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On the Balance of Intercalation and Conversion Reactions in Battery Cathodes

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S1. Ternary phase diagram for the Mg-Mn-X (X = O, S) system

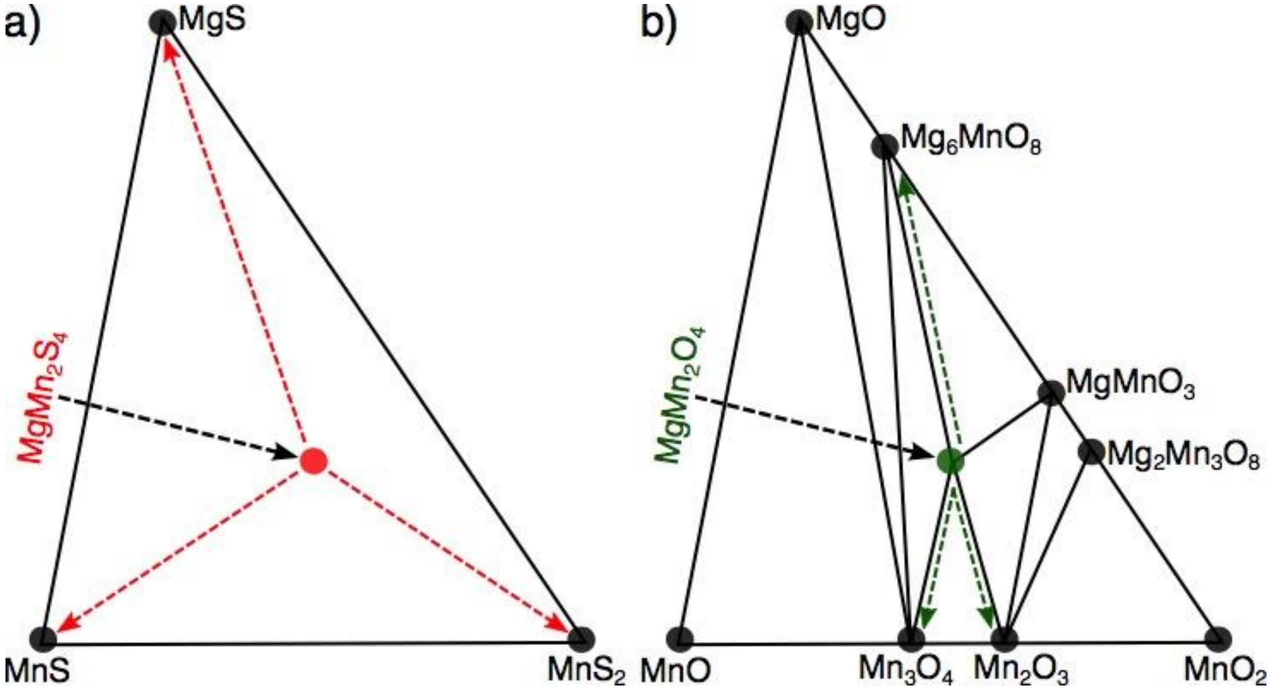

Figure S1: (Color online) Ternary phase diagram for the (a) Mg-Mn-S and (b) Mg-Mn-O systems generated from the Materials Project database. Note that the phase diagrams display only the chemical space of relevance for intercalation or conversion reactions and are hence bound by MgX, MnX and MnX_2 compounds. Thermodynamically stable phases on the borders of the phase diagram are shown as black circles and their corresponding compositions are labeled. Solid black lines indicate tie-lines connecting stable compounds. $MgMn_2S_4$ (panel a), the product of a one-electron intercalation reaction between Mg and MnS_2, is thermodynamically unstable (E^{hull}=61 meV/atom) and shown as a red circle, while $MgMn_2O_4$ (panel b), the product of a one-electron intercalation reaction between Mg and MnO_2, is thermodynamically stable (E^{hull}=0 meV/atom) and is shown as a green circle. Dashed red arrows in panel a indicate the conversion products (MgS, MnS and MnS_2) that form spontaneously when Mg reduces MnS_2. Dashed green arrows in panel b indicate the conversion products (Mg_6MnO_8, Mn_3O_4 and Mn_2O_3) that will form if Mg reduction of MnO_2 does not lead to the intercalation product, spinel-$MgMn_2O_4$. Thermodynamically unstable phases (with the exception of $MgMn_2S_4$) are not shown in both panels.

S2. Two-electron Reduction: LCP voltages

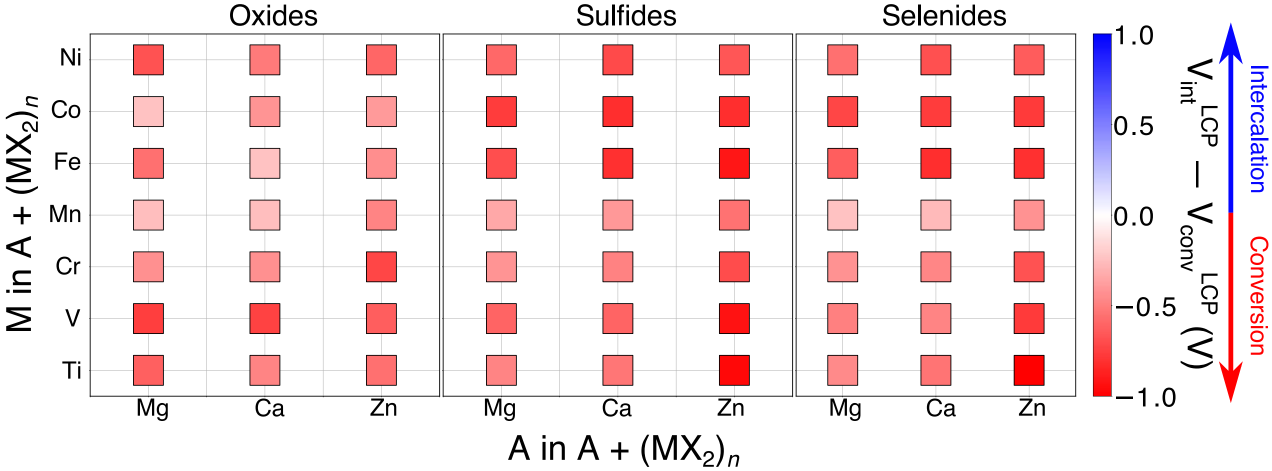

Figure S2: Difference between the intercalation ($V_{\mathrm{int}}^{\mathrm{LCP}}$) and conversion ($V_{\mathrm{conv}}^{\mathrm{LCP}}$) voltage for 2-electron reduction reactions, starting from the lowest energy charged polymorph (LCP). The voltage difference is indicated for three working ions (A = Mg, Ca, and Zn) in various 3*d*-transition metal oxide, sulfide, and selenide hosts. Higher intercalation voltages are indicated by blue-colored squares while higher conversion voltages are red-colored. The intercalation of divalent ions considered is into a MX_2 structure, corresponding to a $2e^-$ (per transition metal ion) reduction.

S3. One-electron reactions considered in this work

Intercalation Reaction	**Conversion Reaction**
$Na + TiO_2 \rightarrow NaTiO_2$	$8Na + 8TiO_2 \rightarrow Na_8Ti_5O_{14} + TiO + Ti_2O$
$Na + TiS_2 \rightarrow NaTiS_2$	$17Na + 17TiS_2 \rightarrow 7TiS + Na_3Ti_{10}S_{20} + 7Na_2S$
$Na + TiSe_2 \rightarrow NaTiSe_2$	$4Na + 4TiSe_2 \rightarrow Na_4TiSe_4 + Ti_3Se_4$
$Na + VO_2 \rightarrow NaVO_2$	$5Na + 5VO_2 \rightarrow V + \frac{1}{2}Na_5V_7O_{14} + Na_3VO_4$
$Na + VS_2 \rightarrow NaVS_2$	$3Na + 3VS_2 \rightarrow V_3S_4 + \frac{1}{2}Na_3VS_4 + Na_2S$
$Na + VSe_2 \rightarrow NaVSe_2$	$5Na + 5VSe_2 \rightarrow 2Na_2Se + \frac{1}{2}Na_3V_5Se_{10} + V_3Se_4$
$Na + CrO_2 \rightarrow NaCrO_2$	$12Na + 12CrO_2 \rightarrow 4Cr_2O_3 + 3Na_4CrO_4 + Cr$
$Na + CrS_2 \rightarrow NaCrS_2$	$2Na + 2CrS_2 \rightarrow Cr_2S_3 + Na_2S$
$Na + CrSe_2 \rightarrow NaCrSe_2$	$2Na + 2CrSe_2 \rightarrow Na_2Se + Cr_2Se_3$
$Na + MnO_2 \rightarrow NaMnO_2$	$5Na + 5MnO_2 \rightarrow NaMn_3O_4 + 2Na_2MnO_3$
$Na + MnS_2 \rightarrow NaMnS_2$	$6Na + 6MnS_2 \rightarrow Na_6MnS_4 + 3MnS_2 + 2MnS$
$Na + MnSe_2 \rightarrow NaMnSe_2$	$10Na + 10MnSe_2 \rightarrow 2Na_2Mn_2Se_3 + Na_6MnSe_4 + 5MnSe_2$
$Na + FeO_2 \rightarrow NaFeO_2$	$6Na + 6FeO_2 \rightarrow Na_3Fe_5O_9 + \frac{1}{2}Na_7Fe_3O_8$
$Na + FeS_2 \rightarrow NaFeS_2$	$2Na + 2FeS_2 \rightarrow FeS_2 + FeS + Na_2S$
$Na + FeSe_2 \rightarrow NaFeSe_2$	$2Na + 2FeSe_2 \rightarrow Na_2Se + FeSe_2 + FeSe$
$Na + CoO_2 \rightarrow NaCoO_2$	$6Na + 6CoO_2 \rightarrow CoO + Na_3CoO_3 + Na_3Co_4O_8$
$Na + CoS_2 \rightarrow NaCoS_2$	$4Na + 4CoS_2 \rightarrow Co_3S_4 + CoS_2 + 2Na_2S$
$Na + CoSe_2 \rightarrow NaCoSe_2$	$20Na + 20CoSe_2 \rightarrow Co_9Se_8 + 10Na_2Se + 11CoSe_2$
$Na + NiO_2 \rightarrow NaNiO_2$	$2Na + 2NiO_2 \rightarrow 0Na_{13}Ni_{11}O_{24} + 0Na_9Ni_{11}O_{20}$
$Na + NiS_2 \rightarrow NaNiS_2$	$4Na + 4NiS_2 \rightarrow Ni_3S_4 + NiS_2 + 2Na_2S$
$Na + NiSe_2 \rightarrow NaNiSe_2$	$4Na + 4NiSe_2 \rightarrow NiSe_2 + 2Na_2Se + Ni_3Se_4$
$Li + TiO_2 \rightarrow LiTiO_2$	$7Li + 7TiO_2 \rightarrow Li_7Ti_5O_{12} + 2TiO$
$Li + TiS_2 \rightarrow LiTiS_2$	$2Li + 2TiS_2 \rightarrow TiS + Li_2S + \frac{1}{2}LiTi_3S_6$
$Li + TiSe_2 \rightarrow LiTiSe_2$	$4Li + 4TiSe_2 \rightarrow 2Li_2Se + Ti_3Se_4 + \frac{1}{2}LiTi_3Se_6$
$Li + VO_2 \rightarrow LiVO_2$	$20Li + 20VO_2 \rightarrow \frac{1}{2}Li_7V_5O_{12} + Li_{17}V_{16}O_{32} + V_2O_3$
$Li + VS_2 \rightarrow LiVS_2$	$3Li + 3VS_2 \rightarrow Li_2S + \frac{1}{2}Li_3VS_4 + V_3S_4$

$Li + VSe_2 \rightarrow LiVSe_2$	$4Li + 4VSe_2 \rightarrow V_3Se_4 + 2Li_2Se + VSe_2$
$Li + CrO_2 \rightarrow LiCrO_2$	$4Li + 4CrO_2 \rightarrow Cr_2O_3 + \frac{1}{2}Li_9Cr_5O_{12}$
$Li + CrS_2 \rightarrow LiCrS_2$	$2Li + 2CrS_2 \rightarrow Li_2S + Cr_2S_3$
$Li + CrSe_2 \rightarrow LiCrSe_2$	$2Li + 2CrSe_2 \rightarrow Cr_2Se_3 + Li_2Se$
$Li + MnO_2 \rightarrow LiMnO_2$	$Li + 1MnO_2 \rightarrow \frac{1}{2}MnO + \frac{1}{2}Li_2MnO_3$
$Li + MnS_2 \rightarrow LiMnS_2$	$3Li + 3MnS_2 \rightarrow LiMn_2S_4 + Li_2S + MnS$
$Li + MnSe_2 \rightarrow LiMnSe_2$	$4Li + 4MnSe_2 \rightarrow 2Li_2Se + 0LiMn_9Se_{10} + 2MnSe_2$
$Li + FeO_2 \rightarrow LiFeO_2$	$7Li + 7FeO_2 \rightarrow \frac{1}{3}Li_5Fe_7O_{12} + \frac{2}{3}Li_8Fe_7O_{15}$
$Li + FeS_2 \rightarrow LiFeS_2$	$2Li + 2FeS_2 \rightarrow FeS_2 + FeS + Li_2S$
$Li + FeSe_2 \rightarrow LiFeSe_2$	$2Li + 2FeSe_2 \rightarrow Li_2Se + FeSe_2 + FeSe$
$Li + CoO_2 \rightarrow LiCoO_2$	$34Li + 34CoO_2 \rightarrow Co_3O_4 + Li_{20}Co_{21}O_{40} + 2Li_7Co_5O_{12}$
$Li + CoS_2 \rightarrow LiCoS_2$	$4Li + 4CoS_2 \rightarrow CoS_2 + 2Li_2S + Co_3S_4$
$Li + CoSe_2 \rightarrow LiCoSe_2$	$20Li + 20CoSe_2 \rightarrow Co_9Se_8 + 11CoSe_2 + 10Li_2Se$
$Li + NiO_2 \rightarrow LiNiO_2$	$Li + 1NiO_2 \rightarrow \frac{1}{2}NiO + \frac{1}{2}Li_2NiO_3$
$Li + NiS_2 \rightarrow LiNiS_2$	$4Li + 4NiS_2 \rightarrow Ni_3S_4 + 2Li_2S + NiS_2$
$Li + NiSe_2 \rightarrow LiNiSe_2$	$4Li + 4NiSe_2 \rightarrow NiSe_2 + 2Li_2Se + Ni_3Se_4$
$Mg + 2TiO_2 \rightarrow MgTi_2O_4$	$Mg + 2TiO_2 \rightarrow Ti_2O_3 + MgO$
$Mg + 2TiS_2 \rightarrow MgTi_2S_4$	$5Mg + 10TiS_2 \rightarrow 3TiS + Ti_7S_{12} + 5MgS$
$Mg + 2TiSe_2 \rightarrow MgTi_2Se_4$	$2Mg + 4TiSe_2 \rightarrow Ti_3Se_4 + TiSe_2 + 2MgSe$
$Mg + 2VO_2 \rightarrow MgV_2O_4$	$Mg + 2VO_2 \rightarrow MgO + V_2O_3$
$Mg + 2VS_2 \rightarrow MgV_2S_4$	$2Mg + 4VS_2 \rightarrow VS_2 + 2MgS + V_3S_4$
$Mg + 2VSe_2 \rightarrow MgV_2Se_4$	$2Mg + 4VSe_2 \rightarrow 2MgSe + VSe_2 + V_3Se_4$
$Mg + 2CrO_2 \rightarrow MgCr_2O_4$	$Mg + 2CrO_2 \rightarrow Cr_2O_3 + MgO$
$Mg + 2CrS_2 \rightarrow MgCr_2S_4$	$Mg + 2CrS_2 \rightarrow Cr_2S_3 + MgS$
$Mg + 2CrSe_2 \rightarrow MgCr_2Se_4$	$Mg + 2CrSe_2 \rightarrow Cr_2Se_3 + MgSe$
$Mg + 2MnO_2 \rightarrow MgMn_2O_4$	$3Mg + 6MnO_2 \rightarrow \frac{1}{2}Mn_3O_4 + \frac{1}{2}Mg_6MnO_8 + 2Mn_2O_3$
$Mg + 2MnS_2 \rightarrow MgMn_2S_4$	$Mg + 2MnS_2 \rightarrow MnS_2 + MnS + MgS$
$Mg + 2MnSe_2 \rightarrow MgMn_2Se_4$	$Mg + 2MnSe_2 \rightarrow MgSe + MnSe + MnSe_2$
$Mg + 2FeO_2 \rightarrow MgFe_2O_4$	$Mg + 2FeO_2 \rightarrow Fe_2O_3 + MgO$
$Mg + 2FeS_2 \rightarrow MgFe_2S_4$	$Mg + 2FeS_2 \rightarrow FeS_2 + FeS + MgS$
$Mg + 2FeSe_2 \rightarrow MgFe_2Se_4$	$Mg + 2FeSe_2 \rightarrow FeSe_2 + FeSe + MgSe$

$Mg + 2CoO_2 \rightarrow MgCo_2O_4$	$11Mg + 22CoO_2 \rightarrow Mg_2Co_3O_8 + Mg_5Co_{19}O_{32} + 4MgO$
$Mg + 2CoS_2 \rightarrow MgCo_2S_4$	$2Mg + 4CoS_2 \rightarrow CoS_2 + Co_3S_4 + 2MgS$
$Mg + 2CoSe_2 \rightarrow MgCo_2Se_4$	$10Mg + 20CoSe_2 \rightarrow Co_9Se_8 + 11CoSe_2 + 10MgSe$
$Mg + 2NiO_2 \rightarrow MgNi_2O_4$	$3Mg + 6NiO_2 \rightarrow 3MgO + 2Ni_3O_4 + \frac{1}{2}O_2$
$Mg + 2NiS_2 \rightarrow MgNi_2S_4$	$2Mg + 4NiS_2 \rightarrow Ni_3S_4 + NiS_2 + 2MgS$
$Mg + 2NiSe_2 \rightarrow MgNi_2Se_4$	$2Mg + 4NiSe_2 \rightarrow NiSe_2 + 2MgSe + Ni_3Se_4$
$Ca + 2TiO_2 \rightarrow CaTi_2O_4$	$Ca + 2TiO_2 \rightarrow CaTiO_3 + TiO$
$Ca + 2TiS_2 \rightarrow CaTi_2S_4$	$3Ca + 6TiS_2 \rightarrow 2TiS + CaTi_4S_8 + 2CaS$
$Ca + 2TiSe_2 \rightarrow CaTi_2Se_4$	$2Ca + 4TiSe_2 \rightarrow Ti_3Se_4 + TiSe_2 + 2CaSe$
$Ca + 2VO_2 \rightarrow CaV_2O_4$	$Ca + 2VO_2 \rightarrow CaO + V_2O_3$
$Ca + 2VS_2 \rightarrow CaV_2S_4$	$2Ca + 4VS_2 \rightarrow VS_2 + 2CaS + V_3S_4$
$Ca + 2VSe_2 \rightarrow CaV_2Se_4$	$2Ca + 4VSe_2 \rightarrow 2CaSe + VSe_2 + V_3Se_4$
$Ca + 2CrO_2 \rightarrow CaCr_2O_4$	$Ca + 2CrO_2 \rightarrow Cr_2O_3 + CaO$
$Ca + 2CrS_2 \rightarrow CaCr_2S_4$	$Ca + 2CrS_2 \rightarrow Cr_2S_3 + CaS$
$Ca + 2CrSe_2 \rightarrow CaCr_2Se_4$	$Ca + 2CrSe_2 \rightarrow Cr_2Se_3 + CaSe$
$Ca + 2MnO_2 \rightarrow CaMn_2O_4$	$6Ca + 12MnO_2 \rightarrow 3Mn_3O_4 + 4CaO + Ca_2Mn_3O_8$
$Ca + 2MnS_2 \rightarrow CaMn_2S_4$	$Ca + 2MnS_2 \rightarrow MnS_2 + MnS + CaS$
$Ca + 2MnSe_2 \rightarrow CaMn_2Se_4$	$Ca + 2MnSe_2 \rightarrow CaSe + MnSe + MnSe_2$
$Ca + 2FeO_2 \rightarrow CaFe_2O_4$	$2Ca + 4FeO_2 \rightarrow Ca_2Fe_2O_5 + Fe_2O_3$
$Ca + 2FeS_2 \rightarrow CaFe_2S_4$	$Ca + 2FeS_2 \rightarrow FeS_2 + FeS + CaS$
$Ca + 2FeSe_2 \rightarrow CaFe_2Se_4$	$Ca + 2FeSe_2 \rightarrow FeSe_2 + FeSe + CaSe$
$Ca + 2CoO_2 \rightarrow CaCo_2O_4$	$6Ca + 12CoO_2 \rightarrow 3Co_3O_4 + Ca_2Co_3O_8 + 4CaO$
$Ca + 2CoS_2 \rightarrow CaCo_2S_4$	$2Ca + 4CoS_2 \rightarrow CoS_2 + Co_3S_4 + 2CaS$
$Ca + 2CoSe_2 \rightarrow CaCo_2Se_4$	$10Ca + 20CoSe_2 \rightarrow Co_9Se_8 + 11CoSe_2 + 10CaSe$
$Ca + 2NiO_2 \rightarrow CaNi_2O_4$	$3Ca + 6NiO_2 \rightarrow 2NiO + 2CaO + CaNi_4O_8$
$Ca + 2NiS_2 \rightarrow CaNi_2S_4$	$2Ca + 4NiS_2 \rightarrow Ni_3S_4 + NiS_2 + 2CaS$
$Ca + 2NiSe_2 \rightarrow CaNi_2Se_4$	$2Ca + 4NiSe_2 \rightarrow NiSe_2 + Ni_3Se_4 + 2CaSe$
$Zn + 2TiO_2 \rightarrow ZnTi_2O_4$	$Zn + 2TiO_2 \rightarrow Zn + 2TiO_2$
$Zn + 2TiS_2 \rightarrow ZnTi_2S_4$	$5Zn + 10TiS_2 \rightarrow 3TiS + Ti_7S_{12} + 5ZnS$
$Zn + 2TiSe_2 \rightarrow ZnTi_2Se_4$	$2Zn + 4TiSe_2 \rightarrow Ti_3Se_4 + TiSe_2 + 2ZnSe$
$Zn + 2VO_2 \rightarrow ZnV_2O_4$	$Zn + 2VO_2 \rightarrow ZnO + V_2O_3$
$Zn + 2VS_2 \rightarrow ZnV_2S_4$	$2Zn + 4VS_2 \rightarrow VS_2 + 2ZnS + V_3S_4$
$Zn + 2VSe_2 \rightarrow ZnV_2Se_4$	$2Zn + 4VSe_2 \rightarrow VSe_2 + 2ZnSe + V_3Se_4$

$Zn + 2CrO_2 \rightarrow ZnCr_2O_4$	$Zn + 2CrO_2 \rightarrow Cr_2O_3 + ZnO$
$Zn + 2CrS_2 \rightarrow ZnCr_2S_4$	$Zn + 2CrS_2 \rightarrow Cr_2S_3 + ZnS$
$Zn + 2CrSe_2 \rightarrow ZnCr_2Se_4$	$Zn + 2CrSe_2 \rightarrow Cr_2Se_3 + ZnSe$
$Zn + 2MnO_2 \rightarrow ZnMn_2O_4$	$Zn + 2MnO_2 \rightarrow ZnO + Mn_2O_3$
$Zn + 2MnS_2 \rightarrow ZnMn_2S_4$	$Zn + 2MnS_2 \rightarrow MnS_2 + MnS + ZnS$
$Zn + 2MnSe_2 \rightarrow ZnMn_2Se_4$	$Zn + 2MnSe_2 \rightarrow MnSe_2 + MnSe + ZnSe$
$Zn + 2FeO_2 \rightarrow ZnFe_2O_4$	$Zn + 2FeO_2 \rightarrow Fe_2O_3 + ZnO$
$Zn + 2FeS_2 \rightarrow ZnFe_2S_4$	$Zn + 2FeS_2 \rightarrow FeS_2 + FeS + ZnS$
$Zn + 2FeSe_2 \rightarrow ZnFe_2Se_4$	$Zn + 2FeSe_2 \rightarrow FeSe_2 + FeSe + ZnSe$
$Zn + 2CoO_2 \rightarrow ZnCo_2O_4$	$11Zn + 22CoO_2 \rightarrow Zn_2Co_3O_8 + Zn_5Co_{19}O_{32} + 4ZnO$
$Zn + 2CoS_2 \rightarrow ZnCo_2S_4$	$2Zn + 4CoS_2 \rightarrow CoS_2 + Co_3S_4 + 2ZnS$
$Zn + 2CoSe_2 \rightarrow ZnCo_2Se_4$	$10Zn + 20CoSe_2 \rightarrow Co_9Se_8 + 11CoSe_2 + 10ZnSe$
$Zn + 2NiO_2 \rightarrow ZnNi_2O_4$	$3Zn + 6NiO_2 \rightarrow \frac{1}{2}O_2 + 3ZnO + 2Ni_3O_4$
$Zn + 2NiS_2 \rightarrow ZnNi_2S_4$	$2Zn + 4NiS_2 \rightarrow Ni_3S_4 + NiS_2 + 2ZnS$
$Zn + 2NiSe_2 \rightarrow ZnNi_2Se_4$	$2Zn + 4NiSe_2 \rightarrow NiSe_2 + Ni_3Se_4 + 2ZnSe$

S4. Polymorphs considered in the determination of one-electron reaction voltages

The accompanying supplementary file `structures_SI.xlsx` contains information about the polymorphs used as electrode structures for the purposes of calculating the voltages displayed in the main manuscript. Structural information for the one-electron reactions can be found in the *1-electron reactions* tab of the spreadsheet. The spreadsheet contains, for each combination of working ion, transition metal, and anion considered in this work, an ID and spacegroup for the following structures:

1. ID for the discharged structure used to calculate the LDP voltage (Column name: `ID for LDP discharged structure`)

2. Spacegroup for the discharged structure used to calculate the LDP voltage (Column name: `Spacegroup for LDP discharged structure`)

3. ID for the charged structure to calculate the LCP voltage (Column name: `ID for the LCP charged structure`)

4. Spacegroup for the charged structure used to calculate the LCP voltage (Column name: `Spacegroup for the LCP charged structure`)

5. ID for the discharged structure used to calculate the LCP voltage (Column name: `ID for the LCP discharged structure`)

6. Spacegroup for the discharged structure used to calculate the LCP voltage (Column name: `Spacegroup for the LCP discharged structure`)

The `ID` fields contain either a Materials Project ID (an alphanumeric string beginning with "mp-" or "mvc-") or the stoichiometry of the compound. Any compound with a Materials Project ID can be accessed freely at `http://www.materialsproject.org`. Note that no ID is given for the charged structures used to calculate the LDP voltages; these structures in all cases were generated by removing the working ion from the stable discharged structure and re-relaxing the empty host according to the computational procedure described in the main manuscript. An asterisk (*) in the ID cell on the spreadsheet indicates that a local calculation was used for that particular structure.

Some fields contain the phrase “Hypothetical structure” - in this case, a hypothetical structure exhibiting E^{hull}=100 meV/atom was used, as described in the main manuscript.

S5. Two-electron reactions considered in this work

Intercalation Reaction	**Conversion Reaction**
$Mg + TiO_2 \rightarrow MgTiO_2$	$Mg + TiO_2 \rightarrow TiO + MgO$
$Mg + TiS_2 \rightarrow MgTiS_2$	$Mg + TiS_2 \rightarrow TiS + MgS$
$Mg + TiSe_2 \rightarrow MgTiSe_2$	$8Mg + 8TiSe_2 \rightarrow Ti_3Se_4 + Ti_5Se_4 + 8MgSe$
$Mg + VO_2 \rightarrow MgVO_2$	$3Mg + 3VO_2 \rightarrow V + MgV_2O_4 + 2MgO$
$Mg + VS_2 \rightarrow MgVS_2$	$8Mg + 8VS_2 \rightarrow V_5S_4 + 8MgS + V_3S_4$
$Mg + VSe_2 \rightarrow MgVSe_2$	$4Mg + 4VSe_2 \rightarrow V + 4MgSe + V_3Se_4$
$Mg + CrO_2 \rightarrow MgCrO_2$	$3Mg + 3CrO_2 \rightarrow Cr + MgCr_2O_4 + 2MgO$
$Mg + CrS_2 \rightarrow MgCrS_2$	$4Mg + 4CrS_2 \rightarrow Cr_3S_4 + Cr + 4MgS$
$Mg + CrSe_2 \rightarrow MgCrSe_2$	$3Mg + 3CrSe_2 \rightarrow Cr_2Se_3 + Cr + 3MgSe$
$Mg + MnO_2 \rightarrow MgMnO_2$	$Mg + MnO_2 \rightarrow MnO + MgO$
$Mg + MnS_2 \rightarrow MgMnS_2$	$Mg + MnS_2 \rightarrow MnS + MgS$
$Mg + MnSe_2 \rightarrow MgMnSe_2$	$Mg + MnSe_2 \rightarrow MnSe + MgSe$
$Mg + FeO_2 \rightarrow MgFeO_2$	$Mg + FeO_2 \rightarrow MgO + FeO$
$Mg + FeS_2 \rightarrow MgFeS_2$	$Mg + FeS_2 \rightarrow FeS + MgS$
$Mg + FeSe_2 \rightarrow MgFeSe_2$	$Mg + FeSe_2 \rightarrow FeSe + MgSe$
$Mg + CoO_2 \rightarrow MgCoO_2$	$Mg + CoO_2 \rightarrow CoO + MgO$
$Mg + CoS_2 \rightarrow MgCoS_2$	$12Mg + 12CoS_2 \rightarrow Co_3S_4 + Co_9S_8 + 12MgS$
$Mg + CoSe_2 \rightarrow MgCoSe_2$	$10Mg + 10CoSe_2 \rightarrow Co_9Se_8 + CoSe_2 + 10MgSe$
$Mg + NiO_2 \rightarrow MgNiO_2$	$Mg + NiO_2 \rightarrow NiO + MgO$
$Mg + NiS_2 \rightarrow MgNiS_2$	$12Mg + 12NiS_2 \rightarrow Ni_3S_4 + Ni_9S_8 + 12MgS$
$Mg + NiSe_2 \rightarrow MgNiSe_2$	$Mg + NiSe_2 \rightarrow NiSe + MgSe$
$Ca + TiO_2 \rightarrow CaTiO_2$	$3Ca + 3TiO_2 \rightarrow CaTiO_3 + 2CaO + Ti_2O$
$Ca + TiS_2 \rightarrow CaTiS_2$	$Ca + TiS_2 \rightarrow TiS + CaS$
$Ca + TiSe_2 \rightarrow CaTiSe_2$	$8Ca + 8TiSe_2 \rightarrow Ti_3Se_4 + Ti_5Se_4 + 8CaSe$
$Ca + VO_2 \rightarrow CaVO_2$	$3Ca + 3VO_2 \rightarrow V + CaV_2O_4 + 2CaO$
$Ca + VS_2 \rightarrow CaVS_2$	$8Ca + 8VS_2 \rightarrow V_5S_4 + V_3S_4 + 8CaS$
$Ca + VSe_2 \rightarrow CaVSe_2$	$4Ca + 4VSe_2 \rightarrow V + V_3Se_4 + 4CaSe$
$Ca + CrO_2 \rightarrow CaCrO_2$	$3Ca + 3CrO_2 \rightarrow CaCr_2O_4 + Cr + 2CaO$
$Ca + CrS_2 \rightarrow CaCrS_2$	$4Ca + 4CrS_2 \rightarrow Cr_3S_4 + Cr + 4CaS$
$Ca + CrSe_2 \rightarrow CaCrSe_2$	$3Ca + 3CrSe_2 \rightarrow Cr + Cr_2Se_3 + 3CaSe$
$Ca + MnO_2 \rightarrow CaMnO_2$	$Ca + MnO_2 \rightarrow MnO + CaO$

$Ca + MnS_2 \rightarrow CaMnS_2$	$Ca + MnS_2 \rightarrow MnS + CaS$
$Ca + MnSe_2 \rightarrow CaMnSe_2$	$Ca + MnSe_2 \rightarrow MnSe + CaSe$
$Ca + FeO_2 \rightarrow CaFeO_2$	$Ca + FeO_2 \rightarrow CaO + FeO$
$Ca + FeS_2 \rightarrow CaFeS_2$	$Ca + FeS_2 \rightarrow FeS + CaS$
$Ca + FeSe_2 \rightarrow CaFeSe_2$	$Ca + FeSe_2 \rightarrow FeSe + CaSe$
$Ca + CoO_2 \rightarrow CaCoO_2$	$Ca + CoO_2 \rightarrow CoO + CaO$
$Ca + CoS_2 \rightarrow CaCoS_2$	$12Ca + 12CoS_2 \rightarrow Co_3S_4 + Co_9S_8 + 12CaS$
$Ca + CoSe_2 \rightarrow CaCoSe_2$	$10Ca + 10CoSe_2 \rightarrow Co_9Se_8 + CoSe_2 + 10CaSe$
$Ca + NiO_2 \rightarrow CaNiO_2$	$Ca + NiO_2 \rightarrow NiO + CaO$
$Ca + NiS_2 \rightarrow CaNiS_2$	$12Ca + 12NiS_2 \rightarrow Ni_3S_4 + Ni_9S_8 + 12CaS$
$Ca + NiSe_2 \rightarrow CaNiSe_2$	$Ca + NiSe_2 \rightarrow NiSe + CaSe$
$Zn + TiO_2 \rightarrow ZnTiO_2$	$Zn + 1TiO_2 \rightarrow Zn + TiO_2$
$Zn + TiS_2 \rightarrow ZnTiS_2$	$Zn + TiS_2 \rightarrow TiS + ZnS$
$Zn + TiSe_2 \rightarrow ZnTiSe_2$	$3Zn + 3TiSe_2 \rightarrow Zn + Ti_3Se_4 + 2ZnSe$
$Zn + VO_2 \rightarrow ZnVO_2$	$2Zn + 2VO_2 \rightarrow Zn + ZnV_2O_4$
$Zn + VS_2 \rightarrow ZnVS_2$	$8Zn + 8VS_2 \rightarrow V_5S_4 + 8ZnS + V_3S_4$
$Zn + VSe_2 \rightarrow ZnVSe_2$	$4Zn + 4VSe_2 \rightarrow V + 4ZnSe + V_3Se_4$
$Zn + CrO_2 \rightarrow ZnCrO_2$	$2Zn + 2CrO_2 \rightarrow Zn + ZnCr_2O_4$
$Zn + CrS_2 \rightarrow ZnCrS_2$	$3Zn + 3CrS_2 \rightarrow Cr + ZnCr_2S_4 + 2ZnS$
$Zn + CrSe_2 \rightarrow ZnCrSe_2$	$3Zn + 3CrSe_2 \rightarrow ZnCr_2Se_4 + Cr + 2ZnSe$
$Zn + MnO_2 \rightarrow ZnMnO_2$	$Zn + MnO_2 \rightarrow MnO + ZnO$
$Zn + MnS_2 \rightarrow ZnMnS_2$	$Zn + MnS_2 \rightarrow MnS + ZnS$
$Zn + MnSe_2 \rightarrow ZnMnSe_2$	$Zn + MnSe_2 \rightarrow MnSe + ZnSe$
$Zn + FeO_2 \rightarrow ZnFeO_2$	$Zn + FeO_2 \rightarrow ZnO + FeO$
$Zn + FeS_2 \rightarrow ZnFeS_2$	$Zn + FeS_2 \rightarrow FeS + ZnS$
$Zn + FeSe_2 \rightarrow ZnFeSe_2$	$Zn + FeSe_2 \rightarrow FeSe + ZnSe$
$Zn + CoO_2 \rightarrow ZnCoO_2$	$Zn + CoO_2 \rightarrow CoO + ZnO$
$Zn + CoS_2 \rightarrow ZnCoS_2$	$12Zn + 12CoS_2 \rightarrow Co_3S_4 + Co_9S_8 + 12ZnS$
$Zn + CoSe_2 \rightarrow ZnCoSe_2$	$10Zn + 10CoSe_2 \rightarrow Co_9Se_8 + CoSe_2 + 10ZnSe$
$Zn + NiO_2 \rightarrow ZnNiO_2$	$Zn + NiO_2 \rightarrow NiO + ZnO$
$Zn + NiS_2 \rightarrow ZnNiS_2$	$12Zn + 12NiS_2 \rightarrow Ni_3S_4 + 12ZnS + Ni_9S_8$
$Zn + NiSe_2 \rightarrow ZnNiSe_2$	$Zn + NiSe_2 \rightarrow NiSe + ZnSe$

S6. Polymorphs considered in the determination of two-electron reaction voltages

The *2-electron reactions* tab of the supplementary spreadsheet `structure_SI.xlsx` contains information about which structures were considered in the calculation of voltages for two-electron reduction reactions presented in this work. The notations are the same as those described in Section S4.

S7. Thermodynamic analysis of intercalation and conversion reactions in sulfides and selenides

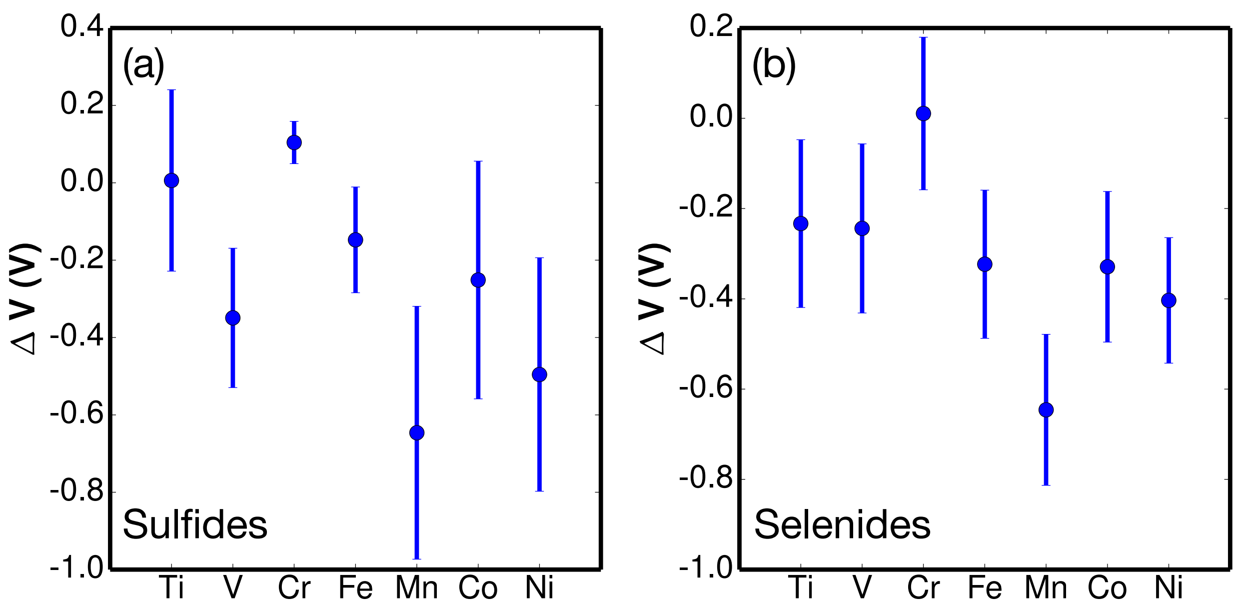

Figure S3: The difference between intercalation and conversion voltages for each transition metal (a) sulfide and (b) selenide. Specifically, $\Delta V = V_{\mathrm{int}}^{\mathrm{LDP}} - V_{\mathrm{conv}}^{\mathrm{LDP}}$. The error bars represent the variation across possible working ions.

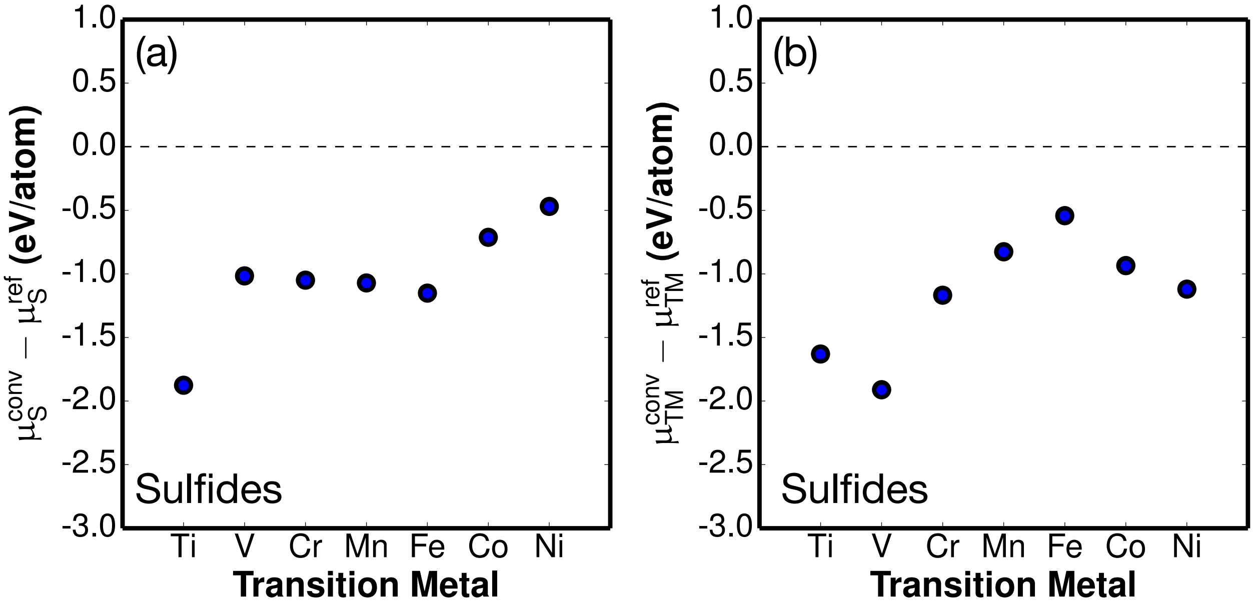

Figure S4: (a) and (b) show the referenced chemical potential set by the products of the conversion reaction for each particular transition metal sulfide. (a) displays the sulfide chemical potential, and (b) displays the transition metal chemical potential. In (a) and (b), we take the reference chemical potential to be the DFT energy of the bulk material.

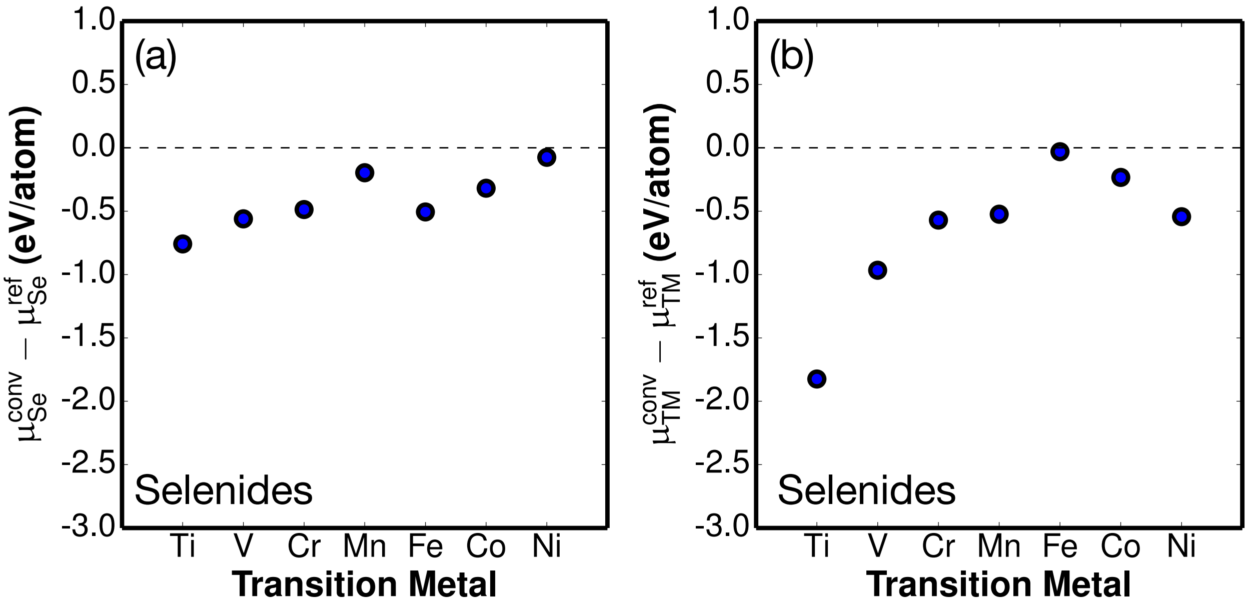

Figure S5: (a) and (b) show the referenced chemical potential set by the products of the conversion reaction for each particular transition metal selenide. (a) displays the selenide chemical potential, and (b) displays the transition metal chemical potential. In (a) and (b), we take the reference chemical potential to be the DFT energy of the bulk material.

S7.1 Chemical potentials

To understand the thermodynamic underpinnings the competition between intercalation and conversion reactions, we can consider the reaction voltages (which are related to the free energy change of the reaction – Δ*G* – via Eq. 1 in the main text) in terms of chemical potential changes. As an example, we analyze the balance of conversion and intercalation in $MgCr_2O_4$:

$$MgCr_2O_4 \leftarrow_{Intercalation} Mg + 2CrO_2 \rightarrow MgO + Cr_2O_{3\,Conversion}$$

If we difference the intercalation and conversion reactions shown above we arrive at the (hypothetical) reaction $MgCr_2O_4 \rightarrow MgO + Cr_2O_3$, which does not evolve spontaneously if the $\Delta G>0$. This is equivalent to stating that intercalation is the favored process if $\Delta V>0$. ΔG can in turn be described by Equation 1, wherein μ_i indicates the chemical potential of species *i*.

$$\Delta G=\Delta\mu_{Mg}+\Delta\mu_{Cr}+\Delta\mu_{O} \qquad (1)$$

Expanding each of the terms in Equation 1 yields Equation 2:

$$\Delta G=\left(\mu_{Mg}^{MgO}-\mu_{Mg}^{MgCr_2O_4}\right)+\left(2\mu_{Cr}^{Cr_2O_3}-2\mu_{Cr}^{MgCr_2O_4}\right)+\left(\mu_{O}^{MgO}+3\mu_{O}^{Cr_2O_3}-4\mu_{O}^{MgCr_2O_4}\right) \qquad (2)$$

where for example, μ_{Mg}^{MgO} represents the chemical potential of Mg within MgO. The oxygen chemical potential in MgO and Cr_2O_3 that form upon conversion, i.e. the terms μ_{O}^{MgO} and $\mu_{O}^{Cr_2O_3}$ in Equation 2, are necessarily the same since the two conversion products, if they form, should be in equilibrium with each other. Henceforth, we will denote the oxygen chemical potential in conversion products as μ_{O}^{conv}. Equation 2 then becomes:

$$\Delta G=\left(\mu_{Mg}^{MgO}-\mu_{Mg}^{MgCr_2O_4}\right)+2\left(\mu_{Cr}^{Cr_2O_3}-\mu_{Cr}^{MgCr_2O_4}\right)+4\left(\mu_{O}^{conv}-\mu_{O}^{MgCr_2O_4}\right) \qquad (3)$$

From Equation 3 it becomes clear that for a given reaction, higher chemical potentials in the conversion products will favor intercalation, i.e. $\Delta G>0$. Further, only two out of the three chemical potentials are truly independent in Equation 3, owing to the Gibbs phase rule. To facilitate the analysis in a way that does not directly depend on the choice of the working ion, we consider μ_{TM} and μ_{O} as the independent chemical potentials.

To examine how variation in the transition metal chemistry affects the chemical potential of the transition metal and oxygen in the conversion product equilibrium, we computed each chemical potential for the conversion reaction associated with each transition metal oxide. Note that two distinct definitions of the chemical potential arise:

1. When three products form as a result of the conversion reaction, as is the case in $Mg + 2MnO_2 \rightarrow \frac{1}{6}Mn_3O_4 + \frac{1}{6}Mg_6MnO_8 + \frac{2}{3}Mn_2O_3$, the composition of the reduced system ($Mg+2MnO_2$) is bound by three phases on the ternary (Mg-Mn-O) phase diagram. In such scenarios, all three chemical potentials are uniquely defined by the free energies of the bounding phases.

2. When two products form as a result of the conversion reaction, (for example, $Mg + 2CrO_2 \rightarrow MgO + Cr_2O_3$) the reduced composition lies on a tie line between the conversion products. In this case, we calculate the chemical potential of each species as the average of the triangular facets shared by the tie line (MgO-Cr_2O_3-Cr and MgO-Cr_2O_3-$MgCrO_4$ in the Mg-Cr-O example).

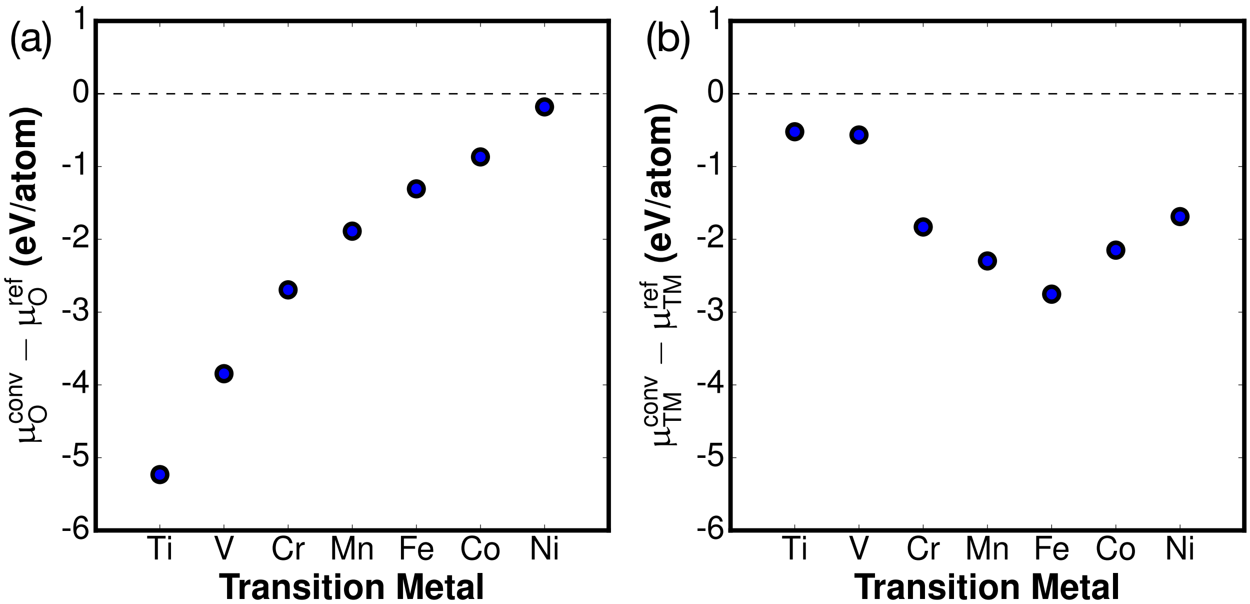

Figure S6: (a) and (b) show the referenced chemical potential set by the products of the conversion reaction for each particular transition metal. (a) displays the oxygen chemical potential, and (b) displays the transition metal chemical potential. In (b) and (c), we take the reference chemical potential to be the DFT energy of the bulk material.

Figures **Error! Reference source not found.**a and b display the variation of the oxygen and transition metal chemical potential, respectively, in the conversion products for several transition metals. In Figure **Error! Reference source not found.**, each chemical potential is referenced to the chemical potential of the corresponding element in its pure, bulk state μ_{TM}^{ref}. The trends in Figures **Error! Reference source not found.**a and b exhibit different trends: The transition metal chemical potential tends to decrease initially across the 3*d* period before increasing marginally for Co and Ni, while the oxygen chemical potential increases monotonically from Ti to Ni. The increase of oxygen chemical potential in the 3*d*-oxides is consistent with the well-known decrease in oxygen affinity across the transition metal period.[1] The differing trends presented in Figure **Error! Reference source not found.** highlight an important optimization problem - some transition metals, such as Ti, exhibit a high transition metal chemical potential which favors intercalation, but the oxygen chemical potential in Ti-oxides is low, favoring conversion. Evidently an optimal balance of these quantities is attained by Cr-oxides, which favor intercalation most strongly (Figure 6b in the main text).

S8. *U* values used in calculations

Table S3: To be compatible with the Materials Project database,[2] we used the following *U* values, only for oxides. Note that the pseudopotentials used in Materials Project are different from those used in the fit by Jain *et al.*,[3] resulting in different *U* values.

Transition metal	***U* (eV)**
Ti	–
V	3.25
Cr	3.7
Mn	3.9
Fe	5.3
Co	3.32
Ni	6.2

References

[1] K Kusabiraki, J Ikegami, T Nishimoto, T Ooka, *Oxidation of metals* **1997**, *47*, 411.

[2] A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, K. A. Persson, *APL Mat.* **2013**, *1*, 011002.

[3] A. Jain, G. Hautier, S. P. Ong, C. J. Moore, C. C. Fischer, K. A. Persson, G. Ceder, *Phys. Rev. B* **2011**, *84*, 045115.