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Electronic Supplementary Information

for

High-Charge Capacity Polymer Electrodes Comprising Alkali Lignin from the Kraft Process

Samuel Leguizamon, Kryssia P. Díaz-Orellana, Julian Velez, Mark C. Thies, and Mark E. Roberts*

Department of Chemical & Biomolecular Engineering, Clemson University

*e-mail: mrober9@clemson.edu

Effect of H_2SO_4 concentration on Electrochemical Performance

The influence of H_2SO_4 concentration on the electrochemical performance of the composite films is shown in figure S1. The films were prepared using a 10mL solution of 15.3 M AA, 0.124 g of AL, and 69 µL of pyrrole monomer. After polymerization, the film was rinsed and inserted into H_2SO_4 with a specific concentration: 1 M, 0.5 M, 0.1 M, 0.01 M, 0.001 M, and 0.0001 M. The film was left in the electrolyte solution for 5 min before testing. Cyclic voltammetry shows than higher H_2SO_4 concentrations lead to sharper redox peaks and decreased peak separation, as expected for a proton-dependent process (Figure S1 a and b).

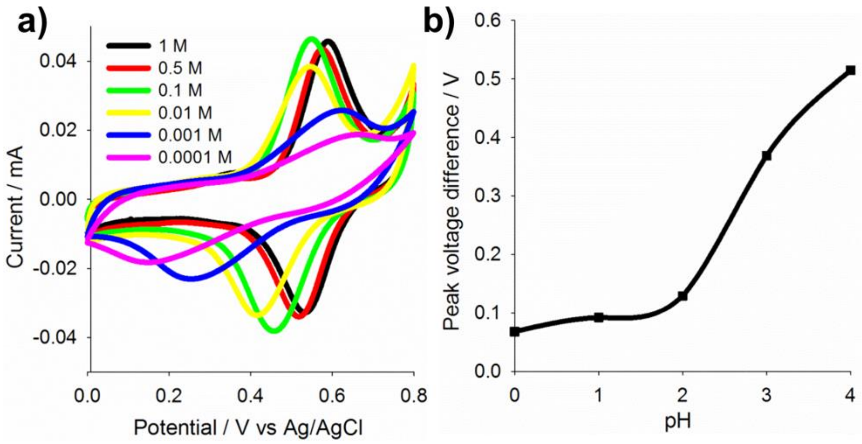

Figure S1. a) Cyclic voltammetry profiles for PPy/AL (prepared in 15.3M AA) at different H_2SO_4 concentrations. b) Voltage difference between catholic and anodic peaks on (a) vs the pH. Measurements are carried out in a 3-electrode cell on Pt working electrodes with Ag/AgCl as the reference and Pt mesh as the counter.

Nyquist plots

Nyquist plots from Electrochemical Impedance Spectrscopy are shown below in Figure S2 for single electrode measurements in 0.5 M H2SO4 (A) and in Devices with PPY-lignin cathodes and activated carbon (AC) anodes.

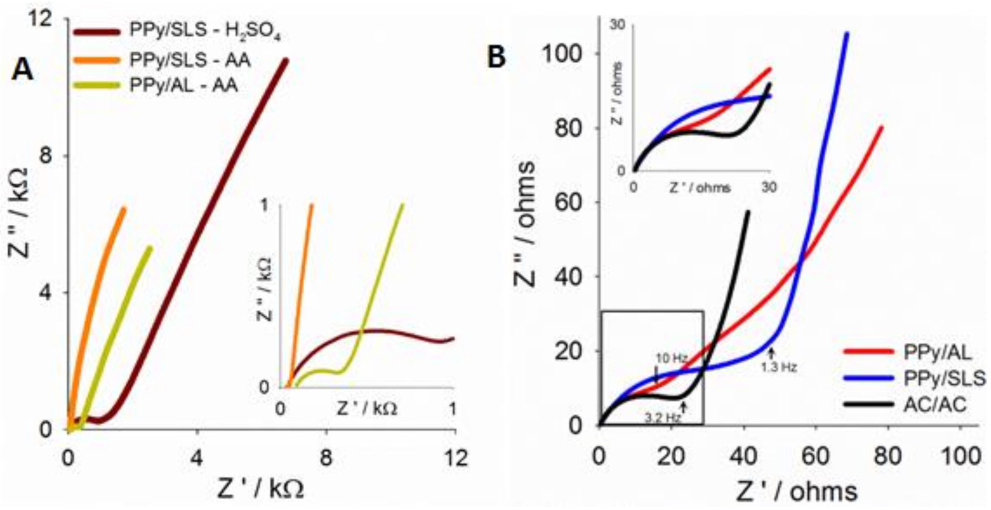

Figure S2. A) Nyquist plot of PPy-Lignin composite electrodes in 0.5 M H_2SO_4 obtained from 3 electrode measurements with Ag/AgCl reference and Pt counter electrodes. B) Nyquist plot of 2 electrode cells with PPy-Lignin cathodes and AC anodes. Measurements were made using an applied potential of 0.7 V over a frequency range of 10000 to 0.1 Hz using a perturbation amplitude of 10 mV.

Electrochemical characteristics of electrodes prepared in 5 M AA polymerization solution

Because AL/PPy exhibited peculiar behavior, each electrode type (pure PPy, SLS/PPy, and AL/PPy) was prepared in 5 M AA solutions and testing in 0.5 M H_2SO_4. Figure S3 shows that SLS/PPy exhibited the highest capacitance when prepared under these conditions, while AL, which has the highest capacitance at 15.3M, showed little capacitance and no redox peak. The standard PPy electrode had lower performance compared to films prepared in H_2SO_4, but wasn't very different than electrodes prepared in 15.3 M AA. These observations are attributed to the poor solubility of AL in AA at this molarity. SLS and Py showed similar solubility compared to the 15.3 M AA, however, very little AL dissolved under these conditions. The low electrochemical performance is likely do to some of the solid particles finding their way into the film. Currently, the phase behavior of the AL in AA is being investigated to understand this anomaly.

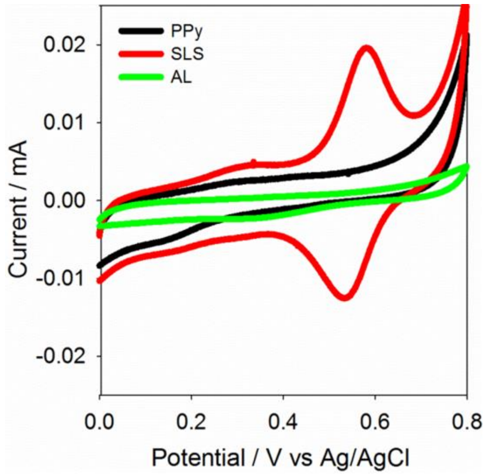

Figure S3. Cyclic voltammetry profiles of PPy, PPy/SLS and PPy/AL polymerized from a 5M AA solution. Measurements are carried out in a 3-electrode cell on Pt working electrodes with Ag/AgCl as the reference and Pt mesh as the counter.

Mass composition of the PPy/Lignin films

Electrodes were assumed to be formed with PPy, H_2SO_4 (from polymerization or subsequent testing), acetic acid and either SLS or AL. The resulting film formula composition is of the form:
$[(PPy)_{x=1}\ (C_2H_3O_2^{-})_y\ (SO_4^{-2})_w]\ [Lignin]_z$

Previous studies [36] have reported approximate "molecular formulas" for AL and SLS. These formulas were used as the lignin monomeric units for the calculations. The molecular formulas were modified to give the approximated sulfur content found in the specific lignin reactants (AL, SLS, and pH fractions 9.5 and 10.5) determined by ICP-AES (table 1). The molecular formulas utilized in the calculations are presented on table S1.

The elemental composition (i.e. weight % of nitrogen, carbon, and oxygen) of the films was determined by EDX, and these values were used to calculate the composition of each species. Electrodes prepared from AA were assumed to have the same doping level (y= 0.61 for x =1), which was found for pure PPY synthesized in AA. Similarly, electrodes prepared from H_2SO_4 were assumed to have the same H_2SO_4 doping level (w=0.09 for x=1), as determined in the reference electrodes. Therefore, the parameters allowed to change during the fitting for the compositions are: 1) the lignin fraction, **z** (for SLS or AL), and 2) sulfate content, **w** (HSO_4^{-}/SO_4^{-2}), except in the case for PPy/SLS in H_2SO_4, where w is fixed by the H_2SO_4 dopant level. Using the film formula given above, and initial values for the fitting parameters, w and z, the weight % of each element was calculated. A weighted error between the "calculated weight %" and the "EDX weight %" was calculated, and w and z were determined by minimizing the error. A range of compositions is reported to reflex how much the composition can change and still achieve within 5% of the minimum error. Details of the calculations are shown below.

Table S1. Assumed monomeric units for the different constituents in PPy/Lignin films

Reactant	Formula[a]
Pyrrole	C_4H_3N
Acetic Acid	$C_2H_3O_2$
Sulfuric Acid	H_2SO_4
Sulfonated Lignin	$C_{10}H_{12}O_6S_{0.36}$
Alkali Lignin	$C_{10}H_{12}O_3S_{0.19}$
pH 9.5 fraction	$C_{10}H_{12}O_3S_{0.15}$
pH 10.5 fraction	$C_{10}H_{12}O_3S_{0.13}$

[a] Hydrogen mass was neglected in the calculations

The elemental compositions were calculated by dividing the contribution of each element by the total AMU (Atomic Mass Unit) of the composite (Eq. 1 and 2). (Example shown for the PPy/SLS in AA)

$$\begin{aligned} N_{fxn} &= x \qquad Eq.1 \\ C_{fxn} &= 4x + 2y + 10z \\ O_{fxn} &= 2y + 6z + 4w \\ S_{fxn} &= 0.36z + 1w \end{aligned}$$

$$AMU_T = N_{fxn}\,(AMU_N) + C_{fxn}\,(AMU_C) + O_{fxn}\,(AMU_O) + S_{fxn}\,(AMU_S) \qquad Eq.2$$

In order to compare with the EDX results, the wt. % of each element can be calculated using Eq. 3.

$$N\,wt.\% = \frac{N_{fxn}\,(AMU_N)}{AMU_T} \ldots \qquad Eq.3$$

Equations 1-3 show the calculations for weight % of C, O, N, S in the electrodes based on the elemental composition in each species, and initial guesses for w and z. A spreadsheet was set to change the values of z and w (x is set to 1, y is determined from reference PPy electrodes) to minimize the error between the elemental analysis values (weight %) from EDX and the calculated values from Eqns 1-3. The range of compositions in table 1 reflects a variation of parameter analysis in which the error did not significantly change (< 5%). In order to minimize the influence from the most abundant elements (C, O) within the film, a weighted error was used (Eq. 4-5):

$$\% \, individual \; eror = \frac{|EDX_{element} - Calculated|}{EDX_{element}} \; x \; 100 \qquad Eq.4$$

$$\% \, Weighted \; eror = \sum \frac{Individual \; errors}{EDX_{each \; element}} \qquad Eq.5$$

The contributions (wt. %) of each individual component in the composite film ([$(PPy)_x$ $(C_2H_3O_2^-)_y$ $(SO_4^{-2})_w$] $[Lignin]_z$) were given by Eq. 6 and 7, where MM is the molecular weight of each monomeric unit.

$$MM_{composite} = MM_{PPy}\,(x) + \; MM_{C2H3O2}\,(y) + MM_{Lignin}\,(z) + \; MM_{H2SO4}\,(w) \qquad Eq.6$$

$$wt.\% \; PPy = \frac{MM_{PPy}\,(x)}{MM \; composite} \; x \; 100 \; \ldots \qquad Eq.7$$

Cycle life of PPy/Lignin electrodes and PPy/Lignin device

The cycle life of PPy/AL single Pt electrode films and PPy/AL-AC device are shown in figure S3. The single electrode was prepared on a Pt electrode at 20 µA for 3300 s (1:1 wt-% PPy:AL). The PPy/AL for the device was prepared on stainless steel foil as explained in the experimental section (1.34 g/L AL). It was found that the ideal concentration of AL varies with the size of the electrode: higher area electrodes (0.5 cm^2) required lower concentrations of AL (1.34 g/L AL) in solution to obtain optimal hydroquine/quinone redox behavior, whereas smaller area electrodes (0.02 cm^2) required a higher concentration of lignin (6.7 g/L AL) to obtain optimal HQ/Q redox behavior. Figure S3a shows the cyclic voltammetry profiles of the device (PPy/AL-AC) before and after 1700 charge/discharge cycles; hydroquinone/quinone groups get irreversibly oxidized, which causes a loss in the characteristic redox peak from AL. After 25 charge/discharge cycles the device starts losing its specific capacitance (figure S3b), although, the charge drop is slower when compared with the single electrode (Pt) (figure S3c) indicating that, even though, the stability of the mixed electrodes is low in solution, it is improved in a two-electrode cell.

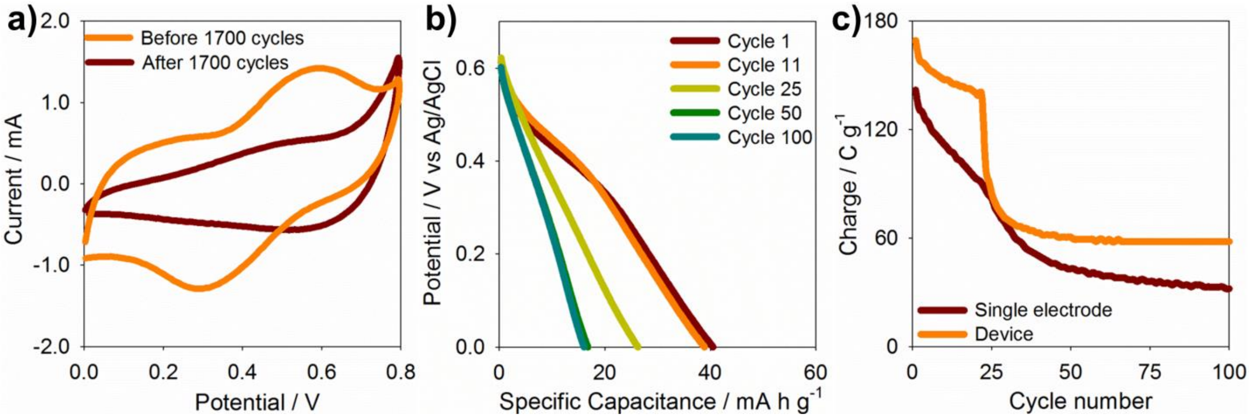

Figure S4. Cycle life experiments on PPy/AL single electrodes and for asymmetric supercapacitors with PPy/AL and AC electrodes. a) Cyclic voltammetry profiles of the PPy/AL - AC cell before and after 1700 charge/discharge cycles. b) Discharge profiles for the cell in (a) at 0.46 mA for various cycles. c) Cycle stability of PPy/AL single electrode and PPy/AL-AC device at 0.46mA.