

Supplemental Information

Magnesium Insertion and Related Structural Changes in Spinel-Type Manganese Oxides

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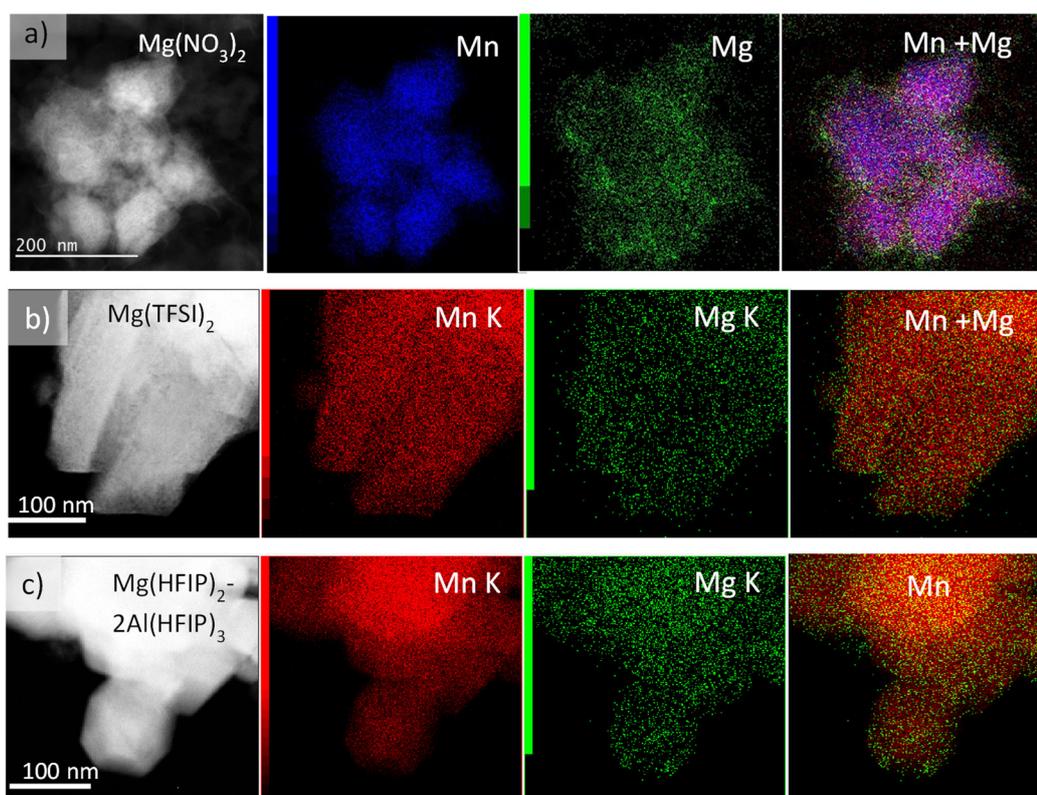


Figure S1. STEM-EDX Mg and Mn maps of Aqua, TFSI and HFIP samples.

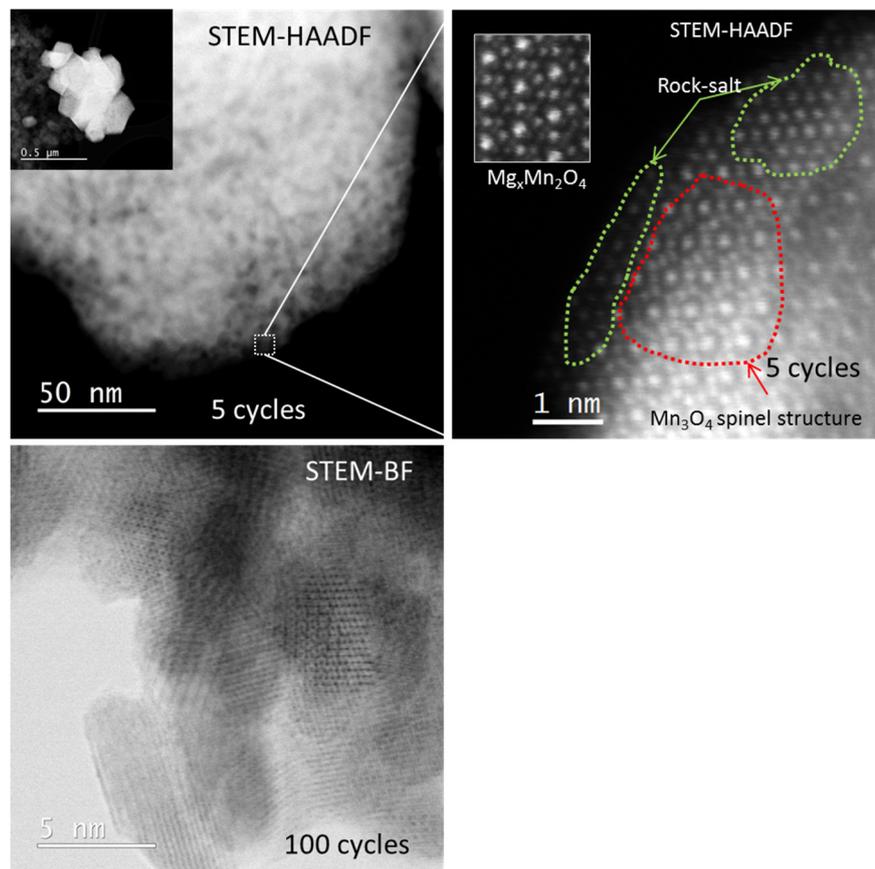


Figure S2. Magnesiated $(\text{Mg}_x\text{Li}_{1-x})\text{Mn}_2\text{O}_4$ structure after 5 cycles (STEM-HAADF images above), and after failure at 100 cycles (STEM-BF image below).

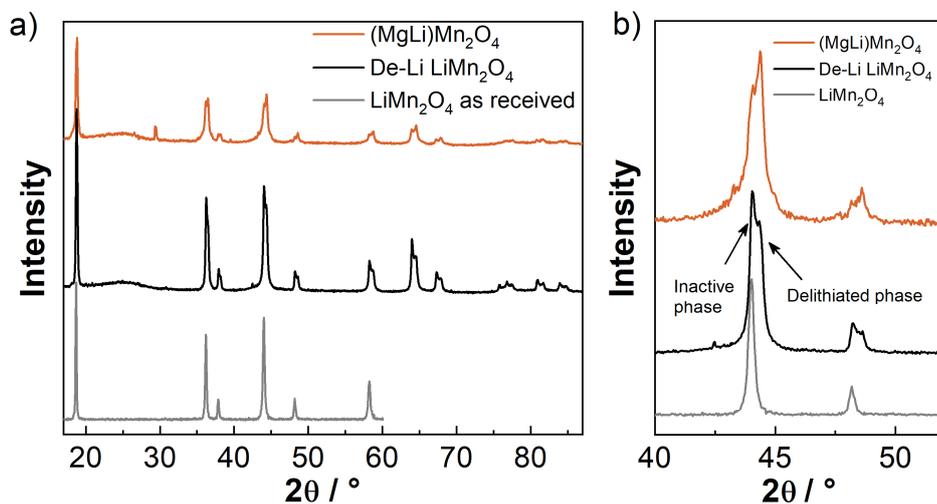


Figure S3. a) XRD patterns of delithiated LiMn_2O_4 and magnesiated $(\text{Mg}_x\text{Li}_{1-x})\text{Mn}_2\text{O}_4$. Pattern of pristine LiMn_2O_4 is added as a reference. The samples were obtained from $\text{Mg}(\text{NO}_3)_2/\text{H}_2\text{O}$ electrolyte. b) Magnified region, where the two-phase behaviour can be observed.

Presented XRD patterns in Figure S3a show the materials, obtained from $\text{Mg}(\text{NO}_3)_2/\text{H}_2\text{O}$ electrolyte upon delithiation and magnesiation. Additional analysis showed that there are two phases present in cycled samples, which are depicted in Figure S3b. One phase shows no changes in comparison to non-reacted starting material, so we have labeled it as

“inactive”. The other phase is retaining the original cubic structure. However, the decrease of lattice parameter from $a = 8,227 \text{ \AA}$ in pristine LiMn_2O_4 , to $a = 8,174 \text{ \AA}$ in delithiated state, to $a = 8,163 \text{ \AA}$ in magnesiated state was observed, as described in main text. Smaller unit cells when doping with small amounts of Mg in LiMn_2O_4 structure, were also reported by Singh et al [1].

The phases are in approximate ratio of 1:1. Upon magnesiation, appearance of additional peak around 29.4° could be observed. This would correspond to (220) peak of $\text{Li}_{0.5}\text{Mg}_{0.5}\text{Mn}_2\text{O}_3$ structure, reported by Singh et al. [2] indicating there was unwanted Mn-Mg substitution taking place. Such substitution would result in accelerated degradation of material upon cycling and severe capacity losses. For more detailed XRD analysis and successful determination of mixing on different sites we would need much more sample to obtain better measurements, which was not feasible with our setup, as described in Experimental section.

[1] Singh, P.; Sil, A.; Nath M.; Ray, S. Preparation and characterization of lithium manganese oxide cubic spinel $\text{Li}_{1.03}\text{Mn}_{1.97}\text{O}_4$ doped with Mg and Fe. *Physica B: Condensed Matter* **2010**, *405*, 649-654.

<https://doi.org/10.1016/j.physb.2009.09.081>

[2] Singh, V.; Seehra, M. S.; Manivannan, A.; Kumta, P. N. Magnetic characteristics of a new cubic defect spinel $\text{Li}_{0.5}\text{Mg}_{0.5}\text{Mn}_2\text{O}_3$. *J. Appl. Phys.* **2021**, *111*, 07E302. <https://doi.org/10.1063/1.3670504>