Ordered Mesoporous MFe<sub>2</sub>O<sub>4</sub> (M = Co, Cu, Mg, Ni, Zn) Thin Films with Nanocrystalline Walls, Uniform 16 nm Diameter Pores and High Thermal Stability: Template-Directed Synthesis and Characterization of Redox Active Trevorite

Jan Haetge, Christian Suchomski and Torsten Brezesinski\*

Institute of Physical Chemistry, Justus-Liebig-University Giessen, Heinrich-Buff Ring 58,

Giessen 35392, Germany



**Figure S1.** Morphology of KLE-templated NFO thin films calcined at 600 °C. (a) Lowmagnification top view SEM image. It is evident from this micrograph that the crack-free NFO materials employed in this work are homogeneous on the micrometer length scale and that the pores at the top surface are open. In addition, it can be seen that the nanostructured domains have a size of up to 1 micrometer in diameter. (b) 3D-AFM height image of the hexagonal top surface. The rms roughness is less than 1 nm. (c) Low-magnification bright-field TEM image showing that the periodic structure observed at the top surface persists throughout the films.



**Figure S2.** SAXS patterns taken in Bragg-Brentano geometry on KLE-templated NFO thin films heated to 250 °C as well as 450 and 650 °C (inset). It can be clearly seen that the films achieved their maximum contraction of ~75% after calcination at 250 °C because the ligands of both inorganic precursors are fully decomposed under the aging conditions. The result that even a  $2^{nd}$  order reflection can be observed for amorphous NFO underlines the high degree of pore ordering. The fact that the samples loose their out-of-plane-periodicity when the crystalline phase is achieved can be attributed to the small number of repeat units normal to the substrate (note that the crystallization is always accompanied by a certain restructuring).



**Figure S3.** Voltammetry sweeps obtained on KLE-templated NFO thin film electrodes at 25 mV/s rate comparing lithium (Li<sup>+</sup>) and tetrabutylammonium (TBA<sup>+</sup>) electrolytes. We note that a rate of 25 mV/s does not allow much time for charge storage by lithium intercalation. It is evident from this data that only a small fraction of the charge storage in these materials stems from double layer capacitance (~40 C/g), which implies that some 70% of the capacitance arises from the fact that Li<sup>+</sup> is electrochemically adsorbed onto the surface through charge-transfer

processes. We explain this level of pseudocapacitance with high BET surface area and good connectivity of pores (the latter provides for short diffusion path lengths and facilitates solvent diffusion through the bulk of the films).



**Figure S4.** Low-magnification SEM images of a KLE-templated NFO thin film before (a) and after (b) galvanostatic cycling. The image in (b) was collected after 100 cycles at a rate of 1C. It can be clearly seen that the intercalation of lithium ions into the inverse spinel lattice does not lead to severe restructuring of the pore network. This result helps explain the excellent cycling stability and supports the hypothesis of a topotactic intercalation. In addition, it can be seen that the NFO thin film electrodes remain crack-free at the micrometer level, which demonstrates that these samples can readily accommodate the volume expansion associated with  $Li^+$  intercalation.