Supporting Information

Revealing Transport Kinetics for Efficient Electrochemical Conversion of Captured CO_2 in Amine Solutions

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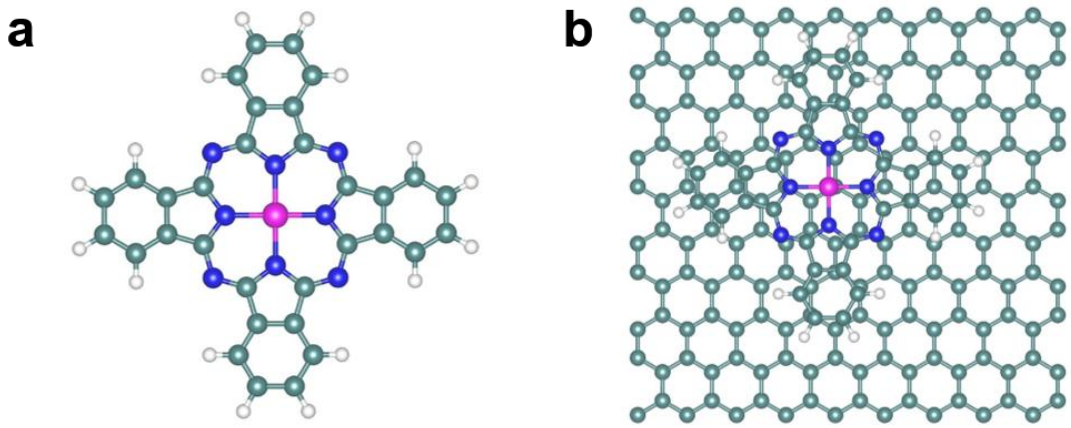

Figure S1. The structures of (a) CoPc and (b) CoPc/CB for DFT calculations. The green, blue, pink, and white balls denote C, N, Co, and H atoms, respectively.

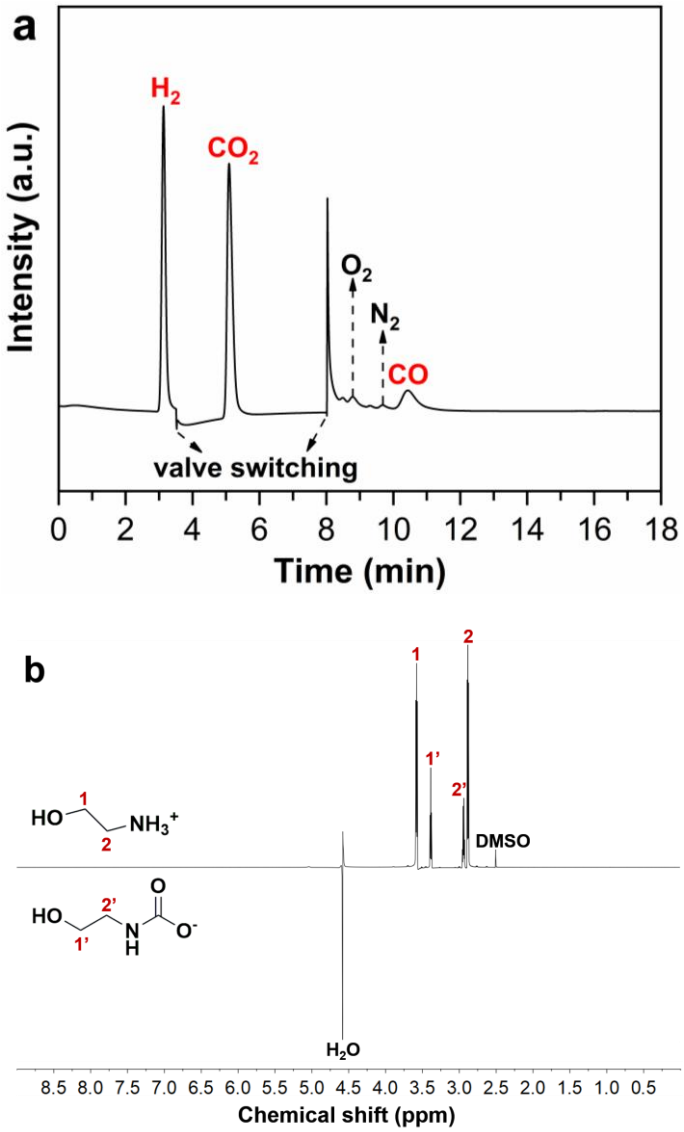

Figure S2. (a) Gas chromatogram of the gaseous products and (b) ^{1}H NMR spectrum of the electrolyte solution after electrolysis of CO_2-loaded 2 M MEA at –0.85 V vs RHE for 15 min using CoPc/CB catalyst. Since the concentration of MEA-derived species is too high, the electrolyte is diluted with ultrapure water for 10 times before ^{1}H NMR measurement.

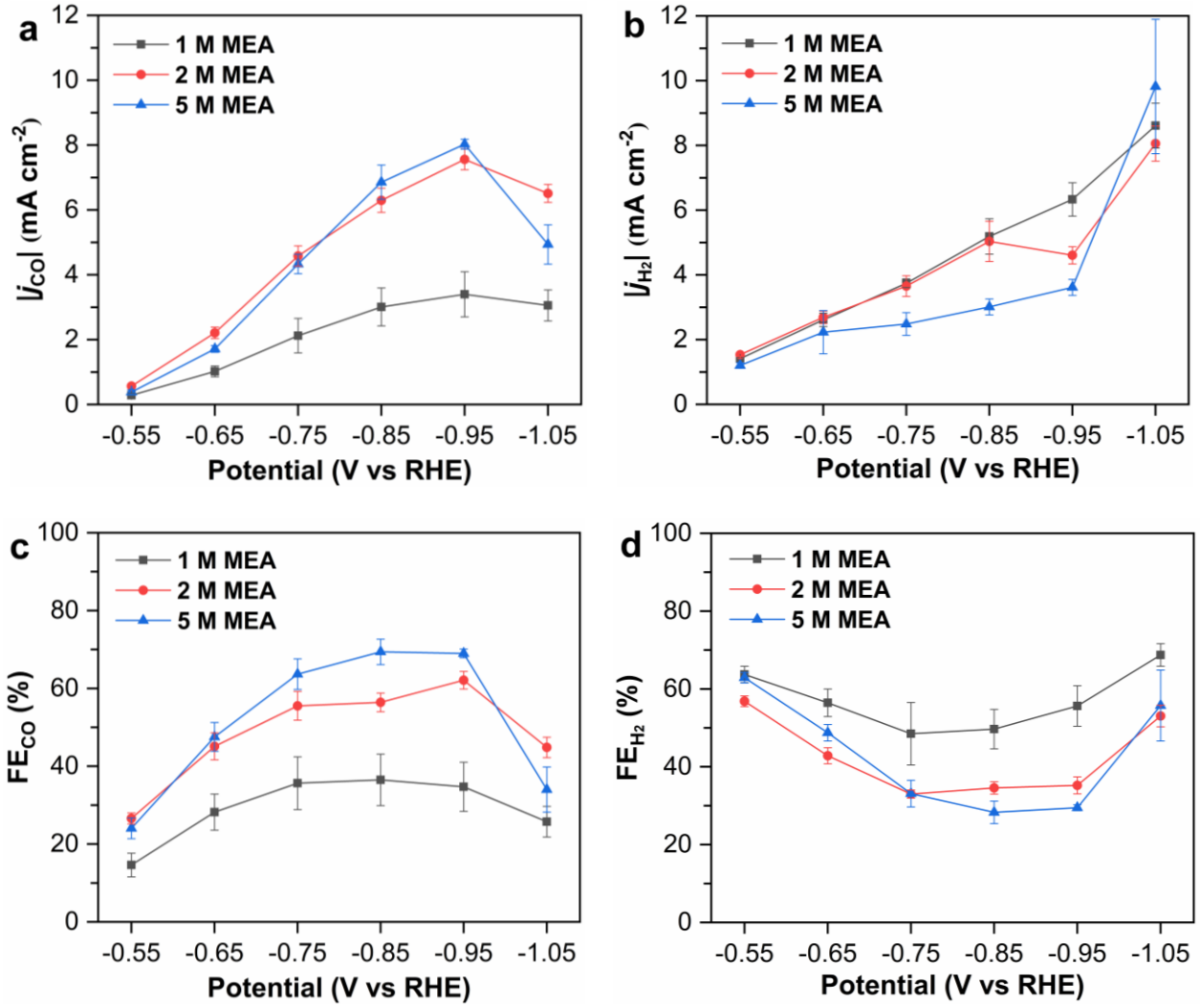

Figure S3. (a) $|j_{CO}|$, (b) $|j_{H2}|$, (c) FE_{CO}, and (d) FE_{H2} recorded for the electrolysis of captured CO_2 in MEA solutions of varying concentrations using CoPc/CB catalyst.

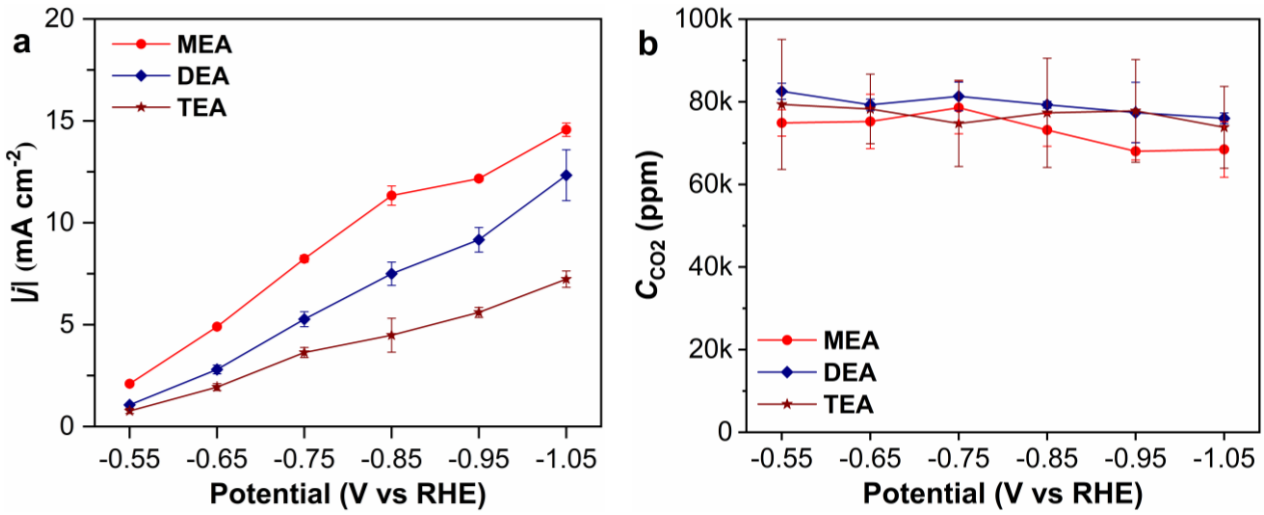

Figure S4. (a) $|j|$ and (b) concentrations of CO_2 in the headspace recorded for the electrolysis of CO_2-loaded 2 M MEA, DEA, and TEA solutions using CoPc/CB catalyst.

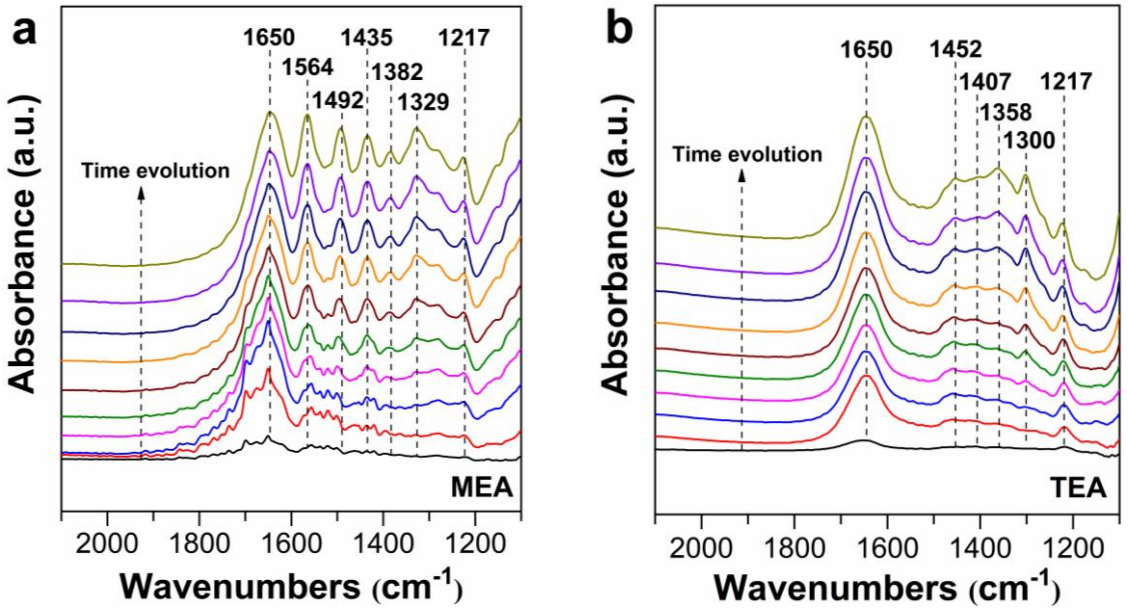

Figure S5. *In-situ* ATR-FTIR recorded during the process of CO_2 capture in 2 M (a) MEA and (b) TEA solutions for 30 min.

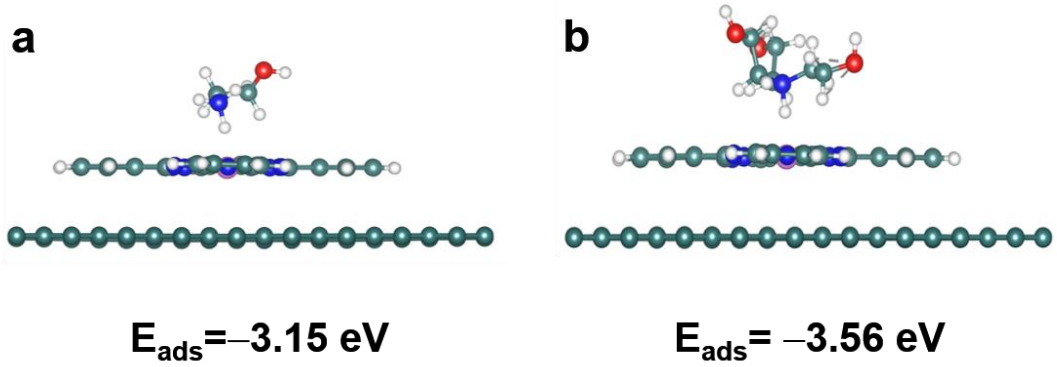

Figure S6. E_{ads} of (a) MEA-H^+ and (b) TEA-H^+ on the Co active site. The green, blue, red, and white balls denote C, N, O, and H atoms, respectively.

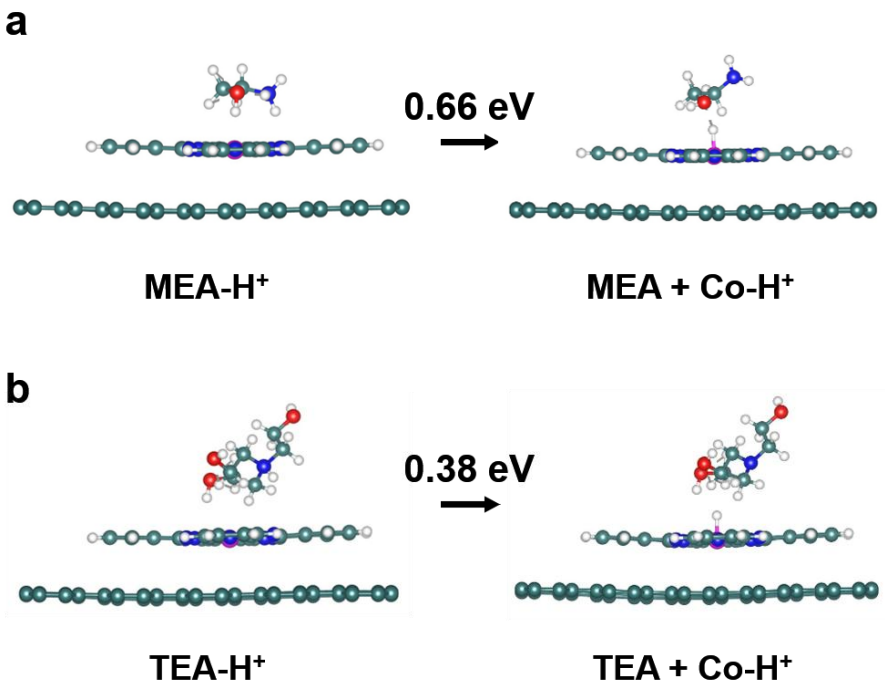

Figure S7. The energy required for H transferred from (a) MEA-H^+ and (b) TEA-H^+ to the Co active site. The green, blue, red, and white balls denote C, N, O, and H atoms, respectively.

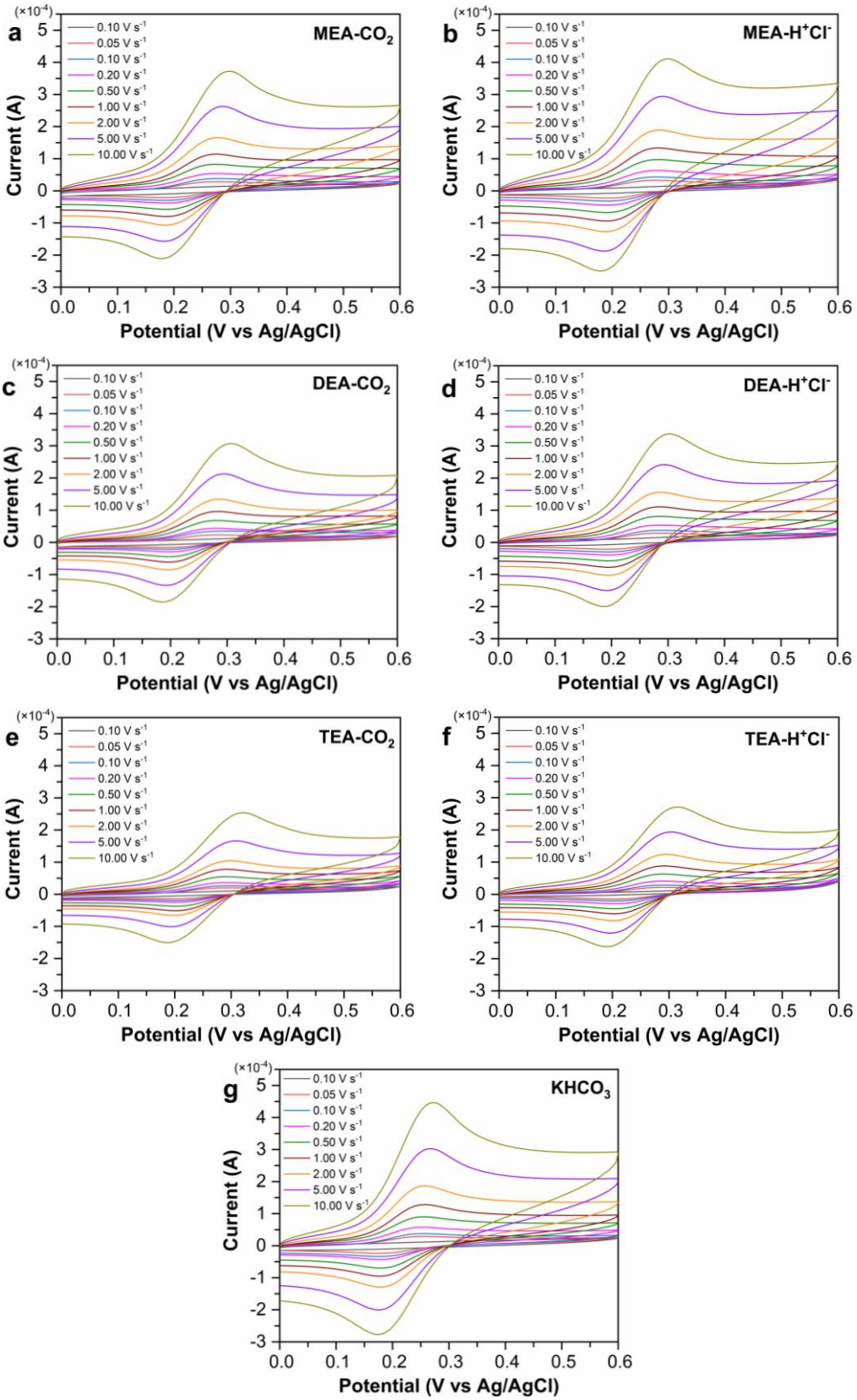

Figure S8. Cyclic voltammograms recorded in (a,c,e) CO_2-loaded 2 M amine solutions, (b,d,f) ammonium chloride solutions of the corresponding amines, and (g) 2 M $KHCO_3$ solution at differernt scan rates.

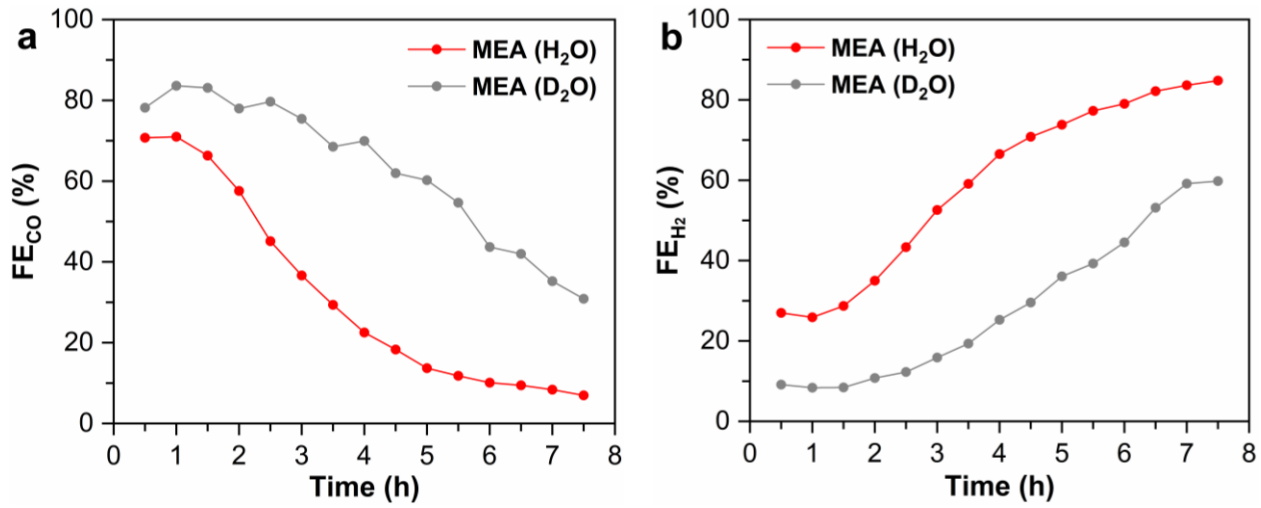

Figure S9. (a) FE_{CO} and (b) FE_{H2} recorded for the prolonged electrolysis of captured CO_2 in 2 M MEA at –0.85 V vs RHE using CoPc/CB catalyst and H_2O or D_2O as solvent.

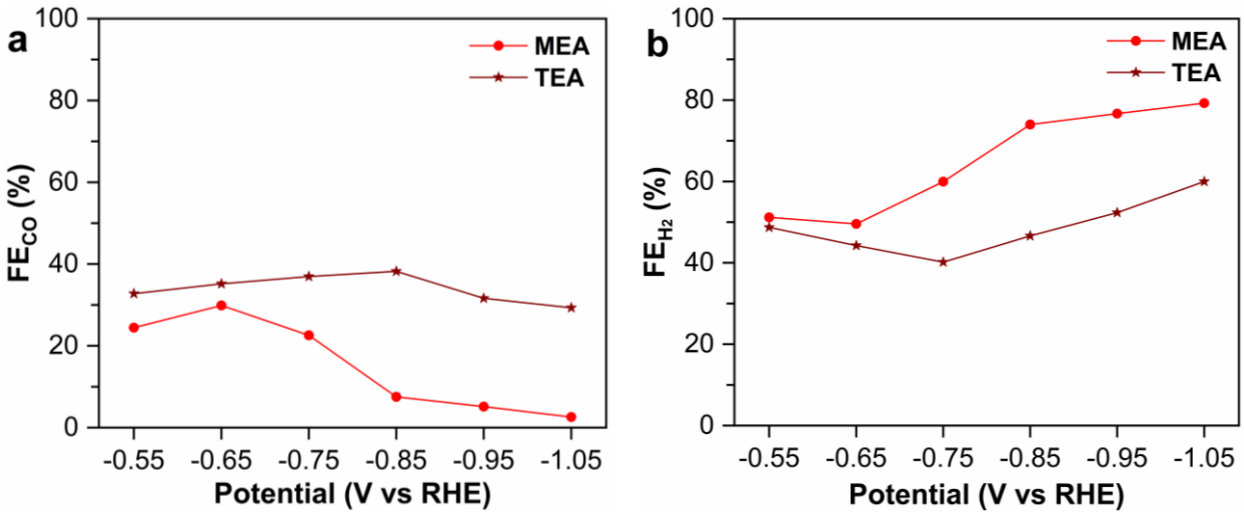

Figure S10. (a) FE_{CO} and (b) FE_{H2} recorded for the electrolysis of captured CO_2 in 2 M MEA and TEA solutions using Ni–N–C catalyst.

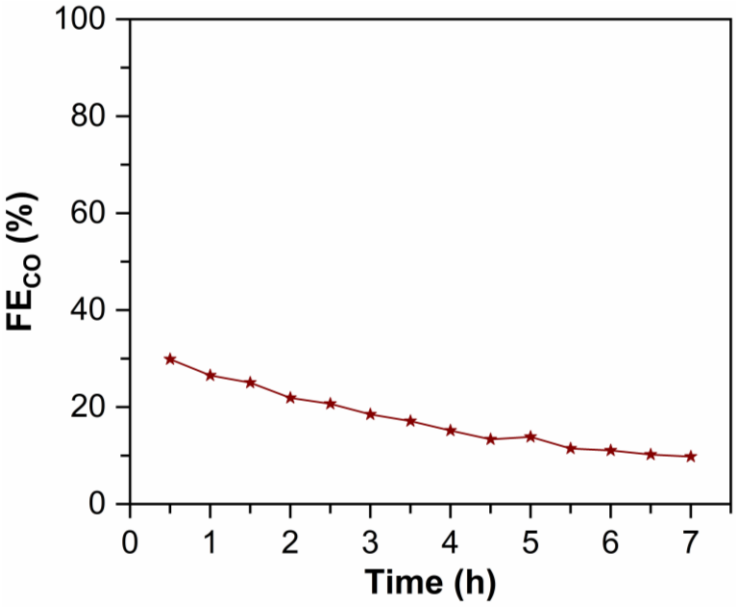

Figure S11. FE_{CO} recorded for the prolonged electrolysis of captured CO_2 in 2 M TEA solution at −0.85 V vs RHE using Ni–N–C catalyst.

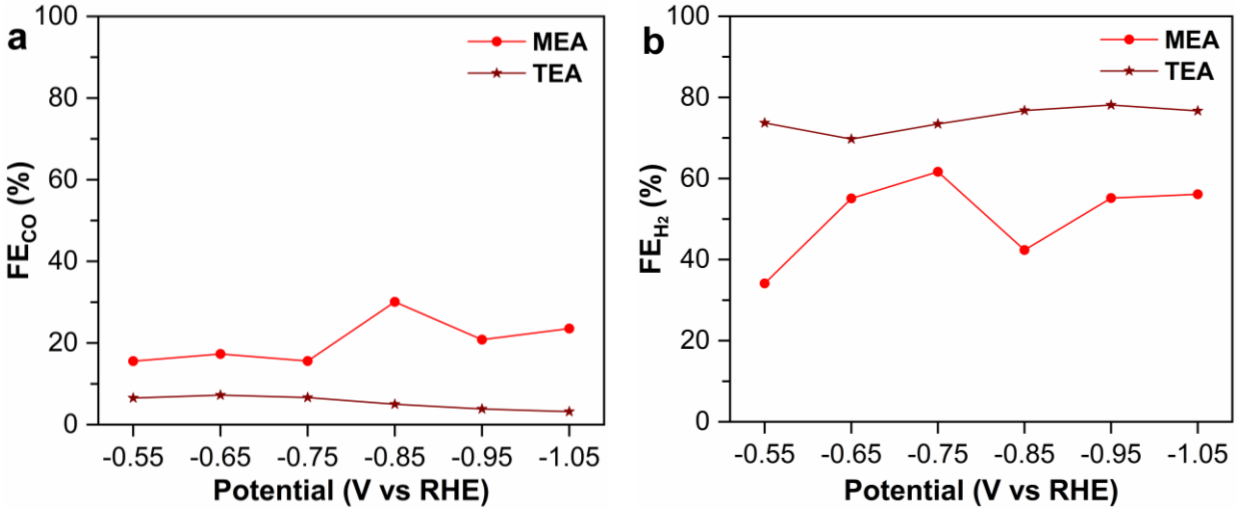

Figure S12. (a) FE_{CO} and (b) FE_{H2} recorded for the electrolysis of captured CO_2 in 2 M MEA and TEA solutions using Ag catalyst.

Table S1. The pH values of various amine solutions.

Amine solutions	pH
2 M MEA	12.04
CO_2-loaded 2 M MEA	7.45
Ar-purged CO_2-loaded 2 M MEA	7.64
2 M DEA	11.55
CO_2-loaded 2 M DEA	7.53
Ar-purged CO_2-loaded 2 M DEA	7.76
2 M TEA	10.93
CO_2-loaded 2 M TEA	7.53
Ar-purged CO_2-loaded 2 M TEA	7.71

Table S2. Performance comparison for electrochemical conversion of captured CO_2 in various amine solutions within an H-cell.

Catalyst	Electrolyte (pH)	FE_{CO}[a] (%)	$\|j\|$[b] (mA cm^{-2})	Potential[c]	Ref.
CoPc/CB	Ar-purged CO_2-loaded 2 M MEA (7.64)	69	12.2	–0.95 V vs RHE	This work
	Ar-purged CO_2-loaded 2 M DEA (7.76)	76	7.5	–0.85 V vs RHE	
	Ar-purged CO_2-loaded 2 M TEA (7.71)	80	4.5	–0.85 V vs RHE	
Ag	N_2-purged CO_2-loaded 2 M MEA + 3 M KCl (8.3)	38	N. A.	–0.66 V vs RHE	S1
Ag	N_2-purged CO_2-loaded 2 M KCl + 2 M MEA (7.6)	19	30	–0.85 V vs RHE[d]	S2
Ni–N/C	Ar-purged CO_2-loaded 1 M MEA (pH not reported)	78	1.7[e]	–0.58 V vs RHE	S3
	Ar-purged CO_2-loaded 1 M DEA (pH not reported)	65	1.5[e]	–0.64 V vs RHE	
$Ni(cyclam)Cl_2$	Ar-purged CO_2-loaded 0.1 M MEA + 0.05 M phosphate (7.9)	77	1.41	–0.74 V vs RHE[d]	S4
	Ar-purged CO_2-loaded 0.1 M DEA + 0.05 M phosphate (8.0)	41	1.42	–0.74 V vs RHE[d]	

[a] Maximum FE_{CO} under reported conditions. [b] Current density achieved at the listed potential. [c] The electrolysis potential at which the maximum FE_{CO} achieved. [d] Potentials converted from reported potentials against SHE or Ag/AgCl according to the pH of electrolyte in the reference. [e] $|j|$ calculated from the reported $|j_{CO}|$ and FE_{CO} in the reference. N. A. denotes data not available.

Table S3. The coefficients of viscosity for different CO_2-loaded amine solutions.

Electrolyte	Coefficient of viscosity (mPa·s)
CO_2-loaded 1 M MEA	1.0
CO_2-loaded 2 M MEA	1.1
CO_2-loaded 5 M MEA	2.0
CO_2-loaded 2 M DEA	1.4
CO_2-loaded 2 M TEA	1.8

References

S1. G. Lee, Y. C. Li, J.-Y. Kim, T. Peng, D.-H. Nam, A. Sedighian Rasouli, F. Li, M. Luo, A. H. Ip, Y.-C. Joo and E. H. Sargent, Electrochemical upgrade of CO_2 from amine capture solution, *Nat. Energy*, 2020, **6**, 46-53.

S2. G. Leverick, E. M. Bernhardt, A. I. Ismail, J. H. Law, A. Arifutzzaman, M. K. Aroua and B. M. Gallant, Uncovering the active species in amine-mediated CO_2 reduction to CO on Ag, *ACS Catal.*, 2023, **13**, 12322-12337.

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