Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information for

Thermochemical heat storage based on the Mn_2O_3/Mn_3O_4 redox couple: influence of the initial particle size on the morphological evolution and cyclability

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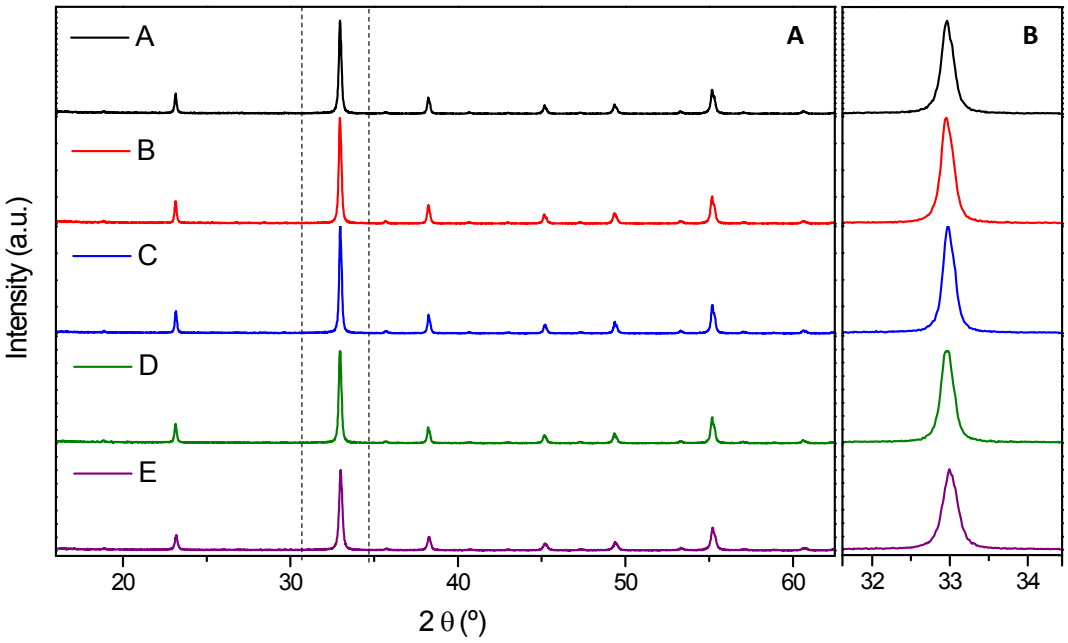

Figure S1. A: X-ray diffraction patterns of the Mn_2O_3 samples. XRD patterns are plotted without applying any correction. The dashed lines indicate the zone shown in B, which depicts the most intense reflection used for crystallite size calculations.

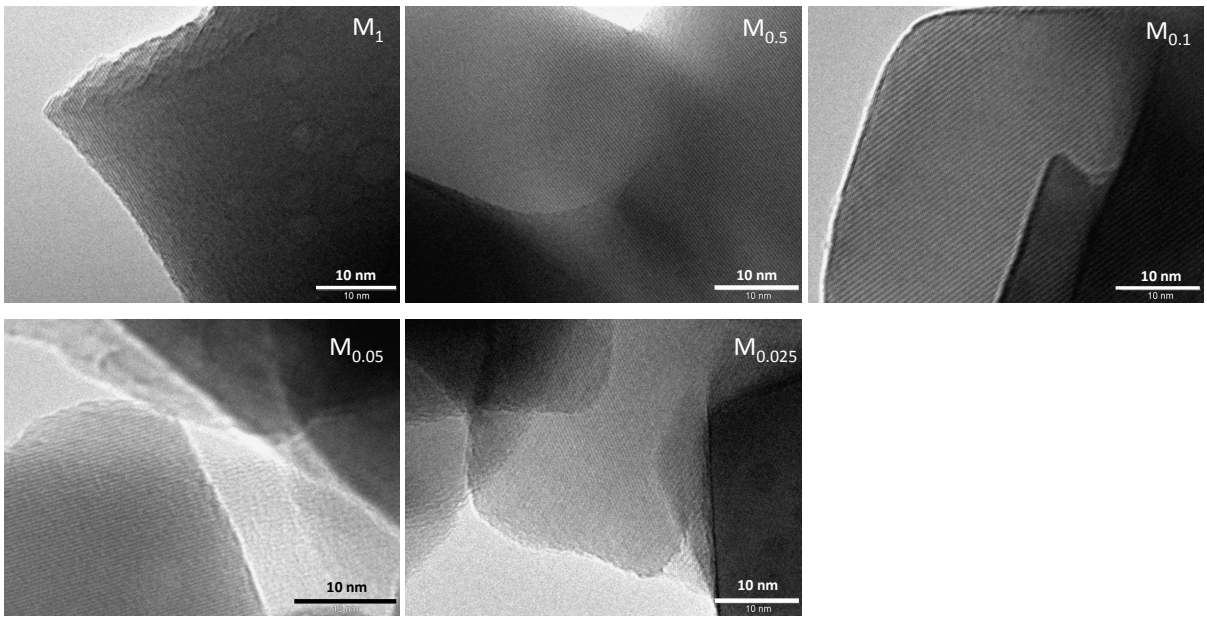

Figure S2. High resolution TEM micrographs of the Mn_2O_3 samples prepared with different precursor concentrations.

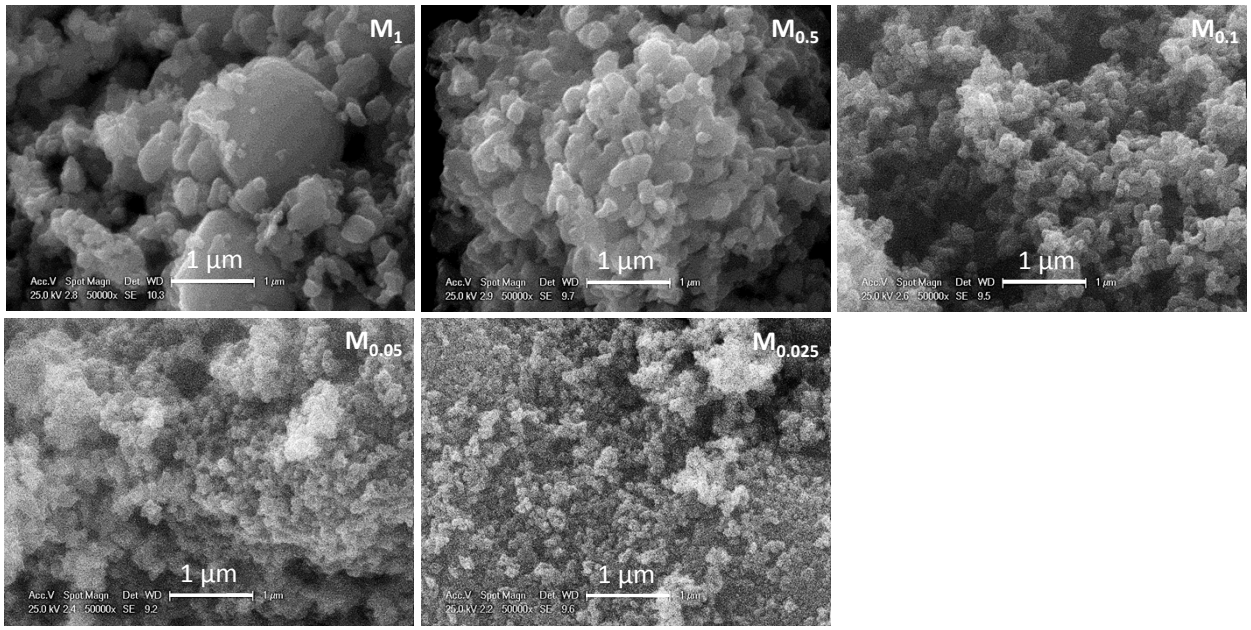

Figure S3 SEM micrographs of the Mn_2O_3 samples after calcination at 700 ºC.

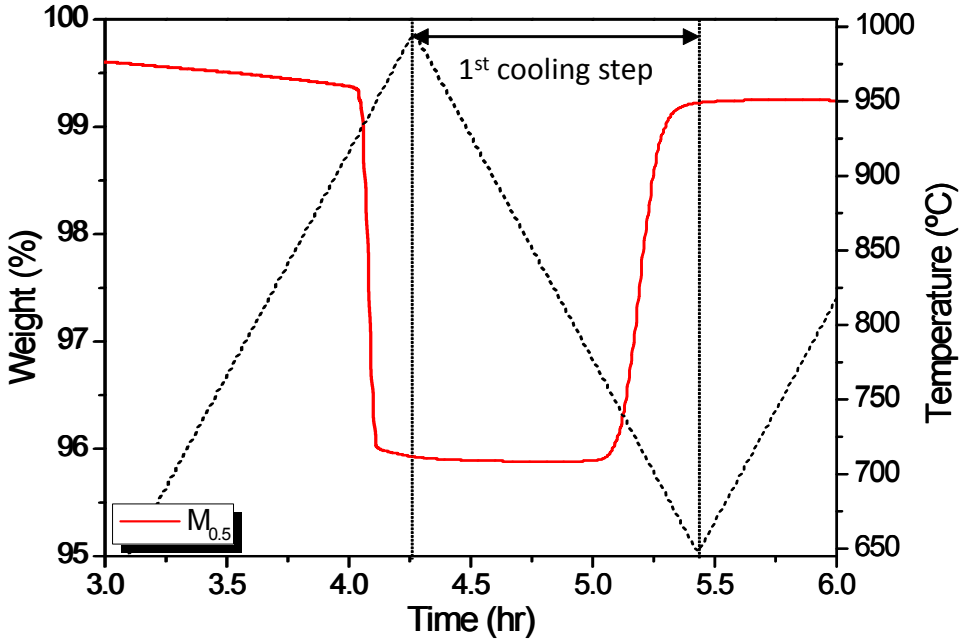

Figure S4. First cooling step interval taken from the 30 redox cycles run performed to $M_{0.5}$ sample.

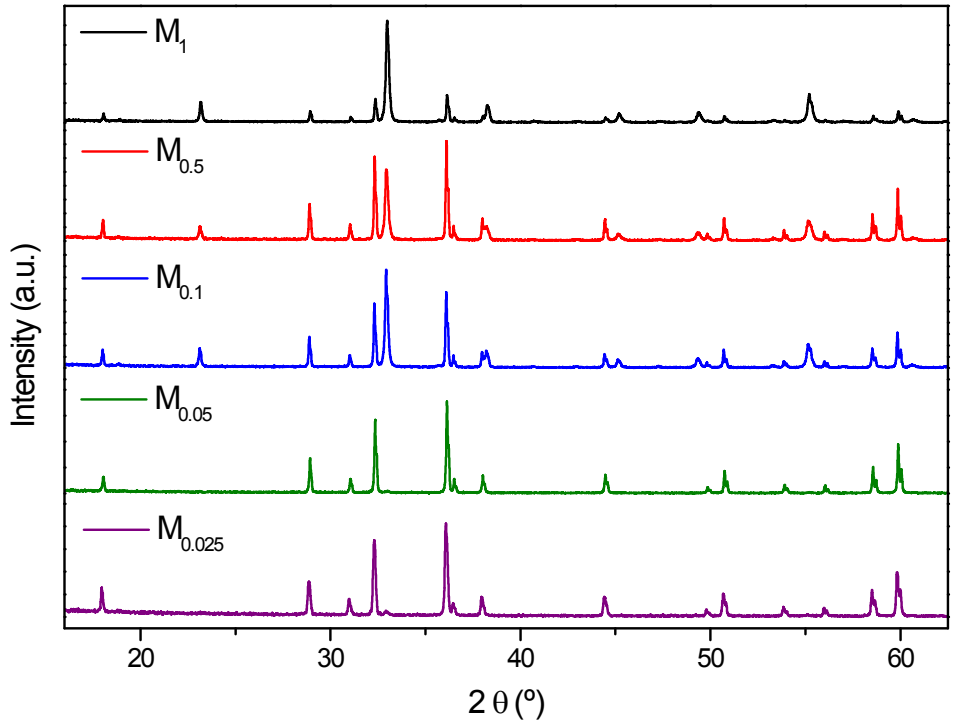

Figure S5. X-ray diffraction patterns for each sample after the 30 redox cycle assays carried out in thermobalance. M_1-$M_{0.1}$ samples presented a mixture of Mn_3O_4 tetragonal (ICDD- 00-024-0734) phase and Mn_2O_3 cubic phase, as on the last cycle, oxidation was not fully completed on the last cooling step. For $M_{0.05}$-$M_{0.025}$ solely Mn_3O_4 phase was observed, since such materials showed a complete loss of reversibility on the first redox cycles assayed.

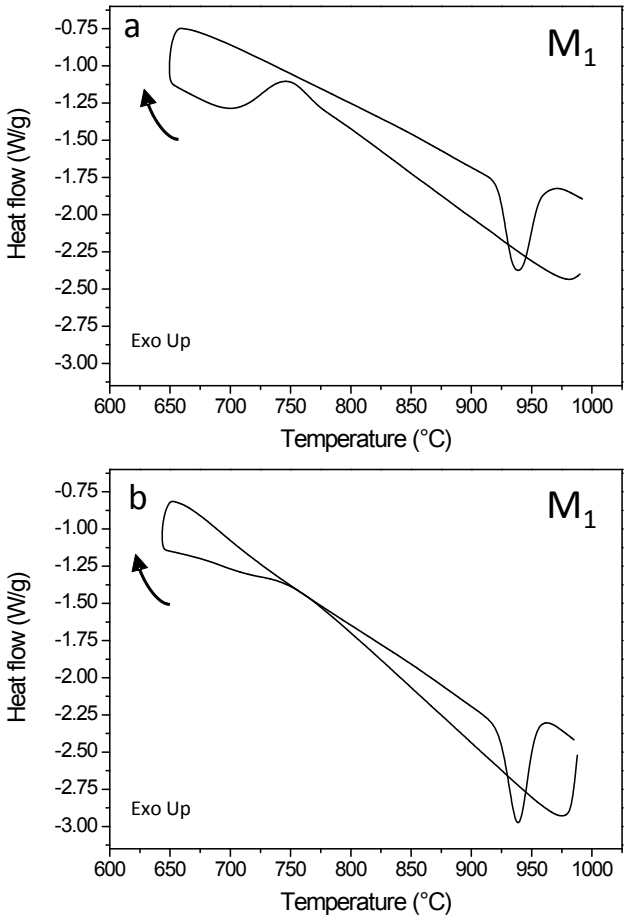

Figure S6. DSC curves for M_1 sample: (a) first oxidation and second reduction and (b) oxidation in cycle 29th and reduction in cycle 30th. As it can be observed reduction peak kept its shape after the entire assay, whereas oxidation peak exhibited a broadening for the last cycle. This is due to the slowdown on the oxidation rate caused by particle sintering. The arrow indicates the cycle direction.