Supporting Information for Promising anode materials for alkali metal ion batteries: A case study on cobalt anti-MXenes

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Phonon spectra of cobalt anti-MXenes

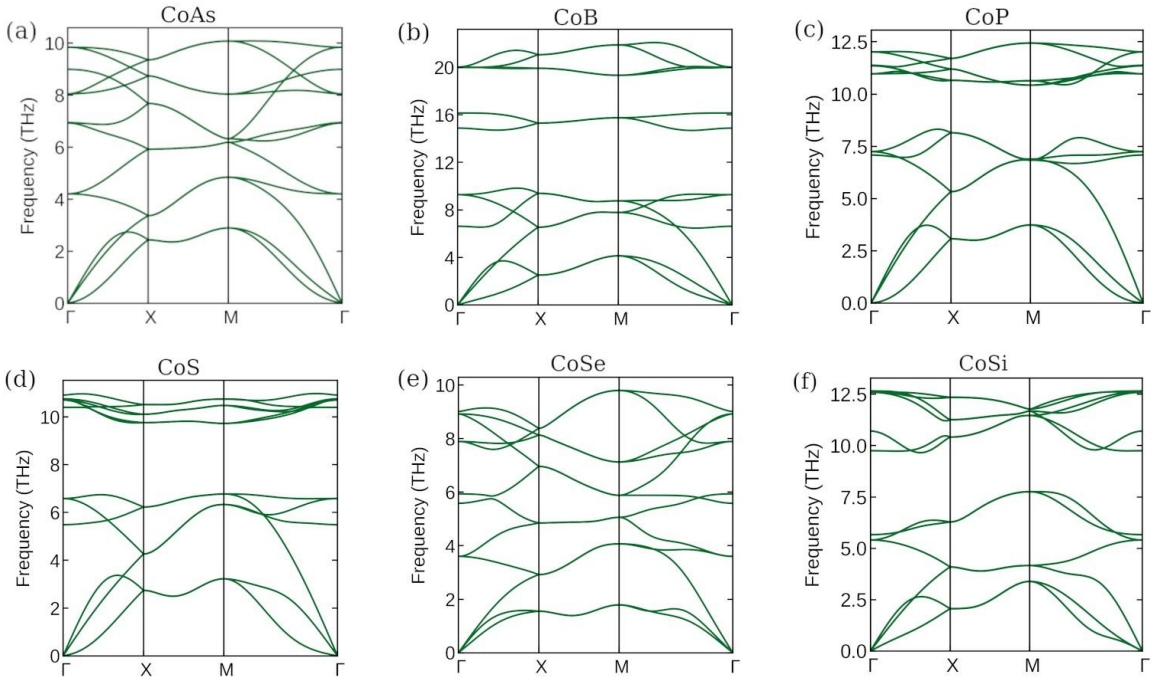

Figure S1. Phonon spectra of cobalt anti-MXenes. Positive frequencies indicate the dynamical stability of all systems.

Band structures and projected density of states of Co-anti-MXenes

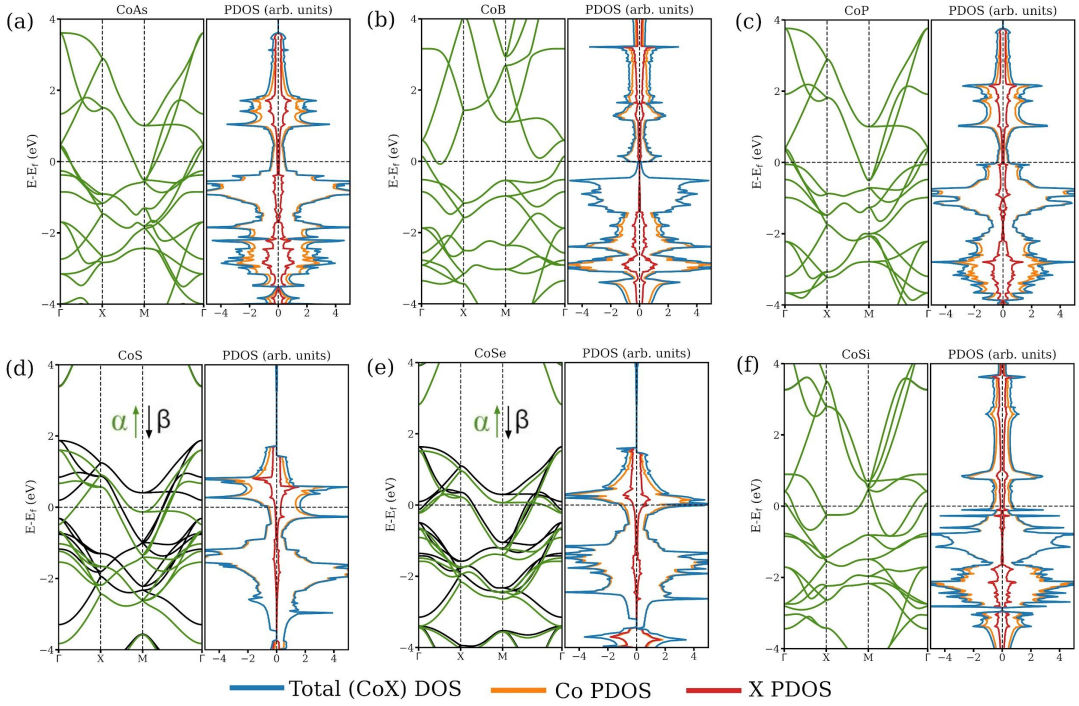

Figure S2. Band structure and projected density of states (PDOS) of (a) CoAs, (b) CoB, (c) CoP, (d) CoS, (e) CoSe, and (f) CoSi. All the anti-MXenes have a finite DOS near the Fermi level, indicating that they are metallic and have the potential to be used as electrodes. States across the Fermi level have a major contribution from the cobalt atoms, indicating their contribution to the metallicity. This figure is reproduced from reference 28 with permission.[28] (Copyright © 2022, American Chemical Society).

Co-PDOS in pristine Co-anti-MXenes

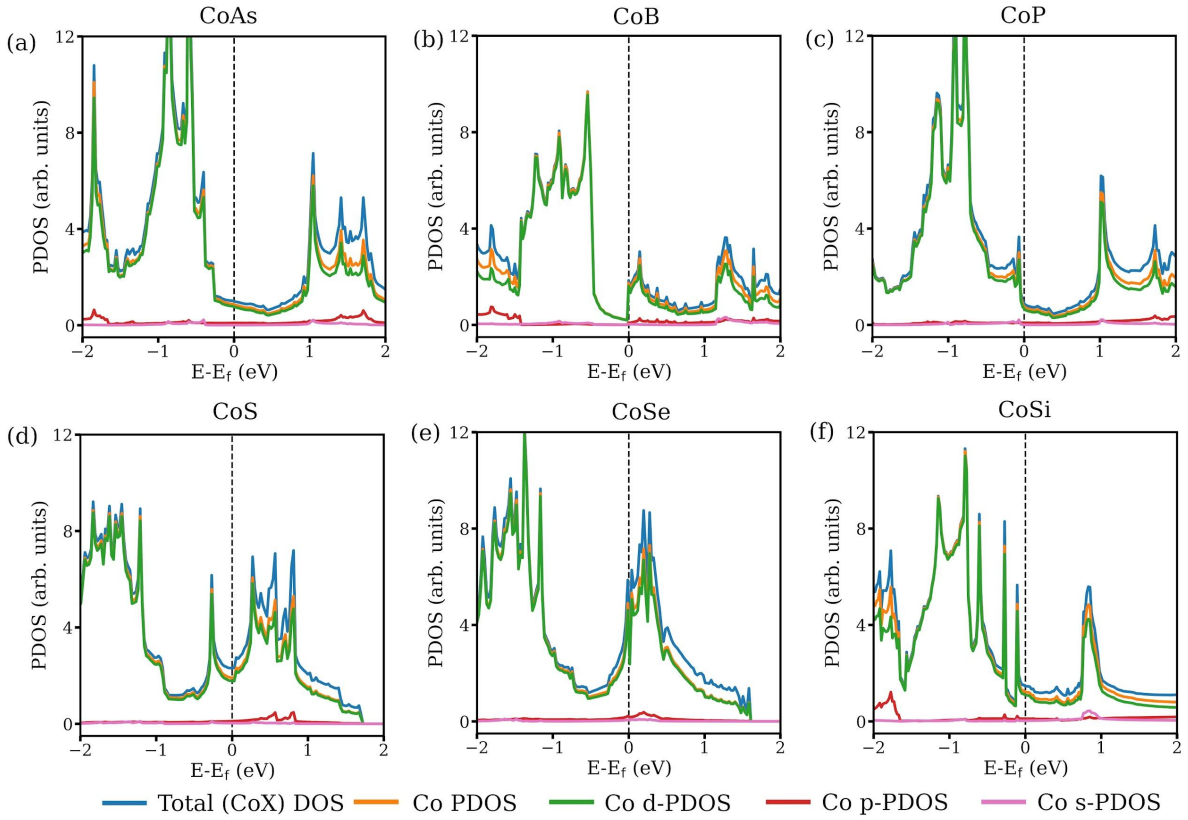

Figure S3. Projected density of states of 'Co' in pristine Co-anti-MXenes. The metallicity of Co-anti-MXenes is arising due to the d-orbitals of the Co. This figure is reproduced from reference 28 with permission.[28] (Copyright © 2022, American Chemical Society).

Table S1. Height (Å) of the Li/Na/K-atom from the CoX surface at the S1, S2, and S3 sites of a 3✕3 supercell of Co-anti-MXenes.

System	Height (Å), Li			Height (Å), Na			Height (Å), K		
	S3	S1	S2	**S3**	S1	S2	**S3**	S1	S2
CoAs	***0.654***	1.507	2.388	***1.307***	2.041	2.703	***2.016***	2.524	3.050
CoB	***1.205***	1.627	2.081	***1.659***	2.018	2.386	***2.184***	2.450	2.736
CoP	***0.835***	1.553	2.323	***1.437***	2.045	2.646	***2.044***	2.500	2.989
CoS	***0.731***	1.385	2.187	***1.279***	1.885	2.543	***1.860***	2.359	2.874
CoSe	***0.530***	1.415	2.330	***1.307***	2.088	2.722	***2.223***	2.473	3.025
CoSi	***0.781***	1.578	2.411	***1.341***	2.018	2.718	***2.009***	2.517	3.029

Table S2. Bader charges on the alkali metal atom at various adsorption sites.

System	Charges, Li			Charges, Na			Charges, K		
	S3	S1	S2	S3	S1	S2	S3	S1	S2
CoAs	**0.856**	0.870	0.903	**0.818**	0.832	0.825	**0.833**	0.857	0.873
CoB	**0.874**	0.889	0.904	**0.829**	0.849	0.867	**0.856**	0.871	0.884
CoP	**0.866**	0.876	0.907	**0.832**	0.840	0.836	**0.843**	0.866	0.878
CoS	**0.872**	0.878	0.910	**0.849**	0.861	0.854	**0.855**	0.881	0.906
CoSe	**0.846**	0.862	0.877	**0.812**	0.779	0.693	**0.823**	0.844	0.836
CoSi	**0.851**	0.867	0.889	**0.797**	0.810	0.791	**0.818**	0.847	0.867

Table S3. Mulliken and Löwdin charges on the alkali metal atoms at the S3 adsorption sites.

Systems	Charges, Li		Charges, Na		Charges, K	
	Löwdin	Mulliken	Löwdin	Mulliken	Löwdin	Mulliken
CoAs	0.86	1.20	0.86	1.08	0.90	1.03
CoB	0.93	1.20	0.93	1.08	0.97	1.02
CoP	0.86	1.18	0.86	1.08	0.91	1.04
CoS	0.89	1.20	0.90	1.12	0.94	1.05
CoSe	0.81	1.09	0.76	0.89	0.84	0.92
CoSi	0.87	1.20	0.88	1.12	0.94	1.08

CDD plots for the adsorption of Li/Na/K on various Co-anti-MXenes

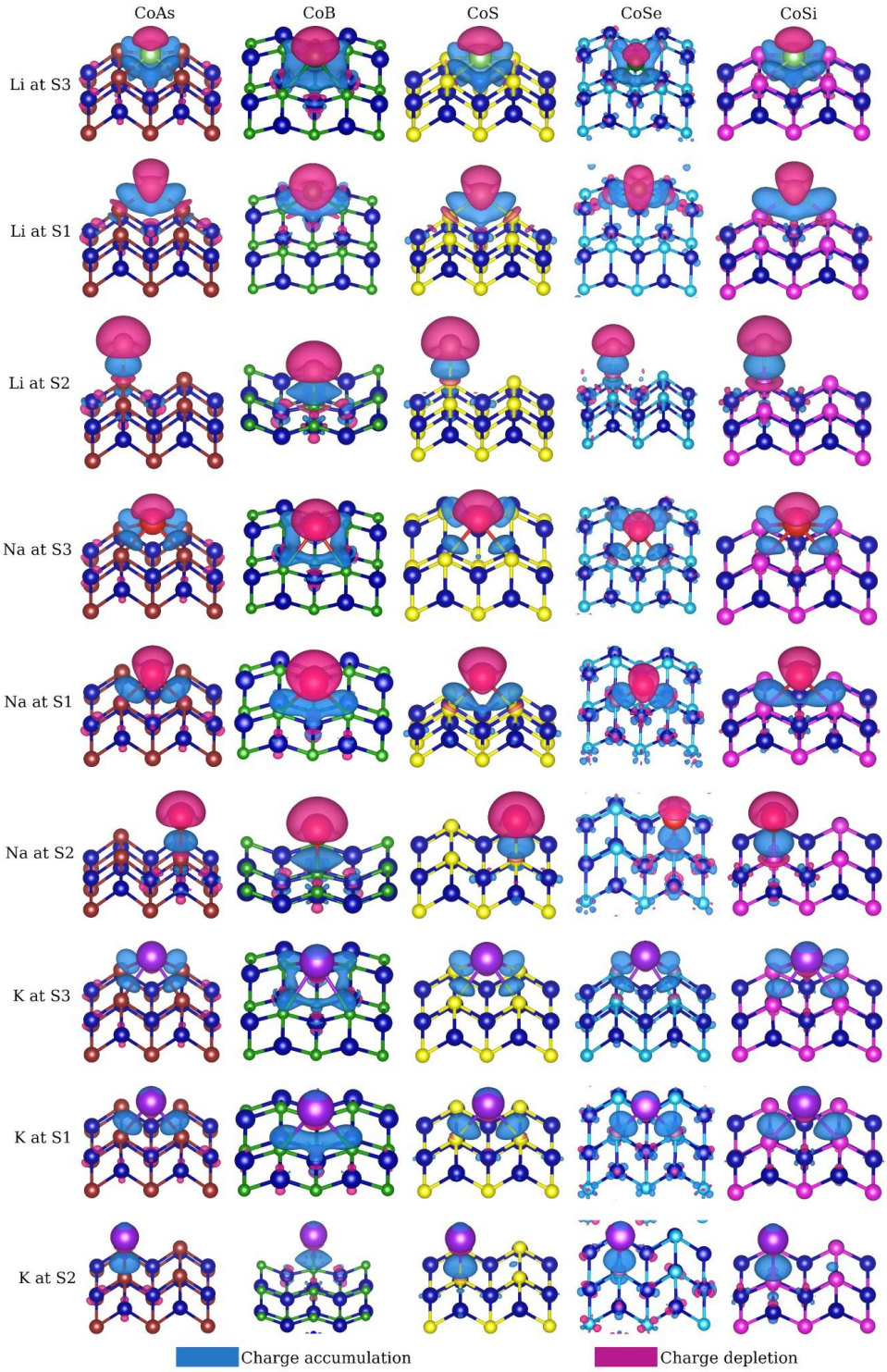

Figure S4. Charge density difference plots for the adsorption of Li/Na/K at the S1, S2, and S3 sites of Co- anti-MXenes. See the main text for calculation details and for the interpretation of the plots.

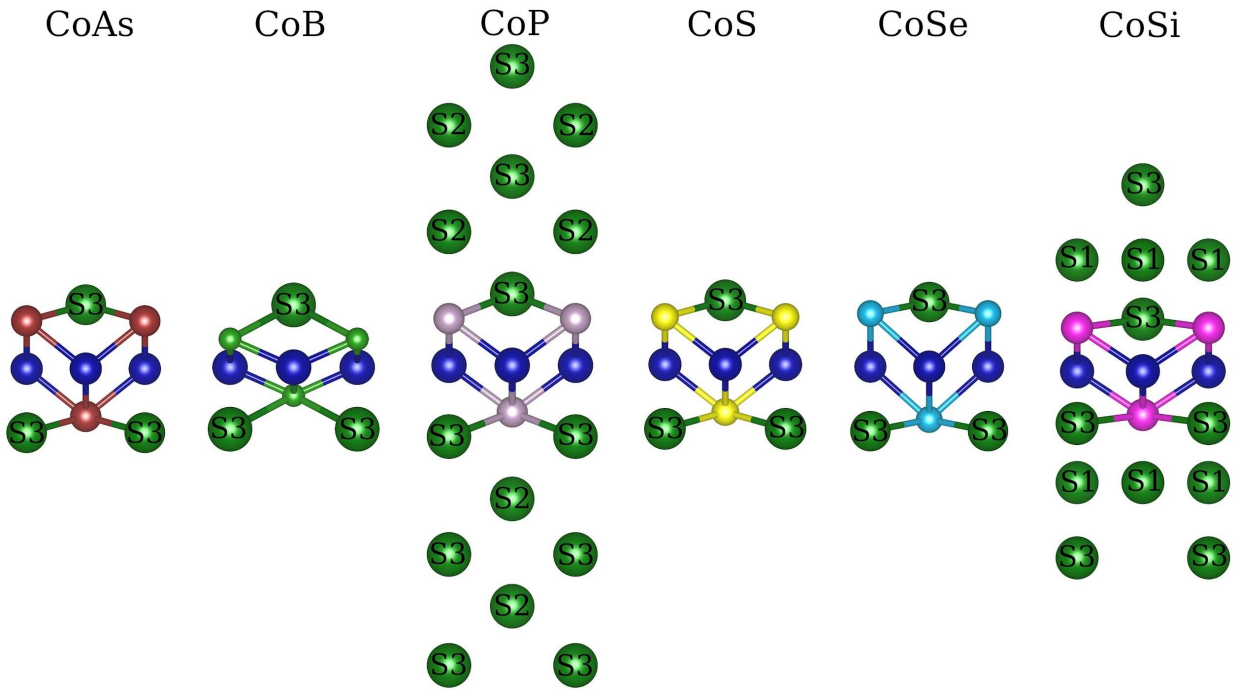

Figure S5. Optimized structures of various Co-anti-MXenes after the adsorption of a maximum number of lithium atoms. The molecular formulas of the maximally lithiated Co-anti-MXenes are LiCoAs, LiCoB, Li_5CoP, LiCoS, LiCoSe, and Li_4CoSi, respectively.

Optimized structures of maximally sodiated Co-anti-MXenes

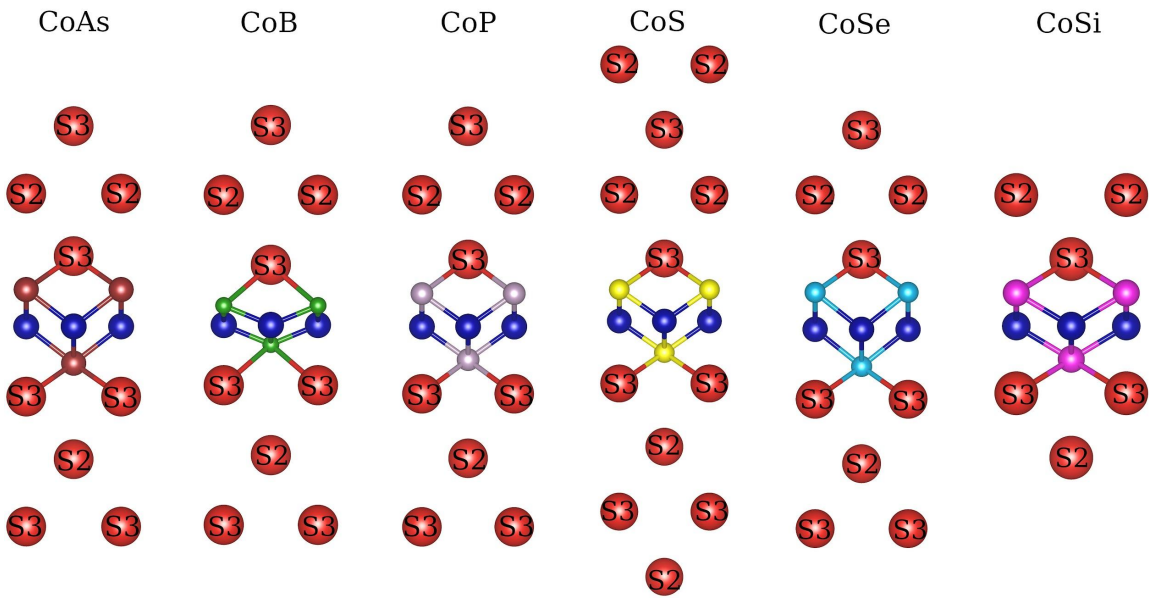

Figure S6. Optimized structures of various Co-anti-MXenes after the adsorption of a maximum number of sodium atoms. The molecular formulas of the maximally sodiated Co-anti-MXenes are Na_3CoAs, Na_3CoB, Na_3CoP, Na_4CoS, Na_3CoSe, and Na_2CoSi. This figure is reproduced from reference 28 with permission.[28] (Copyright © 2022, American Chemical Society).

Optimized structures of maximally potassiated Co-anti-MXenes

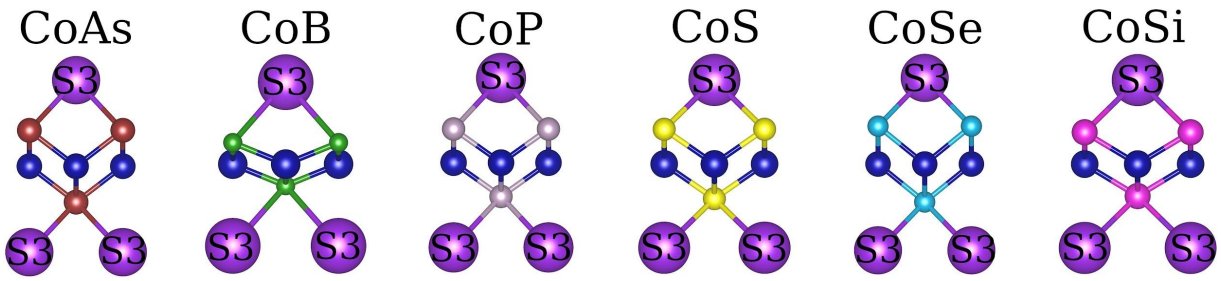

Figure S7. Optimized structures of various Co-anti-MXenes after the adsorption of a maximum number of potassium atoms. The molecular formula for all the maximally potassiated Co-anti-MXenes is the same: KCoX (X = As, B, P, S, Se, and Si).

Thermal stability of maximally sodiated structures

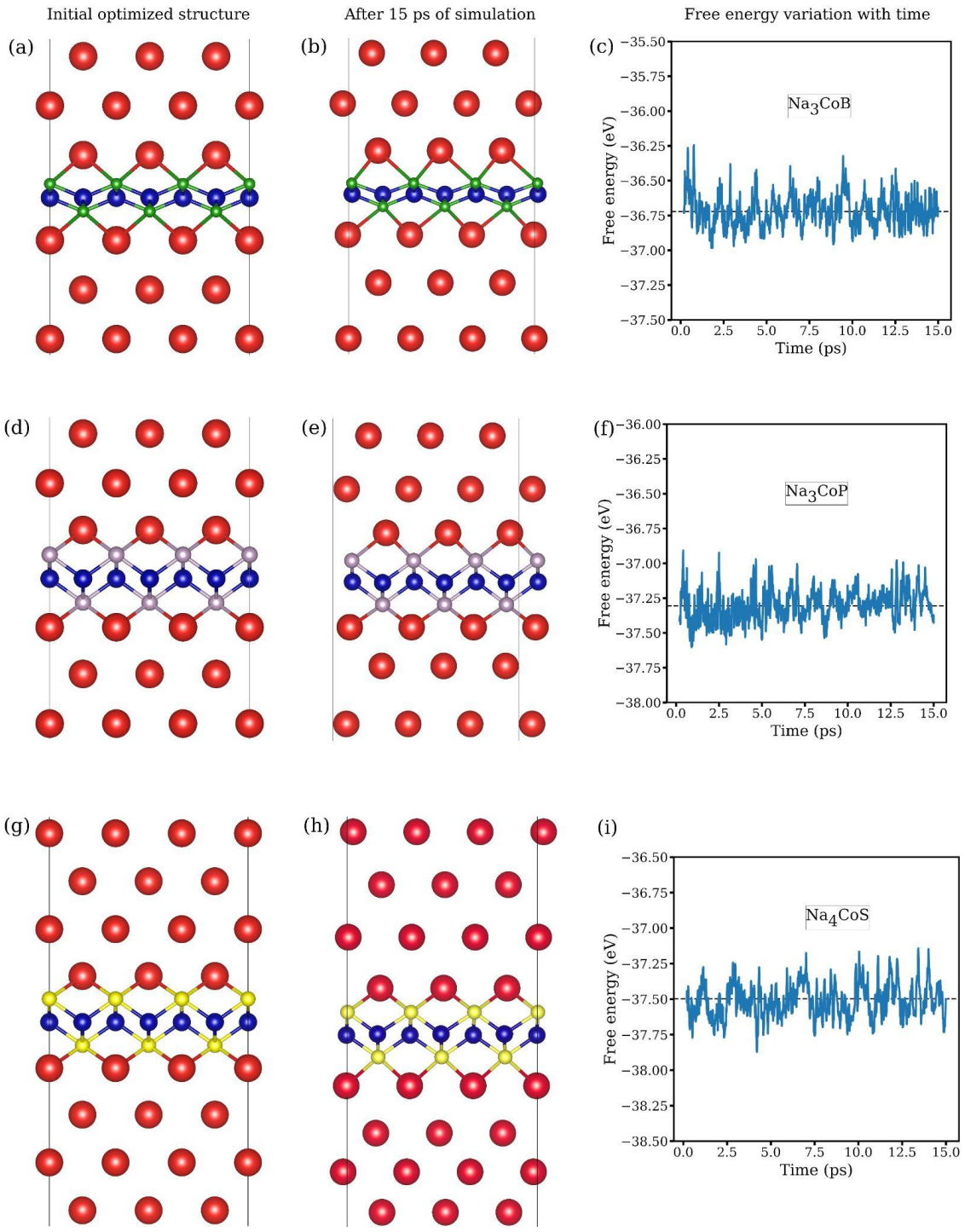

Figure S8. (a), (d), and (g) depict the optimized structures of Na_3CoB, Na_3CoP, and Na_4CoS systems, respectively, at the 0^{th} ps of the NVT simulation. (b), (e) and (h) depict the corresponding structures after a 15 ps NVT simulation. (c), (f) and (i) show the fluctuations in the free energy of Na_3CoB, Na_3CoP, and Na_4CoS during the 15 ps NVT simulation (at 300 K). This figure is reproduced from reference 28 with permission.[28] (Copyright © 2022, American Chemical Society).

ELF plots of maximally lithiated Co-anti-MXenes

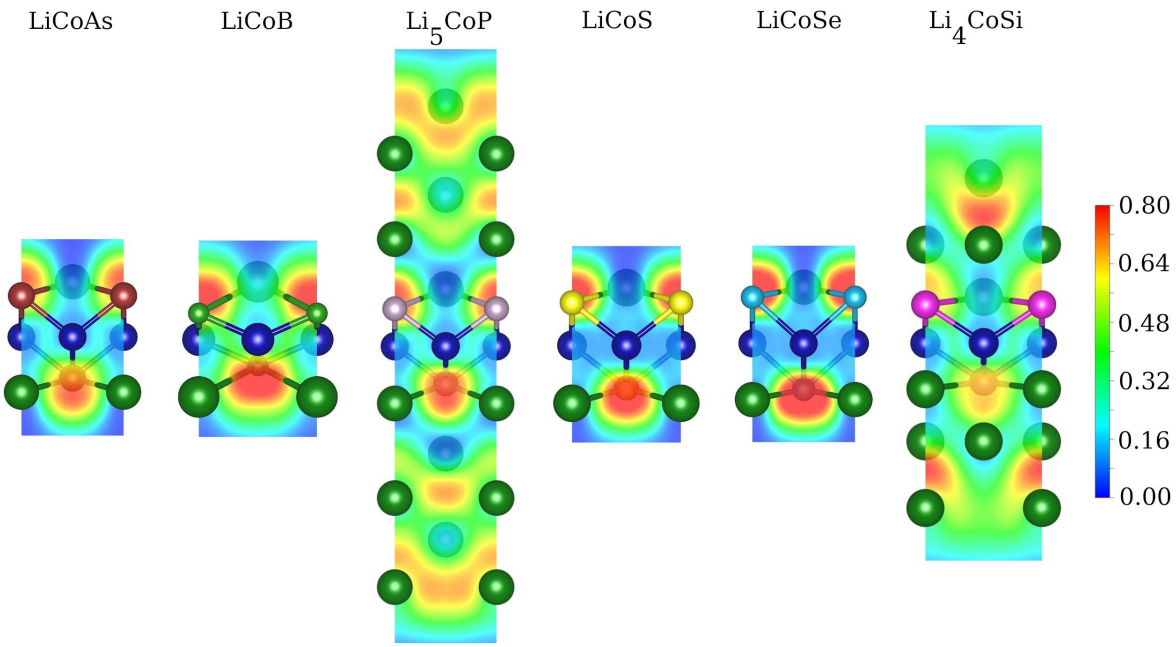

Figure S9. ELF plots of maximally lithiated Co-anti-MXenes. Plots are projected along the (010) plane.

ELF plots of maximally potassiated Co-anti-MXenes

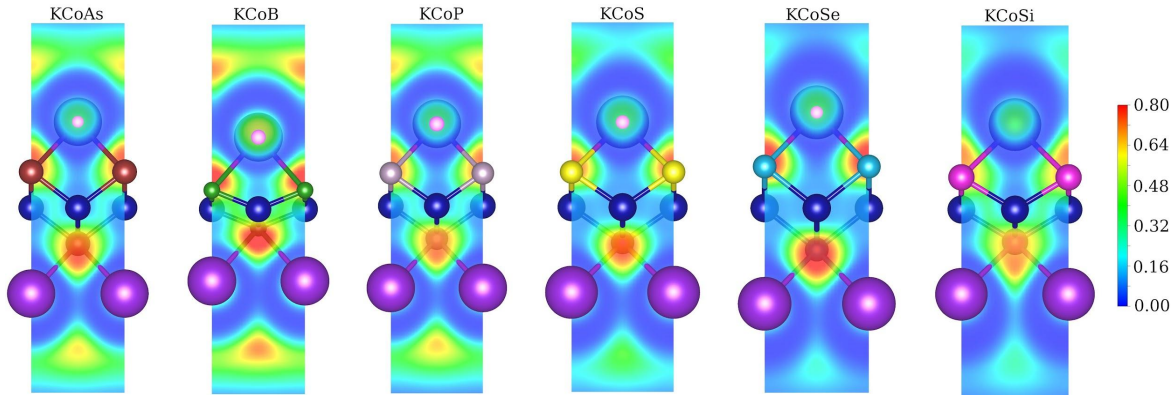

Figure S10. ELF plots of maximally potassiated Co-anti-MXenes. Plots are projected along the (010) plane.

ELF plots of Co-anti-MXenes with two layers of K atoms

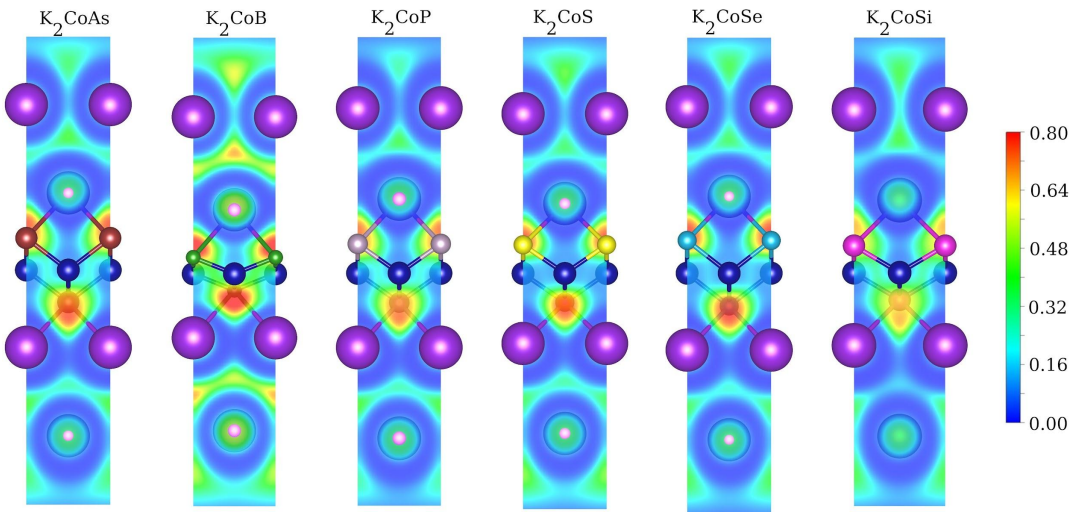

Figure S11. ELF plots of Co-anti-MXenes with two layers of K atoms (the maximally potassiated structures have only one layer of potassium atoms). Plots are projected along the (010) plane.

Expansion of the CoP bilayer after the intercalation of Li

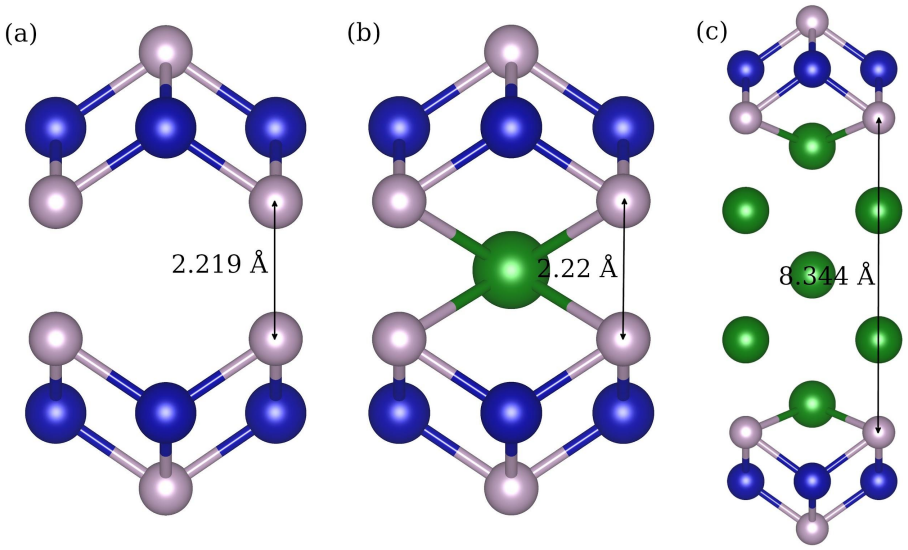

Figure S12. Optimized structures of (a) pristine CoP bilayer, (b) CoP bilayer with one layer of lithium atoms, and (c) CoP bilayer with five layers of Li atoms, respectively. The interlayer spacings between the CoP layers in these structures are 2.219 Å, 2.22 Å, and 8.344 Å, respectively.

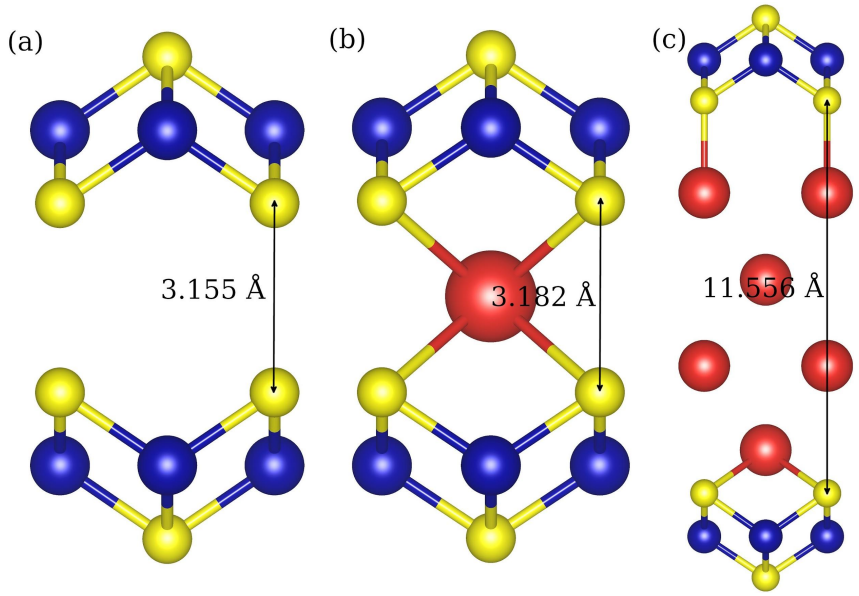

Figure S13. Optimized structures of (a) pristine CoS bilayer, (b) CoS bilayer with one layer of sodium atoms, and (c) CoS bilayer with four layers of Na atoms, respectively. The calculated interlayer spacings between the CoS layers in these structures are 3.155 Å, 3.182 Å, and 11.556 Å, respectively. This figure is reproduced from reference 28 with permission. [28] (Copyright © 2022, American Chemical Society).

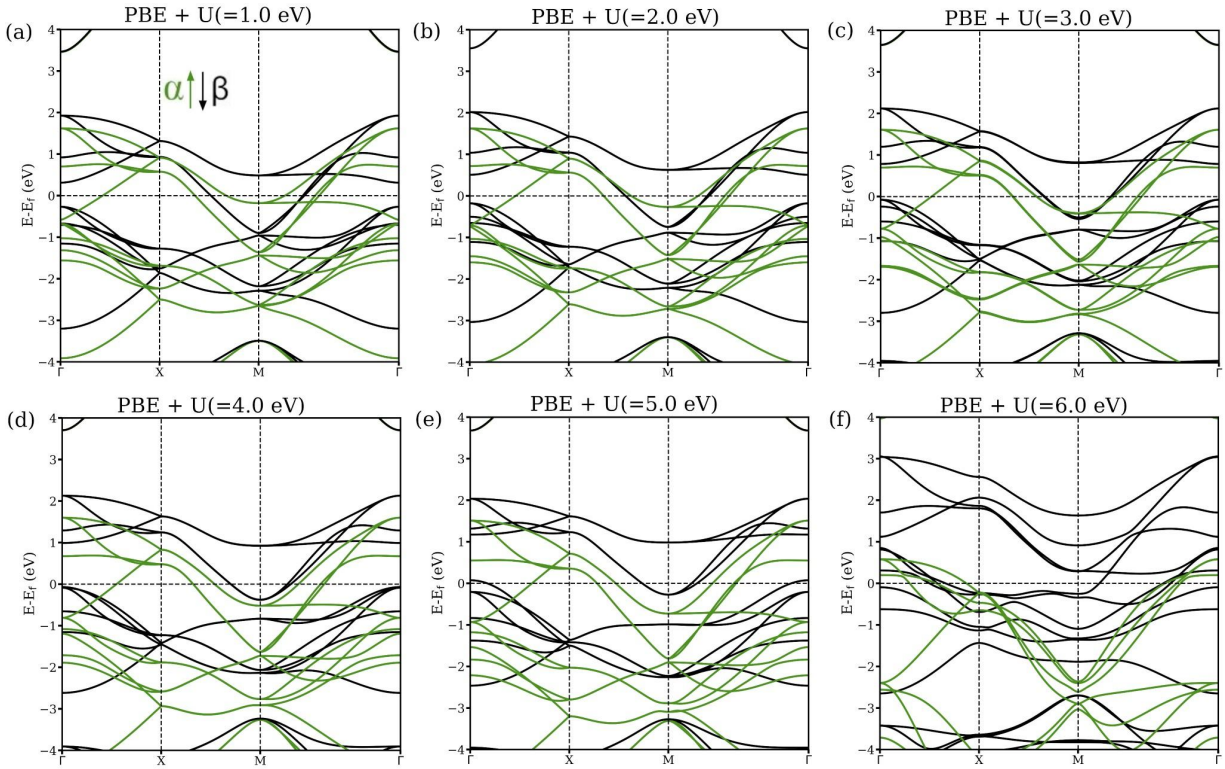

Figure S14. Computed bandstructures of the CoS system for both $\propto$ and β-spin channels at various U values (1eV ≤ U ≤ 6eV). The corresponding U values are provided in the title of each panel.

Validation for the kinetic energy cutoff and the k-mesh

Table S4. Variation in the total energy of a CoS unit cell with different kinetic energy cutoffs. All calculations are performed with a 12×12×1 k-mesh (only SCF optimization is performed)

ENCUT value (eV)	Total energy of the system (eV)	Energy difference (eV)
350	-24.845	–
400	-24.839	0.006
450	-24.837	0.002
500	-24.838	-0.001
550	-24.838	0.000
600	-24.838	0.000

Table S5. Variation in the total energy of a CoS unit cell with different k-mesh values. All calculations are performed with a 450 eV kinetic energy cutoff (only SCF optimization is performed).

K-mesh	Total energy of the system (eV)	Energy difference (eV)
6×6×1	-24.845	–
8×8×1	-24.830	0.015
10×10×1	-24.840	-0.010
12×12×1	-24.837	0.003
14×14×1	-24.836	0.001
16×16×1	-24.837	-0.001