

Novel Screen-Printed Sensor with Chemically Deposited Boron-Doped Diamond Electrode: Preparation, Characterization, and Application

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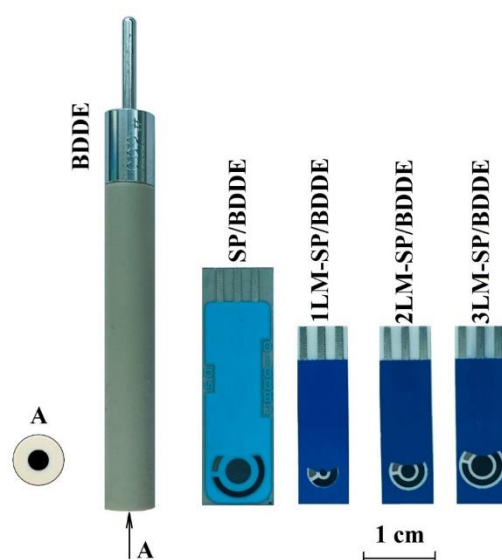


Figure S1. Applied sensors.

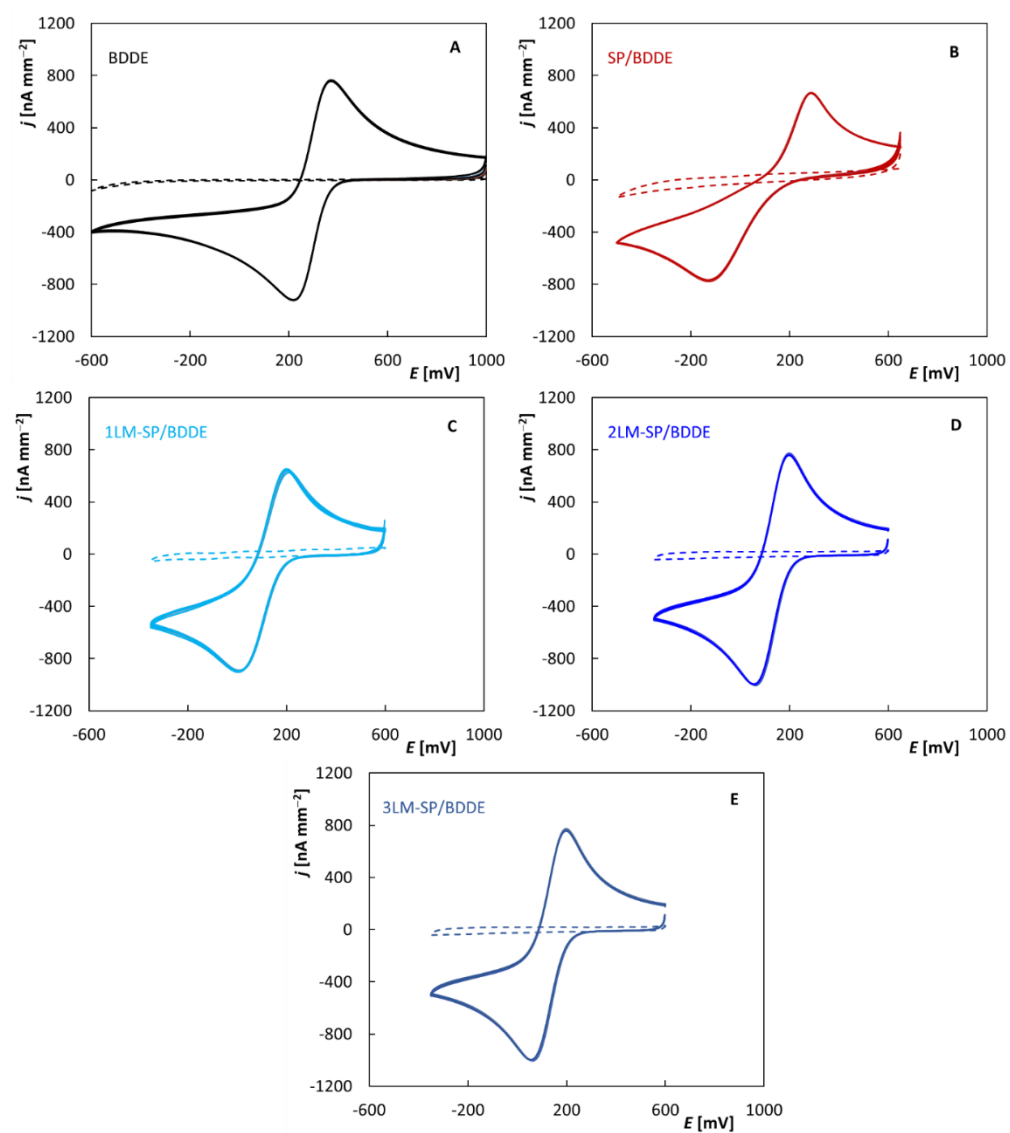


Figure S2. Cyclic voltammograms of $[\text{Fe}(\text{CN})_6]^{4-/3-}$ recorded on all tested sensors (electrolyte – 0.1 mol L⁻¹ KCl, $v = 100 \text{ mV s}^{-1}$, $c([\text{Fe}(\text{CN})_6]^{4-/3-}) = 6.25 \times 10^{-4} \text{ mol L}^{-1}$).

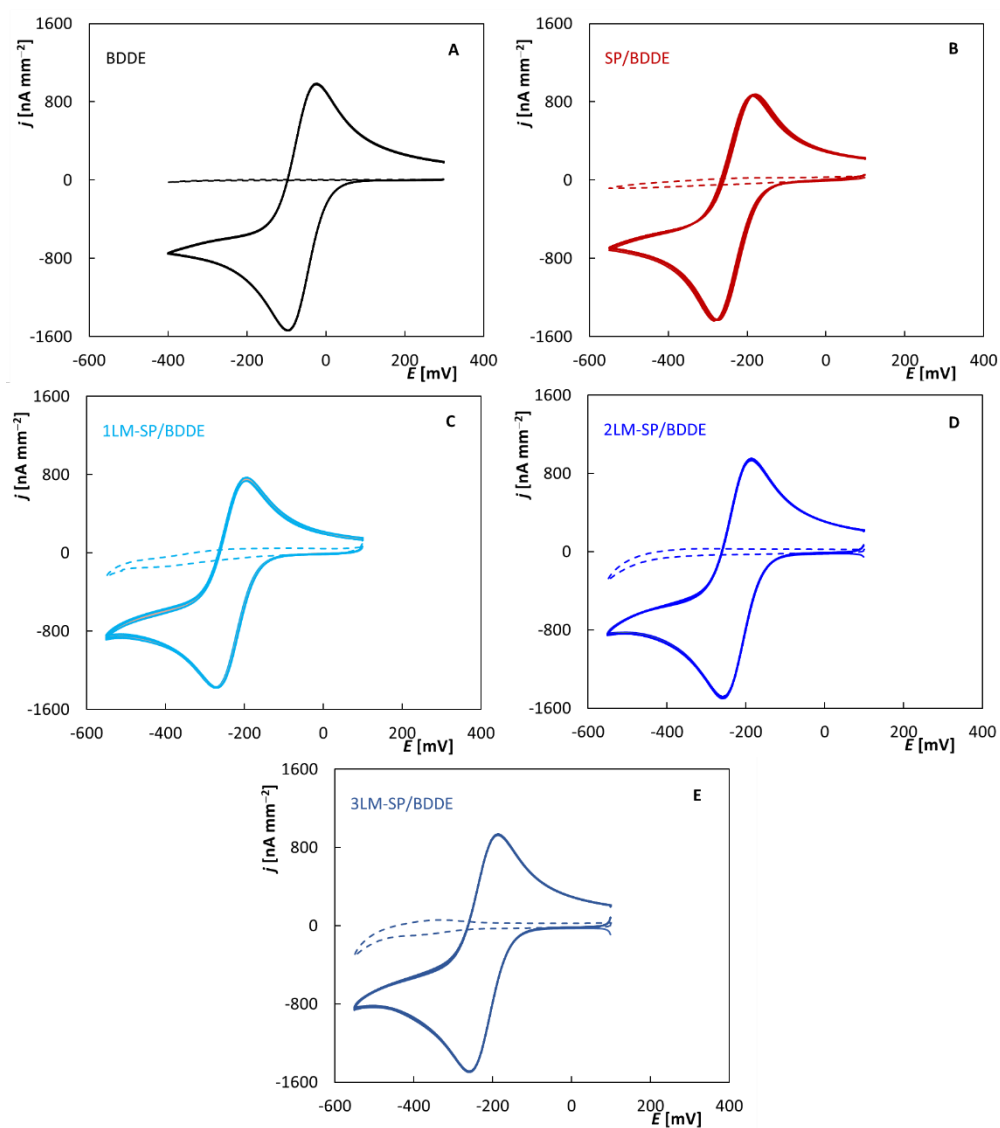


Figure S3. Cyclic voltammograms of $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ recorded on all tested sensors (electrolyte – $0.1 \text{ mol L}^{-1} \text{ KCl}$, $v = 100 \text{ mV s}^{-1}$, $c([\text{Ru}(\text{NH}_3)_6]^{2+/3+}) = 6.25 \times 10^{-4} \text{ mol L}^{-1}$).

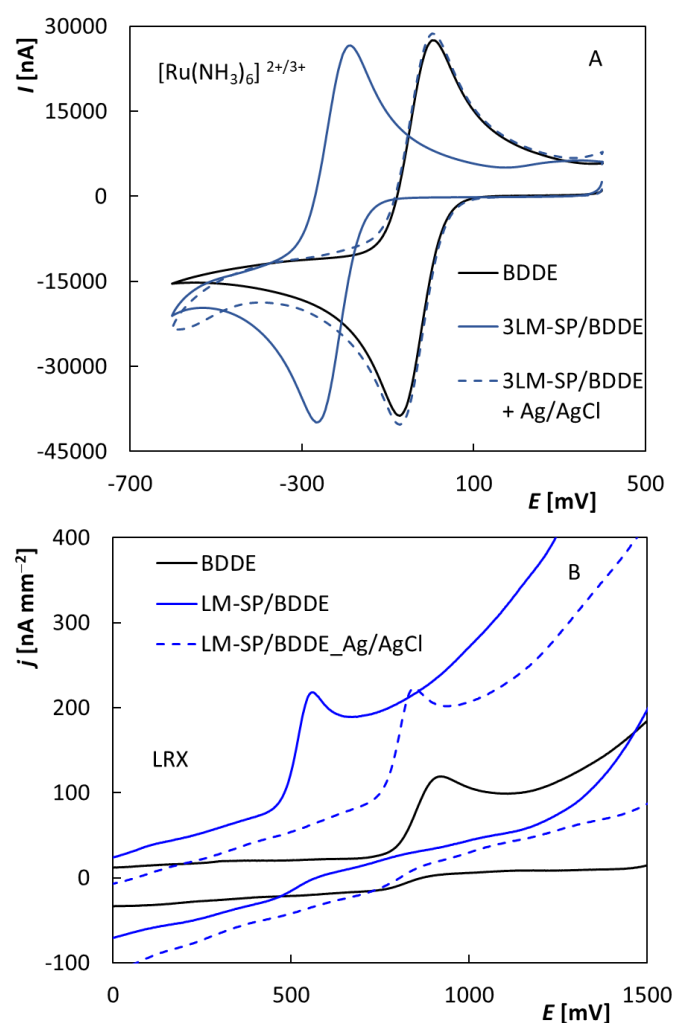


Figure S4. Cyclic voltammograms of $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ recorded on BDDE with Ag/AgCl(KCl. sat.), on 3LM-SP/BDDE, and on 3LM-SP/BDDE with external reference electrode (Ag/AgCl(KCl sat.)) (A), and cyclic voltammograms of LRX recorded using the same 3 electrochemical cell arrangements (B) (A: electrolyte – 0.1 mol L⁻¹ KCl, $v = 100 \text{ mV s}^{-1}$, $c([\text{Ru}(\text{NH}_3)_6]^{2+/3+}) = 2.5 \times 10^{-3} \text{ mol L}^{-1}$; B: electrolyte – BRB (pH 3), $v = 100 \text{ mV s}^{-1}$, $c(\text{LRX}) = 40 \text{ } \mu\text{mol L}^{-1}$).

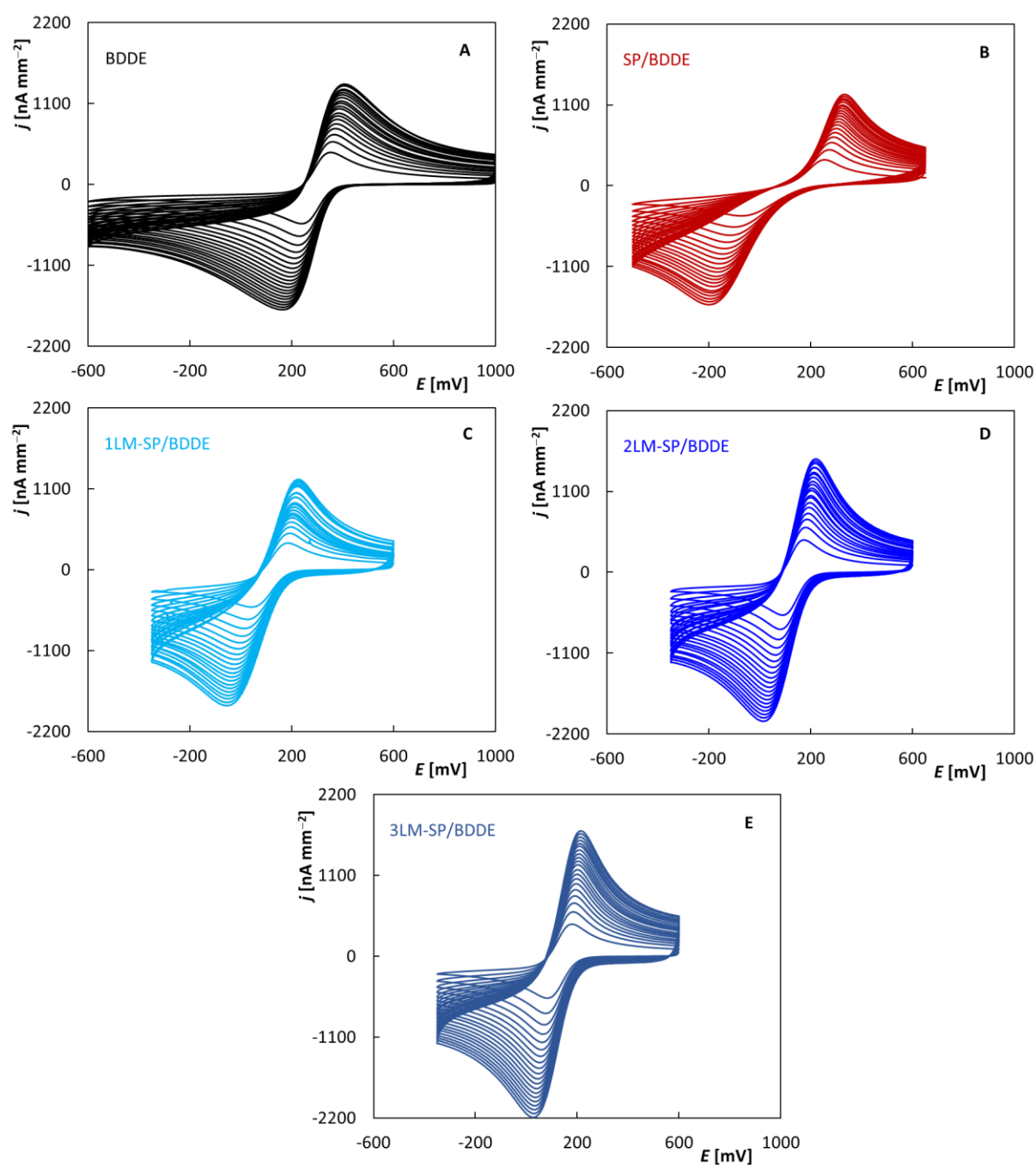


Figure S5. Cyclic voltammograms of [Fe(CN)₆]^{4-/3-} recorded on tested sensors at various scan rates (electrolyte – 0.1 mol L⁻¹ KCl, $v = 25$ –500 mV s⁻¹, $c([Fe(CN)_6]^{4-/3-}) = 6.25 \times 10^{-4}$ mol L⁻¹).

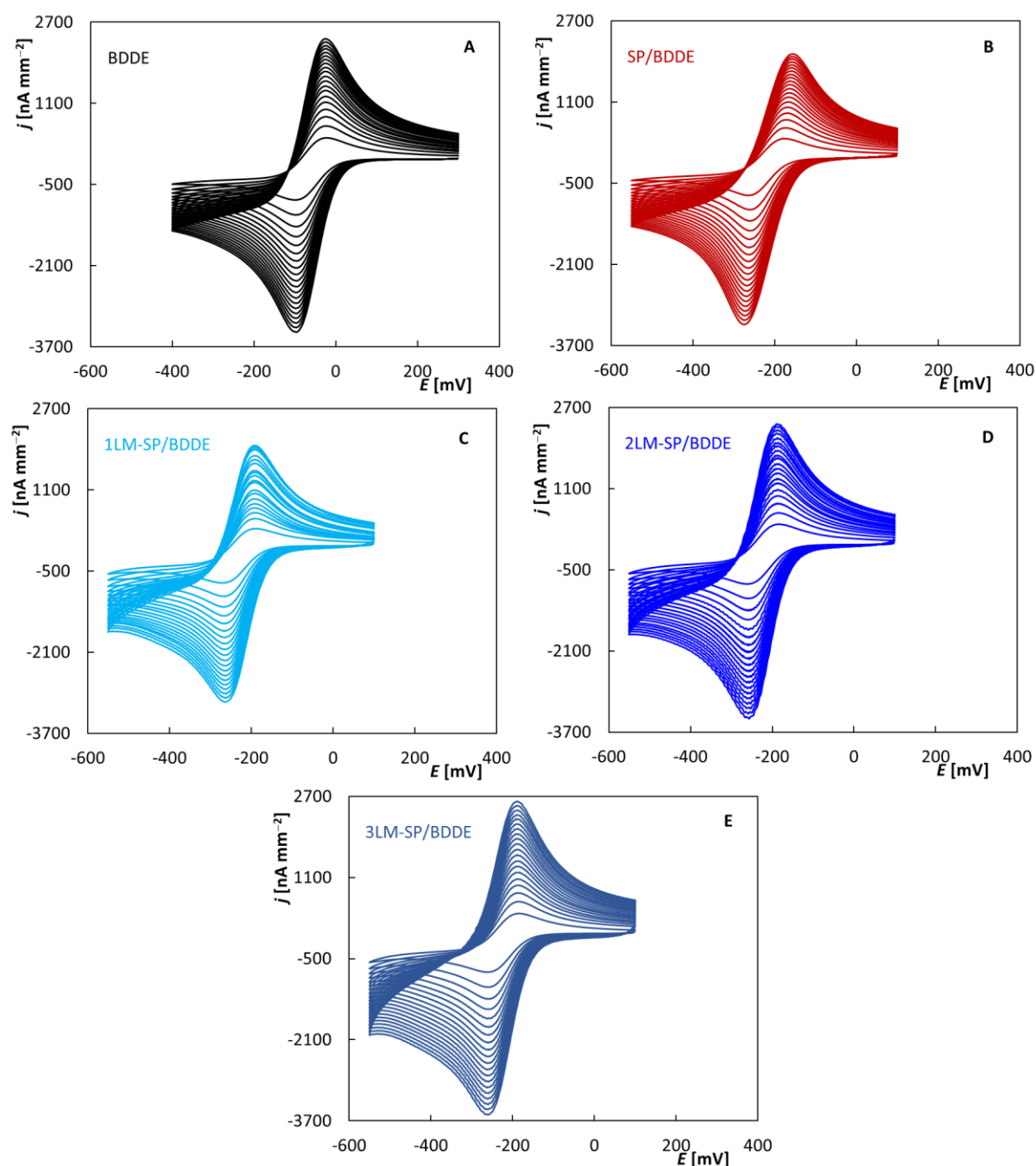


Figure S6. Cyclic voltammograms of $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ recorded on tested sensors at various scan rates (electrolyte $0.1 \text{ mol L}^{-1} \text{ KCl}$, $v = 25\text{--}500 \text{ mV s}^{-1}$, $c([\text{Ru}(\text{NH}_3)_6]^{2+/3+}) = 6.25 \times 10^{-4} \text{ mol L}^{-1}$).

Table S1. Statistical parameters of dependences of $\log(j_p)$ on $\log(v)$ for $[\text{Fe}(\text{CN})_6]^{4-/3-}$ and $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ (electrolyte $0.1 \text{ mol L}^{-1} \text{ KCl}$, $v = 25\text{--}500 \text{ mV s}^{-1}$, $c([\text{Fe}(\text{CN})_6]^{4-/3-}) = 6.25 \times 10^{-4} \text{ mol L}^{-1}$, $c([\text{Ru}(\text{NH}_3)_6]^{2+/3+}) = 6.25 \times 10^{-4} \text{ mol L}^{-1}$).

	Electrode	j_p	Slope	Intercept	r
			$[\text{nA s mV}^{-1} \text{ mm}^{-2}]$	$[\text{nA mm}^{-2}]$	
$\text{Fe}(\text{CN})_6]^{4-/3-}$	BDDE	a	(0.363 ± 0.003)	(2.120 ± 0.008)	0.9992
		c	(0.366 ± 0.002)	(2.182 ± 0.005)	0.9997
	SP/BDDE	a	(0.377 ± 0.003)	(2.042 ± 0.007)	0.9995
		c	(0.388 ± 0.023)	(1.950 ± 0.005)	0.9997
	1LM-SP/BDDE	a	(0.388 ± 0.007)	(2.107 ± 0.016)	0.9973
		c			

Ru(NH ₃) ₆] ^{2+/3+}	2LM-SP/BDDE	c	(0.374±0.004)	(2.070±0.010)	0.9989
		a	(0.383±0.003)	(2.200±0.007)	0.9995
	3LM-SP/BDDE	c	(0.362±0.001)	(2.200±0.003)	0.9999
		a	(0.413±0.002)	(2.144±0.005)	0.9997
		c	(0.405±0.002)	(2.133±0.004)	0.9998
	BDDE	a	(0.489±0.001)	(2.129±0.003)	0.9999
		c	(0.509±0.001)	(2.084±0.002)	0.9999
	SP/BDDE	a	(0.469±0.001)	(2.092±0.002)	0.9999
		c	(0.521±0.001)	(2.027±0.001)	0.9999
	1LM-SP/BDDE	a	(0.489±0.004)	(2.050±0.009)	0.9994
		c	(0.510±0.004)	(2.000±0.008)	0.9996
	2LM-SP/BDDE	a	(0.507±0.006)	(2.057±0.013)	0.9989
		c	(0.527±0.002)	(2.015±0.005)	0.9998
	3LM-SP/BDDE	a	(0.525±0.006)	(2.016±0.014)	0.9989
		c	(0.533±0.001)	(2.002±0.002)	0.9999

a – anodic, c – cathodic.

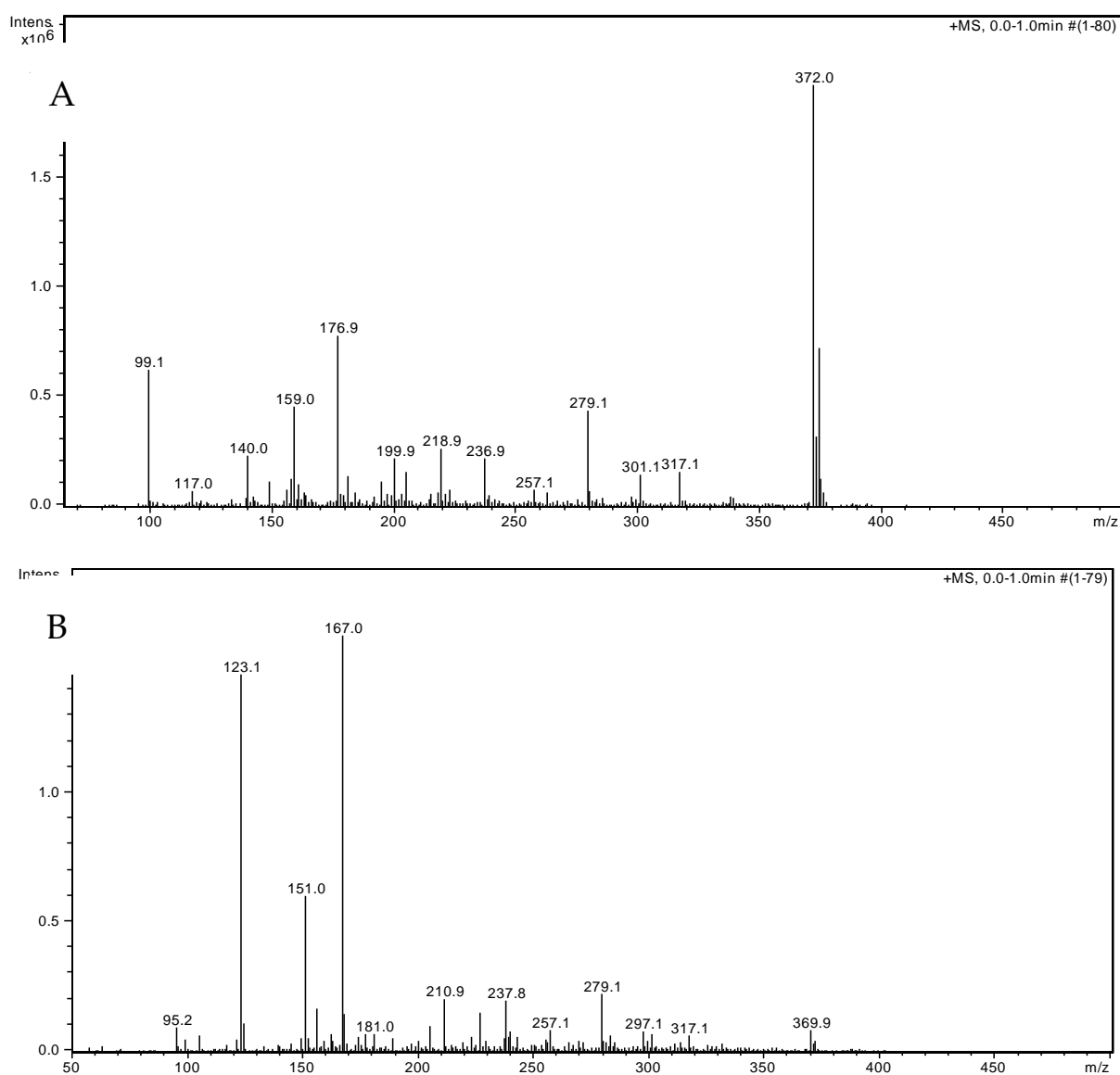


Figure S7. Mass spectra recorded in EC-MS experiment with LRX ($c = 50 \mu\text{mol L}^{-1}$) in aqueous $0.1 \text{ mol L}^{-1} \text{CH}_3\text{COOH}$ with acetonitrile (1:1, v/v) at potential 0 mV (A) and 200 mV (B) on porous

graphite carbon electrode *vs.* Pd/H₂ reference electrode. ESI-MS conditions: nitrogen pressure in the nebulizer 15 psi, dry gas 5 L h⁻¹, dry temperature 300 °C, capillary voltage −3.5 kV, end plate offset +0.5 kV (positive mode). Ion at *m/z* 369.9 corresponds to [M+H]⁺ of intermediate **II** (or the rearranged structure **VI**) in Scheme 4, ion *m/z* 167 belongs to [M+H]⁺ of intermediate **IX** (ions at *m/z* 151, 123 and 95 are fragment ions of the ion *m/z* 167).

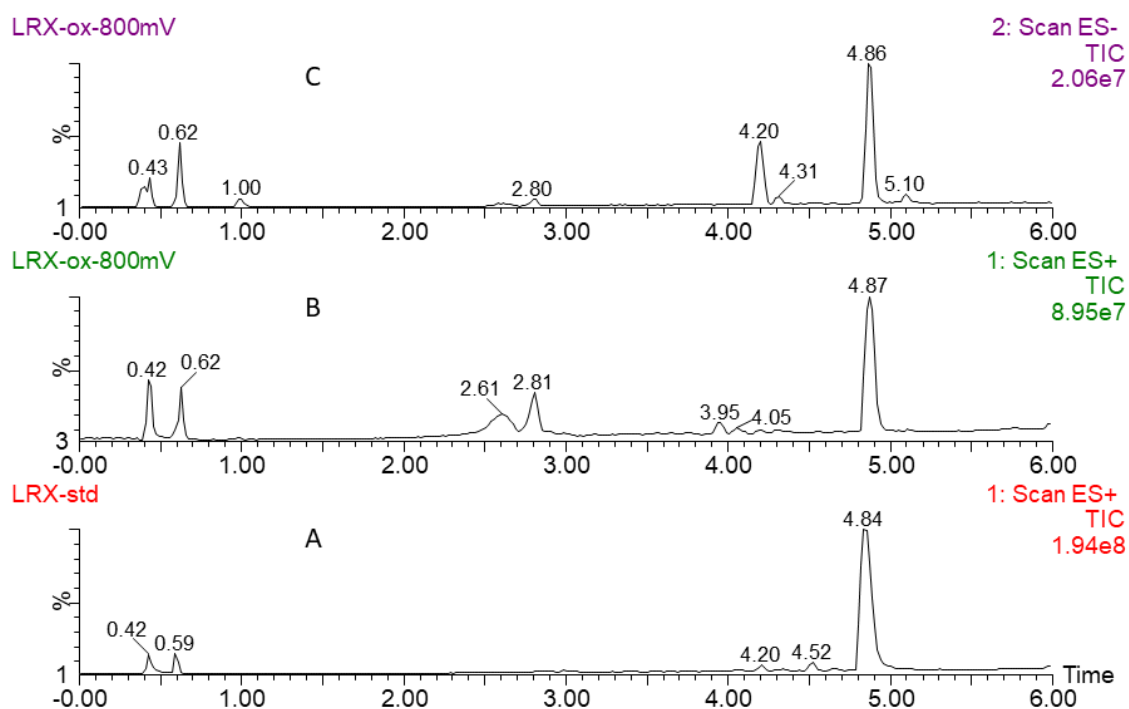


Figure S8. Total ion chromatograms of LRX solution ($c = 50 \mu\text{mol L}^{-1}$) in aqueous $0.1 \text{ mol L}^{-1} \text{CH}_3\text{COOH}$ with acetonitrile (1:1, v/v) before (A) and after (B, C) electrolysis on the carbon fiber brush electrode at constant potential 800 mV *vs.* SCE for 60 min. Chromatograms were recorded in positive (A, B) and negative (C) ionization mode of ESI.

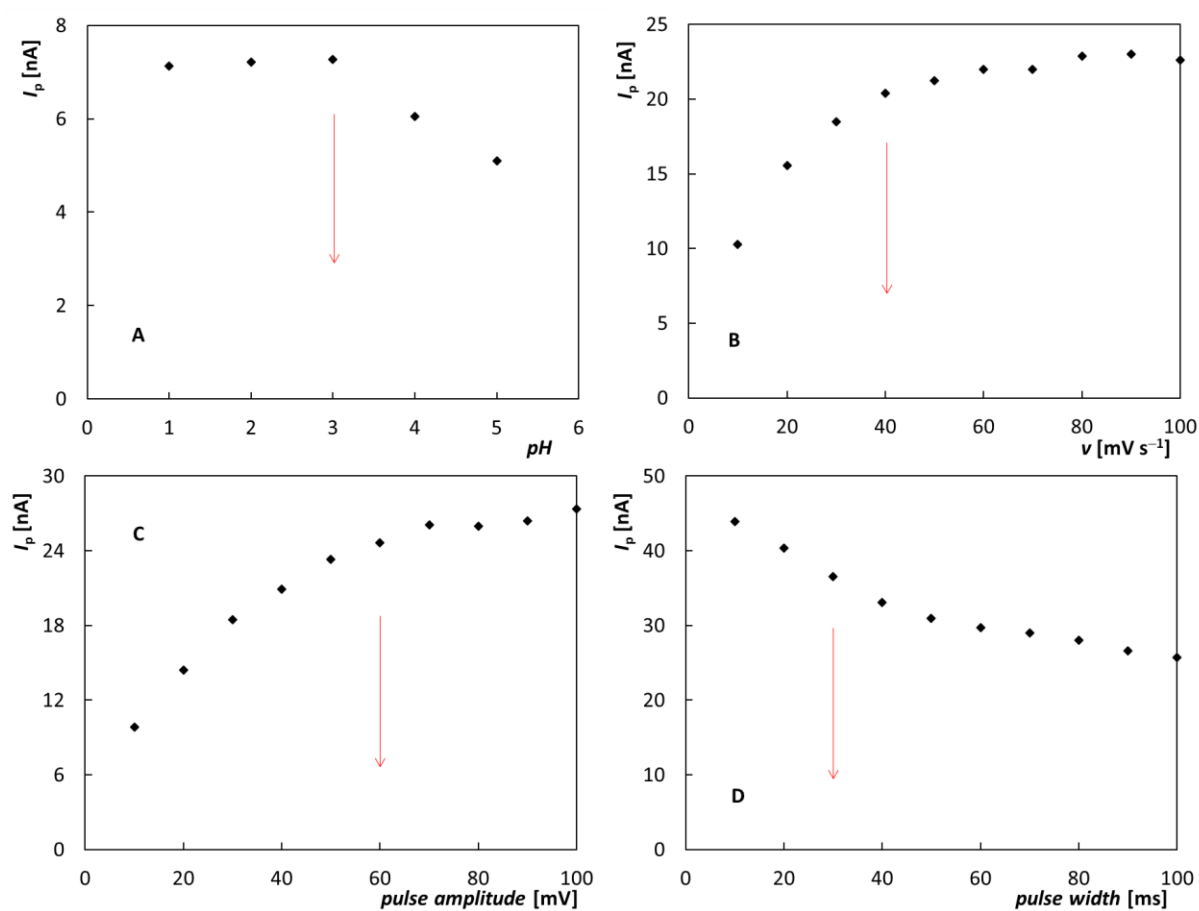


Figure S9. Optimization of DPV parameters for LRX determination using BDDE dependences of I_p on pH of supporting electrolyte (A), I_p on v (B), I_p on pulse amplitude (C), and I_p on pulse width (D) (DPV, electrolyte – BRB (pH 1–5 (A) and 3 (B–C)), $E_{in} = 0$ mV, $E_{fin} = +2000$ mV, $v = 20$ (A), 10–100 (B), and 40 (C, D) mV s⁻¹, pulse amplitude = +50 (A, B), 0–100 (C), and +60 (D) mV, pulse width = 50 (A–C), and 10–100 (D) ms, $c(\text{LRX}) = 2.0 \mu\text{mol L}^{-1}$).