Supporting Information

of

Mechanistic Insights into CO_2 Capture and Electrochemical Conversion in Nonaqueous Na-CO_2 Batteries

Rahul Jayan[b,#], Satheesh Mani[a,#], Md Mahbubul Islam[a,*]

[a] Department of Mechanical Engineering, Wayne State University, Detroit, Michigan 48202, USA

[b] Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87544, USA

[*]Corresponding Author: gy5553@wayne.edu

[#]These authors contributed equally to this work.

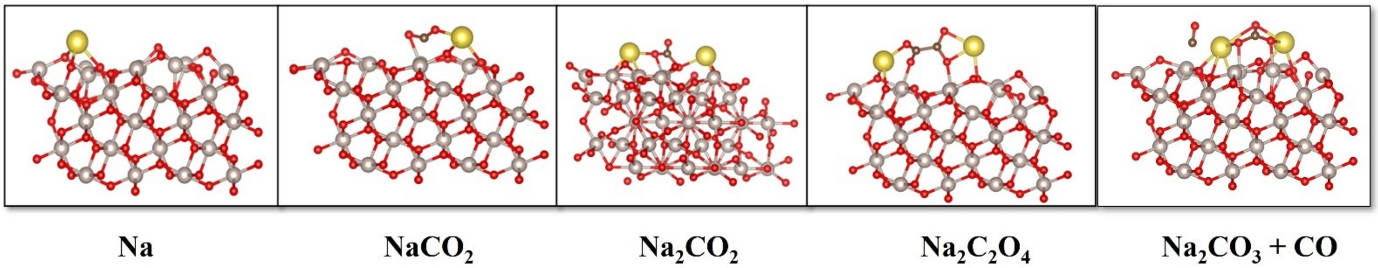


Figure S1: Side view of the most stable geometric configuration of $Na_2CO_3 + CO$ product via $Na_2C_2O_4$ (Path I) intermediate at 0V.

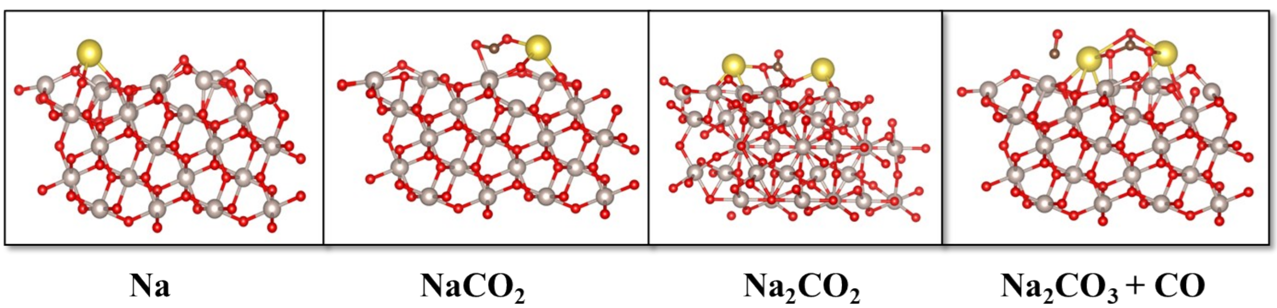


Figure S2: Side view of the most stable geometric configuration of the $Na_2CO_3 + CO$ nucleation (Path IV') at 0V.

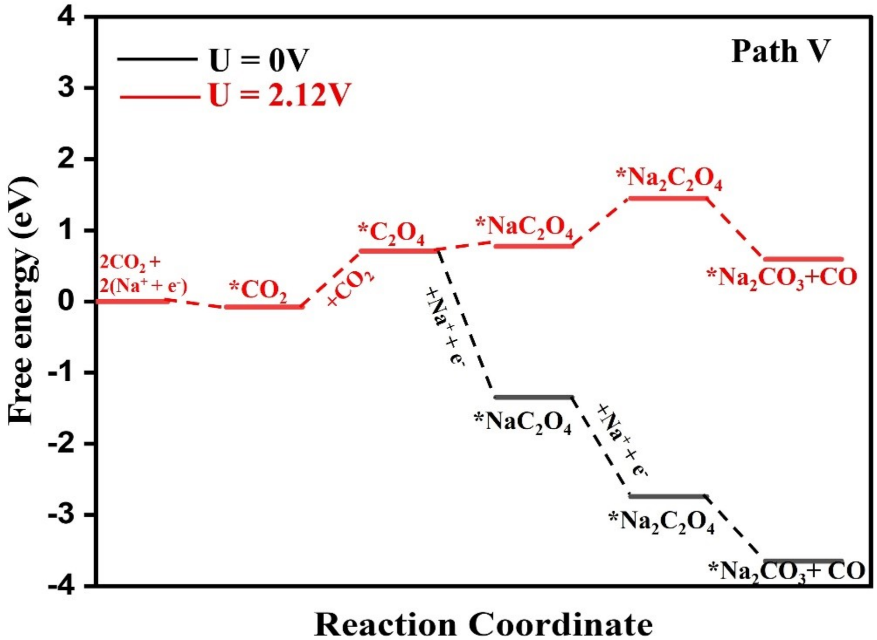


Figure S3: Computed Gibbs free energy path (path-V) for Na_2CO_3 + CO via $Na_2C_2O_4$ nucleation at U = 0V and U =2.12V

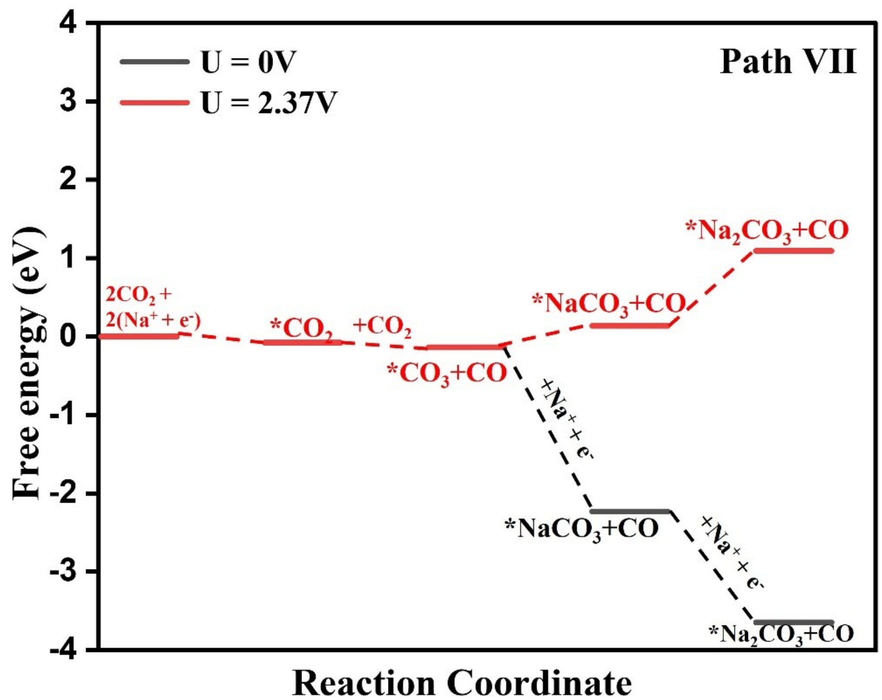
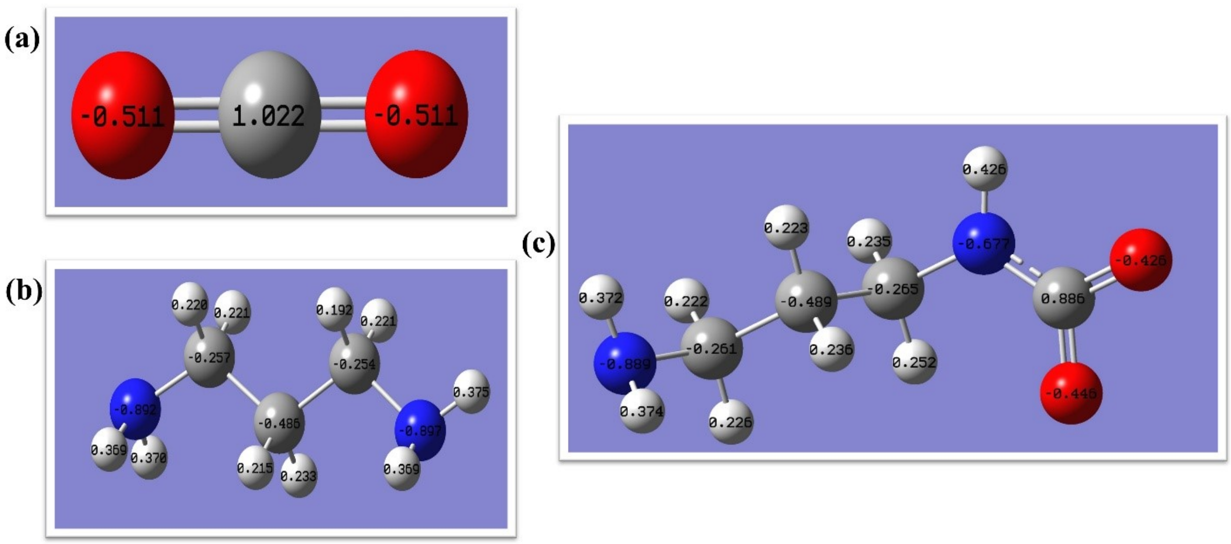


Figure S4: Computed Gibbs free energy path (path-VII) for Na_2CO_3 + CO nucleation at U = 0 V and U



=2.37V

Figure S5. NBO analysis of (a) isolated CO_2 molecule showing symmetric charge distribution, (b) pristine PDA structure with atomic charges, and (c) PDA-CO_2 adduct illustrating charge redistribution upon CO_2 interaction. All atomic charges are shown in electron units. Color code: Red – O; Light grey – C; Blue– N; White – H.

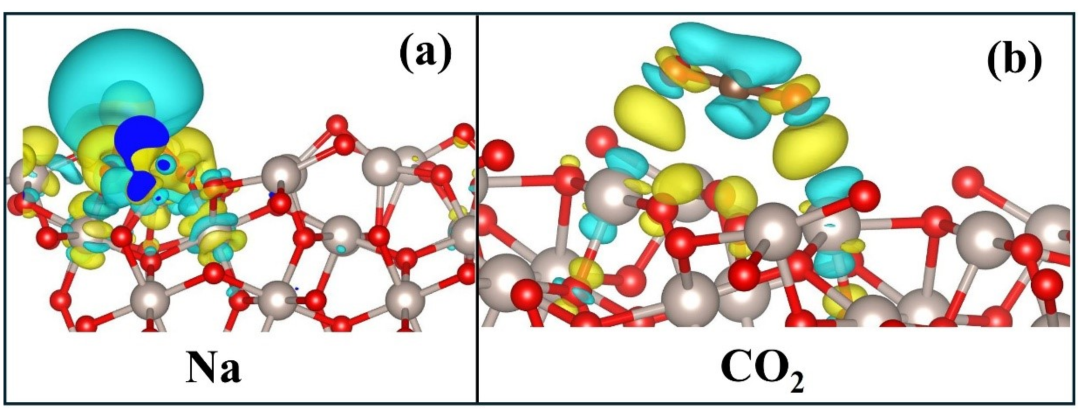


Figure S6. DCD images of (a). Na (b). CO_2 adsorbed on RuO_2 catalyst.

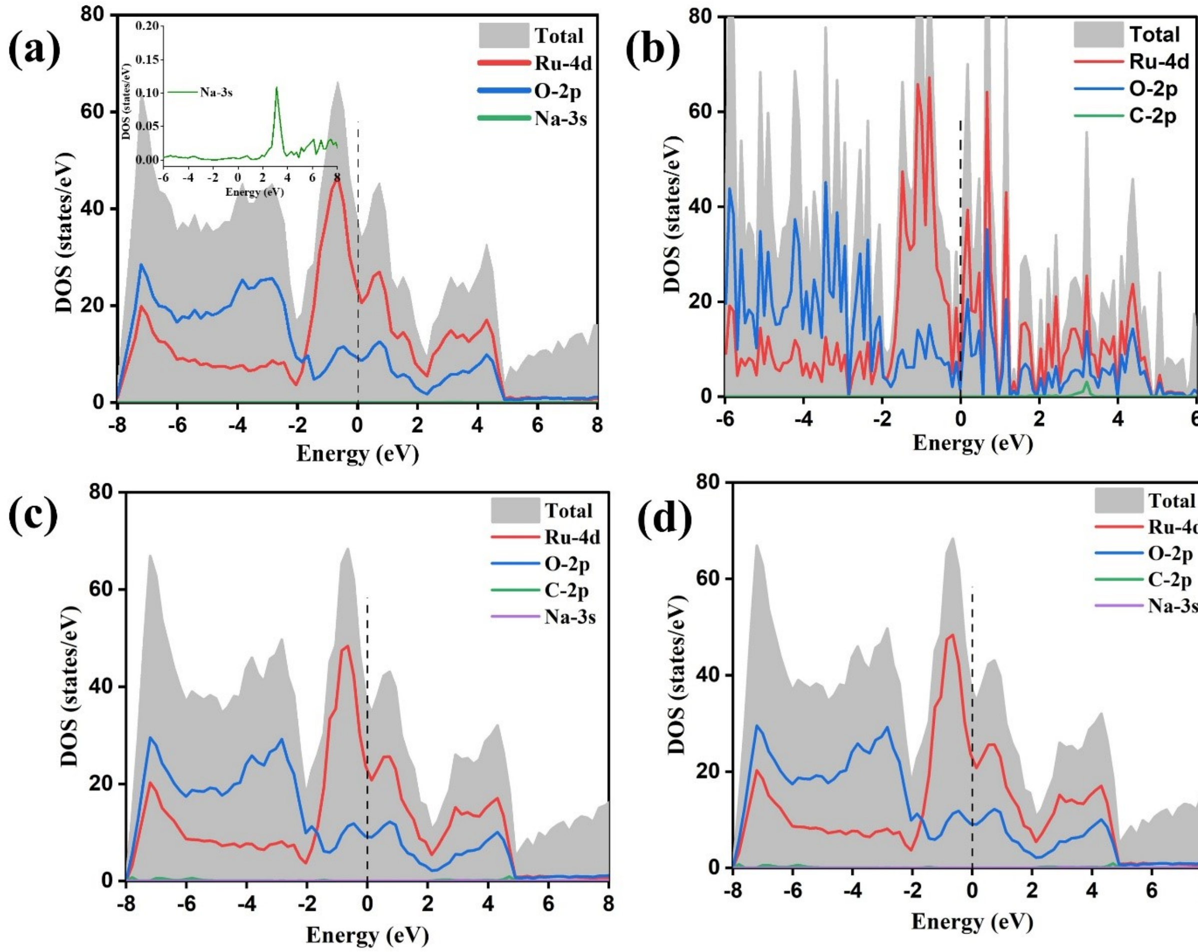


Figure S7. PDOS for various reaction intermediates (a). Na (b) CO_2 (c). $Na_2C_2O_4$ and (d) Na_2CO_3 +CO adsorbed on RuO_2 catalyst.

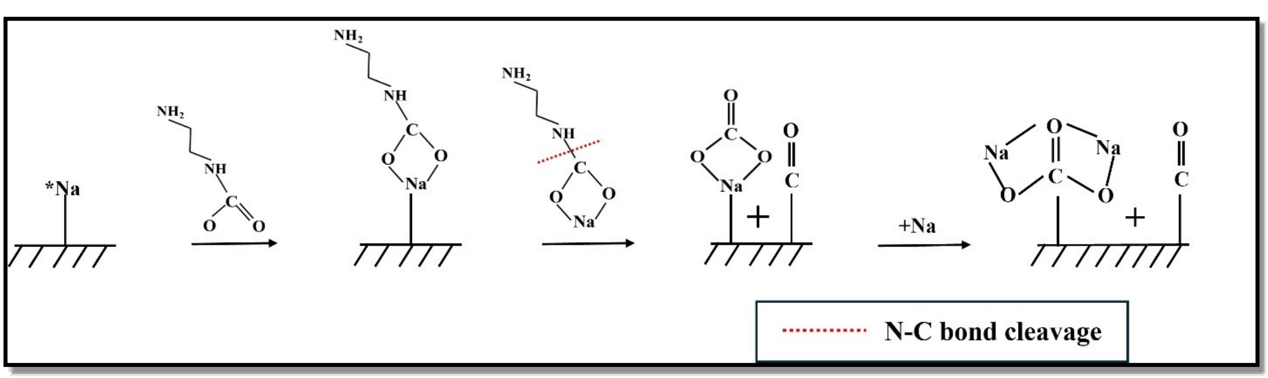


Figure S8. Proposed favorable reaction pathway with amine adducts leading to end discharge products.

Standard Gibbs free energies and equilibrium voltages:

For Na-CO_2 reactions, possible nucleation pathways involve the formation of $Na_2C_2O_4$ (sodium oxalate) and Na_2CO_3 +CO (sodium carbonate) as discharge products.

$$2Na\ (s) + 2CO_2\ (g) \rightleftharpoons Na_2C_2O_4\ (s)$$

$$2Na\ (s) + 2CO_2\ (g) \rightleftharpoons Na_2CO_3\ (s) + CO\ (g)$$

From the above chemical reaction, the standard Gibbs free energies for both $Na_2C_2O_4$ (s) and Na_2CO_3 (s) nucleation can be calculated as

$$\Delta G^0{}_f (Na_2C_2O_4)\ s = G^0\ (Na_2C_2O_4)\ s - 2\ G^0\ (Na)\ s - 2\ G^0\ (CO_2)\ g$$

$$\Delta G^0{}_f (Na_2CO_3)\ s = G^0\ (Na_2CO_3)\ s + \ G^0\ (CO)\ g - 2\ G^0\ (Na)\ s - 2\ G^0\ (CO_2)\ g$$

These expressions allow for the computation of standard Gibbs free energy ($\Delta G^0{}_f$) values, which can then be used to determine equilibrium potentials using the Nernst equation:

$$\mathbf{U_0 = -\Delta G^0{}_f / ne}$$

where n and e represent the number of transferred electrons and electronic charge and the value of equilibrium potential U_0 (Na_2CO_3+CO) and U_0 ($Na_2C_2O_4$) was calculated to be 2.37 V and 2.12 V respectively.

The electrochemical free energy change for the most favorable pathway during the discharging and charging processes of the studied catalyst is determined using the following expression:

$$(\Delta G_E\ (Na\text{-}CO_2)) = E_{total} - \{E_{prev} + n_{Na}\ (\mu_{Na}) + nCO_2\ (\mu CO_2)\}$$

E_{total} and E_{prev} represents energy of the total system and energy of the previous step. n_{Na}, nCO_2, μ_{Na} and μCO_2 denotes the number of Na, CO_2 and chemical potential of Na and CO_2.

Discharge overpotential (η_{dis}) = $U_{eq} - U_{dis}$,

Charge overpotential (η_{chg}) = $U_{chg} - U_{eq}$,

Total overpotential (ΔE_{total}) =$\eta_{dis} + \eta_{chg}$

Table S1: The calculated zero-point energies and entropies for all the studied reaction intermediates for the studied RuO_2 (211) substrate.

Reaction Intermediate	ZPE (eV)	TS (eV)
Na	0.0581	0.1343
CO_2	0.3324	0.1784
$NaCO_2$	0.3909	0.2101
Na_2CO_2	0.4069	0.2636
NaC_2O_4	0.705	0.308
$Na_2C_2O_4$	0.7614	0.2973
$NaCO_3$+CO	0.6579	0.3064
Na_2CO_3+CO	0.7614	0.2973

Reference:

(1) Jayan, R.; Islam, M. M. Understanding Catalytic Mechanisms and Cathode Interface Kinetics in Nonaqueous Mg–CO2 Batteries. *ACS Appl. Mater. Interfaces* **2023**, *15* (39), 45895–45904. https://doi.org/10.1021/acsami.3c09599.

(2) Jayan, R.; Islam, M. M. Advancing Next-Generation Nonaqueous Mg–CO2 Batteries: Insights into Reaction Mechanisms and Catalyst Design. *J. Mater. Chem. A* **2023**, *11* (29), 15915–15923. https://doi.org/10.1039/D3TA03287F.