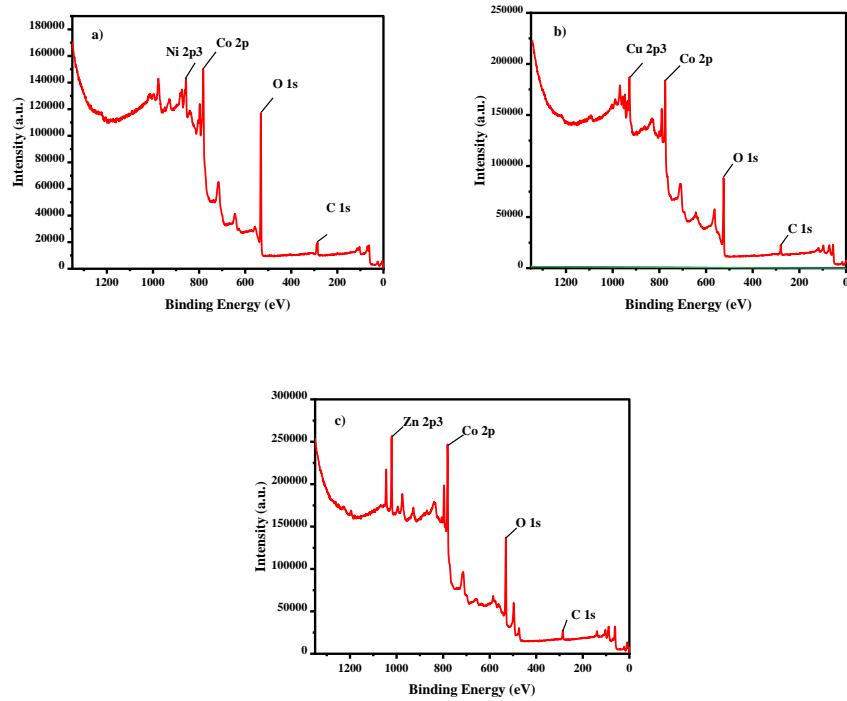


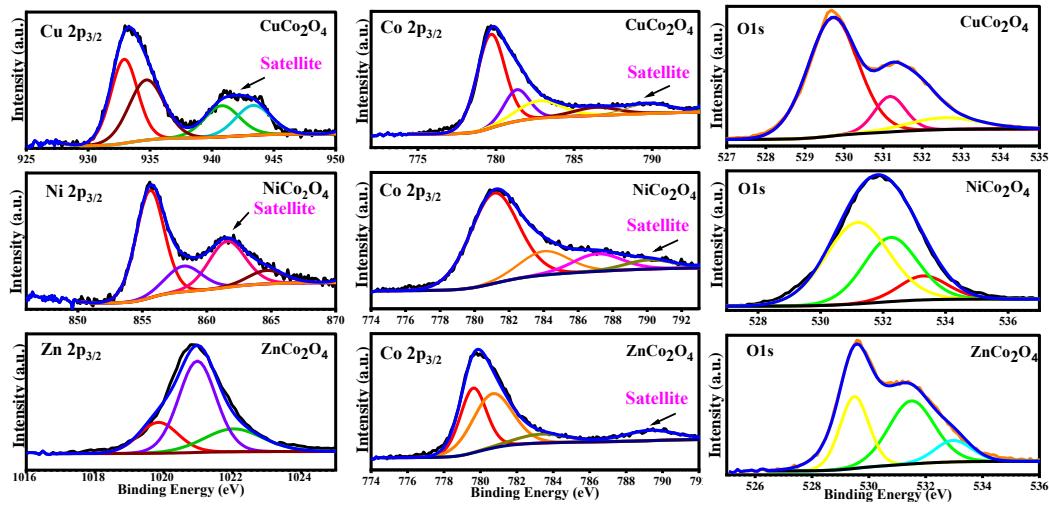
*Supplementary Information (SI)*

## Electrochemical Characteristics of Nanosized Cu, Ni, and Zn Cobaltite Spinel Materials

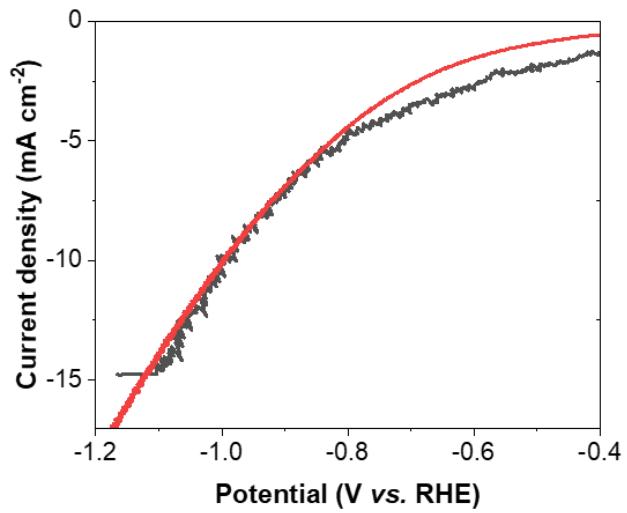
### 1. Supplementary Figures



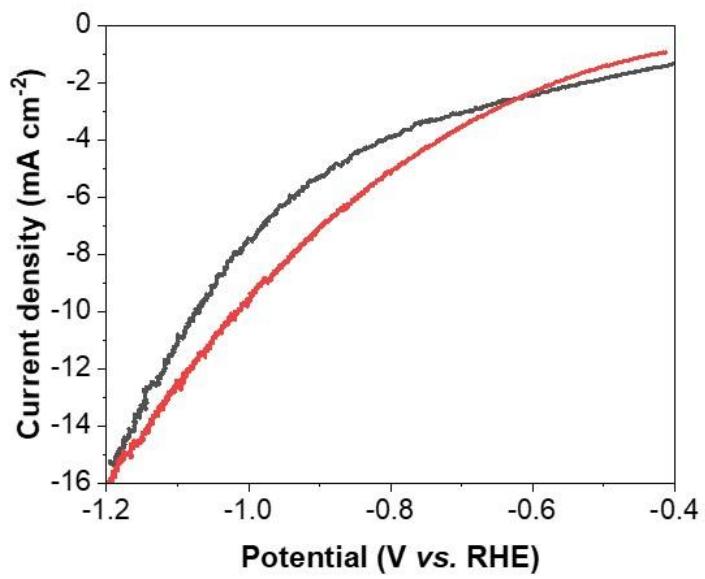
**Figure S1.** XPS survey spectrum of a) NiCo<sub>2</sub>O<sub>4</sub>, b) CuCo<sub>2</sub>O<sub>4</sub>, c) ZnCo<sub>2</sub>O<sub>4</sub>.



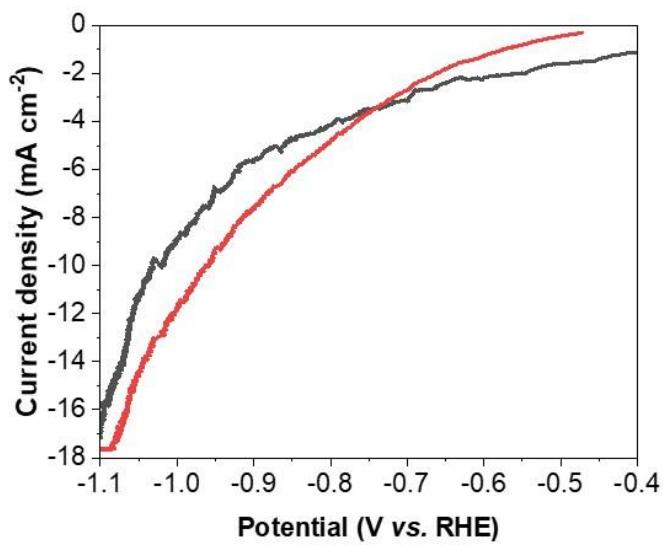
**Figure S2.** Deconvoluted X-ray photoelectron spectra for  $\text{CuCo}_2\text{O}_4$ ,  $\text{NiCo}_2\text{O}_4$  and  $\text{ZnCo}_2\text{O}_4$  before reaction.



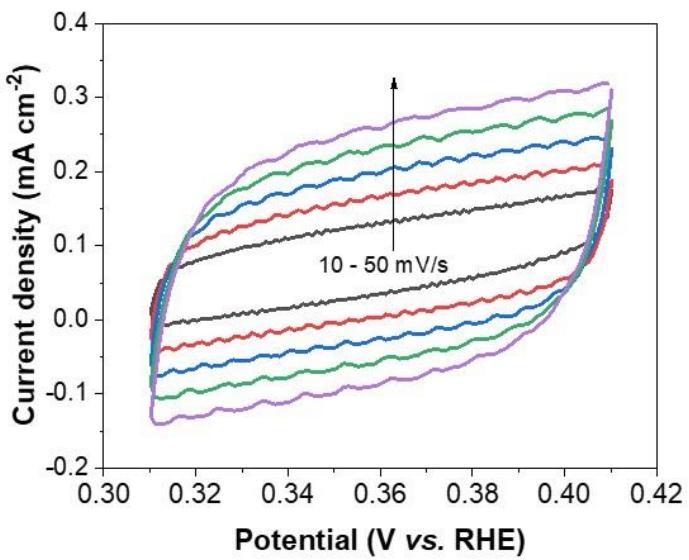
**Figure S3.** Ni spinel was evaluated at different times in  $\text{CO}_2$ -saturated 0.1 M  $\text{KHCO}_3$  and reproduced independently by two different systems.



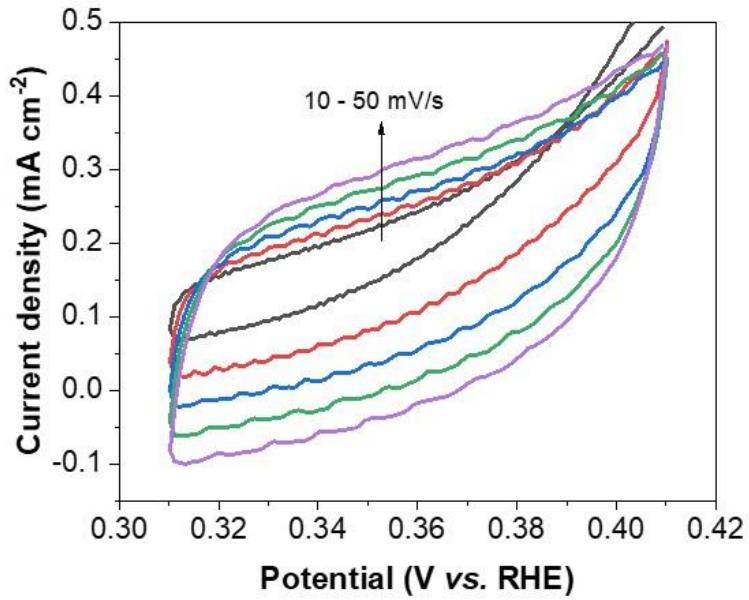
**Figure S4.** Cu spinel was evaluated at different times in  $\text{CO}_2$ -saturated 0.1 M  $\text{KHCO}_3$  and reproduced independently by two different systems.



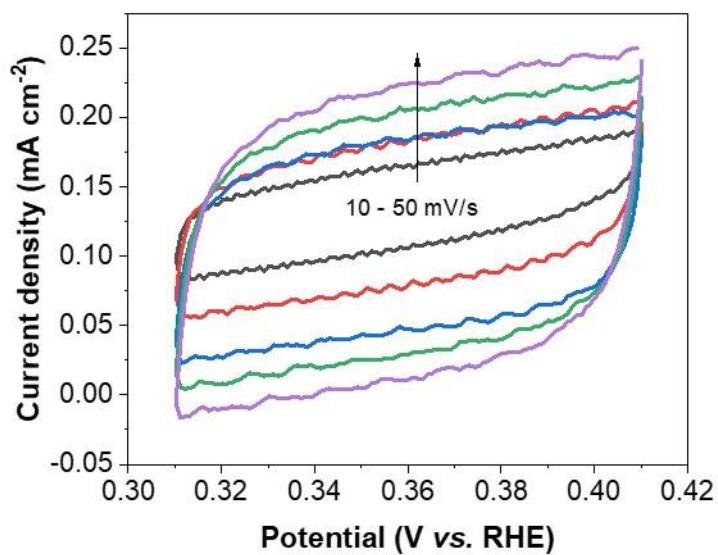
**Figure S5.** Zn spinel was evaluated at different times in  $\text{CO}_2$ -saturated 0.1 M  $\text{KHCO}_3$  and reproduced independently by two different systems.



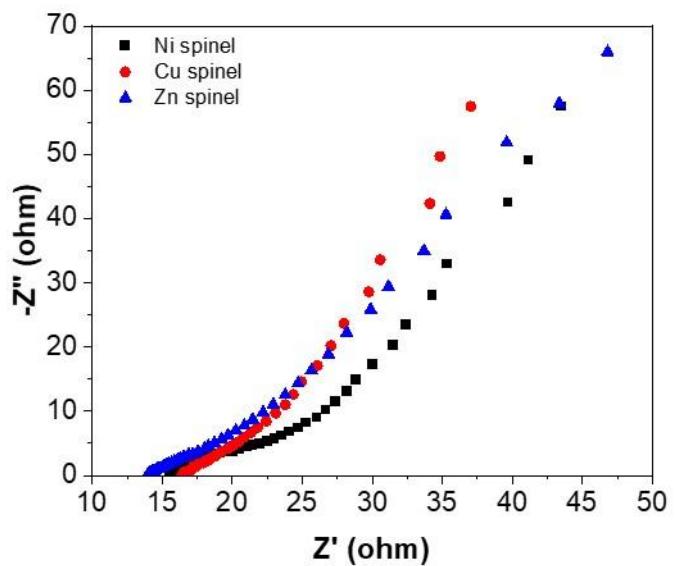
**Figure S6.** Cyclic voltammogram (CV) curves of Ni spinel materials in the non-Faradaic potential region recorded at different scan rates (10-50 mV s<sup>-1</sup>).



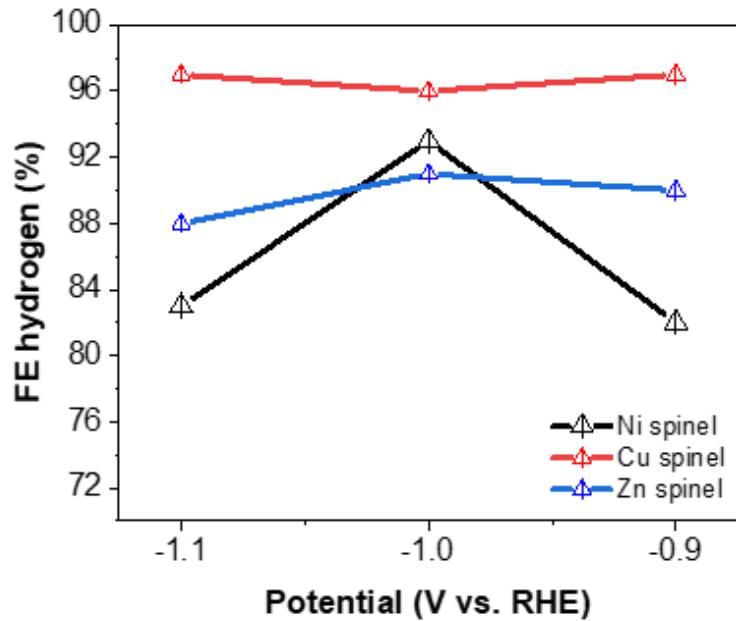
**Figure S7.** Cyclic voltammogram (CV) curves of Cu spinel materials in the non-Faradaic potential region recorded at different scan rates ( $10\text{-}50 \text{ mV s}^{-1}$ ).



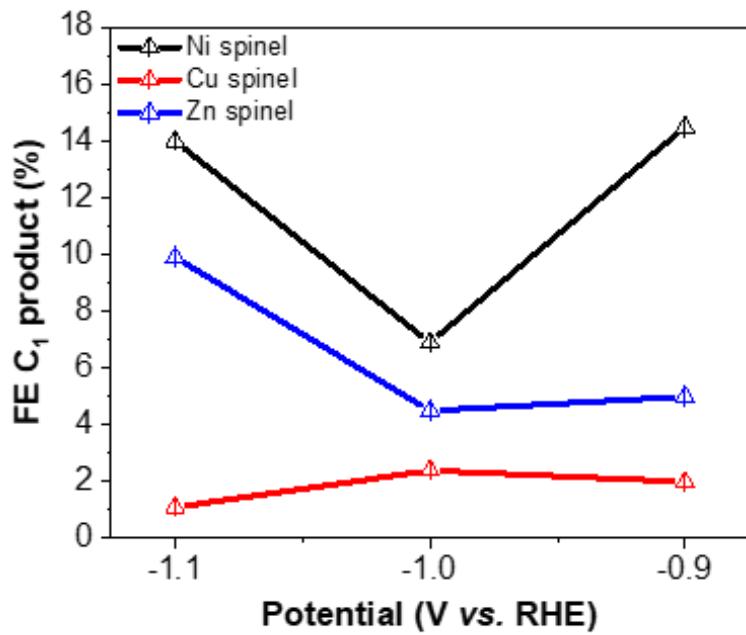
**Figure S8.** Cyclic voltammogram (CV) curves of Zn spinel materials in the non-Faradaic potential region recorded at different scan rates (10-50 mV s<sup>-1</sup>).



**Figure S9.** Nyquist plots of Ni, Zn and Cu spinel in CO<sub>2</sub>-saturated 0.1 M KHCO<sub>3</sub>.



**Figure S10.** The FE of H<sub>2</sub> for the different catalysts in the potential range of -0.9 to -1.1 V.



**Figure S11.** The FE of C<sub>1</sub> product for the different catalysts in the potential range of -0.9 to -1.1 V.

## 2. Supplementary Tables

**Table S1.** Summary of the electrocatalysts toward the CO<sub>2</sub> reduction reaction.

| Catalysts  | HCOOH<br>(FE%) | CO<br>(FE%) | MeOH<br>(FE%) | EtOH<br>(FE%) | Ref. |
|--|----------------|-------------|---------------|---------------|------|
| Co <sub>3</sub> O <sub>4</sub> -20@CNCo-20         | 84             | -           | -             | -             | [38] |
| Ultrathin Co <sub>3</sub> O <sub>4</sub><br>Layers | 60             | -           | -             | -             | [39] |
| NGCo <sub>3</sub> O <sub>4</sub> -20               | 64             |             |               | -             | [30] |
| NGCo <sub>3</sub> O <sub>4</sub> -30               | 83             | -           | -             | -             | [30] |
| NGCo <sub>3</sub> O <sub>4</sub> -40               | 72             |             |               | -             | [30] |
| CuBi <sub>2</sub> O <sub>4</sub>                   | 60             | -           | -             | -             | [40] |
| CuFe <sub>2</sub> O <sub>4</sub> @PANI             | -              | -           | 73            | -             | [41] |
| CdSeCuFe <sub>2</sub> O <sub>4</sub>               | -              | -           | 72            | -             | [42] |
| Ni <sub>2</sub> FeS <sub>4</sub>                   | -              | 5.9         | -             | -             | [43] |