

Macromolecular Rapid Communications

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

--Manuscript Draft--

Manuscript Number:	marc.202000428R1
Article Type:	Communication
Corresponding Author:	Hoyong Chung, Ph.D. Florida State University Tallahassee, FL UNITED STATES
Corresponding Author E-Mail:	hchung@fsu.edu
Order of Authors:	Hailing Liu, Ph.D. Logan Mulderrig Daniel Hallinan, Ph.D. Hoyong Chung, Ph.D.
Keywords:	Lignin, biomass, solid polymer electrolytes, poly(ethylene glycol), battery.
Section/Category:	Polymers for a Sustainable Future (guest-edited by Philip Scholten, Jie Cai & Robert Mather)
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 includes 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 1.4×10^{-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.
Author Comments:	
Additional Information:	
Question	Response
Please submit a plain text version of your cover letter here.	Uploaded separately.
Do you or any of your co-authors have a conflict of interest to declare?	No. The authors declare no conflict of interest.
Response to Reviewers:	Responses to reviewers' comments Reviewer #1: The authors present the synthesis and testing of a novel polymer electrolyte based on PEGylated lignin. The goal was to utilize this important biopolymer and improve the low ionic conductivity and mechanical properties of PEG electrolytes, which limit the performance of lithium ion batteries. Different synthetic approaches were explored in this work and preliminary testing of conductivity indicates that the PEGylated lignins have performance that is competitive with commercial materials. This is an exciting preliminary result and it is expected that this robust system will lead to significant expansion of research into these novel materials.

Response: The author appreciates reviewer #1's insight regarding the potential of the manuscript.

Reviewer #2:

The characterization of PEG graft onto modified lignin is well done and the conductivity study is ok. It

would be useful for the authors to add (1) performance as a battery electrolyte and (2) some insight on the scalability of the syntheses steps, technical and economic challenges.

Response:

A paragraph has been added after the conductivity results, discussing the performance as a battery electrolyte.

Addressing the problem of low room temperature ionic conductivity is essential for practical application of polymer electrolytes in batteries. (Reference: Long et al. "Polymer Electrolytes for Lithium Polymer Batteries" J. Mater. Chem. A 2016, 4 (26), 10038–10069) The room temperature conductivity of lignin-graft-PEG 2000 is nearly double that of homopolymer PEO reported by Marzantowicz. (Reference: Marzantowicz et al. "Crystalline Phases, Morphology and Conductivity of PEO: LiTFSI Electrolytes in the Eutectic Region" J. Power Sources 2006, 159 (1), 420–430) Regarding battery performance, a doubling of ionic conductivity will enable a battery to achieve more than twice the specific power. (Reference: Doyle et al. "The Importance of the Lithium Ion Transference Number in Lithium/Polymer Cells" Electrochim. Acta 1994, 39 (13), 2073–2081) Based on prior work with PEO-based electrolytes, (Reference: Hallinan et al. "Lithium Metal Stability in Batteries with Block Copolymer Electrolytes" J. Electrochem. Soc. 2013, 160 (3), A464–A470) these lignin-graft-PEG electrolytes are expected to be compatible with lithium iron phosphate cathodes and lithium titanate anodes. Improvement in the mechanical properties of the lignin-graft-PEG electrolytes are most likely needed to enable long-term cycling with lithium metal anodes and for compatibility with other next-generation electrodes.

An additional discussion regarding scalability of the developed lignin-based polymer is on page 5 of "Revised manuscript for review only" as follows.

The molecular structure of polymers (Figure 1) in present work is designed for convenient scalability. The synthesis step was minimized (two steps) and used reagents are all not expensive chemicals. The synthesis does not require special conditions such as high temperature, high pressure, and large amount of pricy catalysts. Although it is not within the scope of the present work, additional work already underway to produce the lignin-based polymers in large scale. A particular technical challenge of the lignin-based polymer production is poor solubility of lignin. However, intensive studies are solving the solvent issue through testing and optimizing various solvents with multiple industrial lignins. (References: Tricker et al. "Similarities in Recalcitrant Structures of Industrial Non-Kraft and Kraft Lignin" ChemSusChem 2020, 13, 4624-4632.; Kwok et al. "Pretreatment efficacy and lignin solubility of organic solvents on juvenile slash pine chips for lignin value prior to pulping," BioRes. 2020, 14, 5988-6003.; Kwok et al. "Solvent Selection for Lignin Value Prior to Pulping" ChemSusChem 2020, 13, 267-273) In addition, in depth discussion of scalability can be found from literatures. (References: Lancefield et al. "The synthesis and analysis of advanced lignin model polymers." Green Chemistry 2015, 17, 4980-4990.; Kai et al. "Towards lignin-based functional materials in a sustainable world." Green Chemistry 2016, 18, 1175-1200.; Moreno et al. "Lignin-based smart materials: a roadmap to processing and synthesis for current and future applications." Materials Horizons 2020, 7, 2237.; Ganewatta et al. "Lignin biopolymers in the age of controlled polymerization." Polymers 2019, 11, 1176) These works demonstrate potentials of industrial scale production of lignin-based polymers the used of lignin as a low-cost renewable resource comes with high economic value.



FAMU-FSU
Engineering

FAMU-FSU College of Engineering
Department of Chemical and Biomedical Engineering
2525 Pottsdamer Street, Suite A131
Tallahassee, FL 32310
<https://chy979797.wixsite.com/chunggroup>

September 22, 2020

Dear Dr. Staffilani,

Please find our attached revised manuscript “Lignin-based Solid Polymer Electrolytes: Lignin-graft-Poly(ethylene glycol)”. I appreciate your effort to handle our manuscript and the opportunity of resubmission for your further consideration. We would like to also express our appreciation to the reviewers for their constructive comments.

Following your suggestions, we have included appropriate responses to reviewers’ comments and questions in this cover letter and have revised the manuscript accordingly. We have uploaded a copy of “Revised manuscript for review only” and “Revised manuscript” to your online submission system. The documents point out our changes, either highlighted or in red, in response to reviewers’ comments and questions.

Thank you for considering our revised manuscript for publication in *Macromolecular Rapid Communications*.

Sincerely yours,

Hoyong Chung

Assistant Professor

Department of Chemical and Biomedical Engineering

FAMU-FSU College of Engineering

Florida State University

Tel) +1-850-644-1768

E-mail) hchung@fsu.edu

Responses to reviewers' comments

Reviewer #1:

The authors present the synthesis and testing of a novel polymer electrolyte based on PEGylated lignin. The goal was to utilize this important biopolymer and improve the low ionic conductivity and mechanical properties of PEG electrolytes, which limit the performance of lithium ion batteries. Different synthetic approaches were explored in this work and preliminary testing of conductivity indicates that the PEGylated lignins have performance that is competitive with commercial materials. This is an exciting preliminary result and it is expected that this robust system will lead to significant expansion of research into these novel materials.

Response: The author appreciates reviewer #1's insight regarding the potential of the manuscript.

Reviewer #2:

The characterization of PEG graft onto modified lignin is well done and the conductivity study is ok. It would be useful for the authors to add (1) performance as a battery electrolyte and (2) some insight on the scalability of the syntheses steps, technical and economic challenges.

Response:

A paragraph has been added after the conductivity results, discussing the performance as a battery electrolyte.

Addressing the problem of low room temperature ionic conductivity is essential for practical application of polymer electrolytes in batteries. (Reference: Long et al. "Polymer Electrolytes for Lithium Polymer Batteries" J. Mater. Chem. A 2016, 4 (26), 10038–10069) The room temperature conductivity of lignin-graft-PEG 2000 is nearly double that of homopolymer PEO reported by Marzantowicz. (Reference: Marzantowicz et al. "Crystalline Phases, Morphology and Conductivity of PEO: LiTFSI Electrolytes in the Eutectic Region" J. Power Sources 2006, 159 (1), 420–430) Regarding battery performance, a doubling of ionic conductivity will enable a battery to achieve more than twice the specific power. (Reference: Doyle et al. "The Importance of the Lithium Ion Transference Number in Lithium/Polymer Cells" Electrochim. Acta 1994, 39 (13), 2073–2081) Based on prior work with PEO-based electrolytes, (Reference: Hallinan et al. "Lithium Metal Stability in Batteries with Block Copolymer Electrolytes" J. Electrochem. Soc. 2013, 160 (3), A464–A470) these lignin-graft-PEG electrolytes are expected to be compatible with lithium iron phosphate cathodes and lithium titanate anodes. Improvement in the mechanical properties of the lignin-graft-PEG electrolytes are most likely needed to enable long-term cycling with lithium metal anodes and for compatibility with other next-generation electrodes.

An additional discussion regarding scalability of the developed lignin-based polymer is on page 5 of "Revised manuscript for review only" as follows.

The molecular structure of polymers (Figure 1) in present work is designed for convenient scalability. The synthesis step was minimized (two steps) and used reagents are all not expensive chemicals. The synthesis does not require special conditions such as high temperature, high pressure, and large amount of pricy catalysts. Although it is not within the scope of the present work, additional work already underway



to produce the lignin-based polymers in large scale. A particular technical challenge of the lignin-based polymer production is poor solubility of lignin. However, intensive studies are solving the solvent issue through testing and optimizing various solvents with multiple industrial lignins. (References: Tricker et al. "Similarities in Recalcitrant Structures of Industrial Non-Kraft and Kraft Lignin" *ChemSusChem* 2020, 13, 4624-4632.; Kwok et al. "Pretreatment efficacy and lignin solubility of organic solvents on juvenile slash pine chips for lignin value prior to pulping," *BioRes.* 2020, 14, 5988-6003.; Kwok et al. "Solvent Selection for Lignin Value Prior to Pulping" *ChemSusChem* 2020, 13, 267-273) In addition, in depth discussion of scalability can be found from literatures. (References: Lancefield et al. "The synthesis and analysis of advanced lignin model polymers." *Green Chemistry* 2015, 17, 4980-4990.; Kai et al. "Towards lignin-based functional materials in a sustainable world." *Green Chemistry* 2016, 18, 1175-1200.; Moreno et al. "Lignin-based smart materials: a roadmap to processing and synthesis for current and future applications." *Materials Horizons* 2020, 7, 2237.; Ganewatta et al. "Lignin biopolymers in the age of controlled polymerization." *Polymers* 2019, 11, 1176) These works demonstrate potentials of industrial scale production of lignin-based polymers the used of lignin as a low-cost renewable resource comes with high economic value.

Revised manuscript for review only

Title:

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

Authors:

Hailing Liu,¹ Logan Mulderrig,^{1,2} Daniel Hallinan Jr.,^{1,2,*} and Hoyong Chung^{1,*}

Affiliations:

1) Department of Chemical and Biomedical Engineering
Florida A&M University-Florida State University College of Engineering
2525 Pottsdamer Street, Suite A131
Tallahassee, FL 32310

2) Aero-propulsion, Mechatronics, and Energy (AME) Center
Florida State University
2003 Levy Avenue
Tallahassee, FL 32310

*Corresponding author emails: hchung@eng.famu.fsu.edu and dhallinan@eng.famu.fsu.edu

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 1.4×10^{-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.^[1] Among various kinds of lignin, more than 85% of lignin product is kraft lignin which is generated through the paper pulping process.^[2] Generally, the isolated lignin has high mechanical strength and high thermal stability.^[3] However, the complex chemical structures and limited solubility has prevented advanced applications of lignin for decades.^[4] 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.^{[5],[6]} Thus, there are abundant phenolic and aliphatic hydroxyl groups in lignin (Figure S1b).^[7] In

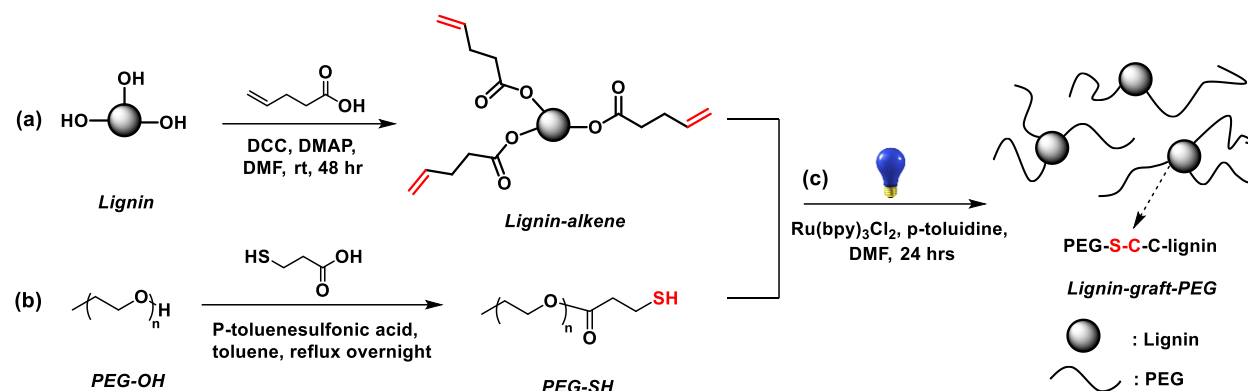
1
2
3
4 this report, the hydroxyl groups in the lignin were used to prepare finely designed lignin-based polymers
5 via graft copolymerization.
6

7 A practically efficient method to prepare covalently linked lignin-based polymers is graft
8 copolymerization.^[8] The commonly used three methods are graft-from, graft-onto and graft-through graft
9 copolymerizations.^[9] 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.^{[10],[11]} 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.^[8] For example, poly(ethylene glycol) (PEG) has been
16 copolymerized with lignin to enhance thermal stability,^{[12],[13]} Young's modulus,^[14] and strength at break.^[15]
17
18
19

20 In lithium ion batteries, electrolytes function to conduct lithium ions traveling between anode and
21 cathode.^[16] According to the physical state, there are liquid electrolytes and solid electrolytes.^[17] 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.^[18] The solid polymer electrolytes are nonvolatile, less flammable, and tend to suffer less severe
25 degradation reactions than liquid electrolytes.^[19] 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.^[16] 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.^[16] Moreover, low mechanical
32 strength and thermal instability of PEG limits the industrial-scale manufacturing of lithium batteries.^[16]
33 Fortunately, these problems can be solved by grafting PEG onto lignin which is mechanically strong due
34 to high aromaticity.
35
36
37
38

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.^{[20], [21]} 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.
45
46
47
48

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.^[22] 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.^[23]
57
58
59
60
61
62
63
64
65



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.

After the carbodiimide-mediated esterification with 4-pentenoic acid, the prepared lignin-alkene is characterized by ^1H 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.^[24] This value corresponds to on average 86 grafting sites per lignin molecule. In addition to the ^1H 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 cm^{-1} is apparent. After esterification, C-H vibrations at 2980 cm^{-1} appear, C=C vibrations from the alkene at 1650 cm^{-1} appear and C=O ester vibration occurs at 1740 cm^{-1} , which shows more ester groups are gained through esterification.

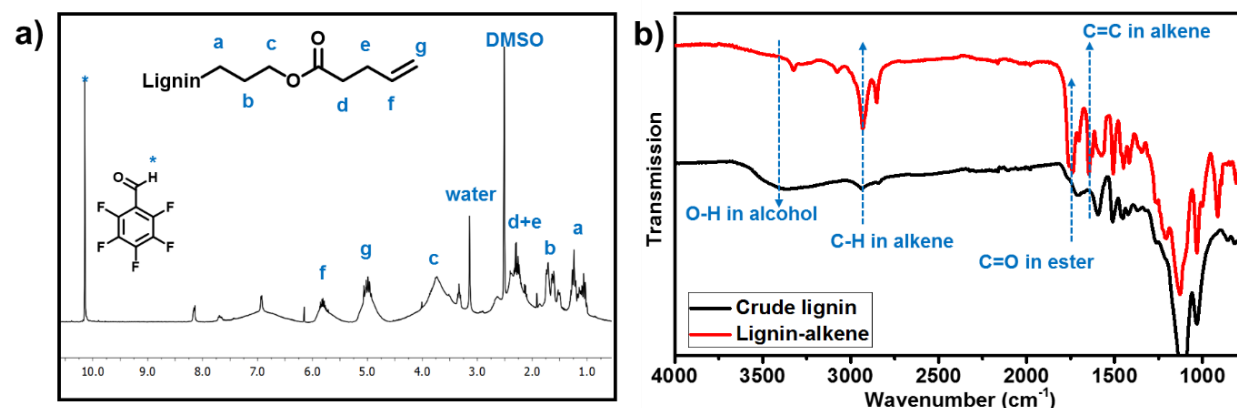


Figure 1. Characterization of lignin-alkene (a) ^1H NMR of lignin-alkene in DMSO- d_6 . (b) FTIR comparison of unmodified lignin and lignin-alkene. A chemical structure of internal standard, 2,3,4,5,6-pentafluorobenzaldehyde, is shown in (a) with an asterisk.

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.^[25] 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 ¹H 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.

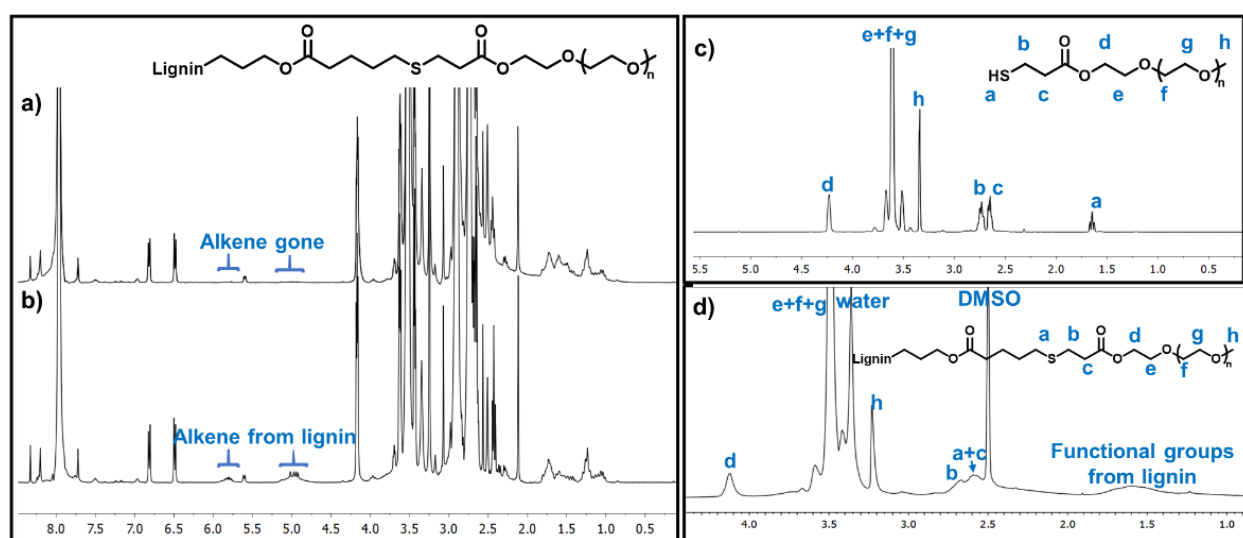


Figure 2. (a) ¹H NMR of the reaction of lignin-alkene and PEG-SH 550 at 24 hours, when the reaction is completed. (b) ¹H NMR of the reaction of lignin-alkene and PEG-SH 550 at 0 hour. (c) ¹H NMR of PEG-SH 550 in CDCl₃. (d) ¹H NMR of lignin-graft-PEG 550 in DMSO-d₆.

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 ¹H 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 ¹H 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 ¹H NMR in DMSO-d₆ (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

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

The molecular structure of polymers (Figure 1) in present work is designed for convenient scalability. The synthesis step was minimized (two steps) and used reagents are all not expensive chemicals. The synthesis does not require special conditions such as high temperature, high pressure, and large amount of pricy catalysts. Although it is not within the scope of the present work, additional work already underway to produce the lignin-based polymers in large scale. A particular technical challenge of the lignin-based polymer production is poor solubility of lignin. However, intensive studies are solving the solvent issue through testing and optimizing various solvents with multiple industrial lignins.^{[1], [26], [27]} In addition, in depth discussion of scalability can be found from literatures.^{[28], [8], [29], [30]} These works demonstrate potentials of industrial scale production of lignin-based polymers the used of lignin as a low-cost renewable resource comes with high economic value.

Ionic Conductivity of Lignin-graft-PEG: As a candidate for solid polymer electrolyte in battery applications, the ionic conductivity of the lignin-graft-PEG was measured by electrochemical impedance spectroscopy (EIS). The test samples were prepared by mixing lithium bis-trifluoromethanesulfonimide (LiTFSI) and lignin-graft-PEG. The prepared samples possess a ratio of 0.085 mole LiTFSI per mole ethylene oxide (EO) repeating unit, equivalently 1/11.8 molar ratio of LiTFSI/EO. Two samples were studied to determine the effect of lignin and PEG ratio on ionic conductivity. The graft polymers are lignin-graft-PEG 550 (66 wt% PEG + 34 wt % lignin) and lignin-graft-PEG 2000 (78 wt% PEG + 22 wt% lignin).

The ionic conductivity is shown in Figure 3 in Arrhenius format. The conductivity between 35 °C and 120 °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-PEG 2000. Both samples have a clear Vogel-Fulcher-Tammann (VFT) temperature dependence. Details of the VFT regressions are reported in the Supporting Information. Overall, the lignin-graft-PEG 2000 has higher conductivity than the lignin-graft-PEG 550 samples at all the tested temperatures. This is true even if the higher PEG content of lignin-graft-PEG 2000 is taken into account (for example by dividing the conductivity of each graft polymer electrolyte by its respective PEG weight or volume fraction). Similar behavior (ionic conductivity increasing with PEG molar mass) has also been observed in block copolymers of polystyrene-block-poly(ethylene oxide).^{[31], [32]} Note that poly(ethylene oxide) (PEO) and PEG are chemically identical. The term 'PEO' is used more commonly in the polymer electrolyte community and often refers to higher molar mass and/or material synthesized with living polymerization methods. On the other hand, 'PEG' is most frequently used in biomedical applications and takes its root from condensation reaction of ethylene oxide. It is often used to refer to low molar mass polymer (less than about 10 kg/mol).

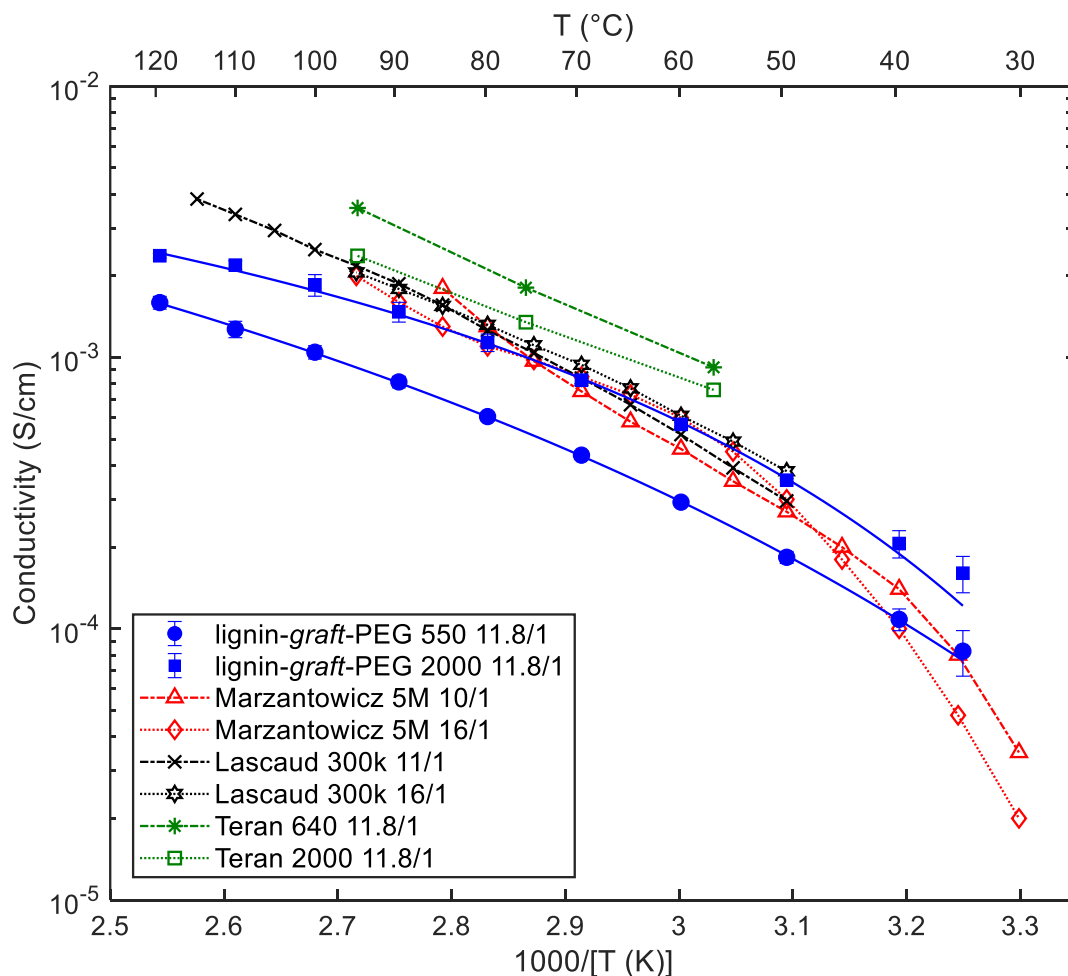


Figure 3. Arrhenius plot of conductivity of lignin-graft-PEG from this work compared to three reports from literature of PEG-LiTFSI mixtures: Marzantowicz,^[33] Lascaud,^[34] and Teran.^[35] In the legend, sample name or first author is followed by PEG molar mass then by EO/LiTFSI molar ratio. 'M' stands 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.^{[34], [35], [33]} In particular, there is data from Teran et al.^[35] 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.^[35] 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.^[36] Grafting of PEG-like moieties to synthetic polymer backbones have shown similar room-temperature enhancement that has been attributed to suppressed crystallinity.^[36] The stable covalent linkage

in lignin-graft-PEG is likely to interfere with PEG crystallization. The efficiently performed graft copolymerization (via photoredox thiol-ene reaction) enabled the synthesis of well-defined lignin-graft-PEG which leads to enhanced ambient-temperature conductivity and increased mechanical strength (observed qualitatively). This result highlights a method to maintain reasonable ambient-temperature conductivity by grafting PEG to a bio-sourced macromolecule, lignin.

Addressing the problem of low room temperature ionic conductivity is essential for practical application of polymer electrolytes in batteries.^[16] The room temperature conductivity of lignin-graft-PEG 2000 is nearly double that of homopolymer PEO reported by Marzantowicz.^[33] Regarding battery performance, a doubling of ionic conductivity will enable a battery to achieve more than twice the specific power.^[37] Based on prior work with PEO-based electrolytes,^[38] these lignin-graft-PEG electrolytes are expected to be compatible with lithium iron phosphate cathodes and lithium titanate anodes. Improvement in the mechanical properties of the lignin-graft-PEG electrolytes are most likely needed to enable long-term cycling with lithium metal anodes and for compatibility with other next-generation electrodes.

In conclusion, a new biomass- based copolymer, lignin-graft-PEG, that is designed as a novel solid polymer electrolyte in battery applications, is successfully synthesized by an environmentally benign photoredox thiol-ene reaction. The polymer synthesis was performed by three simplistic steps: 1) alkene modification of lignin, 2) end group modification of PEG to possess thiol terminals, and 3) graft-onto copolymerization through Ru-catalyzed photoredox thiol-ene reaction. The stable covalent linkage in lignin-graft-PEG suppresses PEG crystallization. The newly synthesized lignin-graft-PEG demonstrated enhanced ambient-temperature conductivity compared to homopolymer PEG precedents. Therefore, the reported lignin-graft-PEG is a promising new material for solid polymer electrolytes in battery applications.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgments

This work was supported by the Florida State University Energy and Materials Hiring Initiative, the FAMU-FSU College of Engineering, Department of Chemical and Biomedical Engineering, NSF award number 1804871, and NSF FAMU CREST center award number 1735968. We would like to thank Siyuan Chen for his help on FTIR, Danyelle Graham for assistance in synthesis, and Dr. Banghao Chen for the support of NMR facilities.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

Lignin, biomass, solid polymer electrolytes, poly(ethylene glycol), battery.

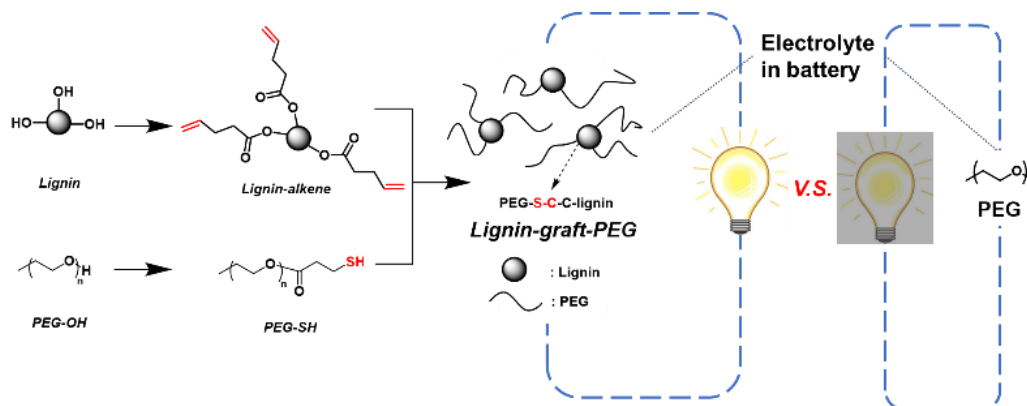
References

- [1] A. W. Tricker, M. J. Stellato, T. T. Kwok, N. S. Kruyer, Z. Wang, S. Nair, V. M. Thomas, M. J. Realff, A. S. Bommarius, C. Sievers, *ChemSusChem* **2020**, *13*, cssc. 202001219.

- [2] A. G. Vishtal, A. Kraslawski, *BioResources*. **2011**, 6.3, 3547
- [3] S. L. Hilburg, A. N. Elder, H. Chung, R. Ferebee, M. R. Bockstaller, N. R. Washburn, *Polymer (Guildf)*. **2014**, 55, 995.
- [4] H. Chung, N. R. Washburn, *Green Mater*. **2012**, 1, 137.
- [5] W. Zhao, B. Simmons, S. Singh, A. Ragauskas, G. Cheng, *Green Chem*. **2016**, 18, 5693.
- [6] B. M. Upton, A. M. Kasko, *Chem. Rev*. **2015**, 116, 2275.
- [7] Y. Z. Xu, L. Yuan, Z. K. Wang, P. A. Wilbon, C. P. Wang, F. X. Chu, C. B. Tang, *Green Chem*. **2016**, 18, 4974.
- [8] D. Kai, M. J. Tan, P. L. Chee, Y. K. Chua, Y. L. Yap, X. J. Loh, *Green Chem*. **2016**, 18, 1175.
- [9] H. Liu, H. Chung, *J. Polym. Sci. Part A Polym. Chem*. **2017**, 55, 3515.
- [10] D. Kai, K. Zhang, S. S. Liow, X. J. Loh, *ACS Appl. Bio Mater*. **2018**.
- [11] H. Liu, H. Chung, *Macromolecules* **2016**, 49, 7246.
- [12] S. Sen, S. Patil, D. S. Argyropoulos, *Green Chem*. **2015**, 17, 4862.
- [13] H. Pohjanlehto, H. M. Setälä, D. E. Kiely, A. G. McDonald, *J. Appl. Polym. Sci*. **2014**, 131.
- [14] Y. Kang, Z. Chen, B. Wang, Y. Yang, *Ind. Crops Prod*. **2014**, 56, 105.
- [15] J. Nakano, Y. Izuta, T. Orita, H. Hatakeyama, K. Kobashigawa, K. Teruya, S. Hirose, *Sen'i Gakkaishi*. **1997**.53, 416
- [16] L. Long, S. Wang, M. Xiao, Y. Meng, *J. Mater. Chem. A* **2016**, 4, 10038.
- [17] A. M. Stephan, K. S. Nahm, *Polymer (Guildf)*. **2006**, 47, 5952.
- [18] A. Manuel Stephan, K. S. Nahm, *Polymer (Guildf)*. **2006**, 47, 5952.
- [19] D. T. Hallinan, S. A. Mullin, G. M. Stone, N. P. Balsara, *J. Electrochem. Soc*. **2013**, 160, A464.
- [20] Q. Lu, Y. He, Q. Yu, B. Li, Y. V. Kaneti, Y. Yao, F. Kang, Q. Yang, *Adv. Mater*. **2017**, 29, 1604460.
- [21] P. Barai, K. Higa, V. Srinivasan, *Phys. Chem. Chem. Phys*. **2017**, 19, 20493.
- [22] H. Liu, H. Chung, *Acs Sustain. Chem. Eng*. **2017**, 5, 9160.
- [23] H. Chung, A. Al-Khouja, N. R. Washburn, in *Green Polym. Chem. Biocatal. Mater. II*, American Chemical Society, **2013**, pp. 373–391.
- [24] H. Liu, N. Mohsin, S. Kim, H. Chung, *J. Polym. Sci. Part A Polym. Chem*. **2019**, 57, 2121.
- [25] K. Öberg, Y. Hed, I. J. Rahmn, J. Kelly, P. Löwenhielm, M. Malkoch, *Chem. Commun*. **2013**, 49, 6938.
- [26] Kwok, Thomas Tai-min, et al. *BioResources*. **2019**, 14.3, 5988-6003.
- [27] T. T. Kwok, J. R. Bright, S. R. Vora, N. J. Chrisandina, C. O. Luetngen, M. J. Realff, A. S. Bommarius, *ChemSusChem* **2020**, 13, 267.
- [28] C. S. Lancefield, N. J. Westwood, *Green Chem*. **2015**, 17, 4980.

- [29] A. Moreno, M. H. Sipponen, *Mater. Horizons* **2020**, 7, 2237.
- [30] M. S. Ganewatta, H. N. Lokupitiya, C. Tang, *Polymers (Basel)*. **2019**, 11, 1176.
- [31] K. Timachova, H. Watanabe, N. P. Balsara, *Macromolecules* **2015**, 48, 7882.
- [32] M. Singh, O. Odusanya, G. M. Wilmes, H. B. Eitouni, E. D. Gomez, A. J. Patel, V. L. Chen, M. J. Park, P. Fragouli, H. Iatrou, N. Hadjichristidis, D. Cookson, N. P. Balsara, *Macromolecules* **2007**, 40, 4578.
- [33] M. Marzantowicz, J. R. Dygas, F. Krok, J. L. Nowiński, A. Tomaszewska, Z. Florjańczyk, E. Zygadło-Monikowska, *J. Power Sources* **2006**, 159, 420.
- [34] S. Lascaud, M. Perrier, A. Vallee, S. Besner, J. Prud'Homme, M. Armand, *Macromolecules* **1994**, 27, 7469.
- [35] A. A. Teran, M. H. Tang, S. A. Mullin, N. P. Balsara, *Solid State Ionics* **2011**, 203, 18.
- [36] W. S. Young, W. F. Kuan, T. H. Epps, *J. Polym. Sci. Part B Polym. Phys.* **2014**, 52, 1.
- [37] M. Doyle, T. F. Fuller, J. Newman, *Electrochim. Acta* **1994**, 39, 2073.
- [38] D. T. Hallinan, S. A. Mullin, G. M. Stone, N. P. Balsara, *J. Electrochem. Soc.* **2013**, 160, A464.

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.



Click here to access/download
Supporting Information
SI Aug 5 2020_accepted.pdf



[Click here to access/download](#)

Production Data

Revised manuscript for publication_Sep 22.docx

