—Supporting Information—

Searching Ternary Oxides and Chalcogenides as Positive Electrodes for Calcium Batteries

Wang Lu,[†] Juefan Wang,[†] Gopalakrishnan Sai Gautam,[*,‡] and Pieremanuele Canepa[*,†,¶]

†*Department of Materials Science and Engineering, National University of Singapore, 9 Engineering Drive 1, 117575, Singapore*

‡*Department of Materials Engineering, Indian Institute of Science, Bangalore 560012, India*

¶*Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, 117585, Singapore*

E-mail: saigautamg@iisc.ac.in; pcanepa@nus.edu.sg

S1 Structural Data Obtained from Initial Screening

Table S1 lists selected intercalation discharged ($Ca_iM_jZ_k$) and charged (M_jZ_k) compound obtained from the Inorganic Chemical Structure Database (ICSD?). The information is completed by the compound space groups, their energy above the convex hull (E^{hull}) as obtained from the Materials Project,[1] and the coordination number ($CN_{disc.}$) of Ca^{2+}. The coordination number is determined by visual inspection of discharged structures. Note, whenever available we report a matching charged composition M_jZ_k and its relevant properties.

Table S1: Discharged $Ca_iM_jZ_k$ and charged M_jZ_k oxide and chalcogenide compounds resulting from the preliminary screening. The ICSD or Materials Project (MP) codes matching the materials are reported. E^{hull} (in meV/atom) is the energy above the convex hull, and Ca^{2+} the coordination number ($CN_{disc.}$) of the discharge compounds.

Material	ICSD/MP	Space Group	E^{hull}	$CN_{disc.}$
CaV_3O_7	2507	*Pnma*	2.0	7
V_3O_7	mvc-13330	*Pnma*	51.0	–
$Ca_2V_2O_6$	241336	*C*2/*m*	24.0	6
CaV_2O_6	21064	*C*2/*m*	0.0	–
CaV_2O_4	164185	*Pnma*	0.0	8
V_2O_4	mp-777479	*Pnma*	26.0	–
CaV_2O_5	82689	*Pmmn*	0.0	8
V_2O_5	15798	*Pmmn*	0.0	–
$CaNb_2O_4$	88779	*Pbcm*	0.0	6
Nb_2O_4	96	$I4_1/a$	3.0	–
$Ca_5Cu_6O_{12}$	91059	$P2_1/c$	28.0	6
$Ca_3Cu_6O_{12}$	mp-1540145	$I4_1/a$	0.0	–
$CaMoO_3$	246082	$P2_1/c$	0.0	8
MoO_3	mp-715584	*Pc*	0.0	–

$CaIrO_3$	420479	$Cmcm$	0.0	8
IrO_3	mp-1097041	$Cmcm$	0.0	–
$CaRh_2O_4$	170597	$Pnma$	0.0	8
Rh_2O_4	28498	$P4_2/mnm$	0.0	–
$CaCu_2S_2$	241336	$P\bar{3}m1$	0.0	6
Cu_2S_2	63328	$Cmcm$	0.0	–
$CaMo_6S_8$	619423	$R\bar{3}$	20.0	8
Mo_6S_8	86788	$R\bar{3}$	66.0	–
$Ca_4Mn_2O_7$	103352	$Cmca$	37.0	7
$Ca_3Mn_2O_7$		$Cmc2_1$	17.0	–
$Ca_3(CoO_3)_2$	153193	$R\bar{3}cH$	0.6	8
$CaCoO_3$		Cm	48.3	–
$Ca_4Fe_9O_{17}$		$C2$	26.0	6
$Ca_3Co_4O_9$		$Cmm2$	73.0	6
$CaMn_2O_4$	280514	$Pbcm$	0.0	8
Mn_2O_4		$Pnma$	4.0	–
$CaMn_3O_6$	172817	$P2_1/c$	13.0	8
Mn_3O_6		$I4/m$	0.0	–
CaV_4O_9	90927	$P4/nZ$	23.00	8
V_4O_9		$Pnma$	25.00	–
$Ca_2Sb_2S_5$	201044	$P2_1/c$	0.0	6/7
$CaSb_2S_5$		Pc	17.8	–
$CaCr_2O_4$	8288	$Pbnm$	54.0	8
CrO_2		$Cmcm$	18.7	–
$CaCuO_2$	75868	$P4/mmm$	16.0	8
CuO_2		$R\bar{3}m$	16.2	–

$CaMn_2O_4$	260389	$Fm\bar{3}m$	39.0	8
MnO_2		$Cmcm$	20.2	–
$Ca(NiO_2)_2$	40470	$R\bar{3}mH$	54.0	6
NiO_2		$Fd\bar{3}m$	10.4	–
$CaTi_2O_4$	51183	$Cmcm$	24.0	8
TiO_2		$Cmcm$	147.0	–
$Ca_2Co_2O_5$	428760	$Pcmb$	20.0	8
$CaCo_2O_5$		$Pmmn$	63.0	–
$Ca_2Cr_2O_5$	238797	I_2mb	16.8	7
Cr_2O_5		$Pmmn$	281.0	–
$Ca_2Fe_2O_5$	255803	$Pnma$	0.0	8
$CaFe_2O_5$		$Pmmn$	105.0	–
$Ca_2Fe_9O_{13}$	100826	$C2/m$	53.00	7
Fe_9O_{13}		$C2/m$	264.0	–
$CaFe_2O_4$	28177	$Pbnm$	0.0	8
FeO_2		$Pnma$	207.0	–
$CaFeO_3$	248483	$Pbnm$	0.0	8
FeO_3		$C2/m$	557.0	–
$Ca_3(Mn_2O_7)$	55666	$Cmc2_1$	17.0	8
Mn_2O_7		$P21/c$	318.0	–
$CaMn_3O_6$	252285	$P2_1/c$	13.	8
MnO_2		$P2/m$	25.0	–
$CaMnO_3$	258991	$Pnma$	35.0	8
MnO_3		$Imma$	512.0	–
Ca_2MnO_4	50789	$I4_1/acd$	7.0	8
MnO_4		$I4_1/amd$	504.0	–

$Ca(Mo_3S_4)_2$	62388	$R\bar{3}$	18.0	8
Mo_3S_4		$R3$	65.0	–
$CaMoO_3$	172790	$Pbnm$	0.0	8
MoO_3		$Pnma$	4.0	–
$CaMoO_4$	62219	$I4_1/a$	0.0	8
MoO_4		$P1$	467.0	–
$CaVO_3$	237336	$Pnma$	0.0	8
VO_3		$Imma$	333.0	–
$Ca_3(Ru_2O_7)$	153769	$Cmc2_1$	14.0	6/8
$Ca_2Ru_2O_7$		$Fd\bar{3}m$	0.0	–
Ca_2CoO_3	95439	Cm	18.2	5
$Ca_3(CoO_3)_2$		$P1$	296.0	–
Ca_2CoO_3	181372	$C2/m$	231.0	4
$CaCoO_3$		$Pnma$	23.0	–
Ca_2CuO_3	68885	$Immm$	2.0	7
$CaCuO_3$		$Pm\bar{3}m$	165.0	–
$Ca_2Nb_2O_7$	26010	$P2_1$	42.0	6/7/8
$CaNb_4O_{14}$		$R\bar{3}m$	380.0	–
$Ca(CoO_2)_2$	245715	$Pnma$	73.0	8
CoO_2		$Cmcm$	224.0	–
$CaCrO_3$	245840	$Pbnm$	36.0	8
CrO_3		$P2_1$	187.0	–
$CaCu_2O_3$	15094	$Pmmn$	31.0	6
Cu_2O_3		$Cmcm$	192.0	–
$Ca(Fe_2O_3)_2$	16355	$Cmcm$	24.0	6
$CaFe_5O_7$	16356	$Cmcm$	29.0	6

Fe_5O_7		$Cmcm$	192.0	–
$Ca(FeO_2)_2$	16695	$Pnma$	2.0	8
Fe_2O_4		$Pnma$	165.0	–
$CaMnSe_2$	52781	$Fm\bar{3}m$	32.0	6
$MnSe_2$		$Pa\bar{3}$	43.0	–
$CaMnO_3$	50997	$Pnma$	35.0	8
MnO_3		$Imma$	51.0	–
$CaNbO_3$	51202	$Pnma$	59.0	8
NbO_3		$P4mm$	187.0	–
$Ca(Ta_2O_6)$	24091	$Pnma$	0.0	8
TaO_3		$Im\bar{3}$	147.0	–
$Ca(YS_2)_2$	619557	$Pnma$	0.0	6/7
YS_2		$Fd\bar{3}m$	1564.0	–
$CaFe_5O_7$	251508	$P2_1/m$	29.0	6/8
Fe_5O_7		$Cmcm$	192.0	–
$Ca_2(Os_2O_7)$	97093	$Imma$	0.0	8
$CaOsO_3$	237732	$Pnma$	76.0	8
Ca_2IrO_4	25500	$P\bar{6}2m$	27.0	6/7/9
$Ca_4(IrO_6)$	81902	$R\bar{3}cH$	22.0	8
$Ca_4Mn_3O_{10}$	86648	$Pbca$	22.0	7/10
$CaMo_5O_8$	280969	$P2_1/c$	263.0	7
$Ca(Mo_5O_8)$	152115	$P2_1/c$	263.	8
Ca_2GeS_4	23416	$Pnma$	0.0	6
$Ca_3V_2O_8$	9332	$R3c$	37.0	6
$Ca_2Mn_3O_8$	24847	$C2/m$	0.0	6
Ca_3NbO_6	91038	$P2_1/c$	51.0	7

$CaFe_3O_5$	16354	$Cmcm$	32.0	8
$Ca(RuO_3)$	69359	$Pnma$	0.0	8
$CaPd_3O_4$	16538	$Pm\bar{3}n$	21.0	8
$Ca_4(PdO_6)$	88134	$R\bar{3}cH$	0.0	6/8
$CaPd_3O_4$	186819	$Pm\bar{3}n$	21.0	8
$Ca_2(Ru_2O_7)$	21064	$C2/m$	–	6
$Ca_5Nb_5O_{17}$	415450	$P2_1/c$	9.0	6/7/8/9
$Ca_2V_2O_7$	421266	$P\bar{1}$	0.0	6/7
$Ca_3Ti_2O_7$	86241	$Cmc2_1$	3.0	6/7
$Ca(MoO_4)$	22351	$I4_1/a$	–	8
$Ca(TiO_3)$	16688	$Pcmn$	–	8
$Ca(VO_3)$	150283	$Pbnm$	–	8
$CaCe_2S_4$	619204	$I\bar{4}3d$	–	8
$CaCoO_3$	230897	$Pbnm$	–	8
$CaSc_2S_4$	27181	$Pnam$	–	8
$CaSm_2S_4$	619544	$I\bar{4}3d$	–	8
$Ca_2Nb_2O_7$	22411	$Fd\bar{3}mS$	41.0	8
$Ca_2Nb_2O_7$	72206	$Fd\bar{3}mZ$	41.0	8
$Ca_3Ti_2O_7$	63705	$Cmc2_1$	3.0	8
$Ca_4Mn_3O_{10}$	85669	$Pbca$	22.0	8
$Ca_2(V_2O_7)$	20609	$P\bar{1}$	–	6/7
$Ca_3(VO_4)_2$	412273	$C2/m$	–	6/8
$Ca_3Ti_2O_7$	259358	$Cmc2_1$	–	6/8
$Ca_4(Nb_2O_9)$	51311	$P2_1/c$	–	6/8
$Ca_4(Ti_3O_{10})$	86242	$Pcab$	–	6/8
$Ca_2Ta_2O_7$	27121	$Fd\bar{3}m$	1.0	8

$Ca(Ta_4O_{11})$	43348	$P6_3$	0.0	8
$CaTa_2O_6$	47121	$Pm\bar{3}$	0.0	8/12
$Ca_2(Ta_2O_7)$	93847	$C2$	0.0	6/8
$CaWO_4$	5510	$I4_1/a$	0.0	8
$CaWO_4$	253259	$P2_1/m$	0.0	9
Ca_3WO_6	262323	$P2_1/m$	0.0	6/8
$Ca_4Fe_9O_{17}$	32698	$C2$	27.0	7
$CaFeO_2$	92353	$Pnma$	92.	8
$Ca_2Fe_2O_5$	15059	$Pnma$	0.0	7
$Ca(V_2O_6)$	166516	$C2/m$	–	6
$Ca_2Mn_3O_8$	258918	$C2/m$	–	6
$Ca_2Fe_2O_5$	5474	$Pcmn$	–	7
$Ca(V_2O_4)$	164188	$Pnam$	–	8
$Ca(FeO_3)$	92343	$P2_1/m$	–	8
$Ca(FeO_3)$	92347	$Pnma$	–	8
$Ca(Fe_2O_4)$	166065	$Pbnm$	–	8
Ca_2SnS_4	619548	$Pnma$	0.0	6
$CaEr_2S_4$	619253	$Pnma$	–	7
$CaHo_2S_4$	619369	$Pnma$	–	7
$CaLu_2S_4$	200013	$Pnma$	–	7
CaS_4Yb_2	619559	$Pnma$	–	7
$CaDy_2S_4$	619247	$I\bar{4}3d$	–	8
$CaGa_2S_4$	46017	$Fddd$	–	8
$CaGa_2S_4$	619292	$Cccm$	–	8
$CaGd_2S_4$	619301	$I\bar{4}3d$	–	8
$CaHfS_3$	619354	$Pnma$	–	8

$CaHo_2S_4$	619368	$I\bar{4}3d$	–	8
$CaLa_2S_4$	619386	$I\bar{4}3d$	–	8
$CaMo_6S_8$	619421	$R\bar{3}$	–	8
$CaNb_2O_6$	15208	$Pbcn$	–	8
$Ca_2Fe_7O_{11}$	100827	$C2/m$	–	7
$Ca_3(CrO_4)_2$	15293	$R3c$	–	3/5/6
$Ca_5Ir_3O_{12}$	120112	$P\bar{6}2m$	–	7/9
$CaMgS_2$	603167	$Fm\bar{3}m$	27.0	6
$CaCdS_2$	52751	$Fm\bar{3}m$	84.0	6
$CaEuS_2$	52753	$Fm\bar{3}m$	14.0	6
$Ca(NdS_2)_2$	619434	$I\bar{4}3d$	12.0	8
$CaTm_2S_4$	619554	$Pnma$	0.0	6/7
$CaZrS_3$	23286	$Pnma$	37.0	6
$CaNd_2S_4$	619436	$I\bar{4}3d$	–	8
$CaPr_2S_4$	619509	$I\bar{4}3d$	–	8
$CaYb_2S_4$	402372	$I\bar{4}3d$	272.	8
$CaCu_2S_2$	241336	$P\bar{3}m1$	0.0.	6
$CaMnS_2$	52779	$Fm\bar{3}m$	63.0	6
$CaAl_2Se_4$	49731	$Cccm$	–	8
$CaGa_2Se_4$	24387	$Fddd$	–	8

S2 Voltage Curves of CaV_2O_4 and $CaNb_2O_4$

Figure S1 shows the voltage profiles of the non-topotactic Ca intercalation in CaV_2O_4 and $CaNb_2O_4$.

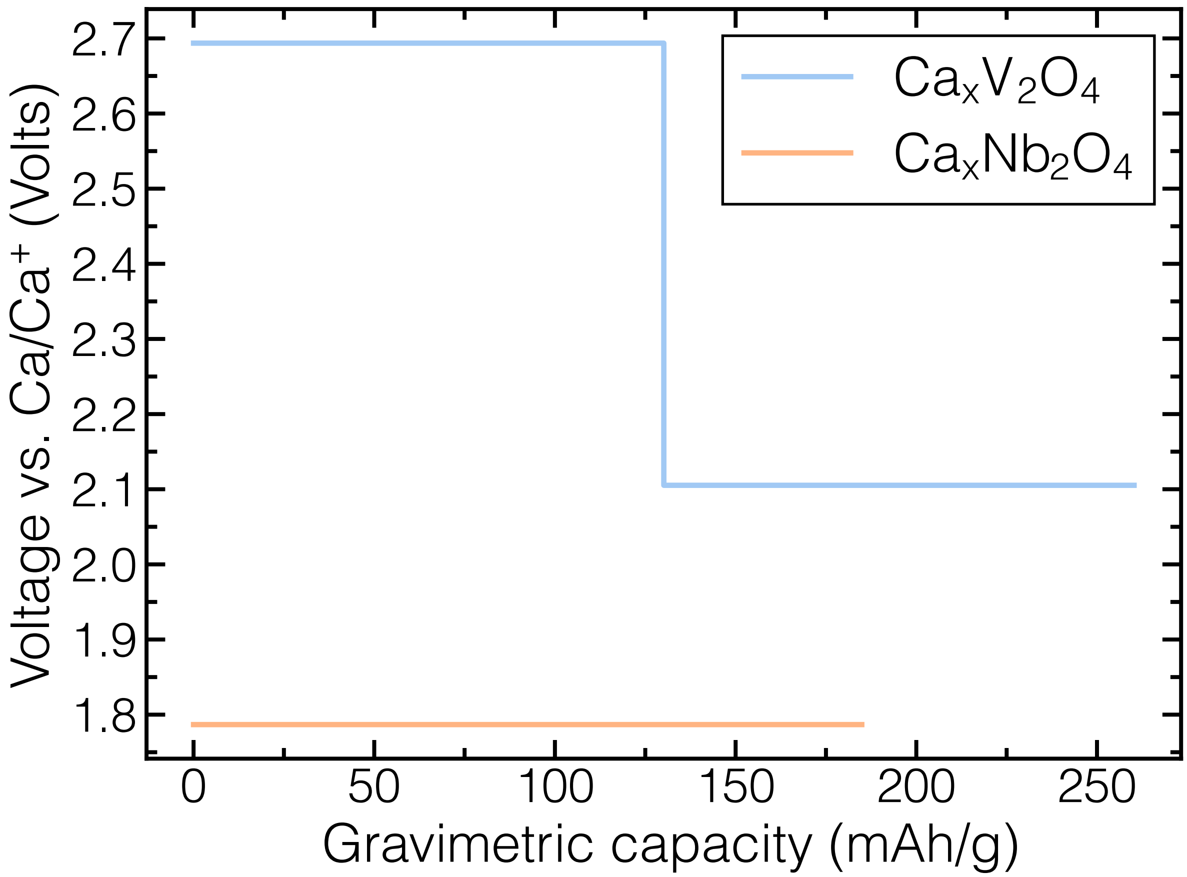

Figure S1: Computed voltage profiles of Ca intercalation in CaV_2O_4 and $CaNb_2O_4$.

S3 Estimation of Maximum Tolerable Migration Barriers

The maximum tolerable migration barrier (E_m) is the migration barrier that a Ca^{2+} can overcome for long-range transport under 'feasible' battery operating conditions. The maximum of E_m can be derived using the following relations. The diffusion length (l) allowed by an ion follows Eq. 1.

$$l = \sqrt{Dt} \tag{1}$$

where D is the diffusivity t the time for the particle to be discharged. We assumed that ion diffusion in the particle is modelled as a random walk, and the local ion migration follows an Arrhenius model as from Eq. 2.

$$D = \nu a^2 e^{\left(-\frac{E_m}{k_B T}\right)} \tag{2}$$

were ν was set to $\sim 10^{12}$ s^{-1} and the atomic jump distance a to ~ 3 Å, which is in the range of typical lattice parameters. k_B is the Boltzmann constant.

Using Eq. 1 together with Eq. 2 one can estimate a maximum tolerable migration barriers if specific particle size (l), times for discharge/charge (t) and temperatures (T) are assumed, which are plotted in Figure S2 for two temperatures of interest, 298 K and 333 K.

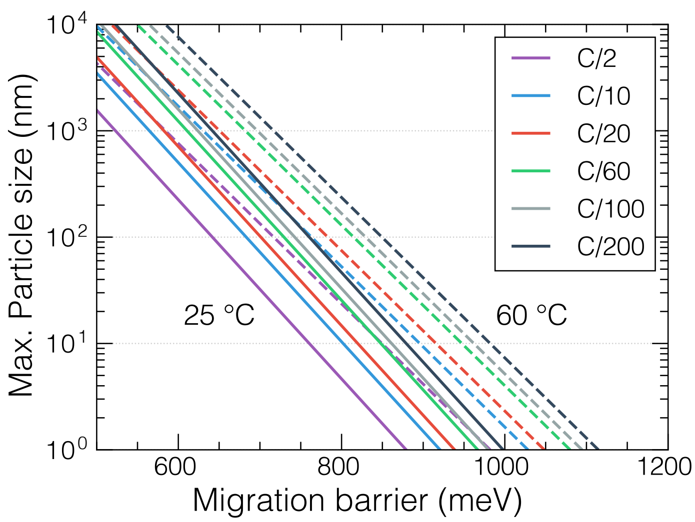

Figure S2: Relationship between tolerable Ca migration barrier (E_m) and the corresponding cathode particle size enabling Ca^{2+} diffusion. Various charging rates are indicated in the figure legend. Solid and dashed lines correspond to 25°C and 60°C.

S4 Computed Migration Energy Paths

The following figures depict the computed migration energy profiles for the cathode materials explored.

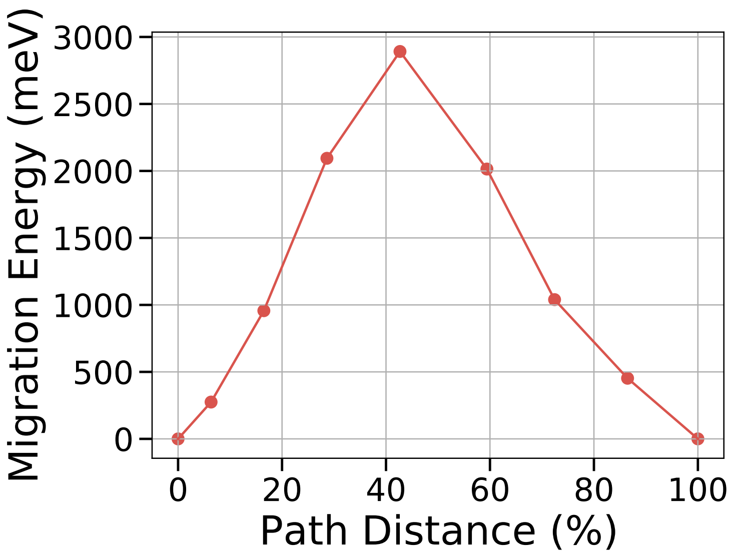

Figure S3: Migration energy path of CaV_3O_7.

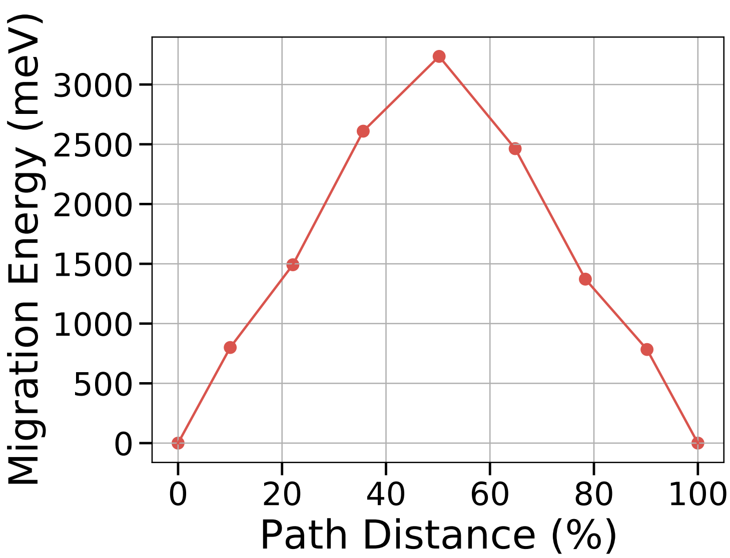

Figure S4: Migration energy path of $Ca_2V_2O_6$.

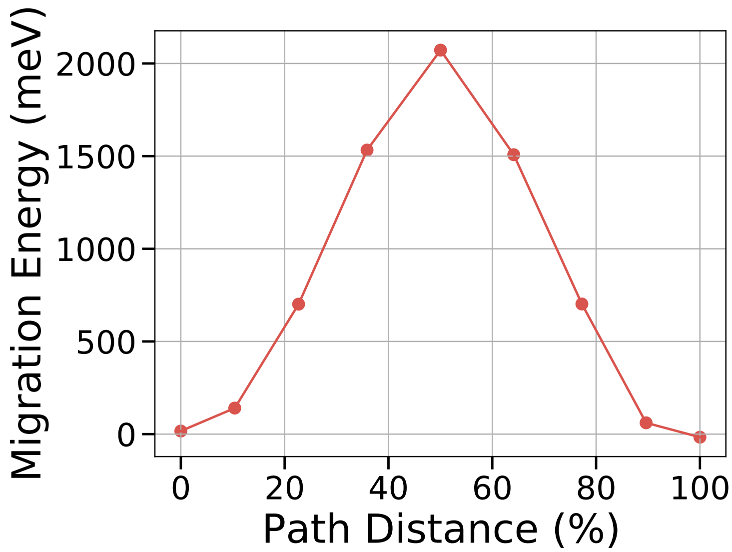

Figure S5: Migration energy path of $CaMoO_3$.

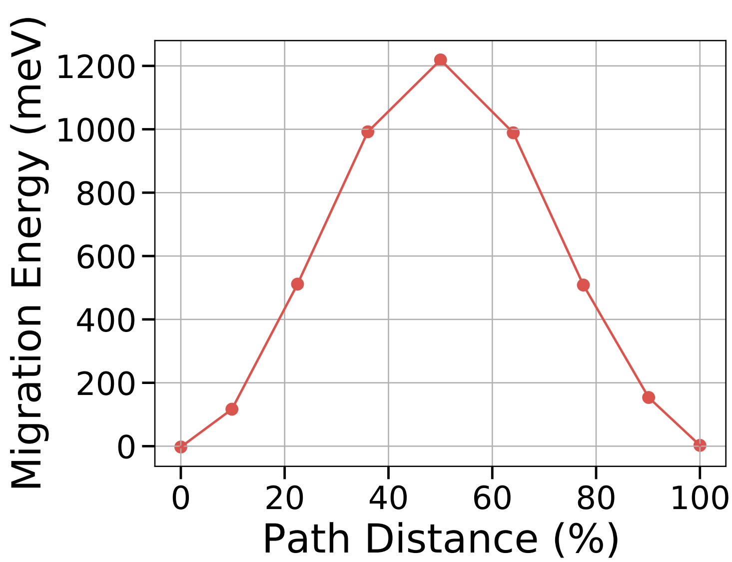

Figure S6: Migration energy path of $CaIrO_3$.

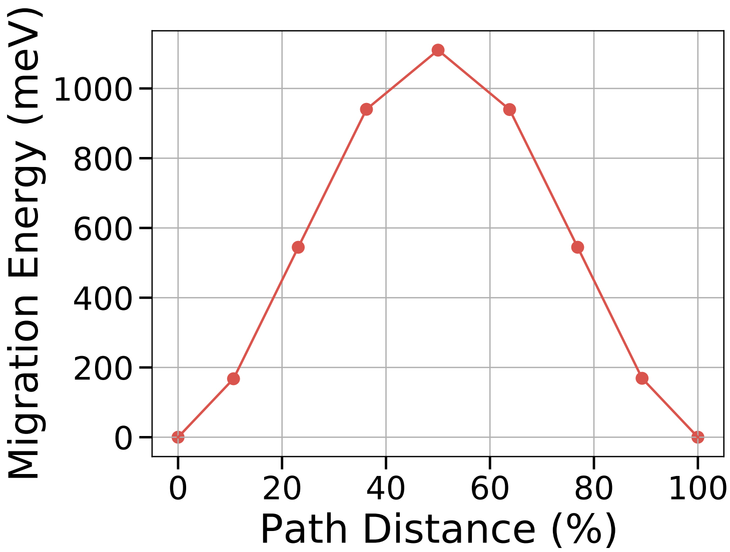

Figure S7: Migration energy path of $CaRh_2O_4$.

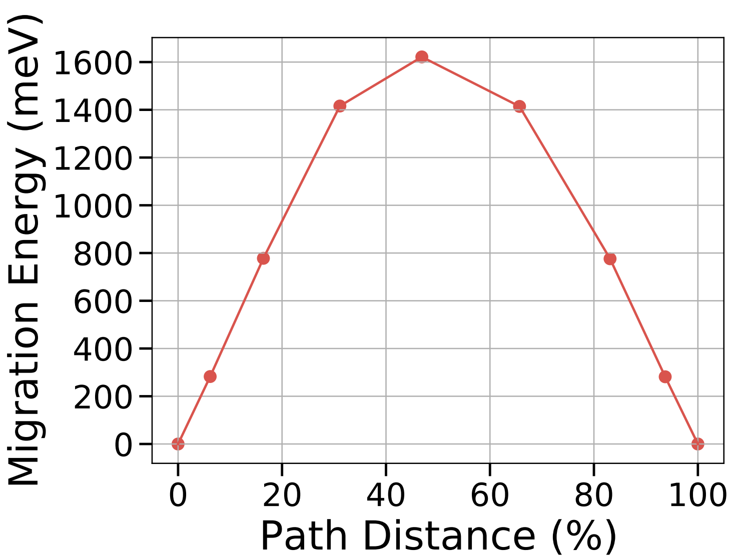

Figure S8: Migration energy path of $CaCu_2S_2$ via intermediate site.

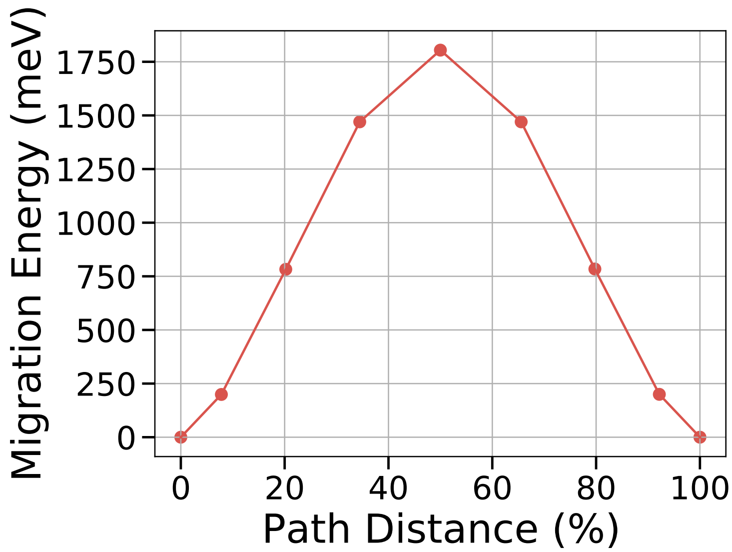

Figure S9: Migration energy path of $CaCu_2S_2$ via edge site.

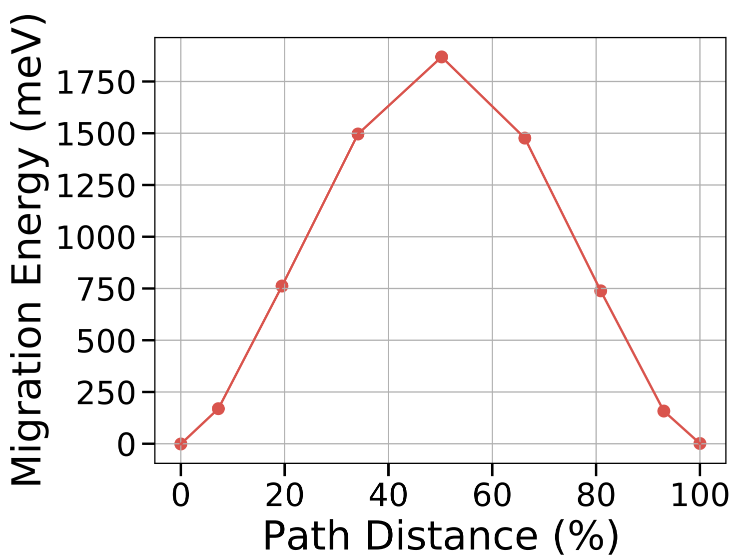

Figure S10: Migration energy path of α-CaV_2O_5.

References

(1) Jain, A.; Ong, S. P.; Hautier, G.; Chen, W.; Richards, W. D.; Dacek, S.; Cholia, S.; Gunter, D.; Skinner, D.; Ceder, G.; Persson, K. A. Commentary: The Materials Project: A materials genome approach to accelerating materials innovation. *APL Materials* **2013**, *1*, 011002.