—Supporting Information— Searching Ternary Oxides and Chalcogenides as Positive Electrodes for Calcium Batteries

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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 | $\mathrm{ICSD}/\mathrm{MP}$ | Space Group | $\mathrm{E}^{\mathrm{hull}}$ | $\mathrm{CN}_{\mathrm{disc.}}$ |
|---|-----------------------------|-------------|------------------------------|--------------------------------|
| CaV_3O_7 | 2507 | Pnma | 2.0 | 7 |
| V_3O_7 | mvc-13330 | Pnma | 51.0 | _ |
| $Ca_2V_2O_6$ | 241336 | C2/m | 24.0 | 6 |
| CaV_2O_6 | 21064 | C2/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 |
| $\mathrm{Ca}_3\mathrm{Cu}_6\mathrm{O}_{12}$ | 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 |
| $\mathrm{Rh}_2\mathrm{O}_4$ | 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 | _ |
| $\mathrm{Ca}_4\mathrm{Mn}_2\mathrm{O}_7$ | 103352 | Cmca | 37.0 | 7 |
| $\mathrm{Ca_3Mn_2O_7}$ | | $Cmc2_1$ | 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 |
| $\mathrm{CaMn_2O_4}$ | 280514 | Pbcm | 0.0 | 8 |
| $\mathrm{Mn}_2\mathrm{O}_4$ | | 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 | _ |

| ${\rm CaMn_2O_4}$ | 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 |
| $\rm NiO_2$ | | $Fd\bar{3}m$ | 10.4 | _ |
| $CaTi_2O_4$ | 51183 | Cmcm | 24.0 | 8 |
| ${\rm TiO}_2$ | | 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 | — |
| $\frac{\text{Fe}_9\text{O}_{13}}{\text{CaFe}_2\text{O}_4}$ | 28177 | C2/m Pbnm | 264.0 0.0 | 8 |
| $\begin{array}{c} \mathrm{Fe_9O_{13}}\\ \mathrm{CaFe_2O_4}\\ \mathrm{FeO_2} \end{array}$ | 28177 | C2/m Pbnm Pnma | 264.0 0.0 207.0 | 8 |
| $Fe_{9}O_{13}$ $CaFe_{2}O_{4}$ FeO_{2} $CaFeO_{3}$ | 28177 248483 | C2/m Pbnm Pnma Pbnm | 264.0 0.0 207.0 0.0 | |
| $Fe_{9}O_{13}$ $CaFe_{2}O_{4}$ FeO_{2} $CaFeO_{3}$ FeO_{3} | 28177 248483 | C2/m Pbnm Pnma Pbnm C2/m | 264.0 0.0 207.0 0.0 557.0 | |
| Fe_9O_{13} $CaFe_2O_4$ FeO_2 $CaFeO_3$ FeO_3 $Ca_3(Mn_2O_7)$ | 28177 248483 55666 | $\begin{array}{c} C2/m\\ Pbnm\\ Pnma\\ Pbnm\\ C2/m\\ Cmc2_1 \end{array}$ | 264.0 0.0 207.0 0.0 557.0 17.0 | |
| Fe_9O_{13} $CaFe_2O_4$ FeO_2 $CaFeO_3$ FeO_3 $Ca_3(Mn_2O_7)$ Mn_2O_7 | 28177 248483 55666 | $\begin{array}{c} C2/m \\ Pbnm \\ Pnma \\ Pbnm \\ C2/m \\ Cmc2_1 \\ P21/c \end{array}$ | 264.0 0.0 207.0 0.0 557.0 17.0 318.0 | |
| Fe_9O_{13} $CaFe_2O_4$ FeO_2 $CaFeO_3$ FeO_3 $Ca_3(Mn_2O_7)$ Mn_2O_7 $CaMn_3O_6$ | 28177 248483 55666 252285 | $\begin{array}{c} C2/m \\ Pbnm \\ Pnma \\ Pbnm \\ C2/m \\ Cmc2_1 \\ P21/c \\ P2_1/c \end{array}$ | 264.0 0.0 207.0 0.0 557.0 17.0 318.0 13. | |
| Fe_9O_{13} $CaFe_2O_4$ FeO_2 $CaFeO_3$ FeO_3 $Ca_3(Mn_2O_7)$ Mn_2O_7 $CaMn_3O_6$ MnO_2 | 28177 248483 55666 252285 | $\begin{array}{c} C2/m \\ Pbnm \\ Pnma \\ Pbnm \\ C2/m \\ Cmc2_1 \\ P21/c \\ P2_1/c \\ P2_1/c \\ P2/m \end{array}$ | $\begin{array}{c} 264.0 \\ 0.0 \\ 207.0 \\ 0.0 \\ 557.0 \\ 17.0 \\ 318.0 \\ 13. \\ 25.0 \\ \end{array}$ | |
| Fe_9O_{13} $CaFe_2O_4$ FeO_2 $CaFeO_3$ FeO_3 $Ca_3(Mn_2O_7)$ Mn_2O_7 $CaMn_3O_6$ MnO_2 $CaMnO_3$ | 28177 248483 55666 252285 258991 | $\begin{array}{c} C2/m \\ Pbnm \\ Pnma \\ Pbnm \\ C2/m \\ C2/m \\ P21/c \\ P21/c \\ P2_1/c \\ P2/m \\ Pnma \end{array}$ | $\begin{array}{c} 264.0 \\ 0.0 \\ 207.0 \\ 0.0 \\ 557.0 \\ 17.0 \\ 318.0 \\ 13. \\ 25.0 \\ 35.0 \end{array}$ | |
| Fe_9O_{13} $CaFe_2O_4$ FeO_2 $CaFeO_3$ FeO_3 $Ca_3(Mn_2O_7)$ Mn_2O_7 $CaMn_3O_6$ MnO_2 $CaMnO_3$ MnO_3 | 28177 248483 555666 252285 258991 | $C2/m$ $Pbnm$ $Pnma$ $Pbnm$ $C2/m$ $C2/m$ $Cmc2_1$ $P21/c$ $P2_1/c$ $P2_1/c$ $P2/m$ $Pnma$ $Imma$ | $\begin{array}{c} 264.0 \\ 0.0 \\ 207.0 \\ 0.0 \\ 557.0 \\ 17.0 \\ 318.0 \\ 13. \\ 25.0 \\ 35.0 \\ 512.0 \end{array}$ | |
| Fe_9O_{13} $CaFe_2O_4$ FeO_2 $CaFeO_3$ FeO_3 $Ca_3(Mn_2O_7)$ Mn_2O_7 $CaMn_3O_6$ MnO_2 $CaMnO_3$ MnO_3 Ca_2MnO_4 | 28177 248483 555666 252285 258991 50789 | $C2/m$ $Pbnm$ $Pnma$ $Pbnm$ $C2/m$ $Cmc2_1$ $P21/c$ $P2_1/c$ $P2_1/c$ $P2/m$ $Pnma$ $Imma$ $I4_1/acd$ | $\begin{array}{c} 264.0 \\ 0.0 \\ 207.0 \\ 0.0 \\ 557.0 \\ 17.0 \\ 318.0 \\ 13. \\ 25.0 \\ 35.0 \\ 512.0 \\ 7.0 \end{array}$ | |

| $\mathrm{Ca}(\mathrm{Mo}_3\mathrm{S}_4)_2$ | 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 |
| $\mathrm{Ca_2Ru_2O_7}$ | | $Fd\bar{3}m$ | 0.0 | — |
| Ca ₂ CoO 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 | _ |
| $CaCoO_3$ Ca_2CuO_3 | 68885 | Pnma Immm | 23.0 2.0 | 7 |
| $CaCoO_3$ Ca_2CuO_3 $CaCuO_3$ | 68885 | Pnma Immm Pm3m | 23.0 2.0 165.0 | 7 |
| $\begin{array}{c} CaCoO_3\\ Ca_2CuO_3\\ CaCuO_3\\ Ca_2Nb_2O_7 \end{array}$ | 68885 26010 | Pnma Immm Pm3m P21 | 23.0 2.0 165.0 42.0 | - 7 - 6/7/8 |
| $\begin{array}{c} CaCoO_3 \\ Ca_2CuO_3 \\ CaCuO_3 \\ Ca_2Nb_2O_7 \\ CaNb_4O_{14} \end{array}$ | 68885 26010 | Pnma Immm Pm3m P21 R3m | 23.0 2.0 165.0 42.0 380.0 | - 7 - 6/7/8 - |
| $\begin{array}{c} CaCoO_{3} \\ Ca_{2}CuO_{3} \\ CaCuO_{3} \\ Ca_{2}Nb_{2}O_{7} \\ CaNb_{4}O_{14} \\ Ca(CoO_{2})_{2} \end{array}$ | 68885 26010 245715 | Pnma Immm Pm3m P21 R3m Pnma | 23.0 2.0 165.0 42.0 380.0 73.0 | - 7 - 6/7/8 - 8 |
| $\begin{array}{c} CaCoO_3 \\ Ca_2CuO_3 \\ CaCuO_3 \\ Ca_2Nb_2O_7 \\ CaNb_4O_{14} \\ Ca(CoO_2)_2 \\ CoO_2 \end{array}$ | 68885 26010 245715 | Pnma Immm Pm3m P21 R3m Pnma Cmcm | 23.0 2.0 165.0 42.0 380.0 73.0 224.0 | - 7 - 6/7/8 - 8 - |
| $\begin{array}{c} CaCoO_3 \\ Ca_2CuO_3 \\ CaCuO_3 \\ CaCuO_2 \\ CaNb_2O_7 \\ CaNb_4O_{14} \\ Ca(CoO_2)_2 \\ CoO_2 \\ CaCrO_3 \end{array}$ | 68885 26010 245715 245840 | Pnma Immm Pm3m P21 R3m Pnma Cmcm Pbnm | 23.0 2.0 165.0 42.0 380.0 73.0 224.0 36.0 | - 7 - 6/7/8 - 8 - 8 |
| $\begin{array}{c} CaCoO_3 \\ Ca_2CuO_3 \\ CaCuO_3 \\ CaCuO_2 \\ Ca2Nb_2O_7 \\ CaNb_4O_{14} \\ Ca(CoO_2)_2 \\ CoO_2 \\ CoO_2 \\ CaCrO_3 \\ CrO_3 \\ CrO_3 \end{array}$ | 68885 26010 245715 245840 | Pnma Immm Pm3m P21 R3m Pnma Cmcm Pbnm P21 | 23.0 2.0 165.0 42.0 380.0 73.0 224.0 36.0 187.0 | - 7 - 6/7/8 - 8 - 8 - 8 - |
| $CaCoO_3$ Ca_2CuO_3 $CaCuO_3$ $Ca_2Nb_2O_7$ $CaNb_4O_{14}$ $Ca(CoO_2)_2$ CoO_2 CaO_2 $CaCrO_3$ CrO_3 $CaCu_2O_3$ | 68885 26010 245715 245840 245840 15094 | Pnma Immm Pm3m P21 R3m Pnma Cmcm Pbnm P21 Pbnm P21 | 23.0 2.0 165.0 42.0 380.0 73.0 224.0 36.0 187.0 31.0 | - 7 - 6/7/8 - 8 - 8 - 8 - 8 - 6 |
| $CaCoO_3$ Ca_2CuO_3 $CaCuO_3$ $CaCuO_2$ $CaNb_4O_{14}$ $Ca(CoO_2)_2$ CoO_2 $CaCrO_3$ CrO_3 CrO_3 $CaCu_2O_3$ Cu_2O_3 | 68885 26010 245715 245840 15094 | Pnma Immm Pm3m P21 R3m Pnma Cmcm Pbnm P21 Pmma Cmcm Pbnm P21 Cmcm Cmcm Cmcm Cmcm Pummn Cmcm | 23.0 2.0 165.0 42.0 380.0 73.0 224.0 36.0 187.0 31.0 192.0 | - 7 - 6/7/8 - 8 - 8 - 8 - 6 - |
| CaCoO ₃ Ca ₂ CuO ₃ CaCuO ₃ Ca ₂ Nb ₂ O ₇ CaNb ₄ O ₁₄ Ca(CoO ₂) ₂ CoO ₂ CaCrO ₃ CrO ₃ CrO ₃ CaCu ₂ O ₃ Cu ₂ O ₃ | 68885 26010 245715 245840 245840 15094 16355 | Pnma Immm Pm3m P21 R3m P21 R3m Pnma Cmcm Pbnm P21 Pmmn Cmcm Cmcm Cmcm Cmcm Cmcm Cmcm | 23.0 2.0 165.0 42.0 380.0 73.0 224.0 36.0 187.0 31.0 192.0 24.0 | - 7 - 6/7/8 - 8 - 8 - 8 - 6 - 6 |

| $\rm Fe_5O_7$ | | Cmcm | 192.0 | — |
|---|--------|--------------|--------|-------|
| $Ca(FeO_2)_2$ | 16695 | Pnma | 2.0 | 8 |
| $\rm Fe_2O_4$ | | 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 | — |
| $\mathrm{Ca}(\mathrm{YS}_2)_2$ | 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 |
| $\rm Fe_5O_7$ | | 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 |
| $\mathrm{Ca}_4\mathrm{Mn}_3\mathrm{O}_{10}$ | 86648 | Pbca | 22.0 | 7/10 |
| $CaMo_5O_8$ | 280969 | $P2_{1}/c$ | 263.0 | 7 |
| ${\rm Ca}({\rm Mo}_5{\rm O}_8)$ | 152115 | $P2_{1}/c$ | 263. | 8 |
| Ca_2GeS_4 | 23416 | Pnma | 0.0 | 6 |
| $Ca_3V_2O_8$ | 9332 | R3c | 37.0 | 6 |
| $\rm Ca_2Mn_3O_8$ | 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 |
| $\mathrm{Ca_5Nb_5O_{17}}$ | 415450 | $P2_{1}/c$ | 9.0 | 6/7/8/9 |
| $Ca_2V_2O_7$ | 421266 | $P\bar{1}$ | 0.0 | 6/7 |
| $\mathrm{Ca}_3\mathrm{Ti}_2\mathrm{O}_7$ | 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 |
| $\begin{array}{c} CaCoO_{3}\\ CaSc_{2}S_{4} \end{array}$ | 230897 27181 | Pbnm Pnam | _ | 8 |
| $\begin{array}{c} CaCoO_{3}\\ CaSc_{2}S_{4}\\ CaSm_{2}S_{4} \end{array}$ | 230897 27181 619544 | Pbnm Pnam I43d | | 8 8 8 |
| $\begin{array}{c} CaCoO_{3}\\ \hline\\ CaSc_{2}S_{4}\\ \hline\\ CaSm_{2}S_{4}\\ \hline\\ Ca_{2}Nb_{2}O_{7} \end{array}$ | 230897 27181 619544 22411 | Pbnm Pnam I43d Fd3mS | 41.0 | 8 8 8 8 |
| $\begin{array}{c} CaCoO_{3}\\ \hline\\ CaSc_{2}S_{4}\\ \hline\\ CaSm_{2}S_{4}\\ \hline\\ Ca_{2}Nb_{2}O_{7}\\ \hline\\ Ca_{2}Nb_{2}O_{7} \end{array}$ | 230897 27181 619544 22411 72206 | Pbnm Pnam I43d Fd3mS Fd3mZ | - - 41.0 41.0 | 8 8 8 8 8 |
| $\begin{array}{c} CaCoO_3\\ CaSc_2S_4\\ CaSm_2S_4\\ Ca_2Nb_2O_7\\ Ca_2Nb_2O_7\\ Ca_3Ti_2O_7\\ \end{array}$ | 230897 27181 619544 22411 72206 63705 | Pbnm Pnam I43d Fd3mS Fd3mZ Cmc21 | - - 41.0 41.0 3.0 | 8 8 8 8 8 8 8 |
| $\begin{array}{c} CaCoO_3\\ CaSc_2S_4\\ CaSm_2S_4\\ Ca_2Nb_2O_7\\ Ca_2Nb_2O_7\\ Ca_3Ti_2O_7\\ Ca_4Mn_3O_{10} \end{array}$ | 230897 27181 619544 22411 72206 63705 85669 | $Pbnm$ $Pnam$ $I\bar{4}3d$ $Fd\bar{3}mS$ $Fd\bar{3}mZ$ $Cmc2_1$ $Pbca$ | - - 41.0 41.0 3.0 22.0 | 8 8 8 8 8 8 8 8 |
| $\begin{array}{c} CaCoO_3\\ CaSc_2S_4\\ CaSm_2S_4\\ Ca_2Nb_2O_7\\ Ca_2Nb_2O_7\\ Ca_3Ti_2O_7\\ Ca_4Mn_3O_{10}\\ Ca_2(V_2O_7)\\ \end{array}$ | 230897 27181 619544 22411 72206 63705 85669 20609 | Pbnm Pnam I43d Fd3mS Fd3mZ Cmc21 Pbca P1 | - - 41.0 41.0 3.0 22.0 - | 8 8 8 8 8 8 8 8 8 8 6/7 |
| $\begin{array}{c} CaCoO_3\\ CaSc_2S_4\\ CaSm_2S_4\\ Ca_2Nb_2O_7\\ Ca_2Nb_2O_7\\ Ca_3Ti_2O_7\\ Ca_4Mn_3O_{10}\\ Ca_2(V_2O_7)\\ Ca_3(VO_4)_2\\ \end{array}$ | 230897 27181 619544 22411 72206 63705 85669 20609 412273 | $Pbnm$ $Pnam$ $I\bar{4}3d$ $Fd\bar{3}mS$ $Fd\bar{3}mZ$ $Cmc2_1$ $Pbca$ $P\bar{1}$ $C2/m$ | - - 41.0 41.0 3.0 22.0 - | 8 8 8 8 8 8 8 8 6/7 6/8 |
| $\begin{array}{c} CaCoO_3\\ CaSc_2S_4\\ CaSm_2S_4\\ Ca_2Nb_2O_7\\ Ca_2Nb_2O_7\\ Ca_3Nb_2O_7\\ Ca_3Ti_2O_7\\ Ca_4Mn_3O_{10}\\ Ca_2(V_2O_7)\\ Ca_3(VO_4)_2\\ Ca_3Ti_2O_7\\ \end{array}$ | 230897 27181 619544 22411 72206 63705 85669 20609 412273 259358 | $Pbnm$ $Pnam$ $I\bar{4}3d$ $Fd\bar{3}mS$ $Fd\bar{3}mZ$ $Cmc2_1$ $Pbca$ $P\bar{1}$ $C2/m$ $Cmc2_1$ | 41.0 41.0 3.0 22.0 | 8 8 8 8 8 8 8 8 8 8 6/7 6/8 6/8 |
| $\begin{array}{c} CaCoO_{3} \\ CaSc_{2}S_{4} \\ CaSm_{2}S_{4} \\ Ca_{2}Nb_{2}O_{7} \\ Ca_{2}Nb_{2}O_{7} \\ Ca_{2}Nb_{2}O_{7} \\ Ca_{3}Ti_{2}O_{7} \\ Ca_{4}Mn_{3}O_{10} \\ Ca_{2}(V_{2}O_{7}) \\ Ca_{3}(VO_{4})_{2} \\ Ca_{3}Ti_{2}O_{7} \\ Ca_{4}(Nb_{2}O_{9}) \end{array}$ | 230897 27181 619544 22411 72206 63705 85669 20609 412273 259358 51311 | $Pbnm$ $Pnam$ $I\bar{4}3d$ $Fd\bar{3}mS$ $Fd\bar{3}mZ$ $Cmc2_1$ $Pbca$ $P\bar{1}$ $C2/m$ $Cmc2_1$ $P2_1/c$ | 41.0 41.0 3.0 22.0 | 8 8 8 8 8 8 8 8 8 6/7 6/8 6/8 6/8 |
| $\begin{array}{c} CaCoO_{3} \\ CaSc_{2}S_{4} \\ CaSm_{2}S_{4} \\ Ca_{2}Nb_{2}O_{7} \\ Ca_{2}Nb_{2}O_{7} \\ Ca_{2}Nb_{2}O_{7} \\ Ca_{3}Ti_{2}O_{7} \\ Ca_{4}Mn_{3}O_{10} \\ Ca_{2}(V_{2}O_{7}) \\ Ca_{3}(VO_{4})_{2} \\ Ca_{3}Ti_{2}O_{7} \\ Ca_{4}(Nb_{2}O_{9}) \\ Ca_{4}(Ti_{3}O_{10}) \end{array}$ | 230897 27181 619544 22411 72206 63705 85669 20609 412273 259358 51311 86242 | $Pbnm$ $Pnam$ $I\bar{4}3d$ $Fd\bar{3}mS$ $Fd\bar{3}mZ$ $Cmc2_1$ $Pbca$ $P\bar{1}$ $C2/m$ $Cmc2_1$ $Pbca$ $P\bar{1}$ $C2/m$ $Pcab$ | | 8 8 8 8 8 8 8 8 8 6/7 6/8 6/8 6/8 6/8 |

| $\mathrm{Ca}(\mathrm{Ta}_4\mathrm{O}_{11})$ | 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 |
| $\mathrm{Ca_2Mn_3O_8}$ | 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 |
| $\begin{array}{c} Ca(FeO_3) \\ Ca(FeO_3) \end{array}$ | 92343 92347 | $P2_1/m$ Pnma | _ | 8 |
| $\begin{array}{c} {\rm Ca(FeO_3)}\\ {\rm Ca(FeO_3)}\\ {\rm Ca(Fe_2O_4)} \end{array}$ | 92343 92347 166065 | P2 ₁ /m Pnma Pbnm | | 8 8 8 |
| $\begin{array}{c} Ca(FeO_3)\\ \hline\\ Ca(FeO_3)\\ \hline\\ Ca(Fe_2O_4)\\ \hline\\ Ca_2SnS_4 \end{array}$ | 92343 92347 166065 619548 | P2 ₁ /m Pnma Pbnm Pnma | 0.0 | 8 8 8 6 |
| $\begin{array}{c} {\rm Ca(FeO_3)} \\ {\rm Ca(FeO_3)} \\ {\rm Ca(Fe_2O_4)} \\ {\rm Ca_2SnS_4} \\ {\rm CaEr_2S_4} \end{array}$ | 92343 92347 166065 619548 619253 | P2 ₁ /m Pnma Pbnm Pnma Pnma | | 8 8 8 6 7 |
| $\begin{array}{c} {\rm Ca(FeO_3)}\\ {\rm Ca(FeO_3)}\\ {\rm Ca(Fe_2O_4)}\\ {\rm Ca_2SnS_4}\\ {\rm CaEr_2S_4}\\ {\rm CaEr_2S_4}\\ {\rm CaHo_2S_4} \end{array}$ | 92343 92347 166065 619548 619253 619369 | P2 ₁ /m Pnma Pbnm Pnma Pnma Pnma | - - 0.0 - | 8 8 8 6 7 7 7 |
| $\begin{array}{c} {\rm Ca(FeO_3)}\\ {\rm Ca(FeO_3)}\\ {\rm Ca(Fe_2O_4)}\\ {\rm Ca_2SnS_4}\\ {\rm CaEr_2S_4}\\ {\rm CaEr_2S_4}\\ {\rm CaHo_2S_4}\\ {\rm CaLu_2S_4}\end{array}$ | 92343 92347 166065 619548 619253 619369 200013 | P2 ₁ /m Pnma Pbnm Pnma Pnma Pnma Pnma | - - 0.0 - - | 8 8 8 6 7 7 7 7 |
| $\begin{array}{c} {\rm Ca(FeO_3)}\\ {\rm Ca(FeO_3)}\\ {\rm Ca(Fe_2O_4)}\\ {\rm Ca_2SnS_4}\\ {\rm CaEr_2S_4}\\ {\rm CaEr_2S_4}\\ {\rm CaHo_2S_4}\\ {\rm CaLu_2S_4}\\ {\rm CaS_4Yb_2}\\ \end{array}$ | 92343 92347 166065 619548 619253 619369 200013 619559 | P2 ₁ /m Pnma Pbnm Pnma Pnma Pnma Pnma Pnma | | 8 8 6 7 7 7 7 7 7 |
| $\begin{array}{c} {\rm Ca(FeO_3)}\\ {\rm Ca(FeO_3)}\\ {\rm Ca(Fe_2O_4)}\\ {\rm Ca_2SnS_4}\\ {\rm CaEr_2S_4}\\ {\rm CaEr_2S_4}\\ {\rm CaHo_2S_4}\\ {\rm CaHo_2S_4}\\ {\rm CaLu_2S_4}\\ {\rm CaS_4Yb_2}\\ {\rm CaDy_2S_4} \end{array}$ | 92343 92347 166065 619548 619253 619369 200013 619559 619247 | P21/mPnmaPbnmPnmaPnmaPnmaPnmaPnmaIIA3d | | 8 8 6 7 7 7 7 7 8 |
| $\begin{array}{c} {\rm Ca(FeO_3)}\\ {\rm Ca(FeO_3)}\\ {\rm Ca(Fe_2O_4)}\\ {\rm Ca_2SnS_4}\\ {\rm CaEr_2S_4}\\ {\rm CaEr_2S_4}\\ {\rm CaHo_2S_4}\\ {\rm CaLu_2S_4}\\ {\rm CaS_4Yb_2}\\ {\rm CaOy_2S_4}\\ {\rm CaGa_2S_4}\\ \end{array}$ | 92343 92347 166065 619548 619253 619369 200013 619559 619247 46017 | P21/m Pnma Pbnm Pnma Pnma Pnma Pnma Pnma I43d Fddd | 0.0 | 8 8 6 7 7 7 7 7 8 8 8 |
| $\begin{array}{c} \mathrm{Ca}(\mathrm{FeO}_3)\\ \mathrm{Ca}(\mathrm{FeO}_3)\\ \mathrm{Ca}(\mathrm{Fe}_2\mathrm{O}_4)\\ \mathrm{Ca}_2\mathrm{SnS}_4\\ \mathrm{Ca}\mathrm{Er}_2\mathrm{S}_4\\ \mathrm{Ca}\mathrm{Er}_2\mathrm{S}_4\\ \mathrm{Ca}\mathrm{Ho}_2\mathrm{S}_4\\ \mathrm{Ca}\mathrm{Lu}_2\mathrm{S}_4\\ \mathrm{Ca}\mathrm{S}_4\mathrm{Yb}_2\\ \mathrm{Ca}\mathrm{Dy}_2\mathrm{S}_4\\ \mathrm{Ca}\mathrm{Ga}_2\mathrm{S}_4\\ \mathrm{Ca}\mathrm{Ga}_2\mathrm{S}_4 \end{array}$ | 92343 92347 166065 619548 619253 619369 200013 619559 619247 46017 619292 | P21/m Pnma Pbnm Pnma Pnma Pnma Pnma Pnma I43d Fddd Cccm | 0.0 | 8 8 6 7 7 7 7 7 8 8 8 8 |
| $\begin{array}{c} {\rm Ca(FeO_3)} \\ {\rm Ca(FeO_3)} \\ {\rm Ca(Fe_2O_4)} \\ {\rm Ca_2SnS_4} \\ {\rm CaEr_2S_4} \\ {\rm CaEr_2S_4} \\ {\rm CaHo_2S_4} \\ {\rm CaAU_2S_4} \\ {\rm CaS_4Yb_2} \\ {\rm CaOy_2S_4} \\ {\rm CaOy_2S_4} \\ {\rm CaGa_2S_4} \\ {\rm CaGa_2S_4} \\ {\rm CaGd_2S_4} \end{array}$ | 92343 92347 166065 619548 619253 619369 200013 619559 619247 46017 619301 | P21/m Pnma Pbnm Pnma Pnma Pnma Pnma Pnma I43d Fddd Cccm I43d | 0.0 | 8 8 8 6 7 7 7 7 7 7 8 8 8 8 8 8 8 |

| $\mathrm{CaHo}_2\mathrm{S}_4$ | 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 |
| $\mathrm{Ca}(\mathrm{NdS}_2)_2$ | 619434 | $I\bar{4}3d$ | 12.0 | 8 |
| $CaTm_2S_4$ | 619554 | Pnma | 0.0 | 6/7 |
| $CaZrS_3$ | 23286 | Pnma | 37.0 | 6 |
| $\mathrm{CaNd}_2\mathrm{S}_4$ | 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 ${\rm CaV_2O_4}$ and ${\rm CaNb_2O_4}.$

S3 Estimation of Maximum Tolerable Migration Barriers

The maximum tolerable migration barrier (E_m) is the migration barrier that a Ca²⁺ 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 Ca²⁺ 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 CaMoO₃.



Figure S6: Migration energy path of CaIrO₃.



Figure S7: Migration energy path of CaRh₂O₄.



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



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



Figure S10: Migration energy path of α -CaV₂O₅.

References

 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.