Conversion of Lignin Precursors to Carbon Fibers with Nanoscale Graphitic Domains

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Results and Discussion

Lignin is one of the most abundant and inexpensive natural biopolymers. It can be efficiently converted to low cost carbon fiber, monolithic structures, or powders that could be used directly in the production of anodes for lithium-ion batteries. In this work, we report thermomechanical processing methods relevant for the conversion of lignin precursors into carbon fiber-based anode materials, the impact of lignin precursor modification on melt processing, and the microstructure of the final carbon material. Modification of softwood lignin produced functionalities and rheological properties that more closely resemble hardwood lignin thereby enabling the melt processing of softwood lignin in oxidative atmospheres (air). The conversion process encompasses melt spinning of the lignin precursor, oxidative stabilization, and a low temperature carbonization step in a nitrogen/hydrogen atmosphere. We determined resistivities of individual carbon fiber samples and characterized the microstructure by scanning electron microscopy. Neutron diffraction reveals nanoscale graphitic domains embedded in an amorphous carbon matrix. These unique structural characteristics make biomass-derived carbon fibers a suitable material for energy storage applications with enhanced electrochemical performance.

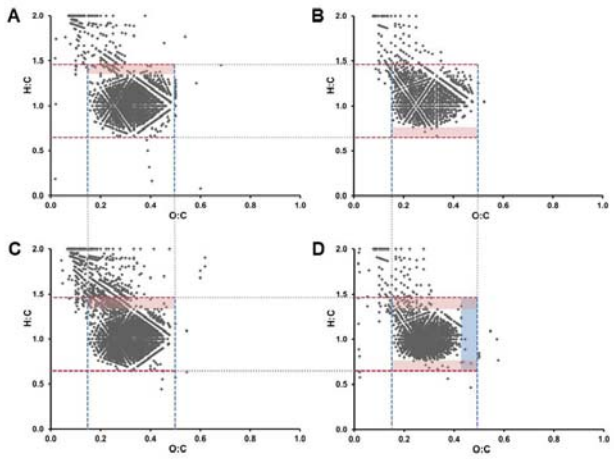

Figure 1. Van Krevelen plots for (A) hardwood Alcell, (B) softwood Kraft, (C) phthalic anhydride modified hardwood Alcell and (D) phthalic anhydride modified softwood Kraft lignin derived from the assigned elemental composition for each peak in the mass spectra. Van Krevelen diagrams plot the molar ratio of hydrogen to carbon (H:C) versus the molar ratio of oxygen to carbon (O:C) and have been applied extensively to study complex organic samples such as natural organic matter. The H:C ratio increases as the number of rings plus double bonds decreases, while the O:C ratio distinguishes heteroatom classes based on the number of O atoms. Because major chemical compound classes, such as lipids, carbohydrates, and lignin, have characteristic H:C or O:C ratios, van Krevelen diagrams provide rapid identification of compound classes and help in identifying changes in the chemical composition based on the distribution of peaks in the plot. Elemental compositions for each peak calculated from negative-ion ESI FT-ICR mass spectra provide H:C and O:C ratios for modified and unmodified AHL and KSL The H:C range for AHL (0.65−1.39) was lower than the range for KSL (0.76− 1.47) while the range of O:C ratios were identical (0.15−0.49). The esterification of AHL with phthalic anhydride results in a negligible change in the range of H:C ratios (0.65−1.38). However, phthalic anhydride modification of KSL had a significant impact on both ranges, H:C (0.76−1.38) and O:C (0.15−0.43).

Acknowledgements

Work performed at the National High Magnetic Field Laboratory was supported by the National Science Foundation (NSF), Division of Materials Research through DMR-1157490, Florida State University, the Future Fuels Institute, BP/The Gulf of Mexico Research Initiative to the Deep-C Consortium, and the State of Florida. Neutron diffraction experiments were performed on the Nanoscale-Ordered Materials Diffractometer (NOMAD) at Oak Ridge National Laboratory's Spallation Neutron Source supported by the Scientific User Facility Division, Office of Basic Energy Sciences, U.S. Department of Energy.

References [1] Chatterjee, S. *et al*., ACS Sustainable Chem. Eng., **2**, 2002-2010 (2014)