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Thermodynamic and Kinetic Properties of Layered-$CaCo_2O_4$ for the Ca-ion batteries: A Systematic First-Principles Study

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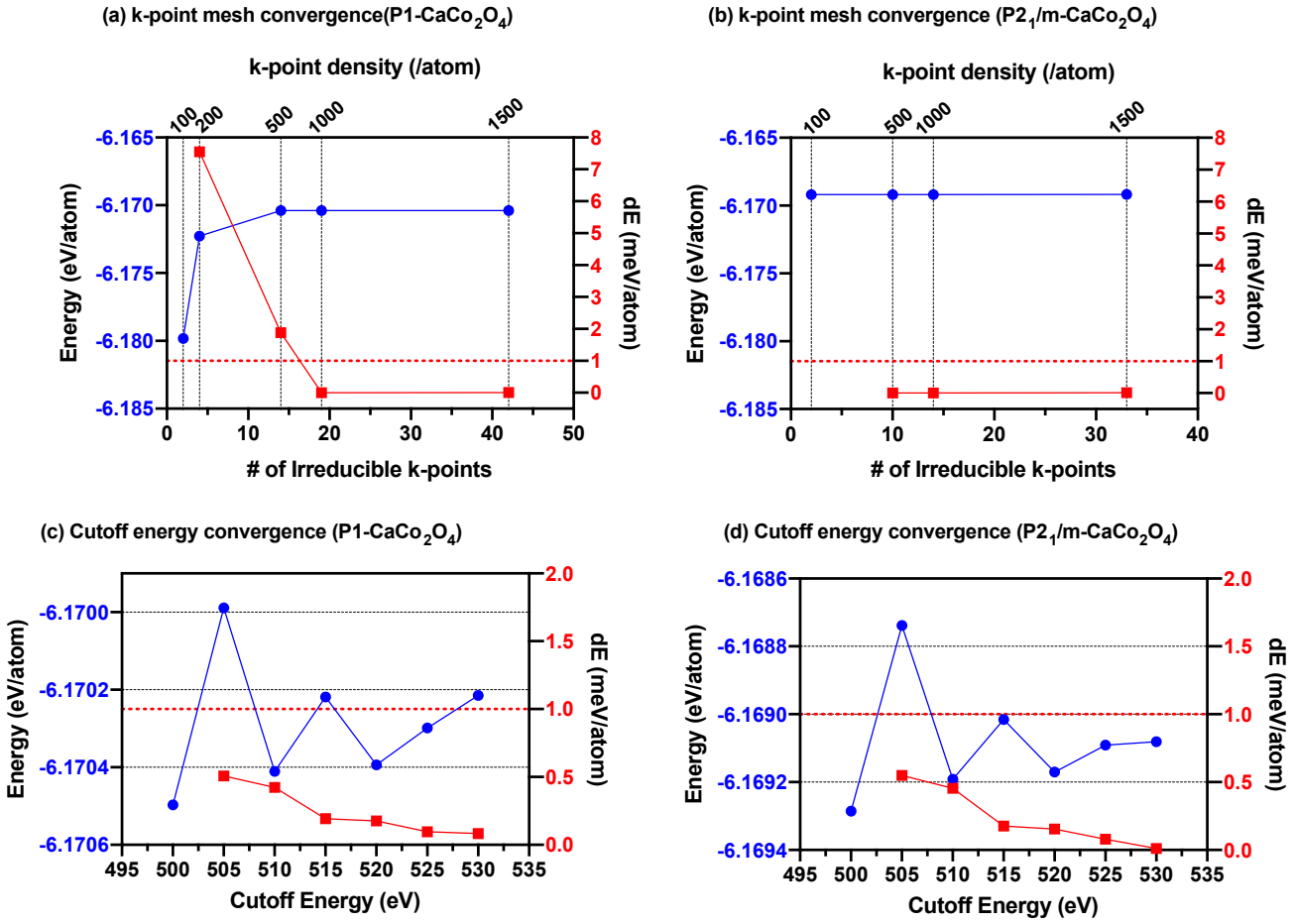

Figure S1. The energy convergence test as a function of the number of the irreducible k-points and cutoff energy. The energy per atom of P1- and $P2_1/m$-$CaCo_2O_4$ structures with respect to the irreducible k-points are plotted in (a) and (b), respectively, where top x-axis represents the k-point density per atom and right y-axis is the energy difference. The energies per atom of P1- and $P2_1/m$-$CaCo_2O_4$ structures as a function of cutoff energy are plotted in (c) and (d), respectively.

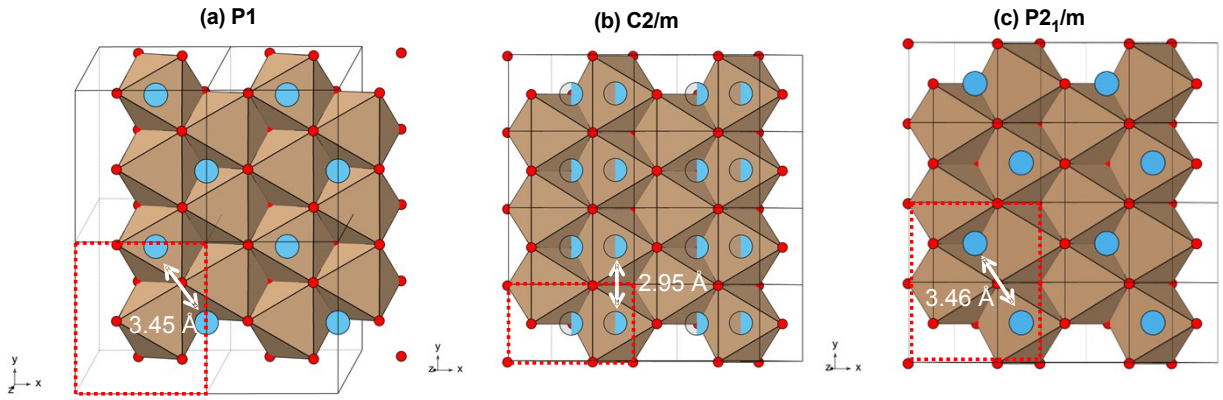

Figure S2. The Ca atom distribution within layer in the structures of P1 (a), C2/m (b), and P2$_1$/m (c). The dashed red boxes represent unit cell.

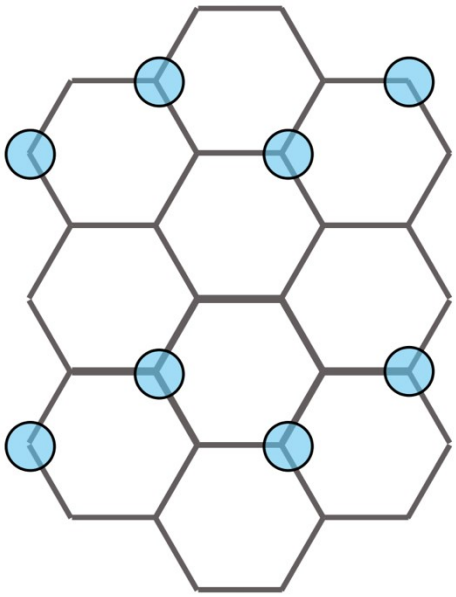

Figure S3. Another Ca distribution with the zigzag pattern with the angle of 60°.

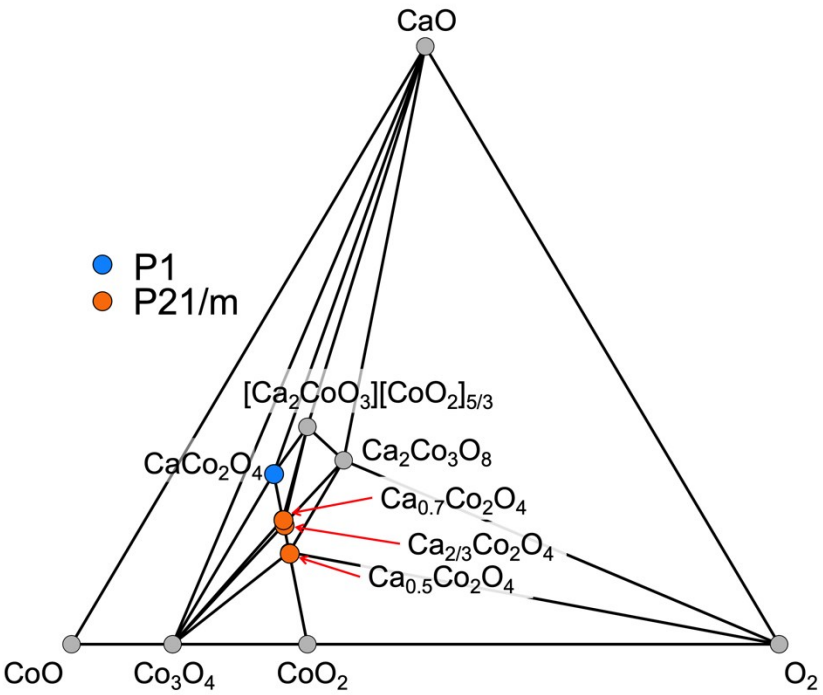

Figure S4. The equilibrium phase diagram of CaO-CoO-O_2, where rutile CoO_2 is the most stable structure.

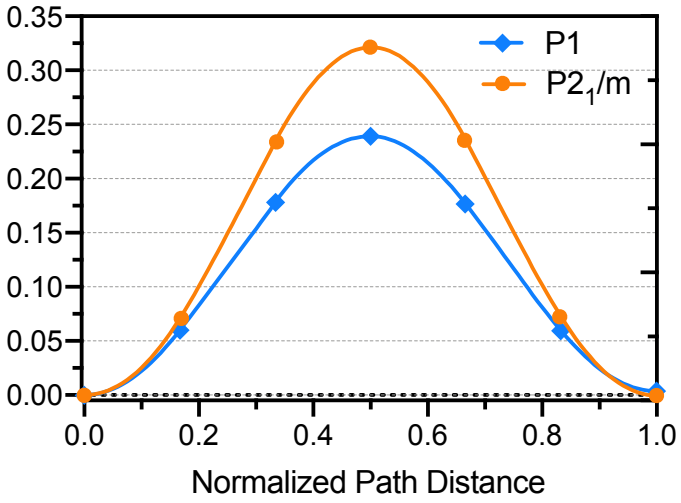

Figure S5. The MEP of Ca-ion migration in the high-concentration vacancy limit in P1 and $P2_1/m$ structures calculated by strongly constrained and appropriately normed semilocal density functional.

Table S1. Ca migration barriers in the layered CoO_2 at various local environments of diffusing Ca atom. The "Limit" in dilute vacancy means a single Ca vacancy (blue box in Figure 3(b) and (e)). The "2Vac_1" and "2Vac_2" represents an additional vacancy at each initial and final states (orange and blue box in Figure 3(b) and (e)); and "4Vac" is for the structure with two additional vacancies at each initial and final states (magenta box in Figure 3(b) and (e)).

Local environments of diffusing Ca		Migration Barrier (eV)			
		P1		$P2_1/m$	
		Intra	Inter	Intra	Inter
Dilute Vacancy	Limit (blue)	0.72	0.36	0.82	0.42
	2Vac_1 (orange)	0.89	0.39	0.96	0.42
	2Vac_2 (purple)	0.90	0.60	1.04	0.59
	4Vac (magenta)	0.35	0.38	0.36	0.31
High Vacancy	Limit	0.27		0.25	

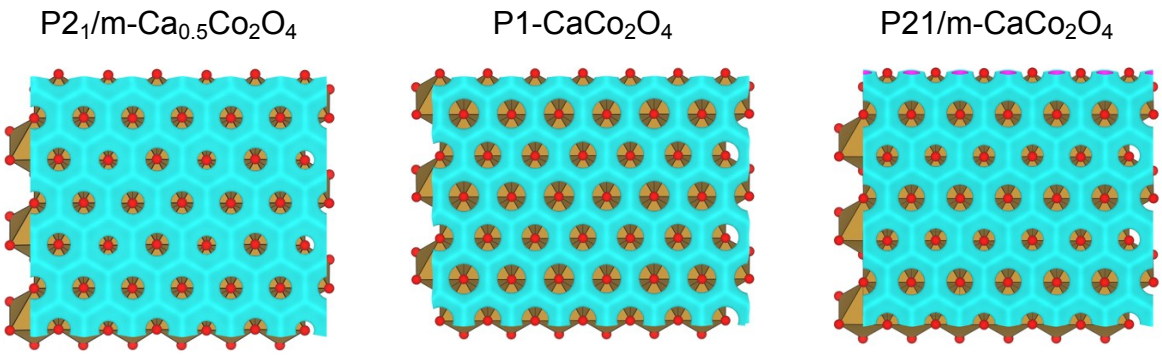

Figure S6. The Ca diffusion path as the isosurface of constant low bond-valence site energy of Ca within the (a)$P2_1/m$-$Ca_{0.5}Co_2O_4$, (b)P1-$CaCo_2O_4$, and (c)$P2_1/m$-$CaCo_2O_4$ structures.

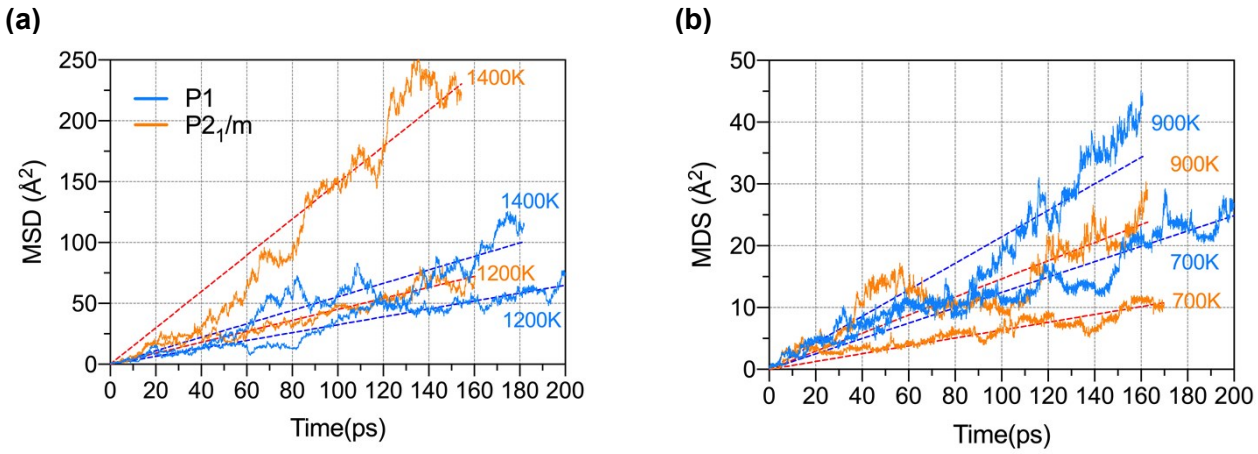

Figure S7. Calculated mean squared displacement (MSD) for P1- and $P2_1/m$-$Ca_{0.5}Co_2O_4$ at (a) high temperatures (1400K, 1200K) and (b) low temperatures (900K and 700K). The dashed lines signify the Einstein relation between MSD and time.

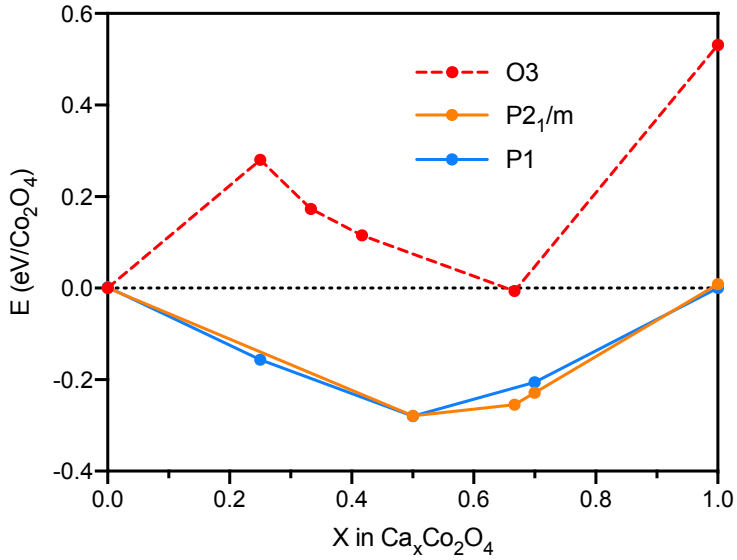

Figure S8. The energies of O3-$Ca_xCo_2O_4$, where X is the Ca concentrations at the hull, and convex hulls of P3-types layered $CaCo_2O_4$. . The energies of O3-$Ca_xCo_2O_4$ phase (dashed line) are referenced to the P1-CaCO2O4 (X=1) and Ca metal.