

LIGNIN-DERIVED ENERGY STORAGE MATERIALS

RESEARCH PROPOSAL

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Abstract

Valorization of lignin to high-value chemicals and products in company with biofuel production will greatly improve the economic viability of a biorefinery. Over the years, with the increasing demand for electrical energy storage materials, lignin-derived activated carbon materials has received increasing attention. Lignin is an amorphous complex biopolymer with a heterogeneous aromatic structure derived mainly from three lignin monomeric precursors, p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S), respectively. However, the effects of the structural and compositional properties of lignin on the electrochemical properties of the derived carbon materials are not well understood. In the present study, activated lignin-derived mesoporous carbon samples were prepared from poplar, pine and switchgrass, which represent distinct H/G/S ratios and structural properties. The activated mesoporous carbon was then employed as the electrode material to investigate its potential use in supercapacitor. The Brunauer–Emmett–Teller (BET) surface area and pore size distributions were analyzed using N₂ adsorption. X-ray photoelectron spectroscopy (XPS) was carried out to analyze the surface chemistry of lignin-derived activated carbon materials. The capacitive performances and cycling stability of the supercapacitor were investigated using cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) respectively. This study provides insight on how the lignin composition and sources affect the derived activated carbon materials for potential supercapacitor application.

Chapter 1 Introduction

Today, lithium-ion battery technology develops fast and enjoys great potential to be extensively applied in the large scale energy storage, such as electrical vehicles, grid storage and solar power storage, because of its extremely high energy density, low self-discharge rate, negligible memory effect and relatively longer lifespan (Galiński, Lewandowski, & Stępnik, 2006). However, serious safety concerns have been raised for the mainstream volatile and flammable organic carbonate electrolytes are able to decompose under high temperature and the released gas accumulated within battery incite risk of fire or explosion (Bandhauer, Garimella, & Fuller, 2011). Because of the inherent non-volatile and non-flammable property, ionic liquids have been treated as a promising safer alternative for the conventional electrolytes and are receiving extensive investigation (Yoon et al., 2013). The properties of ionic liquids related to its electrochemical applications will be briefly reviewed as follow.

1.1 Extraction

Liquid–liquid extraction (LLE) is a separation method based on relative solubility within two immiscible liquids (Han & Row, 2010). Ionic liquids (ILs) have been widely applied into liquid-liquid extraction associated with metal ions (Abdolmohammad-Zadeh & Sadeghi, 2009; Abulhassani, Manzoori, & Amjadi, 2010; Manzoori, Amjadi, & Abulhassani, 2009), organic compounds, such as hydrocarbons (Arce, Earle, Katdare, Rodriguez, & Seddon, 2008; Guerra-Abreu, Pino, Anderson, & Afonso, 2008), acids (Absalan, Akhond, & Sheikhan, 2008) and sulfuric compounds (Bosmann et al., 2001), and large biological compounds, such as proteins (Cheng, Chen, Shu, & Wang, 2008; Pei, Wang, Wu, Xuan, & Lu, 2009; Shimojo et al., 2006) and DNA (Wang, Cheng, Chen,

Du, & Fang, 2007). Diverse physiochemical properties were recognized as the root causes of ILs' fantastic extraction capability. By elaborately adjusting the alkyl chain in cations, the type of anions and symmetry of ionic liquid molecules, ionic liquid can be tailor designed to satisfy a specific solubility and miscibility for extracting a target compound (Huddleston et al., 2001; Visser, Swatoski, Griffin, Hartman, & Rogers, 2001). The distribution coefficients of ionic liquids to water can be significantly affected by PH (Carda-Broch, Berthod, & Armstrong, 2003), so, adjusting the PH of ionic liquid/aqueous system is also a practical method to modify the extraction selectivity of ILs(Han & Row, 2010).

However, LLE was widely criticized for its time consuming and requirement for large amount of pure organic solvents, though it is still a favored extraction method. For these reasons, solid-phase extraction (SPE) and liquid-phase extraction (LPE) were employed as alternative approaches(Lee, Lee, Rasmussen, & Pedersen-Bjergaard, 2008).

SPE, is an extraction technique that involves the use of a fiber coated with an extracting phase as sorbent to extracts analytes from media(Arthur & Pawliszyn, 1990). As a new class of sorbent coating materials, ionic liquids were introduced into SPME for its capability of providing higher selectivity and affinity(Ho, Canestraro, & Anderson, 2011). Since the extraction efficiency is directly related to the quantity of ionic liquid coated on SPME support (Y.-N. Hsieh et al., 2006), ionic liquids were usually either coated(Y.-N. Hsieh et al., 2006) or chemically bonded(Amini, Rouhollahi, Adibi, & Mehdinia, 2011) to high specific surface area materials, such as silica-based materials and functional porous polymers(Han & Row, 2010). Polymeric ionic liquids were also

reported to be utilized as SPME coating materials for its higher thermal stability and resistance to flow at enhanced temperature, which exhibits potential development as reusable SPMA coating materials(López-Darias, Pino, Anderson, Graham, & Afonso, 2010; Meng & Anderson, 2010).

LPE is able to be recognized as a solvent minimized LLE, only trace amount of solvents was required for LPE(Sarafraz-Yazdi & Amiri, 2010). Claimed advantages of higher sensitivity, precision and extraction efficiency, ionic liquids were widely applied into LPE by either single-drop microextraction (SDME), in which ionic liquids were directly immersed or suspended immediately above the headspace of the extraction solution (Aguilera-Heirador, Lucena, Cardenas, & Valcarcel, 2008; Vidal, Domini, Grané, Psillakis, & Canals, 2007; Vidal, Psillakis, et al., 2007) or dispersive liquid-liquid microextraction (DLLME), in which dispersive ionic liquids containing solvent were injected into the extraction solution and then sedimented extractant containing ionic liquid can be acquired by centrifugation(Y. Liu, Zhao, Zhu, Gao, & Zhou, 2009; Pena, Casais, Mejuto, & Cela, 2009; Zhou, Bai, Xie, & Xiao, 2008).

1.2 Separation

An ideal stationary phase is required to exhibit divergent absorptivity for different chemical components, as well as it requires a low vapor pressure and chemically stable and at high operating temperature. For these reasons, ionic liquids were extensively investigated as coating materials of stationary phase(Anderson & Armstrong, 2003, 2005; Armstrong, He, & Liu, 1999; Breitbach & Armstrong, 2008; Huang, Han, Zhang, & Armstrong, 2007; Payagala, Huang, Breitbach, Sharma, & Armstrong, 2007; Payagala et al., 2009; Sharma et al., 2008) and ionic liquid GC columns have been

commercialized by Sigma-Aldrich. Taking advantage of the unusual selectivity with dual-nature, ionic liquid can be used to separate both polar and non-polar molecules(Armstrong et al., 1999). Continuous efforts have been put in improve thermal stability of stationary phase associated with cross-linking ILs(Anderson & Armstrong, 2005), dicationic ILs(Huang et al., 2007; Payagala et al., 2007), trigonal tricationic ILs(Payagala et al., 2009; Sharma et al., 2008) and phosphonium-based IL(Breitbach & Armstrong, 2008). The effects of ionic liquids anions and the structure of cations on selectivity and efficiency of stationary phase separation(Y. N. Hsieh et al., 2007; Y. N. Hsieh et al., 2008). In order to acquire more comprehensive information and higher selectivity on samples, ILs have also been introduced into two-dimensional(Krupčík, Májek, Gorovenko, Sandra, & Armstrong, 2011) and three-dimensional gas chromatography(Siegler, Crank, Armstrong, & Synovec, 2010).

Ionic liquids has also received considerable attention in liquid phase chromatography research as surface-bonded stationary phase and mobile phase modifier(Han, Tian, Park, Choi, & Row, 2009). In addition to tunable property of cations and anions, the electrostatic interaction and ion exchange interaction between analytes and stationary phase were also recognized to contribute to the high separation efficiency(S. J. Liu et al., 2004; Qiu, Jiang, & Liu, 2006). However, more studies related to its complicated separation mechanisms and optimized IL still need to be done(Han et al., 2009). ILs, as mobile phase modifier, were found to be able to effectively block silanol group reside on silica surface of stationary phase so as to fix the tailing problem observed in thin-layer chromatography (TLC)(Kaliszan, Marszał, Jan Markuszewski, Bczek, & Pernak, 2004) and HPLC(Han et al., 2009).

Capillary electrophoresis (CE) is a family of electrokinetic separation method appeared in recent year due to its high resolution and sensitivity. By applying ionic liquids as capillary surface modifier, the EOF of capillary was reversed, which promote an improvement of resolution between analytes(Borissova, Vaheer, Koel, & Kaljurand, 2007; W. D. Qin & Li, 2002; W. Qin, Wei, & Li, 2003). Some long-chain alkylimidazolium ILs were also reported evaluated as surfactant to improve efficiency and selectivity in micellar electrokinetic chromatography (MEKC)(Borissova, Palk, & Koel, 2008).

Chapter 2 Objectives

2.1 Overall Objective

The ultimate objective of my study is to extract lignin from lignocellulosic biomass, including but not limited to, poplar, pine and switchgrass, through multiple poplar pretreatment methods, such as ionic liquids, dilute acids and alkaline, so that to find a practical, both economically and technologically, large scale application for the lignin, for example, energy storage materials.

2.2 Specific objectives

- Multiple pretreatment method, including dilute acid, alkaline and ionic liquids pretreatment, will be evaluated to designate the most suitable pretreatment option and optimized operation condition for a maximized lignin yield.
- The effect of different pretreatment option to lignin structure will also be examined by lignin characterization.
- Diverse biomass feedstock will be involved in the present study to examine the effect of the different proportion of three types of lignin precursors, G-unit, S-unit and H-unit to electrochemical properties.
- The extracted lignin will be used to produce energy storage materials, such as electrodes of supercapacitor and anion of sodium-ion battery
- The potential of ionic liquids as electrolyte will also be investigated in the present study.

The present study assists us to clarify the significant factors that contribute to enhanced electrochemical performance of lignin-derived energy storage materials. Considering the current enormous demands for energy storage material, large scale

application of lignin would be achieved if lignin derived material can compete with the existing material, such as graphite, silica and so on.

Chapter 3 Methods

3.1 Alkaline Pretreatment

Alkali pretreatment will be conducted at 140 °C for 1 h by 10 % ammonia hydroxide loading. Two gram 2 mm biomass particles will be mixed with ammonia hydroxide and soaked for 24 h in a tube reactor. After 60 min heated in an Heidolph MR Hei-End oil bath, the tube reactor will be quickly transferred into iced water for cooling. The pretreated sludge will be transferred to a 50 mL centrifuge tube, and centrifuged at 4000 rpm for 15 min to separate into liquid stream and solid stream. The upper soluble lignin containing liquid stream will be subjected to pH adjustment between 1 and 2. The residue will be separated and washed with 30 mL DI water for 4 times and then enzyme hydrolyzed to recover lignin.

3.2 Ionic Liquids Pretreatment

For ionic liquid pretreatment, 2 g 2 mm biomass particles will be mixed under a 10 % wt solid content. The mixture will be heated at 120°C for 2 hours. After pretreatment, 35 mL of ethanol will be added into the biomass slurry to extract lignin fraction. The sludge will be centrifuged at 4000 rpm for 15 min to separate liquid and solid fractions. Removing solid fraction and then add DI water into the result liquid fraction at ethanol to water ratio of 9 to 1. After adjusting pH of the resultant and recovering the precipitant and enzyme hydrolyzing hemicellulose, the lignin fraction will be acquired.

3.3 Dilute Acid Pretreatment

Two gram 2 mm biomass particles will be mixed with 1 % w/w sulfuric acid in a tube reactor. The mixture will be heated at 160 °C for 40 min in an oil bath. After heating, the tube will be quickly removed from the oven into iced water for cooling. The sludge will be transferred from the tube to a 50ml centrifuge tube and centrifuged at 4000 rpm for 15 min. The separated liquid fraction will be adjusted to a pH value of between 1 and 2. The precipitant will be subjected to an enzyme hydrolysis of hemicellulose to recover lignin.

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Appendix A: Budget

1. Direct Costs	Year 1	Year 2	Year 3	Total
A. Salaries and Wages				
(1) You	\$18,000.00	\$18,000.00	\$18,000.00	\$54,000.00
(2) Your advisor	\$84,500.04	\$88,725.04	\$92,950.04	\$266,175.13
(3) Others as appropriate	\$0.00	\$0.00	\$0.00	\$0.00
Total Salaries and Wages	\$102,500.04	\$106,725.04	\$110,950.04	\$320,175.13
B. Fringe Benefits				
(1) You	\$4,093.00	\$4,168.00	\$4,245.25	\$12,506.25
(2) Advisor	\$29,020.26	\$30,249.99	\$31,489.68	\$90,759.93
(3) Others as appropriate	\$0.00	\$0.00	\$0.00	\$0.00
Total Fringe Benefits	\$33,113.26	\$34,417.99	\$35,734.93	\$103,266.18
C. Travel				
(1) ASABE meeting	\$2,139.00	\$2,200	\$2,200.00	\$6,539.00
(2) Sample collection	\$0.00	\$0.00	\$0.00	\$0.00
(3) Other	\$0.00	\$0.00	\$0.00	\$0.00
Total Travel	\$2,139.00	\$2,200	\$2,200.00	\$6,539.00
D. Materials and Supplies				
(1) Straw bales	\$0.00	\$0.00	\$0.00	\$0.00
(2) Chemical reagents	\$5,000.00	\$5,000.00	\$5,000.00	\$15,000.00
(3) Others	\$5,000.00	\$5,000.00	\$5,000.00	\$15,000.00
Total Materials and Supplies	\$10,000.00	\$10,000.00	\$10,000.00	\$30,000.00
E. Equipment				
(1) Automated sampler	\$2,000.00	\$2,000.00	\$2,000.00	\$6,000.00
(2) Golf cart	\$0.00	\$0.00	\$0.00	\$0.00
(3) Other	\$0.00	\$0.00	\$0.00	\$0.00
Total Equipment	\$2,000.00	\$2,000.00	\$2,000.00	\$6,000.00
F. Other Direct Costs				
(1) Publication costs	\$1,000.00	\$1,001.00	\$1,002.00	\$3,003.00
(2) Tuition and fees	\$28,380.00	\$28,380.00	\$28,380.00	\$85,140.00
(3) Subcontracted sample analysis	\$3,000.00	\$3,000.00	\$3,000.00	\$9,000.00
(4) Recalibration of moisture sensor				
(5) Other				
Total Other Direct Costs	\$32,380.00	\$32,381.00	\$32,382.00	\$97,143.00
G. Modified Total Direct Costs	\$182,132.30	\$187,724.03	\$193,266.98	\$563,123.31
2. Indirect Costs	\$91,066.15	\$93,862.02	\$96,633.49	\$281,561.65
3. Total Costs	\$273,198.45	\$281,586.05	\$289,900.46	\$844,684.96

Budget Justification Format and Examples

1. Direct Costs

A. Salaries and Wages

- (1) Based on current departmental stipend of \$18000/year for a first-year Ph.D Research Assistant.
- (2) Estimated 20% contribution from advisor at a salary of \$84500.04/year.

B. Fringe Benefits

- (1) Current University of Kentucky fringe benefit rate for graduate students is 8.85%, plus a health and life insurance of \$2500 / year for "16-17" with a 3% increase per year in the future.
- (2) Current University of Kentucky fringe benefit rate for faculty is 21.25%, plus a health and life insurance of \$11064 / year for "16-17" with a 3% increase per year in the future.

C. Travel

- (1) Attendance at 2017 International Meeting of ASABE. Air fare estimated as \$500, three days' lodging and per diem at \$240 per day, meeting registration of \$919.

D. Materials and Supplies

- (1) All feedstock in the present project was acquired from Idaho Nation Laboratory for free.
- (2) Estimated costs of NaOH, H₂SO₄, Ionic Liquids, etc. to perform experiment as stated in the proposal are \$5000 per year.
- (3) Estimated other laboratory supplies or consumables are \$5000 per year.

E. Equipment

- (1) FTIR to characterize lignin samples as stated in the proposal.
- (2) EZGO Model AA-BB to transport water samples from storage to laboratory.

F. Other Direct Costs

- (1) Estimated 10-page article to be published in *Transactions of the ASABE* at \$100/page.
- (2) Tuition and fees for non-resident graduate students is \$28380 per year.
- (3) Part of lignin characterization analysis and all activated carbon electrochemical analysis would be sent to chemical engineering department and Center for Applied Energy Research (CAER) to test.

G. Modified Total Direct Costs. As per University of Kentucky guidance, calculated as Total Direct Cost less graduate tuition and equipment.

2. Indirect Costs. Calculated as 50% of Modified Total Direct Costs as per University of Kentucky Office of Sponsored Projects Administration.

Future Years: Salaries and wages are increased by 5%/year based on the 2016 Consumer Price Index (or based on average 2016 salary increase for University of Kentucky employees).

Appendix B: Research Plan

Task	Date															
	8/2	8/23	9/13	10/4	10/25	11/15	12/6	12/27	1/17	2/7	2/28	3/21	4/11	5/2	5/23	
1. Lignin extraction																
1.1 Lignin extraction																
1.1.1 Ionic liquid	█	█	█	█	█	█	█	█	█	█	█	█	█	█	█	
1.1.2 Dilute acid				█	█	█	█	█	█	█	█	█	█	█	█	
1.1.3 Alkali																
1.2 Activated carbon preparation																
1.2.1 Carbonization									█	█	█	█	█	█	█	
1.2.2 Carbonization																
1.3 Electrodes preparation																
2. Electrochemical analysis																
2.1 Cyclic Voltammograms (CV)																
2.2 Electrochemical Impedance Spectroscopy (EIS)																
3. Characterization of precursor and activated carbon																
3.1 Brunauer–Emmett–Teller (BET)																
3.2 Transmission electron microscope (TEM)																
3.3 Scanning electron microscopy image (SEM)																
3.4 X-ray diffraction (XRD)																
3.5 X-ray photoelectron spectroscopy (XPS)																
3.6 NMR																
3.7 FTIR																
3.8 Pyrolysis – GC/MS																
4. Publication manuscript																

Research Plan Milestones:

1. Dec 27th 2016 Lignin preparation completed
2. Jan 17th 2017 Activated carbon preparation completed
3. Jan 24th 2017 Supercapacitor electrodes preparation completed
4. Feb 7th 2017 Electrochemical analysis completed
5. Apr 11th 2017 Activated carbon and precursor characterization
6. May 23th 2017 Publication manuscript completed