

## Supporting Information:

### Is there a universal reaction mechanism of Li insertion into oxidic spinels: A case study using $\text{MgFe}_2\text{O}_4$

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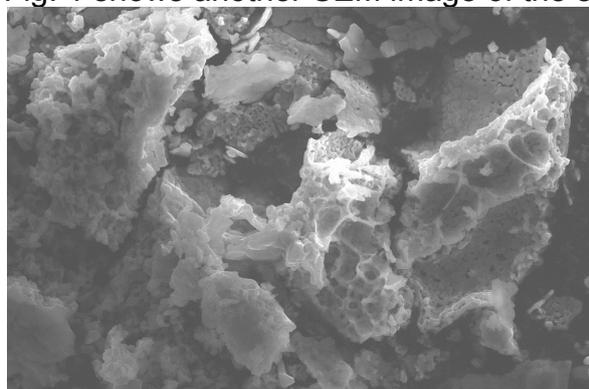
## EDX

Supplementary Table 1:

sample	Measure No.	Mg / At %	Fe / At %	Ratio Mg : Fe
$\text{MgFe}_2\text{O}_4\_A$	1	36.87	63.13	
	2	39.90	60.10	
	3	39.65	60.35	
	4	31.32	68.68	
	<b>Average</b>		<b>36.94</b>	<b>63.07</b>
$\text{MgFe}_2\text{O}_4\_B$	1	28.79	71.21	
	2	34.25	65.75	
	3	31.07	68.93	
	4	40.51	59.49	
	<b>Average</b>		<b>33.66</b>	<b>66.35</b>

## SEM

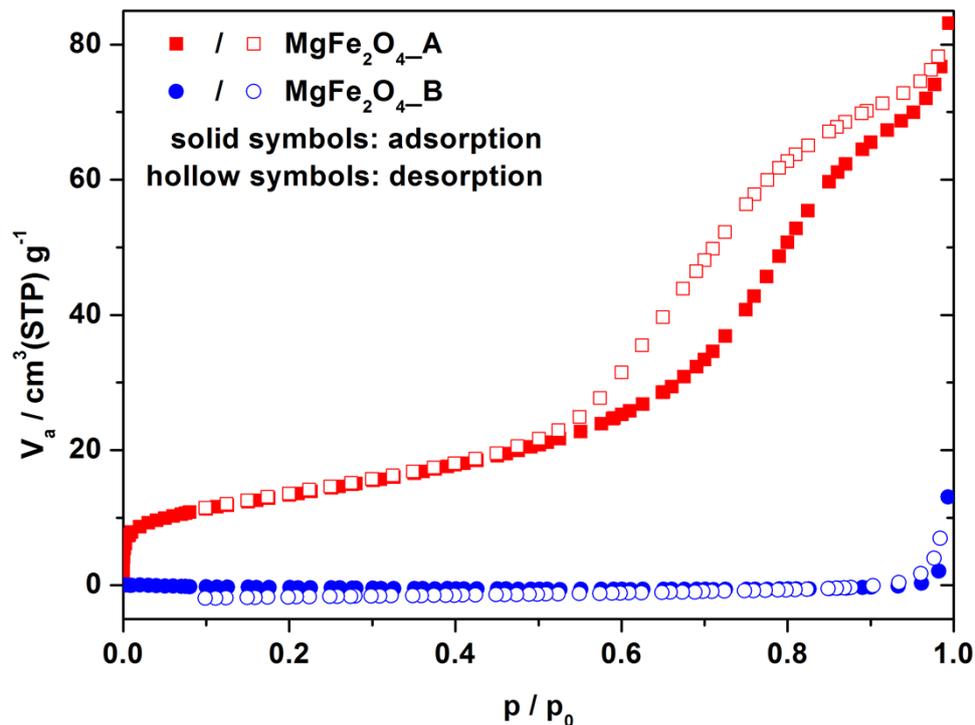
Fig. 1 shows another SEM image of the sample  $\text{MgFe}_2\text{O}_4\_B$ .



Supplementary Fig. 1: SEM map images of the sample  $\text{MgFe}_2\text{O}_4\_B$

## N<sub>2</sub>-Adsorption

Adsorption/Desorption of N<sub>2</sub> samples A and B:

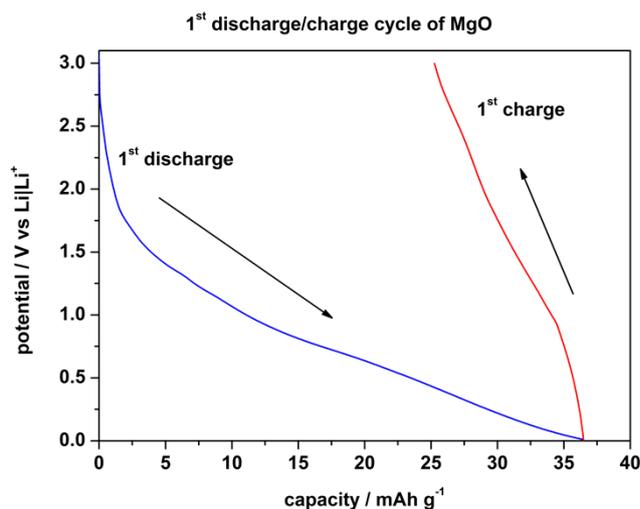


Supplementary Fig. 2: N<sub>2</sub> Adsorption and Desorption for sample MgFe<sub>2</sub>O<sub>4</sub>\_A and B,

## MgO as anode material in Lithium battery

For electrochemical measurement 80 wt% MgO was mixed with 10 wt.% SUPER C65 Carbon (Timcal, Switzerland) and 10 wt.% PVdF (Solvay, Germany). The mixture was dissolved with NMP (N-methyl-2-pyrrolidone), deposited on copper foil and dried overnight at room temperature and sintered at 100 °C for 24 h in a vacuum drying chamber. Afterwards 10 mm discs were cut with about 2 mg active material and used as cathode in a swagelok type test cell, using lithium metal as the anode, glass fiber filter disks (Whatman, United Kingdom) as the separator, and a solution of 1 M LiPF<sub>6</sub> in an ethylene carbonate/dimethyl carbonate mixture (Merck, Germany) as electrolyte. Test cells were discharged/charged with C/10 rate, performed with a Materials Mates 510 DC.

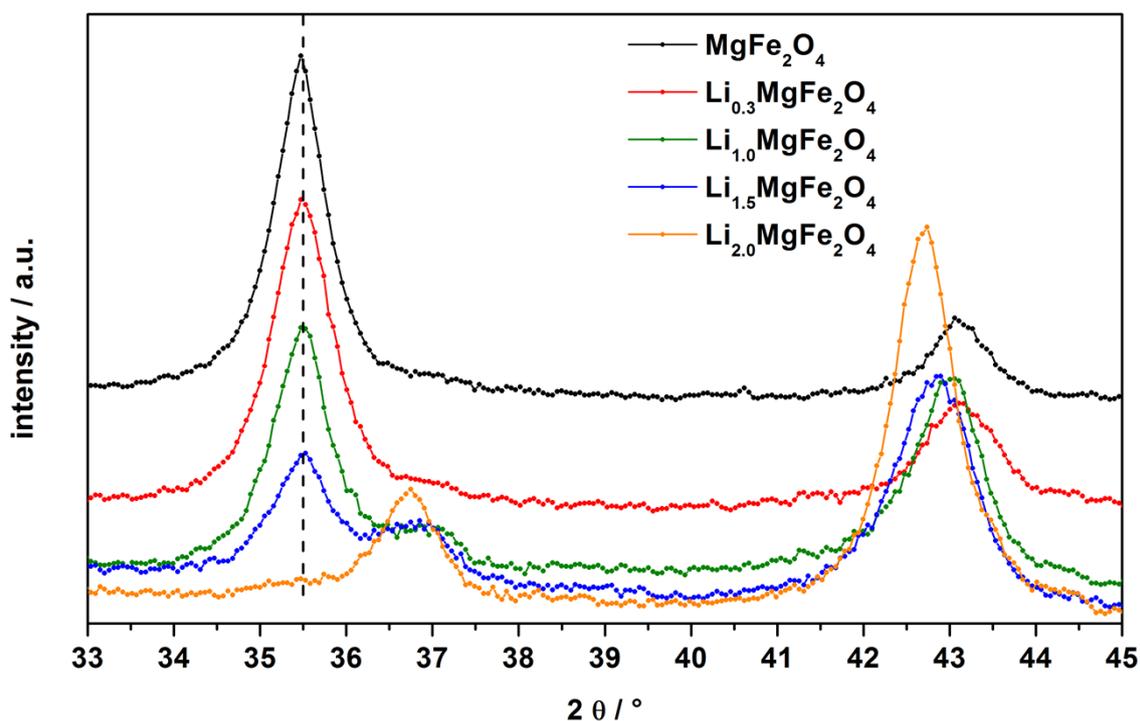
The first discharge curve of MgO is shown in Fig. 3. According to the very low capacity it is supposed that no conversion of MgO takes place.



Supplementary Fig. 3: First discharge (blue)/charge (red) Cycle of nanocrystalline MgO.

### Ex-situ XRD on lithiated $\text{MgFe}_2\text{O}_4$ \_A

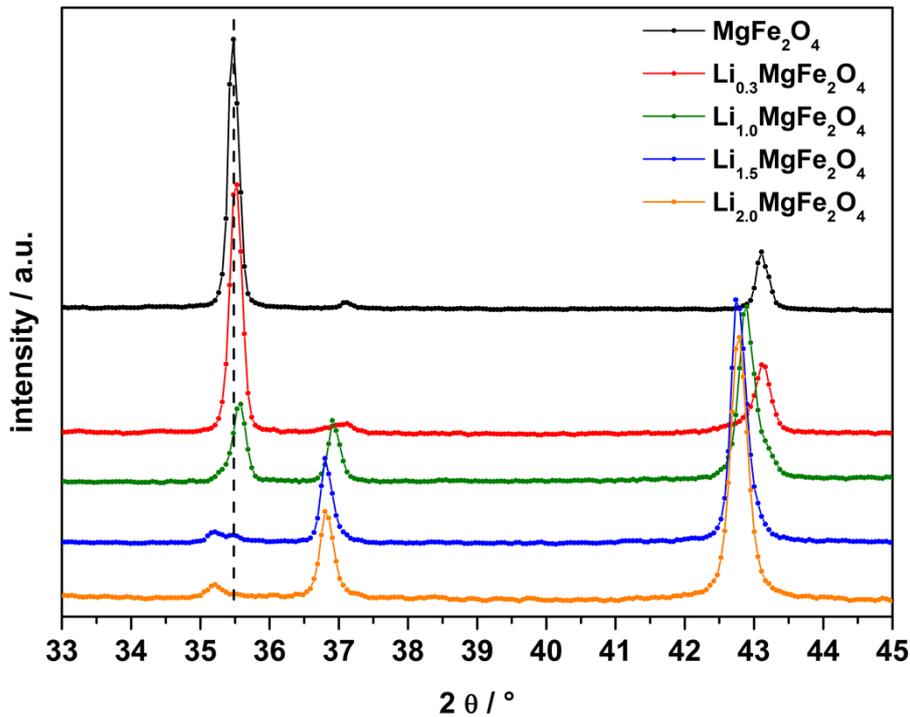
In Fig. 4 the detailed area of the XRD pattern 33–45° 2 $\theta$  is shown for the pristine material and after 0.3, 1.0, 1.5 and 2.0 Li per formula unit of sample A. The shift of the strong 311 peak at 35.5° of the spinel structure of sample A is shifting a little bit 0.3 %, this is not observed for sample B (Fig. 5). The decreasing intensity with increasing Li amount per formula unit can be clearly observed.



Supplementary Fig. 4: XRD pattern of pristine material and after insertion of 0.3, 1.0, 1.5, 2.0 Li of sample  $\text{MgFe}_2\text{O}_4$ \_A.

### Ex-situ XRD on lithiated $\text{MgFe}_2\text{O}_4$ \_B

In Fig. 5 the detailed area of the XRD pattern 33-45° 2 $\theta$  is shown for the pristine material and after 0.3, 1.0, 1.5 and 2.0 Li per formula unit of sample B. Strong 311 peak at 35.5° of the spinel structure is **not** shifting. But for insertion of 0.3 Li the 400 reflection peak 43° has an asymmetric shape because the monoxide is already formed.



Supplementary Fig. 5: XRD pattern of pristine material and after insertion of 0.3, 1.0, 1.5, 2.0 Li of sample  $\text{MgFe}_2\text{O}_4$ \_B.

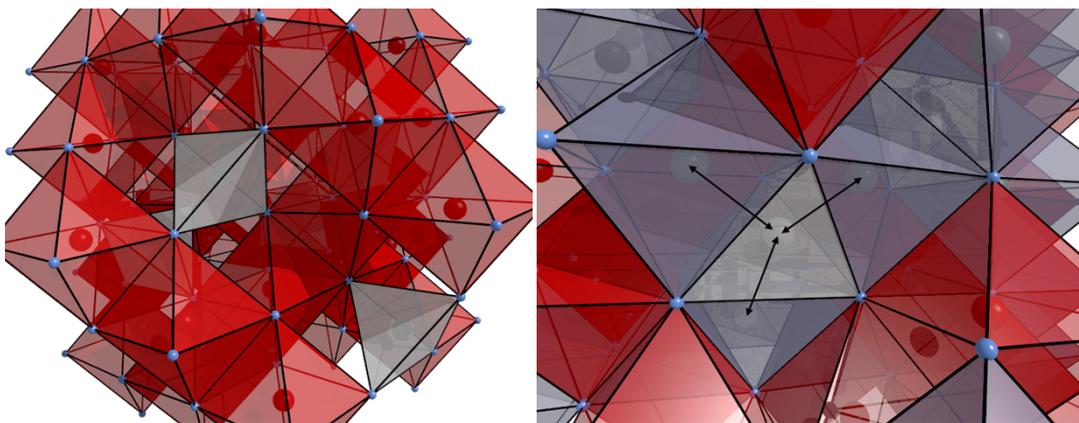
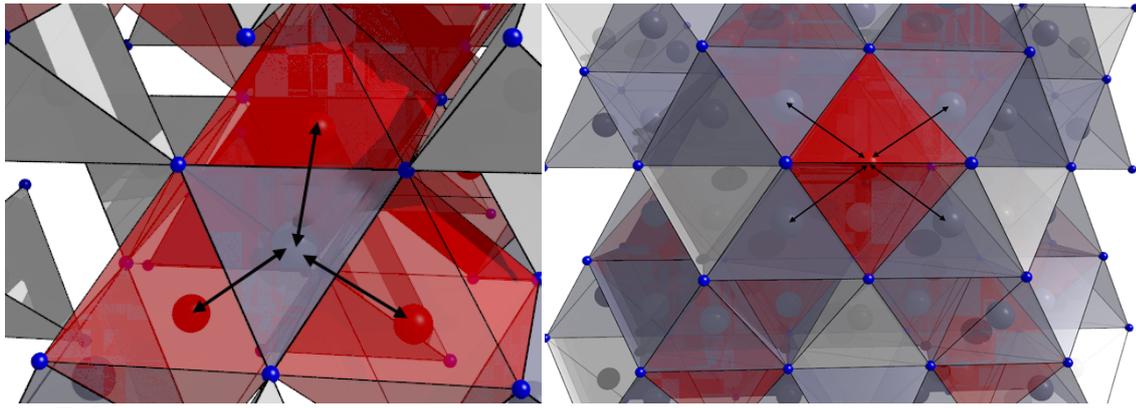


Fig. 6: Schematic illustration of the pristine spinel (left) and with occupied octahedral sites 16d (right) black arrows display the distances under 2 Å next to neighbored occupied octahedral sites.



**Fig. 7: Schematic illustration of the spinel with occupied tetrahedral sites 8b (left) and occupied tetrahedral sites 48f (right) black arrows display the distances under 2 Å next to neighbored occupied octahedral sites.**