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Enhanced ionic conduction in composite polymer electrolyte filled with a plant biomass “lignin”

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An addition of small amount of plant biomass-based lignin causes a large improvement in ionic conductivity of composite polymer electrolytes at room temperature, which can be considered to fabricate easily under a low carbon way for use in future all-solid-state battery applications.

Solid polymer electrolytes (SPE) have attracted much attention as a “soft” solid electrolyte for batteries because of their safe, easy-processible, and flexible properties.^{1–3} Nevertheless, the ionic conductivity of SPE at ambient temperature is generally lower than that of liquid electrolytes.⁴ One innovative method is to prepare composite polymer electrolyte (CPE), in which the added solid particle, known as the filler, incorporated into the host polymer has been proposed to increase the electrochemical properties of SPE.⁵ The poly(ethylene oxide) (PEO) is the most widely used as a polymer matrix for SPE, because it contains ether coordination sites that enable the dissociation of salts together with a flexible macromolecular structure that assists ionic transport. Since the PEO tends to crystallize below 60 °C, the fast ion-transport can occur at higher than 60 °C in the amorphous phase. Therefore, the presence of PEO crystalline domains interferes with ionic transport, which requires an amorphous phase.² Various formulations of composite polymers have been attempted to suppress the crystallization. The introduction of organic plasticizers,^{6, 7} or inorganic fillers such as SiO₂,⁸ TiO₂,⁹ and Al₂O₃,¹⁰ have therefore been researched to improve the conductivity of SPE.

Besides that, a significant number of alternative polymer hosts without PEO have been explored over a few decades,¹¹ poly(ethylene carbonate) (PEC) is recently known to be one of the ion-conductive materials which are synthesized from carbon dioxide (CO₂) with ethylene oxide. There is a good point

that materials can be produced under a low environmental load from using CO₂ as a monomer. The PEC-based electrolytes are based on a new ion-conduction mechanism and have the possibility of exceeding the conventional conductivity level which is fully expected.¹² Motivated by these advantages, it has been proposed to utilize PEC as a novel polymer host for SPE.¹²

On the other hand, it is well known that lignin is one of the main constituents of lignocellulose biomass and is the most abundant aromatic resource on the earth in terrestrial ecosystems, representing nearly 30% of the organic carbon in the biosphere.¹³ Traditionally, lignin as one kind of by-product in paper pulp manufacturing and biomass conversion processes for biofuel production is a readily available, cheap, and underutilized biopolymer.¹⁴ Nowadays, lignin has been increasingly investigated for its potential incorporation in the production of battery materials, which has the advantage of being environmentally friendly.¹⁵ With the increasing manufacturing of lignin in recent years, lignin has been available at a low cost. Although lignin has many outstanding properties that there are still limited studies on lignin as a functional additive applied to Li batteries, already studies mostly on anodes,^{16, 17} binders,^{18, 19} and gel electrolytes.^{20–22} Moreover, the previous studies on electrolytes for battery only focused on lignin which needs complex graft copolymerization.^{23, 24} Furthermore, all the applied lignin use conventional extraction procedures, such as thermochemical treatment.^{24, 25}

Recently, we proposed a novel lignin extraction process without high temperature and toxic reagents, in which wet-type ultrafine bead milling and enzymatic saccharification are used for the simultaneous enzymatic saccharification and comminution (SESC) of plants.²⁶ The SESC lignin can enhance the heat-tolerant properties of a synthetic polymer.²⁷ Herein, innovative utilization of the SESC lignin which is a completely natural product-based functional additive with a superior ability as filler for PEO and PEC-based SPE was investigated for the first time. The CPE can be easily prepared with a very small amount of SESC lignin that is added to PEO or PEC and Li salt (Fig. S1). The PEO and PEC-based CPE samples were named according to the lignin contents as the PEO and PEC-lig CPE 0, 0.1, 0.5, and 1.0%, where the percent values represent the amount of SESC lignin in wt.%. The ion-conductive properties of these

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electrolytes were evaluated, and FT-IR measurement was carried out to examine the functional groups as well as their interaction in chemical structures.

All lignin composites were obtained as homogeneous flexible solid films (Fig. S2). The outstanding film-forming properties and excellent flexibility may arise from the interaction based on the strong hydrogen bond between lignin and electrolyte molecules. The ionic conductivity of lignin-incorporated CPE is superior to the original at all the measurement temperatures. The Arrhenius plots of the conductivity for PEO-based CPE with various lignin contents are shown in Fig. 1 (a). The original PEO electrolyte without lignin

which was Arrhenius behavior with convex curves throughout the entire range of measurement temperatures (Fig. 1 (c)). Whereas the original PEC electrolyte without lignin had a very low conductivity, $3.4 \times 10^{-8} \text{ S cm}^{-1}$ at 40°C , the PEC-lig CPE 0.1% had a much higher conductivity than $10^{-5} \text{ S cm}^{-1}$. An improvement in the conductivity was caused almost three orders of magnitude by the addition of only 0.1% lignin, because the T_g was the lowest (Table. 1). The T_g was lower than that of the original which is most likely ascribed to the plasticizing effect promoted by the bis-(trifluoromethanesulfonyl) imide (TFSI) anion.¹² A decrease in the value of T_g helps smooth migration of ions, and an increase in the conductivity is therefore expected. Reasons for the enhancement of the conductivity have been reported as the higher amorphous content of polymer in CPE, the Lewis acid-base interactions between the filler particles and the electrolyte polar groups, and the association of the filler particles with polymer chains.²⁸ Moreover, ion-conductive properties of CPE are influenced by the type and size of the filler incorporated, and the smaller particles provide more pronounced effects.²⁸ Our previous study indicates that the SESC lignin exists as a platelet-shaped nanoparticle in the PEC matrix.²⁷ The surface morphology of PEC-lig CPE 0.1% was also confirmed using the SEM measurement as shown in Fig. S4, and it was observed that the platelet-shaped lignin is well dispersed in the amorphous dimensional space. Furthermore, it can be confirmed that the PEC electrolytes have an amorphous phase from the DSC measurement, and all T_g values are lower than room temperature (Fig. S3 c), thereby preserving chain mobility leading to facile ionic conduction, resulting in higher conductivity.

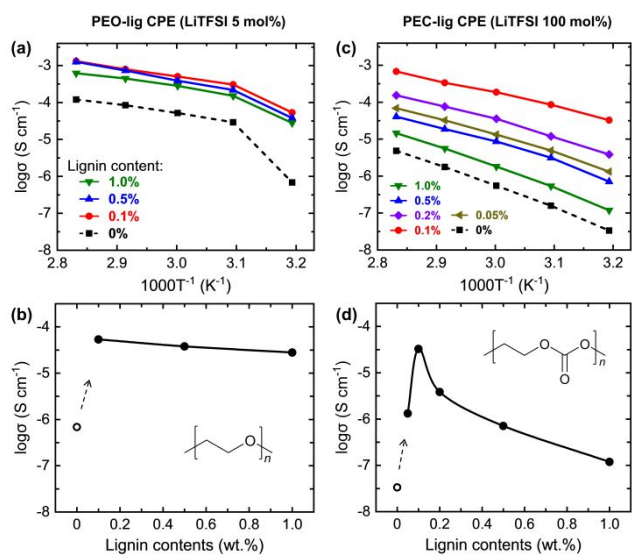


Fig. 1 Temperature dependence of ionic conductivity for (a) PEO-lig CPE and (b) PEC-lig CPE, and lignin contents dependence of the conductivity at 40°C for (b) PEO-lig CPE and (d) PEC-lig CPE.

has low conductivity of the order of $10^{-7} \text{ S cm}^{-1}$ at room temperature because of a transition at approximately 50°C corresponding to the melting temperature of crystalline PEO domains (Fig. S3 a). By the addition of only 0.1% SESC lignin, approximately doubled the conductivity of the original, which was $5.3 \times 10^{-5} \text{ S cm}^{-1}$ at 40°C , appeared in the CPE. The conductivity values of PEO-lig CPE 0.5 and 1.0% were similar, and the PEO-lig CPE 0.5% exhibited the conductivity up to $10^{-5} \text{ S cm}^{-1}$ at 30°C , which is approximately two orders of magnitude higher than that of the original. Previous studies on PEO-based CPE indicated that the addition of nanoparticle fillers such as TiO_2 can lead to a significant increase in the conductivity, inhibit re-crystallization of the polymer, and lower the glass transition temperature (T_g).²⁸ The melting point shifted to a lower temperature as the incorporation of lignin increased, and the peak area also decreased (Fig. S3 a), which suggests a decrease in the degree of crystallinity for PEO. As the amorphous region increases, the PEO chain attains faster internal modes in which bond rotations produce more segmental motion to favor inter and intrachain transport of ions, thus increasing the conductivity.

On the other hand, the temperature dependence of the conductivity for PEC-lig CPE is much different from the PEO system. The PEC-lig CPE exhibited typical amorphous-type

Table 1 Thermal properties of PEO and PEC-lig CPE.

SESC lignin content (%)		0	0.1	0.5	1.0
PEO-CPE	T_g ($^\circ\text{C}$)	-43	-44	-45	-45
	T_{d5} ($^\circ\text{C}$)	368	369	385	373
PEC-CPE	T_g ($^\circ\text{C}$)	-4	-16	-8	-1
	T_{d5} ($^\circ\text{C}$)	168	172	172	187

The lignin contents dependence of ionic conductivity at 40°C for PEO and PEC electrolyte are compared and shown in Fig. 1 (b, d). The conductivity of both PEO- and PEC-lig CPE decreased with increasing the lignin content, but the values were still higher than those of the originals. This behavior indicates that the favorable properties imparted by the lignin addition are prevented at a higher content because of the insulating nature of the lignin. There are enormous aromatic ring structures and abundant polar groups in the lignin, such as phenolic hydroxyl, carboxyl, and methoxy groups on its side chain which can easily cause excessive intermolecular forces, resulting in poor dispersibility in the material which affects the conductivity.²² Thus, as the amount of added lignin increases, the increased terminal groups lead to a decrease in the conductivity when the amount of added lignin is more than 0.1%.

It is known that the PEO chains form a stable complex with cations, thus the change in the formation of interacted PEO units can be confirmed from the vibrational characterization. The FT-IR spectra of neat PEO and PEO-lig CPE are shown in Fig. 2 (a, b). The C-O-C stretching triplet modes and CH₂ bending doublet are confirmed by the existence of the crystalline PEO phase. In neat PEO, the C-O-C stretching mode is divided into three bands at 1145, 1093, and 1059 cm⁻¹, and the CH₂ bending mode appears at 1363 and 1342 cm⁻¹, respectively. After the addition of LiTFSI, the C-O-C stretching and the CH₂ bending mode shifted to lower wavenumbers at 1142, 1098, 1057 cm⁻¹, and at 1354 cm⁻¹, and these intensities were slightly larger. The intensity of these shifted bands increased remarkably compared with neat PEO. Moreover, the C-O-C stretching mode further shifted to 1135, 1095, 1056 cm⁻¹ by increasing of added lignin, while the CH₂ bending mode also shifted to 1351 cm⁻¹. These results are due to the complexation and interaction between the ether oxygen of PEO and Li⁺ and are in good agreement with previous results reported by various researchers.^{29–31} The abundant aliphatic and phenolic ether

shifted to lower wavenumber and were observed at 1727 cm⁻¹ because of the interaction of C=O with Li⁺. The interacting band of C=O appeared to turn slightly higher wavenumber at 1731~1734 cm⁻¹ with increasing the lignin content, which may be aroused from the intramolecular interaction between C=O and ester or carboxy group of lignin.³⁵ The band of PEC-lig CPE 0.1% shifted to the lowest wavenumber at 1731 cm⁻¹ by infinitesimal lignin content. This means that the highest conductivity of PEC-lig CPE 0.1% is associated with the dissociated ions which can migrate faster via the enhanced segmental motion. Moreover, broadbands at 3533~3640 cm⁻¹ in Fig. 2 (d) indicate the presence of OH stretching vibrations in aromatic and aliphatic OH groups of lignin.³⁶ The bands at 3617 and 3540 cm⁻¹ of the CPE 0.1% correspond to the multiple intermolecular hydrogen bonds of aliphatic hydroxyl groups as well as between aliphatic hydroxyl groups and condensed guaiacyl hydroxyl units,^{37, 38} so the intermolecular bonded OH group of PEC-lig CPE was reduced by the addition of lignin as the broad bands shift lower. Furthermore, according to our previous study,³⁹ the antioxidant activity of SESC lignin contributes to its excellent heatproof properties as shown in Fig. S3 and Table. 1, which is beneficial to the improvement in the safety of the battery. The scavenging activity of radicals by the guaiacol groups of lignin prevents the thermal degradation of the PEC main chain which is a beneficial property in electrolyte applications.²⁷ The SESC lignin has a definite absorption property of radicals, and by physically mixing the SESC lignin with the electrolyte, a certain chemical structure on the terminal of the lignin particles can be changed as shown in the upper part of Fig. 3. A small number of radicals is derived from

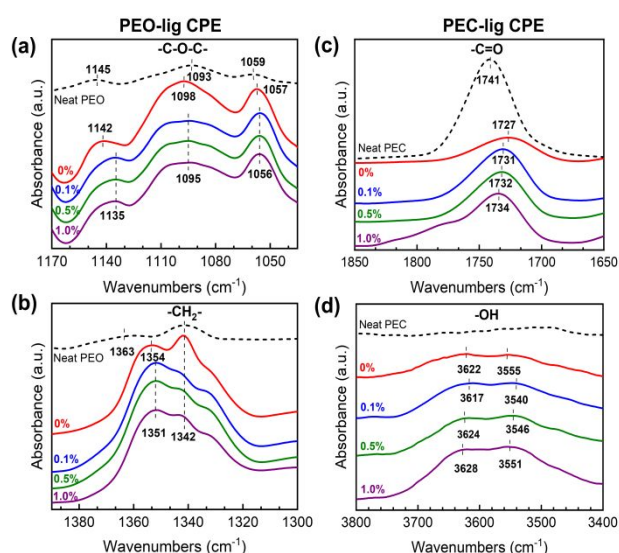


Fig. 2 FT-IR spectra of (a) C-O-C stretching mode and (b) CH₂ bending vibrations for neat PEO and PEO-lig CPE, (c) C=O stretching vibration mode of neat PEC and PEC-lig CPE, and (d) OH stretching vibrations OH groups in lignin.

linkages in lignin also could be related to contributing directly enhancing the ionic conductivity. A previous study reports that the phenolic resin can enhance the conductivity because of lowering pseudo-activation energy for the Li⁺ conduction.³² The hydrogen bond between the hydroxyl group of the phenolic terminal of the lignin and ether oxygen in the PEO chain also results in higher basicity of PEO. The higher basicity of the ether group can dissolve Li salts more easily and results in a greater fraction of “free” ions especially anions for higher conductivity.³³

On the contrary, the structural information on neat PEC and PEC-lig CPE obtained from the FT-IR are shown in Fig. 2 (c, d). In Fig. 2 (c), the band at 1741 cm⁻¹ of neat PEC can be identified as a stretching vibration mode of the carbonyl groups (C=O) on the PEC main chain.³⁴ By the addition of LiTFSI, the C=O bands

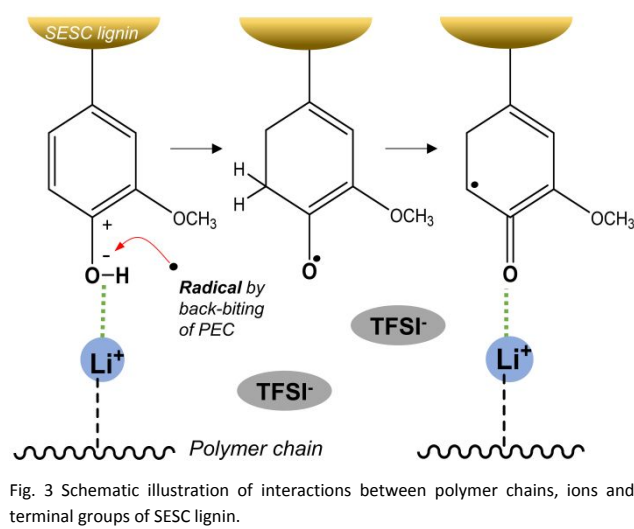


Fig. 3 Schematic illustration of interactions between polymer chains, ions and terminal groups of SESC lignin.

PEC terminals by the partial degradation. The guaiacyl groups generated by the pyrolysis of SESC lignin act as radical scavengers, which inhibit the alkoxide back-biting reaction of PEC chains, and these structural transformations may also affect the ion-conductive property. Based on the FT-IR results, it is believed that a change of local structure occurs as seen in the lower part of Fig. 3. The OH stretching vibrations in aromatic OH groups of lignin were confirmed which provided the chemistry of a possible bonding mechanism. When the Li salt

was added to SPE, the interaction occurs between C-O-C or C=O with Li⁺, and the interactions are probably weakened by the addition of SESC lignin. The decrease in T_g value is proposed to be due to the plasticizing effect of dissociated TFSI anions which further affect the improvement in the conductivity. Furthermore, there is a small amount of ketone structures on the aromatic terminals during the process of radical scavenging by the guaiacol groups in PEC-based CPE. The structure of resulting ketone groups on the terminals also provides dissociation for Li salts and may weaken stable coordination of Li⁺ ions with polymer chains which can lead to the fast migration of ions.

In conclusion, ion-conductive PEO- and PEC-based CPE were prepared for the first time using nano-particulate SESC lignin from plant biomass. This study has a positive impact on the utilization of biomass material from natural resources as a high-value filler, as well as materials that can be produced under low environmental load, thus the application of these materials can greatly reduce the production cost of batteries and meet the concept of sustainable development. The CPE with SESC lignin can therefore demonstrate the potential application of a promising candidate as a low carbon electrolyte material for flexible batteries and perspective to develop all-solid-state polymer batteries under low environmental impact.

There are no conflicts to declare.

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