Electronic Supplementary Material (ESI) for Materials Advances.

Supplementary Information

Green production of hydrogen-doped faceted cobalt microcrystals using water-assisted electro-reduction method

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Table S1. The position and the intensity of reflection peaks observed in XRD pattern of the Co powder produced after 8 h of electrolysis.

Position (2Θ)	Height (cts)	d-spacing (Å)	Relative Intensity (%)	fcc-Co (JCPDS≠001-1259)	hcp-Co (JCPDS≠005-0727)
41.7867	235.07	2.16173	12.07	-	41.685°, (100), 20 cts
44.4614	1947.01	2.03770	100.00	44.370 °, (111),100 cts	44.763°, (002), 60 cts
47.6867	598.98	1.90714	30.76	-	47.569°, (101), 100 cts
51.7319	674.12	1.76712	34.62	51.285°, (200), 8 cts	-
76.0527	700.91	1.25044	36.00	75.374°, (220), 80 cts	75.941 (110), 80 cts

Table S2. A comparison between the various methods available for the reduction of cobalt oxides into metallic cobalt, based on the data available in the literature.

Method	Requirement	Condition	Reference
Direct reduction by reducing agents	Hydrogen reduction of oxides. Pre-production of hydrogen followed by its storage/transportation	400 -800 °C	[1-3]
	Ethanol (C_2H_5OH) reducing agent	800–950 °C	[4]
	Reduction of $Co_SO_4·7H_2O$ by hydrazine hydrate ($N_2H_4·H_2O$) in the presence of chemicals such as cetyl trimethyl ammonium bromide ($(C_{16}H_{33}(CH_3)_3NBr$, and NaOH	Room temperature, ultrasound-assisted reduction	[5]
Electrodeposition in aqueous electrolyte	Electrolyte: acidic $CoSO_4·7H_2O$-Na_2SO_4 in the presence of tetra ethyl ammonium bromide	60 °C, Energy consumption=2.4-3.0 kWh Kg^{-1}	[6]
Electrodeposition in non-aqueous electrolytes	Electrolyte: $CoCl_2$ in urea acetamide-LiBr	80 °C	[7]
	Electrolyte: $Co(TFSA)_2$ in 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide in the presence of coumarin and thiourea	Cathodic potential= −2.2V vs silver QRE	[8]
Molten salt electro-deoxidation	Electrolyte: Molten Na_2CO_3-K_2CO_3	800 °C, Cell voltage> 1.7 V	[9]
Molten salt hydrogen electro-reduction	Electrolyte: LiCl (water)	680 °C, cell voltage=1V, Energy consumption= 1.15 kWh Kg^{-1}	Current study

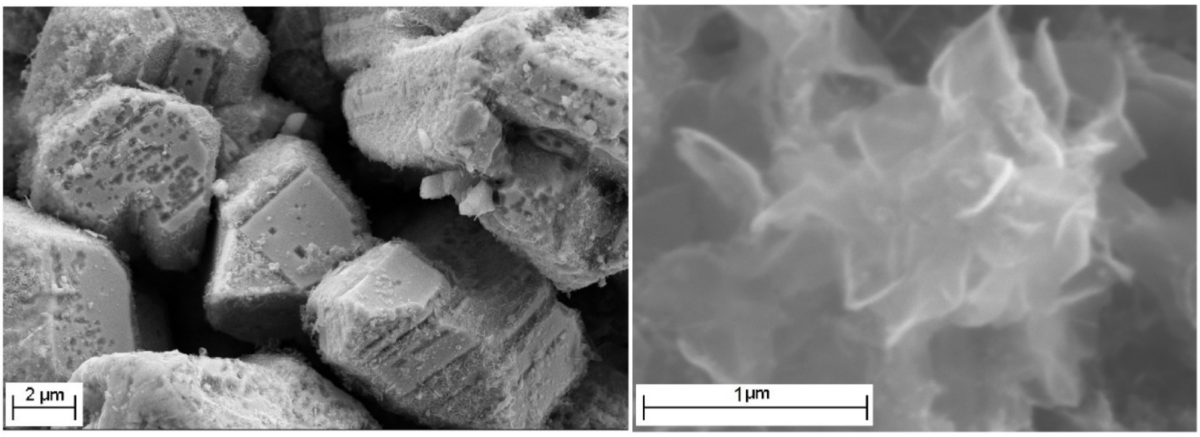

Fig. S1. SEM micrographs of the electrolytic product obtained by the cathodic polarisation of the oxide pellets at 680 °C under the humid Ar atmosphere at the cell voltage of 1V for 2h, at different magnifications.

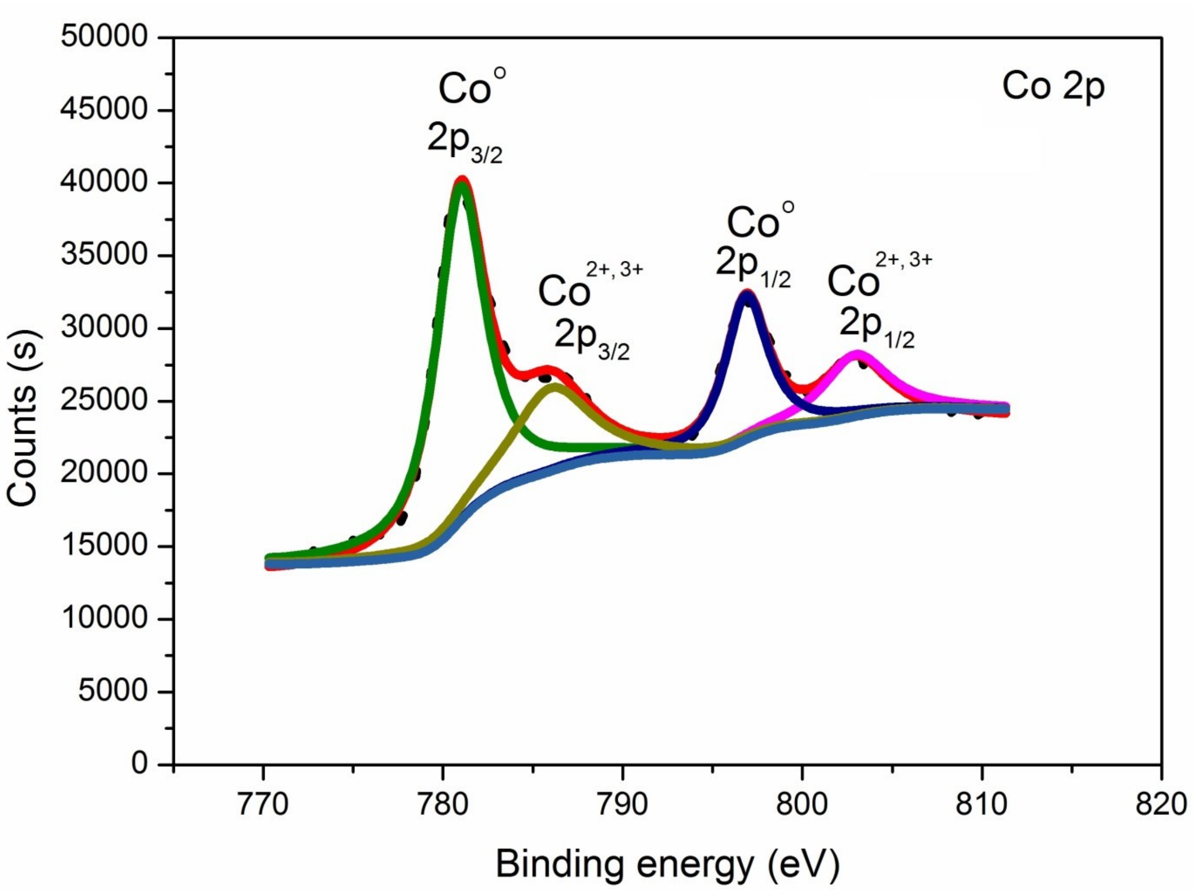

Fig. S2. Co(2p)) XP spectra of electrolytic product obtained by the cathodic polarisation of the oxide pellets at 680 °C under the humid Ar atmosphere at the cell voltage of 1V for 6h.

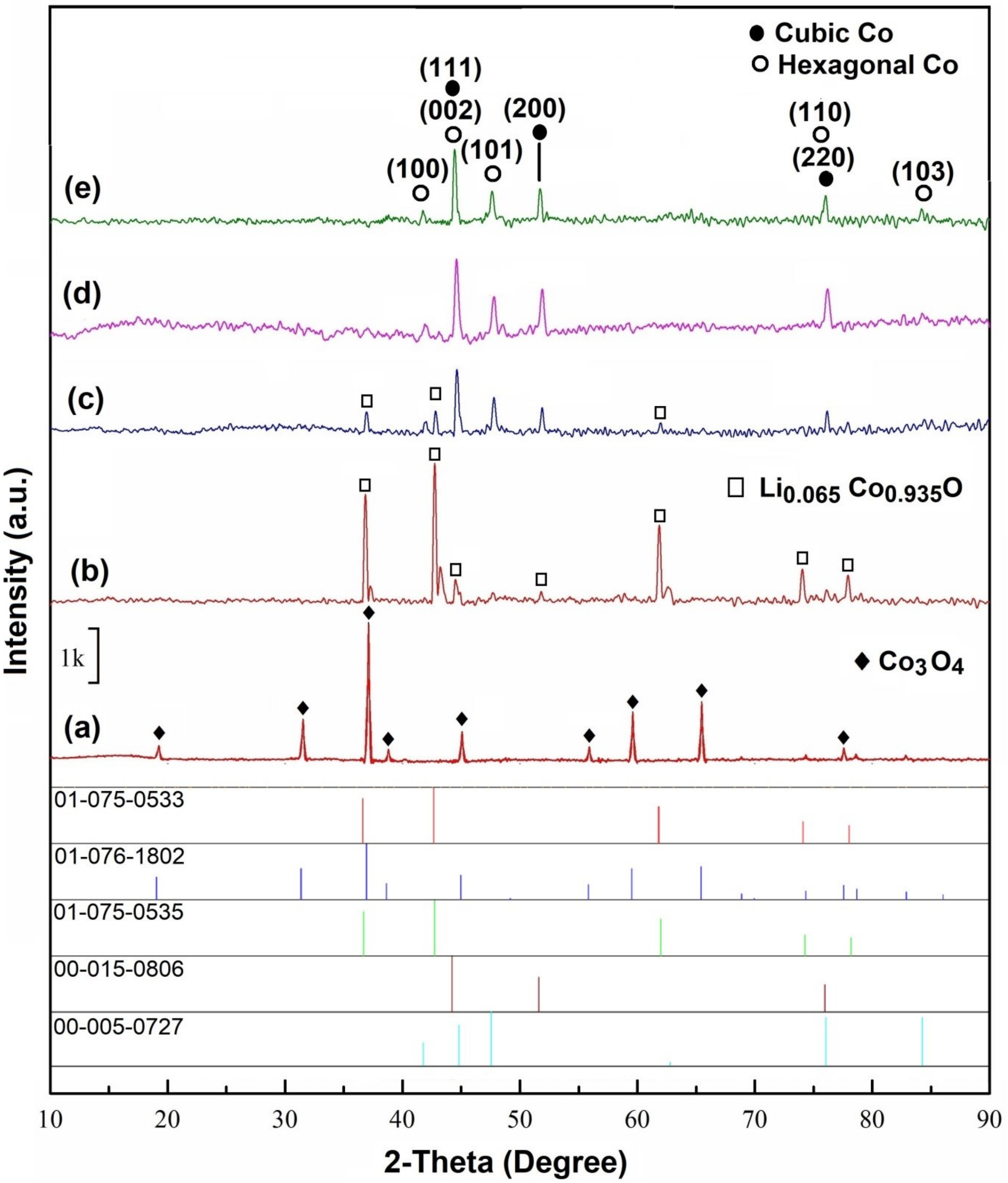

Fig. S3. The X-ray diffraction patterns of (a) the Co oxide after being pressed and sintered at 1300 °C, and (b-e) the electrolytic products obtained after various electrolysis duration under humid Ar at a low cell potential of 1V: (b) 2h, (c) 4h, (d) 6h and (e) 8h. The standard diffraction lines of JCPDS cards are also presented.

Fig. S4 The phase transitions from CoO initial particles to well-faceted cobalt microcrystals occurred during the water-assisted molten salt electro-reduction process.

References

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