Supporting information

Nitro Lignin Derived Nitrogen Doped Carbon as Efficient and Sustainable Electrocatalyst for the Oxygen Reduction Reaction

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Table of Contents

1. Synthetic Methods

1.1 Extraction of Alkali Lignin (L)

The hydrothermal treatment of beech wood is conducted at 220 °C for 15 h in a stainless steel autoclave (Parr). $Ba(OH)_2$ (5.8 g) and distilled water (20 mL) are added to 2.2 g of beech wood. The autoclave is sealed and heated at 220 °C for 15 h in an oven. After cooling down the autoclave, the obtained dark liquor is filtered on paper and the pulp is washed with HCl 1 M and water until pH is neutral. The pulp is dried overnight at 38 °C in a vacuum oven. The dried solid is dissolved in THF and filtered on paper to remove insoluble residues. Thus the solvent is removed in vacuum and the residue is dried overnight at 38 °C in a vacuum oven. THF-soluble alkali lignin

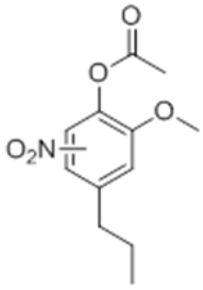
(L) is isolated in 10 wt % yield and was characterized by GPC, elemental analysis (Table 1), 2D-HSQC-NMR (Fig. 2A) and FT-IR (Fig. 2C).

1.2 Lignin acetylation

L (500 mg) is stirred over night at room temperature in 10 mL of an acetic anhydride/pyridine solution (5 mL/ 5 mL). The reaction is quenched by addition of water while cooling the flask. The acetylated product is extracted with $CHCl_3$, dried over sodium sulfate anhydrous and the organic solvent is distilled off to recover the acetylated L.

1.3 Nitration and derivatization of 2-methoxy-4-propylphenol

2-methoxy-3/5-nitro-4-propylphenyl acetate (S1)



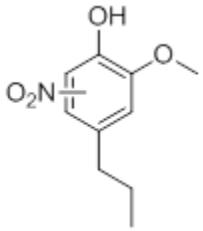
In a round bottom flask, nitric acid (0.4 mL, 9.6 mmol) is slowly added into cold (0 °C) acetic anhydride (1.2 mL, 12.7 mmol). The mixture is thus added to a solution of 2-methoxy-4-propylphenol (1.0 mL, 6.2 mmol) in acetic anhydride (20 mL, 0.21 mmol) followed by one drop

of sulfuric acid. The solution is stirred at room temperature for 3 h. The reaction is quenched by addition of ice and the pH is neutralized using potassium hydroxide in pellets, finally the solution is extracted with diethyl ether (200 mL). The organic phase is dried over anhydrous sodium sulfate, filtered and the solvent is removed by rotary evaporation. The product (S1) (567.8 mg, 3.4 mmol, 55 %) is obtained as a mixture of isomers (5-nitro/3-nitro1: 3) (Fig. S1)

^{1}H-NMR (400 MHz, Methanol-d4, δ): 7.79 (s, 1H), 7.21 (dd, J1 = 4 Hz, J2 = 8 Hz, 2H), 7.08 (s, 1H), 3.94 (s, 3H), 3.88 (s, 3H), 2.96 (t, J = 8 Hz, 2H), 2.54 (t, J = 8 Hz, 2H), 2.36 (s, 3H), 2.30 (s, 3H), 1.70 (m, 2H), 1.64 (m, 2H), 1.03 (t, J = 8 Hz, 3H), 0.96 (t, J = 8 Hz, 3H).

EI-MS (m/z): Mw calc. for $C_{12}H_{15}NO_5$: 253.25 g/mol, found: 253.1 g/mol.

2-methoxy-3/5-nitro-4-propylphenol (S2)

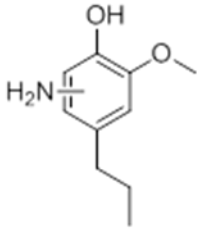


S1 (550 mg, 3.3 mmol) is dissolved in a methanolic solution of potassium hydroxide (0.3 M, 25 mL). The reaction is stirred at 60 °C for 4h, then cooled to room temperature and hydrochloric acid (37 %) is slowly added until pH<6. The solution is extracted with diethyl ether (200 mL), the organic phase is dried over anhydrous sodium sulfate and then concentrated in vacuum. The crude residue is dried overnight at 38 °C under vacuum yielding the desired product (669 mg, 3.2 mmol) in 96 % yield as a mixture of isomers (5-nitro/3-nitro: 2.7).

^{1}H-NMR (400 MHz, Methanol-d4, δ); 7.44 (s, 1H), 6.92 (m, 2H), 6.86 (s, 1H), 3.93 (s, 3H), 3.85 (s, 3H), 2.83 (m, 2H), 2.41 (m, 2H), 1.62 (m, 2H), 1.56 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H), 0.90 (t, J = 7.4 Hz, 3H).

EI-MS (m/z): Mw calc. for $C_{10}H_{13}NO_4$: 211.21g/mol, found: 211.1 g/mol.

3/5-amino-2-methoxy-4-propylphenyl acetate (S3)



The reduction is performed using a H-Cube Pro™ reactor equipped with a hydrogen feed (generated in situ) and a liquid feed. A filtered solution of S2 in methanol (0.05 M) is pumped by a HPLC pump through a 70 mm column packed with Raney-Nichel with a flow of 0.3 mL/min at 130 °C in the presence of hydrogen. H_2 is mixed with the eluent at a pressure of 6 Bar. The collected sample is dried at 38 °C overnight under vacuum affording S3 in 95 % yield.

^{1}H NMR (400 MHz, Methanol-d4, δ): 6.58 (s, 1H), 6.30 (s, 1H), 3.73 (s, 3H), 2.40 (m, 2H), 1.57 (m, 2H), 0.95 (t, J = 8 Hz, 3H).

EI-MS (m/z): Mw calc. for $C_{10}H_{15}NO_2$: 181.23, found: 181.1 g/mol.

1.4 Nitration and derivatization of Lignin

Nitro Lignin (NL)

L (2.7 g) is dissolved in acetic anhydride (20 mL, 0.21 mol) and three drops of concentrated sulfuric acid are added. A solution of nitric acid (6 mL, 0.14 mol) in acetic anhydride (20 mL, 0.21 mol) is thus added at 0 °C. The mixture is stirred for 3 h at room temperature and then quenched by addition of ice. The pH is neutralized using potassium hydroxide in pellets. The so obtained nitrated lignin (NL) is extracted with 2-methyltetrahydrofuran (400 mL). The organic phase is dried over anhydrous sodium sulfate, filtered and concentrated in vacuum affording NL (2.0 g) in 75 wt % yield.

Nitro Deacetylated Lignin (NDL)

NL (1.80 g) is dissolved in a methanolic solution of potassium hydroxide (0.3 M, 120 mL). The reaction is stirred at 60 °C for 4 h, thus the flask is cooled to room temperature and hydrochloric acid (37%) is added until pH<6.

The mixture is concentrated by rotary evaporation and the solid suspended in THF. The solid phase is separated by centrifugation and the organic solvent is removed in vacuum affording NDL (1.1 g, 60 wt %).

Amino Lignin (AmL)

The reduction of the NDL to amino lignin (AmL) was performed using the H-Cube ProTM reactor. A filtered solution of NDL in methanol (4 mg/mL) is flushed at a flow rate of 0.3 mL/min through a 70 mm column packed with Raney-Nichel at 130 °C in presence of H_2 and at a pressure of 6 Bar. The collected sample is dried affording crude amino lignin in 73 wt % yield. The course of the reaction (reduction of NDL to AmL) is followed by colorimetric ninhydrin test. The color comparison of L, NL, NDL and AmL solutions (Fig. S2) shows the dark-blue color caused by Ruhemann's purple compounds developed in the presence of free amino/aniline groups.

1.5 General Procedure for the synthesis of Mesoporous N-doped Carbon

The selected precursor (L, NL or AmL, 100 mg) is frozen using liquid nitrogen and then grinded in an agate mortar cooled in an ice bath. The fine powder is blended with a mixture of $KCl/ZnCl_2$ (500 mg) prepared in a glovebox in a molar ratio of 51:49. The mixture is transferred into a ceramic crucible and heated under nitrogen condition to a final temperature of 850 °C using the following gradient program: 2 h at 25 °C, heating rate of 3 °C/min to 240 °C, 240 °C for 2 hours and then heating rate of 1 °C/min to 850°C. At the end of the process, the temperature is kept at 850 °C for two hours and then the system is cooled down to room temperature. The powder is suspended in water, stirred overnight in order to remove all the salts, and then filtered. The washing procedure is repeated twice. The final sample is dried under vacuum at 60 °C over night.

2. Electrochemical characterization

For ink preparation 5 mg of the catalyst was mixed with 95 µl of Nafion® solution (5 wt.% in lower aliphatic alcohols and water, Sigma Aldrich) and 350 µl of absolute ethanol (VWR). After sonication for 30 min, 5 µl of the homogenous dispersion was dropcasted on the well-polished glassy carbon electrode and dried at room temperature under ambient conditions for 5 min resulting in a catalyst loading of 290 µg cm^{-2}. A commercial 20 wt % Pt on carbon (Pt/C; Alfa Aesar) served as reference material. The reference ink was prepared in the same way as the sample inks resulting in a high Pt loading of 60 µg cm^{-2} (Pt/C loading, 290 µg cm^{-2}). The measured potentials were converted to RHE scale and corrected to the internal resistance determined by impedance at high frequencies. All the samples were pretreated by cycling for 10 cycles between 0.0 and 1.0 V (vs. RHE) in O_2-saturated solution to obtain stable cyclic voltammograms (CVs). The working electrode was kept at the starting potential for 5 s prior to each measurement. CVs were executed with a sweep rate of 50 mV s^{-1} and linear sweep voltammograms (LSVs) with 5 mv s^{-1}. From all LSVs the LSV measured in N_2-saturated solution was subtracted to eliminate the capacitive currents. Limiting currents were determined at 0.3 V (vs. RHE).

The data obtained at different rotation speeds was used for Koutecky-Levich (KL) analysis by plotting the reciprocal current (i^{-1}) *vs*. the reciprocal square route of the angular rotating speed ($\omega^{-1/2}$) at different potentials. Following the KL equation the electron transfer number (n) can be calculated by the use of the slopes of the linear fit lines (Equation 1).

$$\frac{1}{i} = \frac{1}{i_L} + \frac{1}{i_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{i_K} \qquad (1)$$

$$with\ B = 0.62nFAC_0D^{2/3}\upsilon^{-1/6}$$

Here i_L and i_K stand for the kinetic and the diffusion limiting and current, respectively. F is the Faraday constant (96485 C mol^{-1}), C_0 represents the saturated O_2 concentration (1.21 x 10^{-6}mol cm^{-3}), A is the area of the electrode (0.196 cm^2), D is the diffusion coefficient of the dissolved O_2 (1.86 x 10^{-5} cm^2 s^{-1}) and υ stands for the electrolyte's kinematic viscosity (0.01 cm^2 s^{-1}). All values are applicable for 0.1 M KOH at room temperature.

A rotating ring disc electrode (RRDE) set-up (Gamry Instruments) was used to detect *in-situ* the amount of H_2O_2 formed. Typically, 6.5 µl catalyst ink were deposited on the RRDE-electrodes (diameter, 5.7 mm) resulting in the same loading as used in the RDE experiments. The collection efficiency ($N = 0.36$) of the RRDE-electrode was specified prior to the experiment using LSVs at different rotation rates in a 10 mmol potassium ferrocyanide solution. The ring was kept at a constant potential of 1.20 V (vs. RHE) during all RRDE-measurements. The recorded ring (i_R) and disc currents (i_D) are used for the calculation of the number of transferred electrons (n) and the yield of hydrogen peroxide ($H_2O_2(\%)$) according to Equation 2 and Equation 3, respectively.

$$H_2O_2(\%) = 200\frac{i_R/N}{i_R/N+i_D} \quad (2)$$

$$n = 4\frac{i_D}{i_R/N+i_D} \quad (3)$$

The stability was tested performing chronoamperometric measurements at 0.80 V (vs. RHE) in O_2-saturated 0.1 M KOH applying a rotation rate of 1600 rpm. MeOH-crossover experiments

were conducted using the same parameters as used for the stability test and injecting 6.3 mL of MeOH after 1600 s leading to a final MeOH concentration of 1 M.

3. Tables and Figures

Table S1: Elemental composition (derived by combustion analyses) and N_2-physisorption data of the samples prepared using an eutectic NaCl/$ZnCl_2$-mixture.

sample	*N-content* / wt%	*C-content* / wt%	S_{BET} / $m^2\ g^{-1}$	V_{tot} / $cm^3\ g^{-1}$	*Total yield* / wt%	*carbon yield*/ wt%
AmL-C	4.4	80.8	1240	1.00	15.6	19.0
NDL-C	4.3	73.5	1640	0.99	13.6	15.1
NL-C	4.0	77.1	1610	1.00	10.0	11.6

Table S2. Total nitrogen content and absolute amount of *N* sites present in the carbonized samples according to XPS analysis.

sample	*N (total)* / wt%	*pyridinic – N* / wt%	*pyrrolic - N* / wt%	*graphitic - N* / wt%	*N - oxide* / wt%
AmL-C	3.5	1.1	1.0	1.1	0.3
NDL-C	4.8	1.1	1.2	2.0	0.5
NL-C	6.7	2.2	1.7	2.4	0.4

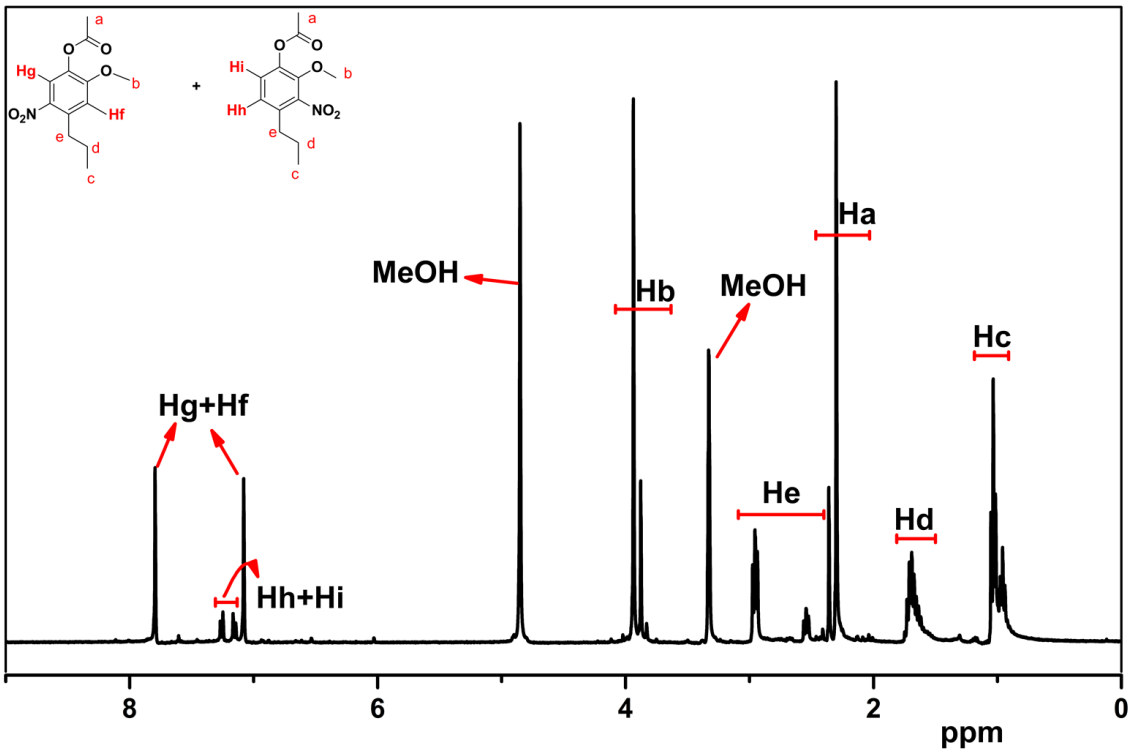


Figure S1. ^{1}H-NMR of 2-methoxy-3/5-nitro-4-propylphenyl acetate

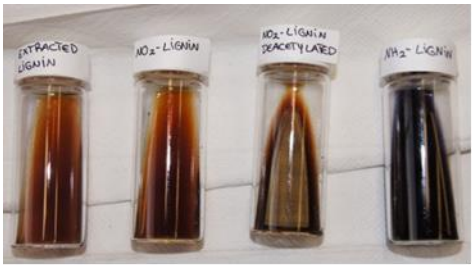


Figure S2. Colorimetric Ninhydrin test performed on L, NL, NDL, AmL

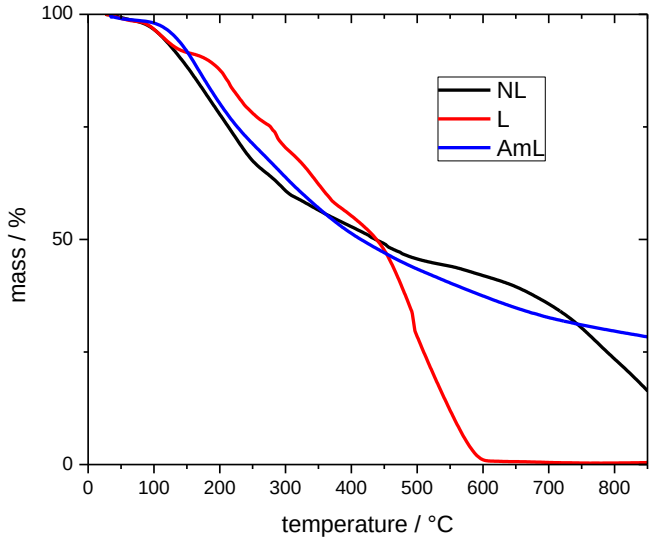


Figure S3. Thermal gravimetric analysis for L, NL, AmL. The analysis were conducted under nitrogen atmosphere. The temperature was increased from 30° to 1000° C with a rate of 2.5 °C/min.

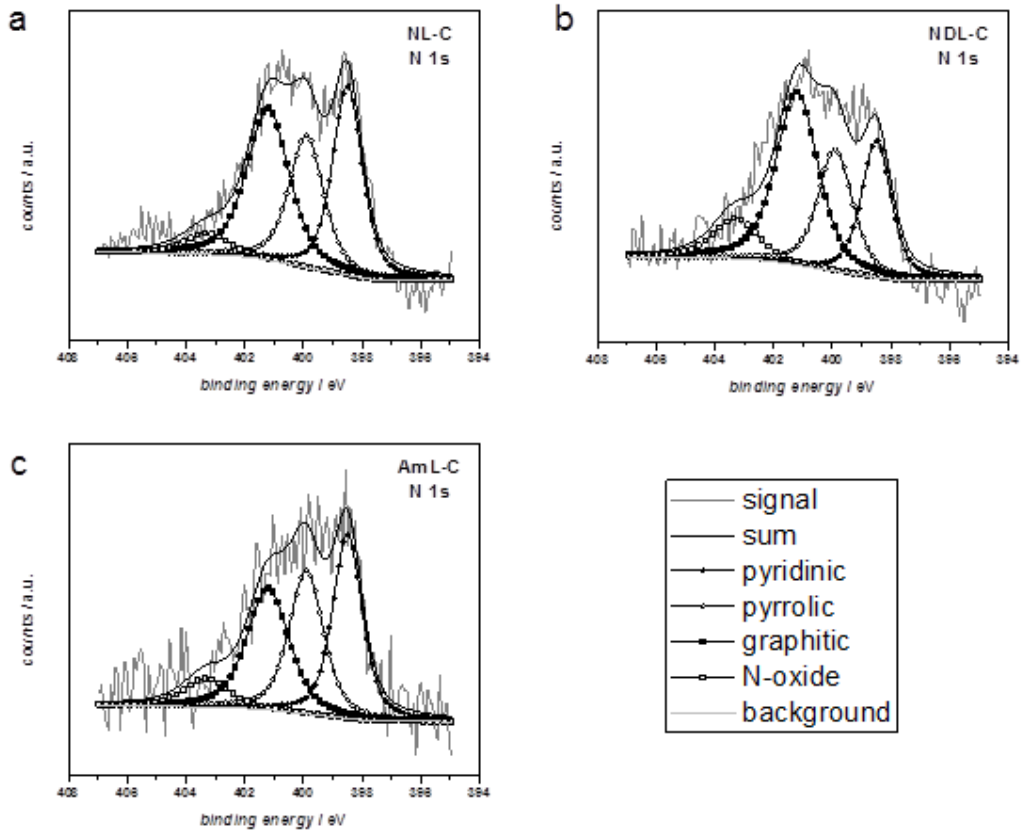


Figure S4. N 1s XPS spectra of a) NL-C, b) NDL-C, and c) AmL-C. Deconvoluted nitrogen peaks: pyridinic-N (398.5 eV); pyrrolic-N (399.9 eV); graphitic-N (401.2 eV), oxidized-N (403.3 eV).

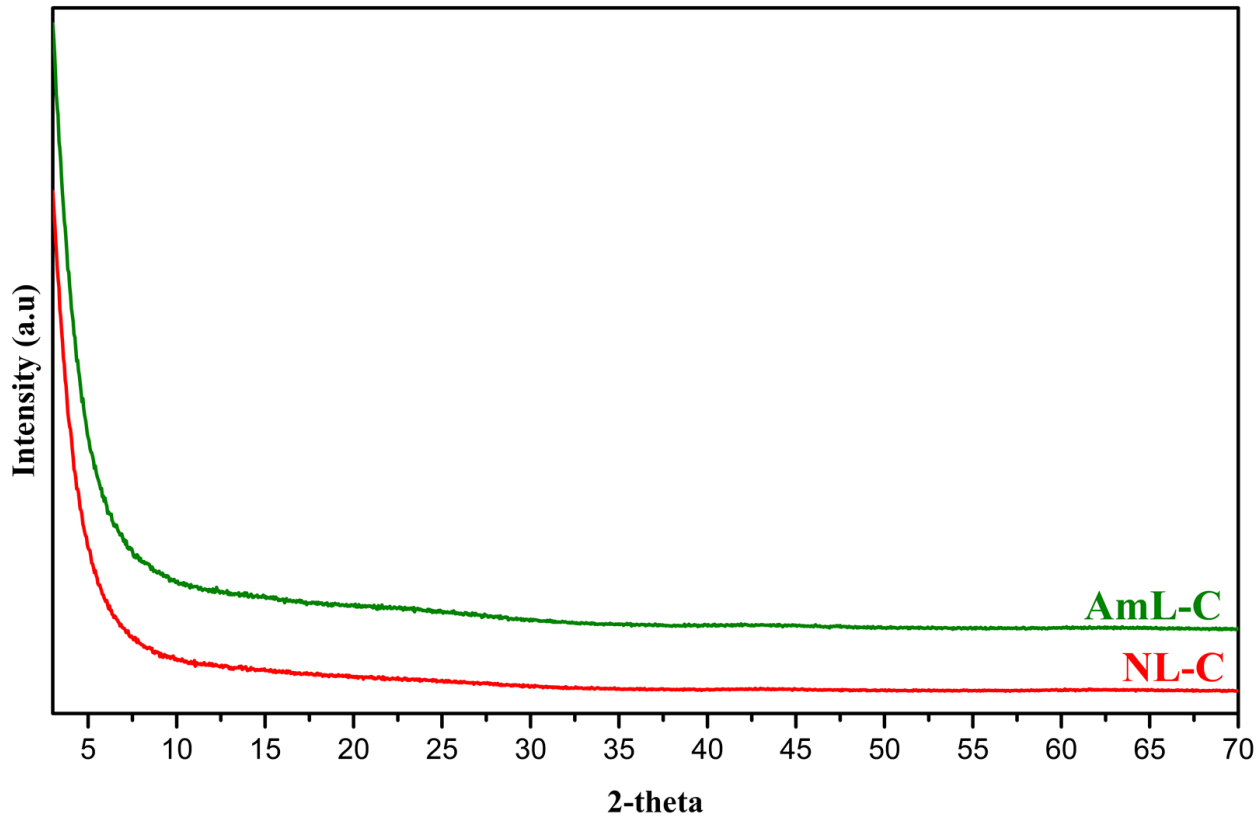


Figure S5. XRD Pattern of Nitro-Lignin (NL-C) and Amino-Lignin (AmL) after carbonization

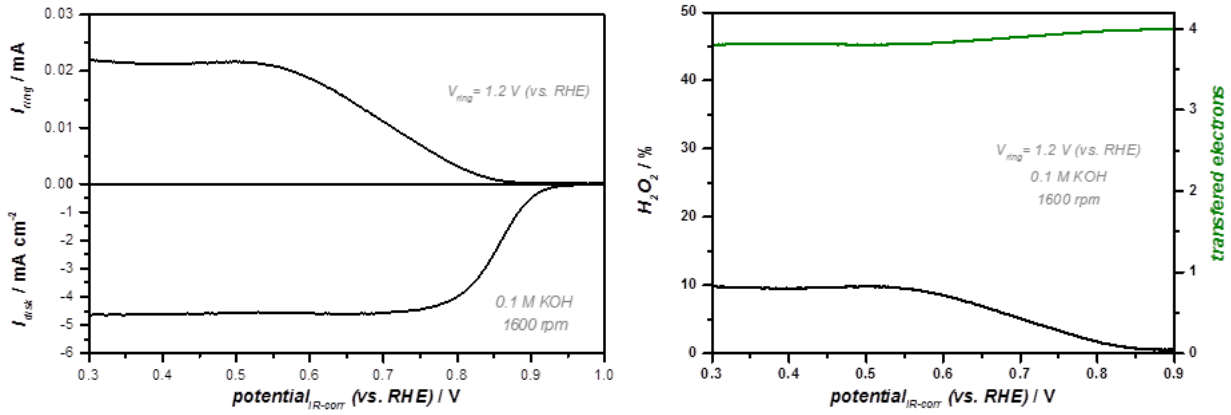


Figure S6. Left: RRDE-measurements of NL-C in O_2-saturated 0.1 M KOH with a sweep rate of 5 mV s^{-1}, 1600 rpm. Right: Number of transferred electrons and hydrogen peroxide yield for NL-C obtained by RRDE-measurements.

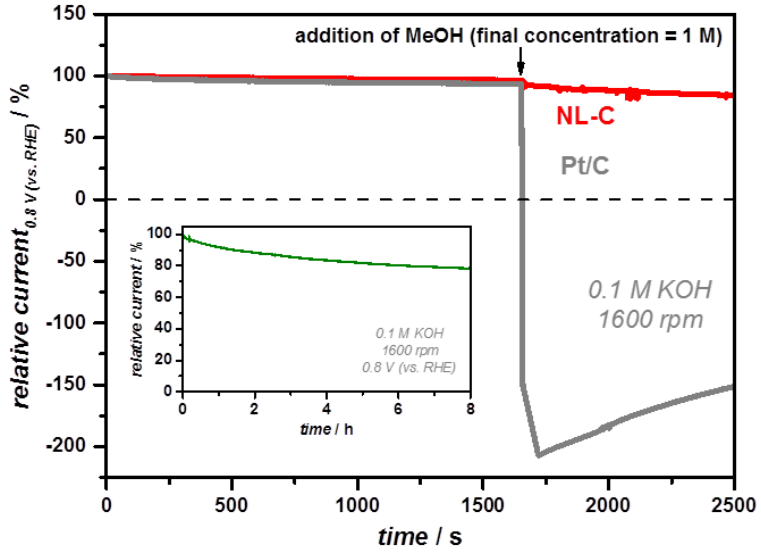


Figure S7: Methanol crossover test for NL-C and the commercial Pt/C (Pt-loading = 60 µg cm^{-2}). Chronoamperometric response at 0.8 V (vs. RHE) in O_2-saturated 0.1 M KOH (rotating rate = 1600 rpm) with the addition of MeOH after 1600 s (reaching a MeOH concentration in the electrolyte of 1 mol l^{-1}). The inset shows the stability before MeOH addition

References

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