Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

Role of Inorganic Layers on Polysulfide Decomposition at Sodium-Metal Anode Surfaces for Room Temperature Na/S Batteries

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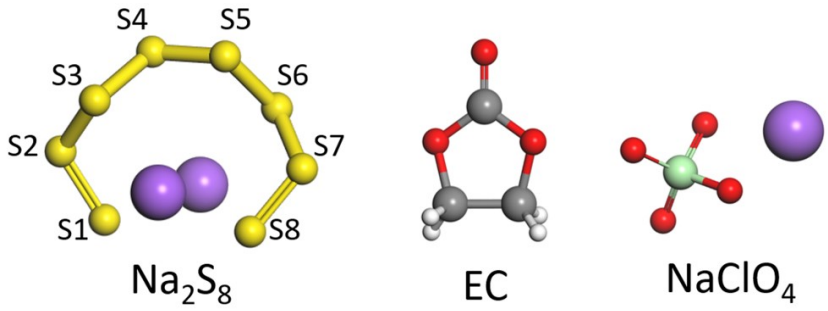

Figure S1. Optimized Na_2S_8, ethylene carbonate (EC), and $NaClO_4$ molecule.

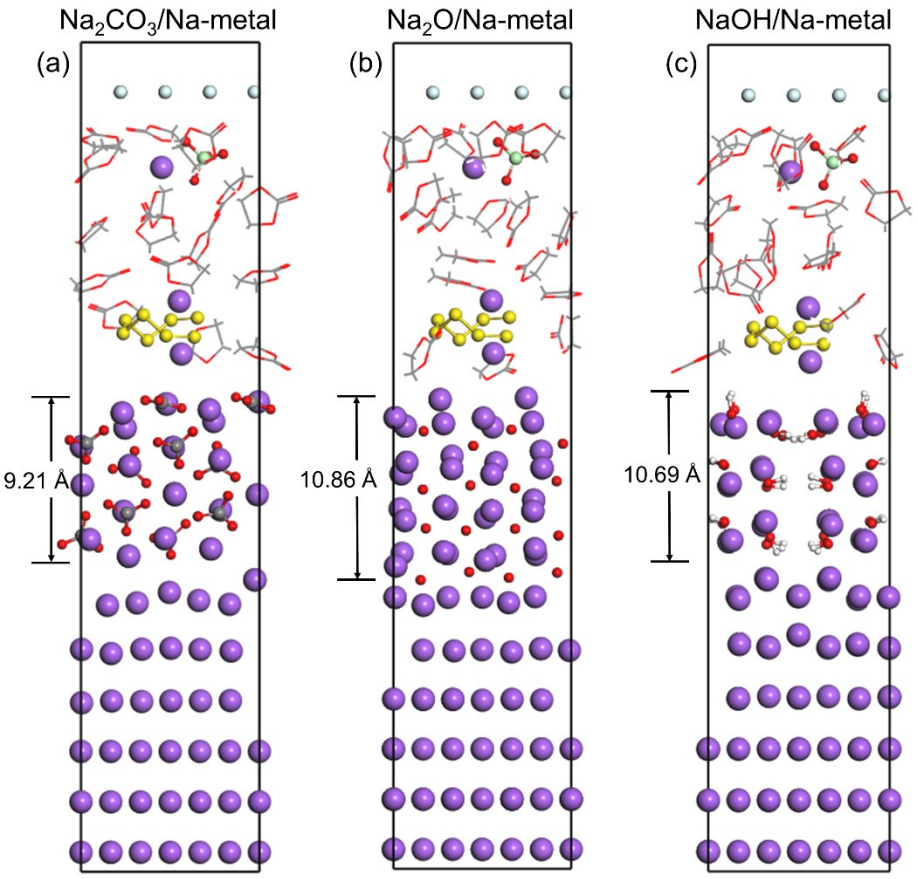

Figure S2. Initial configurations used for AIMD simulation of Na_2S_8 decomposition with the introduction of different SEI layers in EC solvent for (a) Na_2CO_3, (b) Na_2O, and (c) NaOH. The wireframe structures are EC molecules. Code colors: Na atom; purple, F; blue, Cl; green, O; red, C; gay, and H; white.

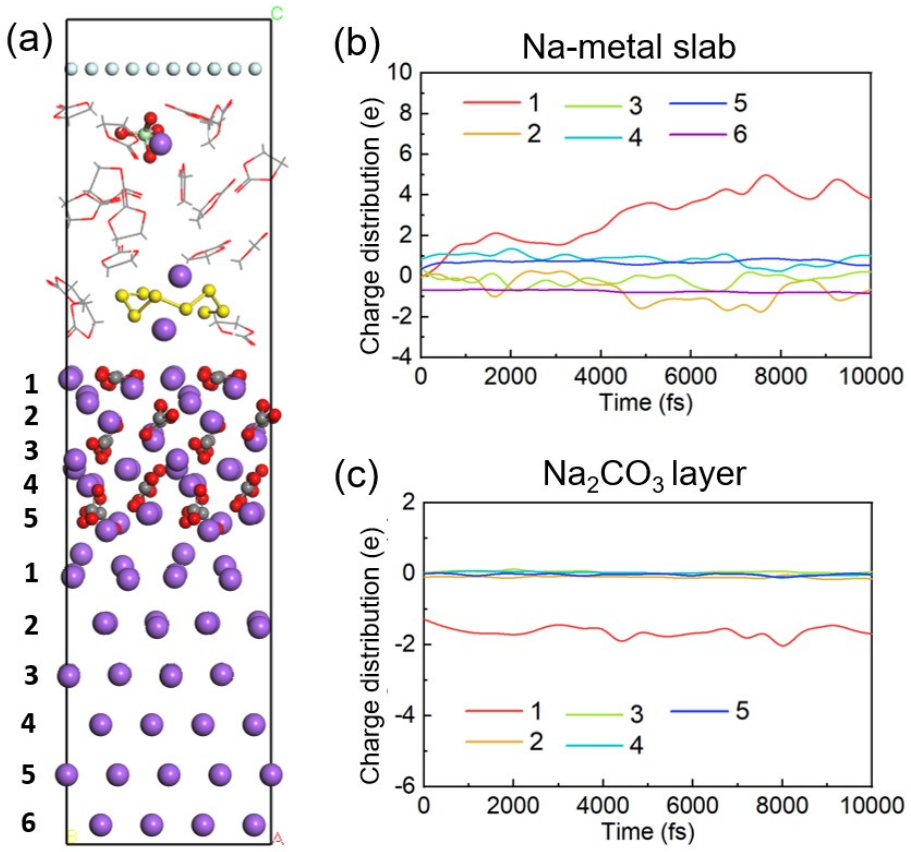

Figure S3. (a) Initial Na_2CO_3/Na-metal configuration with the labels of the Na_2CO_3 layers (above) and the Na-metal layers (below). The corresponding charge distribution evolution in (b) the Na-metal layers and (c) the Na_2CO_3 layers. Code colors: Na atom; purple, F; blue, Cl; green, O; red, C; gay, and H; white.

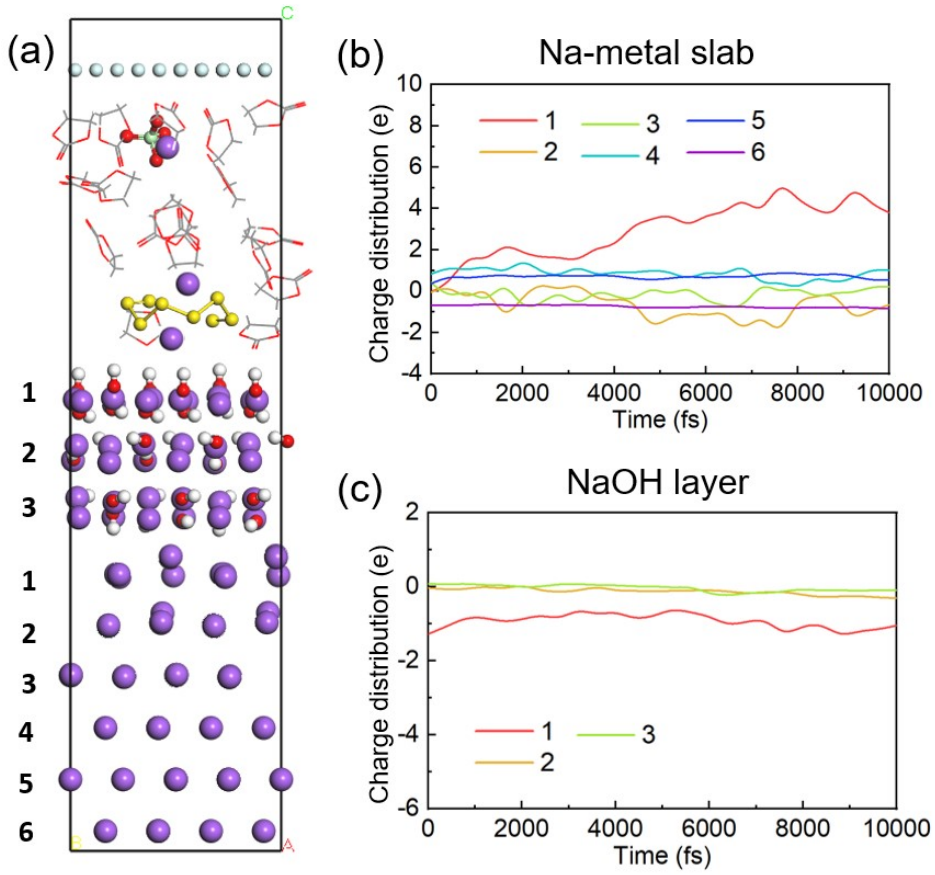

Figure S4. (a) Initial NaOH/Na-metal configuration with the labels of the NaOH layers (above) and the Na-metal layers (below). The corresponding charge distribution evolution in (b) the Na-metal layers and (c) the NaOH layers. Code colors: Na atom; purple, F; blue, Cl; green, O; red, C; gay, and H; white.

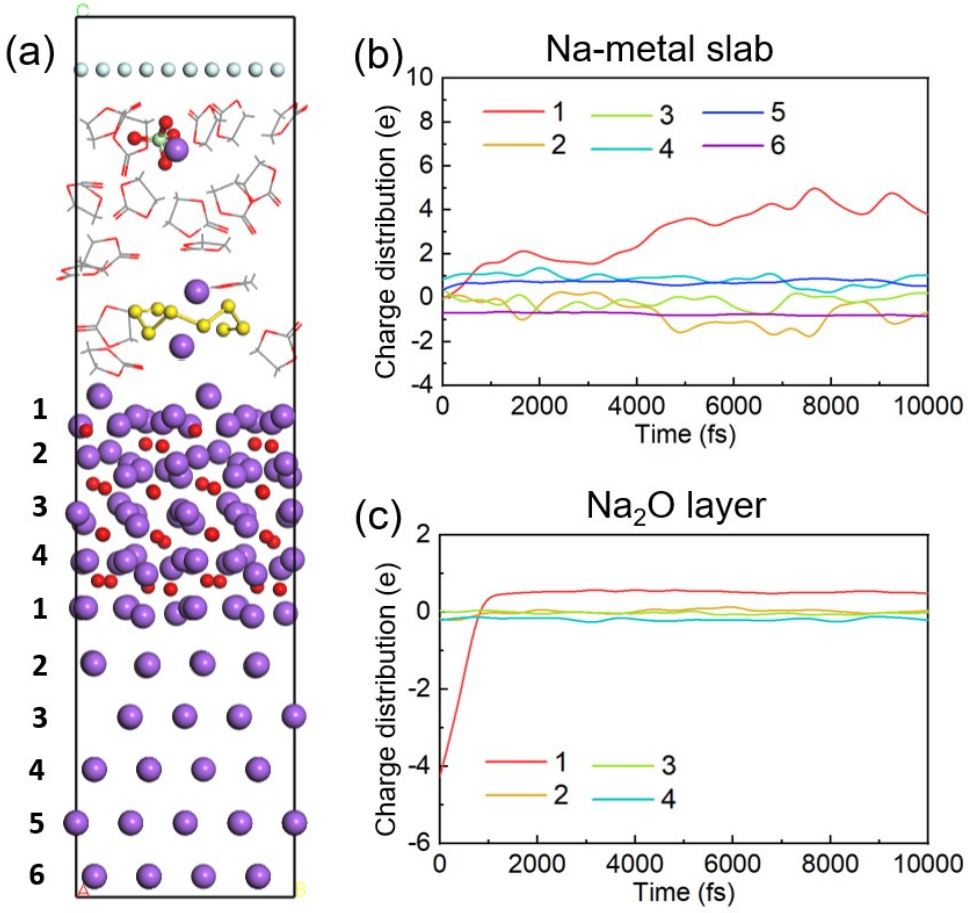

Figure S5. (a) Initial Na_2O/Na-metal configuration with the labels of the Na_2O layers (above) and the Na-metal layers (below). The corresponding charge distribution evolution in (b) the Na-metal layers and (c) the Na_2O layers. Code colors: Na atom; purple, F; blue, Cl; green, O; red, C; gay, and H; white.

Table S1. Summary of geometric parameters of the bulk structures

Structures	Lattice constants (Å)			Angle (°)		
	a	*b*	*c*	*α*	*β*	*γ*
Na-metal	3.582	3.582	6.080	90	90	120
Na_2CO_3	8.749	5.259	5.911	90	103.4	90
NaOH	3.351	10.685	3.334	90	90	90
Na_2O	5.431	5.431	5.431	90	90	90

Table S2. The summary of the lattice parameters of SEI layer supercells with different facets before making heterostructure and the lattice mismatch of the SEI layers against the Na-metal slab upon combining the Na-metal slab.

Materials	supercell	facet	lattice parameters (Å)		lattice mismatch (%)	
			a	b	a	b
Na_2CO_3	2 × 2	(100)	10.52	11.82	-2.15	-4.74
	1 × 2	(010)	8.75	11.82	-18.60	-4.74
	1 × 2	(001)	8.75	10.52	-18.60	-15.25
	3 × 1	(110)	10.00	10.68	-6.95	-13.95
Na_2O	2 × 2	(100)	10.86	10.86	1.03	-12.45
	2 × 2	(010)	10.86	10.86	1.03	-12.50
	2 × 2	(001)	10.86	10.86	1.03	-12.50
	1 × 2	(110)	7.68	10.86	-28.54	-12.50
NaOH	3 × 1	(100)	10.3	12.56	-4.18	1.20
	3 × 3	(010)	10.3	10.68	-4.18	-13.90
	3 × 1	(001)	10.3	12.56	-4.18	1.20
	3 × 1	(110)	10.3	11.12	-4.18	-10.40

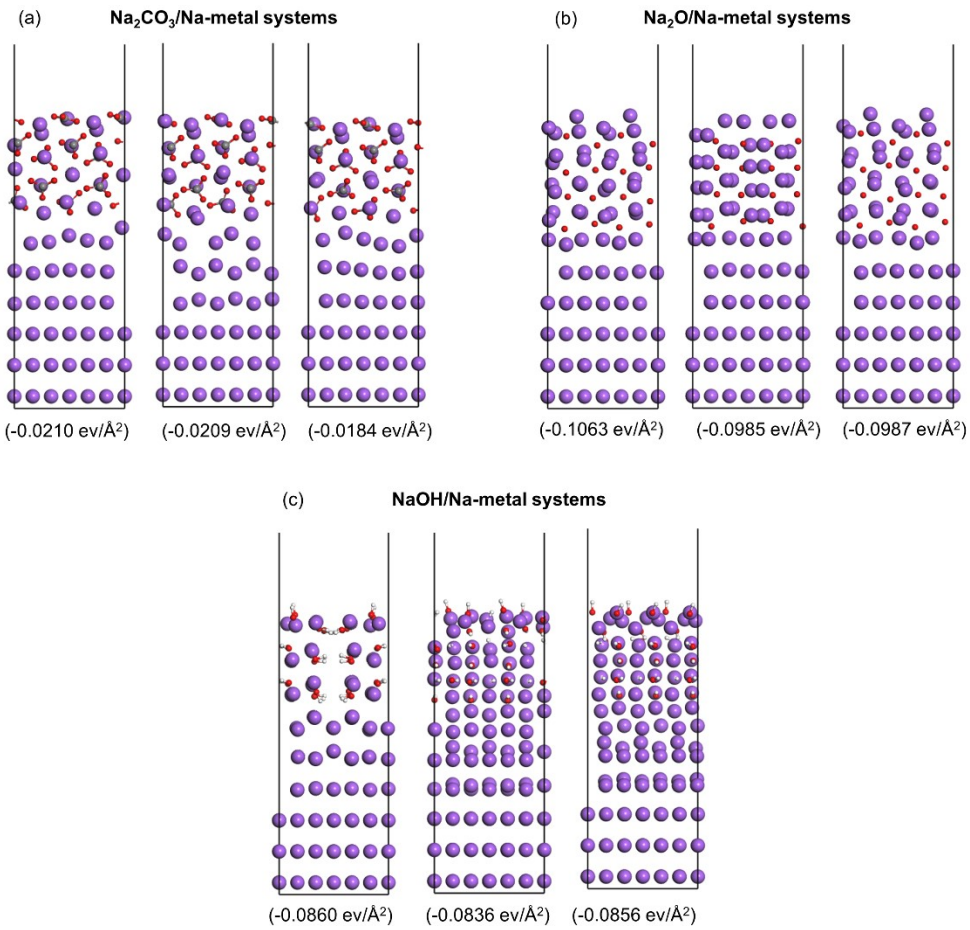

Figure S6. Three possible configurations of (a) Na_2CO_3, (b) Na_2O, and (c) NaOH layer on the Na-metal surface. The values of the interface formation energies are shown in the parentheses. Color codes depict purple; Na, red; O, black; C, and white; H atoms.