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Charge storage properties of biopolymer electrodes with (sub) tropical lignins

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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 fulfil 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 *koso* is used for timber and firewood, and in Ethiopia, *koso* 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 ($CDCl_3$) were purchased from Sigma-Aldrich and were used as received. Lignin (LG2-4) samples were supplied by Innventia AB, Stockholm, Sweden.

The ^{31}P NMR spectra were recorded on a BrukerAvance 500MHz instrument using cyclohexanol (δ = 144.5 ppm) as an internal standard, with 90◦ pulse angle, inverse gated proton decoupling, delay time 2 second and 1024 scans. The phosphitylating reagent remained and its water adduct were identified at δ = 174.7 ppm and δ = 131.8 ppm respectively.

Lignin (20 mg) sample was dried in 40◦ C oven overnight to remove water and then dissolved totally in 100 µl DMF. DMF/pyridine (1:1, v/v) solution 100 µl contained cyclohexanol (1.1 mg, 1.1×10^{-2} mmol) as internal standard and chromium (III) acetylacetonate (0.5 mg, 1.4×10^{-3}mmol) as relaxation agent was added subsequently. Phosphitylating reagent (100µl) was added to the lignin mixture and CDCl3 (500 µl) was then added. The final mixture was vortexed and transferred to a 5mm NMR tube for ^{31}P NMR analysis.

The PPy/LG composites were synthesized by galvanostatic polymerization at a current density of 250 µA/cm^2 (until a charge of 100 mC/cm^2) in a three-electrode system consisting of a gold working electrode, a Ag/AgCl/KCl (3.0 M NaCl) reference electrode and a platinum wire counter electrode from a solution consisting of 0.025 M Py and 5 mg/mL of LG in 0.1 M $HClO_4$/water:acetonitrile (1:1) mixed solvent. Cyclic voltammetry and galvanostatic experiments were carried out using an Autolab PGStat 10 (EchoChemie, the Netherlands). The quartz cystal microbalance studies were carried done using a Q-Sense E4 using gold deposited quartz crystals. The frequency change was monitored during the deposition of the material, and analysed using the Sauerbrey equation to deduce the masses for these stiff materials.

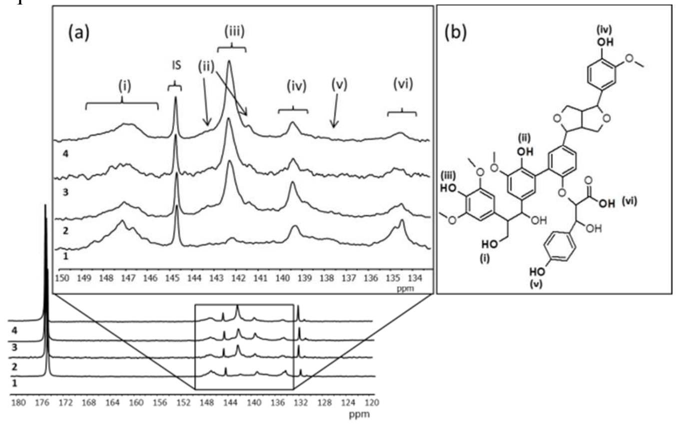

Figure 1. (a) Quantitative ^{31}P NMR spectra and signal assignment of different lignins 1(LG1), 2 (LG2), 3 (LG3), 4 (LG4). Internal standard 144.5 ppm, phosphitylating regent 174.7 ppm, water adduct 131.8 ppm. (b) Scheme of kraft lignin chemical structure. (i) aliphatic hydroxyl, 145.4-150 ppm (ii) 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.

Lignin samples isolated from different biomass sources including *Hagenia Abysinica* (LG1), acacia (LG2), eucalypt-soda AQ (LG3), eucalypt-kraft (LG4) were phosphitylated with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (phosphitylating regent) 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 (δ = 174.7 ppm) and the water adduct (δ = 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)).

C_5 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 (G) (iv) at 138.5-140.2 ppm has been observed in all lignin samples. The *p*-hydroxyphenyl (H) hydroxyl (v)(δ =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.

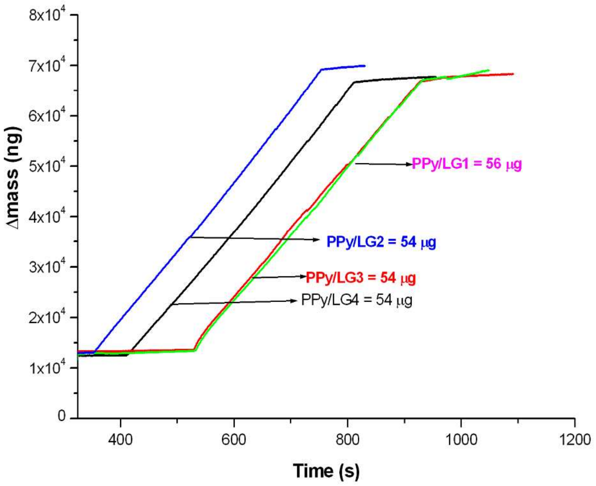

Figure 2. Mass changes obtained for the deposition of the different lignins/PPy composites on gold electrode.

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 studies[17-19]. The characteristic quinone redox peaks and peak capacitances were found to increase with increasing S/G ratio (Table 1).

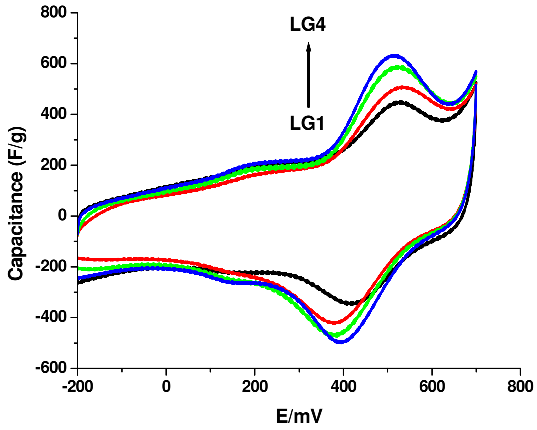

Figure 3. Cyclic voltammograms of the different lignins/PPy composites at 20 mV/s.

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.

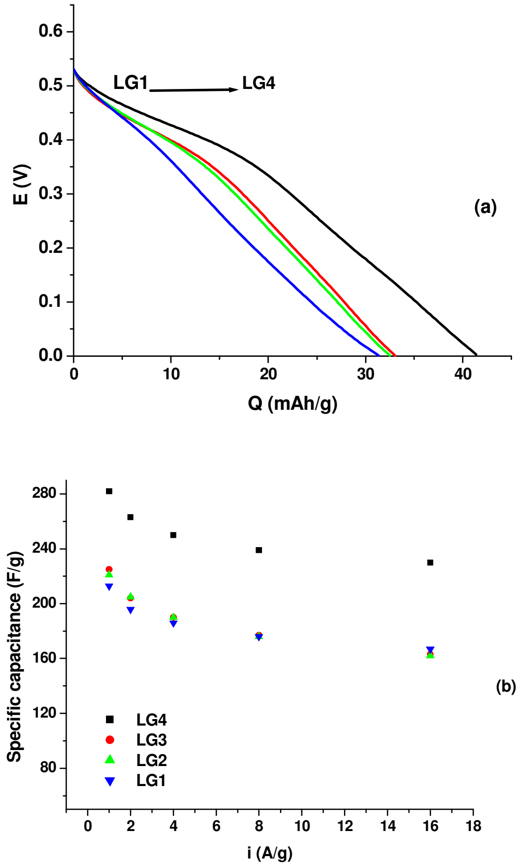

Figure 4. (a).Comparison of the charge capacity of different lignins/PPy composites at 1A/s.(b). Comparison of the specific capacitances of different lignin/polypyrrole composites at different currents.

Table 1. Summary of the NMR and electrochemical data.

Lignin sample	Composition determined from NMR (mmol/g)			Peak Pseudocapacitance (F/g) from CV	Capacitance (F/g) from galvanostatic	Charge capacity (mAh/g) from galvanostatic
	S-unit	G-unit	S/G ratio			
LG1	0.4	1.6	0.3	401	206	30.4
LG2	1.8	1.9	1.0	469	220	32.3
LG3	2.3	1.1	2.1	528	239	35
LG4	3.0	1.1	2.6	563	282	41.6

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[20] which do not contribute to charge storage. Accordingly, we noted that compared to previous results [16, 17] 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 $QH_2 \rightarrow Q + 2e^- + 2H^+$. 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 (≈50%)[17] 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.

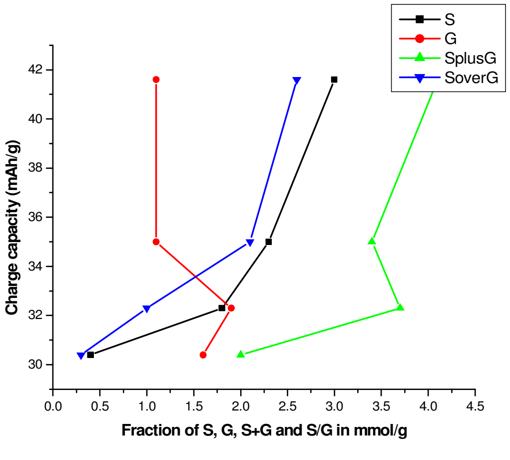

Figure 5. A plot of the variation of the charge capacity against the S(■), G(●), S + G(▲) fractions as well as the S/G ratio(▼) (no units) found in the different lignins studied.

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 ≈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

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