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# Supporting Information

## Effects of Temperature on Amine-Mediated CO<sub>2</sub> Capture and Conversion in Li Cells

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## Experimental Methods

**Materials** – All chemicals, electrodes, and cell-making materials were dried prior to use and stored in an argon-filled glovebox (MBRAUN, H<sub>2</sub>O < 0.1 ppm and O<sub>2</sub> < 0.1 ppm). Tetraethylene glycol dimethyl ether (TEGDME, > 99.9%), dimethyl sulfoxide (DMSO, > 99.9%), and lithium perchlorate (LiClO<sub>4</sub>, battery grade, 99.9% metals basis) were purchased from Sigma Aldrich. 2-ethoxyethylamine (EEA, CAS Registry Number 110-76-9, 99%, TCI America) was purchased from Fisher Scientific and diisopropylamine (DIPA, >99%) was purchased from Sigma Aldrich. Both amines were used as received. Prior to use, LiClO<sub>4</sub> was dried for 24 hours under active vacuum in a glass oven (Buchi) at 120 °C and was transferred to the glovebox without exposure to ambient. All solvents were dried over molecular sieves (Type 3Å, Sigma Aldrich) inside the glovebox for at least 48 hours at room temperature. The molecular sieves had been previously dried under active vacuum in the glass oven at 200°C for a minimum of 24 hours prior to their transfer into the glovebox. The water content in the electrolyte was measured using a Karl Fisher titrator (Mettler Toledo) and was typically found to be < 18 ppm.

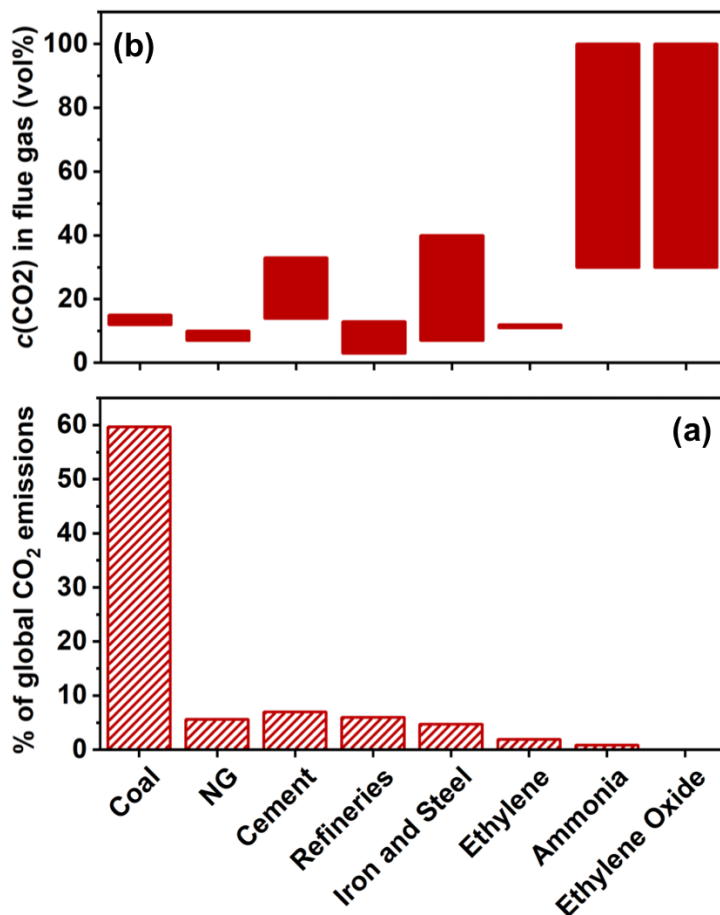
**ATR-IR spectroscopy** – Discharged electrodes were rinsed with 1,2 dimethoxyethane (DME) and subsequently dried under Ar. After being sealed in glass vials inside the glovebox, the samples were transferred outside for FTIR measurements on a Nicolet 6700 FT-IR spectrometer (Thermo Scientific). All measurements were performed in transmission mode over a wavenumber range of 650 to 4000 cm<sup>-1</sup> using a Germanium (Ge) crystal.

**Scanning Electron Microscopy (SEM)** - Discharged electrodes were rinsed with 1,2 dimethoxyethane (DME) and subsequently dried under Ar and sealed in a glass vial inside the glovebox. Prior to imaging, the sealed vial was opened and the sample was quickly transferred (<1 min.) to the SEM chamber. All images were collected using a Zeiss Merlin High-resolution SEM operating at an accelerating voltage of 5 kV and beam current of 100 pA.

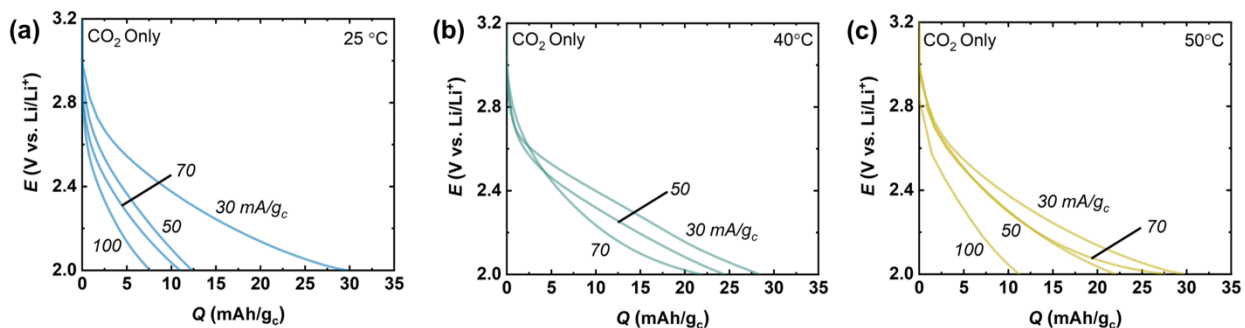
**<sup>1</sup>H NMR**– Room temperature (RT) and variable-temperature (VT) <sup>1</sup>H NMR measurements were performed using Bruker Avance Neo spectrometers operating at 400.17 MHz and 500.18 MHz, respectively. Both systems were equipped with a 5 mm BBFO Smart Probe. The equilibrium proportion of carbamate at varying temperatures was determined from the VT <sup>1</sup>H NMR spectra using a quantification method reported previously.<sup>1</sup> Note that RT <sup>1</sup>H NMR measurements in this study were typically performed on previously aged electrolyte solutions containing 0.1 M EEA-CO<sub>2</sub>. These were prepared by heating small electrolyte volumes (1-2 mL) over a hot plate maintained at a fixed temperature (40°C-130°C) for 24 hours inside an Ar glovebox. The samples were then subsequently cooled to room-temperature, prior to being analyzed via <sup>1</sup>H NMR. All NMR measurements were conducted using capped Wilmad NMR tubes (528-PP-7), each containing a typical electrolyte sample volume of ~700 μL.

**Cyclic Voltammetry Measurements** – Cyclic voltammetry measurements were conducted in a hermetically sealed Mbraun glovebox using a 3-electrode electrolysis-type cell containing a fritted Pt counter electrode, a fritted, nonaqueous AgNO<sub>3</sub> reference electrode (Ag wire immersed in 0.1 M TBAClO<sub>4</sub> / 0.01 M AgNO<sub>3</sub> in acetonitrile), and a carbon Super-P coated (preparation details reported elsewhere)<sup>1</sup> glassy carbon (GC, Pine, A = 0.196 cm<sup>2</sup>) mounted to a Modulated Speed Rotator (Pine) working electrode. Prior to measurement with Li<sup>+</sup>-containing electrolyte, the potential of the fritted, non-aqueous Ag/Ag<sup>+</sup> reference electrode relative to Li/Li<sup>+</sup> was measured by immersing a piece of Li foil in neat electrolyte (0.3 M LiClO<sub>4</sub> in TEGDME) and monitoring the potential of Li metal vs. Ag/Ag<sup>+</sup> for approximately 20 minutes until the potential stabilized. At that point, the potential difference between the reference electrode and Li/Li<sup>+</sup> was measured, and was typically found to be around  $0 V_{Li} = -3.26 V$  vs. Ag/Ag<sup>+</sup>. Furthermore, note the prior to performing CV in the presence of DIPA-CO<sub>2</sub>, the electrolyte (0.1 M DIPA in 0.3 M LiClO<sub>4</sub>/TEGDME) was purged with CO<sub>2</sub> and rested for several hours before being re-saturated with CO<sub>2</sub> to ensure a CO<sub>2</sub> headspace before the measurement began.

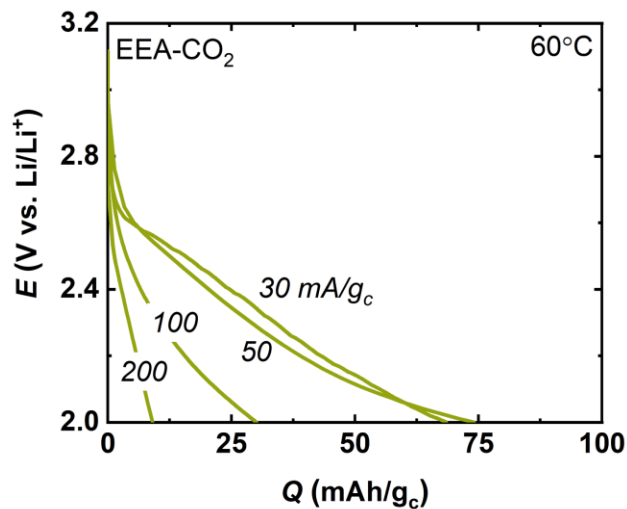
## Supplementary Figures



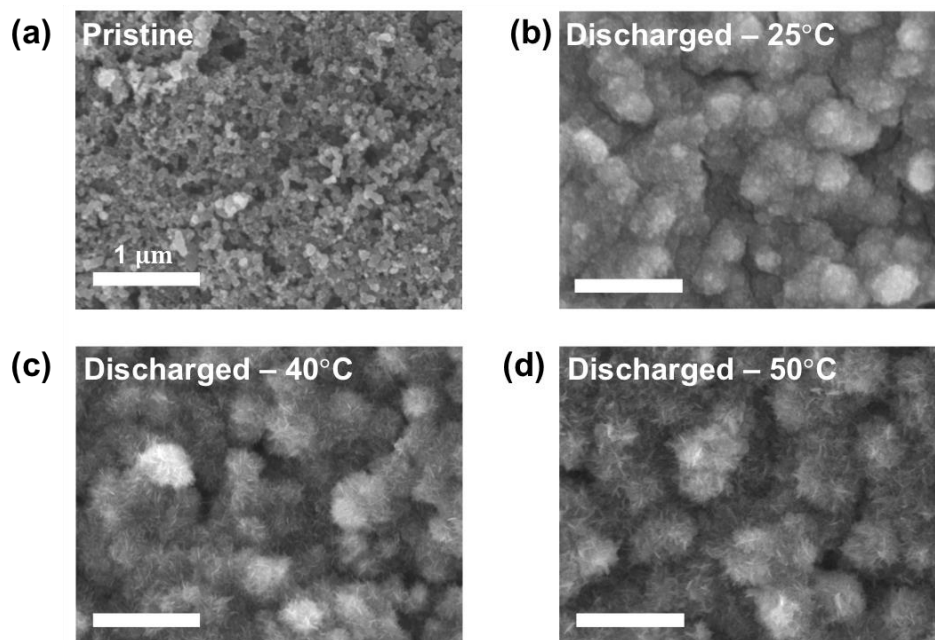
**Figure S1:** (a) Percentage contribution of various CO<sub>2</sub>-emitting processes to the global CO<sub>2</sub> emissions. (b) Carbon dioxide concentrations (vol%) in flue gases emitted from various processes.<sup>2-4</sup>



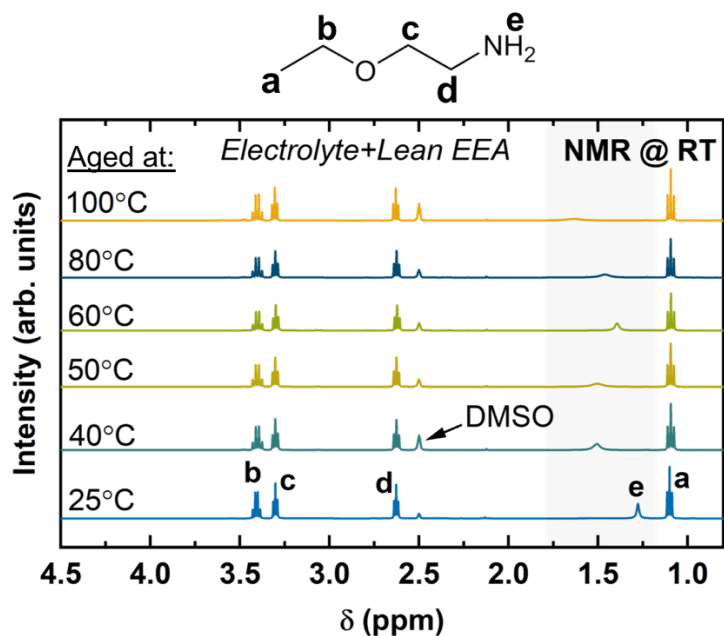
**Figure S2:** Discharge profiles of Li-CO<sub>2</sub> cells containing 0.3 M LiClO<sub>4</sub>/DMSO electrolyte (no amine) at (a) 25 °C, (b) 40 °C, and (c) 50 °C over a range of current densities.



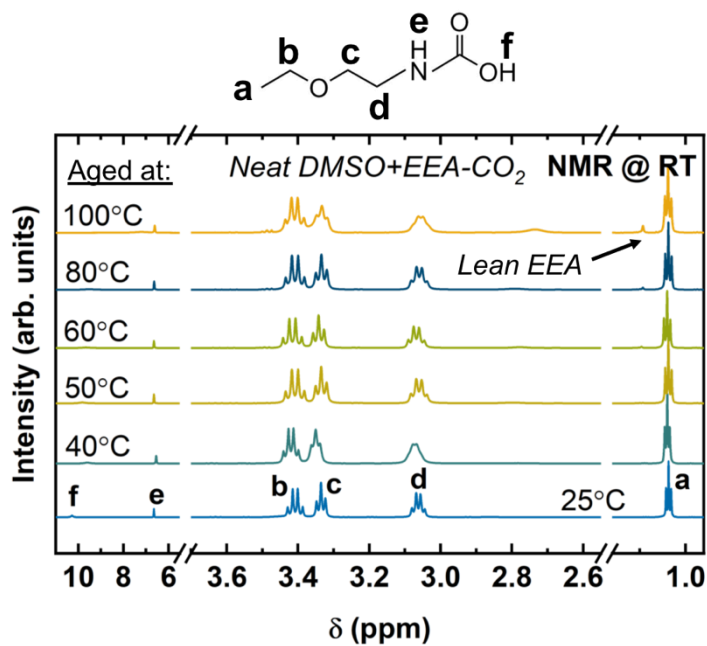
**Figure S3:** Zoomed-in view of Figure 3d. Discharge profiles of Li-CO<sub>2</sub> cells containing 0.1 M EEA-CO<sub>2</sub> in a DMSO-based electrolyte at 60°C over a range of current densities (30 – 200 mA/g<sub>c</sub>).



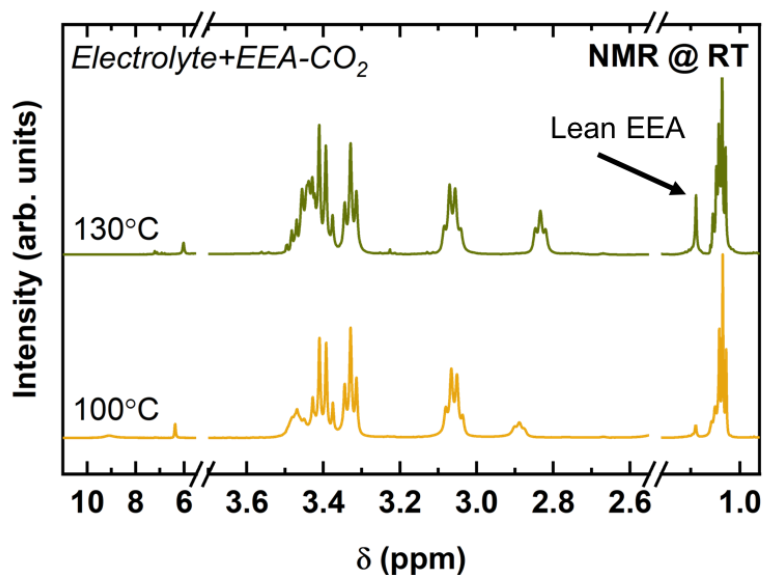
**Figure S4:** SEM images of (a) pristine electrode, and electrodes discharged at (b) 25°C, (c) 40°C, and (d) 50°C at a fixed rate of 70 mA/g<sub>c</sub>.



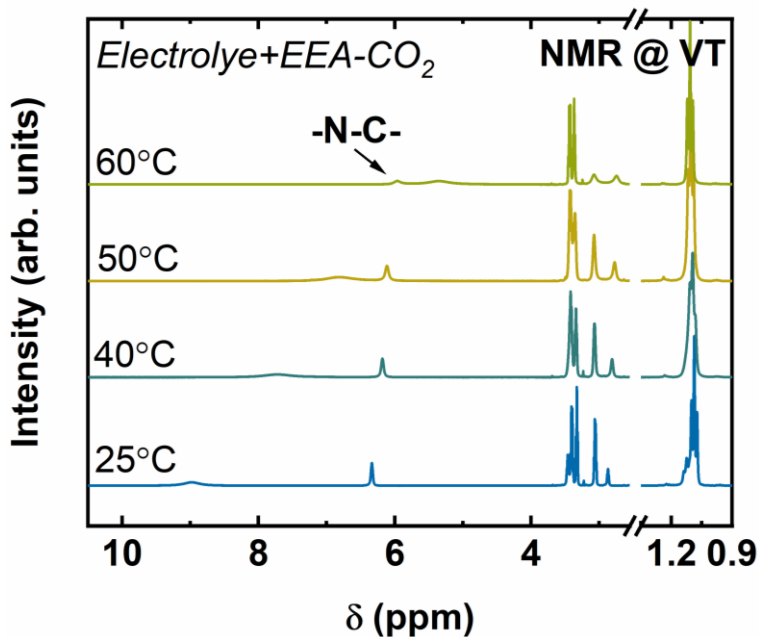
**Figure S5:** Room-temperature  $^1\text{H}$  NMR spectra of solutions containing 50 mM lean EEA (no  $\text{CO}_2$ ) in 0.3 M  $\text{LiClO}_4/\text{DMSO-d}_6$  after heating at the specified temperature for 24 hours.



**Figure S6:** Room-temperature  $^1\text{H}$  NMR spectra of solutions containing 50 mM EEA- $\text{CO}_2$  in  $\text{DMSO-d}_6$  (no  $\text{Li}^+$  salt) after aging at the specified temperature for 24 hours.

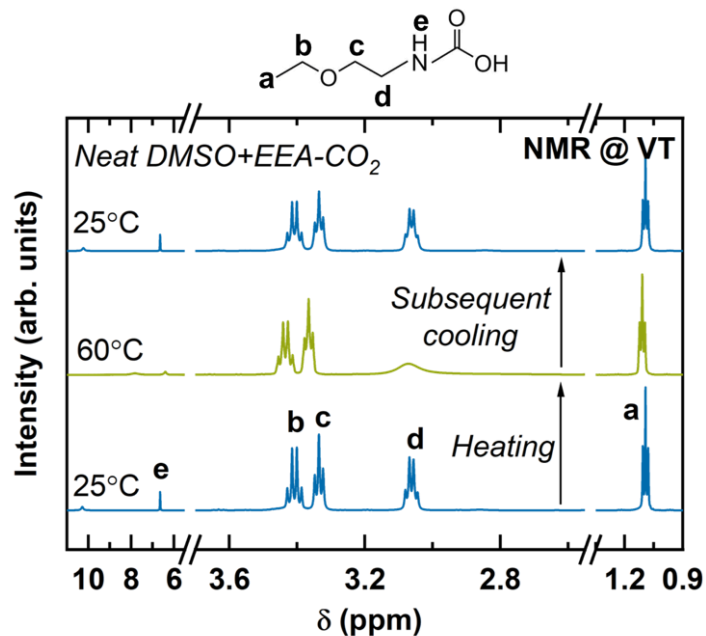


**Figure S7:** (a) Room-temperature  $^1\text{H}$  NMR spectra of solutions containing 50 mM EEA- $\text{CO}_2$  in 0.3 M  $\text{LiClO}_4/\text{DMSO-d}_6$  after 24-hour aging at 100°C and 130°C.

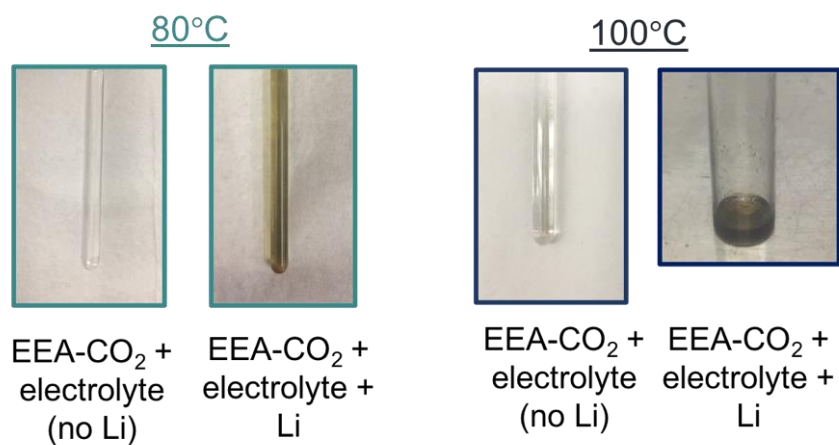


**Figure S8:** Zoomed-in view of Figure 4b in the range  $4 \text{ ppm} < \delta < 11 \text{ ppm}$ . Variable-temperature (VT)  $^1\text{H}$  NMR spectra of solutions containing 50 mM  $\text{CO}_2$ -loaded EEA in  $\text{DMSO-d}_6$  24 hours after the addition of 0.3 M  $\text{LiClO}_4$ .

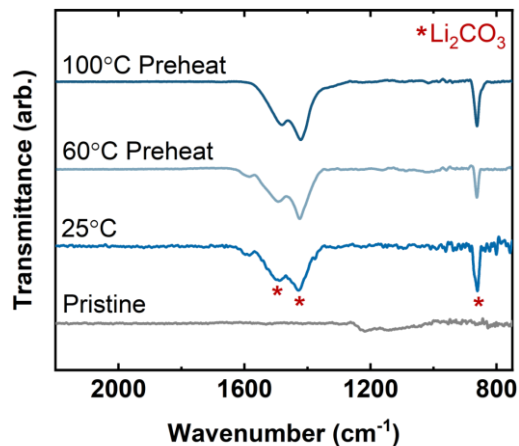




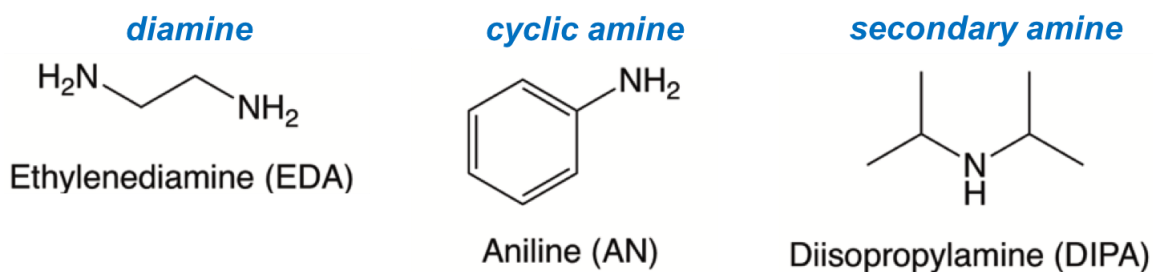
**Figure S9:** Variable-temperature (VT)  $^1\text{H}$  NMR spectra of deuterated electrolyte containing 50 mM  $\text{CO}_2$ -loaded EEA in  $\text{DMSO-d}_6$  that was first heated from  $25^\circ\text{C}$  (bottom) to  $60^\circ\text{C}$  (middle), and then was subsequently cooled back down to  $25^\circ\text{C}$  (top).



**Figure S10:** Photographs of electrolyte ( $0.3\text{ M LiClO}_4/\text{DMSO-d}_6$ ) containing  $50\text{ mM EEA-CO}_2$  after 24-hour aging at the specified temperatures in the absence and presence of PC-stabilized Li.



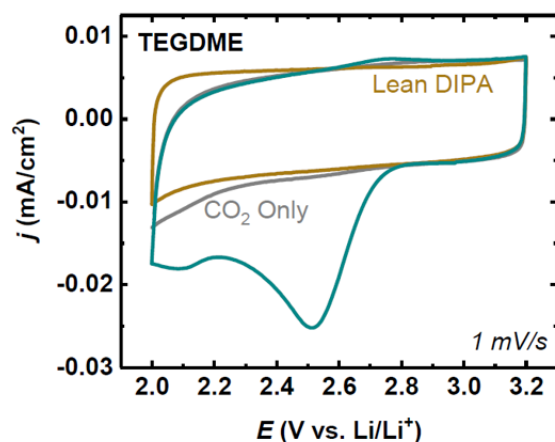
**Figure S11:** ATR-IR spectra of a pristine Vulcan Carbon electrode, and electrodes discharged at 50 mA/g<sub>c</sub> at room temperature using electrolytes that had been aged for 24 hours at the indicated temperature.



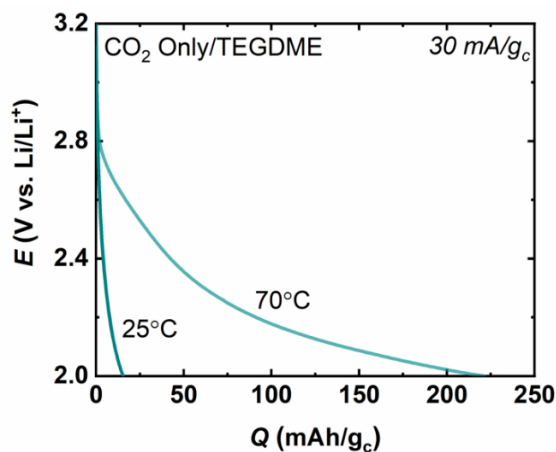
**Figure S12:** Chemical structures of ethylenediamine (EDA), aniline (AN), and diisopropylamine (DIPA).

Electrolyte containing 0.3 M LiClO <sub>4</sub> with:	Solvent	
	DME	TEGDME
0.1 M DIPA- CO <sub>2</sub>	<p>(a)</p>	<p>(b)</p>

**Figure S13:** Photographs showing solutions containing 0.1 M DIPA-CO<sub>2</sub> and 0.3 M LiClO<sub>4</sub> in (a) DME and (b) TEGDME.



**Figure S14:**  $iR$ -corrected cyclic voltammograms at 1 mV/s in a 3-electrode cell containing 0.1 M DIPA- $\text{CO}_2$  and 0.3 M  $\text{LiClO}_4/\text{TEGDME}$ . The background scans with Ar-saturated electrolyte containing either lean DIPA (no  $\text{CO}_2$ ) or  $\text{CO}_2$  only-saturated electrolytes (no DIPA) are provided as a reference. The working electrode used in all cases was a super P-coated glassy carbon (GC) electrode. Current densities are normalized to the GC geometric surface area ( $0.196 \text{ cm}^2$ ).



**Figure S15:** Discharge profiles of Li- $\text{CO}_2$  cells containing 0.3 M  $\text{LiClO}_4/\text{TEGDME}$  electrolyte (no amine) at  $25^\circ\text{C}$  and  $70^\circ\text{C}$  at  $30 \text{ mA/g}_c$ .



**Figure S16:** Photograph of Li metal anode post discharge with DIPA- $\text{CO}_2$  in 0.3 M  $\text{LiClO}_4/\text{TEGDME}$  at  $70^\circ\text{C}$ .

## References:

1. Khurram, A.; Yan, L.; Yin, Y.; Zhao, L.; Gallant, B. M., Promoting Amine-Activated Electrochemical CO<sub>2</sub> Conversion with Alkali Salts. *J. Phys. Chem. C* **2019**, *123* (30), 18222-18231.
2. Rubin, E.; De Coninck, H., IPCC special report on carbon dioxide capture and storage. UK: Cambridge University Press. *TNO (2004): Cost Curves for CO<sub>2</sub> Storage, Part* **2005**, *2*, 14.
3. Zakkour, P.; Cook, G., CCS Roadmap for Industry: High-purity CO<sub>2</sub> sources. *Carbon Counts Company Ltd: UK* **2010**.
4. Wiley, D. E.; Ho, M. T.; Bustamante, A., Assessment of opportunities for CO<sub>2</sub> capture at iron and steel mills: an Australian perspective. *Energy Procedia* **2011**, *4*, 2654-2661.