To tackle safety issue and electronic conductivity limitation , recently solid polymer electrolytes (SPEs) have been considered as a promising candidate to replace the liquid electrolyte for rechargeable lithium batteries[1, 2]. Herein, we represented an in situ cross-linked solid-state polymer electrolytes (CSPEs) based on diepoxy group through lithium salt catalyzed ring-opening polymerization with additive FSO_2NH_2 [3]. We employed a series of technology to measure characters of precursor and synthesized electrolytes. NMR and FTIR spectra revealed precursor FSO_2NH_2 was received successfully, and as-prepared CSPEs exhibited good thermal ability, low glass transition temperature (T_g), comparable ion conductivity (σ) and high lithium-ion transport number (t_{Li+}). Noteworthy, CSPE-2 exhibits a capacity of t_{Li+}=0.61 and electrochemical oxidation stability (up to 5.2V). The full cell of $LiFePO_4$|CSPE-2|graphite showed an initial discharge specific capacity of 146 mAh g^{-1} at 0.1 C and coulomb efficiency of ca. 90.2% after 200 cycles, Moreover, the $LiFePO_4$|CSPE-2|Li cell delivered an initial discharge specific capacity of 165 mAh g^{-1} at 0.1 C and coulomb efficiency of ca. 96.7% after 200 cycles. In addition, CSPE-2 shows better anode interfacial compatibility with additive FSO_2NH_2. These results could provide another strategy for development of recharge lithium solid polymer electrolyte.

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Interface studies of anode-less lithium batteries using photoelectron spectroscopy and in-situ lithium deposition

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Solid polymer electrolytes (SPEs) can play an important part in achieving a lithium-based anode-less battery technology [1]. The interface in cells of this type is a major bottleneck for achieving this technology, as this is where serious degradation of the electrolyte material can be observed [2]. Our work uses soft X-ray photoelectron spectroscopy to investigate the stability of three different SPEs (PEO, PCL, and PTMC, with LiTFSI salt) after the deposition of lithium metal in vacuum.

Lithium alkoxide, lithium fluoride and $Li_xS_yO_z$, were found among the degradation products. A competing degradation between polymer and salt (dependent on the polymer) was also identified. As summarized in the illustration below (**Fig. 1**) PTMC:LiTFSI is degraded the most, in regards to the polymer and the salt. This is followed by PCL:LiTFSI where the polymer is more decomposed than the salt, and PEO:LiTFSI, where it's the other way around. The degradation products also move throughout the interface to different degrees depending in the polymer host.

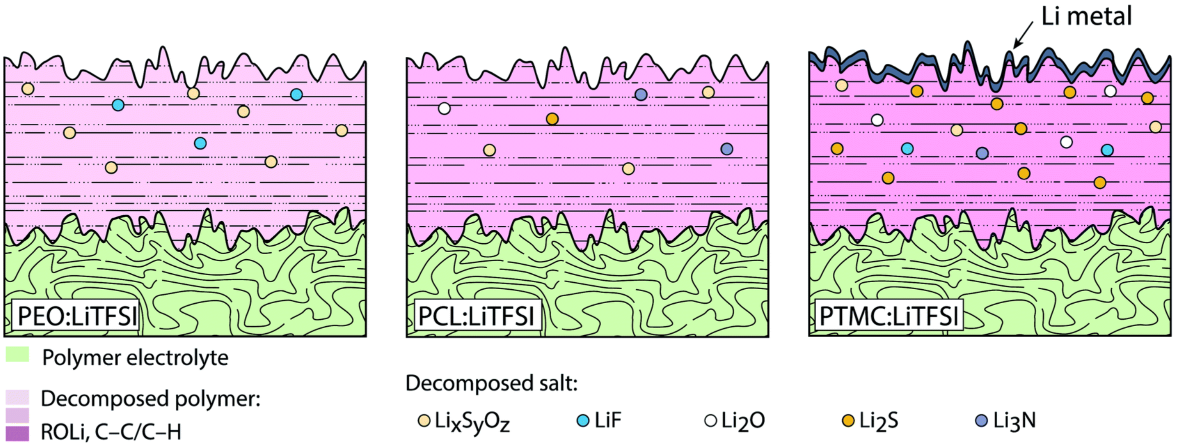

Figure 1. Summary of the polymer electrolyte films after lithium deposition. Polymer is green, degradation region is purple. Darker purple means a higher degree of polymer degradation. The small dots are the decomposed salt. Lithium metal is grey. [3]

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Optimization of solid polymer electrolytes for anode-free Li-ion batteries

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Li-ion batteries are nowadays an essential part of everyday life but are still limited by low energy density, hindering a further penetration of the technology. Anode-free batteries, eliminating the negative electrode material, represents one of the most promising solutions to overcome this issue. Moreover, the direct exploitation of Li-metal plating–stripping reaction theoretically guarantees higher energy density compared to traditional anodes (i.e. graphite). However, the usage of Li-metal in the anode-free configuration has two main critical aspects: dendritic growth and low coulombic efficiency, causing safety concerns on one hand and poor cyclability on the other.[1,2] The properties of a solid polymer electrolyte (SPE) can help mitigating these issues, compared to liquid electrolytes.[3] For this reason, a PEO-based SPE was investigated by evaluating the effect of different Li^+ salts and optimizing the structure with the addition of plasticizer and inorganic particles and blending with polymers containing carbonate ester groups. The purpose has been to increase the ionic conductivity of the PEO-salt system and the coulombic efficiencies of the Li plating–stripping process. Finally, the effect of zinc on the Li deposition process was assessed. Zinc is one of the most easily accessible "lithophilic" materials, showing a very low overpotential of Li deposition and a consequent growth of a uniform layer of Li.[4] Therefore the incorporation of Zn^{2+} salts, alongside Li^+ salts, in the formulation of the SPE was explored here for the first time. In depth chemical, morphological and electrochemical characterization was conducted to understand the influence of the strategies employed, building the foundation for the effective utilization of SPEs in anode-free systems.

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Degradation control of all-solid-state Na batteries by inorganic oxide coated positive electrode active material

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All-solid-state Na batteries (ASSBs) are attracted attention owing to their high safety and resource properties for next-generation batteries. In general, cell degradation of ASSBs using polymer electrolyte occurs with the positive electrode (PE)/electrolyte interface during charge process. To suppress interfacial degradation, the inorganic oxides coated for Li batteries were reported in the previous study[1]. In this study, Na_3PO_4 or $Na_3Zr_2Si_2PO_{12}$ (NZSP) coated PEs were applied for ASSBs to suppress degradation. The degradation behavior of ASSBs was investigated by charge / discharge test and XRD analysis using extracted PE sheet from cell.

NaTFSA as Na salt, P(EO/PO) as polyether-based macromonomer, and DMPA as photoinitiator were mixed into Ar-filled glovebox. Polymer electrolyte films were prepared by UV irradiation of obtained homogeneous solution. $NaCoO_2$ (NCO) as active material, acetylene black (AB) as conductive additive, and P(EO/MEEGE)-NaTFSA as binder were mixed by 82:5:13 of weight ratio. The Na_3PO_4 and NZSP of inorganic oxides were added 5 wt.% and 10 wt.% for NCO, respectively. Applied slurry (thick. 50 μm) onto Al foil was cut to ϕ16 mm after vacuum dry. The PE sheet, Na metal negative electrode, and polymer electrolyte were assembled into coin-cell to fabricate ASSBs. The charge/discharge tests for over 10 cycles were performed at 333 K after heat-treated at 363 K for 48 h.

Fig. 1 shows the charge / discharge profiles of non-coated and 10 wt.% NZSP coated PE in the ASSBs. Although the 1st discharge capacity exhibited 36 mAhg^{-1} in the non-coated system, the sufficient capacity was not obtained about 30% of the theoretical capacity of NCO. In contrast, the NZSP-coated PE improved the 1st discharge capacity to 60 mAhg^{-1}. Fig. 2 shows the cycle number dependences of capacity and Coulombic efficiency. ASSB with NZSP-coated PE showed high discharge capacity retention and Coulombic efficiency in comparison with non-coated system. These results are suggesting that NZSP coating are the active material surface suppresses interfacial resistance degradation of the PE/electrolyte derived from the suppression of side products such as Co_3O_4.[1] In this presentation, a detailed evaluation of degradation behavior by XRD analysis will be also reported.

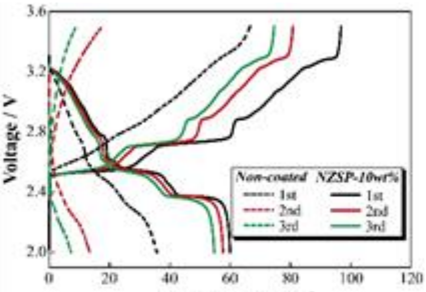

Fig. 1 Charge / discharge profiles of ASSBs with NZSP and without NZSP.

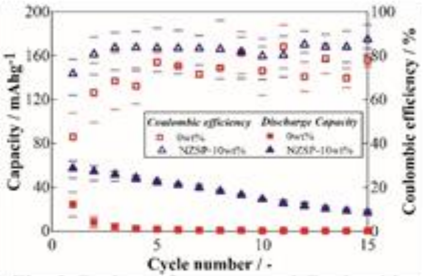

Fig. 2 Cycle performance and Coulombic efficiency of ASSBs.

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Investigation of the suitability of polymer host materials for solid-state anode-less lithium batteries

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Lithium metal batteries boast a multitude of advantageous properties in the pursuit of high-density energy storage such as a high energy density of 3862 mAh g^{-1} and a low standard electrochemical potential of −3.040 V.[1] Using excess Li-metal as an anode material compromises several of these factors by adding additional weight and volume of unused Li foil which also is problematic in the way that lithium is a critical resource with limited reserves. As such, the approach of an "anode-less lithium battery" has been suggested, indicating that the entirety of the available lithium in the cell is contained in the cathode material and electrolyte and is plated on the current collector during charging.[2,3] Attempts using this approach in combination with liquid electrolytes have been made, but show the typical problems of liquid electrolytes such as leaking, chemical stability, volatility and flammability.[4,5] An additional challenge with liquid electrolytes is the formation of dendrites due to a lack of mechanical stability of the electrolyte.

Solid polymer electrolytes appear to be an option that can address most of the above-mentioned issues and give access to reliable anode-less lithium batteries. As such, a comparison of three different polymers – poly(ethylene oxide), polycaprolactone and poly(trimethylene carbonate) – to assess them as candidates for anode-less lithium batteries will be presented. This comparison consists by cycling batteries assembled using each polymer with varying amounts of LiTFSI (20–40 wt%). To adhere to the above-mentioned goals, the cells used copper foil to deposit the lithium on and an LFP-based (lithium iron phosphate) cathode. The comparison shows that poly(trimethylene carbonate) shows the highest capacity retention followed by polycaprolactone and poly(ethylene oxide) performing the worst among the three chosen polymer hosts This goes against expectations as poly(ethylene oxide) has been the most commonly used solid polymer electrolyte to date.

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Effects of Molecular Structure of PEO-Based Solid Polymer Electrolytes for Ionic Conduction Behavior

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Solid polymer electrolytes (SPEs) are desired to the development of rechargeable battery systems owing to their high safety properties. However, SPEs exhibits relatively low ionic conductivity of less than 10^{-4} order at room temperature. The introduction of free side chains into network polymer with high mobility is known to improve cationic transport performances.¹⁾ If the main chains and side chains exhibit different relaxation times independent, ionic conduction is expected derived from each glass transition temperatures (T_gs). In this study, various PEO-based SPEs were prepared and evaluated physicochemical properties and dissociation to clarify relationship between ionic conduction and solvation structure.

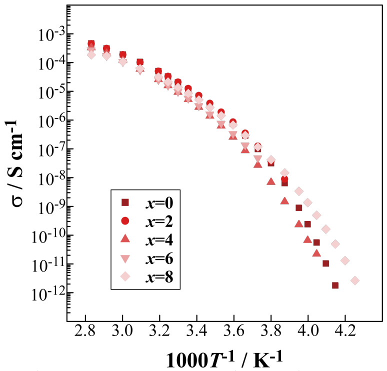

Fig.1 Temperature dependence of ionic conductivity of SPE with side chain.

SPEs were prepared with LiTFSA as an electrolyte salt, trifunctional P(EO/PO) and monofunctional PEO as a polyether-based monomer. LiTFSA was added by varying ratio of [Li]/[O]=0.02~0.16 per molar of oxygen units of P(EO/PO) and PEO. The mixed solutions with changing weight ratio of (10-*x*)P(EO/PO) : *x*PEO (*x*=0, 2, 4, 6, 8). Self-standing and transparent SPE films were obtained by UV irradiation for 5 minutes after addition of DMPA as a photo initiator. Obtained SPE samples were evaluated for thermal properties, ionic conductivity, and Raman spectroscopy.

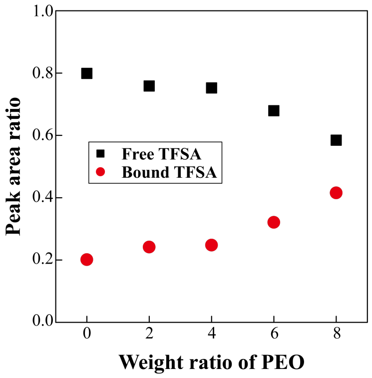

Fig.2 Raman spectra of SPE with side chain.

Fig.1 shows temperature dependence of ionic conductivity of SPEs for each weight ratio of side chain. Prepared SPEs with side chain were not confirmed significant effect of the introduction of side chains on ionic conductivity above room temperature. However, ionic conductivity improved by introduction of side chains in the low temperature near T_g. Fast ionic conduction path should be formed by side chain into main chain. Fig.2 shows peak area ratio of free TFSA relative to bound TFSA measured by Raman spectroscopy.²⁾ The peak area ratio of bound TFSA relative to free TFSA increased by introduction of side chains. Therefore, salt dissociability might be deteriorated by close to pure PEO structure with the ratio of side chains. We will also report the effect of chemically/physically cross-linking of SPEs.

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Densification of Lithium Metal via Particle Brush Artificial SEI Interpreted by X-ray Computed Tomography

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Alone, ex-situ analysis and postmortem teardowns often convolute interpretations of lithium metal cell failure modes, especially involving delicate polymer-lithium interfaces. In this study, x-ray micro-computed tomography (micro-CT) renders cycled lithium metal morphology interfaced with hybrid coatings comprised of poly(ethylene glycol) grafted to silica nanoparticles. Improved cycling performance in symmetric lithium metal cells as well as in lithium metal-LTO half cells is linked to denser lithium morphology obtained with the hybrid coating in ether and carbonate-based liquid electrolyte systems. Furthermore, the hybrid coatings eliminate the need for stack pressure, a sacrifice of energy density, by inherently tuning the lithium metal morphology. Finally, the findings inform best practices of lithium metal cell design with the hybrid coating, including rolling lithium foils as well as coating thickness and uniformity.

Cheap and easily processable polymer-based electrolytes for sustainable sodium-ion batteries

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Nowadays, research is directed towards alternative systems to Li-ion batteries (LIB), because lithium is expensive and its resources are geographically constrained. Sodium exhibits suitable electrochemical properties and it is very abundant, which makes Na-based batteries (NIB) suitable candidates to replace LiBs, particularly when large-scale energy storage is envisaged [1].

In this context, here we offer an overview of our recent developments on polymer-based electrolytes for NIB, which were prepared through different techniques, exploiting both simple casting and UV-curing and using various additives to improve specific characteristics (e.g., RTILs, cellulose derivatives, glymes) [2]. UV-curing allowed obtaining self-standing polymer electrolytes with desirable properties of flexibility, shape retention upon thermal stress, improved interfacial contact with the electrodes and ionic conductivity suitable for practical application. The resulting materials thermal, mechanical, morphological and electrochemical properties were thoroughly investigated. They exhibited excellent ionic conductivity (>1 mS/cm at 25 °C) and wide electrochemical stability window (> 4.2 V vs. Na^+/Na), ensuring safe operation at ambient conditions.

The best polymer electrolytes were assembled in lab-scale sodium cell coupled with nanostructured electrodes (e.g., hard carbons by biowaste carbonisation, TiO_2, MX-enes, high voltage phosphates like NaVPF, $NaMnO_2$), and showed remarkably stable ambient temperature cycling behaviour (about 250 mAh/g at 0.1 mA/cm^2 and remarkable overall stability upon long term cycling > 1000 reversible cycles at 0.5 mA/cm^2 corresponding to > 5000 h of continuous operation).

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Acknowledgements

Part of this work was carried out within the activities “Ricerca Sistema Elettrico” funded through contributions to research and development by the Italian Ministry of Economic Development. Financial support from the Italian Government - MIUR (PRIN N° 2017MCEEY4 funding) is gratefully acknowledged.

Investigation of High Ionic Conductive Polymer-Glass Ceramic Composite Electrolytes and Application for All-Solid-State Batteries

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All-solid-state batteries are attracting attention as next generation energy storage devices owing to their high safety and high energy density. Although we proposed composite solid electrolytes (CSEs) consisting of PEO-based polymer electrolytes and inorganic electrolytes, significant improvement of their performances, such as ionic conductivities hasn't been confirmed[1). In this study, to achieve high conductivity, we proposed the CSE consisting of polymer electrolytes introducing side chain and NASICON-type glass-ceramic electrolytes. The application of glass-ceramic electrolytes for CSE are expected to reduce grain boundary resistance (R_{GB}) because of their amorphous phase property. Therefore, in this study the CSEs using glass-ceramics were evaluated by thermal and electrochemical properties to investigate the conduction mechanism.

The CSEs were prepared by mixing polyether-based macromonomer (P (EO/PO=8:2)), $\mathrm{Li(CF_3SO_2)_2N}$ as an alkaline salt, 2,2-dimethoxy-2-phenylacetophenone as a photo initiator, acetonitrile as a solvent, and $\mathrm{Li_2O\text{-}Al_2O_3\text{-}SiO_2\text{-}P_2O_5\text{-}TiO_2}$ (LICGC) powder as an inorganic electrolyte. The composition percentage of LICGC (x) was changed between 0 to 200wt%. In addition, methoxytriethylene glycol acrylate was added as a free chain at 0 wt% and 40 wt% to P(EO/PO). After vacuum drying to remove the solvent, prepared solutions were cast onto a glass substrate and polymerized by UV irradiation. Thermal and electrochemical properties of prepared electrolytes were measured by DSC and AC impedance, respectively. Also, [Li | CSE | Li] cells were assembled, and impedance measurements of these cells were carried out to investigate apparent activation energies of grain boundary and Li / CSE interface.

Fig. 1 shows the Nyquist plot of [Li | P(PO/EO)+x wt% LICGC | Li] cells at 283 K. By the introduction of LICGC, R_{GB} appeared in the middle frequency region between bulk resistance (R_{B}) and interface resistance (R_{Li}) 1). This result suggests the formation of the percolation phase of LICGC particles in the CSE. Fig. 2 shows the x dependencies of the appearance activation energies of R_{GB} ($E_{a,\mathrm{GB}}$) and R_{Li} ($E_{a,\mathrm{Li}}$) calculated from Arrhenius plots. $E_{a,\mathrm{Li}}$ exhibited the maximum value at x=50 wt%. $E_{a,\mathrm{GB}}$ linely decreased with LICGC content, $\mathrm{Li^+}$ transport might be promoted by the active LICGC particle surface. In this presentation, we will report the structure effects of polymer chain (side free chain) and chemical / physical cross linking.

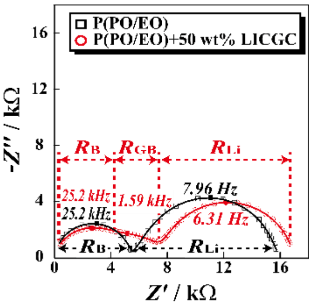

Fig.1 Nyquist plot of [Li | CSE | Li]at 283 K.

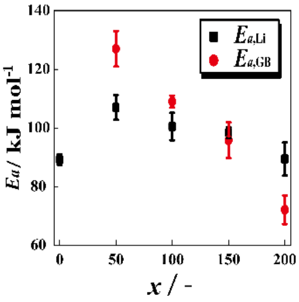

Fig.2 x dependencies of the $E_{a,\mathrm{GB}}$ and $E_{a,\mathrm{Li}}$.

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