# Supporting Information

# Cyanamide Route to Calcium-Manganese Oxide Foams for Water Oxidation

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The Supporting information contains:

1. Details on oxygen evolution experiments

2. The following additional figures and tables;

Figure S9. SEM image and EDS-mapping of $CaMn_2O_x$-0.8-400.

Figure S10. SEM image and EDS-mapping images of o $CaMn_2O_x$-0.8-550.

Figure S11. SEM image and EDS-mapping images of $CaMn_2O_x$-0.8-700.

Figure S12. Structure of $Ca_2Mn_3O_8$. A – side view where the $MnO_6$ layers and the Ca ions between them are visible. B – top view illustrating the two binding positions of Ca: on the top of Mn vacancies (3.84 Å Mn-Ca distance) and in a cubane motif (3.17 Å Mn-Ca distance). Mn atoms are shown in magenta, Ca in green, and O in red.

Table S2. Oxygen evolution data from refs.[1,2] and this investigation).

Figure S13. Oxygen evolution results for the reaction of CaMn oxides suspended in 0.5 M $Ce^{4+}$ aqueous solution.

Table S3: Amount of dissolved oxides (mg/ml) in solution (0.5M Ce(IV)).

Figure S14: Long term oxygen evolution test (100mg catalyst in 38ml of Ce(IV) solution, $CaMn_2O_x$-0.8-400, Ce(IV)= 0.5M). Oxygen evolution was measured by gas chromatography. The result shows that although the oxygen evolution rate has been decreased after first 20h but it is producing oxygen until the end of reaction time and the catalyst remains active for longer time either by addition of fresh oxidant or using less amount of catalyst.

Figure S15: Recycling experiments using $CaMn_2O_x$-0.8-400 = 2.8 mg/ml, Ce(IV)= 0.5M.

Table S4: Details of catalytic test experiments by gas chromatography.The data show small change in T.O.F. even with different amount of catalyst or using the same one for second and third run (T.O.F. has been calculated based on the oxygen amount(mmol)produced in the first 30min of the reaction and divided by the amount of manganese content of the catalyst(mol).

Figure S16. XANES spectra measured at the Mn *K*-edge (top) and the Ca *K*-edge (bottom) from the CaMn material before annealing (100 °C) and after annealing for 4h at different temperatures. Insets: comparison of the XANES spectra from CaMn oxide with and without cyanamide, annealed at 550 °C.

Figure S17. $k^3$ weighted EXAFS spectra measured at the Mn *K*-edge (top) and the Ca *K*-edge (bottom) from the CaMn material before annealing (100 °C) and after annealing for 4h at different temperatures. Black: experimental curves, red - simulations. The simulation parameters are shown in Table S1.

Table S5. EXAFS simulation parameters.

Figure S18. Coordination numbers deduced from the simulations, as shown also in Table S1. A: measurements at the Mn *K*-edge, B: at the Ca *K*-edge.

Figure S19. Rate of $O_2$-formation ($R_{O2}$) per surface area ($A$). If $O_2$-rate were proportional to the surface area, $R_{O2}/A$ should be independent on the surface (A). Instead, a decreased activity per surface area by two orders of magnitude is observed meaning that the surface area is not a crucial determinant of the rate of catalysis (see dotted line drawn to guide the eye) (refs.[1,2] and this investigation).

## 1. *Details on the oxygen evolution experiments*

For a typical catalytic experiment, oxides were suspended in water in a Schlenk tube. Then these solutions were made anaerobic by nitrogen purging ($[O_2] < 1$ µmol/l) and the oxygen level was monitored by a Clark electrode. After an equilibriation time of 2 min, an anaerobic solution of Ce(IV) was injected into the tube using a nitrogen-purged syringe. The dissolved oxygen produced during the reaction was monitored by a Clark electrode. The initial oxygen evolution rates as shown in Table 1 and 2 were determined by a linear fit of the Clark cell data of the first three minutes and divided by the amount of the overall manganese content in the oxide suspended in the 2 ml reaction solution (Table S2). In pursuing these experiments, it was been considered that the Clark electrode can detect dissolved oxygen reliably only below the $O_2$-saturation point of water (258 µmol/l, T=25°C).

*The long term experiments were carried out as follows: Millipore water was sonicated under reduced pressure for 1 h.* Millipore water was sonicated under reduced pressure for 1 h. Afterwards the water solution was flushed with argon for 1 h to remove all oxygen. The catalyst and the magnetic stir bar were placed into the reaction chamber and the reactor was closed. Subsequent oxygen was removed by applying vacuum and flushing the reactor with argon. This procedure was repeated 3 times. The reaction mixture, consisting of Ce(IV) in water (0.5 M), with a total volume of 38 mL, was prepared in an oxygen evacuated flask. Then the reaction solution was added to the reaction chamber under reverse argon flow using a dosing valve. After closing the dosing valve, thermostat, magnetic stirrer, and the online measurement software were started. For the second injection the reactor has been opened under Argon, flushed with this gas, and then closed after the injection. The data after oxidant addition was added to the first graph assuming that flushing the reactor with Ar removed all oxygen produced in the first step (See ref 3 for more details about setup).[1]

The TOF has been calculated based on the oxygen amount (in mmol) produced in the first 30 min of the reaction and divided by the amount of manganese of the catalyst (in mol).

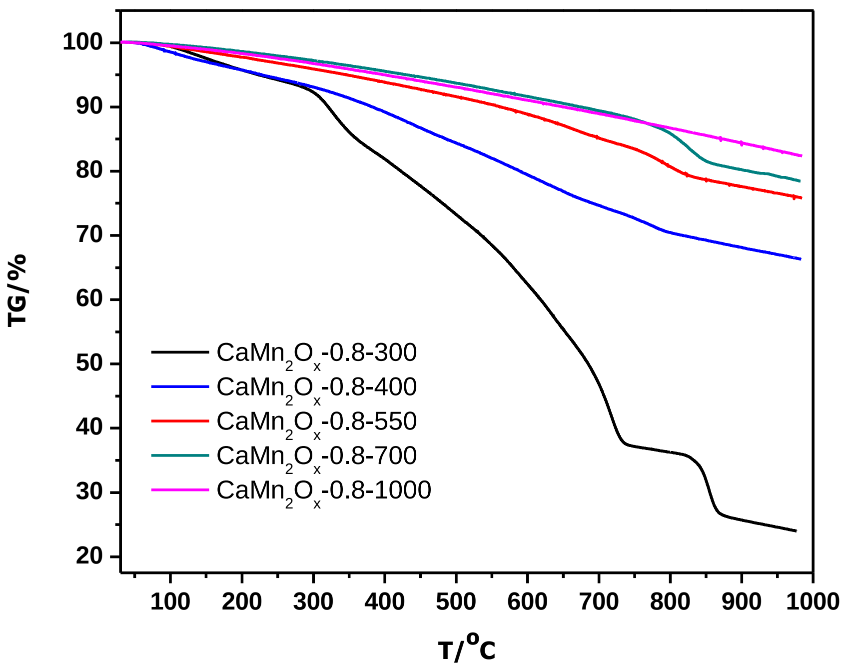


Figure S1. TGA curves for the thermal decomposition of calcium manganese oxides (measurements were carried out on a STA6000 from Perkin-Elmer in ambient condition at a temperature range of 30-1000 $^{\circ}$C with the heating rate of 10 $^{\circ}$C/min.)

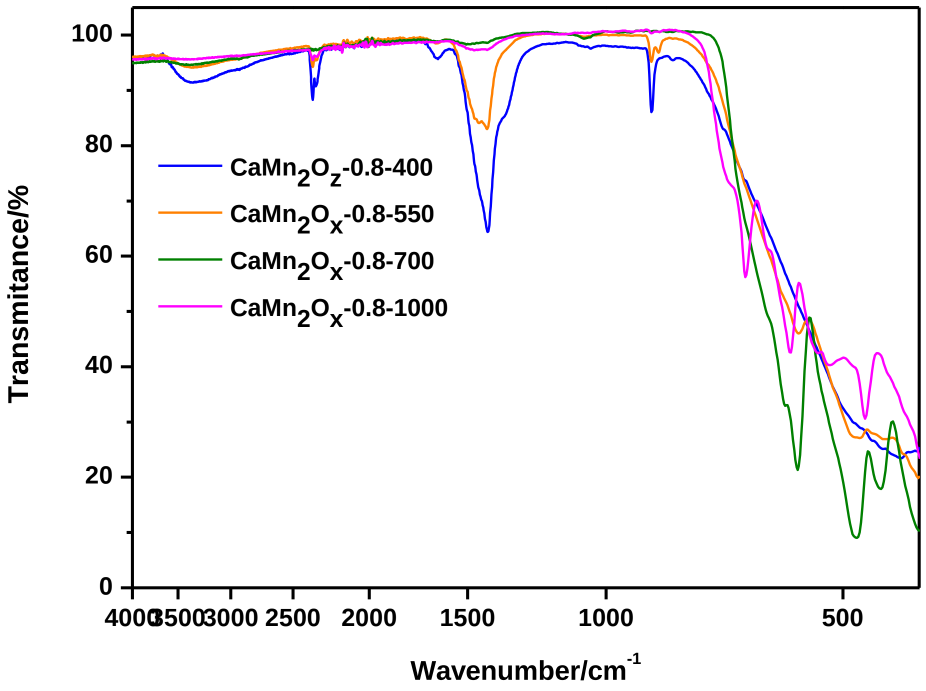


Figure S2. IR spectra of CaMn oxides calcined at 400 $^{\circ}$C, 550 $^{\circ}$C, 700 $^{\circ}$C and 1000 $^{\circ}$C.

Table S1. ICP data of $CaMn_2O_x$-samples

| Sample | %Mn(w) | %Ca(w) |
|---|---|---|
| $CaMn_2O_x$-0.8-300 | 27.64 | 11.27 |
| $CaMn_2O_x$-0.8-400 | 40.71 | 14.75 |
| $CaMn_2O_x$-0.8-550 | 50.40 | 18.00 |
| $CaMn_2O_x$-4-550 | 52.35 | 18.63 |
| $CaMn_2O_x$-8-550 | 54.30 | 18.77 |
| $CaMn_2O_x$-0.8-700 | 41.82 | 21.95 |

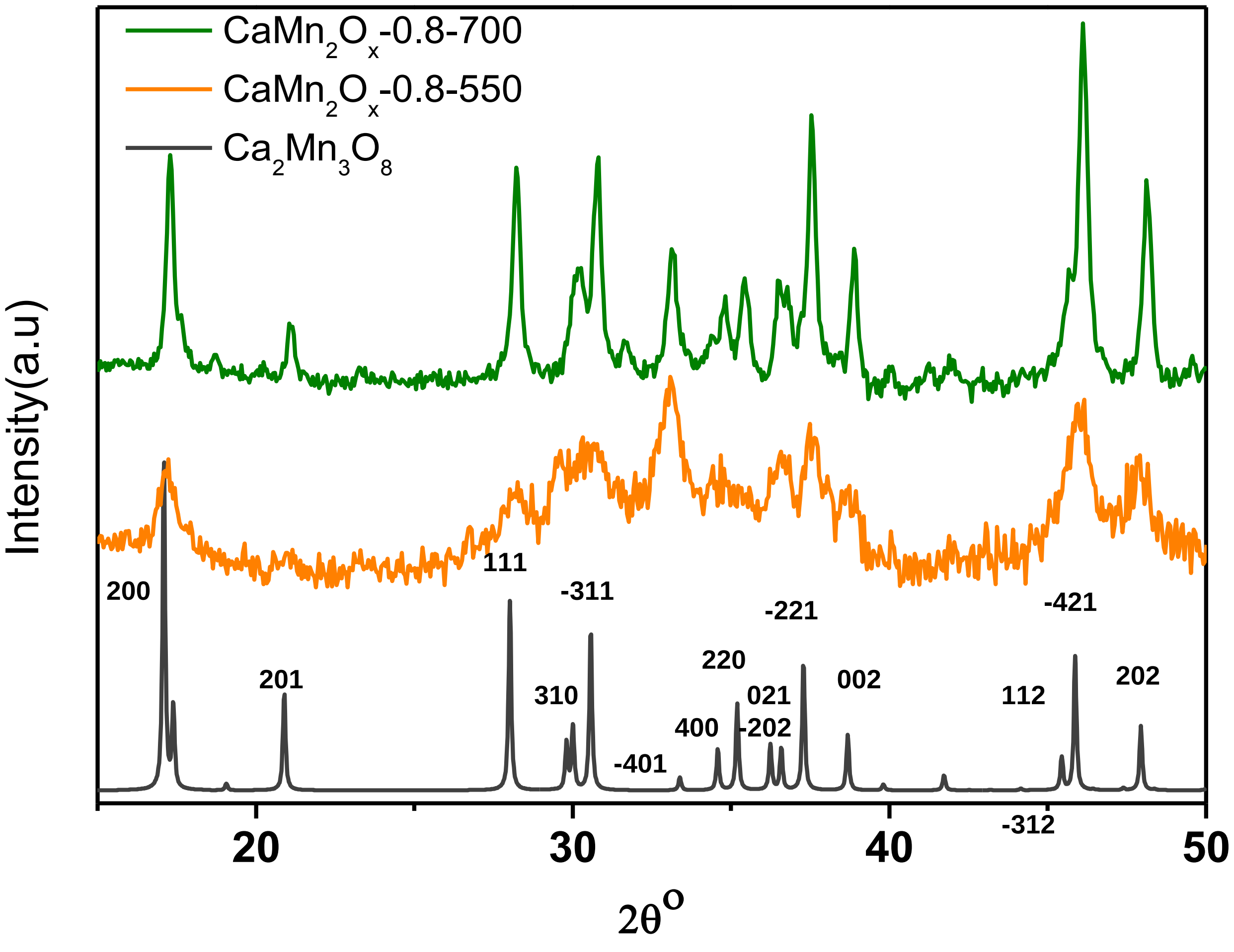


Figure S3. XRD patterns of oxides $CaMn_2O_x$-0.8-550, $CaMn_2O_x$-0.8-700 and $Ca_2Mn_3O_8$.

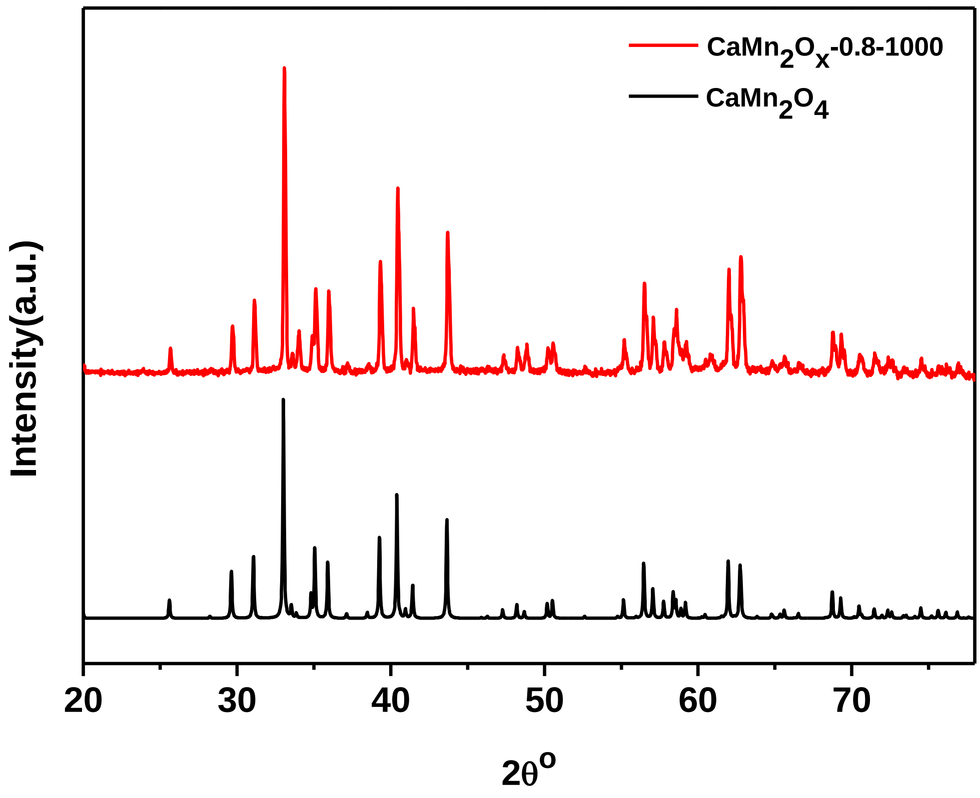
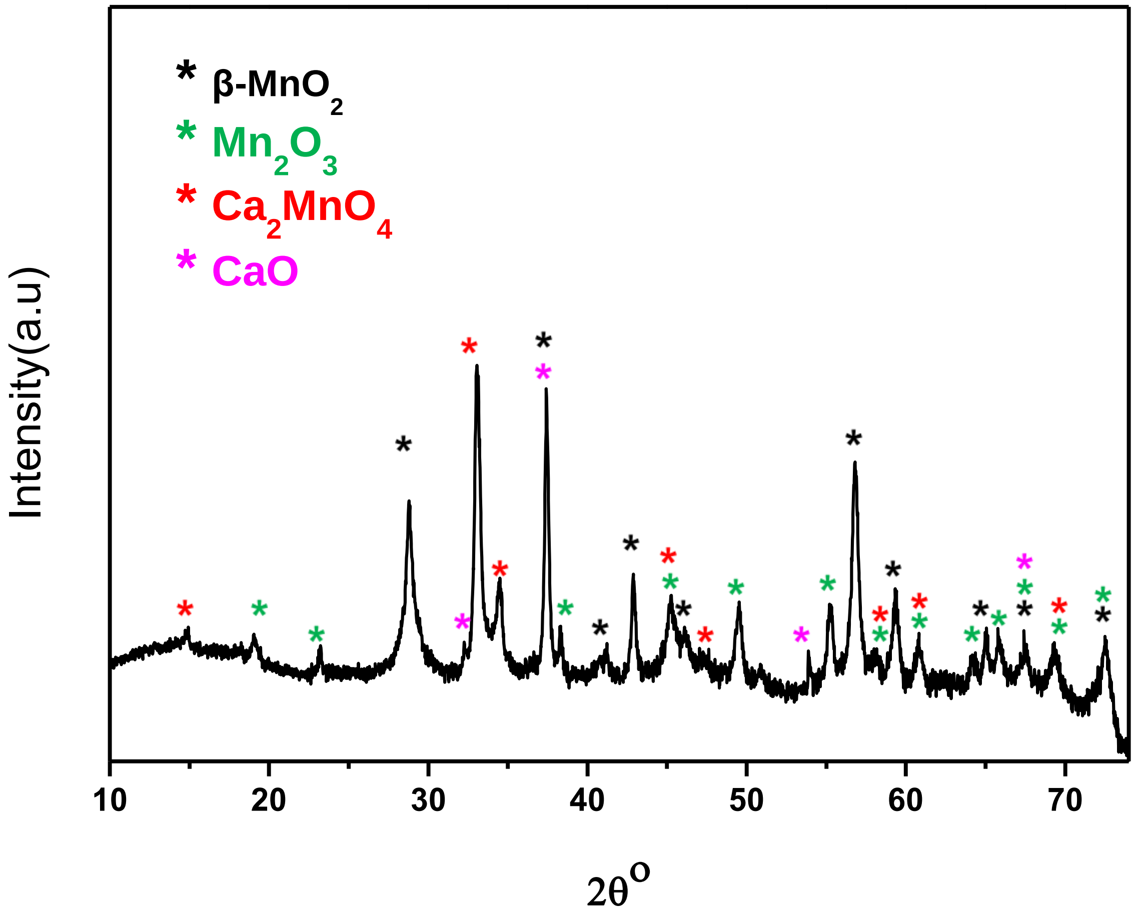


Figure S4. XRD patterns of $CaMn_2O_x$-0.8-1000 and $CaMn_2O_4$, for comparison.



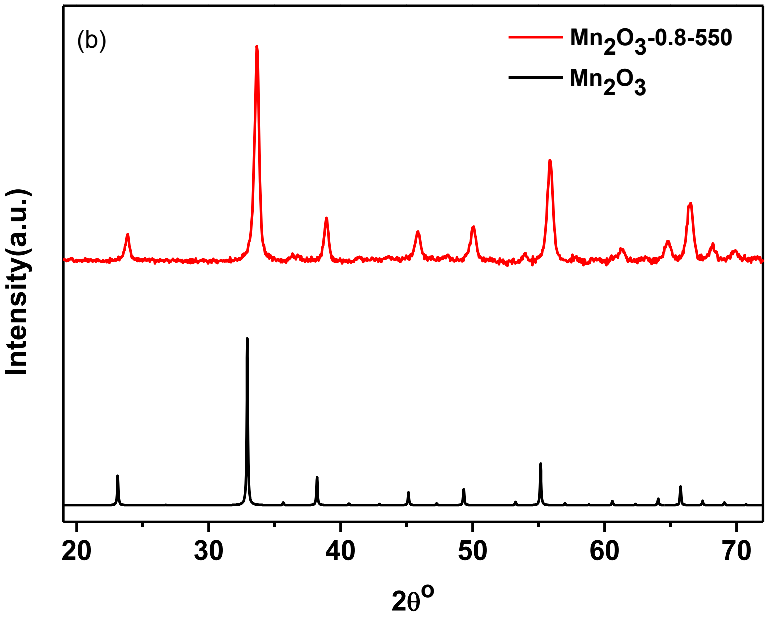


Figure S5. XRD patterns of a) CaMn$_2$O$_x$-0-550 and b) Mn$_2$O$_3$-0.8-550. In a), the stars label reflections that are found in crystalline calcium and manganese oxides at similar diffraction angles. We note that this assignment does not necessarily mean that there is a phase separation involving four distinct oxide phases. For amorphous materials, the XRD pattern reflects the pair distribution function (as obtained by appropriate Fourier-transformation of the XRD pattern); a single amorphous phase may be characterized by reflections of several parent structures. In b), the reflection pattern of Mn$_2$O$_3$ is shown for comparison.

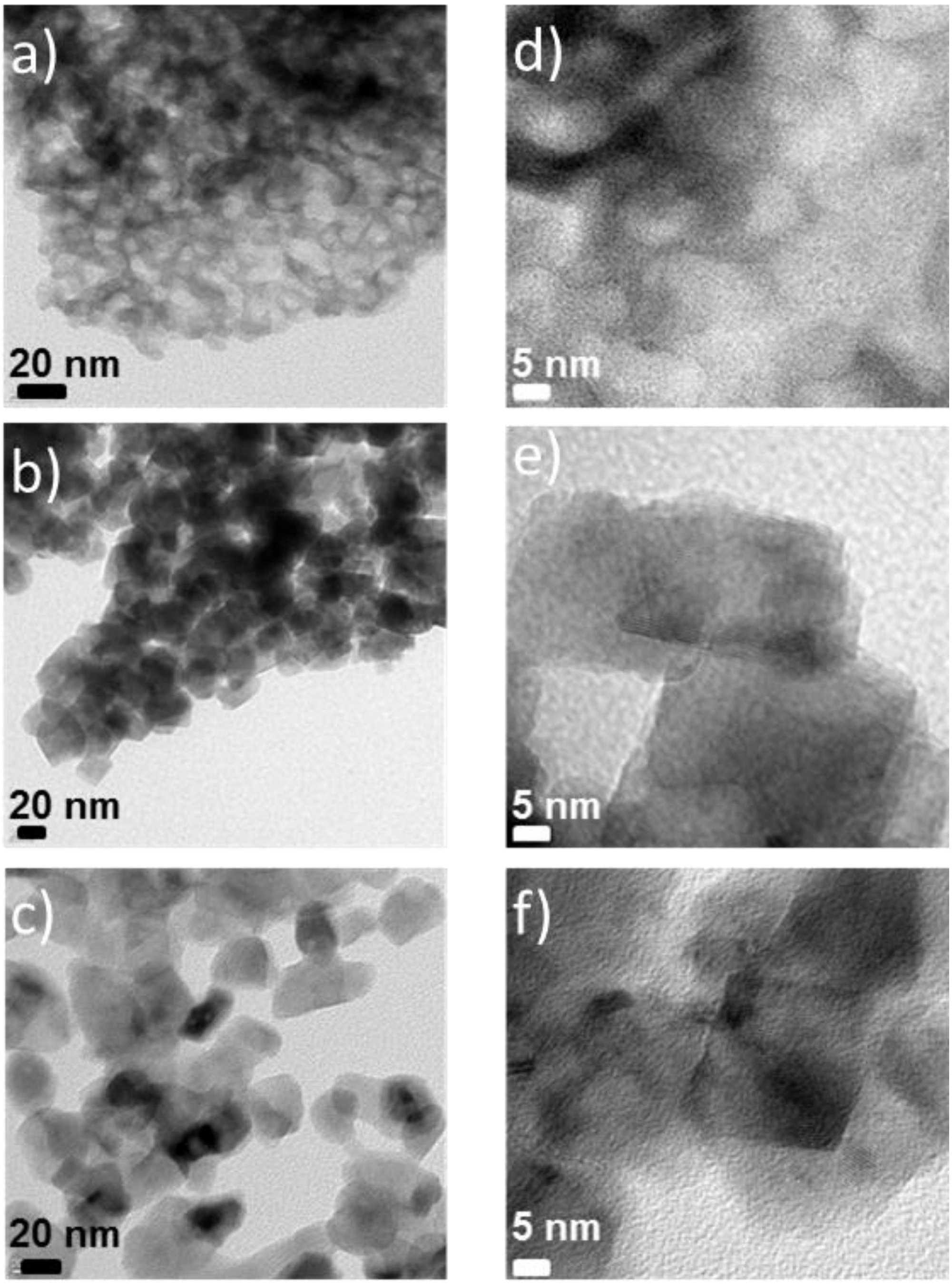


Figure S6. TEM images of a) $CaMn_2O_x$-0.8-550, b) $CaMn_2O_x$-4-550, c) $CaMn_2O_x$-8-550 and (HR)TEM images of d) $CaMn_2O_x$-0.8-550, e) $CaMn_2O_x$-4-550, f) $CaMn_2O_x$-8-550.

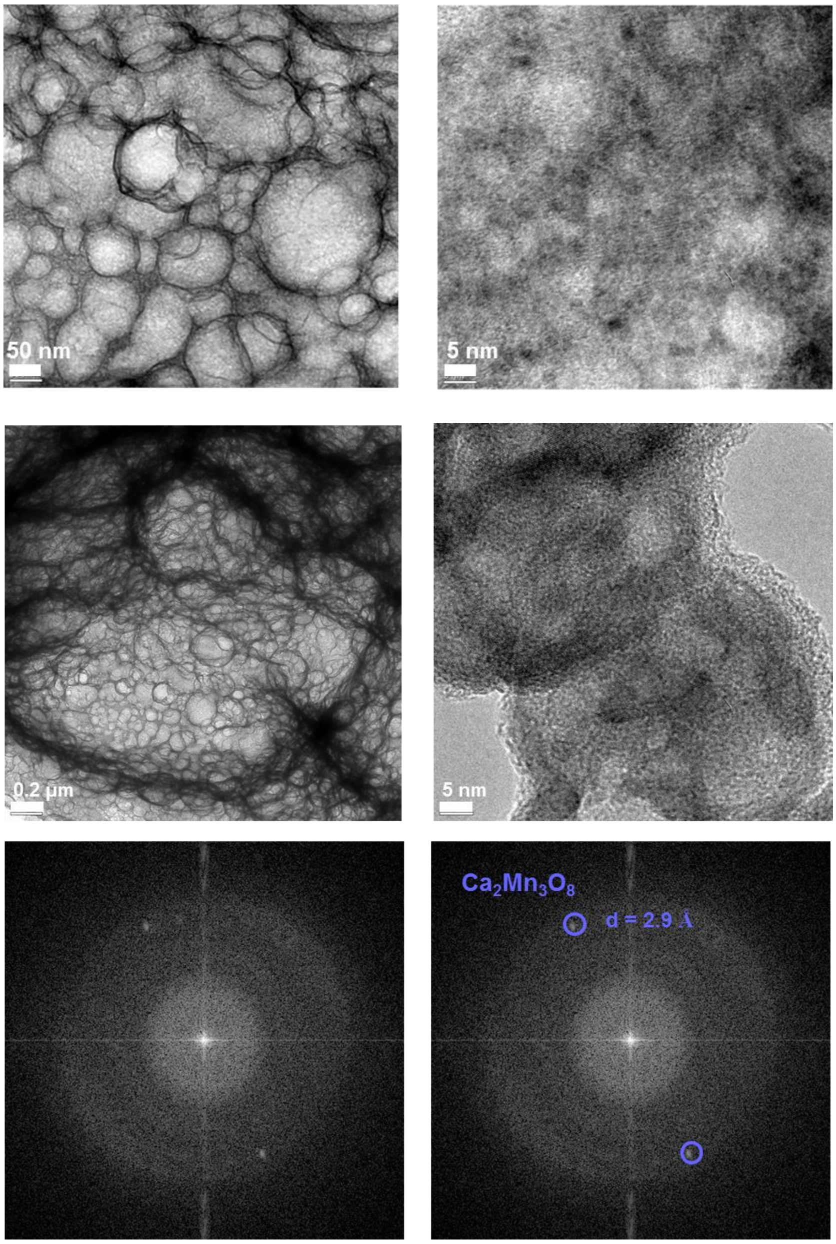


Figure S7. (HR)TEM images and FFTs of $CaMn_2O_x$-0.8-400 which shows d-values corresponding to $Ca_2Mn_3O_8$ (hkl=-311).

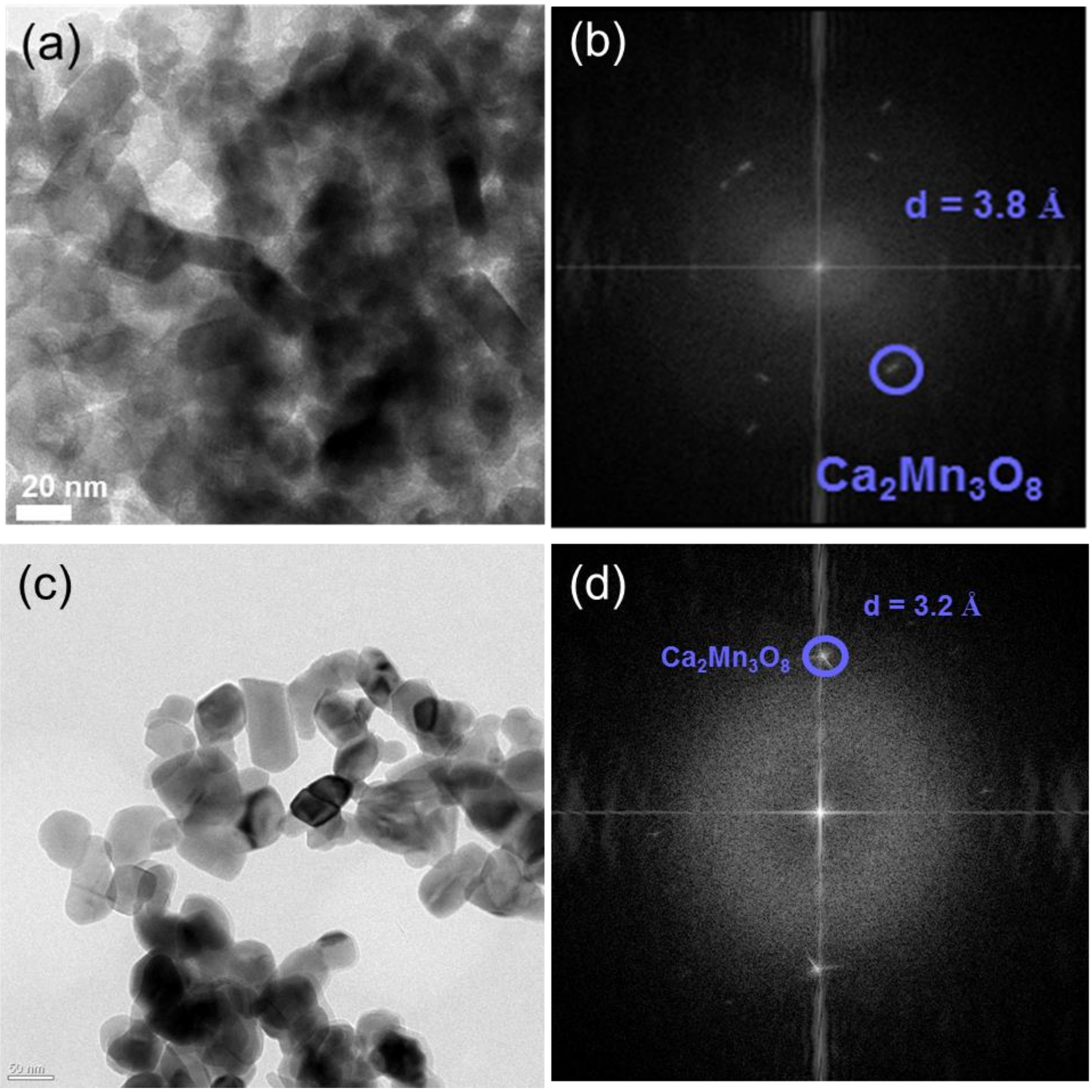


Figure S8. TEM images and FFTs of a,b) $CaMn_2O_x$-0.8-550 which shows d-values corresponding to $Ca_2Mn_3O_8$ (hkl=-111) and c,d) $CaMn_2O_x$-0.8-700 with d-values corresponding to $Ca_2Mn_3O_8$ (hkl=111).

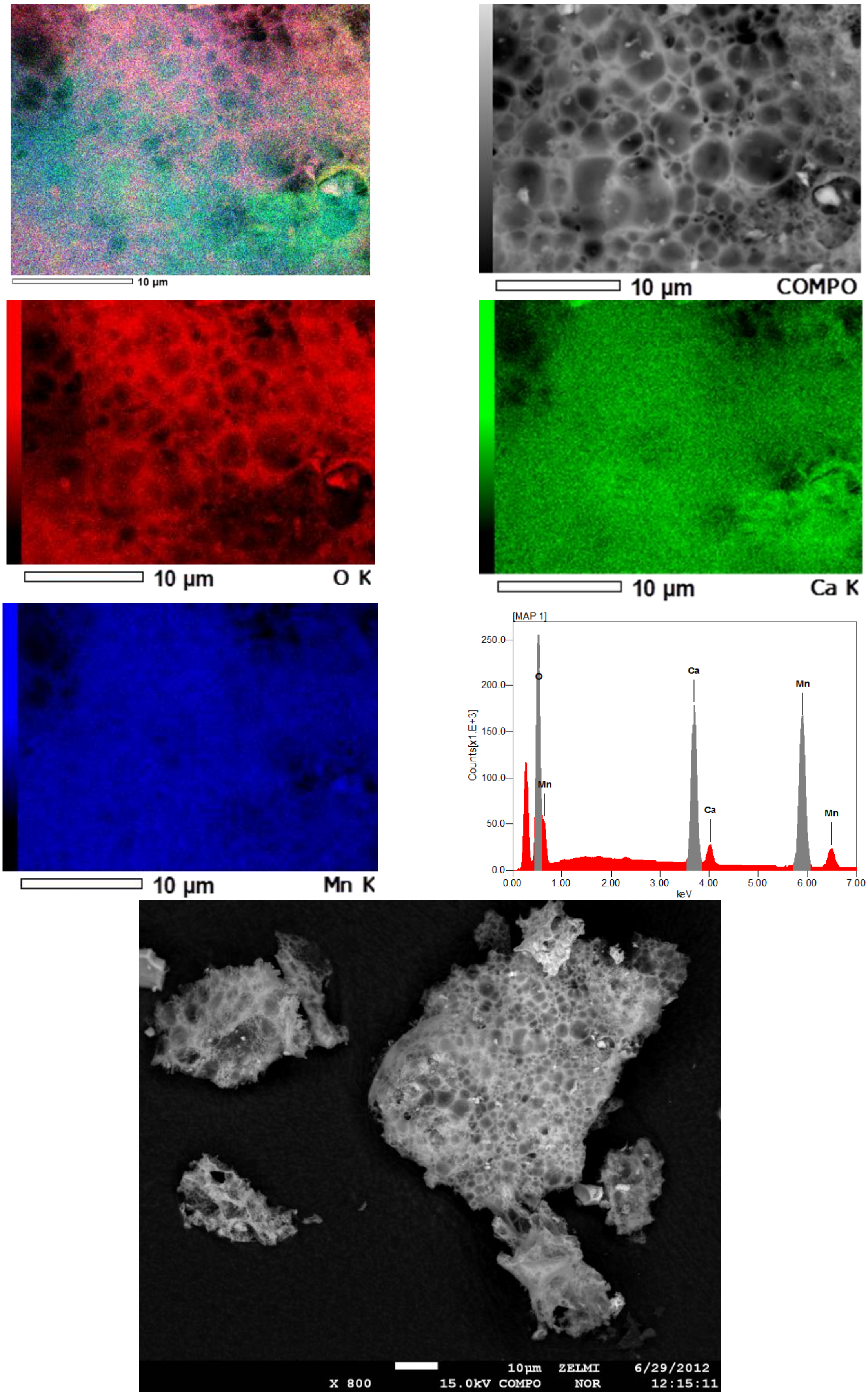


Figure S9. SEM image and EDS-mapping of $CaMn_2O_x$-0.8-400.

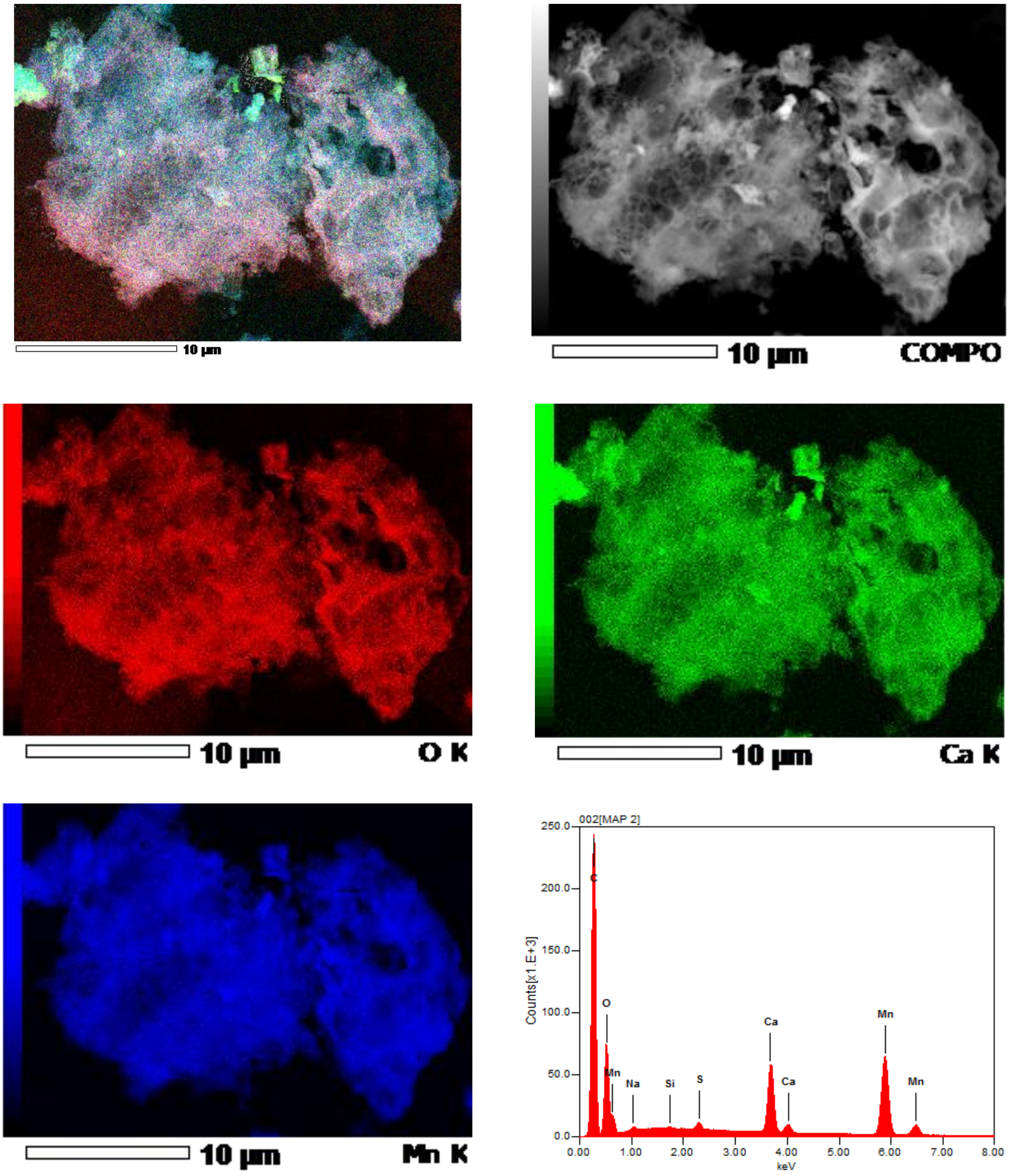


Figure S10. SEM image and EDS-mapping images of o $CaMn_2O_x$-0.8-550.

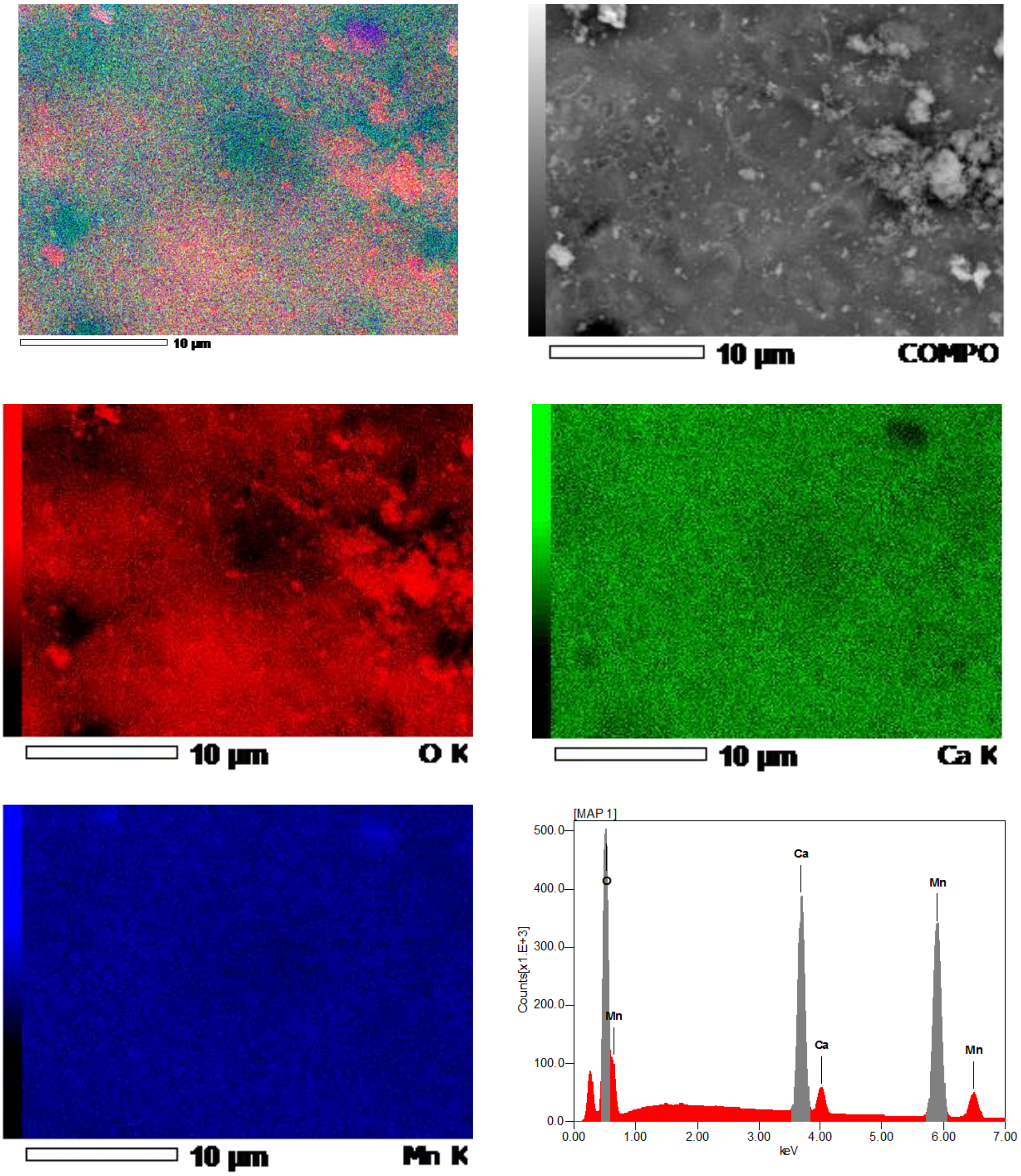


Figure S11. SEM image and EDS-mapping images of $CaMn_2O_x$-0.8-700.

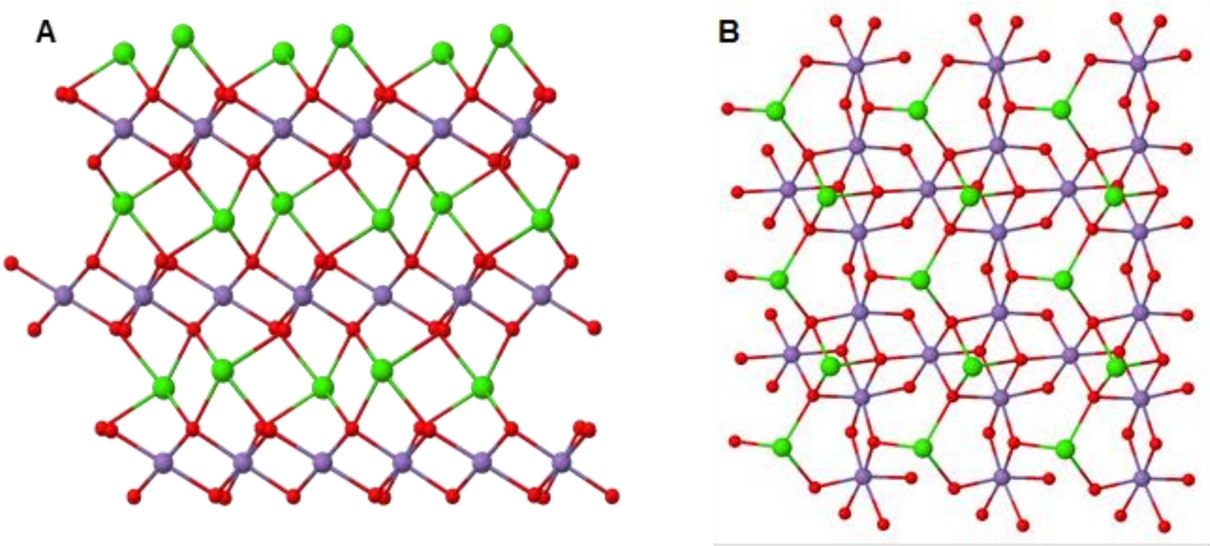


Figure S12. Structure of $Ca_2Mn_3O_8$. A – side view in which the $MnO_6$ layers of edge-sharing octahedral and the Ca ions connecting $MnO_6$ layers are visible. B – top view illustrating the two binding positions of Ca: (i) on the top of Mn vacancies (3.7 Å Mn-Ca distance) and in a cubane motif (3.3 Å Mn-Ca distance). Mn atoms are shown in magenta, Ca in green, and O in red.

Table S2. Oxygen evolution data from refs.[2,3] and as determined in the present investigation.

| Sample | Rate (mmol $O_2$.mol $Mn^{-1}$. $s^{-1}$) |
|---|---|
| $CaMn_2O_x$-8-550 | 0,14 |
| $CaMn_2O_x$-4-550 | 0,219 |
| $CaMn_2O_x$-0.8-550 | 0,62 |
| $CaMn_2O_x$-0-550 | 0,029 |
| $CaMn_2O_x$-0.8-300 | 0,011 |
| $CaMn_2O_x$-0.8-400 | 3/2.7[a] |
| $CaMn_2O_x$-0.8-700 | 0,082 |
| $CaMn_2O_x$-0.8-100 | 0,018 |
| $Mn_2O_3$-0.8-550 | 0,101 |
| α-$Mn_2O_3$ [1] | 0,027 |
| $CaMn_2O_4.4H_2O$(2)[1] | 0,325 |
| $CaMn_2O_4.H_2O$(3)[1] | 0,54 |
| $CaMn_2O_4.4H_2O$(5)[1] | 0,29 |
| $Ca_{0.14}$-birnessite[2] | 0,311 |
| $Ca_{0.27}$- birnessite [2] | 0,239 |

[a] TOFs calculated from 0.05 mg/ml catalyst after 3 min and of 0.5 mg/ml catalyst after 15 s are shown. To determine the reaction rate after 3 min a lower amount of $CaMn_2O_x$-0.8-400 had to be used, as with a concentration of 0.5 mg/ml the oxygen evolution reached the detection limit of the Clark electrode already after 30 seconds.

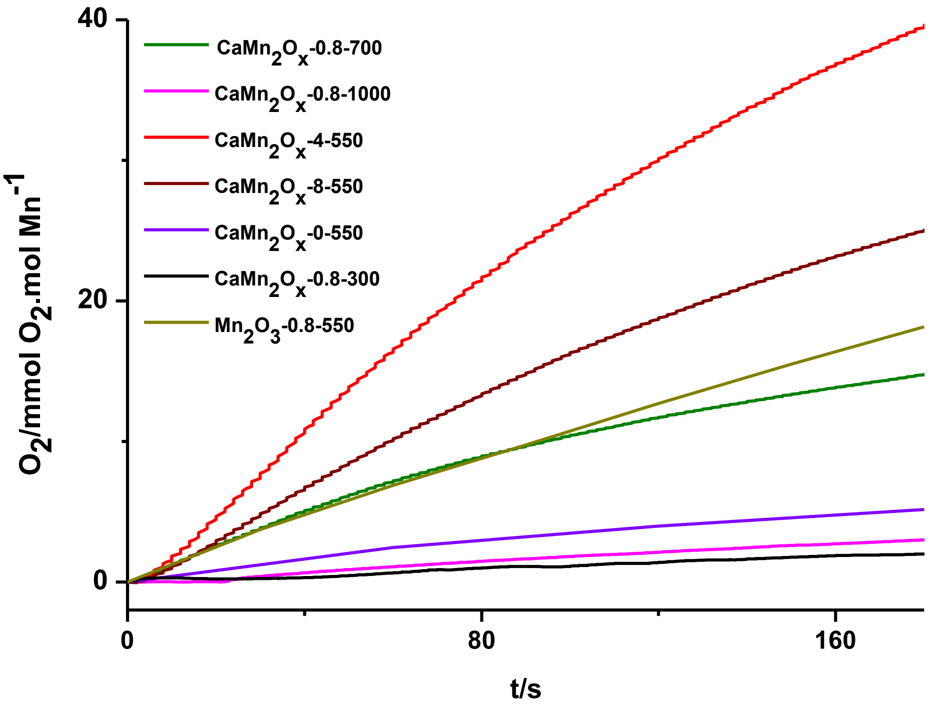


Figure S13. Oxygen evolution results for the reaction of CaMn oxides suspended in 0.5 M aqueous solution of $Ce^{4+}$.

Table S3: Amount of dissolved oxides (mg/ml) in solution (0.5M Ce(IV)).

| Sample | Oxide amount(mg/ml) |
|---|---|
| $CaMn_2O_x$-0.8-300 | 0.5 |
| $CaMn_2O_x$-0.8-400 | 0.05/0.5[a] |
| $CaMn_2O_x$-0.8-550 | 0.5 |
| $CaMn_2O_x$-0.8-700 | 0.5 |
| $CaMn_2O_x$-0.8-1000 | 0.5 |
| $CaMn_2O_x$-8-550 | 0.5 |
| $CaMn_2O_x$-4-550 | 0.5 |
| $CaMn_2O_x$-0-550 | 0.5 |
| $Mn_2O_3$-0.8-550 | 0.45 |

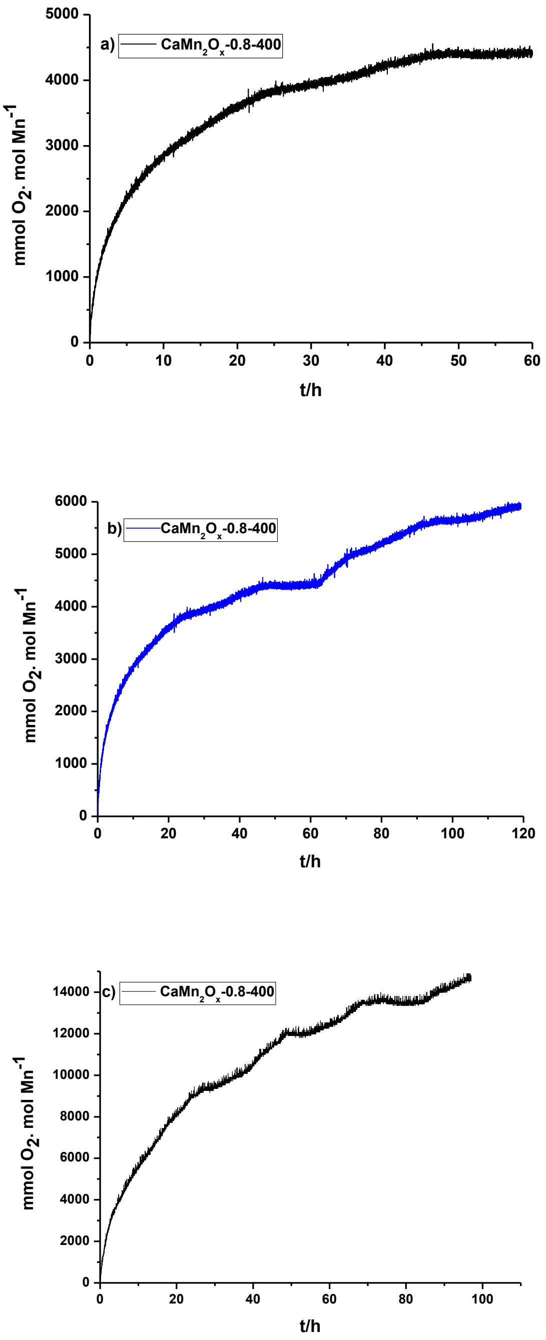
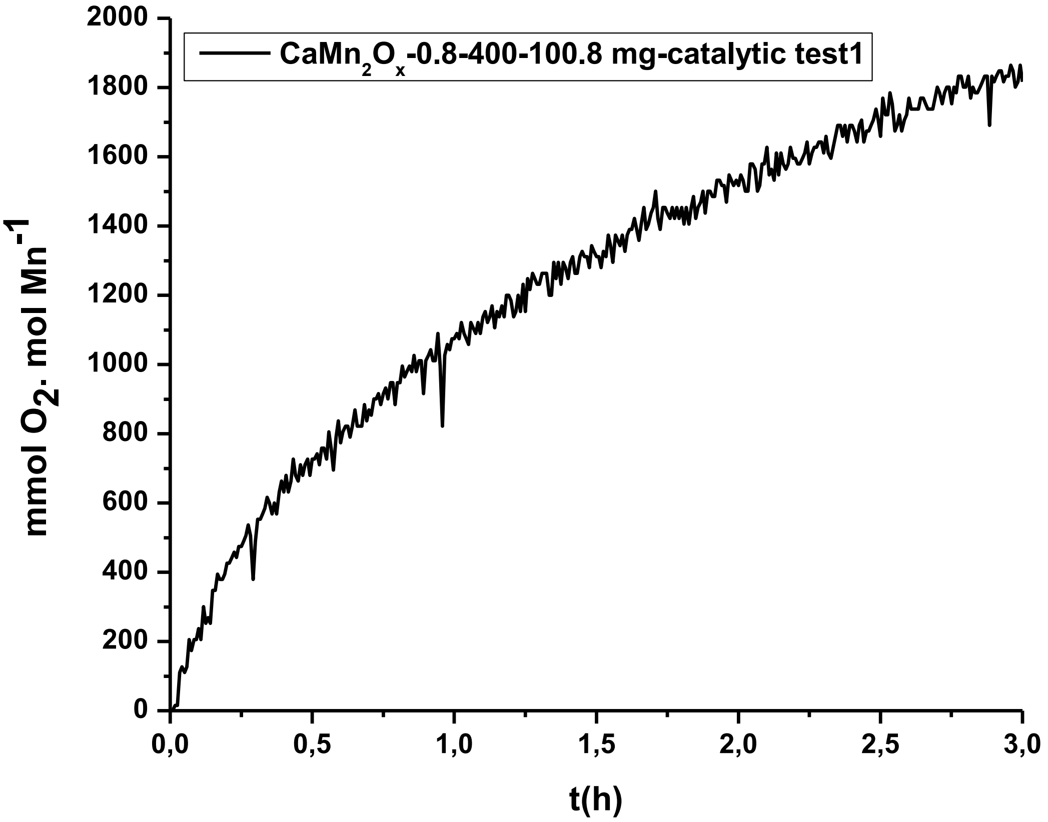
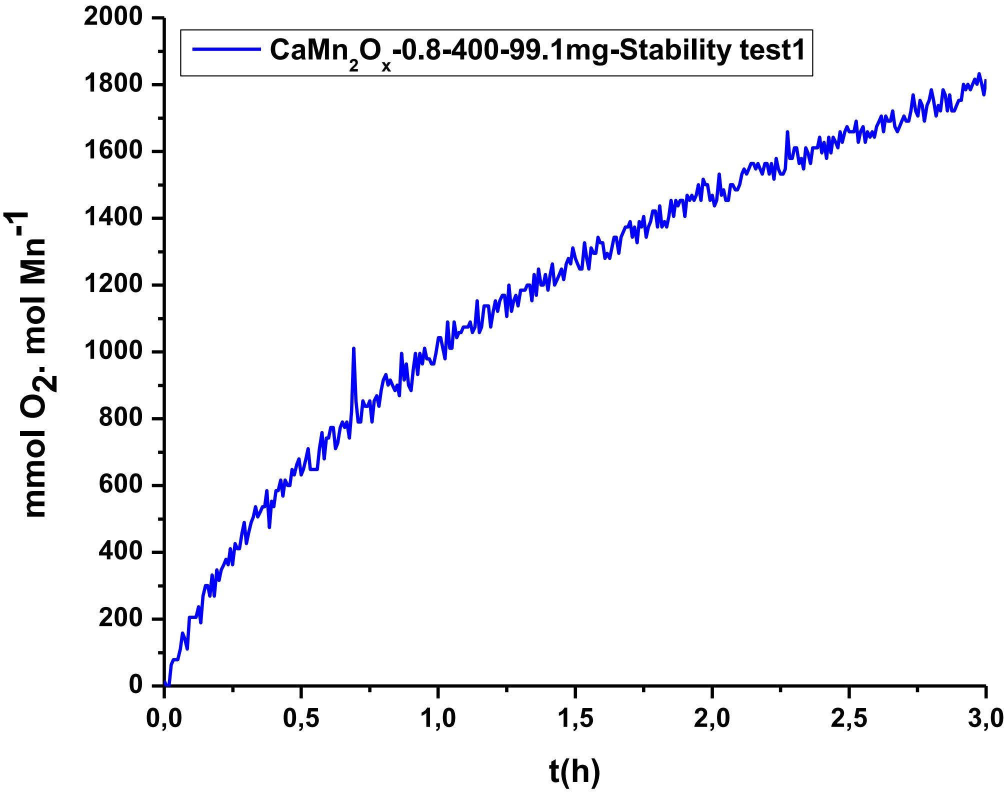


Figure S14: a) Long-term oxygen evolution test (100 mg catalyst in 38 ml of 0.5M Ce(IV) solution) by gas chromatography. The oxygen evolution rate is continuously decreasing likely because the oxidant, Ce(IV), is consumed. Nonetheless, oxygen evolution is detectable for more than two days. b) Regaining the activity after injection of 12 ml fresh Ce(IV) solution. Slower rate observed due to lower concentration of Ce(IV) in solution (0.12 M) after injection. c) Catalytic activity test with less amount of catalyst (20 mg in 38 ml of 0.5 M Ce(IV) solution.)


CaMn$_2$O$_x$-0.8-400-100.8 mg-catalytic test1
mmol O$_2$. mol Mn$^{-1}$
0
200
400
600
800
1000
1200
1400
1600
1800
2000
0,0
0,5
1,0
1,5
2,0
2,5
3,0
t(h)


CaMn$_2$O$_x$-0.8-400-99.1mg-Stability test1
mmol O$_2$. mol Mn$^{-1}$
0
200
400
600
800
1000
1200
1400
1600
1800
2000
0,0
0,5
1,0
1,5
2,0
2,5
3,0
t(h)

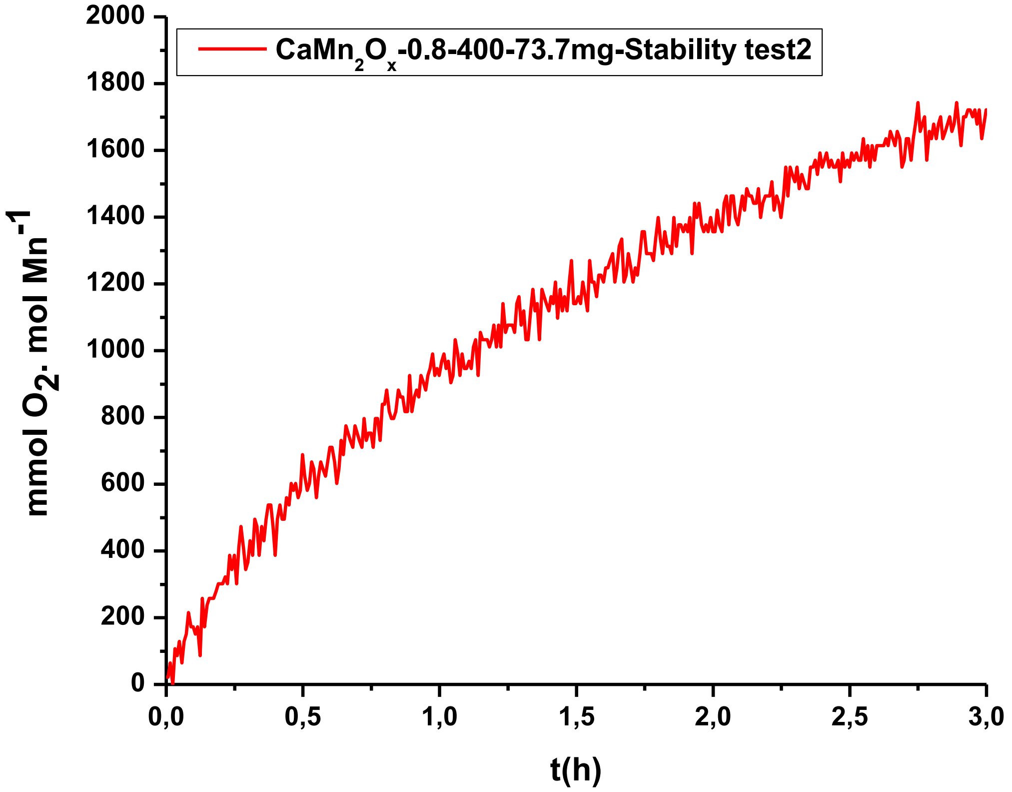


Figure S15: Recycling experiments using $CaMn_2O_x$-0.8-400; Black) first run, blue) second and red) third run. After each run the catalyst was recovered by filtration, washed several times with water, dried and then used again.

Table S4: Catalytic test results from gas chromatography (in 0.5 M Ce(IV)) for repeated addition of Ce(IV) (0.5 M Ce(IV) per run.

The TOF has been calculated based on the oxygen amount (in mmol) produced in the first 30 min of the reaction and divided by the amount of manganese of the catalyst (in mol).

| Test | T ($^{o}$C) | Cat amount (mg) | TOF (mmol$O_2$.molMn.$s^{-1}$) |
|---|---|---|---|
| Long-term | 23 | 100.8 | 0.42 |
| Run 1 | 24.2 | 100.8 | 0.40 |
| Run2 | 25 | 99.1 | 0.35 |
| Run3 | 25 | 73.7 | 0.35 |

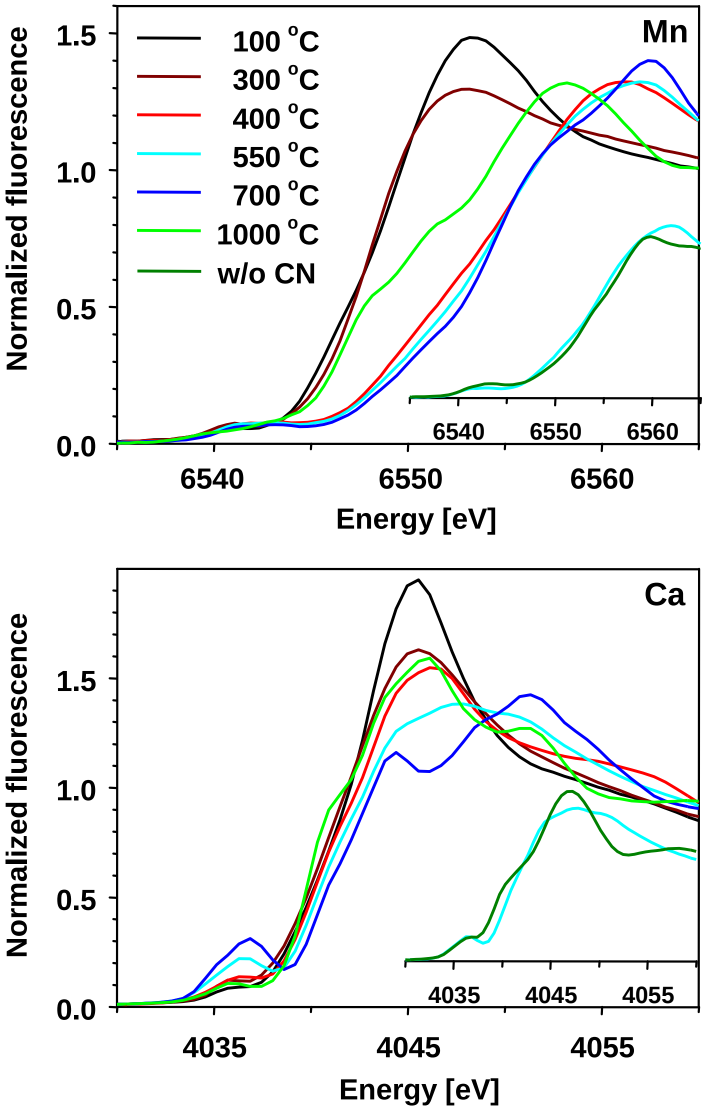


Figure S16. XANES spectra measured at the Mn *K*-edge (top) and the Ca *K*-edge (bottom) from the CaMn material before annealing (labeled '100 °C') and after annealing for 4 h at the indicated temperature. Insets: comparison of the XANES spectra from CaMn oxide with and without cyanamide, annealed at 550 °C.

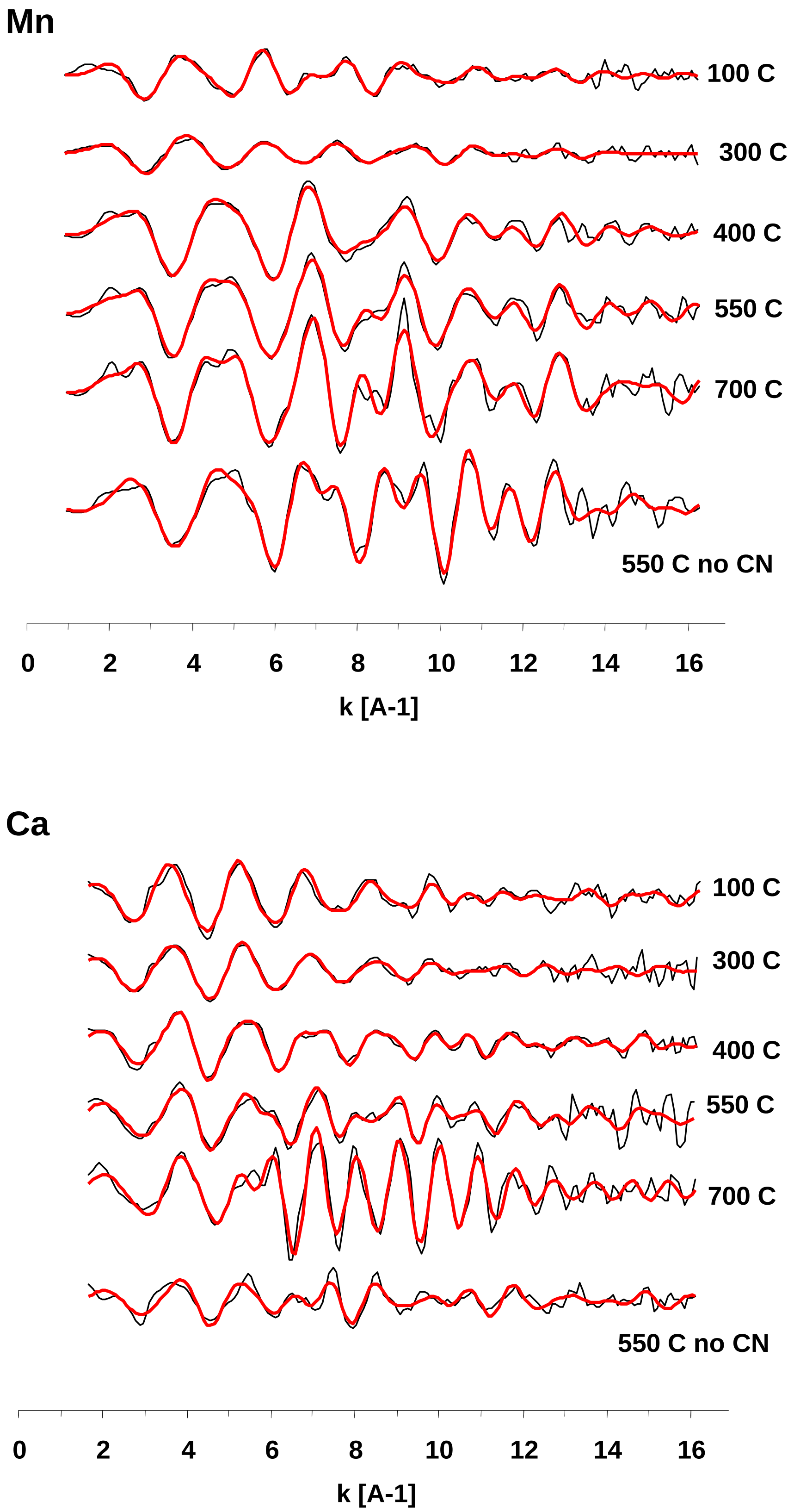


Figure S17. $k^3$-weighted EXAFS spectra measured at the Mn *K*-edge (top) and the Ca *K*-edge (bottom) from the CaMn material before annealing (labeld '100 °C') and after annealing for 4 h at the indicated temperature. Black: experimental curves, red - simulations. The simulation parameters are shown in Table S1.

Table S5. EXAFS simulation parameters and 1σ uncertainty ranges in the EXAFS fit parameters. Parameters marked by * were constrained. All Mn-Ca distances were constrained to be equal in the Mn and Ca spectra, e.g., equal Mn-Ca distances in the Mn-EXAFS and the Ca-EXAFS (joint-fit approach). For simulation of the first manganese coordination sphere, two shells of backscattering atoms were used and the sum of the two coordination numbers was constrained to be equal to six. In the two-shell simulation of the first Ca and Mn coordination sphere, the values of the Debye-Waller parameter (denoted as σ or s) were constrained to be equal.

| | N | | R, A | | s, A | | N | | R, A | | s, A | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Mn-O** | | | | | | **Ca-O** | | | | | |
| **100 oC** | 0.9 ± | 0.2 | 1.91 ± | 0.026 | 0.09 ± | 0.005 | 3.4 ± | 0.2 | 2.36 ± | 0.006 | 0.05 ± | 0.005 |
| **300 oC** | 1.4 ± | 0.1 | 1.90 ± | 0.009 | 0.09 ± | 0.003 | 2.0 ± | 0.2 | 2.30 ± | 0.011 | 0.07 ± | 0.007 |
| **400 oC** | 5.5 ± | 0.1 | 1.88 ± | 0.00 | 0.08 ± | 0.00 | 3.7 ± | 0.4 | 2.35 ± | 0.01 | 0.06 ± | 0.01 |
| **550 oC** | 5.4 ± | 0.2 | 1.89 ± | 0.00 | 0.07 ± | 0.00 | 3.4 ± | 0.3 | 2.33 ± | 0.01 | 0.05 ± | 0.01 |
| **700 oC** | 5.5 ± | 0.2 | 1.89 ± | 0.00 | 0.06 ± | 0.00 | 3.0 ± | 1.1 | 2.28 ± | 0.03 | 0.08 ± | 0.02 |
| **550 oC no CN** | 5.2 ± | 0.2 | 1.89 ± | 0.00 | 0.06 ± | 0.00 | 2.6 ± | 0.3 | 2.37 ± | 0.01 | 0.0632* ± | 0.00 |
| | | | | | | | | | | | | |
| | **Mn-O** | | | | | | **Ca-O** | | | | | |
| **100 oC** | 5.14* ± | 0.0 | 2.17 ± | 0.01 | 0.0911* ± | 0.00 | 3.8 ± | 0.3 | 2.50 ± | 0.006 | 0.0541* ± | 0.00 |
| **300 oC** | 4.61* ± | 0.0 | 2.15 ± | 0.01 | 0.0933* ± | 0.00 | 3.9 ± | 0.4 | 2.44 ± | 0.01 | 0.0698* ± | 0.00 |
| **400 oC** | 0.52* ± | 0.0 | 2.29 ± | 0.04 | 0.0797* ± | 0.00 | 2.1 ± | 0.2 | 2.48 ± | 0.01 | 0.0622* ± | 0.00 |
| **550 oC** | 0.641* ± | 0.0 | 2.29 ± | 0.03 | 0.0732* ± | 0.00 | 1.8 ± | 0.2 | 2.48 ± | 0.01 | 0.0548* ± | 0.00 |
| **700 oC** | 0.529* ± | 0.0 | 2.31 ± | 0.04 | 0.0605* ± | 0.00 | 3.0 ± | 1.0 | 2.39 ± | 0.03 | 0.0818* ± | 0.00 |
| **550 oC no CN** | 0.849* ± | 0.0 | 2.21 ± | 0.02 | 0.0624* ± | 0.00 | 1.4 ± | 0.3 | 2.55 ± | 0.02 | 0.0632* ± | 0.00 |
| | | | | | | | | | | | | |
| | **Mn-Mn** | | | | | | **Ca-Ca** | | | | | |
| **100 oC** | 0.3 ± | 0.1 | 2.90 ± | 0.026 | 0.0632* ± | 0.00 | 1.3 ± | 0.3 | 4.41 ± | 0.013 | 0.0632* ± | 0.00 |
| **300 oC** | 0.2 ± | 0.1 | 2.87 ± | 0.02 | 0.0632* ± | 0.00 | 0.8 ± | 0.6 | 3.61 ± | 0.08 | 0.0632* ± | 0.00 |
| **400 oC** | 1.5 ± | 0.1 | 2.87 ± | 0.00 | 0.0632* ± | 0.00 | 2.4 ± | 0.3 | 4.08 ± | 0.01 | 0.0632* ± | 0.00 |
| **550 oC** | 1.8 ± | 0.1 | 2.87 ± | 0.00 | 0.0632* ± | 0.00 | 1.1 ± | 0.4 | 4.76 ± | 0.02 | 0.0632* ± | 0.00 |
| **700 oC** | 2.7 ± | 0.3 | 2.88 ± | 0.00 | 0.0620 ± | 0.00 | 2.9 ± | 0.6 | 3.46 ± | 0.01 | 0.0632* ± | 0.00 |
| **550 oC no CN** | 1.3 ± | 0.2 | 2.87 ± | 0.01 | 0.0632* ± | 0.00 | 1.3 ± | 0.3 | 4.07 ± | 0.02 | 0.0632* ± | 0.00 |
| | | | | | | | | | | | | |
| | **Mn-O/C/Mn** | | | | | | **Ca-O/C** | | | | | |
| **100 oC** | 3.9 ± | 1.0 | 3.22 ± | 0.03 | 0.0632* ± | 0.00 | 3.1 ± | 1.1 | 3.73 ± | 0.02 | 0.0632* ± | 0.00 |
| **300 oC** | 1.9 ± | 0.4 | 3.11 ± | 0.02 | 0.0632* ± | 0.00 | 5.2 ± | 1.2 | 3.73 ± | 0.03 | 0.0632* ± | 0.00 |
| **400 oC** | 3.4 ± | 1.0 | 3.52 ± | 0.02 | 0.0632* ± | 0.00 | 1.4 ± | 0.7 | 3.66 ± | 0.03 | 0.0387* ± | 0.00 |
| **550 oC** | 6.8 ± | 2.3 | 3.487* ± | 0.00 | 0.0387* ± | 0.00 | 3.37 ± | 0.9 | 3.707 ± | 0.044 | 0.0632* ± | 0.00 |
| **700 oC** | 6.0 ± | 0.0 | 3.58 ± | 0.01 | 0.0632* ± | 0.00 | 4.6 ± | 1.6 | 3.69 ± | 0.05 | 0.0632* ± | 0.00 |
| **550 oC no CN** | 3.9 ± | 0.3 | 3.43 ± | 0.00 | 0.0632* ± | 0.00 | | | | | | |
| | | | | | | | | | | | | |
| | **Mn-Ca** | | | | | | **Ca-Mn** | | | | | |
| **400 oC** | 0.2 ± | 0.2 | 3.17 ± | 0.01 | 0.0632* ± | 0.00 | 0.4 ± | 0.1 | 3.166* ± | 0.00 | 0.0632* ± | 0.00 |
| **550 oC** | 2.8 ± | 0.8 | 3.24 ± | 0.01 | 0.0632* ± | 0.00 | 0.3 ± | 0.2 | 3.239* ± | 0.00 | 0.0632* ± | 0.00 |
| **700 oC** | 0.2 ± | 0.3 | 3.31 ± | 0.01 | 0.0632* ± | 0.00 | 1.6 ± | 0.4 | 3.313* ± | 0.00 | 0.0632* ± | 0.00 |
| **550 oC no CN** | 2.6 ± | 0.3 | 3.18 ± | 0.01 | 0.0632* ± | 0.00 | 1.1 ± | 0.2 | 3.18* ± | 0.00 | 0.0632* ± | 0.00 |
| | | | | | | | | | | | | |
| | **Mn-Mn** | | | | | | **Ca-Ca** | | | | | |
| **100 oC** | 1.4 ± | 0.3 | 3.35 ± | 0.01 | 0.0632* ± | 0.00 | 0.6 ± | 0.2 | 3.549 ± | 0.02 | 0.0632* ± | 0.00 |
| **300 oC** | 0.3 ± | 0.1 | 3.38 ± | 0.02 | 0.0632* ± | 0.00 | 0.3 ± | 0.6 | 3.50 ± | 0.13 | 0.0632* ± | 0.00 |
| **400 oC** | 1.0 ± | 0.3 | 3.38 ± | 0.01 | 0.0632* ± | 0.00 | 0.4 ± | 0.3 | 3.53 ± | 0.03 | 0.0632* ± | 0.00 |
| **550 oC** | 4.0 ± | 1.4 | 3.36 ± | 0.01 | 0.0632* ± | 0.00 | 1.2 ± | 0.3 | 3.46 ± | 0.01 | 0.0632* ± | 0.00 |
| | | | | | | | | | | | | |
| | **Mn-Ca** | | | | | | **Ca-Mn** | | | | | |
| **400 oC** | 0.0 ± | 0.2 | 3.84 ± | 0.01 | 0.0632* ± | 0.00 | 1.0 ± | 0.3 | 3.84* ± | 0.00 | 0.0632* ± | 0.00 |
| **550 oC** | 2.0 ± | 0.5 | 3.68 ± | 0.01 | 0.0632* ± | 0.00 | 0.8 ± | 0.7 | 3.679* ± | 0.00 | 0.0632* ± | 0.00 |
| **700 oC** | 2.0 ± | 0.4 | 3.70 ± | 0.02 | 0.0632* ± | 0.00 | 3.4 ± | 0.7 | 3.701* ± | 0.00 | 0.0632* ± | 0.00 |
| | | | | | | | | | | | | |
| | | | | | | | **Ca-Ca** | | | | | |
| **400 oC** | | | | | | | 0.2 ± | 0.7 | 4.45 ± | 0.07 | 0.0632* ± | 0.00 |
| **550 oC** | | | | | | | 1.8 ± | 0.9 | 5.42 ± | 0.02 | 0.0632* ± | 0.00 |
| **700 oC** | | | | | | | 2.3 ± | 0.4 | 4.34 ± | 0.01 | 0.0632* ± | 0.00 |
| **550 oC no CN** | | | | | | | 0.2 ± | 0.4 | 4.48 ± | 0.12 | 0.0632* ± | 0.00 |

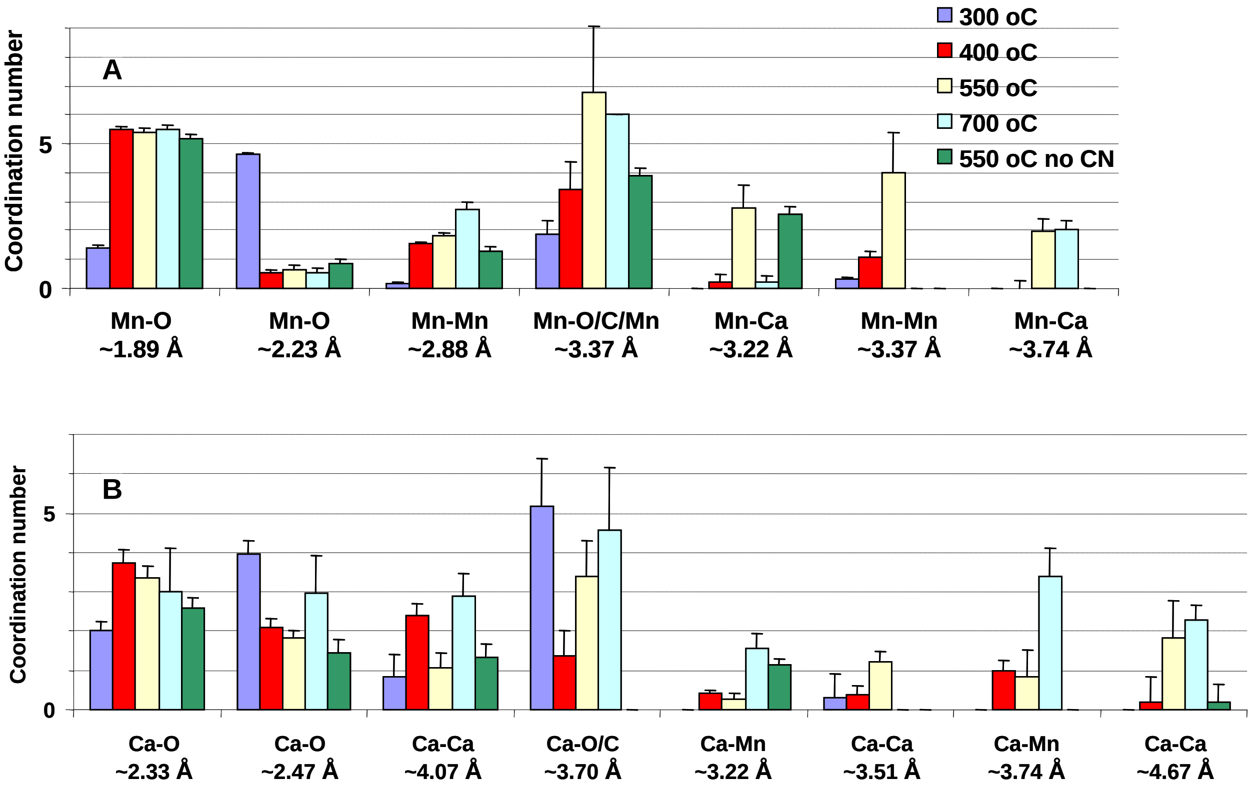


Figure S18. Graphical presentation of the coordination numbers from Table S5.
A, measurements at the Mn *K*-edge; B, at the Ca *K*-edge.

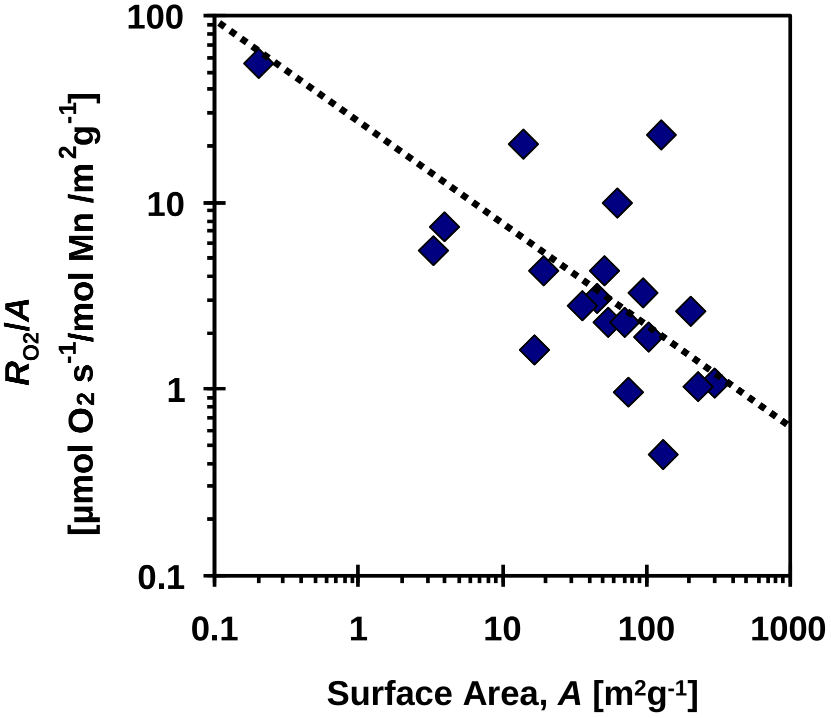


Figure S19. Rate of $O_2$-formation ($R_{O2}$) per surface area (*A*) derived from the values in Table S1. If $O_2$-rate were proportional to the surface area, $R_{O2}/A$ should be independent on the surface (A). Instead, a decreased activity per surface area by two orders of magnitude is observed meaning that the surface area is not the decisive determinant of the rate of catalysis (see dotted line drawn to guide the eye) (refs.[1,2] and this investigation).

**References**:

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