Operando Raman Analysis for Reaction of Electrode / Electrolyte Interface using Solid Polymer Electrolytes

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All-solid-state batteries using various cation species (Li^+, Na^+, Ca^{2+}, Mg^{2+}) as reaction carriers are intense studied because of their high safety and resource abundant. Although solid polymer electrolytes (SPE) has high flexibility and formability with electrode, electrode / electrolyte interface are progressed involute reaction processes extremely such as solvation / desolvation, oxidation / reduction. Hence, *Operando* technique, which can observe reaction directly is required to understand interfacial reactions each cation. Herein, *Operando* Raman analysis was applied to evaluate concentration polarization inside electrolyte for Li- and Na- based SPEs under electrochemical reactions.

The SPE films (thick.: 0.5 mm) were prepared by using cast and photo-polymerization methods from P(EO/PO) as polyether-based macromonomer, MN(SO_2CF_3)$_2$ (TFSA) (M = Li, Na) as salts with cation concentration of [M]/[O] = 0.1. The obtained SPE films were constructed [Cu| SPE | metallic electrode (Li, Na)] and [metallic electrode| SPE| metallic electrode] cells for cyclic voltammetry (CV) and chronoamperometry (CA), respectively. After assembled, these samples were cut to 9 mm×9 mm and introduced into *Operando* cell having observation window. The CV and CA conditions were 0.1 mV s^{-1} of scan rate, -1.0 V to 3.0 V of voltage range and 100 mV of applied voltage, 10 h of measurement time, respectively. The Raman spectroscopies were measured to working (W.E.), counter electrode sides (C.E.) and SPE center of cross-sectional cell under CV or CA at room temperature every constant time. The intensities of Raman spectrum were normalized by peak area of CH_2 band. [1]

Operando Raman analysis was obtained clearly peaks originated from SNS–CF_3 vibration in the TFSA anion[1] for P(EO/PO)-LiTFSA, and these normalized peak areas (A/A_0) changed with CV time as shown Fig. 1. Although electrolyte center exhibited relatively constant value, C.E. and W.E. sides had strong time dependencies. These results suggest concentration change of TFSA anion owing to their Li^+ stripping/dissolution reaction properties. To further evaluation of concentration change, *Operando* Raman analysis using symmetric cell under CA was measured as shown Fig. 2. The C.E. side tended to increase value while the W.E. side decreased. Since C.E. and W.E. sides occur Li stripping and dissolution, respectively, these results can conduct to increase/decrease Li concentration. This presentation, we will also report *Operando* Raman analysis for Na - based SPEs compared to Li - based system.

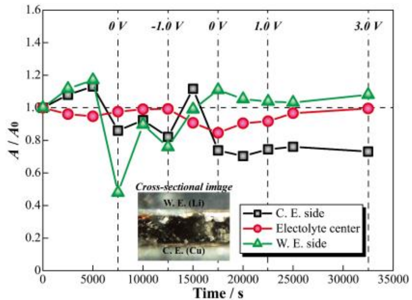

Fig. 1 Concentration change under CV in the [Cu| SPE | Li] cell.

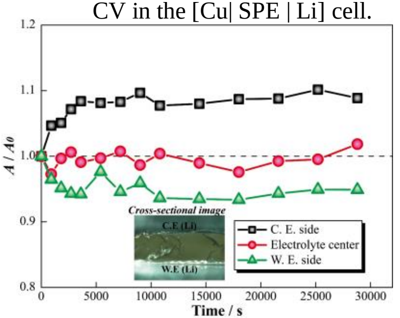

Fig. 2 Concentration change under CA in the [Li| SPE | Li] cell.

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Alternative Li-based salts in Solid Polymer Electrolytes: Is LiTFSI the Best Electrolyte Salt for Polymer Electrolytes?

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One major issue that solid polymer electrolytes are tackling is the electrochemical stability. [1] At minimum, the solid polymer electrolyte is composed of two components, the polymer host and the salt. Currently, the majority of research is utilizing the LiTFSI salt, which has shown good solubility and high ionic conductivity in PEO, and regardless of the chosen polymer host, it is typically assumed to be the best-suited salt, but this has rarely been confirmed. Most research is currently either focusing on modifying the polymer host or on introducing additives to the electrolyte. But the question presents itself of whether or not LiTFSI is the most suitable for all polymer host materials. In this work, we will present the effect of different Li-based salts in a polyester–polycarbonate system, poly(ε-caprolactone-*co*-trimethylene carbonate) (PCL-PTMC).

The PCL-PTMC system has shown good ionic conductivity at ambient temperature, good cycling properties, and a decent electrochemical stability, but to enable cycling against high-voltage cathodes, the electrochemical properties need to be further improved. [2, 3] Six different salts, including LiTFSI, were introduced to the PCL-PTMC system. It was shown that electrolytes with LiBOB and LiDFOB both have a higher conductivity compared to with LiTFSI. Additionally, both borate-based salts also show an improved electrochemical response, as shown in Fig. 1. With galvanostatic methods, the salt which is best suited for cycling with high-voltage cathodes will also be revealed.

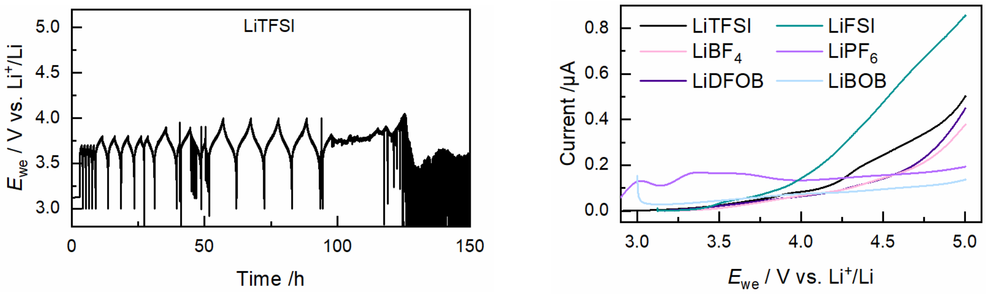

Fig. 1. (Left) galvanostatic cycling with LiTFSI, and (right) LSV of different salts in PCL-PTMC.

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Influence of Different Additives on Ion Transport in PEO Electrolytes

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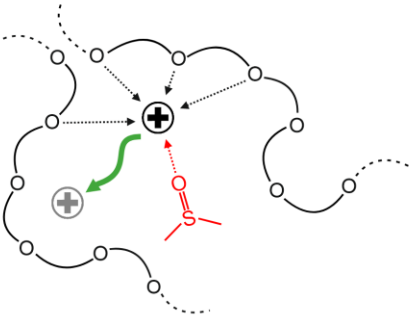
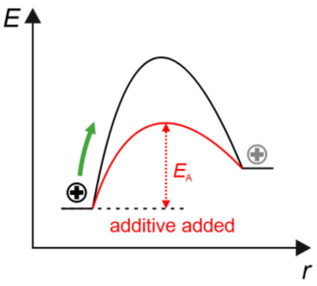
The main concern with solid polymer electrolytes, impeding their widespread commercial application as solid polymer electrolytes, is their low conductivity and lithium ion transference. For that reason, gel polymer electrolytes with incorporated low molecular weight additives are being researched. However, while the range of investigated polymers for polymer electrolytes is ever increasing, much less attention is drawn to the solvating additives.[1]

In our study, we compare ten diverse additives, from carbonates to crown ethers to amides and sulfoxides, regarding their effects on ion transport in concentrated electrolytes comprised of poly (ethylene oxide) (PEO) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). In a competitive selection process, involving nuclear magnetic resonance (NMR) diffusion measurements and Raman spectroscopy data, the four additives 15-crown-5 (15C5), tetraethylene glycol dimethyl ether (G4), *N*,*N*-dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) are ranked first in the resulting transport properties. Further investigations by NMR titration reveal a close relation between additive binding strength and ion transport in the PEO/LiTFSI electrolytes. The results are discussed in terms of competitive coordination of PEO and additive to the Li^+ ion.

Deeper insight is gained using electrophoretic NMR, providing distinct mobilities of each molecular species. For some additives, high lithium ion transference numbers and high effective charges are obtained, which are employed for better understanding the ongoing transport processes. At last, one additive was found to be most beneficial for lithium ion transport, showing an excellent salt dissociation and high lithium ion transport coefficients.





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Quantification of the ion coordination strength in solid polymer electrolytes

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To fully implement solid polymer electrolytes (SPEs) into batteries, a more fundamental understanding of the ion transport is required. One step forward was attained when the impact of the ion coordination strength, *i.e.* the interaction strength between the cations and the polymer chains (**Figure 1**), on the cation transport properties was observed – in particular its strong correlation to the transference number (T_+) for Li systems. [1]

Recently, further advances were gained with a novel method based on conventional FTIR measurements to qualitatively determine the ion coordination strength. By resolving the equilibrium constant K of the cation coordination to the anion *vs.* coordination sites in the polymer backbone at different temperatures and utilizing the van't Hoff equation, the dissociation energy of a salt in a polymer, which is an indirect measure of the coordination strength in a solvent-free system, can be derived. This permits a direct comparison of the the ion coordination strength between different polymer electrolyte systems and, furthermore, the possibility to translate the T_+ trends observed for one cation system to another. [2] In addition, fresh results of how the ion coordination strength in polyether's is affected by the polymer size and structure will be unveiled.

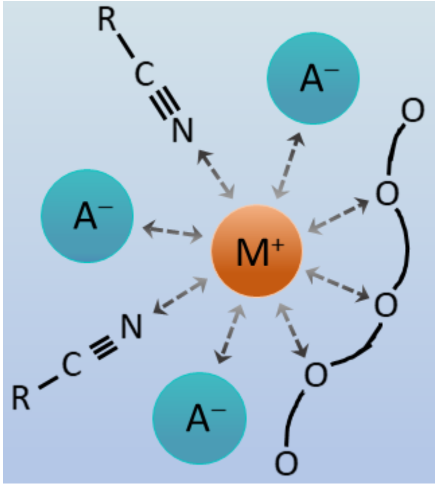

Figure 1. The ion coordination strength is the combined interaction strength from the ion–dipole interaction and the coordination number (CN).

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Solid-state poly(trimethylene carbonate)-based composite electrolytes with a garnet ceramic filer: exploring the ionic transport mechanism

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Polymer-based composite electrolytes, both with conductive and non-conductive ceramic fillers, have been extensively investigated in attempts to reach enhanced ionic conductivity in polymer electrolytes.[1] This category of materials has been dominated by poly(ethylene oxide) (PEO) as the conductive polymer matrix, where the inclusion of additives affect the PEO crystallinity. This renders in difficult to explore the fundamentals behind the ionic transport mechanism in these electrolytes, since the effects of increased amorphicity and novel modes and pathways for ionic conductivity cannot be separated. Therefore, polycarbonates and polyesters provide a better polymer platform to elucidate these phenomena.[2,3] In this work, we focus on assessing the effect of ceramic particles concentration on the ionic conduction behavior in a series of solid composite electrolytes based on the fully amorphous poly(trimethylene carbonate) (PTMC) polymer doped with LiTFSI, together with a garnet-type $Li_{6.7}Al_{0.3}La_3Zr_2O_{12}$ ionically conductive filler. Ionic conductivity measurements showed that at low contents of ceramic particles, they contribute to the ionic conduction primarily by providing an additional transport pathway along polymer-ceramic interfaces, rather than through the bulk. Higher ceramic loadings, however, resulted in a drastic decrease of the ionic conductivity. X-ray photoelectron spectroscopy revealed the presence of a Li_2CO_3 layer partially covering the surface of ceramic particles. As a result, these interfaces within the electrolyte matrix become more resistive, which can explain the observed trend in ionic conductivity for the PTMC-LLZO composites (Fig. 1).

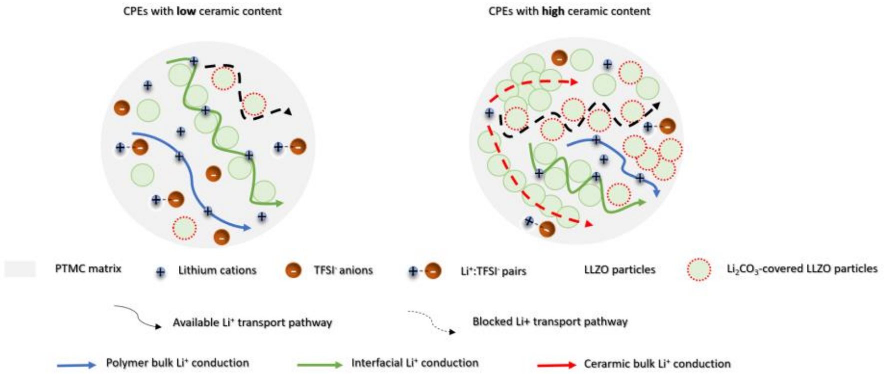

Figure 1: Schematic representation of potential Li-ion transport pathways in PTMC-LLZO composite electrolytes. Straight and dashed lines represent the accessible and blocked conduction pathways, respectively.

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Novel RAFT polymerization of ionic quasi-block copolymer electrolytes

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Advances in battery technology have been driven by the need for increased safety alongside higher capacity devices. Solid-state electrolytes are an ideal solution towards both problems, removing the highly flammable solvent electrolyte while allowing for the use of higher capacity alkali metal anodes. However, these systems have fallen short in offering an electrochemically and mechanically stable membrane whilst providing the required ion transport properties at ambient temperatures[1]. Polymers as electrolytes in solid-state electrolytes have been heavily investigated due their benefits in terms of safety, flexibility, and ease of processing. Among these materials, block copolymers (BCPs) offer a route to combine properties of individual homopolymers in a single macromolecule. As a result, a strong ion conducting polymer, *e.g.*, a poly-ionic liquid (PIL) can be paired with a mechanically robust polymer, *e.g.,* polystyrene (PS) to produce a prime solid polymer electrolyte candidate[2]. This work looks at adapting the polymerization of a select ionic BCP that has previously been characterized and shown strong electrolyte properties[3, 4]. The approach looks at transitioning from a multi-step block by block synthesis to a reduced waste and cost-effective *in situ* polymerization for the whole polymer. This results in block-like copolymers, (quasi-blocks) whereby early results have demonstrated polymer and electrolyte performance compared to their tradition BCP counterparts.

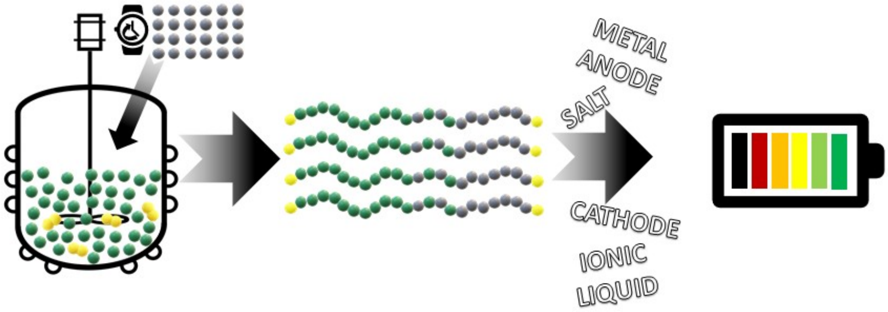

Figure 1: Synthesis and production process for quasi-block copolymer electrolytes

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Ion Transport in Crosslinked Acrylate Gel Electrolyte Systems

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The growing demand for energy storage devices worldwide combined with the claim to develop high safety Lithium ion batteries has drawn researchers' interest towards gel electrolytes which cannot leak and therefore provide safer alternatives.

We prepared electrolytes consisting of polyethylene glycol (PEG), Lithium bis(trifluormethylsulfonyl)amid (LiTFSA), Polyethylene glycol diacrylate (PEGDA; 13 monomers), 2-Phenoxyethyl acrylate (PEA), Dimethylformamide (DMF) and a photoinitiator (2-hydroxy-2-methylpropiophenone; 3 wt%). Here, the Li to ethylene oxide units (EO) was kept at a constant value of 0.1 (i.e. 10 EO per Li cation). The chain length of the PEGs was varied between approx. 5 to 77 monomers. The crosslinker content (PEGDA and PEA) were kept at a constant 5 mol% and 20 mol%, respectively. DMF serves as a plasticsizer. The liquid samples were irradiated at 350 nm for 15 min to sustain solid gel electrolytes.

Impedance spectroscopy, Raman spectroscopy, diffusion NMR (PFG NMR) and electrophoretic NMR measurements were performed and the transference numbers, effective charges and partial conductivities were calculated, which provide information of the underlying transport mechanism. PEG-Li cation-complexes are observed that migrate through the crosslinked matrix.

All results are compared to binary liquid electrolytes employing the respective molecular weight of the PEGs, in which a vehicular transport mechanism of the Li is known. Here, the same vehicular transport mechanism is found in the solid-gel samples, suggesting efficient transport of mobile Li-PEG complexes through the solid crosslinked network.

Investigation of ion transport in polycaprolactone electrolytes in dependency on salt concentration and molecular weight

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In order to improve the ion conduction of solid polymer electrolytes (SPEs), using poly(ε-caprolactone) (PCL) as the polymer host is a promising alternative to the commonly used poly(ethylene oxide) (PEO). While PCL has a good molecular flexibility comparable to PEO, the Li^+ complexation of the functional group is weaker leading to a less restricted cation motion.[1] For other SPEs, increasing the salt concentration was further found to be promising.[2] However, to achieve the full potential of this SPE, it is crucial to understand the underlying ion transport mechanisms and its dependency on polymer properties such as functional groups or molecular weight, as well as the electrolyte composition, i.e. the salt concentration.[3]

Hence, in this work a SPE based on PCL and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) is analyzed systematically with regard to ion transport properties depending on the salt concentration and the chain length of PCL. We aim to identify conditions that promote the different transport mechanisms, namely ion–polymer co-diffusion, continuous motion, and inter-segmental hopping. Therefore, we increase the chain length of PCL starting from oligomeric chains up to long polymer chains, since we expect a strong influence on the transport mechanisms. By using various methods including rheology, PFG NMR, and impedance spectroscopy, as well as MD simulations, a broad picture and deepened understanding is gained.

Moreover, the results are compared to the most extensive studied SPE based on PEO.[1,4,5] It is shown that the weaker-coordinating ester group of PCL in comparison to the ether group of PEO leads to an opposite trend of the transport number with the molecular weight and a larger dominance of anion-mediated ion transport, especially at high salt concentration and molecular weights.

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Effects of Organic Molecules as Electrolyte's Additives in Dye-Sensitized Solar Cell

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Main challenge to commercialise dye-sensitized solar cells (DSSC) are their low power conversion efficiency (η), and short-term stability. The current optimized η of DSSC is still far from the theoretical expectation. In improving the η, additives are introduced to promote free mobile iodide ion (I^-/I_3^-) and also to reduce recombination resistance at the semiconductor/electrolyte interface of DSSC by forming charge barrier. This will allow more electrons to be transferred from the excited dye, increase regenerative of I^-/I_3^- redox electrolyte and enhance the η. Most additives employed in highly efficient DSSC are nitrogenous cyclic compound based with one to three nitrogen atoms. To improve the η of DSSC, we explore new organic structures and investigate their effect as additives in DSSC. Synthesis of new triazole moiety has been conducted by azide-alkyne cycloaddition using a quinoline pharmacophore and characterized spectroscopically. The effects of nitrogenous cyclic compound on photovoltaic properties of DSSC, photo-response behaviour and internal charge transport properties of DSSC has been examined by light-current-voltage, incident photon-to-current efficiency and impedance measurements. Density Functional Theory (DFT) methods also is used to establish the optimized geometry for adsorption of organic compounds onto electrode. This study provide an alternatives additives to improve the photocurrent/photovoltage and thus increases the η of DSSC. The DSSC has successfully increased the photocurrent with optimum power conversion efficiency of 1.8 % under a standard AM 1.5G illumination.