polymers

MDPI

Article

Electrochemical Activity of Lignin Based Composite Membranes as Battery Electrodes.

Marya Baloch [1], Mikel Alberro Astarbe [2] and Jalel Labidi [1,*]

1 Department of Chemical and Environmental Engineering, Faculty of Engineering, Gipuzkoa, Donostia-San Sebastian;
2 Department of Electronic Technology, Faculty of Engineering, University of the Basque Country (UPV/EHU), Plaza Europa 1, 20018, San Sebastian, Spain
marya.baloch@ehu.eus, mikel.alberro@ehu.eus, jalel.labidi@ehu.eus
* Correspondence: jalel.labidi@ehu.eus; Tel.: +34-943-01-7178

Received: date; Accepted: date; Published: date

Supplementary Materials:

2. Materials and Methods

Label	Lignin Type	Lignin wt. %	Nafion® (NF) wt. %	PEO(PO) wt. %
OLPO	Organosolv (OL)	20	0	80
OLPONF	Organosolv (OL)	20	60	20
OLNF	Organosolv (OL)	20	80	0
KLPONF	Kraft (KL)	20	60	20
KLPO	Kraft (KL)	20	0	80
KLNF	Kraft (KL)	20	80	0

Table S1: Demonstration of different ratios of lignin based composite membranes.

2.2. Characterization

Water Uptake (WU), Swelling Ratio (SR) and Gel Content (GC) % tests

The water uptake, swelling ratio and gel content test were carried out on 20mm (~2.49 x 1.5 x 0.075) size bucchi vacuum oven dried (50°C for 24 hours) membranes in a petri dish full of de-ionised (DI) water at room temperature. The membranes were weighed and measured before and after the experiment. The thickness of membrane was measured using a digital micrometer and an electronic digital caliper was used for measurement of the size. The experiment was duplicated in order to collect an average value. The WU/SR amount was calculated by equation S1, and S2, respectively.

$$WU = \frac{Wwet - Wdry}{Wdry} \quad \text{(S1)}$$

Where W_{dry} is weight of the dry membrane and W_{wet} is weight of hydrated membrane after WU experiment. L_{dry} is the length of the dry and L_{wet} corresponds to the hydrated membrane after the SR test.

$$SR = \frac{Lwet - Ldry}{Ldry} \quad \text{(S2)}$$

Some of the membranes were totally disintegrated in DI water, therefore a GC% test has been conducted and the values were calculated by equation S3.

$$Gel\ content\ \% = \frac{m_2}{m_1}\ x\ 100 \quad \text{(S3)}$$

Where, m_2 represents the dried residue mass and m_1 the mass of the original membrane.

Conductivity and resistance measurements

Interfacial contact resistance (ICR) measurements were done by using Keithley meter. The 20mm membranes were dried under vacuum in bucchi glass oven at 50°C for 24 hours, the membranes with an average thickness of 70µm were collected from desiccator and were introduced between two copper (Cu) plates sandwich of high purity. The contacts between pellet and electrode was improved by pressure applied through a steel compression spring arrangement. The superficial contact was maintained to reserve only up to surface of sample membrane, the rest was covered with Teflon. The bulk resistance of the sample from 0 to 200 tons at 25°C was measured. The sample resistance was then calculated by equation S4. 1 Ampere of DC current was applied to the assembly through the cu plates. The resulting potential led to the total resistance value, which is the sum of two interfacial components located between the membrane sample and the Cu plates.

$$R_S = 2R_{Cu} - 2R_{Cu/S} \quad \text{(S4)}$$

The sample resistance R_S is derived from the resistance of a single sample disc sandwiched between the 2 Cu plates, to which we will add two resistors of the Cu plates ($2R_{Cu}$) and those corresponding to the two interfaces between the plates Cu and the material ($2R_{Cu\,/\,M}$). The total resistance, R_T, is expressed by equation S5.

$$R_T = 2R_{Cu} + 2R_{Cu/S} + R_S \quad \text{(S5)}$$

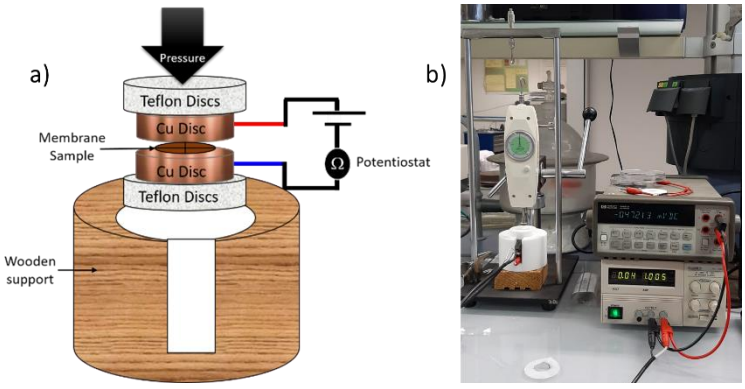

Figure. S1: a) Assembly diagram of the ICR test unit. b) Experimental setup used in the measurement for ICR tests.

The resistivity (Ω-cm) of the membrane was calculated by equation S6.

$$R = \rho \frac{l}{A} \quad \text{(S6)}$$

Where R is the resistance (Ω), l is the thickness of the membrane (cm) and A is the surface area of cross section (cm^2).

The bulk conductivity ($S\text{-}cm^{-1}$) of the membrane has been calculated using equation S7.

$$\sigma = \frac{1}{\rho} \quad \text{(S7)}$$

Where σ is the conductivity and ρ is the resistivity of the bulk material.

Functional groups	Wavenumber cm^{-1}	
	Lignin	OLPONF/KLPONF
O–H	3045-3562	2465, 3223
$-CH_3$, $-CH_2$, -CH	2939, 2844	2932, 2879
C=O	1656	1712
$-CH_3$, $-CH_2$, -CH deformations	1452	1458
C=C	1602, 1504	1604, 1516
Aromatic O-H	1459, 1424, 1393, 1328	1459, 1424, 1394, 1348
C-O-C	1211, 1108, 1030	1211, 1107
Aromatic Syringyl & Guaiacyl	1328, 1210, 1168	1349, 1212, 1147
Aromatic C–H deformation	834	842
Si-OH	--	980
Si-O-Si	--	804
CF_2	--	1100-1200

Table S2: Representation of the peak position of different functional groups of lignin and Nafion ® in composite membranes with comparison to blank lignin.

Electrochemical Impedance Spectroscopy (EIS)

Electrochemical EIS measurements were achieved in a conventional three-electrode electrochemical cell with a Lignin working electrode (WE), Ag/AgCl reference electrode (REF)and a wide platinum foil as a counter electrode (CE), figure S2. The electrochemical activity of the composite materials was evaluated in aqueous solutions of 1 M H_2SO_4. Measurements were done with a Solartron Multipotentiostat 1480 and impedance analysis were done on Solartron mobrey SI 1260 (Impedance-Gain phase analyser). Before and during the measurements, a gentle gas flow of nitrogen was introduced just beneath the electrolyte surface. All measurements were carried out at room temperature, 25.0 ± 0.5 °C. EIS spectra were scanned within a frequency range of 0.01Hz to 100000 Hz with AC amplitude of 10 mV at room temperature.

3. Results

3.3. Conductivity measurements

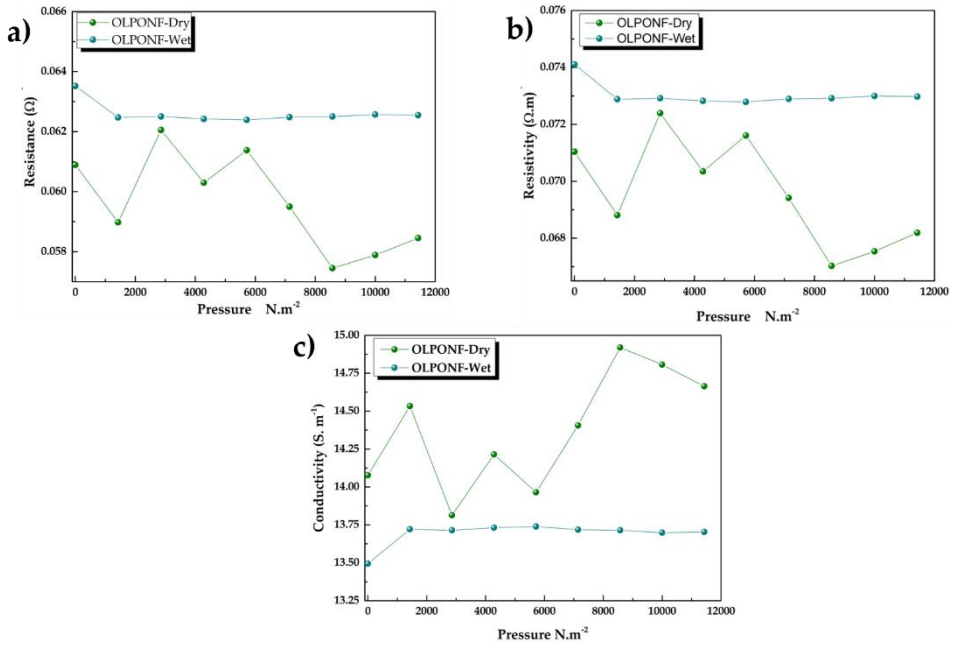

Figure. S2: The comparison of OLPONF membrane before and after the wetting test experiments, shows a) Resistance, b) Resistivity and c) Conductivity with reference to applied pressure.

3.5. Electrochemical Impedance Spectroscopy (EIS).

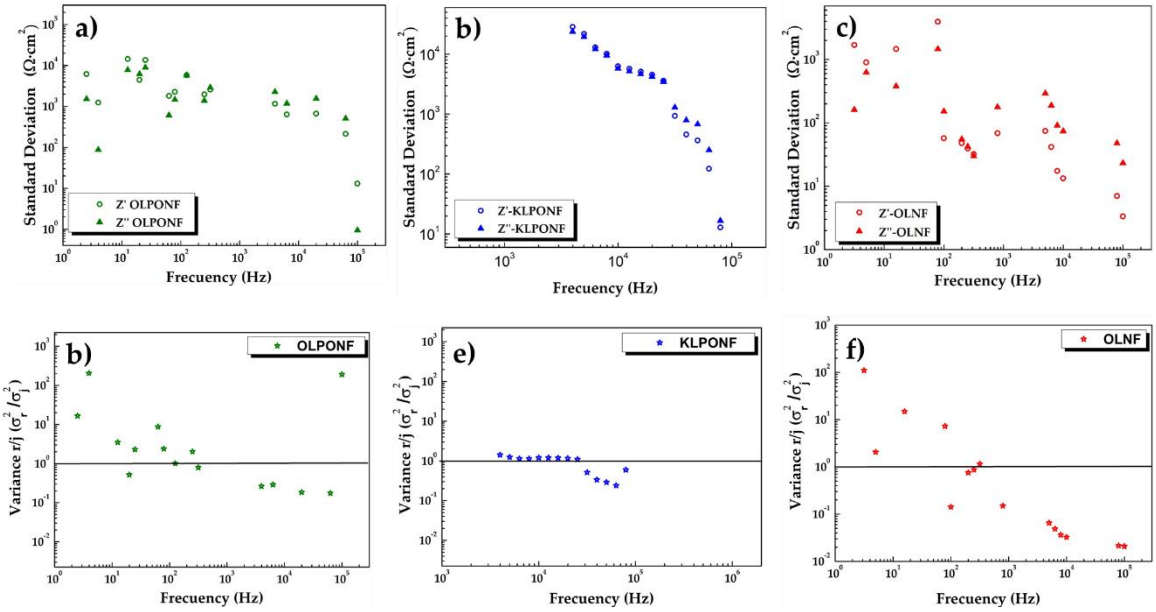

Figure. S3: Statistical analysis via standard deviation (SD) and ratio of variances plots corresponding to the Z′ (real) and Z′′ (Imaginary)-axes of the EIS spectra of a-b) OLPONF, c-d) KLPONF and e-f) OLNF electrodes before the GCPL cycling measurement.

CNLS ECM Series	R1	R2	CPE1-T	CPE1-P	C1	R3	CPE2-T	CPE2-P	C2
	Ω/cm²	Ω/cm²	S^p/ Ω cm²		F/cm²	Ω/cm²	S^p/ Ω cm²		F/cm²
OLPONF Initial	31,56	164410	$1{,}56\times10^{-7}$	0,85813	$7{,}46\times10^{-8}$	15286	$6{,}64\times10^{-8}$	0,90045	$3{,}10\times10^{-8}$
OLPONF Final	$8{,}36\times10^{-5}$	12285	$2{,}78\times10^{-6}$	0,79523	$8{,}92\times10^{-7}$	252,3	$2{,}57\times10^{-5}$	0,42518	$9{,}07\times10^{-10}$
KLPONF Initial	$6{,}42\times10^{-6}$	253750	$1{,}55\times10^{-6}$	0,56119	$1{,}87\times10^{-8}$	954,4	$1{,}89\times10^{-9}$	1,378	$2{,}53\times10^{-8}$
KLPONF Final	$2{,}66\times10^{-6}$	67715	$4{,}14\times10^{-5}$	0,65088	$1{,}38\times10^{-5}$	79,34	$5{,}78\times10^{-5}$	0,36002	$7{,}71\times10^{-11}$

Table S2: Electrical parameters adjustment of the impedance spectra of OLPONF, and KLPONF, to the electric equivalent circuit before and after electrochemical cycling.

Samples	CNLS						(RBF, λ, μ)	
	R2	C1	τ_1	R3	C2	τ_2	τ_1	τ_2
	Ω/cm²	F/cm²	s	Ω/cm²	F/cm²	s	s	s
OLPONF Initial	164410	$7{,}46\times10^{-8}$	$1{,}23\times10^{-2}$	15286	$3{,}10\times10^{-8}$	$4{,}74\times10^{-4}$	$1{,}43\times10^{-3}$	$3{,}40\times10^{-1}$
OLPONF Final	12285	$8{,}92\times10^{-7}$	$1{,}10\times10^{-2}$	252,3	$9{,}08\times10^{-10}$	$2{,}29\times10^{-7}$	$1{,}36\times10^{-3}$	$3{,}72\times10^{-2}$
KLPONF Initial	253750	$1{,}87\times10^{-8}$	$4{,}75\times10^{-3}$	954,4	$2{,}53\times10^{-8}$	$2{,}41\times10^{-5}$		$1{,}38\times10^{-1}$
KLPONF Final	67715	$1{,}38\times10^{-5}$	$9{,}34\times10^{-1}$	79,34	$7{,}71\times10^{-11}$	$6{,}12\times10^{-9}$	$3{,}50\times10^{-2}$	2,00

Table S3: of OLPONF, and KLPONF before and after electrochemical cycling.

a)

CNLS ECM Series	R1	R2	CPE1-T	CPE1-P	C1	R3	CPE2-T	CPE2-P	C2
	Ω/cm²	Ω/cm²	S^p/ Ω cm²		F/cm²	Ω/cm²	S^p/ Ω cm²		F/cm²
OLNF	3,814	5585	$1{,}57\times10^{-6}$	0,923	$1{,}08\times10^{-6}$	9083	$4{,}05\times10^{-6}$	0,935	$3{,}30\times10^{-6}$

b)

Samples	CNLS						(RBF, λ, μ)	
	R2	C1	τ_1	R3	C2	τ_2	τ_1	τ_2
	Ω/cm²	F/cm²	s	Ω/cm²	F/cm²	s	s	s
OLNF	5585	$1{,}08\times10^{-6}$	$6{,}05\times10^{-3}$	9083	$3{,}30\times10^{-6}$	$3{,}00\times10^{-2}$	$1{,}72\times10^{-1}$	$7{,}19\times10^{-4}$

Table S4: a) Electrical parameters adjustment and b) DRT values adjusted to the experimental impedance spectra of OLNF before and after electrochemical cycling.

The Specific capacitances of the samples are calculated by cathodic current from the cyclic voltammogram and by equation S8.

$$Cp = A/2mk(\Delta V) \qquad S8$$

Samples	Specific Capacitance (Cp) F/g
OLPONF	3,59
KLPONF	$1{,}38X10^{-1}$
OLNF	$7{,}18X10^{-1}$

Table. S5: The specific capacitance calculated from experimental data.

Where Cp is the specific capacitance (F g^{-1}) A is area of the CV charge/discharge process (cm^2), m is the active mass of the material (g), k is CV scan rate (s) and ΔV is voltage window difference (V).