Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Aluminium and Magnesium Insertion in Sulfur-Based Spinels: a First-Principles Study

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Supplementary information

Electronic structure analysis

The electronic structure and electronic transport are important properties for electrode materials since they affect their rate capability. Ideally, facile electron and ionic transport would be desirable for fast charge/discharge rate. Our calculations show that sulfur-based spinels have metallic density of states (DOS, Figure S1). Inserted Mg and Al atoms introduce electronic states across the entire energy region (Figure S2). The total DOS of Mg- and Al-inserted spinels is similar to that of pristine hosts. Overall, the electron transport in sulfur-based spinels is expected to be sufficiently fast for Mg and Al-ion battery applications.

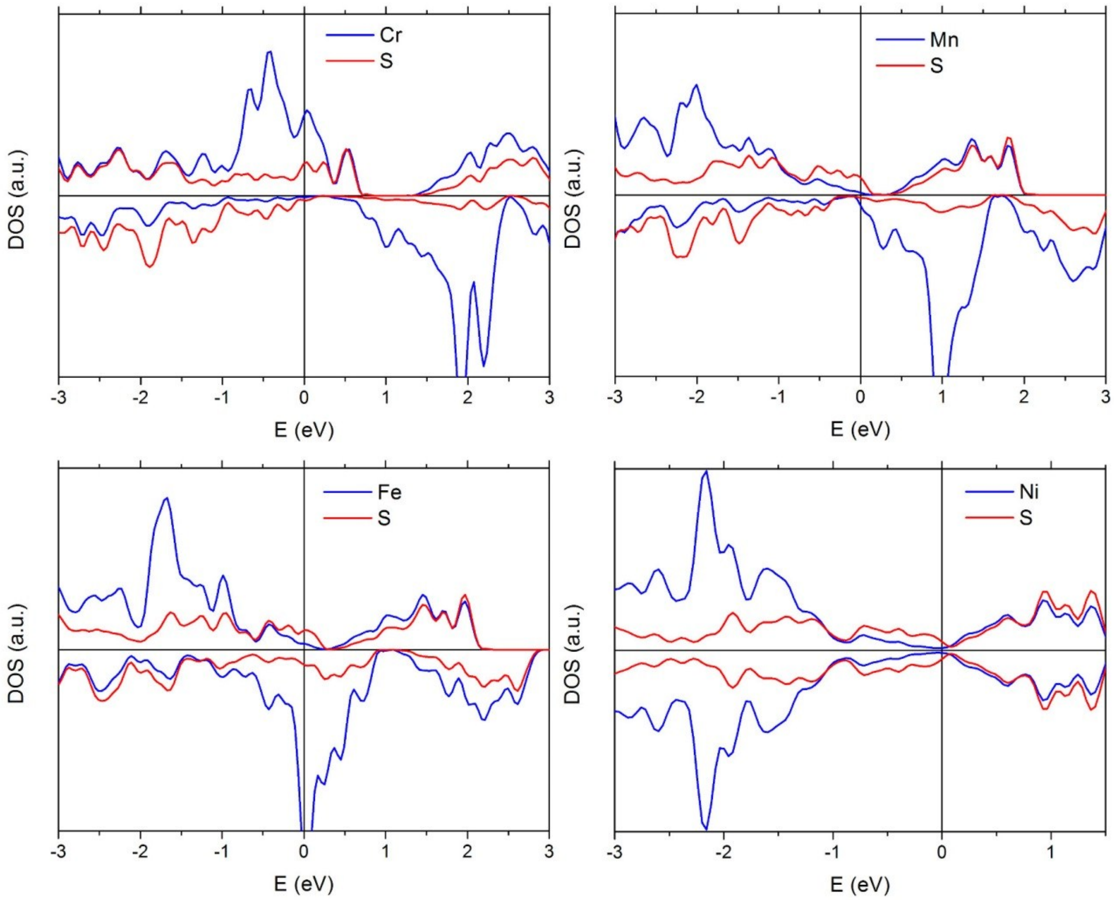

Figure S1. Density of states (DOS) of pristine spinels. The Fermi level is set to zero and is shown by a vertical line.

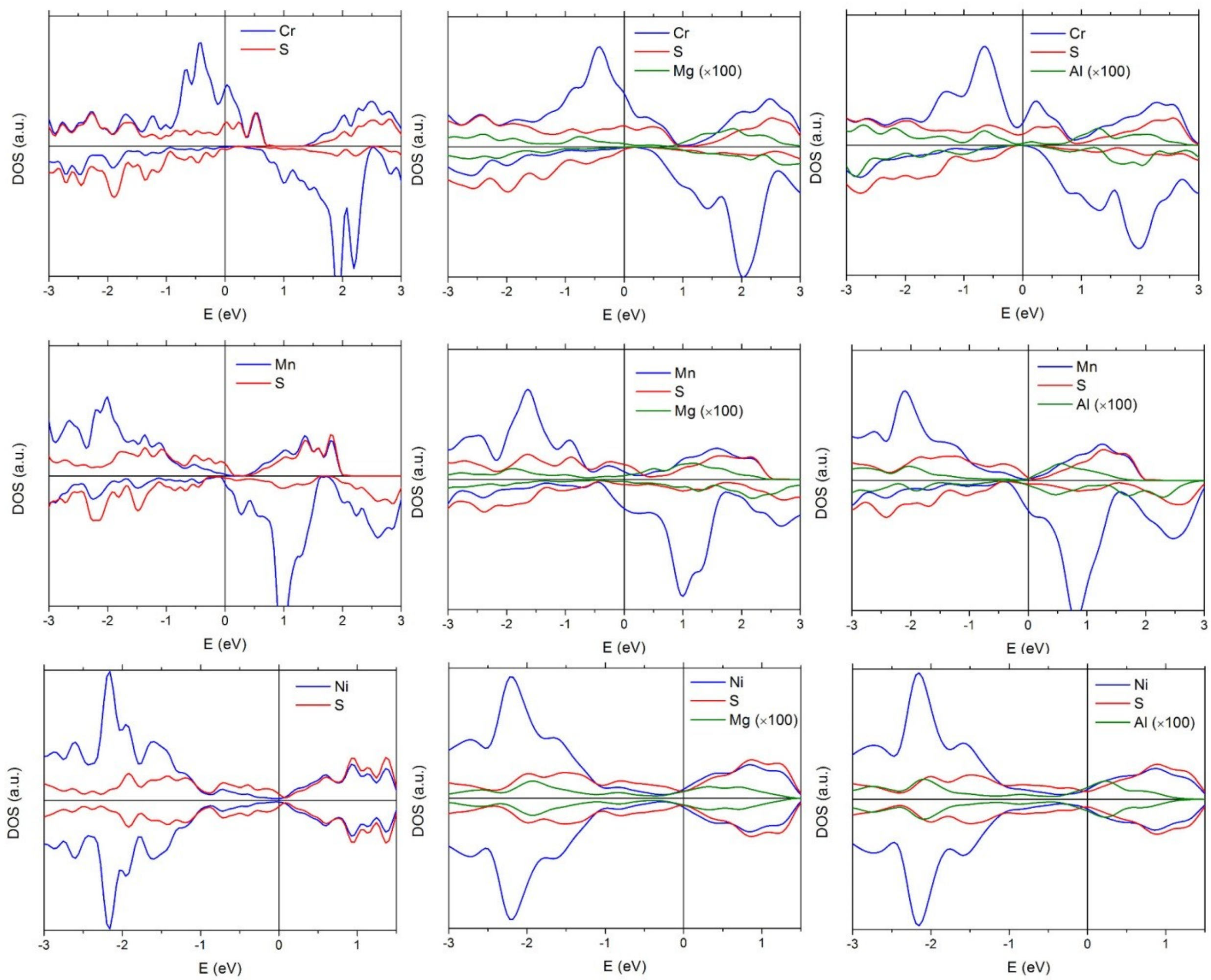

Figure S2. Density of states (DOS) of Cr-, Mn- and Ni-based spinels after Mg and Al insertion. The Fermi level is set to zero and is shown by a vertical line. Note that Mg and Al states are magnified for a viewing convenience.

Table S1. Cathode reactions used to calculate insertion voltage

Chemical reaction
$Mg + Cr_2S_4 \rightarrow MgCr_2S_4$ $Mg + Mn_2S_4 \rightarrow MgMn_2S_4$ $Mg + Fe_2S_4 \rightarrow MgFe_2S_4$ $Mg + Co_2S_4 \rightarrow MgCo_2S_4$ $Mg + Ni_2S_4 \rightarrow MgNi_2S_4$