# $CO_2$ valorisation towards alcohols by Cu-based electrocatalysts: Challenges and perspectives

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# Supporting Information

## Summary

### *S1. $CO_2$-to-methanol via thermochemical route*

Outstanding results following TC reactions for methanol production from our work1 with data taken from references2–[6.] Table S1 shows the best results following thermochemical reactions for methanol production.

Table S1**.** Outstanding results following TC reactions for methanol production from our work[1] with data taken from references[2–6].

| Catalysts | $CO_2$ conversion, % | Selectivity Methanol, % | Temperature, °C | Pressure, MPa | Ref. |
|---|---|---|---|---|---|
| Cu/ZnO | 5.5 | 50 | 240 | 2 | [3] |
| $Cu/ZrO_2$ | 2.5 | 78 | 240 | 2 | [3] |
| Cu/ZnO/Ga | 6 | 88 | 270 | 2 | [5] |
| $Cu/ZrO_2$/Ga | 13.7 | 75.5 | 250 | 2 | [5] |
| $Cu/ZnO/ZrO_2$ | 13 | 32 | 240 | 2 | [3] |
| $Cu/ZnO/ZrO_2/SiO_2$ | 13.9 | 36 | 240 | 2 | [4] |
| $Cu/ZnO/ZrO_2/TiO_2$ | 17.4 | 43.8 | 240 | 3 | [2] |
| $Cu/ZnO/ZrO_2/Al_2O_3/SiO_2$ | 11.7 | 99.7 | 250 | 5 | [6] |

## *S2. $CO_2$-to-methanol via liquid phase electrochemical route*

Table S2**.** State-of-the-art performance of the best catalysts to produce methanol from liquid-phase electrochemical $CO_2$ conversion.

| Electrocatalysts | Faradaic efficiency to Methanol, % | Total current density, mA $cm^{-2}$ | Cell configuration | Ref. |
|---|---|---|---|---|
| $Cu_{63,9}Au_{36,1}$/NCF | 15.9 | - | H-type cell (Nafion 117) | 7 |
| Anodiz. Cu foils | 100.0 | 1.4 | Traditional undivided 3 electrode cell | 8 |
| Electroch. Anodiz. Cu foils | 20.0 | 5.0 | Traditional undivided 3 electrode cell | |
| $Cu_2O$/stainless steel | 38.0 | 5.0 | Traditional undivided 3 electrode cell | |
| $Cu\backslash_{88}Sn_6Pb_6$ alloy foil | 34.0 | 0.6 | Two compartmentss (Nafion 117) | |
| Cu/Carbon paper | 0.4 | 8.9 | Two compartmentss (SPEEK) | |
| Electropolished Cu | 0.1 | 10.0 | Two compartmentss (AMV Selemion) | |
| Cu/ZnO | 2.8 | 12.0 | Two compartmentss (Nafion 117) | |
| $Cu_2O$ /Carbon paper | 20.0 | 2.4 | Two compartmentss SPE (AMI-7001/ MEA) | |
| Cu/CuO | 2.5 | 17.3 | Two compartmentss (Nafion 117) | |
| Ru/Cu | 42.0 | 0.1 | Two compartmentss (agar bridge) | |
| Mo/Cu | 84.0 | 0.8 | Traditional undivided 3 electrode cell | |
| $Cu_2O$/ZnO | 17.7 | 10.6 | Two compartmentss (Nafion 117) | 9 |
| Cu-10-CNT/C | 8.3 | 16.7 | Two compartmentss (Nafion 117) | 10 |
| $Cu_2O$-MWCNTs | 38.0 | 7.5 | Two compartmentss (Nafion 117) | 11 |
| Oxide-der, Cu/ C (MOF) | 18.0 | 1.0 | Two compartmentss (Nafion 117) | 12 |
| $CuO_x$/ZnO | 34.0 | 2.7 | Traditional undivided 3 electrode cell | 13 |
| CuCNT-nanowires | 47.4 | 0.9 | Traditional undivided 3 electrode cell | 14 |
| CuCNT-Impregnation | 23.3 | 0.9 | Two compartmentss (Nafion 117) | 14 |
| Cu/Graphene | 12.7 | 0.3 | Two compartmentss (Nafion 117) | 15 |
| Cu/$TiO_2$/Graphene | 19.5 | 0.3 | Two compartmentss (Nafion 117) | 15 |
| Cu/$Cu_2O$ | 47.5 | 7.8 | Two compartmentss (Nafion 117) | 16 |
| Cu-Y/CS:PVA MCE | 68.0 | 0.3 | Membrane coated electrode (MCE) | 17 |
| $Pd_{83}Cu_{17}$ Aerogels | 80.0 | 31.8 | H-type cell (Nafion 117) | 18 |
| $Cu_{1,63}Se_{1/3}$ | 77.6 | 41.5 | H-type cell (Nafion 117) | 19 |
| CuSAs/TCNFs | 44.0 | 93.0 | H-type cell (Nafion 117) | 20 |

***S3. Faradaic efficiencies for different $CO_2R$ products of the best liquid-phase electrocatalysts.***

| | Faradaic efficiency, % * | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Electrocatalysts | $H_2$ | CO | $C_2H_4$ | $HCOO^-$ /HCOOH | $CH_3OH$ | $C_2H_5OH$ | $C_3H_8O$ | $C_2H_6$ | $CH_3COO^-$ | $CH_4$ | $J_{total}$, mA $cm^{-2}$ | Ref. |
| $Pd_{83}Cu_{17}$ Aerogels | | <1.0 | | | 80.0 | | | | | | 31.8 | [18] |
| $Cu_{1.63}Se1/3$ | <1.0 | 2.0 | - | 22.0 | 77.6 | - | - | - | - | - | 41.5 | [19] |
| CuSAs/TCNFs | <1.0 | 54.0 | - | - | 44.0 | - | - | - | - | - | 93.0 | [20] |
| $Cu_2O$ | | | | | 42.3 | 10.1 | 2.4 | | | | 10.0 | [43] |
| $Cu_2O$/ZnO | | | | | 27.5 | 3.9 | - | | | | 10.0 | [43] |
| $CuB_9$ MOF | 34.0 | 11.0 | 6.0 | 13.0 | 10.0 | 17.0 | - | - | - | - | 20.0 | [33] |
| $CuBi_{12}$ MOF | 30.0 | 9.0 | 7.0 | 16.0 | 9.0 | 28.0 | - | - | - | - | 20.0 | [33] |
| B-OD-Cu | 45.0 | <1.0 | 20.0 | 5.0 | - | 20.0 | - | 8.0 | - | - | 33.4 | [44] |
| Cu 25nm thickness | 5.0 | 5.0 | 70.0 | 1.0 | - | 11.0 | - | - | 5.0 | - | 275.0 | [35] |
| $Ag_{0.14}/Cu_{0.86}$ /PTFE | 10.0 | 3.0 | 31.0 | - | - | 41.0 | - | - | 10.0 | 5.0 | 250.0 | [36] |
| Electrodeposited CuAg alloy | 9.8 | 6.5 | 55.2 | 3.0 | - | 25.9 | 2.4 | - | 1.6 | 1.6 | 300.0 | [37] |
| Nanoporous Cu | 7.6 | 14.7 | 38.6 | 1.9 | - | 16.6 | 4.5 | - | 2.2 | - | 653.0 | [34] |
| Cu Nps/Carbon paper | 10.6 | 38.9 | 35.0 | 7.6 | - | 11.2 | 2.1 | - | 0.4 | - | 430.0 | [38] |
| $Cu_2S$–Cu-V | 12.6 | 5.5 | 21.2 | 15.4 | - | 25.0 | 7.0 | - | 3.0 | 1.1 | 400.0 | [39] |
| Ce(OH)x/Cu/PTFE | 14.2 | 0.5 | 33.8 | 1.1 | - | 42.6 | 0.6 | - | 3.3 | 2.9 | 300.0 | [45] |
| NGQ/Cu-nr | 10.0 | 5.0 | 23.0 | 5.0 | - | 45.0 | 7.0 | - | 4.0 | - | 282.0 | [46] |
| 34% N-C/Cu/PTFE | 7.4 | 0.3 | 37.5 | 1.7 | - | 52.3 | 1.4 | - | 2.3 | 1.2 | 300.0 | [40] |
| $La_{1.8}SrO_{0.2}CuO_4$ | | | | | 2.0 | 30.5 | 10.0 | | | | 180.0 | [41] |
| Porous copper foam | 69.2 | 4.6 | 4.0 | 5.9 | - | 3.2 | 4.9 | 2.8 | 0.7 | - | 37.5 | [42] |

Empty cells: no information available. (-) These products were not detected. * All values were approximated from the reported literature data.

## *S4. Ethanol and n-propanol production from $CO_2$ via liquid-phase electrochemical route*

Table S3**.** State-of-the-art performance of the production of ethanol and n-propanol from liquid-phase electrochemical $CO_2$ conversion.

| Electrocatalysts | Faradaic efficiency to Ethanol, % | Faradaic efficiency to n-Propanol, % | Total current density, mA $cm^{-2}$ | Cell configuration | Ref. |
|---|---|---|---|---|---|
| Graphene/$Cu_2O$/Cufoil | 9.9 | - | 5.3 | Two compartments 3-electrodes cell separated by a glass frit | 21 |
| Cu(100) | 9.7 | 1.5 | 5.0 | Traditional undivided 3 electrode cell | 22 |
| Polycrystalline Cu | 21.9 | - | 5.0 | Two compartments separated by Selemion | 23 |
| 3,6 μm film of $Cu_2O$ | 16.4 | - | 35.0 | Two compartments separated by Selemion | 24 |
| CuO/$TiO_2$ | 37.5 | 5.6 | 8.3 | H-type cell (Nafion 117) | 25 |
| $Cu_{63,9}Au_{36,1}$/NCF | 12.0 | - | - | H-type cell (Nafion 117) | 7 |
| Cu/N-Graphene | 63.0 | - | 2.8 | Two compartments separated by Selemion | 26 |
| Graphene/ZnO/$Cu_2O$/Cufoil | - | 30.0 | 8.0 | Two compartments cell separated by a glass frit | 27 |
| Cu nanocrystals | - | 10.6 | 16.4 | Two compartments separated by Selemion | 28 |
| Cu Nps/ Carbon paper x22.5 loading | 13.3 | 5.9 | 12.7 | Two compartments separated by Selemion | 29 |
| Cu/Graphene | 24.1 | 3.1 | 1.3 | Gas Diffusion electrode (Nafion 117) | 30 |
| CuO/$TiO_2$/Graphene | 43.6 | 3.3 | 1.4 | Gas Diffusion electrode (Nafion 117) | 30 |
| $Cu_{1ML}$/THH Pd NCs | 20.4 | - | 0.6 | H-type cell (Nafion 115) | 31 |
| Electrodeposited Cu onto Cu mesh | 10.0 | 13.0 | 10.0 (normalized to the ECSA) | H-type cell (Nafion 117) | 32 |
| $CuBi_9$ MOF | 17.0 | - | 20.0 | Two compartmentss (Nafion 117) | 33 |

| | | | | | |
|---|---|---|---|---|---|
| $CuBi_{12}$ MOF | 28.0 | - | 20.0 | Two compartmentss (Nafion 117) | [33] |
| Nanoporous Cu | 16.6 | 4.5 | 653.0 | Gas Diffusion electrode | [34] |
| Cu 25nm thickness | 11.0 | - | 275.0 | Flow cell reactor | [35] |
| $Ag_{0,14}/Cu_{0,86}$ /PTFE | 41.0 | - | 250.0 | Gas Diffusion electrode | [36] |
| Electrodeposited CuAg alloy | 25.0 | - | 300.0 | Flow cell reactor | [37] |
| Cu Nps/Carbon paper | 11.0 | 2.1 | 430.0 | Flow cell reactor | [38] |
| $Cu_2S$–Cu-V | 25.0 | 7.0 | 400.0 | Gas Diffusion electrode | [39] |
| 34% N-C/Cu/PTFE | 52.0 | 1.0 | 300.0 | Gas Diffusion electrode | [40] |
| $La_{1,8}Sr_{0,2}CuO_4$ | 30.5 | 10.0 | 180.0 | H-cell | [41] |
| Porous copper foam | - | 4.93 | 37.5 | H-cell | [42] |

## *S5. $CO_2$-to-alcohols via catholyte-free electrochemical route.*

Table S4**.** State-of-the-art performance of the production of alcohols from solvent-less electrochemical $CO_2$ conversion .

| Electrocatalysts | Relative FE to methanol, % | Relative FE to ethanol, % | Relative FE to n-Propanol, % | Total current density, mA $cm^{-2}$ | Cell configuration | Ref. |
|---|---|---|---|---|---|---|
| $Fe_{10}$-CNTox/GDL | 21.7 | 70.5 | 3.3 | 1.4 | Continuous gas-phase $CO_2$ electroreduction. MEA Configuration. | [47] |
| $Pt_{10}$-CNTox/GDL | 16.1 | 25.1 | 34.8 | 1.4 | Continuous gas-phase $CO_2$ electroreduction. MEA Configuration. | [47] |
| Cu-Graphite/C | 75.0 | - | - | 2.4 | Continuous gas-phase $CO_2$ electroreduction. MEA Configuration. | [48] |
| Cu-AC/C | 45.0 | - | - | 2.4 | Continuous gas-phase $CO_2$ electroreduction. MEA Configuration. | [48] |
| Cu-CNF/C | 2.5 | 2.0 | 2.5 | 2.4 | Continuous gas-phase $CO_2$ electroreduction. MEA Configuration. | [48] |
| Cu-CNF/C (PBI) | 5.0 | 2.0 | 0.2 | 1.6 | Continuous gas-phase $CO_2$ electroreduction. MEA Configuration. | [49] |
| Cu powder | 92.8 | - | - | 1.6 | Continuous gas-phase $CO_2$ electroreduction. MEA Configuration. | [50] |
| Cu_C powder | 14.1 | - | - | 1.6 | Continuous gas-phase $CO_2$ electroreduction. MEA Configuration. | [50] |
| Cu Oxide/ZnO | 0.2 | 0.2 | | 7.5 | Continuous gas-phase $CO_2$ electroreduction. MEA Configuration. | [51] |
| Pb/CNT | 6.3 | - | - | 16.0 | Continuous gas-phase | [52] |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | | | | $CO_2$ electroreduction. MEA Configuration. | |
| Cu(250nm)-C-G/PTFE | - | 20.3 | 5.4 | 150.0 | Continuous gas-phase $CO_2$ electroreduction. MEA Configuration. | [53] |
| Cu/$TiO_2$ NTs | 23.5 | - | - | 120.0 | Continuous Solid Polymer Electrolyte Membrane (SPE) Reactor | [54] |
| 34% N-C/Cu/PTFE | - | 56.5 | 2.7 | 160.0 | Continuous gas-phase $CO_2$ electroreduction. MEA Configuration. | [40] |
| Commercial $Cu_2O$ (solid-state electrolyte) | - | 7.0 | 7.0 | 90.0 | $CO_2$ electroreduction. MEA Configuration. | [55] |

***S6. Total Faradaic efficiencies of the best catholyte-free EC $CO_2R$ electrocatalysts***

| | Relative Faradaic efficiency, % | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Electrocatalysts | $CH_3OH$ | $C_2H_4O$ | $C_2H_5OH$ | $C_3H_6O$ | $C_3H_8O$ | $CH_3COOH$ | $CH_4$ | $C_2H_4O_2$ | CO | $C_2H_4$ | $HCOO^-$ /HCOOH | $J_{total}$, mA $cm^{-2}$ | Ref. |
| $Fe_{10}$-CNTox/GDL | 21.7 | 2.0 | 70.5 | 0.1 | 3.3 | 2.53 | - | - | - | - | - | 1.4 | 47 |
| $Pt_{10}$-CNTox/GDL | 16.1 | 19.8 | 25.1 | 0.2 | 34.8 | 4.1 | - | - | - | - | - | 1.4 | 47 |
| Cu-Graphite/C | 75.0 | 8.0 | - | 12.0 | - | - | 2.5 | 2.5 | - | - | - | 2.4 | 48 |
| Cu-AC/C | 45.0 | 48.0 | - | 5.0 | - | - | 1.0 | 1.0 | - | - | - | 2.4 | 48 |
| Cu-CNF/C | 2.5 | 70.0 | 2.0 | - | 2.5 | - | 5.0 | 12.0 | 10.0 | - | - | 2.4 | 48 |
| Cu-CNF/C (PBI) | 5.0 | 68.0 | 2.0 | - | 0.2 | - | 0.6 | 19.0 | 5.0 | - | - | 1.6 | 49 |
| Cu_25nm powder | - | - | - | - | - | - | 2.1 | - | 0.1 | 97.8 | - | 7.5 | 56 |
| Cu powder | 92.7 | 1.9 | - | - | - | - | 5.3 | - | - | - | - | 1.6 | 50 |
| Cu_C powder | 14.1 | 60.7 | - | - | - | - | 25.8 | - | - | - | - | 1.6 | 50 |
| Cu Oxide/ZnO | 0.2 | - | 0.2 | 0.2 | - | - | 0.5 | - | 0.3 | 98.5 | - | 7.5 | 51 |
| Pb/CNT | 6.3 | - | - | - | - | - | 34.4 | - | 9.4 | - | 50.0 | 16.0 | 52 |
| Cu(250nm)-C-G/PTFE | - | - | 20.3 | - | 5.4 | 6.7 | - | - | 13.5 | 54.1 | - | 150.0 | 53 |
| Cu/$TiO_2$ NTs | 23.5 | - | - | - | - | - | 17.6 | - | 58.8 | - | - | 120.0 | 54 |
| 34% N-C/Cu/PTFE | - | - | 56.5 | - | 2.7 | 2.7 | - | - | - | 38.0 | - | 160.0 | 40 |
| Commercial $Cu_2O$ (solid-state electrolyte) | - | - | 7.0 | - | 7.0 | 1.4 | - | - | 35.2 | 28.2 | 21.1 | 90.0 | 55 |

(-) These products were not detected.

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