## Highly selective CO<sub>2</sub> conversion to methane or syngas tuned by CNTs@non-noble metal cathode in Zn-CO<sub>2</sub> flow battery

Yang Chen,<sup>a, b, c</sup> Yuxin Mei,<sup>d</sup> Mengli Li,<sup>\*b</sup> Chenyang Dang,<sup>b</sup> Lin Huang,<sup>b</sup> Weiguo Wu,<sup>c</sup> Yuanyuan Wu,<sup>b</sup> Xinhao Yu,<sup>c</sup> Kai Wang,<sup>b</sup> Li Gu,<sup>\*c</sup> Lujia Liu,<sup>\*b, e</sup> and Xuebo Cao<sup>\*b</sup>

a. School of Materials Science and Engineering Changzhou University, Changzhou, Jiangsu

213164, China

b. College of Biological, Chemical Sciences and Engineering, Jiaxing University, Jiaxing, 314001,

China

c. School of Materials and Textile Engineering, Jiaxing University, Jiaxing, Zhejiang, 314001,

China

d. School of Arts and Sciences, University of Toronto (St. George campus), 27 King's College Cir,

Toronto, ON M5S

e. MacDiarmid Institute for Advanced Materials and Nanotechnology, School of Chemical and

Physical Sciences, Victoria University of Wellington, Wellington 6012, New Zealand

## **Corresponding Author**

E-mail: xbcao@zjxu.edu.cn (X. Cao); guli@zjxu.edu.cn (L. Gu); menglil@zjxu.edu.cn (M. Li); luke.liu@vuw.ac.nz (L. Liu).



**Fig. S1** Morphology and composition characterizations of the as-prepared electrode. (a) Schematic diagram of CNTs@Cu electrode preparation. SEM images of CNTs@Cu (b-d), (e) C and (f) Cu element mapping of CNTs@Cu electrode.

A rolled Cu wire grid (100 meshes) was used to react with CNTs solution at room temperature (Fig. S1), which leads to the formation of tubular CNTs@Cu composite structure. As presented by scanning electron microscopy (SEM) images in Fig. S1b and S1c, the as-prepared CNTs@Cu maintains the pristine grid morphology of copper wire mesh, which has a unique hollow tubular structure with channel width of 800 µm and wall thickness of 100 µm. Intertwined CNTs with a porous network structure are uniformly grown on copper mesh's surface. CNTs are uniformly distributed on the surface of Cu mesh, as can be seen in Fig. S1e and S1f.



Fig. S2 (a) XRD patterns and (b) XPS survey spectrum of CNTs@Cu electrode.

As can be seen in Fig. S2a and inset, X-ray diffraction (XRD) pattern of CNTs display one weak and broad peak at around 26° assigned to (002) planes of graphite carbon in CNTs. Three sharp peaks centered at  $2\theta$ =43°, 50°, and 74° belong to (111), (200) and (220) lattice plane diffraction of face-centered cubic copper (JCPDF card No. 65-9026).<sup>1</sup> The existence of Cu substrate in CNTs@Cu is further demonstrated by X-ray photoelectron spectroscopy (XPS) as shown in Fig. S2b.



Fig. S3 (a) Chemical structure and (b) ball-and-spoke model of EMIM-BF<sub>4</sub>.



**Fig. S4** Chromatogram of CO<sub>2</sub> (purity 99.9999%) feed in Zn-CO<sub>2</sub> battery.

CO<sub>2</sub> was continuously supplied into CNTs@Cu electrode until GC signals indicated that off-gas was pure CO<sub>2</sub>. Therefore, the additional GC signal that appeared in subsequent electrochemical process was directly related to gas products produced by CO<sub>2</sub> conversion. In addition, the GC signals showed that no other gas products were detected from effluent gases of battery when battery did not discharge.



**Fig. S5** Use Copper tube and Nickel tube as cathode to assemble batteries to work. (a) Corresponding GC results, and (b) discharge curves at a constant current density j=0.267 mA cm<sup>-2</sup>.



**Fig. S6** <sup>1</sup>H-NMR spectra for [EMIM][BF<sub>4</sub>] electrolyte in Zn-CO<sub>2</sub> battery with CNTs@Cu cathode: (a) Before discharge and (b) after extensive discharge.

The basically identical spectra suggest that no liquid products could be obtained by  $CO_2$  conversion in  $Zn-CO_2$  flow battery.



**Fig. S7** SEM characterizations of the Zn anode in Zn-CO<sub>2</sub> battery with CNTs@Cu cathode: (a) Before discharge and (b) after extensive discharge.

It can be seen from Fig. S7 that the zinc anode is seriously corroded after discharge, indicating that electrochemical oxidation has indeed occurred.



Fig. S8 SEM characterizations of CNTs@Cu cathode after discharged.



Fig. S9 XRD characterizations of CNTs@Cu cathode before (a) and after (b) discharge.

Except for metallic copper, a small amount of copper oxide diffraction peak (20=36.4°) were detected in the CNTs@Cu electrode before discharge by XRD (Fig. S9a), resulted from the growth mechanism of CNTs and Cu oxidation in the air. However, only metallic copper diffraction peaks were detected in CNTs@Cu electrode after discharge as demonstrated by XRD (Fig. S9b), due to electrochemical reduction process involving copper oxide or cuprous oxide. These results are consistent with that of the XPS characterizations (Fig. S10b and S10d) as shown below.



**Fig. S10** The high-resolution XPS spectra of CNTs@Cu cathode before (a, b) and after (c-f) discharge.

Cu and C elements (Fig. S10a-d) were detected on CNTs@Cu cathode. Different from CNTs@Cu electrode before discharge, additional N and Zn peaks (Fig. S10e and S10f) were also detected after discharge by XPS. The results substantiated that CNTs@Cu electrode did undergo an electrochemical reaction. According to the properties of this system and previous reports,<sup>2</sup> we speculate that the additional N and Zn elements found after discharge in XPS data may be related to ZnNHC. And the increase in peak area at the binding energy of 285.5 eV is due to increase in C-N bonds, which is also consistent with the formation of ZnNHC.



Fig. S11 The Nyquist diagrams of CNTs@Cu in battery after long-term discharging.



**Fig. S12** XPS spectra of the Zn anode in  $Zn-CO_2$  battery with CNTs@Cu cathode after discharge: (a) Zn 2p, (b) C 1s, (c) N 1s. Before characterizations, the electrode was rinsed thoroughly with absolute ethanol in order to remove possible electrolyte and/or solid residues.

As expected, Zn, C, and N elements were detected in XPS characterization, resulted from ZnNHC complex formed on the surface of the Zn anode, which was consistent with previous report.



Fig. S13 (a-c) SEM images, (d) C and (e) Ni element mapping of CNTs@Ni electrode.

The as-prepared CNTs@Ni maintains pristine grid morphology of nickel mesh, which has a unique hollow tubular structure with channel width of 800  $\mu$ m and wall thickness of 100  $\mu$ m.



Fig. S14 (a) XRD pattern and (b) XPS survey spectra of CNTs@Ni electrode.

X-ray diffraction (XRD) patterns of CNTs only display one weak peak at about 26° due to their poor crystallinity when compared with that of metal Ni. The other three peaks at 44°, 52° and 76° can be easily observed in Fig. S14a, which can be assigned to (111), (200) and (220) planes of Ni (JCPDF: 031051), respectively.<sup>3</sup> The existence of Ni substrate in CNTs@Ni is further demonstrated by X-ray photoelectron spectroscopy (XPS) as shown in Fig. S14b.



Fig. S15 Impedance spectra of CNTs@Ni before and after discharge in battery.



**Fig. S16** (a) Galvanostatic discharge curves of battery withe CNTs@Ni cathode at j=0.267 mA  $cm^{-2}$  with CO<sub>2</sub>, O<sub>2</sub>, Ar feed. (b, c) GC analysis for effluent gases from CNTs@Ni based battery with CO<sub>2</sub> feed.

The above results prove that  $CO_2$  can be converted into CO and  $H_2$  over  $Zn-CO_2$  flow battery with CNTs@Ni as cathode during discharge.



**Fig. S17** <sup>1</sup>H-NMR spectra for [EMIM][BF<sub>4</sub>] electrolyte in Zn-CO<sub>2</sub> battery with CNTs@Ni cathode. (a) Before discharge, (b) after extensive discharge.

The basically identical spectra suggest that  $CO_2$  was not reduced to liquid products in the battery.



**Fig. S18** SEM characterizations of the Zn anode in  $Zn-CO_2$  battery with CNTs@Ni cathode. (a) Before discharge, (b) after extensive discharge.

It can be seen from the figure that the zinc anode is seriously corroded after discharge, indicating that electrochemical oxidation has indeed occurred.



Fig. S19 SEM characterizations of CNTs@Ni cathode after discharged.

Compared with CNTs@Ni electrode before reaction (Fig. S13), macroscopically, there was no change observed in after discharged electrode, but under high-power SEM, some coverings on the surface of CNTs were found.



**Fig. S20** XPS spectra of the Zn anode. High-resolution binding energy spectra of CNTs@Ni as cathode after discharge, (a) Zn 2p, (b) C 1s, (c) N 1s.

As shown in images, Zn, C and N elements were detected by XPS. This may be related to formation of ZnNHC.



**Fig. S21** Chemical composition characterizations of the CNTs@Ni cathode. The high-resolution XPS spectra of CNTs@Ni cathode before (a, b) and after (c-f) discharge.

Similar to CNTs@Cu electrode, additional N or Zn peaks were also detected in CNTs@Ni cathode after discharge by XPS.



Fig. S22 XRD characterization of CNTs@Ni cathode before (a) and after (b) discharge.

There is basically no change in XRD spectra of cathode before and after the reaction.



Fig. S23 Open circuit potential (OCP) of CNTs@Cu based  $Zn-CO_2$  flow battery.



**Fig. S24** The OCP change of CNTs@Cu based  $Zn-CO_2$  battery during the process of excluding oxygen out by inputing  $CO_2$  for one hour.

	Obvio	usly,	the OCP	stabilized	at 0.9	V for	the fir	rst 30	minutes,	and	gradually	decrease	d to
0.3	82	V	with	CO <sub>2</sub> i	nput,	whic	ch	was	consist	ent	with	Fig.	S23.

Cathode	Anode	Electrolyte	Open circuit voltage (V)	Main Product	Faradic Efficiency (%)	Stability	Refs
Cu-N <sub>2</sub> /GN	Zn	KOH+Zn(Ac) <sub>2</sub> /KHCO <sub>3</sub>	-	СО	64%	40h (120 cycles)	4
CHF	Zn	[EMIM][BF <sub>4</sub> ]	1.01	$CH_4$	94%	8 days	2
Fe <sub>1</sub> NC	Zn	KOH+Zn(Ac) <sub>2</sub> /KHCO <sub>3</sub>	0.727	СО	96%	25h (72 cycles)	5
SAs-Ni-N-C	Zn	KOH+Zn(Ac) <sub>2</sub> /KHCO <sub>3</sub>	-	СО	93.30%	50h	6
Cu <sub>3</sub> P/C	Zn	NaOH/NaHCO <sub>3</sub>	1.5	CO	47%	-	7
Ir@Au	Zn	KOH/KHCO <sub>3</sub>	-	СО	85%	30h (90 cycles)	8
Pd-based	Zn	KOH/NaCl	0.89	НСООН	90%	33h (100 cycles)	9
DNG-SAFe	Zn	KOH+Zn(Ac) <sub>2</sub> /KHCO <sub>3</sub>	-	СО	86.50%	50h (150 cycles)	10
CNTs@Cu	Zn	[EMIM][BF <sub>4</sub> ]	0.82	$CH_4$	93.30%	18 days	This work
CNTs@Ni	Zn	[EMIM][BF <sub>4</sub> ]	0.98	$CO,\ H_2$	50%, 48%	9 days	This work

 Table S1
 Summary of current Zn-CO2 batteries for CO2 conversion



Fig. S25 Specific capacity of the Zn-CO<sub>2</sub> batteries with (a) CNTs@Cu and (b) CNTs@Ni cathode.

Specific capacity was normalized to the mass of consumed Zn. According to mass change of zinc consumed before and after discharge, the specific capacity of  $Zn-CO_2$  battery with CNTs@Ni cathode is 293.9 mAh  $g_{Zn}^{-1}$ , with an energy density of 208.7 Wh kg<sup>-1</sup>.



**Fig. S26** (a) Discharge curves of Zn-CO<sub>2</sub> flow battery with CNTs@Ni cathode at varied current densities (j=0.26, 0.53, 1.06, and 4.26 mA cm<sup>-2</sup>). (b) Long-time discharge curve of the Zn-CO<sub>2</sub> flow battery with CNTs@Ni cathode at a constant current density j=0.267 mA cm<sup>-2</sup>. (c) Polarization and power density curves of Zn-CO<sub>2</sub> flow battery with CNTs@Ni cathode at CO<sub>2</sub> flow rate of 1 mL min<sup>-1</sup> (scan rate, 5 mv s<sup>-1</sup>). (d) Open circuit voltage of Zn-CO<sub>2</sub> flow battery with CNTs@Ni cathode.

Obviously, in parallel comparison, the operating voltage and stability of CNTs@Ni based battery is lower than that of CNTs@Cu based. The battery with CNTs@Ni cathode exhibits a peak power density of 1.397 mW cm<sup>-2</sup> and a stable open circuit potential of 0.98V.



Fig. S27 The OCP change of CNTs@Ni based  $Zn-CO_2$  battery during the process of excludingoxygenoutbyinputing $CO_2$ foronehour.



**Fig. S28** The discharge curves with regenerated Zn or refreshed electrolyte after long-term discharge at a constant current density j=0.267 mA cm<sup>-2</sup>. (a) CNTs@Cu and (b) CNTs@Ni based Zn-CO<sub>2</sub> batteries.



**Fig. S29** The discharge curves after adding about 0.01 mol of water to the system after the batteries were deactivated at a constant current density j=0.267 mA cm<sup>-2</sup>. (a) CNTs@Cu and (b) CNTs@Ni based batteries.



**Fig. S30** The corresponding Faraday efficiency of the batteries product after adding 0.01, 0.02 and 0.04 moles water, respectively: (a) CNTs@Cu and (b) CNTs@Ni based batteries.

The main reason for deactivation of these two batteries lies in the excessive oxidation of Zn anode. The other reason is ascribed to the consumption of reactive C2-H in imidazolium ring, which causes relatively fast attenuation of the batteries performance. It is reported that if a proton source such as H<sub>2</sub>O is present, the de-proton imidazolium would be regenerated.<sup>11</sup> Interestingly, with 0.01 mol deionized water addition, the discharge curves of these deactivated batteries were immediately enhanced (Fig. S29). So far, the role of water in ionic liquids for CO<sub>2</sub> reduction is still controversial.<sup>12</sup> Therefore, water content was also considered to investigate its influence on these batteries' performance in this work (Fig. S30). As expected, the amount of generated H<sub>2</sub> was enhanced as water content increased, while the concentration of CH<sub>4</sub> and CO decreased.



Fig. S31 Schematic diagram of the battery reaction mechanism.

According to the XPS, XRD, SEM before and after the cathode and anode reaction, we speculate that the internal reaction occurs in the battery as shown in the figure.

## Reference

- 1. L. Shi, B. Duan, Z. Zhu, C. Sun, J. Zhou and A. Walsh, Ultrason. Sonochem., 2020, 64, 105013.
- 2. K. Wang, Y. Wu, X. Cao, L. Gu and J. Hu, *Adv. Funct. Mater.*, 2020, **30**, 1908965.
- 3. L. Wang, Y. Li, X. Yin, Y. Wang, L. Lu, A. Song, M. Xia, Z. Li, X. Qin and G. Shao, *Int. J. Hydrog. Energy*, 2017, **42**, 22655-22662.
- 4. W. Zheng, J. Yang, H. Chen, Y. Hou, Q. Wang, M. Gu, F. He, Y. Xia, Z. Xia, Z. Li, B. Yang, L. Lei, C. Yuan, Q. He, M. Qiu and X. Feng, *Adv. Funct. Mater.*, 2019, **30**, 1907658.
- 5. T. Wang, X. Sang, W. Zheng, B. Yang, S. Yao, C. Lei, Z. Li, Q. He, J. Lu, L. Lei, L. Dai and Y. Hou, *Adv. Mater.*, 2020, **29**, 2002430.
- 6. W. Zheng, F. Chen, Q. Zeng, Z. Li, B. Yang, L. Lei, Q. Zhang, F. He, X. Wu and Y. Hou, *Nano-Micro Lett.*, 2020, **12**, 108.
- 7. M. Peng, S. Ci, P. Shao, P. Cai and Z. Wen, J. Nanosci. Nanotechnol., 2019, 19, 3232-3236.
- X. Wang, J. Xie, M. A. Ghausi, J. Lv, Y. Huang, M. Wu, Y. Wang and J. Yao, *Adv. Mater.*, 2019, 31, 1807807.
- 9. J. Xie, X. Wang, J. Lv, Y. Huang, M. Wu, Y. Wang and J. Yao, *Angew. Chem. Int. Ed.*, 2018, **57**, 16996-17001.
- 10. Y. Wang, M. Hatakeyama, K. Ogata, M. Wakabayashi, F. Jin and S. Nakamura, *Phys. Chem. Chem. Phys.*, 2015, **17**, 23521-23531.
- 11. B. Ratschmeier, A. Kemna and B. Braunschweig, *ChemElectroChem*, 2020, 7, 1765-1774.
- 12. W. Ni, Z. Liu, Y. Zhang, C. Ma, H. Deng, S. Zhang and S. Wang, *Adv. Mater.*, 2021, **33**, e2003238.