Electronic Supplementary Information

Gismondine Cobalt Phosphate ($CoPO_4$) as Monovalent-ion Battery Cathode Material: A First-Principles Study

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1.1 Characteristics of Pure $CoPO_4$ (C2/c)

Table S1 shows the experimental lattice parameters of $CoPO_4$ (C2/c) as compared to the ones calculated using *VASP* with the (1) generalized gradient approximation (GGA) and (2) GGA with Hubbard correction (GGA+U) exchange-correlation functionals. Our calculated values are similar to experimental ones. Although pure $CoPO_4$ (C2/c) is predicted to be a semiconductor with a 1.1 eV bandgap under GGA+U, it is predicted to be metallic with no bandgap under GGA (see **Figure S1**).

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Table S1. Comparison of the experimental[1] and our calculated lattice parameters of $CoPO_4$ (C2/c).

	a (Å)	b (Å)	c (Å)	β (°)	Volume (Å^3)
Expt. lattice	14.744	8.850	10.062	131.609	981.7
GGA lattice	14.499	9.201	10.125	134.294	966.8
% diff fr Expt	-1.7	4.0	0.6	2.0	-1.5
GGA+U lattice	14.768	8.879	10.360	135.619	950.1
% diff fr Expt	0.2	0.3	3.0	3.0	-3.2

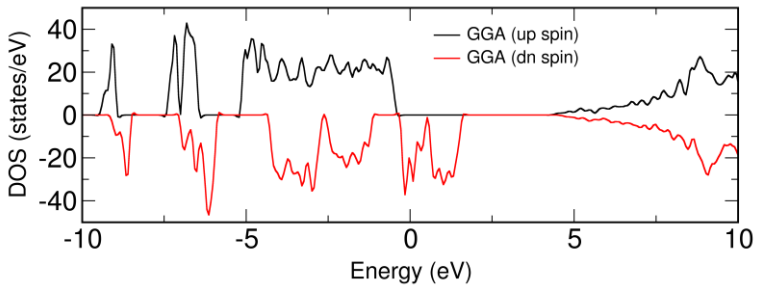

Figure S1. DOS of pure $CoPO_4$ (C2/c) calculated using the GGA exchange-correlation functional.

1.2 Variations of the Repeating Unit in $CoPO_4$ (C2/c)

The volume of $CoPO_4$ (C2/c) shrinks on increasing lithiation/sodiation. **Table S2** shows how much the diameters of ring_Co and ring_p, as well as the widths of cradle_Co and cradle_P, change as Li/Na atoms are adsorbed onto the $CoPO_4$ (C2/c) framework. The $CoPO_4$ (C2/c) framework shrinks more to accommodate the smaller Li atoms.

Table S2. Measurements of the repeating unit of pure $CoPO_4$ (C2/c), $CoPO_4$ with 8 Li atoms adsorbed in the framework, and $CoPO_4$ with 8 Na atoms adsorbed in the framework.

	Pure $CoPO_4$	$CoPO_4$ + 8 Li	$CoPO_4$ + 8 Na
Aver. diameter ring_P (Å)	5.00	3.65	4.25
Aver. diameter ring_Co (Å)	5.20	3.37	3.88
Aver. width cradle_P (Å)	4.71	4.36	4.93
Aver. width cradle_Co (Å)	5.33	3.86	4.32

1.3 Diffusion Routes for Li

Figure S2 shows the diffusion routes taken by Li as it moves from various adsorption sites to another.

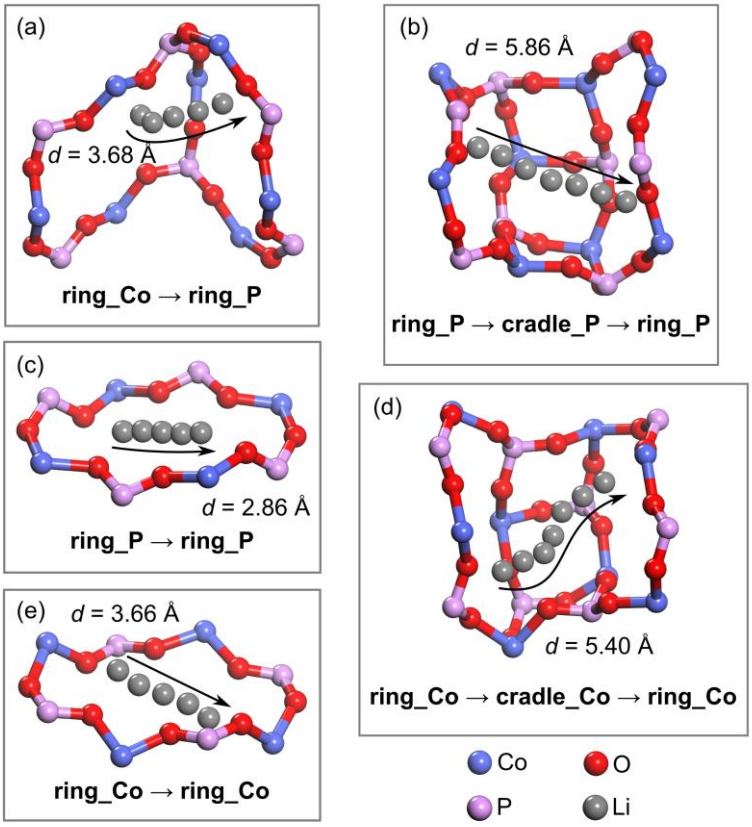

Figure S2. (**a-e**) Molecular models showing the actual route and distance, *d*, taken by Li as it diffuses between different adsorption sites. The Li atom from each geometry-optimized image of the CI-NEB calculations was superimposed onto the pure $CoPO_4$ (C2/c) unit cell; all other atoms in the $CoPO_4$ (C2/c) unit cell have been removed for visual clarity.

1.4 Ab Initio Molecular Dynamics Results

We conducted ab initio molecular dynamics (MD) calculations to observe the actual preferred diffusion pathways of Li/Na within the $CoPO_4$ (C2/c) channels. The generalized gradient approximation (GGA) exchange-correlation functional was used. We placed 4 Li/Na atoms in random positions in a 1 × 2 × 2 supercell and equilibrated the supercell for 2 picoseconds (ps) at 800 K under the canonical (NVT) ensemble using the Nosé-Hoover thermostat.[2] A time step of 1 femtosecond (fs) was used. After equilibration, an NVT production run of 6 ps was conducted and the trajectories of the atoms were saved every 50 fs. The temperature of 800 K was chosen so that we could observe significant diffusion of Li/Na under a reasonable simulation timeframe.[3]

Figure S3 shows the diffusion of Li and Na atoms in $CoPO_4$ (C2/c) during the 6 ps ab initio MD simulation at 800 K. The framework was stable during the simulation and no phase transitions were observed. The MD trajectories coincide with our proposed proposed pathways: we observe that pathways 1 and 2 are the most favored by Li while pathway 1 is the most favored by Na; pathway 3 is not less favored by Li or Na.

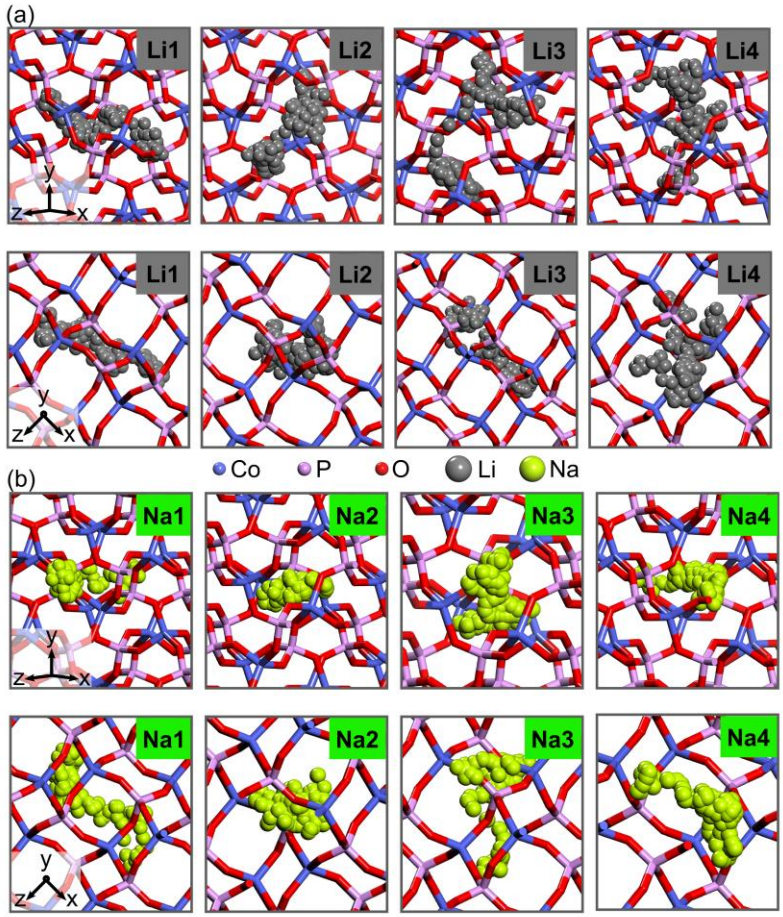

Figure S3. Molecular models showing, from two different perspectives, the trajectories of (**a**) four Li atoms and (**b**) four Na atoms in a 1 × 2 × 2 $CoPO_4$ (C2/c) supercell during a 6 ps ab-initio molecular dynamics simulation at 800 K. Each sphere represents the spatial coordinates of each Na atom captured at every 50-fs interval of the 6 ps simulation. For visual clarity, we did not show the movement of the atoms in the $CoPO_4$ (C2/c) supercell.

References

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2 Nosé, S. *J. Chem. Phys.*, 1984, **81**, 511–519.
3 Wang, Y.; Richards, W. D.; Ong, S. P.; Miara, L. J.; Kim, J. C.; Mo, Y.; Ceder, G. *Nat. Mater.*, 2015, **14**, 1026–1031.