

Supplementary information

## Crossing the paths: the possible role of Co-based materials from lithium-ion battery recycling in the efficient electrocatalytic hydrogen production

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**Table S1** – CHNS and ICP results for the elemental composition of all the samples considered in this study.

Sample	C / %	H / %	N / %	S / %	Co / %	Li / %	Ni / %	Mn / %
Black Mass	2.61	0.08	0.45	0.14	63	5	-	< 0.4
Metal_Pre_300	69.00	6.12	3.82	0	22	-	-	-
Metal_Pre_400	53.54	2.78	3.43	0	31	-	-	-
Metal_Pre_500	13.73	0.76	1.17	0	58	-	-	-
Res_Cath_550	0.19	0.15	0	0.10	54	5	-	-
Res_Cath_650	0.09	0.05	0	0.04	58	5	-	-
Res_Cath_750	0.09	0.05	0	0.07	63	6	-	-
Res_Cath_850	0.04	0	0.03	0.13	59	6	-	-

**Table S2** – Binding energy positions and assignment of peaks resulting from curve-fitting of the XPS spectra from the two representative samples reported in **Figure S2**.

Sample	Position (eV)	Assignment	Chemical species
Metal_Pre_500	780.9	$2p_{3/2}^{-1}3d^8L^{-1} Co^{2+}$	CoO
	783.0	$2p_{3/2}^{-1}3d^9L^{-2} Co^{2+}$	CoO
	787.4	$2p_{3/2}^{-1}3d^7 Co^{2+}$	CoO
Res_Cath_650	779.9	$2p_{3/2}^{-1}3d^7L^{-1} Co^{3+}$	LiCoO <sub>2</sub> , Co <sub>3</sub> O <sub>4</sub>
	781.2	$2p_{3/2}^{-1}3d^8L^{-1} Co^{2+}$	LiCoO <sub>2</sub> , Co <sub>3</sub> O <sub>4</sub>
	782.6	$2p_{3/2}^{-1}3d^9L^{-2} Co^{2+}$	LiCoO <sub>2</sub> , Co <sub>3</sub> O <sub>4</sub>
	785.7	$2p_{3/2}^{-1}3d^7 Co^{2+}$	LiCoO <sub>2</sub> , Co <sub>3</sub> O <sub>4</sub>
	789.9	$2p_{3/2}^{-1}3d^6 Co^{3+}$	LiCoO <sub>2</sub> , Co <sub>3</sub> O <sub>4</sub>

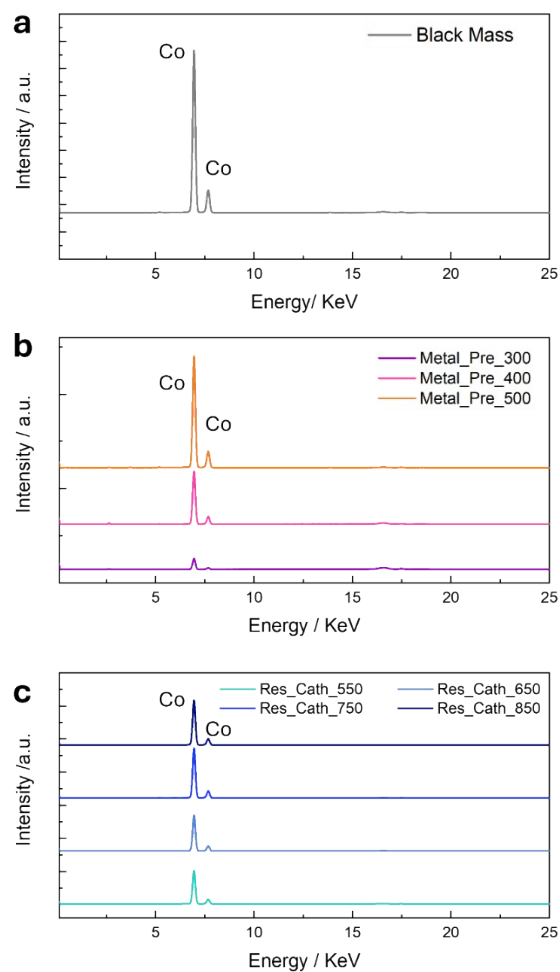


Figure S1 – XRF spectra for all the samples considered in the present study.

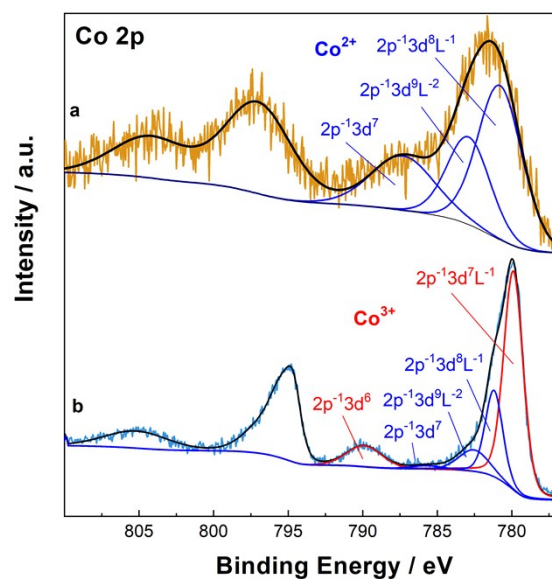
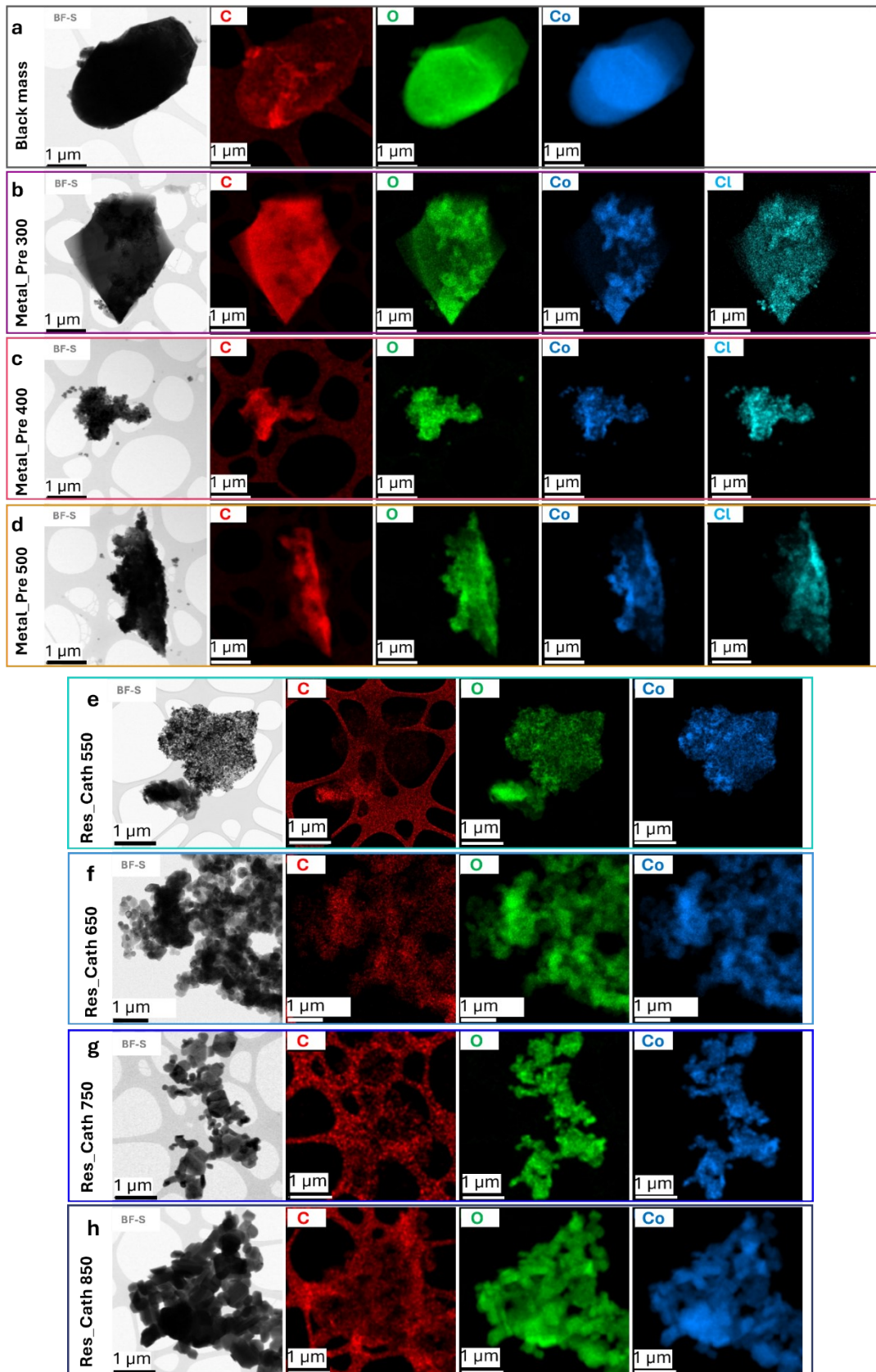
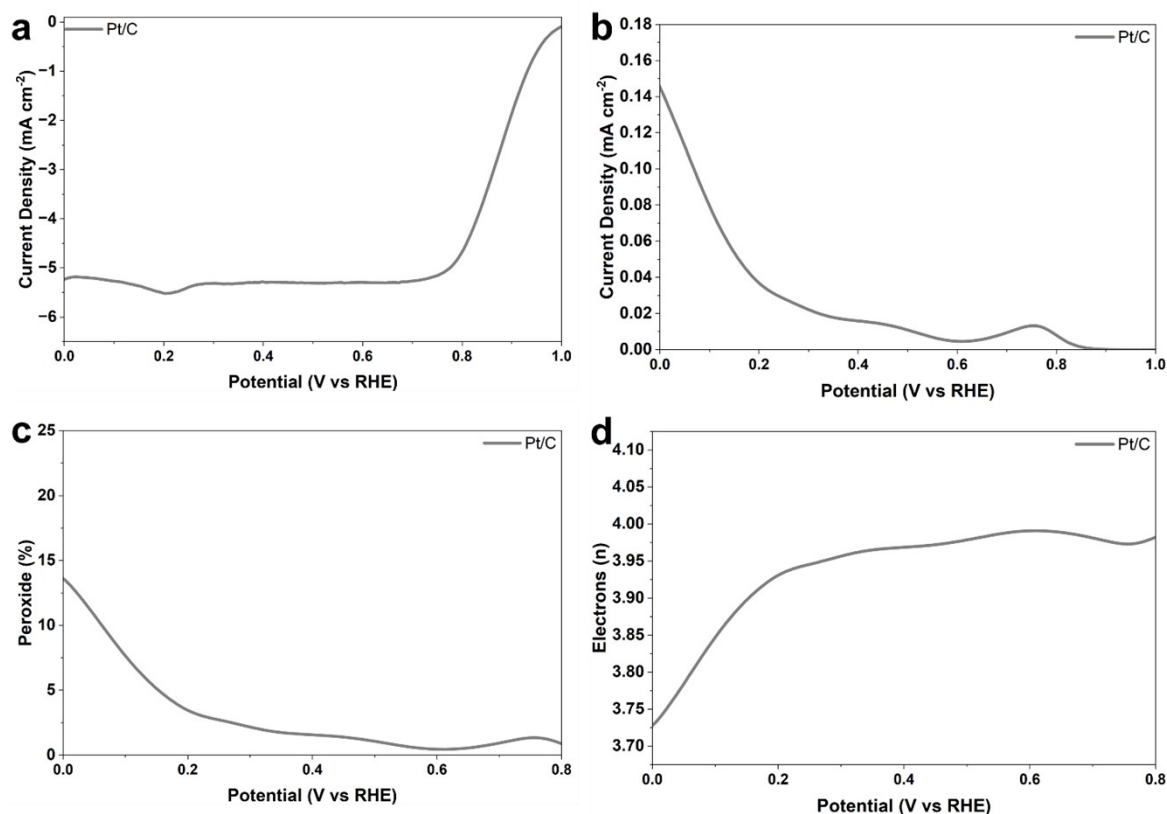


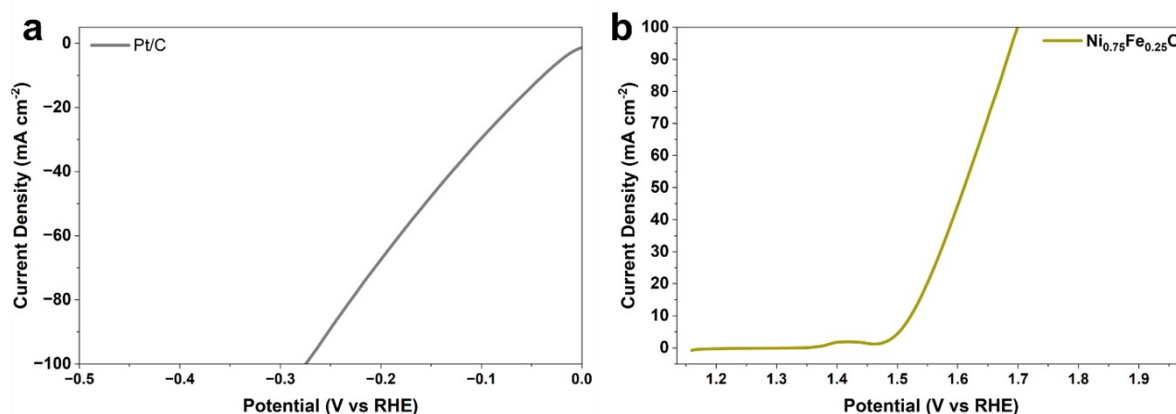
Figure S2 - Curve-fitting deconvolution of high-resolution Co 2p XPS spectra recorded with Al K $\alpha$  radiation of representative samples of the two series investigated in this work: a) Metal\_Pre\_500; b) Res\_Cath\_650.



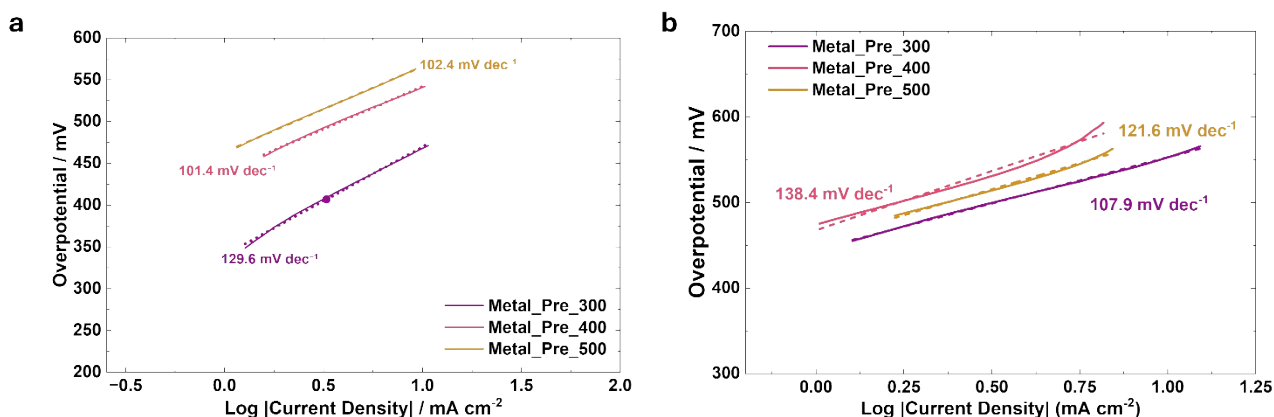
**Figure S3** – STEM images and EDX maps of samples: a) black mass, b) Metal\_pre 300, c) Metal\_Pre 400, d) Metal\_Pre 500, e) Res\_Cath 550, f) Res\_Cath 650, g) Res\_Cath 750, h) Res\_Cath 850.



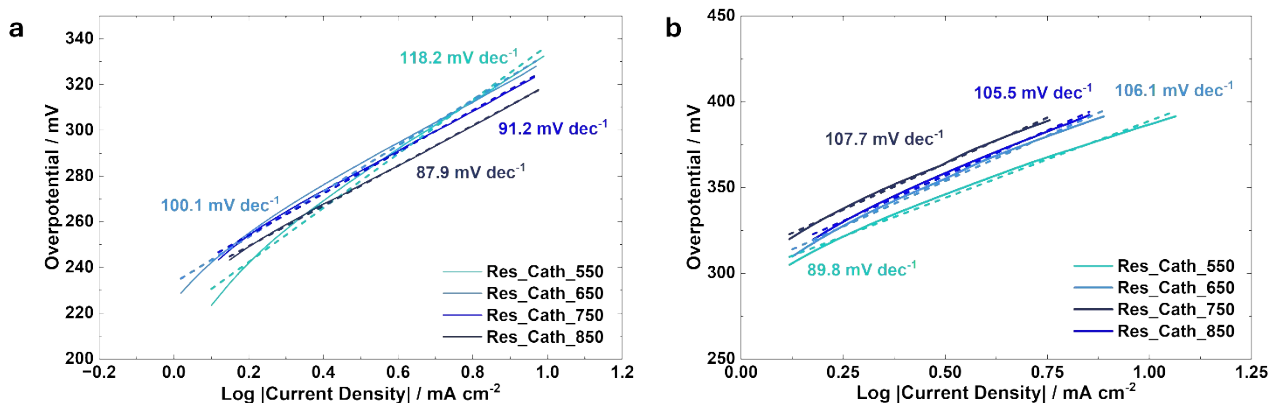
**Figure S4** – Oxygen reduction reaction performance of the samples of the benchmark Pt/C. a) Disk current density, b) ring current density, c) peroxide and d) number of electrons exchanged. The benchmark Pt/C electrocatalyst used in this study was 20 wt.% Pt supported on carbon (Pt/C), with a loading of 30  $\mu\text{g Pt cm}^{-2}$  on RRDE electrode rotating at 1600 rpm in 0.1 M KOH. (Image adapted from Mirshokraee SA, Muhyuddin M, Lorenzi R, et al. Litchi-derived platinum group metal-free electrocatalysts for oxygen reduction reaction and hydrogen evolution reaction in alkaline media. *SusMat.* 2023;3:248–262. Licensed under CC BY 4.0.)<sup>1</sup>



**Figure S5** – a) HER electrocatalytic activity of 20 wt.% Pt/C with loading of 30  $\mu\text{g Pt cm}^{-2}$  on RDE electrode rotating at 1600 rpm in 1 M KOH and b) OER electrocatalytic activity of state of the art NiFe oxide with 0.6 mg cm<sup>-2</sup> loading on RDE electrode rotating at 1600 rpm in 1 M KOH. The Pt/C HER is an image adapted from Mirshokraee SA, Muhyuddin M, Lorenzi R, et al. *SusMat.* 2023, **3**, 248–262. (Licensed under CC BY 4.0.)<sup>1</sup>, whereas the OER data of NiFe oxide are adapted from L. Mirizzi, M. Muhyuddin, C. Lo Vecchio, et al. *Ind. Chem. Mater.*, 2025, **3**, 485 (Licensed under CC BY 3.0.)<sup>2</sup>



**Figure S6** – a) HER Tafel plots and b) OER plots of the samples of the Metal\_Pre\_X series supported over 50% KJB (continuous line: experimental data, dotted lines: fitted curves).



**Figure S7** – a) HER Tafel plots and b) OER plots of the samples of the Res\_Cath\_X series supported over 50% KJB (continuous line: experimental data, dotted lines: fitted curves).

**Table S3** - The comparison of HER and OER activities with other spent LIB-derived electrocatalysts reported in literature

Sample	HER Overpotential (mV vs RHE)	OER Overpotential (mV vs RHE)	Electrolyte	Reference
Res_Cath_850	330	418	1M KOH	This work
CoN NFs	188	282	1M KOH	3
Waste LCOd 50-50	277	-	1M KOH	4
CP3	-	550	1M KOH	5
Q-LDH-0.1	-	270	1M KOH	6
CMS-NF	118	317	1M KOH	7
Spinel MnCo <sub>2</sub> O <sub>4</sub>	-	400	1M KOH	8
$\beta$ -Ni(OH) <sub>2</sub>	-	264	1M KOH	9

**Table S4** - The comparison of ORR activity with other spent LIB-derived electrocatalysts reported in the literature

Sample	$E_{on}$ V vs RHE	$E_{1/2}$ V vs RHE	Peroxide %	Electrons transferred n	Electrolyte	Reference
Res_Cath_850	0.865	0.7	Up to ca. 15	above ca. 3.7	0.1 M KOH	This Work
N-Co/rGO-AT	0.98	0.86	-	Ca. 3.7	0.1 M KOH	10
ChCl.Citric 50:50	0.85	0.76	Up to ca. 20	above ca. 3.5	0.1 M KOH	4
Co <sub>3</sub> O <sub>4</sub> /rGO-2	0.936	0.865	-	4.03	1M KOH	11
Co@NG-800	0.92	0.88	Below 12	3.95	1M KOH	12
NC-1000	0.925	0.828	1.59	Ca. 4	0.1 M KOH	13
CoN NFs	0.938	0.819	Up to 5	Ca. 4	1M KOH	3

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