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**Revised manuscript for review only**

**Title:**

Lignin-based Solid Polymer Electrolytes: Lignin-graft-Poly(ethylene glycol)

**Authors:**

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**Abstract**

Lignin is an aromatic-rich biomass polymer that is cheap, abundant, and sustainable. However, its application in the solid electrolyte field is rare due to challenges in well-defined polymer synthesis. In this report, we demonstrate synthesis of lignin-graft-poly(ethylene glycol) (PEG), and its conductivity test for a solid electrolyte application. The main steps of synthesis include functionalization of natural lignin's hydroxyl to alkene, followed by graft-copolymerization of PEG thiol to the lignin via photoredox thiol-ene reaction. Two lignin-graft-PEGs were prepared having 22 wt% lignin (lignin-graft-PEG 550) and 34 wt% lignin (lignin-graft-PEG 2000). Then, new polymer electrolytes for conductivity tests were prepared via addition of lithium bis-trifluoromethanesulfonimide (LiTFSI). The polymer graft electrolytes exhibited ionic conductivity up to  $1.4 \times 10^{-4}$  S/cm at 35 °C. The presence of lignin moderately impacts conductivity at elevated temperature compared to homopolymer PEG. Furthermore, the ionic conductivity of lignin-graft-PEG at ambient temperature is significantly higher than homopolymer PEG precedents.

Lignin is the second most abundant biopolymer after cellulose. In particular, lignin is the largest renewable aromatic resource, with 50 million tons produced each year globally.<sup>[1]</sup> Among various kinds of lignin, more than 85% of lignin product is kraft lignin which is generated through the paper pulping process.<sup>[2]</sup> Generally, the isolated lignin has high mechanical strength and high thermal stability.<sup>[3]</sup> However, the complex chemical structures and limited solubility has prevented advanced applications of lignin for decades.<sup>[4]</sup> Lignin's monomeric unit structures are known: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol (Figure S1a) are connected by aromatic and aliphatic ether linkages to build the highly networked polymer structure.<sup>[5],[6]</sup> Thus, there are abundant phenolic and aliphatic hydroxyl groups in lignin (Figure S1b).<sup>[7]</sup> In

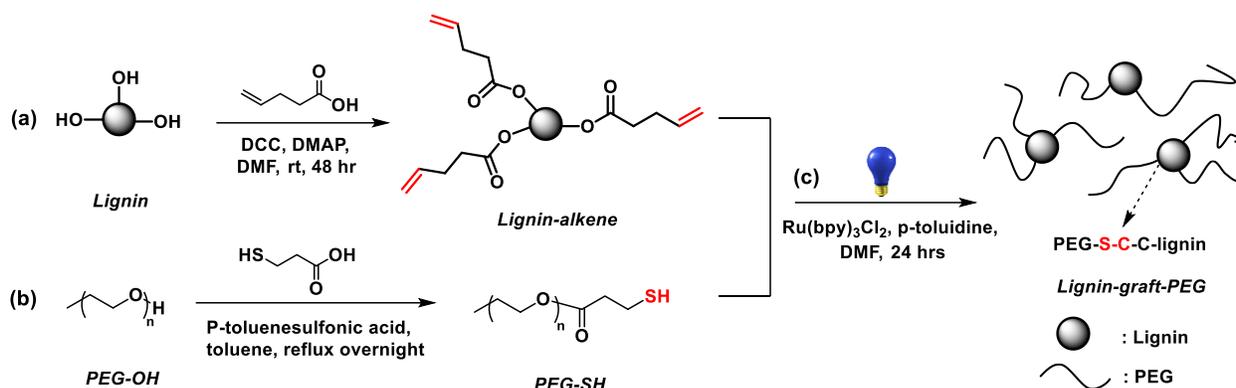
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4 this report, the hydroxyl groups in the lignin were used to prepare finely designed lignin-based polymers  
5 via graft copolymerization.  
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7 A practically efficient method to prepare covalently linked lignin-based polymers is graft  
8 copolymerization.<sup>[8]</sup> The commonly used three methods are graft-from, graft-onto and graft-through graft  
9 copolymerizations.<sup>[9]</sup> Among them, the graft-onto method can be used for various functional groups,  
10 multiple types of synthetic polymers, and diverse degrees of polymerization. In graft-onto method, the  
11 lignin and synthetic polymer are covalently linked by the end group coupling reaction. The covalent  
12 linkages of the lignin graft copolymer assure enhanced reproducibility of mechanical/thermal properties  
13 over different batches and high miscibility when it was used as compatibilizers.<sup>[10],[11]</sup> The lignin-based graft  
14 copolymer can be readily tuned by using different synthetic polymers, grafted polymer arm lengths, and  
15 lignin weight content in the copolymer.<sup>[8]</sup> For example, poly(ethylene glycol) (PEG) has been  
16 copolymerized with lignin to enhance thermal stability,<sup>[12],[13]</sup> Young's modulus,<sup>[14]</sup> and strength at break.<sup>[15]</sup>  
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20 In lithium ion batteries, electrolytes function to conduct lithium ions traveling between anode and  
21 cathode.<sup>[16]</sup> According to the physical state, there are liquid electrolytes and solid electrolytes.<sup>[17]</sup> Generally,  
22 liquid electrolytes provide high ionic conductivity. However, solid electrolytes are gaining strong interest  
23 recently due to their high safety and ability to be used at elevated temperature compared to liquid  
24 electrolytes.<sup>[18]</sup> The solid polymer electrolytes are nonvolatile, less flammable, and tend to suffer less severe  
25 degradation reactions than liquid electrolytes.<sup>[19]</sup> In addition, solid electrolytes alleviate concerns of leaking  
26 and catastrophic reaction with lithium metal anodes. Among solid polymer electrolytes, PEG is one of the  
27 most promising candidates due to its electrochemical stability. That comes from flexible ethylene oxide  
28 (EO) segments, which function to dissolve lithium salt.<sup>[16]</sup> Well above the glass transition temperature ( $T_g$ )  
29 and above the crystallization temperature, where the polymer electrolyte is fully amorphous, lithium ion  
30 transport is facile. However, when the temperature is low at ambient temperature, lithium ion transport is  
31 slow. This is a major issue that limits rapid battery charge and discharge.<sup>[16]</sup> Moreover, low mechanical  
32 strength and thermal instability of PEG limits the industrial-scale manufacturing of lithium batteries.<sup>[16]</sup>  
33 Fortunately, these problems can be solved by grafting PEG onto lignin which is mechanically strong due  
34 to high aromaticity.  
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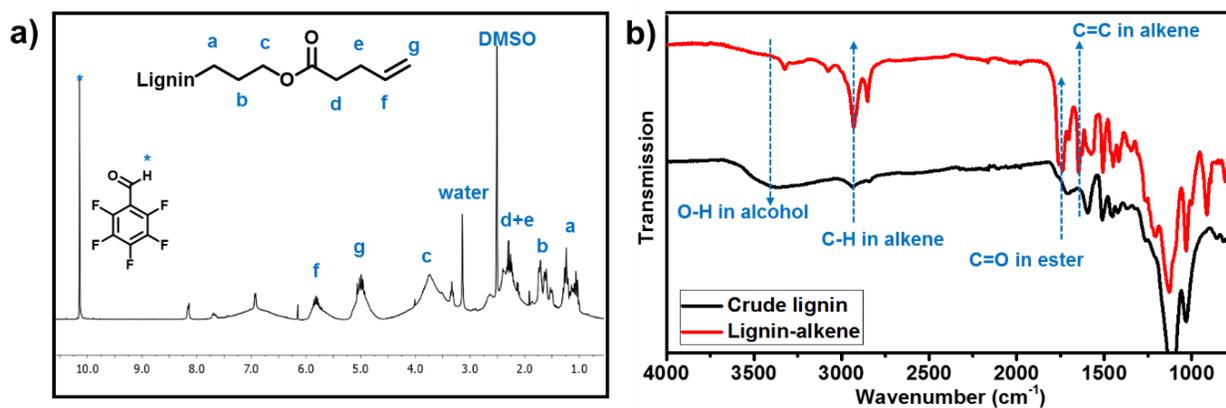
39 In the newly synthesized lignin-graft-PEG, lignin works as rigid segments to enhance the mechanical and  
40 thermal properties, while PEG provides flexibility as well as high ion transportation ability. Highly efficient  
41 ion transport has recently been shown to be important for preventing dendrite formation, a serious safety  
42 concern in Li ion batteries.<sup>[20],[21]</sup> Our graft-onto copolymerization approach yields a new material with  
43 similar elevated-temperature conductivity to homopolymer PEG, while enhancing ambient temperature  
44 conductivity. Lignin-graft-PEG is thus a promising candidate for sustainable solid polymer electrolyte.  
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49 **Synthesis of Lignin-graft-PEG:** Initial examples of Ru-catalyzed photoredox thiol-ene reaction for lignin  
50 modification were developed recently by our group.<sup>[22]</sup> In this report, the developed photoredox lignin  
51 modification was used to covalently link lignin and PEG as a graft copolymerization method. The overall  
52 synthesis of lignin-graft-PEG is depicted in Scheme 1. Softwood kraft lignin (TCI L0045) was modified to  
53 convert the abundant hydroxyl group to alkene group via an esterification (Scheme 1a). Herein, the used  
54 natural lignin is a paper industry byproduct and directly used as received to provide a practical lignin  
55 modification method. The molecular weight of the lignin is 24,000 g/mol with a polydispersity index (PDI)  
56 of 2.4 as reported previously.<sup>[23]</sup>  
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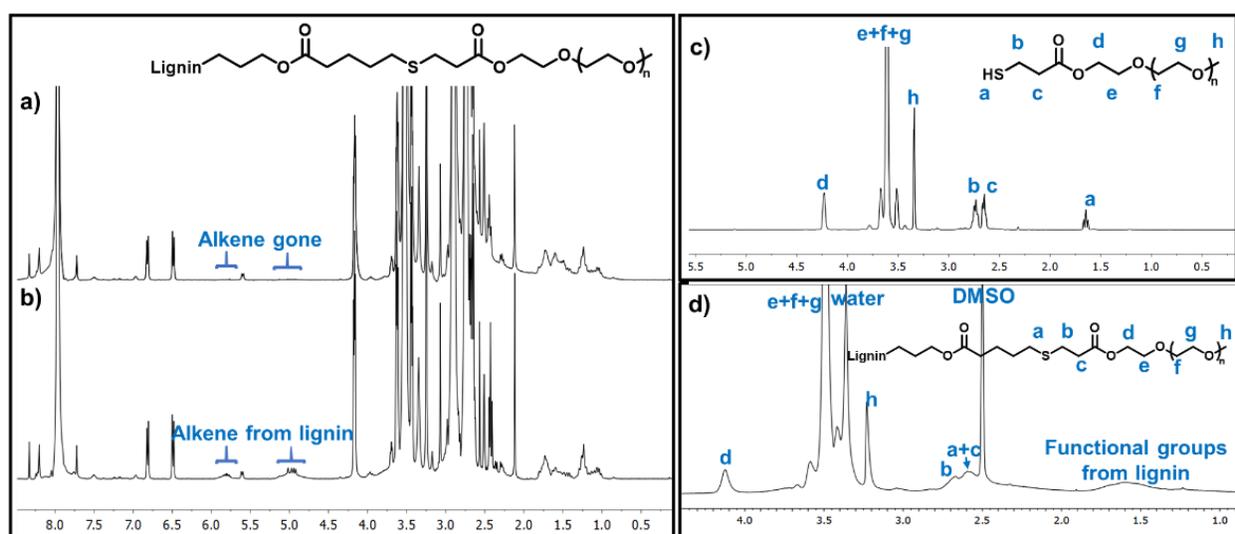
19 **Scheme 1.** The synthesis procedure for lignin-graft-PEG 550. (a) Lignin modification to lignin-alkene. (b) PEG-OH 550 modification with 3-mercaptopropionic acid to synthesize PEG-SH 550. (c) Thiol-ene reaction for lignin-graft-PEG 550. The lignin is represented by a spherical symbol, and the true chemical structure is shown in Figure S1b.

24 After the carbodiimide-mediated esterification with 4-pentenoic acid, the prepared lignin-alkene is characterized by  $^1\text{H}$  NMR (Figure 1a). The appearance of protons d, e, f, and g confirms the introduction of alkene. Protons f and g, which come from alkenes of the modified lignin, are used to measure the alkene amount per gram of lignin. An internal standard, 2,3,4,5,6-pentafluorobenzaldehyde (10.2 ppm, singlet) is used in this process and the details are described in the Supporting Information. As a result, the modified lignin has 0.00357 mol alkene per gram lignin.<sup>[24]</sup> This value corresponds to on average 86 grafting sites per lignin molecule. In addition to the  $^1\text{H}$  NMR, Fourier-transform infrared spectroscopy (FTIR, Figure 1b) was used to determine the consumption of hydroxyl groups as a result of the esterification (Scheme 1a) between lignin and 4-pentenoic acid. In the comparison of crude lignin and lignin alkene, the consumption of hydroxyl groups at  $3400\text{ cm}^{-1}$  is apparent. After esterification, C-H vibrations at  $2980\text{ cm}^{-1}$  appear, C=C vibrations from the alkene at  $1650\text{ cm}^{-1}$  appear and C=O ester vibration occurs at  $1740\text{ cm}^{-1}$ , which shows more ester groups are gained through esterification.



57 **Figure 1.** Characterization of lignin-alkene (a)  $^1\text{H}$  NMR of lignin-alkene in DMSO- $d_6$ . (b) FTIR comparison of unmodified lignin and lignin-alkene. A chemical structure of internal standard, 2,3,4,5,6-pentafluorobenzaldehyde, is shown in (a) with an asterisk.

Commercially available PEGs (PEG-OH 550 and 2000) were modified by an esterification reaction to convert the hydroxyl groups to thiol groups in Scheme 1b.<sup>[25]</sup> This end group modification is a preparation for the grafting of PEG onto lignin using photoredox thiol-ene reaction. The modified PEG was characterized by <sup>1</sup>H NMR as shown in Figure 2c. Proton d, adjacent to a terminal hydroxyl group of PEG-OH, is shifted to 4.24 ppm after the ester linkage is formed between PEG and 3-mercaptopropionic acid. Moreover, the formed ester linkage was confirmed by the appearance of protons a, b, and c from the thiol group and its adjacent protons. Herein, two different PEG-OHs (PEG-OH 550 and 2000) were modified to PEG-SHs. PEG-OH 550 has a number-averaged molecular weight of 550 g/mol, and PEG-OH 2000 has a number-averaged molecular weight of 2000 g/mol. The modified PEG-SH 550 and PEG-SH 2000 were grafted onto lignin separately yielding two different lignin weight contents. Briefly, lignin-graft-PEG 550 has 66 wt% PEG and 34 wt% lignin, and lignin-graft-PEG 2000 has 78 wt% PEG and 22 wt% lignin.



**Figure 2.** (a) <sup>1</sup>H NMR of the reaction of lignin-alkene and PEG-SH 550 at 24 hours, when the reaction is completed. (b) <sup>1</sup>H NMR of the reaction of lignin-alkene and PEG-SH 550 at 0 hour. (c) <sup>1</sup>H NMR of PEG-SH 550 in CDCl<sub>3</sub>. (d) <sup>1</sup>H NMR of lignin-graft-PEG 550 in DMSO-d<sub>6</sub>.

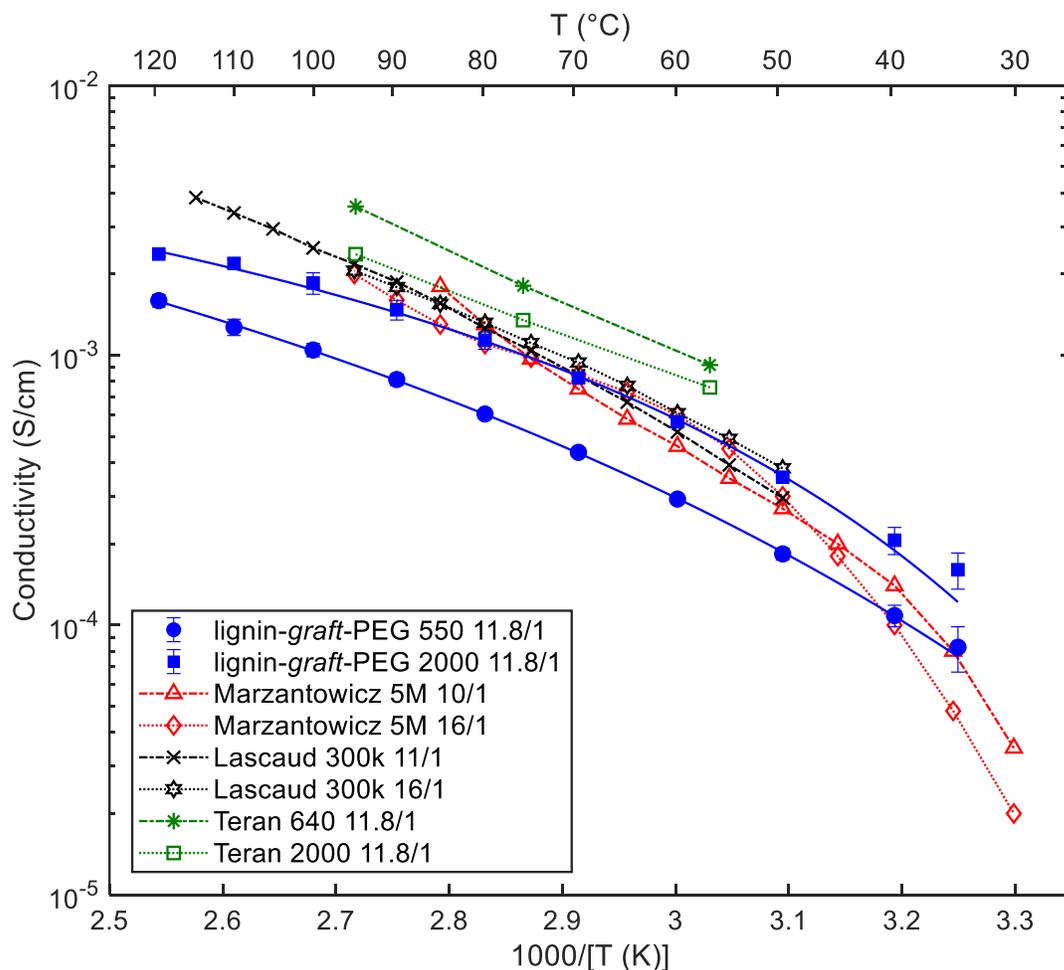
The PEG-SH was grafted onto lignin via Ru-catalyzed photoredox thiol-ene reaction (Scheme 1c). The Ru-catalyzed photoredox thiol-ene reaction is done under moderate reaction conditions with visible blue light irradiation at room temperature. The completion of thiol-ene reaction was confirmed by <sup>1</sup>H NMR after 24 hours as shown in Figure 2a and b. At the beginning of the reaction (0 hour), all the reagents were homogeneously mixed in dark environment. The alkene protons on lignin-alkene were observed at 5.0 and 5.7 ppm in <sup>1</sup>H NMR (Figure 2b). After 24 hours irradiation under blue LED light, the alkenes of lignin-alkene were consumed as a result of a reaction with the thiol groups from PEG-SH (Figure 2a). After purification, lignin-graft-PEG 550 is characterized by <sup>1</sup>H NMR in DMSO-d<sub>6</sub> (Figure 2d). The chemical structure and their NMR signal assignment demonstrates the synthesis of the copolymer, lignin-graft-PEG. According to visual observation, the synthesized lignin-graft-PEG 550 and lignin-graft-PEG 2000 are soft dark brown solids. Prior to graft-onto polymerization (thiol-ene reaction), the lignin-alkene, PEG-SH 550, and PEG-SH 2000 were separately brown powder, transparent liquid, and white solid. The color and phase changes are additional indications for the successful synthesis. From visual observation and manual handling, the mechanical strength of lignin-graft-PEG is much stronger than homopolymer PEG. In addition, it was

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4 previously proven that the covalent incorporation of lignin to polymer enhances mechanical properties  
5 according to related studies.<sup>[3], [9], [11]</sup> During thermal processing to prepare samples for conductivity  
6 measurements, it was found that the newly synthesized lignin-graft-PEG melted at higher temperature than  
7 ungrafted homopolymer PEG. The detailed mechanical and thermal property tests are under investigation  
8 and therefore the present report emphasize synthesis of new lignin-based polymers and their ionic  
9 conductivity.

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12 The molecular structure of polymers (Figure 1) in present work is designed for convenient scalability. The  
13 synthesis step was minimized (two steps) and used reagents are all not expensive chemicals. The synthesis  
14 does not require special conditions such as high temperature, high pressure, and large amount of pricy  
15 catalysts. Although it is not within the scope of the present work, additional work already underway to  
16 produce the lignin-based polymers in large scale. A particular technical challenge of the lignin-based  
17 polymer production is poor solubility of lignin. However, intensive studies are solving the solvent issue  
18 through testing and optimizing various solvents with multiple industrial lignins.<sup>[1], [26], [27]</sup> In addition, in  
19 depth discussion of scalability can be found from literatures.<sup>[28], [8], [29], [30]</sup> These works demonstrate  
20 potentials of industrial scale production of lignin-based polymers the used of lignin as a low-cost renewable  
21 resource comes with high economic value.  
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27 **Ionic Conductivity of Lignin-graft-PEG:** As a candidate for solid polymer electrolyte in battery  
28 applications, the ionic conductivity of the lignin-graft-PEG was measured by electrochemical impedance  
29 spectroscopy (EIS). The test samples were prepared by mixing lithium bis-trifluoromethanesulfonimide  
30 (LiTFSI) and lignin-graft-PEG. The prepared samples possess a ratio of 0.085 mole LiTFSI per mole  
31 ethylene oxide (EO) repeating unit, equivalently 1/11.8 molar ratio of LiTFSI/EO. Two samples were  
32 studied to determine the effect of lignin and PEG ratio on ionic conductivity. The graft polymers are lignin-  
33 graft-PEG 550 (66 wt% PEG + 34 wt % lignin) and lignin-graft-PEG 2000 (78 wt% PEG + 22 wt% lignin).  
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36 The ionic conductivity is shown in Figure 3 in Arrhenius format. The conductivity between 35 °C and 120  
37 °C ranged from 0.0715 to 1.66 mS/cm for lignin-graft-PEG 550 and 0.143 to 2.41 mS/cm for lignin-graft-  
38 PEG 2000. Both samples have a clear Vogel-Fulcher-Tammann (VFT) temperature dependence. Details of  
39 the VFT regressions are reported in the Supporting Information. Overall, the lignin-graft-PEG 2000 has  
40 higher conductivity than the lignin-graft-PEG 550 samples at all the tested temperatures. This is true even  
41 if the higher PEG content of lignin-graft-PEG 2000 is taken into account (for example by dividing the  
42 conductivity of each graft polymer electrolyte by its respective PEG weight or volume fraction). Similar  
43 behavior (ionic conductivity increasing with PEG molar mass) has also been observed in block copolymers  
44 of polystyrene-block-poly(ethylene oxide).<sup>[31], [32]</sup> Note that poly(ethylene oxide) (PEO) and PEG are  
45 chemically identical. The term 'PEO' is used more commonly in the polymer electrolyte community and  
46 often refers to higher molar mass and/or material synthesized with living polymerization methods. On the  
47 other hand, 'PEG' is most frequently used in biomedical applications and takes its root from condensation  
48 reaction of ethylene oxide. It is often used to refer to low molar mass polymer (less than about 10 kg/mol).  
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**Figure 3.** Arrhenius plot of conductivity of lignin-graft-PEG from this work compared to three reports from literature of PEG-LiTFSI mixtures: Marzantowicz,<sup>[33]</sup> Lascaud,<sup>[34]</sup> and Teran.<sup>[35]</sup> In the legend, sample name or first author is followed by PEG molar mass then by EO/LiTFSI molar ratio. 'M' stands for million and 'k' stands for thousand. Note that lines connecting literature data are guides for the eye. Solid curves through lignin samples are VFT regressions.

The ionic conductivity for the synthesized lignin-graft-PEG is compared to previous reports with homopolymer PEG (no lignin segment) to investigate the role of lignin on the conductivity.<sup>[34], [35], [33]</sup> In particular, there is data from Teran et al.<sup>[35]</sup> for a homopolymer PEO with the same molar mass and with the same salt concentration as that used in this study. Based on an Arrhenius regression, which fits the data from Teran et al.<sup>[35]</sup> quite well over this narrow temperature range, the conductivity of the homopolymer electrolyte at 80 °C is 2.15 mS/cm, whereas the lignin-graft-PEG 2000 electrolyte has an ionic conductivity of 1.47 mS/cm at the same temperature, a difference of approximately 50%. Looking more broadly, there appears to be some penalty from lignin presence at elevated temperature, but some benefit from lignin presence at and near ambient temperature. This result suggests that lignin enhances the conductivity at ambient temperature. This could be due to suppression of PEG crystallinity or could be related to the abundant aliphatic and phenolic ether linkages in lignin contributing directly to enhancing the ionic conductivity.<sup>[36]</sup> Grafting of PEG-like moieties to synthetic polymer backbones have shown similar room-temperature enhancement that has been attributed to suppressed crystallinity.<sup>[36]</sup> The stable covalent linkage

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4 in lignin-graft-PEG is likely to interfere with PEG crystallization. The efficiently performed graft  
5 copolymerization (via photoredox thiol-ene reaction) enabled the synthesis of well-defined lignin-graft-PEG  
6 which leads to enhanced ambient-temperature conductivity and increased mechanical strength (observed  
7 qualitatively). This result highlights a method to maintain reasonable ambient-temperature conductivity by  
8 grafting PEG to a bio-sourced macromolecule, lignin.  
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11 Addressing the problem of low room temperature ionic conductivity is essential for practical application of  
12 polymer electrolytes in batteries.<sup>[16]</sup> The room temperature conductivity of lignin-graft-PEG 2000 is nearly  
13 double that of homopolymer PEO reported by Marzantowicz.<sup>[33]</sup> Regarding battery performance, a doubling  
14 of ionic conductivity will enable a battery to achieve more than twice the specific power.<sup>[37]</sup> Based on prior  
15 work with PEO-based electrolytes,<sup>[38]</sup> these lignin-graft-PEG electrolytes are expected to be compatible  
16 with lithium iron phosphate cathodes and lithium titanate anodes. Improvement in the mechanical properties  
17 of the lignin-graft-PEG electrolytes are most likely needed to enable long-term cycling with lithium metal  
18 anodes and for compatibility with other next-generation electrodes.  
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21 In conclusion, a new biomass- based copolymer, lignin-graft-PEG, that is designed as a novel solid polymer  
22 electrolyte in battery applications, is successfully synthesized by an environmentally benign photoredox  
23 thiol-ene reaction. The polymer synthesis was performed by three simplistic steps: 1) alkene modification  
24 of lignin, 2) end group modification of PEG to possess thiol terminals, and 3) graft-onto copolymerization  
25 through Ru-catalyzed photoredox thiol-ene reaction. The stable covalent linkage in lignin-graft-PEG  
26 suppresses PEG crystallization. The newly synthesized lignin-graft-PEG demonstrated enhanced ambient-  
27 temperature conductivity compared to homopolymer PEG precedents. Therefore, the reported lignin-graft-  
28 PEG is a promising new material for solid polymer electrolytes in battery applications.  
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### 33 **Supporting Information**

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35 Supporting Information is available from the Wiley Online Library or from the author.  
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### 37 **Acknowledgments**

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43 of NMR facilities.  
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### 46 **Conflict of Interest**

47  
48 The authors declare no conflict of interest.  
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### 50 **Keywords**

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52 Lignin, biomass, solid polymer electrolytes, poly(ethylene glycol), battery.  
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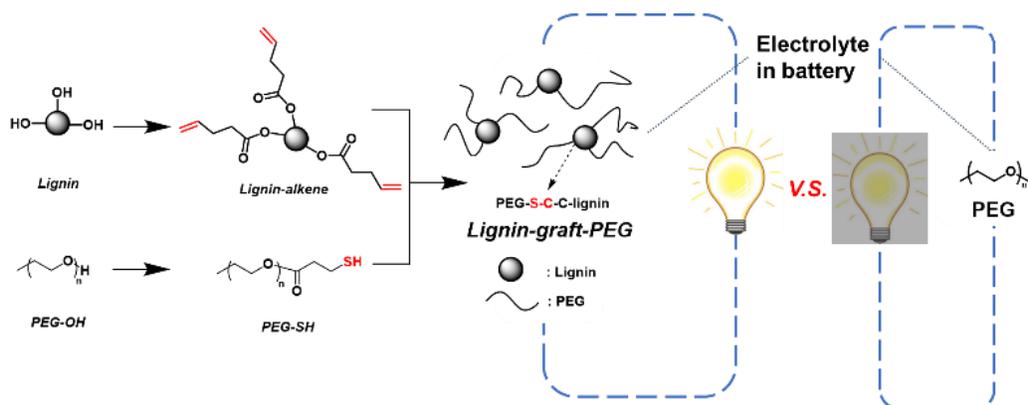
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29 TOC:



Poly(ethylene glycol) (PEG) is grafted onto natural lignin to synthesize a new solid polymer electrolyte, lignin-graft-PEG. The new polymer is biomass-based and a promising candidate in lithium battery applications. The lignin-graft-PEG shows higher ionic conductivity than homopolymer PEG at ambient temperature. This feature solves low conductivity issue of homoPEG at ambient temperature.



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