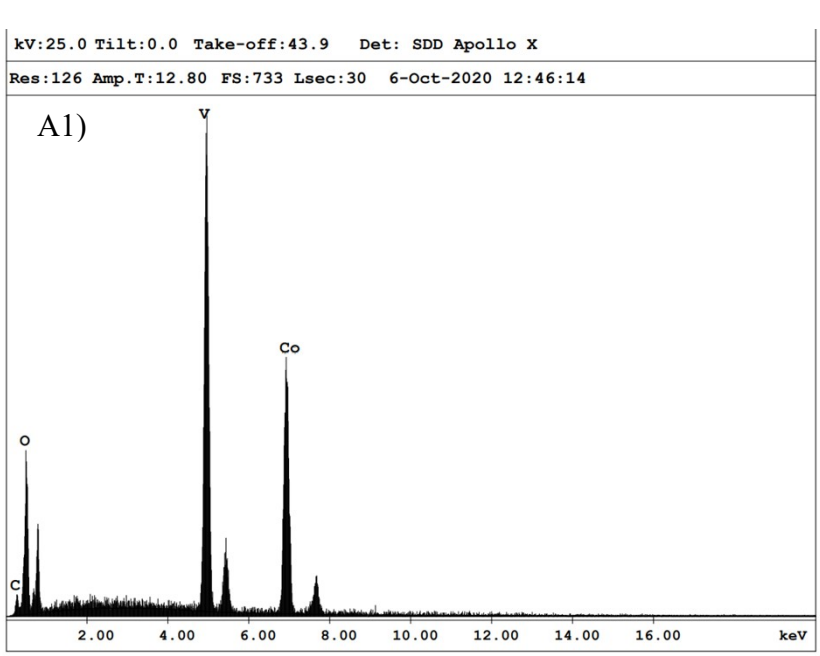
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

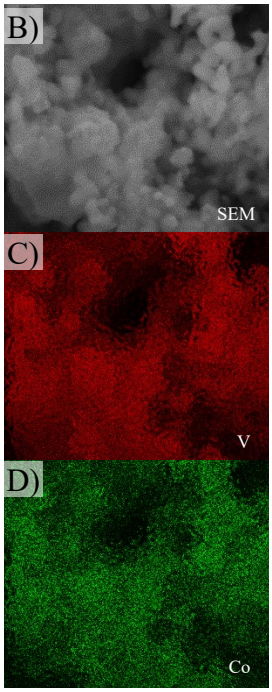
One-step preparation of $Co_2V_2O_7$: synthesis and application as Fenton-like catalyst in gas diffusion electrode

Murilo Fernando Gromboni[a], Paulo Jorge Marques Cordeiro-Junior[a], Patricia Gon Corradini[b,c],Lucia Helena Mascaro[b], Marcos Roberto de Vasconcelos Lanza[a]

[a]São Carlos Institute of Chemistry, University of São Paulo, São Carlos, SP, 13566-590, Brazil
[b]Department of Chemistry, Federal University of São Carlos, São Carlos, SP, 13565-905, Brazil
[c]Fluminense Federal Institute of Education, Science and Technology, Campus Itaperuna, Itaperuna, RJ, 28300-000, Brazil

SUPPLEMENTARY MATERIAL



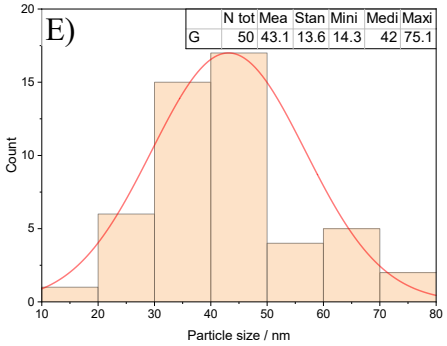


A2)

EDAX PhiZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

Element	Wt %	At %	K-Ratio	Z	A	F
C K	3.86	10.22	0.0104	1.1878	0.2267	1.0007
O K	24.05	47.87	0.0400	1.1505	0.1443	1.0007
V K	34.81	21.76	0.3380	0.9293	0.9960	1.0492
CoK	37.29	20.15	0.3304	0.9274	0.9554	1.0000
Total	100.00	100.00				

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
C K	4.43	0.17	8.99	26.60
O K	37.90	0.60	3.01	63.17
V K	231.43	3.03	1.22	76.30
CoK	137.00	2.00	1.58	68.50



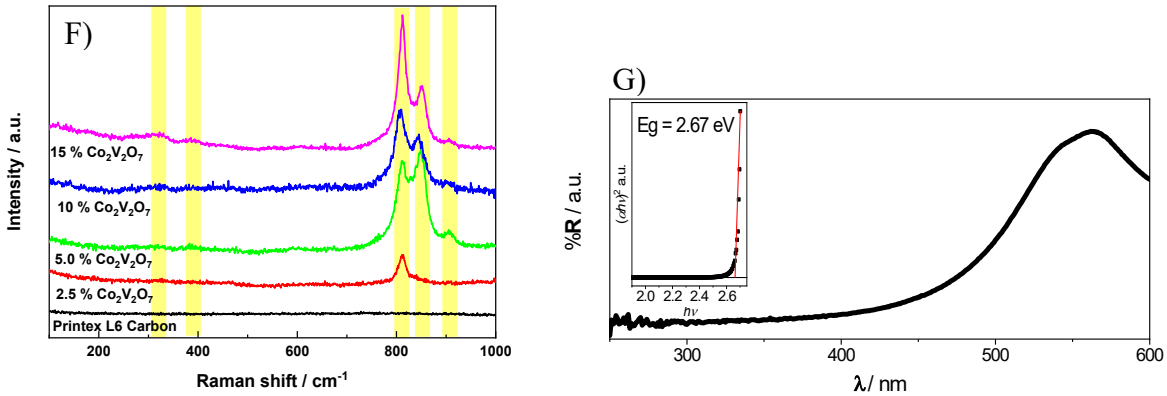


Figure S1. A1) Energy dispersive X-ray (EDS) spectra of as-synthesized sample and A2) the table with quantification results. B) SEM images from $Co_2V_2O_7$ layer over silicon and SEM EDX elemental maps of C) Vanadium and D) Cobalt. E) A particle size distribution histogram determined from the SEM images. F) Raman spectra of PL6C and mixture with different composition of $Co_2V_2O_7$. G) UV-VIS diffuse reflectance spectroscopy (DRS) spectra for as-synthesized sample and the insets show the plots of $(\alpha h\nu)^2$ versus bandgap of $Co_2V_2O_7$.

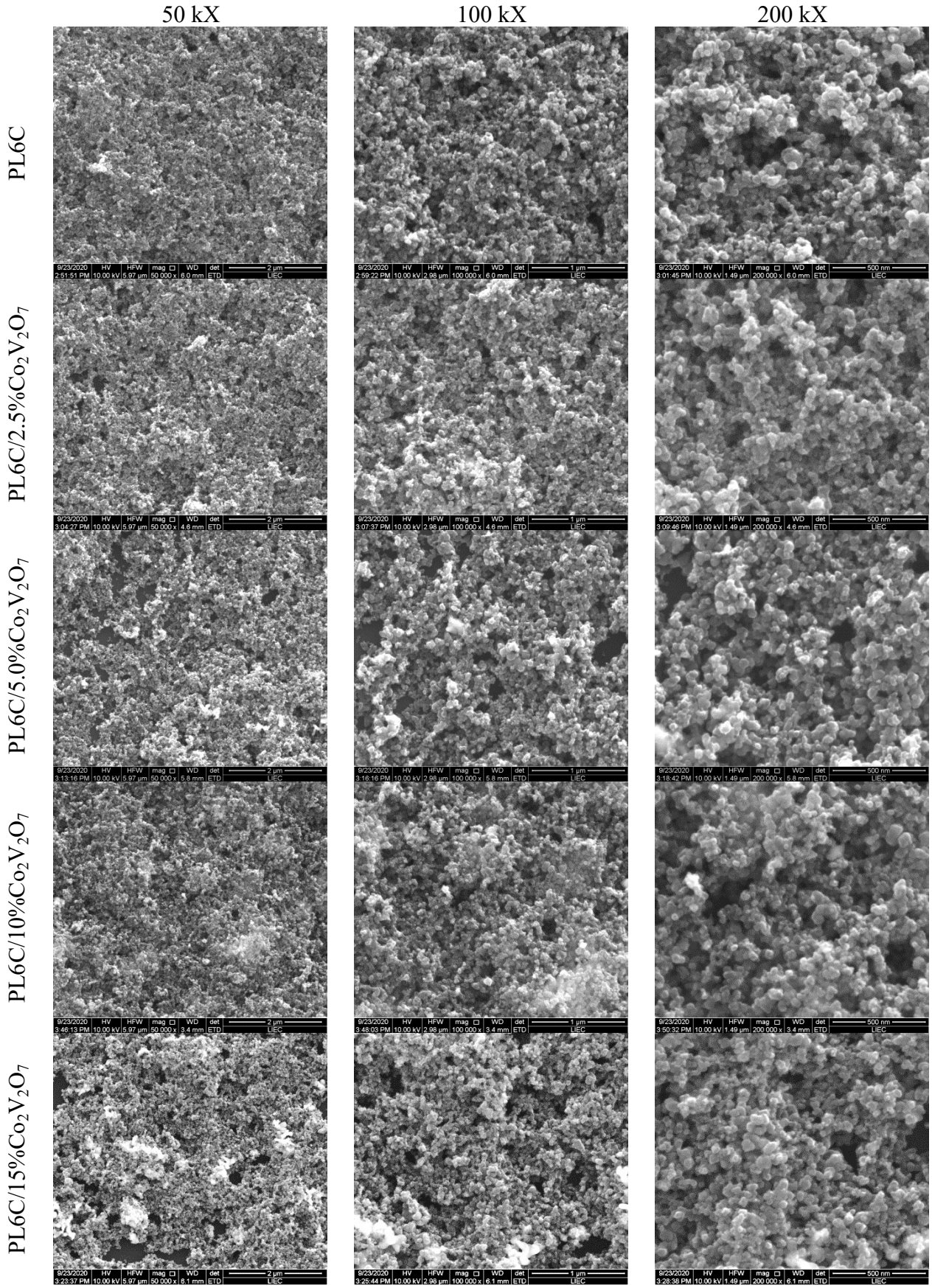
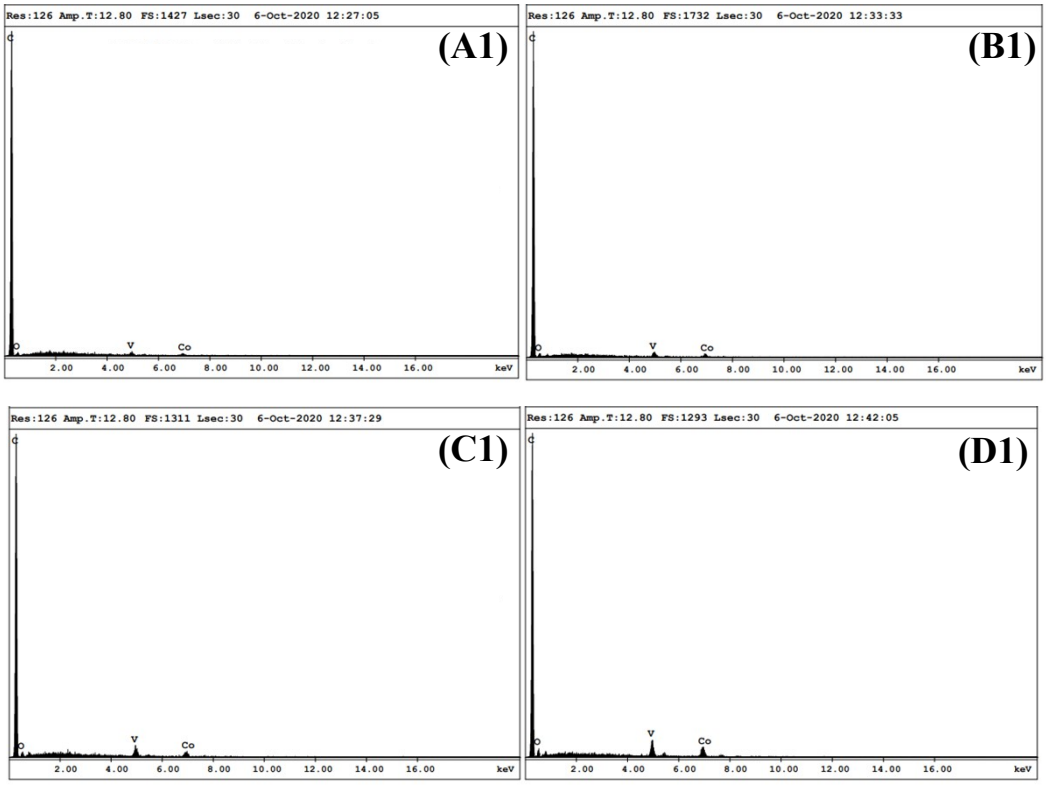


Figure S2. SEM images of PL6C and $Co_2V_2O_7$/PL6C with different ratio and magnification.



EDAX PhiZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

(A2)

Element	Wt %	At %	K-Ratio	Z	A	F
C K	92.88	96.12	0.7895	1.0069	0.8442	1.0000
O K	5.42	3.21	0.0038	0.9765	0.0930	1.0000
V K	0.79	0.33	0.0112	0.7842	1.0455	1.0143
CoK	0.91	0.35	0.0131	0.7780	1.0296	1.0000
Total	100.00	100.00				

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
C K	205.53	0.17	1.27	1233.20
O K	2.17	0.40	14.51	5.42
V K	4.67	0.70	9.64	6.67
CoK	3.30	0.50	11.47	6.60

EDAX PhiZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

(B2)

Element	Wt %	At %	K-Ratio	Z	A	F
C K	90.64	95.20	0.7284	1.0101	0.7955	1.0001
O K	6.25	3.74	0.0044	0.9796	0.0946	1.0001
V K	1.46	0.53	0.0181	0.7869	1.0445	1.0184
CoK	1.65	0.53	0.0197	0.7807	1.0278	1.0000
Total	100.00	100.00				

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
C K	233.53	0.33	1.20	700.60
O K	3.13	0.80	12.68	3.92
V K	9.30	0.87	6.52	10.73
CoK	6.13	0.50	7.95	12.27

EDAX PhiZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

(C2)

Element	Wt %	At %	K-Ratio	Z	A	F
C K	87.90	94.13	0.6640	1.0146	0.7445	1.0001
O K	5.31	4.27	0.0050	0.9839	0.0964	1.0001
V K	3.49	0.88	0.0293	0.7905	1.0429	1.0206
CoK	3.31	0.72	0.0266	0.7844	1.0246	1.0000
Total	100.00	100.00				

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
C K	188.03	0.17	1.33	1128.20
O K	3.17	0.20	10.89	15.83
V K	13.30	0.43	5.17	30.69
CoK	7.30	0.50	7.21	14.60

EDAX PhiZAF Quantification (Standardless)
Element Normalized
SEC Table : Default

(D2)

Element	Wt %	At %	K-Ratio	Z	A	F
C K	82.97	92.04	0.5554	1.0222	0.6548	1.0001
O K	6.51	5.42	0.0066	0.9913	0.1019	1.0002
V K	4.55	1.19	0.0389	0.7968	1.0397	1.0310
CoK	5.97	1.35	0.0482	0.7909	1.0215	1.0000
Total	100.00	100.00				

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
C K	181.30	0.17	1.36	1087.80
O K	4.77	0.20	8.71	23.83
V K	20.30	1.27	4.30	16.03
CoK	15.27	0.50	4.82	30.53

E) *Theoretical values of expected mass*

%weight	2.5%	5%	10%	15%
Carbon	97.5	95.0	90.0	85.0
$Co_2V_2O_7$	*2.5*	*5.0*	*10.0*	*15.0*
Co	**0.9**	**1.8**	**3.6**	**5.3**
V	**0.8**	**1.5**	**3.1**	**4.6**

F) *EDS values*

%weight	2.5%	5%	10%	15%
Co	**0.91**	**1.65**	**3.31**	**5.97**
V	**0.79**	**1.46**	**3.49**	**4.55**
$Co_2V_2O_7$	*2.6*	*4.7*	*10.3*	*15.8*

Figure S3. Energy dispersive X-ray (EDS) spectra of composites PL6C/$Co_2V_2O_7$ at 2.5% (A1); 5% (B1); 10% (C1); and 15% (D1) (A2-D2) the table with quantification. Information of the theoretical values of expected mass (E) and the EDS values obtained (F).

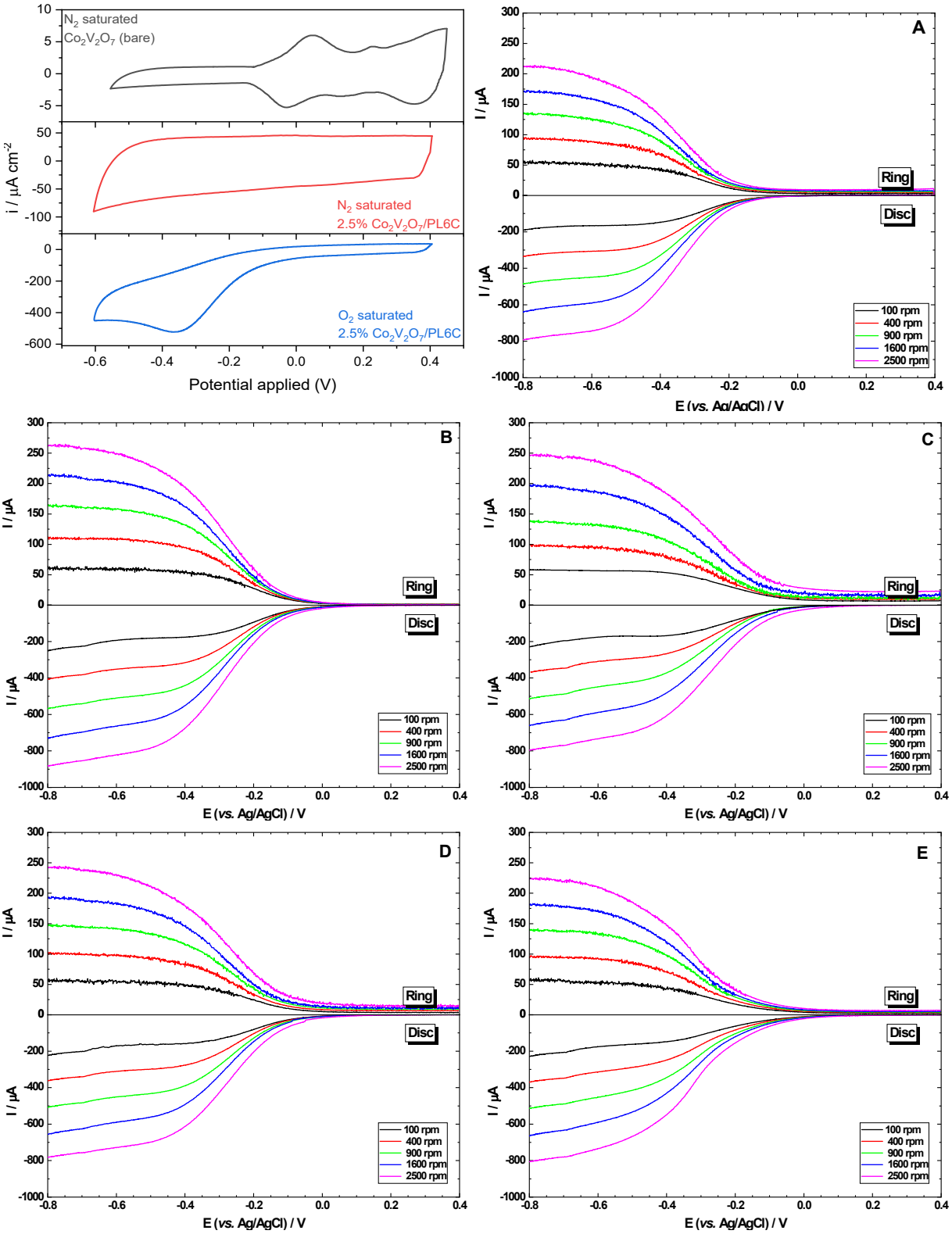


Figure S4. Linear sweep voltammograms for the PL6C (A) and the $Co_2V_2O_7$/PL6C in the proportions of: 2.5% (B), 5.0% (C), 10% (D) and 15% (E) (w/w) at 100, 400, 900, 1600 and 2500 rpm and scan rate 5 mV s^{-1}. Electrolyte support was K_2SO_4 0.1 mol L^{-1} pH 2.5 saturated with O_2.

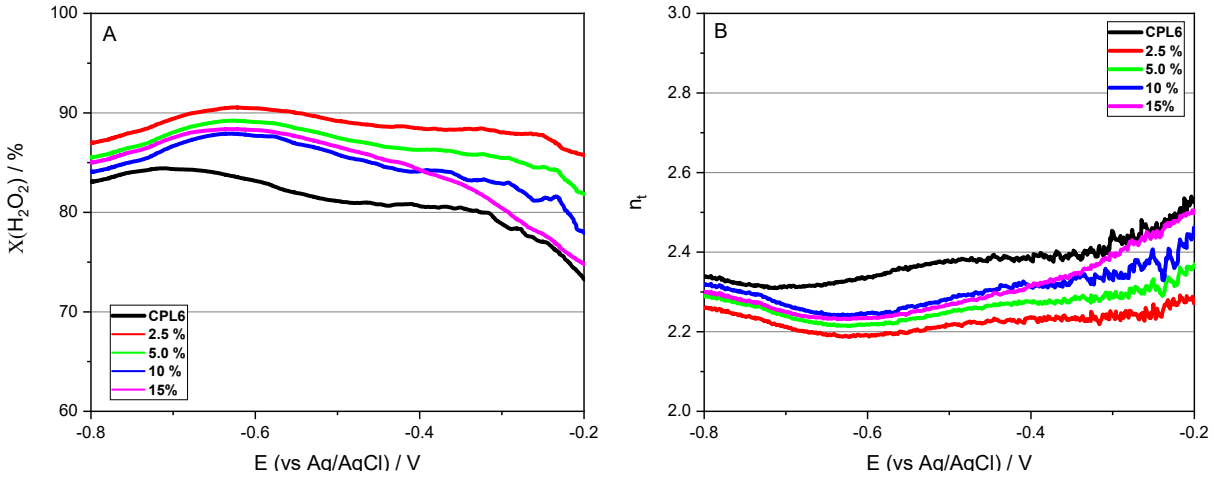


Figure S5. Current efficiency for H_2O_2 electrogeneration **(A)** and number of electrons involved in the ORR **(B)** for the $Co_2V_2O_7$/PL6C in the proportions of 2.5, 5.0, 10, 15% (w/w), and only PL6C at 900 rpm. Electrolyte support was K_2SO_4 0.1 mol L^{-1} pH 2.5 saturated with O_2.

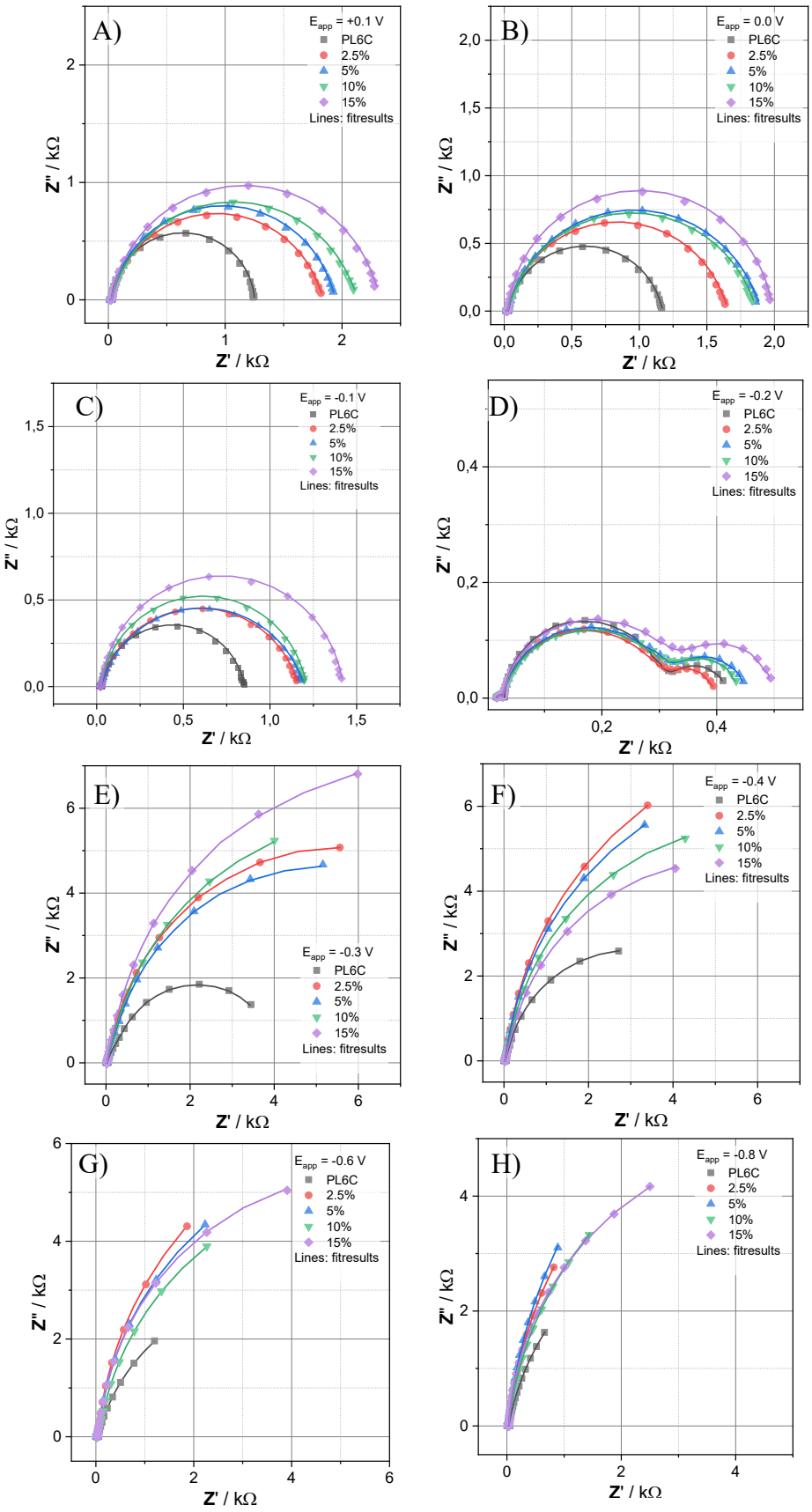


Figure S6: Nyquist plots to PL6C and 2.5-15% $Co_2V_2O_7$/PL6C at different potentials: A)+0.1; B) 0; C) -0.1; D) -0.2; E) -0.3; F) -0.4; G) -0.6 and H)-0.8 V. Electrolyte support was K_2SO_4 0.1 mol L^{-1} pH 2.5 saturated with O_2, and the electrode was spun at 900 rpm.

Table S1: Data fitting EIS

	Eapl[a]	Rsol[b]	Ctrap[c]	Qtrap[d]	n[e]	Rtrns[f]	Cdl[g]	Qdl[h]	n[i]	Rct[j]	Z-R[k]	Z-T[l]	Z-P[m]
PL6C	0.1	16.7	1.8E-06	3.4E-06	0.892	12.1	1.9E-04	1.7E-04	0.959	1219	4	19.9	0.5
	0	16.4	1.8E-06	4.8E-06	0.840	12.5	1.9E-04	1.5E-04	0.891	1141	5	19.2	0.5
	-0.1	16.1	1.1E-06	2.9E-06	0.857	11.6	1.8E-04	1.8E-04	0.910	822	6	14.9	0.5
	-0.2	18.0	1.5E-06	3.2E-06	0.904	12.8	2.2E-04	2.2E-04	0.981	270	119	10.1	0.5
	-0.3	16.7	2.3E-06	3.2E-06	0.965	13.5	4.7E-04	5.8E-04	0.950	56	4013	8.4	0.5
	-0.4	17.2	3.3E-06	5.9E-06	0.933	14.9	1.2E-03	1.6E-03	0.906	49	5887	7.6	0.5
	-0.6	17.7	4.3E-06	1.1E-05	0.888	16.3	2.0E-03	3.2E-03	0.835	69	7699	5.3	0.5
	-0.8	16.0	5.0E-06	9.1E-06	0.920	15.9	4.5E-03	5.3E-03	0.887	99	8943	1.2	0.5

	Eapl[a]	Rsol[b]	Ctrap[c]	Qtrap[d]	n[e]	Rtrns[f]	Cdl[g]	Qdl[h]	n[i]	Rct[j]	Z-R[k]	Z-T[l]	Z-P[m]
25 %	0.1	15.8	1.7E-06	7.7E-06	0.862	11.0	2.3E-04	1.5E-04	0.872	1801	13	22.9	0.5
	0	15.7	1.7E-06	9.9E-06	0.839	11.1	2.3E-04	1.7E-04	0.869	1622	8	18.8	0.5
	-0.1	15.6	1.1E-06	9.2E-06	0.811	10.8	2.3E-04	2.1E-04	0.859	1133	9	15.9	0.5
	-0.2	15.7	1.5E-06	8.9E-06	0.837	11.5	2.5E-04	2.8E-04	0.886	278	94	7.5	0.5
	-0.3	15.8	2.2E-06	5.4E-06	0.915	12.2	6.1E-04	8.4E-04	0.929	36	11215	6.0	0.5
	-0.4	15.6	3.1E-06	1.3E-05	0.859	13.6	1.0E-03	1.3E-03	0.941	16	16800	7.4	0.5
	-0.6	15.8	4.1E-06	8.8E-06	0.920	15.1	1.7E-03	2.1E-03	0.943	22	15081	6.7	0.5
	-0.8	15.9	4.4E-06	1.3E-05	0.889	14.8	3.3E-03	3.8E-03	0.944	35	15186	1.1	0.5

	Eapl[a]	Rsol[b]	Ctrap[c]	Qtrap[d]	n[e]	Rtrns[f]	Cdl[g]	Qdl[h]	n[i]	Rct[j]	Z-R[k]	Z-T[l]	Z-P[m]
5%	0.1	16.6	1.7E-06	7.4E-06	0.862	10.8	2.4E-04	1.7E-04	0.892	1904	12	23.3	0.5
	0	16.9	1.7E-06	9.7E-06	0.839	11.0	2.4E-04	1.7E-04	0.860	1865	7	23.3	0.5
	-0.1	16.6	1.0E-06	9.0E-06	0.811	10.6	2.3E-04	2.0E-04	0.843	1165	7	16.7	0.5
	-0.2	16.6	1.5E-06	8.7E-06	0.837	11.3	2.5E-04	2.5E-04	0.888	283	142	7.2	0.5
	-0.3	16.8	2.2E-06	5.4E-06	0.915	12.1	5.9E-04	8.4E-04	0.917	41	10424	7.8	0.5
	-0.4	16.9	3.1E-06	1.3E-05	0.859	13.4	9.6E-04	1.2E-03	0.939	22	16800	7.4	0.5
	-0.6	16.8	4.0E-06	8.7E-06	0.920	14.8	1.6E-03	1.9E-03	0.943	30	12892	8.5	0.5
	-0.8	17.0	4.4E-06	1.3E-05	0.889	14.6	3.1E-03	3.4E-03	0.946	49	17763	0.9	0.5

	Eapl[a]	Rsol[b]	Ctrap[c]	Qtrap[d]	n[e]	Rtrns[f]	Cdl[g]	Qdl[h]	n[i]	Rct[j]	Z-R[k]	Z-T[l]	Z-P[m]
10%	0.1	16.3	1.6E-06	7.3E-06	0.862	10.7	2.8E-04	1.7E-04	0.856	2092	16	28.2	0.5
	0	16.3	1.6E-06	9.6E-06	0.839	10.9	3.0E-04	2.0E-04	0.852	1833	8	18.4	0.5
	-0.1	16.3	1.0E-06	8.8E-06	0.811	10.5	2.6E-04	2.4E-04	0.927	1177	10	16.9	0.5
	-0.2	16.3	1.4E-06	8.6E-06	0.837	11.3	3.0E-04	3.3E-04	0.861	285	129	7.8	0.5
	-0.3	16.3	2.1E-06	5.2E-06	0.915	12.0	7.1E-04	1.1E-03	0.898	46	13443	7.5	0.5
	-0.4	16.3	3.1E-06	1.3E-05	0.859	13.3	8.0E-04	1.1E-03	0.935	32	12193	7.6	0.5
	-0.6	16.3	3.9E-06	8.5E-06	0.920	14.7	1.3E-03	1.8E-03	0.905	46	11858	9.2	0.5
	-0.8	16.2	4.4E-06	1.3E-05	0.889	14.5	2.3E-03	2.8E-03	0.933	66	12365	0.8	0.5

	Eapl[a]	Rsol[b]	Ctrap[c]	Qtrap[d]	n[e]	Rtrns[f]	Cdl[g]	Qdl[h]	n[i]	Rct[j]	Z-R[k]	Z-T[l]	Z-P[m]
15%	0.1	17.0	1.6E-06	7.4E-06	0.862	10.7	3.0E-04	2.1E-04	0.901	2282	19	32.8	0.5
	0	17.1	1.6E-06	9.6E-06	0.839	10.8	2.8E-04	2.4E-04	0.946	1951	9	16.2	0.5
	-0.1	17.0	1.0E-06	8.9E-06	0.811	10.5	2.8E-04	2.6E-04	0.952	1387	8	13.0	0.5
	-0.2	17.1	1.4E-06	8.5E-06	0.837	11.1	3.1E-04	3.0E-04	0.929	290	183	6.5	0.5
	-0.3	16.9	2.0E-06	5.0E-06	0.915	11.8	6.5E-04	7.9E-04	0.953	53	14872	9.3	0.5
	-0.4	17.1	2.9E-06	1.2E-05	0.859	13.2	7.8E-04	1.1E-03	0.920	41	10534	8.3	0.5
	-0.6	17.1	3.7E-06	8.1E-06	0.920	14.6	1.2E-03	1.3E-03	0.962	51	11333	7.0	0.5
	-0.8	17.1	4.1E-06	1.2E-05	0.889	14.3	1.9E-03	2.1E-03	0.964	72	10424	0.9	0.5

[a]Eapl = Applied potential (V)
[b]Rsol = Resistance of solution (Ω)
[c]Ctrap = capacitance generated by the trapping of electrons (F)
[d]Qtrap= CPE constant generated by the trapping of electrons
[e]n = CPE exponent of Qtrap
[f]Cdl= double-layer capacitance (F)
[g]Qdl= CPE constant generate by the double-layer
[h]n = CPE exponent of Qdl
[i]Rtrns = resistance to electron transfer (Ω)
[k]Z-R = limiting diffusion resistance frow Finite-Length Warburg (Ω)
[l]Z-T = diffusion time constant generated by the of Finite-Length Warburg
[m]Z-P = exponent of diffusion time constant (to Finite-Length Warburg fixed 0.5)

Table S2. Tables with the values of the slopes calculated for the potential range from -0.5 to -0.1 V for R_{ct} and R_{diff}. Values for the number of electrons calculated by the method of Tan et al. compared to the values obtained by Eq. 6.

	PL6C	2.5%	5%	10%	15%
Slope R_{diff}	-14.0	-15.5	-15.8	-15.6	-16.3
Slope R_{ct}	5.8	7.5	7.2	7.0	7.1
Number e^- by slopes	2.4	2.1	2.2	2.2	2.3
Number e^- by LSV	*2.4*	*2.2*	*2.3*	*2.3*	*2.3*

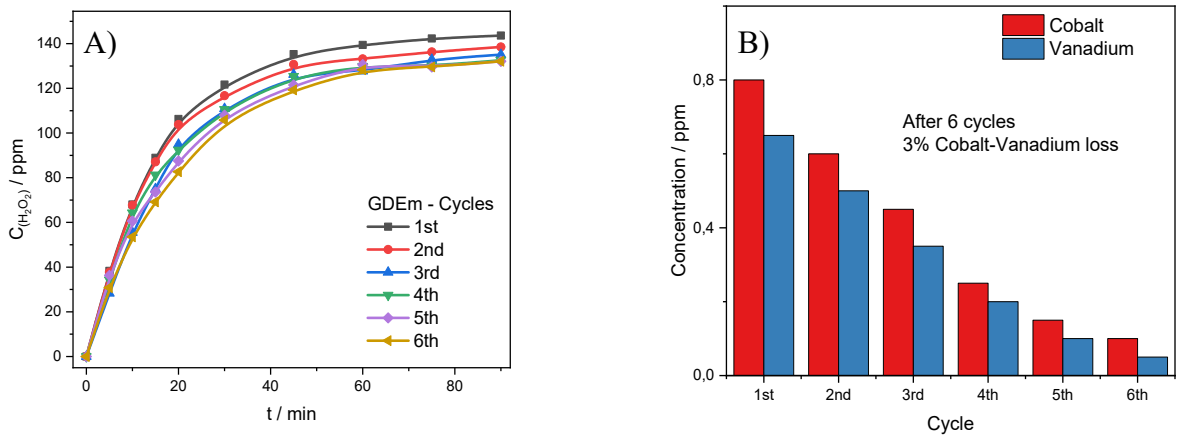


Figure S7: A) Hydrogen peroxide concentration produced as a function of time for GDEm for 90 min of electrolysis at 75 mA cm^{-2} B) Metal leaching test of the Co an V analyzed by an atomic absorption spectrometer

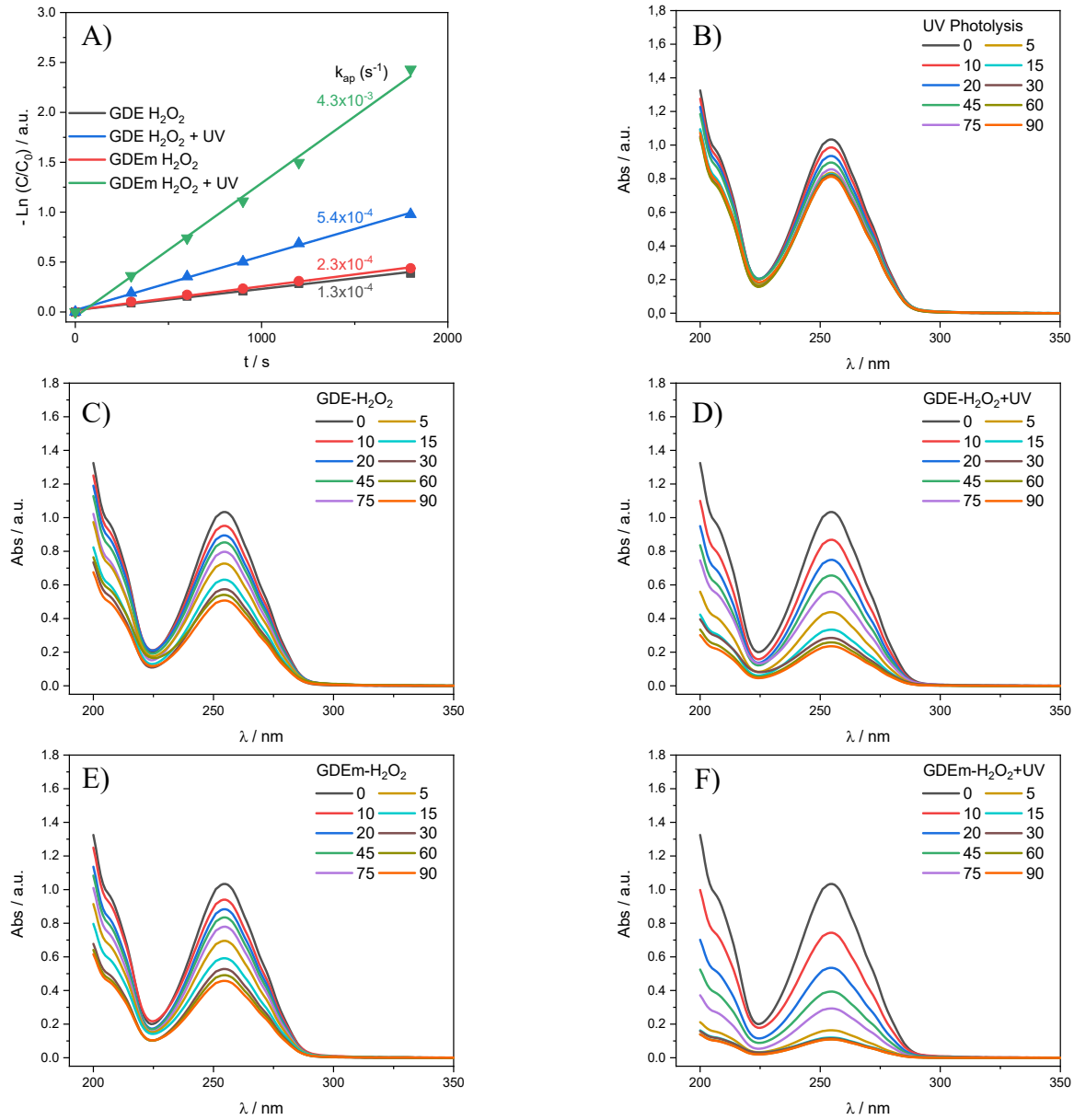


Figure S8: A) Apparent kinetic constants (K_{ap}) for GDE and GDEm to e-H_2O_2 and e-H_2O_2 process and UV-Vis absorption spectra of MeP degradation to UV-Photolysis (B), GDE e-H_2O_2 (C) GDE e-H_2O_2+UV, (D), GDEm e-H_2O_2 (E) GDEm e-H_2O_2+UV

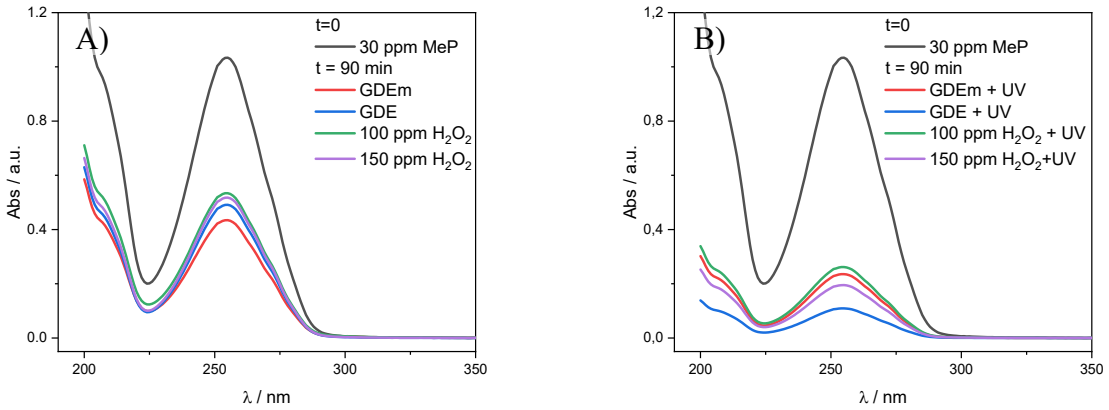


Figure S9: A) UV-Vis absorption spectra of MeP degradation to A) e-H_2O_2 and process without GDE; B) e-H_2O_2+UV and process without GDE