Supporting information for

Rational Design MXene-based Single Atom Catalysts for Na-Se Batteries from Sabatier Principles

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Additional Computational methods

The calculation of electron density difference (EDD)

The charge transfer between Se_8/Na_2Se_n and M_2CO_2/Zn-M_2CO_2 hosts was investigated by electron density difference (EDD). The EDD is expressed according to the following equation

$$\Delta\rho = \rho_{hosts-Se_8/Na_2Se_n} - \rho_{hosts} - \rho_{Se_8/Na_2Se_n} \quad \text{(S1)}$$

where $\rho_{hosts-Se_8/Na_2Se_n}$ and ρ_{hosts} , are the total charge density of the system with and without Se_8/Na_2Se_n, ρ_{Se_8/Na_2Se_n} represents the charge density of Se_8/Na_2Se_n, respectively.

The calculation of Gibbs free energy change (ΔG) of SeRR on M_2CO_2/Zn-M_2CO_2 surface.

Overall, the SeRR during the discharge of Na-Se batteries could be written as following[1, 2]

Total reaction $Se_8 + 16(Na^+ + e^-) \rightarrow 8Na_2Se$ ΔG

Each step involved in the generation is as follows:

$Se_8^* + 2\,(Na^+ + e^-) \rightarrow Na_2Se_8^*$ $\Delta G1$

$Na_2Se_8^* \rightarrow Na_2Se_6^* + 1/4\ Se_8$ $\Delta G2$

$Na_2Se_6^* \rightarrow Na_2Se_4^* + 1/4\ Se_8$ $\Delta G3$

$Na_2Se_4^* \rightarrow Na_2Se_2^* + 1/4\ Se_8$ $\Delta G4$

$Na_2Se_2^* \rightarrow Na_2Se^* + 1/8\ Se_8$ $\Delta G5$

‘*’ represents an active site on the catalytic substrate.

The Gibbs free energy (ΔG) for each SeRR during the Na-Se discharge process is calculated as

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S \quad \text{(S2)}$$

Where ΔE, ΔE_{ZPE} and $T\Delta S$ denotes the changes of total energy, the zero-point energy (ZPE) and entropic contribution, respectively. The ZPE and entropic contribution were calculated from the vibrational frequencies, and a temperature of 298 K was used.

Table S1. E_{ads} of Se_8/Na_2Se_n on different M_2CO_2 or Zn-M_2CO_2 MXene.

Hosts	Se_8	Na_2Se_8	Na_2Se_6	Na_2Se_4	Na_2Se_2	Na_2Se
Ti_2CO_2	-1.274	-3.273	-2.327	-2.630	-2.994	-2.667
Nb_2CO_2	-1.491	-2.426	-1.826	-2.557	-2.959	-3.230
Cr_2CO_2	-1.798	-4.604	-4.174	-4.436	-5.301	-5.224
Zn-Ti_2CO_2	-2.213	-3.919	-3.602	-4.102	-4.438	-5.168
Zn-Nb_2CO_2	-2.588	-4.228	-3.608	-3.984	-4.496	-5.281
Zn-Cr_2CO_2	-3.033	-5.660	-4.335	-5.135	-5.790	-6.426

Table S2. Δ*G* (Gibbs free energy) for each step of the SeRR on M_2CO_2/Zn-M_2CO_2 hosts. The rate-limiting step of SeRR was write in bold.

Hosts	Δ*G1*	Δ*G2*	Δ*G3*	Δ*G4*	Δ*G5*
Ti_2CO_2	-3.835	**1.287**	-0.133	1.019	1.011
Nb_2CO_2	-3.156	0.683	-0.058	**0.893**	0.551
Cr_2CO_2	-4.853	0.414	0.463	0.430	**0.866**
Zn-Ti_2CO_2	-3.857	0.405	0.159	**0.991**	0.014
Zn-Nb_2CO_2	-4.038	0.677	0.268	**0.809**	-0.013
Zn-Cr_2CO_2	-4.784	-0.169	**1.454**	0.632	0.151

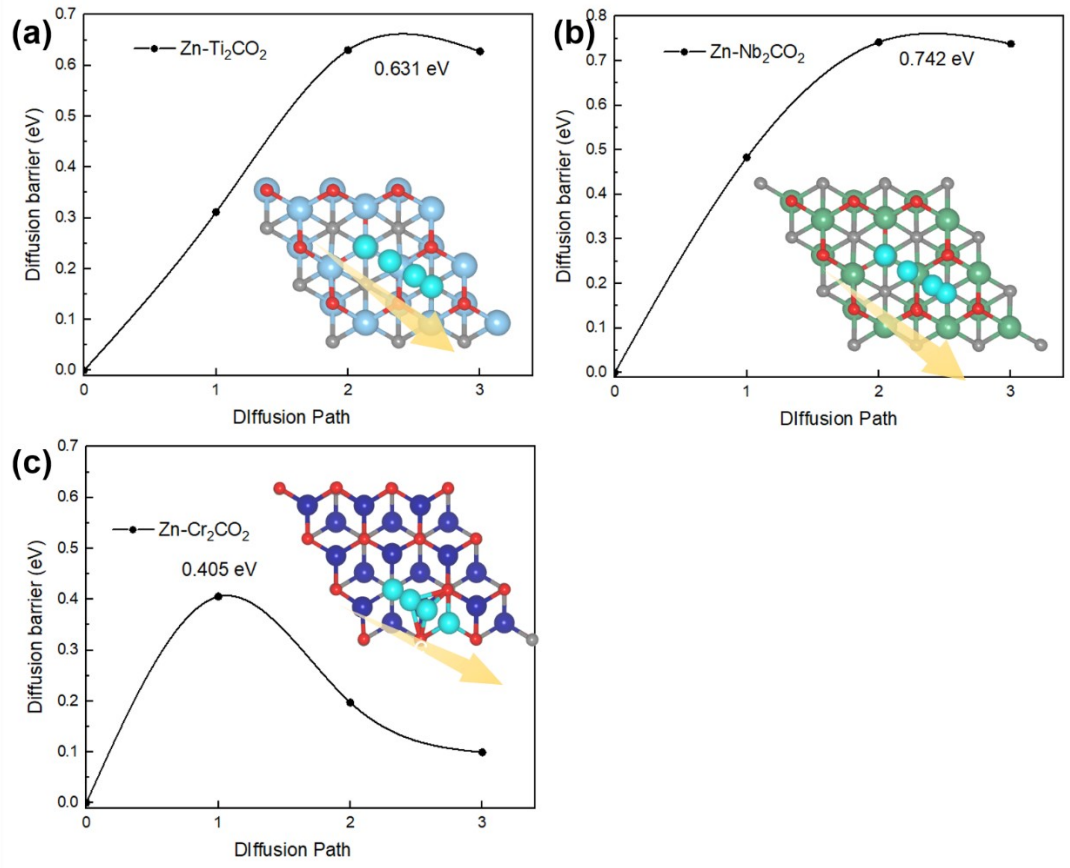
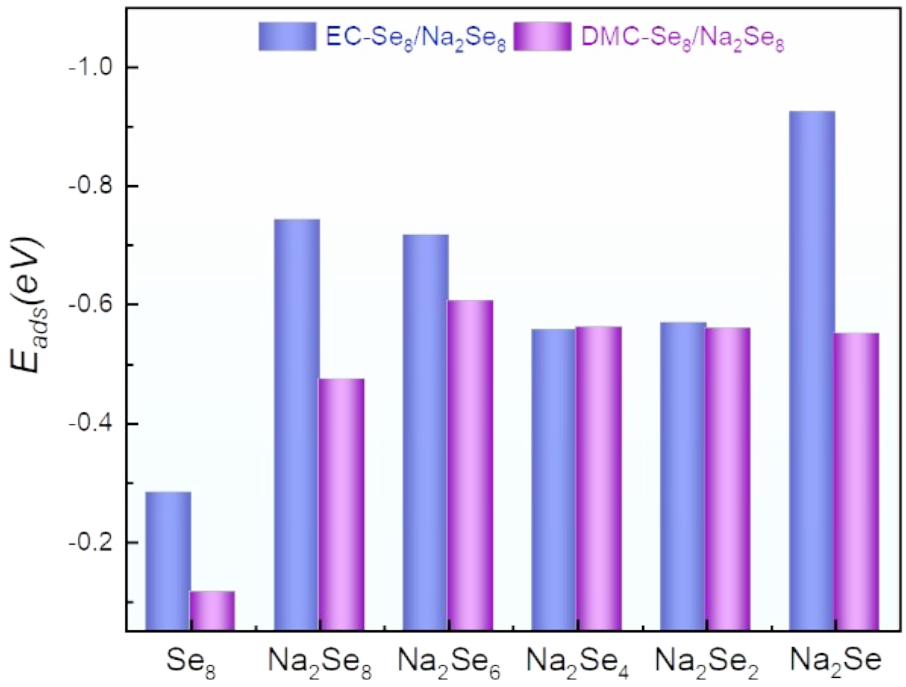


Figure S1. The diffusion energy barrier of zinc atom on the MXene surface.



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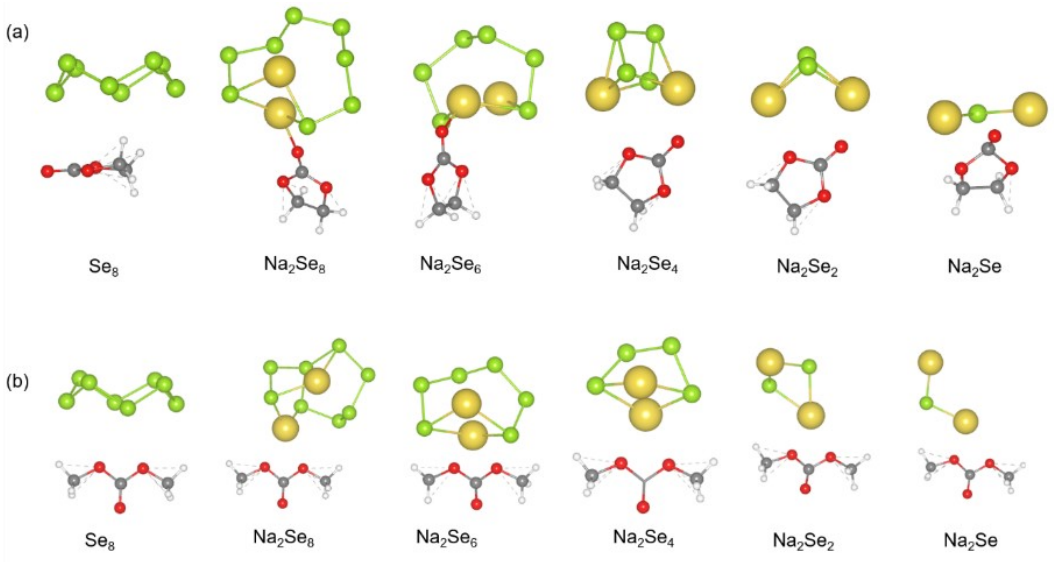

Figure S3. Geometrical structures of Se_8/Na_2Se_n adsorbed on (a) EC and (b) DMC electrolytes.

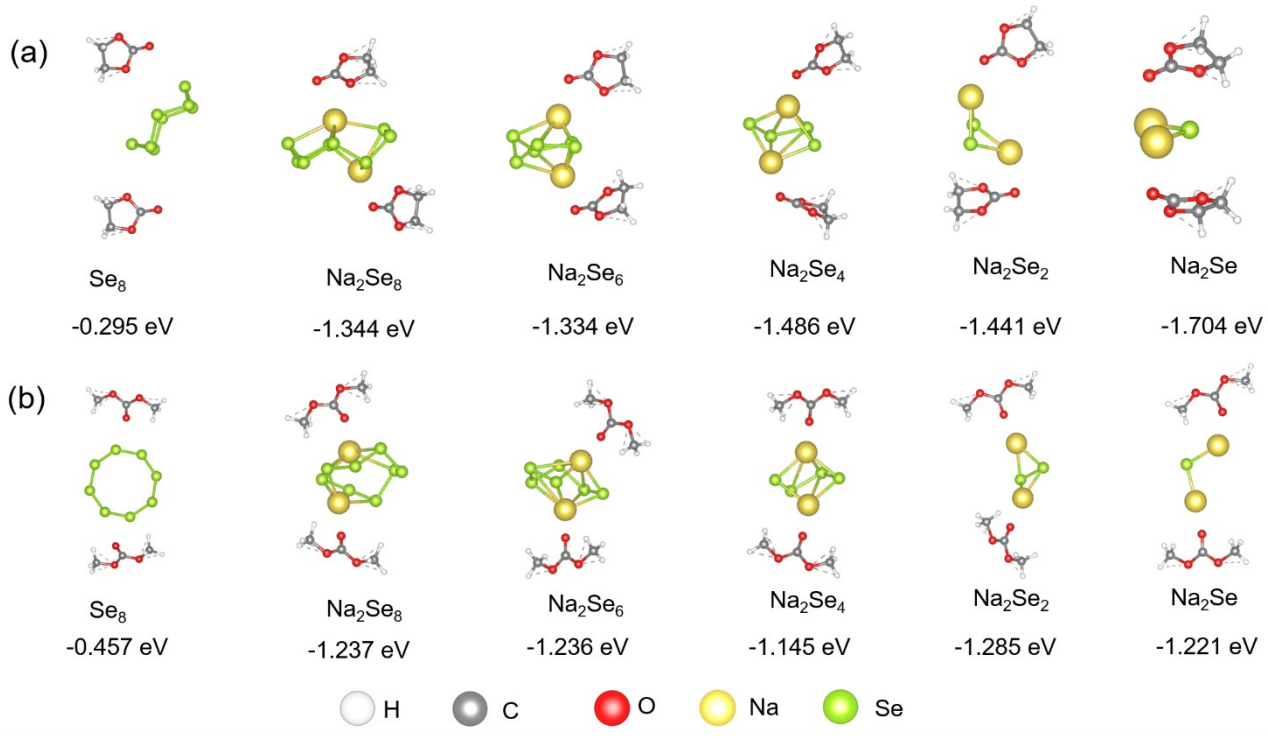

Figure S4. Geometrical structures and adsorption energies of Se_8/Na_2Se_n interact with (a) two EC molecules and (b) two DMC molecules.

References

[1] Q. Xu, T. Yang, W. Gao, R. Zhan, Y. Zhang, S. Bao, X. Li, Y. Chen, M. Xu, Jackfruit-like electrode design for advanced Na-Se batteries, *J. Power Sources*, 2019, **443**.

[2] Q. Li, H. Liu, Z. Yao, J. Cheng, T. Li, Y. Li, C. Wolverton, J. Wu, V.P. Dravid, Electrochemistry of Selenium with Sodium and Lithium: Kinetics and Reaction Mechanism, *ACS Nano*, 2016, **10**, 8788-8795.