Supporting Information

Discovery of Organic Catalysts Boosting Lithium Carbonate Decomp osition toward Ambient Air Operational Lithium-Air Battery

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Figure S1. Schematic illustration of the three-electrode system for RM-catalyzed Li_2CO_3 decomposition test. The RM is oxidized near the working electrode surface. The oxidized RM (RM^{ox}) then freely diffuses and chemically oxidizes pre-loaded Li_2CO_3 through spontaneous hole-electron transfer. Each RM candidate (10 mM) was added to the conventional Li-air electrolyte (1M LiTFSi in TEGDME) with a total volume of 3 ml.



Figure S2. SEM images of Li_2CO_3 before (top) and after (bottom) size-reduction process. The anti-solvent precipitation method can homogeneously reduce the particle size of bulk Li_2CO_3 to a nano-scale (approximately 250 nm in diameter).



Figure S3. XRD patterns of Li_2CO_3 particles before (black) and after (red) anti-solvent precipitation. Characteristic peaks ($2\theta = 21.3^\circ$, 30.6° and 31.8°) of Li_2CO_3 remained unchanged after particle size reduction.



Figure S4. Galvanostatic charge profiles of RM-free cell with and without Li_2CO_3 . The charge process was conducted at a current rate of 0.5 mA within the voltage range of 2.8-4.4 V (vs. Li/Li^+). Only a slight increase in charge capacity was observed after loading Li_2CO_3 on the porous carbon electrode, indicating that Li_2CO_3 barely decomposed in the RM-free condition.



Figure S5. Galvanostatic charge/discharge profiles of MPTZ (a), TMPD (b), DMPZ (c), and DBB (d) cells and same cells using porous carbon electrodes upon 10 cycles at a current rate of 0.5 mA. When charging the Li_2CO_3 -preloaded electrode, all cells exhibited an extended charge plateau near the intrinsic redox potential of each RM (3.71, 3.73, 3.92, and 4.18 V vs. Li/Li^+ for MPTZ, TMPD, DMPZ, and DBB, respectively).



Figure S6. XRD patterns of Li_2CO_3 -preloaded electrodes retrieved from DMPZ (red) and TMPD (green) cells after being cycled within a limited voltage range below 3.5 V (vs. Li/Li⁺). Both electrodes showed no significant changes in characteristic peaks of Li_2CO_3 (30.6°, 31.8°, and 34.15°) compared to the XRD spectra of the electrode retrieved from the RM-free cell.



Figure S7. TOF-SIMS ${}^{6}\text{Li}^{+}$ intensity map for the Li₂CO₃-preloaded electrode retrieved from DMPZ cell after 10 galvanostatic cycles. After being cycled within a voltage range of 2.8-3.5 (V vs. Li/Li⁺), the DMPZ cell showed negligible decreases in ${}^{6}\text{Li}^{+}$ intensity compared to the RM-free cell, in which Li₂CO₃ decomposition barely occurred.



Figure S8. (a-h) EDS mappings of oxygen distribution on Li_2CO_3 -preloaded electrodes after galvanostatic cycling under various electrolyte conditions and voltage limits. Signal intensities for the oxygen atom decreased in the order of MPTZ > DBB > DMPZ > TMPD cells compared to that of the RM-free cell. Negligible decreases in oxygen content were observed in DMPZ and TMPD when cycled within a limited voltage range of 2.8-3.5 (V vs. Li/Li⁺), demonstrating the critical role of redox couples above 3.7 V in decomposing Li₂CO₃.



Figure S9. Galvanostatic charge/discharge profiles of DMPZ cell in two-electrode configuration using 8 mM DMPZ in 1M LiTFSi/TEGDME (100 ul) as the electrolyte and bare Li as the anode. DMPZ cell was cycled at a current rate of 0.146 mA cm⁻². The charge capacity exceeds the theoretical limit of the cell (44 uAh) due to the shuttle behavior of DMPZ: the oxidized DMPZ is constantly reduced by the Li anode during charging.



Figure S10. Initial charge profiles of MPTZ (a), DBB (b), DMPZ (c), and TMPD (D) cells and same cells using porous carbon electrodes in two-electrode configuration at a current rate of 0.146 mA cm⁻². All cells showed an extended charge plateau near the redox potential of each RM (3.71, 3.73, 3.92, and 4.18 V vs. Li/Li⁺ for MPTZ, TMPD, DMPZ, and DBB, respectively). The capacities from each cell were normalized by the input weight of corresponding RMs. The theoretical capacities (based on intrinsic oxidation reactions of RMs) are 125, 107, 254, and 326 mAh/g for MPTZ, DBB, DMPZ, and TMPD, respectively.



Figure S11. In-situ DEMS profiles of DMPZ (a) and TMPD (b) cells with gas evolution for H_2 , ¹³CO₂, and ¹²CO₂ upon charging to 4.3 V (vs. Li/Li⁺) at a current density of 0.146 mA cm⁻². The TMPD cell showed H_2 evolution when charged above 3.2 V (vs. Li/Li⁺), while the DMPZ cell produced a negligible H_2 gas during the charging process.



Figure S12. Galvanostatic charge/discharge profiles of DMPZ (a) and TMPD (b) cells using porous carbon cathode and pretreated Li anode (at 1st, 2nd, 5th, 10th, and 20th cycles) at a current rate of 0.146 mA cm⁻². (c) Accumulated discharge capacity retention of DMPZ and TMPD cells for 100 cycles. TMPD cell showed a rapid decrease in discharge capacity during the initial 10 cycles, maintaining only 10 % of retention after 100 cycles, whereas the DMPZ cell exhibited 70 % of retention after the same number of cycles.



Figure S13. Cyclic voltammograms of TMPD- (a) and DMPZ-electrolyte (b) at a rate of 1 mV s⁻¹ within a voltage range of 2.8-4.2 V (vs. Li/Li⁺). (c) The anodic (I_{pa}) to cathodic peak (I_{pc}) current ratios calculated from the number of scans. Upon cycling, the I_{pa}/I_{pc} ratio starts to deviate from the ideal value of 1 in TMPD, while that of DMPZ is well maintained. The linear fit of I_{pa}/I_{pc} and scan number exhibits a five times larger slope in TMPD (2^{nd}) than that of DMPZ (2^{nd}), implying additional chemical reactions occur during electrochemical oxidation/reduction of TMPD.



Figure S14. (a) Galvanostatic charge/discharge profiles of TMPD upon 30 cycles at a current density of 0.5 mA cm⁻². (b) 1H NMR peaks of TMPD (2.73 and 6.6 ppm) were completely disappeared after cycling.^{1, 2} Instead, new peaks appeared in the range of 6.7-9.0 ppm, indicating the formation of side products induced by the irreversible H-abstraction from TMPD.



Figure S15. In-situ DEMS profiles of RM-free (a), TMPD (b), MPTZ (c), and DMPZ (d) with gas evolution for O_2 upon charging to 4.3 (V vs. Li/Li⁺) at a current rate of 0.146 mA cm⁻². All cells showed a relatively small fraction of O_2 -to-¹³CO₂ evolution (0.035, 0.002, 0.011, and 0.059 for RM-free, TMPD, MPTZ, and DMPZ, respectively) compared to the theoretical value (0.5).



Figure S16. Galvanostatic charge/discharge profiles of RM-free (a), MPTZ (b), TMPD (c), and DMPZ (d) cells in electrolytes with 2.5 mM of DMA additives. The cells were cycled at a current rate of 0.5 mA until Li₂CO₃ was decomposed to the targeted amount (about 0.2 or 0.65 mAh). By comparing the charge capacity between cells with and without Li₂CO₃, all cells were cycled until Li₂CO₃ was decomposed to the targeted amount (approximately 0.21 and 0.65 mAh). The RM-free cell was only cycled until 0.19 mAh of Li₂CO₃ decomposed, as the charge plateau extension became negligible in subsequent cycles (a, inset).



Figure S17. LSV curves of stainless steel electrode (diameter, 14 mm) at a scan rate of 1 mV s⁻¹ in the electrolyte (1M LiTFSi in TEGDME) with or without 2.5 mM DMA. The decomposition of DMA begins at around 4.05 V (vs. Li/Li⁺) with significantly higher current than that from the carbon surface and electrolyte oxidation.



Figure S18. Galvanostatic charge/discharge profiles of RM-free (a), MPTZ (b), TMPD (c), and DMPZ (d) cells in electrolytes with 2.5 mM of DMA additives. The cells were cycled at a current rate of 0.5 mA until Li_2CO_3 was decomposed to the targeted amount (about 0.2 or 0.65 mAh). By comparing the charge capacity between cells with and without Li_2CO_3 , all cells were cycled until Li_2CO_3 was decomposed to the targeted amount (approximately 0.21 and 0.65 mAh). The RM-free cell was only cycled until 0.19 mAh of Li_2CO_3 decomposed, as the charge plateau extension became negligible in subsequent cycles (a, inset).



Figure S19. The standard calibration curve of fluorescence intensity ($\lambda_{ex} = 378 \text{ nm}$, $\lambda_{em} = 431 \text{ nm}$) as a function of DMA concentration (mM). The calibration point of DMA solutions were linearly fitted with a slope of 15708.16 and a correlation coefficient ($R^2=0.99$) close to ideal value, 1.



Figure S20. The multifunctional catalytic effect of DMPZ in decomposing both Li_2O_2 and Li_2CO_3 confirmed by in-situ DEMS analyses. (a) The DMPZ cell was pre-discharged to the capacity cut-off of 0.5 mAh cm⁻² in mixed gas condition at a current rate of 0.2 mA cm⁻² to form both Li_2O_2 and Li_2CO_3 on the electrode. On charging, (b) O_2 and (c) CO_2 gas evolved at potential above 3.2 and 3.7 V (vs. Li/Li^+), respectively. The result confirms the sole decomposition of Li_2O_2 by DMPZ/DMPZ⁺, and the critical role of DMPZ⁺/DMPZ²⁺ in decomposing Li_2CO_3 .



Figure S21. Galvanostatic charge/discharge profiles of RM-free (a) and DMPZ (b) cells at a current rate of 0.2 mA cm⁻² under air-like atmosphere. DMPZ cell exhibited 100% of initial Coulombic efficiency (CE) with clear charge plateaus at 3.2 and 3.7 V (vs. Li/Li⁺), confirming the DMPZ-mediated decomposition of discharge products (e.g. Li₂O₂, Li₂CO₃).



Figure S22. (a) The terminal discharge voltages of the RM-free and DMPZ cells at a current rate of 0.2 mA cm⁻² under an airlike atmosphere. The RM-free cell showed rapid decrease in the terminal voltage approaching the discharge cut-off voltage 2.0 V, while that of the DMPZ cell is well maintained above 2.5 V. (b) The discharge capacity retention of the RM-free and DMPZ cells. The RM-free cell retained only 60% of its initial discharge capacity after 21 cycles, whereas the DMPZ cell exhibited capacity retention of 94 % after the same cycles.



Figure S23. Galvanostatic charge/discharge profiles of the RM-free (a) and DMPZ (b) cells at a 0.5 mA cm^{-2} under an air-like atmosphere. The RM-free cell showed 80% of the initial CE with a large charge overpotential, whereas in the DMPZ cell, an initial CE of 100% was achieved.

	MPTZ	TMPD	DMPZ	DBB
A: Sum of charge capacity (mAh)	0.157	0.603	0.471	0.177
B: Sum of charge capacity from w/o Li ₂ CO ₃ (mAh)	0.124	0.248	0.283	0.105
A-B (mAh), decomposition efficiency of Li_2CO_3 (%)	0.033, 10	0.355, 108	0.188, 57	0.072, 22

Table S1. The charge capacities obtained from each RM cell after 10 galvanostatic cycles in the three-electrode system. Porous carbon electrodes were used before and after loading Li₂CO₃ nanoparticles. From the increased charge capacity after loading Li₂CO₃, the capacities derived from Li₂CO₃ decompositions were calculated as 0.033, 0.355, 0.188, and 0.072 mAh for MPTZ, TMPD, DMPZ, and DBB, respectively. These values could be converted into 0.045, 0.486, 0.256, and 0.099 mg of decomposed Li₂CO₃ for MPTZ, TMPD, DMPZ, and DBB, respectively, using the following equation: $mAh/0.728 = mg_{Li_2CO_3}$. The decomposition efficiencies of each RM cell were calculated based on the mass of pre-loaded Li₂CO₃ (0.45 mg).

1 st cyc	MPTZ	DBB	DMPZ	TMPD
Charge capacity (mAh/g)	119.668	119.947	264.733	451.128
Charge capacity from w/o Li ₂ CO ₃ (mAh/g)	98.244	95.453	189.846	279.548
Decomposed Li_2CO_3 (mAh), decomposition efficiency of Li_2CO_3 (%)	0.022, 6	0.031, 12	0.079, 25	0.140, 35

Table S2. The initial charge capacities obtained from each RM cell after the first charge step in the two-electrode configuration. The capacities from each cell were normalized by the input weight of the corresponding RMs. Considering the theoretical capacities from the intrinsic redox of RMs (125, 107, 254, and 326 mAh/g for MPTZ, DBB, DMPZ, and TMPD, respectively), the shuttle behavior of oxidized RM species was successfully mitigated by using the passivated Li anode. The amount of decomposed Li₂CO₃ was calculated as 0.022, 0.031, 0.079, and 0.140 mAh for MPTZ, DBB, DMPZ, and TMPD, respectively, and these values were converted into decomposition efficiency in the same manner as for the three-electrode system.

	RM-free	TMPD	MPTZ	DMPZ
Integrated area of evolved ¹³ CO ₂ (10 ⁻¹² X mbar*h)	0.130	5.046	1.382	1.129
Integrated area of evolved ¹² CO ₂ (10 ⁻¹² X mbar*h)	0.110	0.221	0.134	0.126
$\frac{{}^{12}CO_2}{{}^{12}CO_2 + {}^{13}CO_2} * 100 \ (\%)$	45.853	4.195	8.839	10.03

Table S3. Quantified data on gaseous species collected from in-situ DEMS cells upon charging to 4.1 (V vs. Li/Li⁺). Because the charging of the RM-free cell was completed in a relatively short time (within half an hour) before the saturation of CO_2 evolution, an extended calibration range (up to 4.3 V vs. Li/Li⁺) was applied to the RM-free cell for a comparative analysis. With the reduced onset potential for ¹³CO₂ gas evolution, the proportions of ¹²CO₂ gas were significantly decreased four- to 10-fold in all RM cells (from 4.195 to 10.03) compared to that of RM-free cell (45.853).

	RM-free	MPTZ	TMPD	DMPZ
A: Sum of charge capacity from w/o Li_2CO_3 (mAh)	0.098	0.185	0.012	0.106
B: Sum of charge capacity from w/o Li_2CO_3 for "subsequent cycles" (mAh)	-	0.562	0.126	0.496
C: Sum of charge capacity (mAh)	0.28942	0.397	0.225	0.302
D: Sum of charge capacity for "subsequent cycles" (mAh)	-	1.193	0.749	1.208
C-A (mAh, umol)	0.190, <mark>3.538</mark>	0.211, <mark>3.930</mark>	0.213, <mark>3.964</mark>	0.196, <mark>3.644</mark>
D-B (mAh, <mark>umol</mark>)	-	0.630, <mark>11.706</mark>	0.623, <mark>11.580</mark>	0.711, <mark>13.22</mark>

Table S4. The charge capacities obtained from each RM cell after galvanostatic cycles in electrolytes containing DMA. By comparing the charge capacity between cells with and without Li₂CO₃, all galvanostatic tests were performed until Li₂CO₃ was decomposed to the targeted amount (about 0.2 mAh, which corresponds to 1/4 of the theoretical capacity from pre-loaded Li₂CO₃). All RM cells were further cycled until approximately 0.65 mAh of Li₂CO₃ decomposed (denoted as "subsequent cycles"). The decomposed amount of Li₂CO₃ could be converted into mole number using the molecular weight of Li₂CO₃ (MW: 73.891 g/mol) and the following equation: $mAh/0.728 = mg_{Li_2CO_3}$.

	RM-free	MPTZ	TMPD	DMPZ
PL intensity at 431 nm (a.u.)				
As-prepared	941.94	928.62	1000.10	743.29
w/o Li ₂ CO ₃	933.15	902.94	1005.80	744.25
After decomposing $^{1\!\!/_{\!\!4}} {\rm Li}_2 {\rm CO}_3$	743.24	836.30	968.07	717.41
After decomposing $\frac{3}{4}$ Li ₂ CO ₃	-	781.18	858.54	602.53
DMA mole number (umol)				
As-prepared	6.71	6.59	7.27	4.82
w/o Li ₂ CO ₃	6.63	6.34	7.32	4.83
After decomposing $\frac{1}{4}$ Li ₂ CO ₃	4.82	5.71	6.96	4.57
After decomposing $\frac{3}{4}$ Li ₂ CO ₃	-	5.18	5.92	3.47

Table S5. The fluorescence intensities and calculated DMA concentrations from each cell during Li₂CO₃ decomposition. Fluorescence spectra for "w/o Li₂CO₃" were recorded after the same period of cycles as "after decomposing 3/4 Li₂CO₃". The mole number of DMA was determined by using the standard calibration curve and the peak intensity at 431 nm was recorded from the corresponding cell. Given that DMA traps ¹O₂ in 1:1 molar equivalent (DMA + ¹O₂ \rightarrow DMA–O₂), the reduction in mole number of DMA could be converted into ¹O₂ production (umol).

Reference

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