### **Supporting Information (SI)**

Mechanistic Investigation of a Ni-catalyzed Electrochemical Reductive Cleavage of the  $\alpha$ -O-4 bond in Lignin Model Compound Benzyl Phenyl Ether

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### <u>General Procedure A: Benzylation of phenols (synthesis of BPE derivative model compounds</u> <u>c, e, f and h)</u>

To a solution of corresponding substituted benzylbromide (2 mmol, 1 equiv) and phenol (3 mmol, 1.5 equiv) in Acetone (9 mL) was added  $K_2CO_3$  (4 mmol, 2 equiv) and the reaction was refluxed overnight. After cooling to room temperature, the reaction was filtered, and the solvent was removed under reduced pressure. Silica gel column chromatography afforded the desired product (elute EtOAc/hexane)

### <u>General Procedure B: Benzylation of substituted phenols (synthesis of BPE derivative model</u> <u>compounds g and i)</u>

To a solution of corresponding substituted phenols (15 mmol, 3 equiv) in tetrahydrofuron (THF) (20 mL) NaOH (10 mmol, 2 equiv) was added and stirred for 15 mins to ensure through mixing. Then benzylbromide (5 mmol, 1 equiv) was added to above solution and the reaction was refluxed overnight. After cooling to room temperature, water and EtOAc were added to the resulting mixture, the organic layer was separated. The aqueous layer was extracted three times with EtOAc. The combined organic layer was washed with brine, dried with Na<sub>2</sub>SO<sub>4</sub>, and then evaporated under reduced pressure. The residue was purified with a flash column chromatography (EtOAc/hexane)

#### Pd/C on carbon paper (Pd/CP) electrode preparation procedure

5 mg of Pd/C (5wt. % loading) (Sigma-Aldrich) was dispersed in a mixture of 340  $\mu$ L of deionized water, 160  $\mu$ L of ethanol (Koptec) and 20  $\mu$ L of Nafion (5 wt%, Sigma-Aldrich) and the suspension was sonicated for 20 min to form a catalyst ink. 400  $\mu$ L of the ink were drop-casted on carbon fiber paper (Spectracarb 2050A-1550, Fuel Cell Store) over a geometric area of 1 × 2 cm<sup>2</sup> to prepare electrodes. The catalyst mass loading is 2 mg/cm<sup>2</sup>.

#### **Deuterium-labeling experiments procedures and quantification**

Deuterium labelling experiments were carried out using a pre-deposited Ni/CP-Ar-1h electrode in 0.1M TBAPF<sub>6</sub> in CD<sub>3</sub>OD for 5h. The completion of reaction was confirmed by both NMR and

GC-MS analysis. The quantification of deuterium content was based on proton on the methyl group of toluene.



<sup>1</sup>HNMR spectra of a) toluene in CD<sub>3</sub>OD, b) phenol in CD<sub>3</sub>OD, c) BPE in TBAPF6- CD<sub>3</sub>OD, d) reaction mixture of deuterium-labelling experiment using Ni/CP-Ar-1h





<sup>1</sup>HNMR of reaction mixture of deuterium-labelling experiment using Ni/CP-Ar-1

<sup>1</sup>H-NMR of a mixture of toluene and phenol in a 1.1:1 ratio in CD<sub>3</sub>OD. The equal ratio mimics the average product ratio observed during the ECH of BPE.



GC-MS spectra of toluene from ECH in CH<sub>3</sub>OH (top); and toluene from ECH in CD<sub>3</sub>OD (bottom)



GC-MS spectra of phenol from ECH in CH<sub>3</sub>OH (top); and phenol from ECH in CD<sub>3</sub>OD (bottom)

### **Supplementary Table S1**

Investigation of the amount of Ni- deposited on the Carbon paper (CP) electrodes surface via Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

Entry	Concentration of Ni <sup>2+</sup> ion in the plating bath solution BEFORE the electroplating (mM)	Plating time (h)	Current (mA)	Concentration of Ni <sup>2+</sup> ion in the plating bath solution AFTER the electroplating (mM)	Plated Ni (mmol)
1	40	5	10	28.3	0.425
2	40	1	10	10.2	0.154
3	40	1	2	4.4	0.066
4	2	1	2	0.01967	0.0295

Reaction conditions: divided cell, 15 mL MeOH, 0.1 M TBAPF<sub>6</sub>, constant current electrolysis,  $2 \text{ cm}^2$  carbon paper as cathode, under air

<u>Supplementary Table S2</u> Investigation of the solvent effects on the yields of ECH of BPE by Ni/CP-Ar, 1h

Entry	Solvent	Electrolyte	Toluene Yield (%)	Phenol Yield (%)
1	МеОН	TBAPF <sub>6</sub>	45	38
2	EtOH	NaClO <sub>4</sub>	28	17
3	ACN	TBAPF <sub>6</sub>	0	0
4	DMF	TBAPF <sub>6</sub>	0	0
5	THF	TBAPF <sub>6</sub>	0	0

Reaction conditions: divided cell, 10 mM BPE, 15 mL solvent, 0.1 M electrolyte, constant current at 10 mA, under air , 5 h

## **Supplementary Table S3**

Investigate the effects of different electrodes doped with various metals on the ECH performance of BPE

			Product Yield (%) <sup>a</sup>	
Entry	Cathode	Additive	$\bigcirc$	Ю
1	Carbon paper	NiCl <sub>2</sub> ·6H <sub>2</sub> O	90	84
2	Carbon paper	PdCl <sub>2</sub>	89	79
3	Pd/CP	no	70	56
4	Cu/CP	no	0	0
5	Fe/CP	no	0	0
6	Co/CP	no	0	0
7*	Pd/CP without electricity, with $H_2$ bubbling	no	31	22
8*	Ni/CP without electricity, with H <sub>2</sub> bubbling	no	0	0

Reaction conditions: divided cell, 15 mL MeOH, 0.1 M TBAPF<sub>6</sub>, 10 mM BPE, constant current at 10 mA, under air, 5 h.

<sup>*a*</sup> Based-on GC analysis with diphenyl as an internal standard

\* Reaction time: 36 h

#### **Supplementary Table S4**

More detailed information for reactions in Scheme 4

Model compound	Conversion (%)	(Substituted-) toluene yield (%)	Starting voltage (V)	Finishing voltage (V)	Faradaic efficiency (%) <sup>a</sup>
a	89	80	15.9	14.0	12.9
b	79	72	16.2	13.9	11.6
c	85	75	16.7	14.2	12.1
d	77	68	16.5	14.2	10.9
e	39	35	16.8	14.5	5.6
f	0	0	17.0	15.0	0
g	73	73	16.2	14.4	11.8
h	75	75	16.5	13.6	12.1
i	72	72	16.3	14.0	11.6
j	95	95	16.4	13.3	15.3
k	92	92	16.7	13.9	14.8

Faraday efficiency(%) =  $\frac{Moles \ of \ isolated \ product \ \times F \ \times n}{Q} \times 100 \ \%$ , where n = number of transferred electrons to the product, F = Faraday's constant, 96,485 C mol<sup>-1</sup>, and Q = total charge passed. (FE calculated based on yield of (substituted-)toluene).

Listed voltages are voltages between anode and cathode.

Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) analysis of Ni/CP-Air, 5h



EDS for the elements (a) Carbon; (b) Oxygen; (c) Chlorine; and (d) the quantification of elemental ratio.

SEM, XRD, and XPS analysis for the Ni/CP-Ar electrode before-and-after the ECH of BPE



SEM of Ni/CP, 1h before ECH of BPE (first row) at different magnifications; and after ECH of BPE (second row) at different magnifications; (b) X-Ray Diffraction (XRD) spectra of Ni/CP-Ar, 1h before ECH of BPE (Black line) & Ni/CP-Ar, 1h after ECH of BPE (Red line); (c) X-ray Photoelectron spectroscopy (XPS) spectra of Ni 2p of Ni/CP-Ar before ECH of BPE (Black line) and after ECH of BPE (Red line).

Investigating the effects of changing the Ni/CP electrode plating currents and concentration of NiCl<sub>2</sub>  $\cdot$  6H<sub>2</sub>O in the plating solution on the corresponding ECH performances



Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) analysis of Ni/CP electrode which was prepared in ethanol



SEM figures (a) & (b) of Ni/CP-Air, 1h which was prepared in ethanol; EDS for the elements (c) Carbon; (d) Chlorine; (e) Nickel; (f) Sodium; (g) oxygen; and (h) the quantification of elemental ratio

X-ray diffraction (XRD) comparison between different Ni/CP electrodes prepared in different solvent-electrolyte systems



Pristine Carbon paper (Blue line); Ni/CP-Air, 5h which was prepared in methanol (Black line) showing the Ni on the carbon paper with a face-centered cubic (fcc) structure; while the fcc structure could not be found for the Ni on the Ni/CP-Air, 1h which was prepared in ethanol (Red line).

Cyclic voltammograms of double-layer capacitance measurements for determination electrochemical surface area



(a) CV scans for Ni/CP-Ar, 1h; (b) CV scans for Ni/CP-Ar, 5h; & (c) CV scans for Ni/CP-Air, 1h

#### **Supplementary Figure S7**

Relationship between electrode capacitance and ECH performance



<sup>1</sup>H NMR of 1,3-dimethyl-2-(phenoxymethyl) benzene

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.36 – 7.28 (m, 2H), 7.16 (dd, *J* = 6.7, 8.3 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 2H), 7.04 – 6.94 (m, 3H), 5.02 (s, 2H), 2.39 (s, 6H).



<sup>13</sup>C NMR of 1,3-dimethyl-2-(phenoxymethyl)benzene

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.28, 138.15, 132.79, 129.47, 128.59, 128.34, 120.86, 114.62, 64.51,19.60.



<sup>1</sup>H NMR of 1,3-di-tert-butyl-5-(phenoxymethyl)benzene

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.42 (t, *J* = 1.8 Hz, 1H), 7.37 – 7.26 (m, 4H), 7.08 – 6.93 (m, 3H), 5.03 (s, 2H), 1.35 (s, 18H).



<sup>13</sup>C NMR of 1,3-di-tert-butyl-5-(phenoxymethyl)benzene

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 159.07, 151.03, 135.92, 129.44, 122.21, 120.82, 114.85, 70.80, 34.87, 31.47.



<sup>1</sup>H NMR of 2-(benzyloxy)-1,3-dimethylbenzen

<sup>1</sup>H NMR (600 MHz, cdcl<sub>3</sub>)  $\delta$  7.48 (t, *J* = 7.1 Hz, 2H), 7.43 – 7.24 (m, 3H), 7.11 – 6.79 (m, 3H), 4.80 (d, *J* = 6.1 Hz, 2H), 2.31 (d, *J* = 7.1 Hz, 6H).



<sup>13</sup>C NMR of 2-(benzyloxy)-1,3-dimethylbenzen

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 155.86, 137.85, 131.19, 128.97, 128.60, 128.03, 127.84, 124.08, 74.00, 16.49.



<sup>1</sup>H NMR of 1-(benzyloxy)-3,5-di-tert-butylbenzene

<sup>1</sup>H NMR (600 MHz, cdcl<sub>3</sub>)  $\delta$  7.53 – 7.42 (m, 2H), 7.42 – 7.35 (m, 2H), 7.34 – 7.26 (m, 1H), 7.04 (t, *J* = 1.7 Hz, 1H), 6.85 (d, *J* = 1.7 Hz, 2H), 5.05 (s, 2H), 1.31 (s, 18H).



<sup>13</sup>C NMR of 1-(benzyloxy)-3,5-di-tert-butylbenzene

<sup>13</sup>C NMR (151 MHz, cdcl<sub>3</sub>) δ 158.45, 152.21, 137.35, 128.57, 127.92, 127.77, 115.19, 109.21, 70.04, 35.02, 31.46.



Optimized structures of intermediates and transition states used in the construction of potential energy diagram shown in Figure 6



Hydrogen atoms are represented with white balls, carbon with gray, oxygen with red, and nickel with blue. Red lines on TS designate displacement vectors for respective transition state.