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The electrochemical and charge storage properties of different lignins inside biopolymer electrodes were studied and correlated with the chemical variations of the lignins as indicated from the nuclear magnetic resonance (NMR) spectroscopic data. The varying fractions of monolignols were found to correlate to charge storage properties. It was found that as the sinapyl to guaiacyl (S/G) ratio increased both the specific capacitance and charge capacity increased considerably. This indicates that quinones generated on S-units can contribute more to charge storage in the biopolymer electrodes.

Renewable energy conversion technologies like solar and wind give intermittent electricity and needs storage, for instance through electrochemical technologies like supercapacitors and batteries. This is of particular importance in areas of the world which still lack an electrical grid; some of these areas also have abundant resources of solar and wind energy. It would be desirable also to use both local and scalable resources for such new technologies.\(^1\)\(^-\)\(^3\) Biopolymers fulfill these criteria and can be used in combinations with electrochemical storage. While cellulose is the most abundant biopolymer, lignin comes as number two, and both are generated in green plant photosynthesis. The waste product from paper production is lignin derivatives in the form of black liquor. Depending on the source of lignin and paper processing chemistry, these lignin derivatives may be more or less suitable for integration into biopolymer electrodes. We here report on our search for sources of high performance lignin derivatives integrated into biopolymer electrodes. This search has been focusing on lignins originating in tropical and subtropical regions, motivated by the need to find local renewable resources close to the ample flux of solar energy around the Equator. Through our analysis of these materials using chemical species labelling and NMR spectroscopy, we have observed that the performance of these materials correlate well with the amount of sinapyl monolignols in the lignin derivative. This enables us to establish a rule and a new metric for the continuing search for scalable and locally available sources of lignins.

**Broader Context**

The contribution of renewable electricity is growing rapidly due to solar photovoltaic and wind turbines being installed in many areas of the world. To enable their expanding use in grid based or grid free economies, storage of this intermittent electrical energy sources becomes necessary. Hence, the searches for cheap, efficient and scalable energy storage materials that can be easily integrated with scalable renewable electricity sources become an urgent global agenda. The use of lignin, which is a naturally occurring second most abundant environmentally friendly and low-cost biomaterial, in electrochemical energy storage may contribute to the realization of scalable energy storage devices.

Supercapacitors store electrical energy through double layer charging, faradaic processes or a combination of both. In recent years many researchers are actively investigating composite electrode materials to improve the energy storage properties of supercapacitors.\(^4\)\(^-\)\(^10\) Several studies proved that conjugated polymers like polypyrrole, polythiophene and polyaniline\(^11\)\(^,\)\(^12\) and their derivatives\(^13\)\(^,\)\(^15\) can improve the electrochemical performances of carbon based supercapacitors by contributing pseudocapacitance to the capacitance of carbon materials resulting from the double-layer.

We have previously demonstrated\(^16\),\(^,\)\(^17\) that lignin derivatives incorporated into polypyrrole electrodes give rise to a quinone groups that can be used to enhance the charge storage density and capacitance of these biopolymer electrode materials. The major objective in this work is to incorporate the biopolymer lignin obtained from different biological sources and chemical processes in composites with polypyrrole and investigate their charge storage properties. Different plants have varying lignin fraction and composition in terms of the relative distribution of the monolignols syringyl (S), guaiacyl (G) and hydroxyphenyl (H) units. We have chosen our biopolymers from plants found in subtropical and tropical regions including Eucalyptus, acacia and Hagenia Abyssinica, or koso, also known as African redwood. Both eucalyptus and acacia are used for industrial production of paper
while this is not the case for *Hagenia Abyssinica*, to the best of our knowledge. The plant *kosso* is used for timber and firewood, and in Ethiopia, *kosso* is traditionally used as anti-tapeworm drug.

A sequential process involving ethanol and sodium hydroxide solution was used to extract acid-insoluble lignin from *Hagenia Abyssinica* at Addis Ababa University, Ethiopia. Pyrrole (Py) was distilled prior to use. Dimethylformamide (DMF), pyridine, acetonitrile, cyclohexanol, chromium (III) acetylacetonate, 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (phosphitylating reagent), deuterated chloroform (CDCl3) were purchased from Sigma-Aldrich and were used as received. Lignin (LG2-4) samples were supplied by Innventia AB, Stockholm, Sweden.

Lignin samples isolated from different biomass sources including *Hagenia Abyssinica* (LG1), acacia (LG2), eucalypt-soda AQ (LG3), eucalypt-kraft (LG4) were phosphorylated with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (phosphitylating reagent) for quantitative $^{31}$P NMR analysis. As can be seen in Figure 1 (a), $^{31}$P NMR spectra show signals for the different hydroxyl groups in lignin samples, the phosphitylating reagent ($\delta = 174.7$ ppm) and the water adduct ($\delta = 131.8$ ppm). Figure 1 (b) presents a scheme of the $^{31}$P NMR phenolic hydroxyl structure in the lignin. The aliphatic hydroxyl (i) at 145.4-150.0 ppm appears in all lignin samples (Figure 1 (a)). C5 substituted guaiacyl phenolic hydroxyl (ii), also termed as condensed phenolic hydroxyls, at 141.0-141.5 and 142.5-144.0 ppm has been observed in all lignin spectra. Guaiacyl hydroxyl (H) hydroxyl (v) ($\delta = 138.0$ ppm) signals are not detectable and the carboxylic acid hydroxyl (vi) showed a broad peak at 134.4-135.5 ppm in all spectra. The amount of syringyl hydroxyl (S) (iii) which appears at 141.5-142.5 ppm, showed significant variation increasing from 0.4 mmol/g (in LG1) up to 3.0 mmol/g (in LG4) while the amount of Guaiacyl hydroxyl (G) decreased from 1.6 mmol/g (in LG1), to 1.1 mmol/g (in LG4) (Table 1).

We note that the present method will detect no sites where quinones are already present. Should these exist, and should they be able to contribute to charge capacity in a biopolymer electrode, they are not included in the count of monolignols potentially forming quinones.

The mass changes estimated (between 54-56 µg)-from EQCM measurements for the PPy/LG composite systems are shown in Figure 2.

![Figure 1](image1.png) **Figure 1.** (a) Quantitative $^{31}$P NMR spectra and signal assignment of different lignins 1(LG1), 2 (LG2), 3 (LG3), 4 (LG4).Internal standard 144.5 ppm, phosphitylating reagent 174.7 ppm, water adduct 131.8 ppm. (b) Scheme of kraft lignin chemical structure. (i) aliphatic hydroxyl, 145.4-150 ppm (ii) condensed phenolic hydroxyl, 141.0-141.5 and 142.5-144.0 ppm, (iii) syringyl 141.5-142.5 ppm, (iv) guaiacyl 138.5-140.2 ppm, (v) p-hydroxyphenyl at 138.0 ppm, (vi) carboxylic acid hydroxyl 134.4-135.5 ppm.

![Figure 2](image2.png) **Figure 2.** Mass changes obtained for the deposition of the different lignins/PPy composites on gold electrode.

Typical cyclic voltammograms of the different lignin composites obtained are depicted in Figure 3. The y-axis in the cyclic voltammograms were converted from ampere units for the current measured to units of F/g by dividing each current value by the scan rate as well as the mass of the materials measured from the EQCM studies17-19. The characteristic quinone redox peaks and peak capacitances were found to increase with increasing S/G ratio (Table 1).
The specific capacitances estimated from the galvanostatic measurements were also found to increase from 206 to 282 F/g as the S/G ratio increased from 0.3 to 2.6 (Table 1). The discharge properties of the different lignins/PPy composites at 1A/g obtained from galvanostatic measurements were compared in Figure 4 (a), where the charge capacity varies from 30.4 to 42 mAh/g (Table 1) as the S/G ratio increased from 0.30 to 2.6.

Table 1. Summary of the NMR and electrochemical data.

<table>
<thead>
<tr>
<th>Lignin sample</th>
<th>Composition determined from NMR (mmol/g)</th>
<th>Peak pseudocapcitance (F/g) from CV</th>
<th>Capacitance (F/g) from galvanostatic</th>
<th>Charge capacity (mAh/g) from galvanostatic</th>
</tr>
</thead>
<tbody>
<tr>
<td>S- unit</td>
<td>G- unit</td>
<td>S/G (ratio)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LG1</td>
<td>0.4 1.6 0.3</td>
<td>401</td>
<td>206</td>
<td>30.4</td>
</tr>
<tr>
<td>LG2</td>
<td>1.8 1.9 0.5</td>
<td>469</td>
<td>220</td>
<td>32.3</td>
</tr>
<tr>
<td>LG3</td>
<td>2.5 1.4 1.7</td>
<td>528</td>
<td>239</td>
<td>35</td>
</tr>
<tr>
<td>LG4</td>
<td>3.0 1.1 2.6</td>
<td>563</td>
<td>282</td>
<td>41.6</td>
</tr>
</tbody>
</table>

The specific capacitance values obtained from the discharge curves were plotted as a function of the current densities in Figure 4(b). The specific capacitance values for the PPy/LG4 composite system were found to be higher than the other polypyrrole/lignin composite at all currents. The various processing conditions are known to lead to different composition of functional groups in the complex lignin structures. Generally, Kraft lignins are richer in the carboxylic functional groups which do not contribute to charge storage. Accordingly, we noted that compared to previous results, numbers are lower for the charge capacity since all the biopolymers investigated in these work were alkaline lignins. The monolignol fraction sinapyl or guaiacyl would give a quinone upon oxidation, with a redox contribution due to $\text{QH}_2 \rightarrow \text{Q} + 2e^- + 2\text{H}^+$. Thus, 1 mmol of S or G per g of lignin would give a charge capacity of 2 milliFaraday/g of lignin or 53 mAh/g. Assuming that the mass fraction of lignin in the biopolymer electrodes is similar to previous determinations ($\approx 50\%$) and not varying much, we expect to see an additional charge capacity of 27 mAh/(g of electrode material) for one more mmol/g of quinone. We note that this correlation is found in Figure 5, where the charge capacity versus S fraction, G fraction, the S+G fraction and the S/G ratio are plotted.

The increase of 12 mAh/g noted as the S+G fraction increases from 2 to 4.1 mmol per gram lignin, or 5.7 mAh/mmol quinone, is only $\approx 20\%$ of the maximum enhancement based on monolignol participation. We are thus not able to extract all potential quinone groups in the composite material. However, the improvement of
charge capacity is more pronounced with increasing S fraction, where there is a monotonous relation, not observed with the G fraction. It is thus hypothesized that the access to redox active quinones is higher with more S groups present in the lignin derivative. This hypothesis is based on only a small selection of lignin samples and with these processing routes, and must be taken with caution. As the S and G fractions of monolignol vary widely across species, plant structures and processing routes, the search for higher performance biopolymer electrodes should focus on higher S content in the precursor materials.

Conclusions

We have characterized different lignins of subtropical origin using $^{31}$P NMR spectroscopy and formed interpenetrating networks of lignin/PPy composites on gold electrodes and studied their electrochemical and charge storage properties. We demonstrated that the charge storage property of the different alkali lignins/PPy composites depends on the amount of sinapyl functional groups present in the lignin. Hence, for improved charge storage in this composite system, it is vital to have more sinapyl groups in the complex lignin structures.

Notes and references

a Biomolecular and organic electronics, Department of Physics, Chemistry and Biology (IFM), Linköping University, 581 83 Linköping, Sweden.
b Department of Chemistry, Addis Ababa University, PO Box 1176, Addis Ababa, Ethiopia (E-mail: shimadm09@gmail.com).

This work was supported by the Knut and Alice Wallenberg Foundation, through the project Power Papers as well as a Wallenberg Scholar grant to O.I.. The authors would also like to acknowledge Innventia for providing lignin samples LG2-4.