Support Information

Proposed electron transmission mechanism between Fe$^{3+}$/Co$^{2+}$ and Fe$^{3+}$/Fe$^{3+}$ in spinel structure and its practical evidence on quaternary Fe$_{0.5}$Ni$_{0.5}$Co$_2$S$_4$

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Table S1. The etching parameters of the two samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Etching element</th>
<th>Source Gun Type</th>
<th>Total acquisition time</th>
<th>Number of Energy steps</th>
<th>Energy step Size</th>
<th>Etching Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₀.₅Ni₀.₅Co₂O₄</td>
<td>Ar ion</td>
<td>Al Kα</td>
<td>1 min 8.0 secs</td>
<td>1361</td>
<td>1.00 eV</td>
<td>~3000 s</td>
</tr>
<tr>
<td>Fe₀.₅Ni₀.₅Co₂S₄</td>
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</tr>
</tbody>
</table>

Figure S1. XPS data of Fe₀.₅Ni₀.₅Co₂O₄ and Fe₀.₅Ni₀.₅Co₂S₄ treated by Ar-cluster etching technique: (a, c, e): Co 3/2p, Ni 3/2p, Fe 3/2p of Fe₀.₅Ni₀.₅Co₂O₄; (b, d, f) Co3/2p, Ni 3/2p, Fe 3/2p of Fe₀.₅Ni₀.₅Co₂S₄.

Figure S2. The Mössbauer of Fe₀.₅Ni₀.₅Co₂O₄ and Fe₀.₅Ni₀.₅Co₂S₄.
According to the Isomer shift value, we can get information that the Fe ions in both two samples presented tervalence. Besides, Fe$^{3+}$ only can be found at B sites.$^{1-2}$