

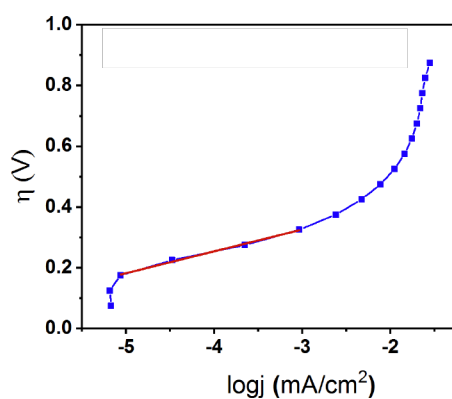
## Supplementary materials

### Positive Effect of Iron Doping in the Electrocatalytic Activity of Cobalt Hexacyanoferrate

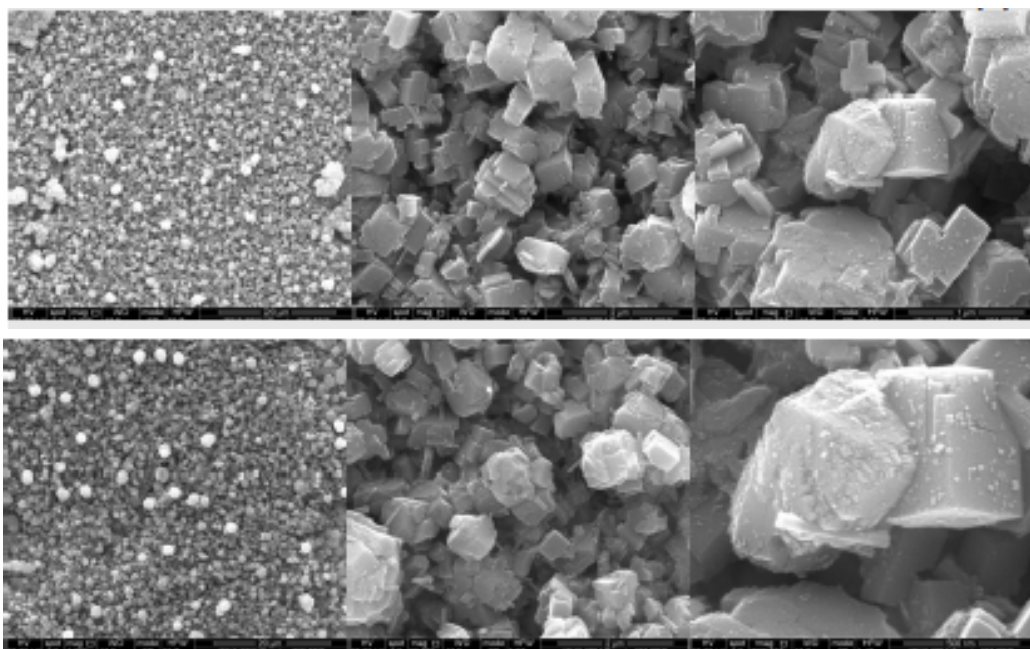
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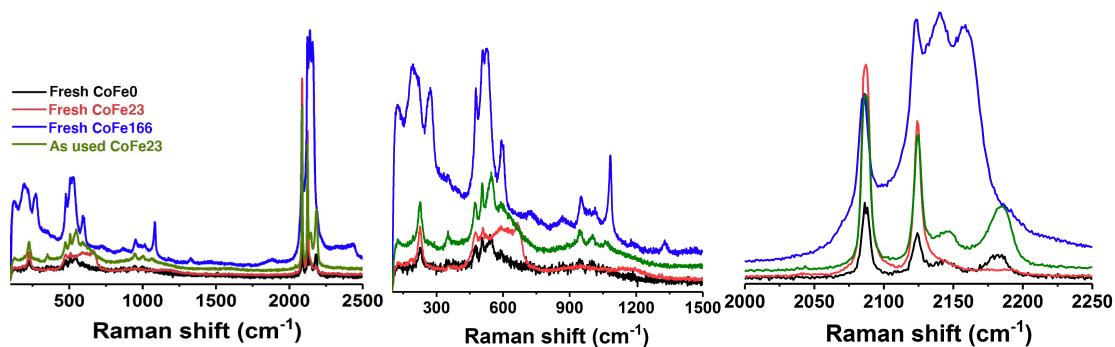
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**Figure S1.** Tafel plot obtained with **CoFe<sub>23</sub>** electrodes in ph 7 KPi electrolyte. Stable current data after 10 minutes operating at constant potential, and averaged over 30 seconds.



**Figure S2.** SEM images of as prepared **CoFe<sub>23</sub>**, and after 10 h electrolysis at  $\eta = 500$  mV in ph 7 KPi electrolyte.



**Figure S3.** Raman spectra of as prepared **CoFe0** , **CoFe23**, **CoFe166**; and of **CoFe23** after 10 h electrolysis at  $\eta = 500$  mv in ph 7 KPi electrolyte.

**Table S1.** Metal ratio in reagents, and final products for the series  $\text{Fe}_x\text{Co}_{2-x}[\text{Fe}(\text{CN})_6]$ .

Fe/Co in solution	Fe/Co in PBA	Fe/Co in active site*	Z (%)	PBA Formula	label
0.00	0.50	0.00	0	$\text{Co}_2[\text{Fe}(\text{CN})_6]$	<b>FeCo0</b>
0.25	0.68	0.10	10	$\text{Fe}_{0.18}\text{Co}_{1.82}[\text{Fe}(\text{CN})_6]$	<b>FeCo10</b>
0.50	0.73	0.15	15	$\text{Fe}_{0.27}\text{Co}_{1.73}[\text{Fe}(\text{CN})_6]$	<b>FeCo15</b>
0.75	0.85	0.23	23	$\text{Fe}_{0.38}\text{Co}_{1.62}[\text{Fe}(\text{CN})_6]$	<b>FeCo23</b>
1.00	0.92	0.27	27	$\text{Fe}_{0.43}\text{Co}_{1.57}[\text{Fe}(\text{CN})_6]$	<b>FeCo27</b>
1.25	1.23	0.40	40	$\text{Fe}_{0.57}\text{Co}_{1.43}[\text{Fe}(\text{CN})_6]$	<b>FeCo40</b>
1.50	1.34	0.56	56	$\text{Fe}_{0.72}\text{Co}_{1.28}[\text{Fe}(\text{CN})_6]$	<b>FeCo56</b>
3.75	3.00	1.66	166	$\text{Fe}_{1.25}\text{Co}_{0.75}[\text{Fe}(\text{CN})_6]$	<b>FeCo166</b>

\*in  $\text{Co}^{\text{II}}$  position.

**Table S2.** Overpotentials required to reach an specific current density in the **FeCoZ** series.

	$\eta @ 1 \text{ mA cm}^{-2}$	$\eta @ 10 \text{ mA cm}^{-2}$	$\eta @ 50 \text{ mA cm}^{-2}$
<b>FeCo0</b>	0.37	0.54	0.98
<b>FeCo10</b>	0.36	0.51	0.86
<b>FeCo15</b>	0.23	0.48	0.81
<b>FeCo23</b>	0.20	0.47	0.77
<b>FeCo27</b>	0.21	0.48	0.82
<b>FeCo56</b>	0.28	0.53	0.83
<b>FeCo166</b>	0.47	0.76	–