Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Electronic Supporting Information

Influence of particle size on the apparent electrocatalytic activity of $LiMn_2O_4$ for oxygen evolution

Max Baumung,[a] Florian Schönewald,[a] Torben Erichsen,[a] Cynthia A. Volkert,[a] Marcel Risch[a,*]

[a] Institute of Materials Physics, University of Goettingen, Friedrich-Hund-Platz 1, Goettingen, 37077, Germany
* mrisch@material.physik.uni-goettingen.de

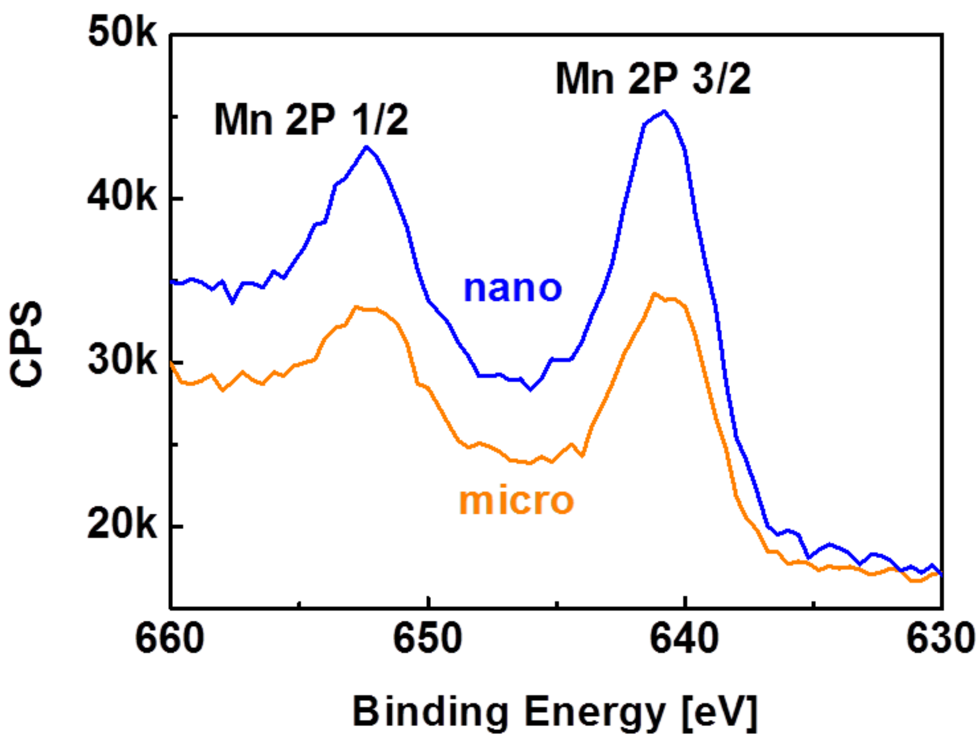

Fig S1 Mn2p XPS of nano and micro-sized particles. The spectra were recorded on a PHI 5000 VersaProbe II and energy calibrated to carbon. No background subtraction was performed.

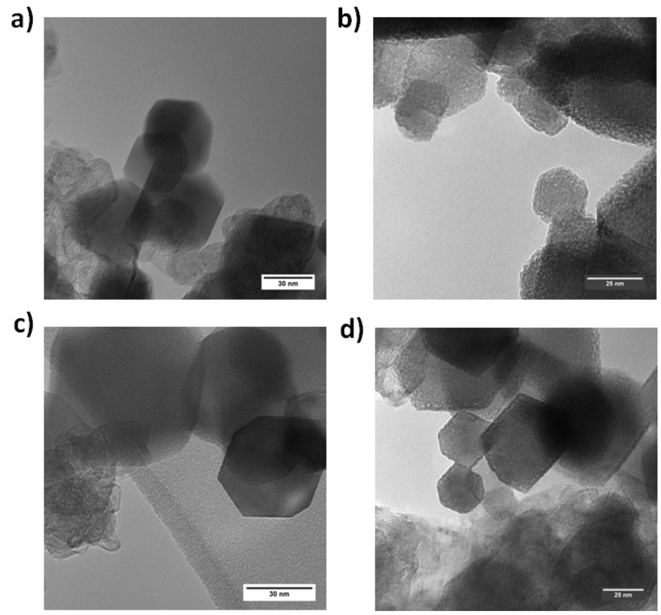

Fig. S2 Additional TEM images of nano-sized particles (a,c) before cycling and (b,d) after cycling.

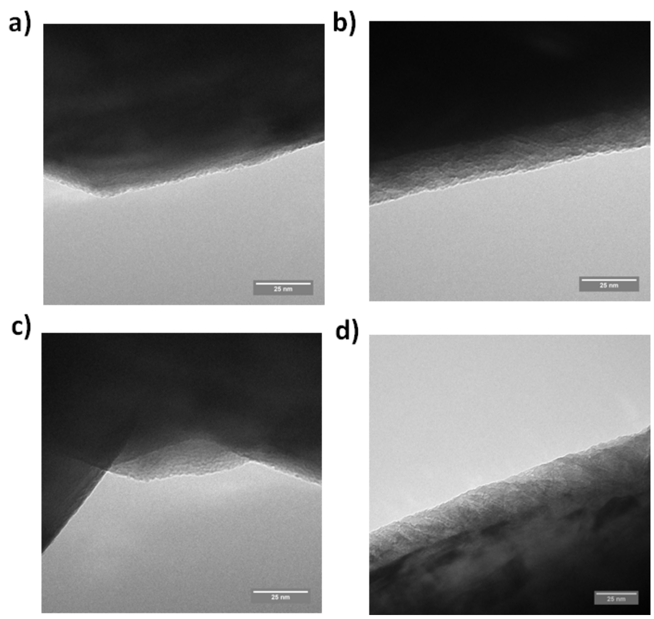

Fig. S3 Additional TEM images of micro-sized particles, (a, c) before cycling and (b, d) after cycling.

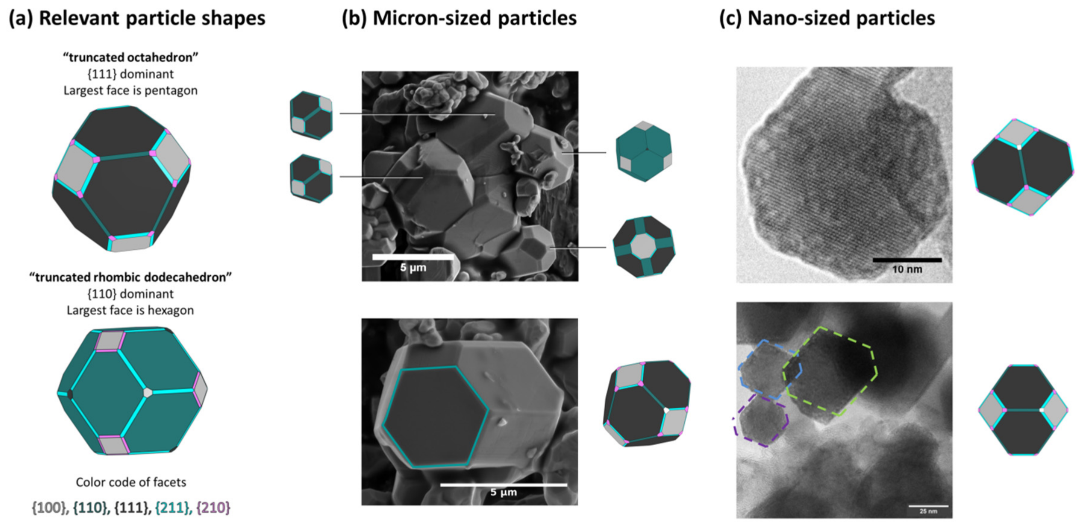

Fig. S4 (a) Geometry of relevant particles shapes and assignment of facets (structure generated by Vesta[1]). (b) SEM images of micro particles to identify the dominant facets. (c) TEM images of nano-sized particles to identify the dominant facets.

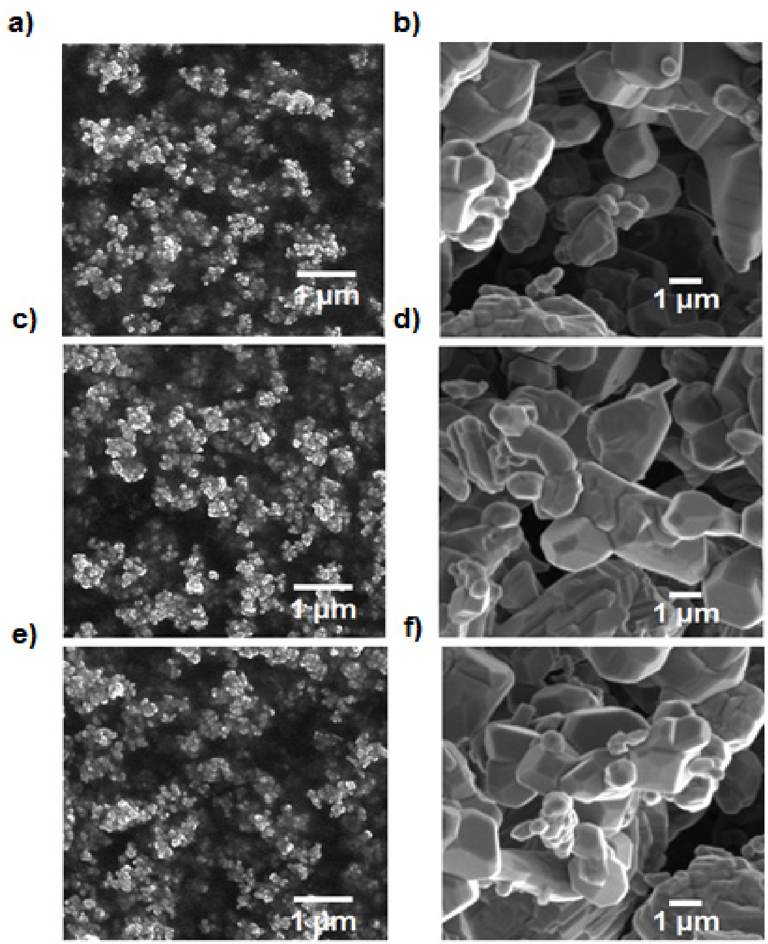

Fig. S5 Additional SEM images of (a, c, e) the nano-sized particles and (b, d, f) micro-sized particles.

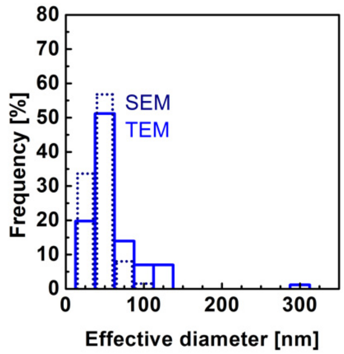

Fig. S6 Particle distributions of nano-sized $LiMn_2O_4$ obtained by TEM (solid line) and SEM (dotted line; same data as Fig. 2c of the main text).

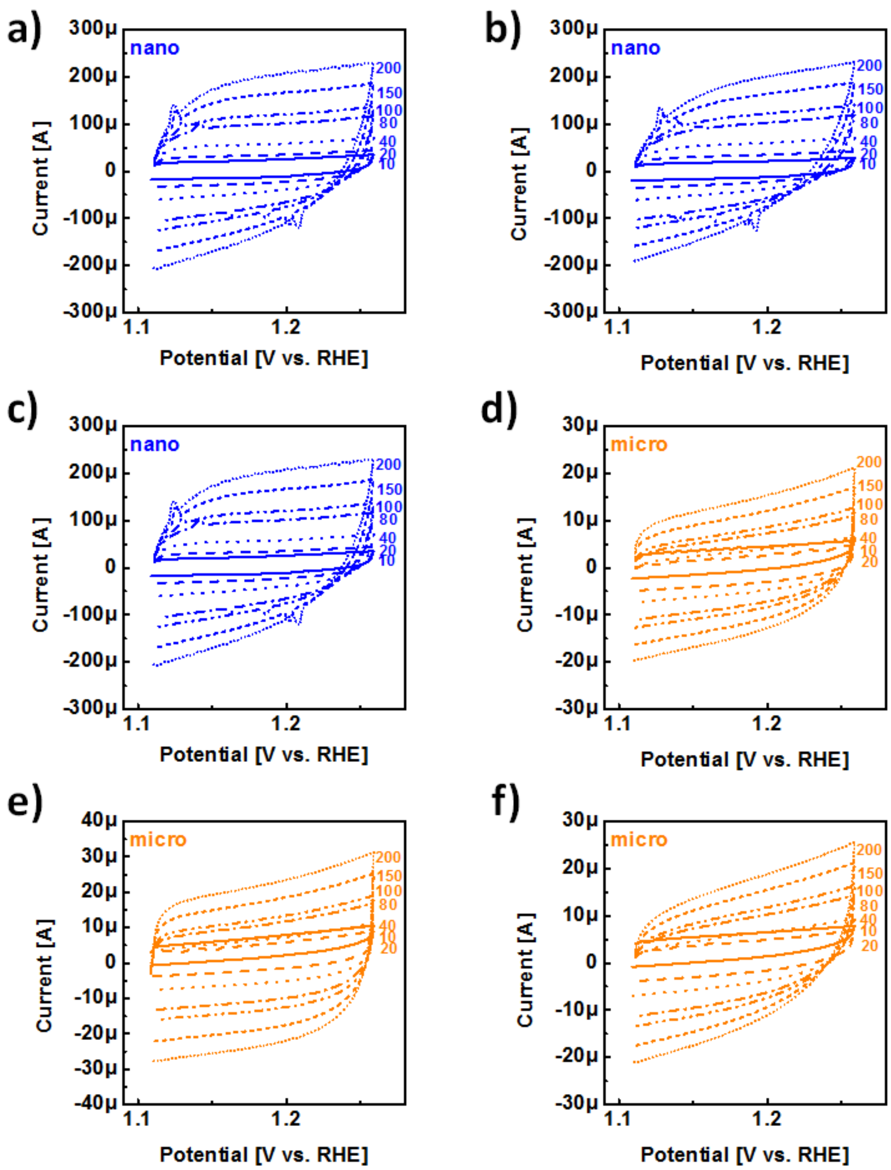

Fig. S7 Representative CV between 1.1 and 1.25 V vs SCE to determine the double layer capacitance of (a-c) nano (d-f) micro particles

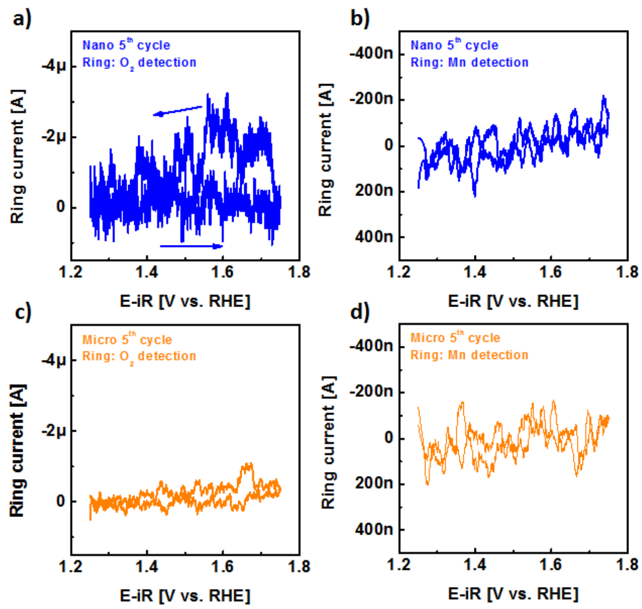

Fig. S8 Investigation of cross talk between disk and ring electrode: (a) Oxygen detection at ring electrode at 0.4 V vs. RHE of a nano-particle casted disk electrode without any rotation. During the backward half cycle, oxygen was detected due to bubble formation which pushes the produced oxygen to the outer part of the electrode to the ring electrode. (b) Manganese detection at ring electrode at 1.2 V vs. RHE of a nano-particle casted disk electrode without any rotation. (c) Oxygen detection at ring electrode at 0.4 V vs. RHE of a micro-particle casted disk electrode without any rotation. (d) Manganese detection at ring electrode at 1.2 V vs. RHE of a micro-particle casted disk electrode without any rotation.

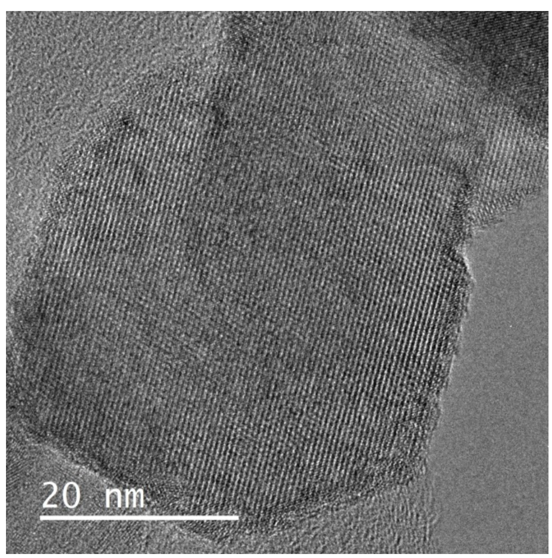

Fig. S9 Additional HRTEM on post-cycle nano-sized powder in an image-corrected FEI Titan affirms that the material is not amorphized on the surface.

Table S1. R^2 of capacitance fit

Data points	R^2 micro anodic / cathodic	R^2 nano (N) anodic / cathodic
1-7	0.95171 / 0.94644	0.98479 / 0.9441
1-6	0.92043 / 0.94714	0.99218 / 0.9599
1-5	0.85417 / 0.95083	**0.9975** / 0.97333
1-4	0.64999 / 0.92461	0.99691 / **0.97986**
2-7	**0.99277** / 0.97365	0.98383 / 0.94986
2-6	0.99008 / 0.97645	0.99117 / 0.9659
2-5	0.9877 / **0.98282**	0.99694 / 0.9795

Table S2. Various current densities of the $LiMn_2O_4$ powders at 1.68 V vs. RHE applied to disk during 5th cycle.

Normalization	Micro		Nano	
	disk	ring	disk	ring
Disk area	0.60(5) mA/cm_{disk}^2	8(2) μA/cm_{disk}^2	1.48(5) mA/cm_{disk}^2	60(1) μA/cm_{disk}^2
Mass loading	1.51(1) A/g	0.06(1) A/g	3.72(1) A/g	0.15(4) A/g
SEM area	38.16(3) μA/cm_{SEM}^2	0.1(4) μA/cm_{SEM}	3.08(9) μA/cm_{SEM}^2	0.13(3) μA/cm_{SEM}^2
ECSA	205(2) μA/cm_{ECSA}^2	-2.0(7) μA/cm_{ECSA}^2	36(4) μA/cm_{ECSA}^2	-1.3(2) μA/cm_{ECSA}^2
Oxygen	n/a	40(14) μA/cm_{ECSA}^2	n/a	26(5) μA/cm_{ECSA}^2
Manganese	n/a	19(12) μA/cm_{ECSA}^2	n/a	8(7) μA/cm_{ECSA}^2

Table S3. Linear combination analysis of the current densities of the $LiMn_2O_4$ powders at 1.68 V vs. RHE.

Coefficient	Nano	Micro
c_{O2}	-20.3(4)	-20.3(4)
c_{Mn}	-269(4)	-269(4)
R^2	0.9996	--

Note that the coefficients should be negative because the ring currents are negative but product currents (and the disk current) are positive. Fitting the coefficients of the micropowder yielded an unreasonable positive c_{O2} coefficient.

Table S4. Various current densities of the $LiMn_2O_4$ powders at 1.58 V vs. RHE applied to disk.

Catalyst	SEM current density (mA/cm_{SEM}^2)	ECSA current density (μA/cm_{ECSA}^2)	Geometric current density (μA/cm_{geo}^2)	Mass activity (A/g)
Micro disk (this work)*	0.006(1)	34(3)	99(7)	0.25(2)
Micro O_2 yield (this work)*	40(3)nA/cm_{SEM}^2	4.0(4)	0.63(5)	0.002(4)
Nano disk (this work)*	0.0005(33)	5.8(4)	245(13)	0.62(4)
Nano O_2 yield (this work)*	3.1(6)nA/cm_{SEM}^2	1(5)	1.5(3)	0.004(1)
Mn_2O_3[2]	-	16(3)	160(30)	0.39(2)
MnO[2]	-	31(25)	220(18)	0.53(9)
MnO_2[2]	-	100(86)	440(35)	1.00(4)
Mn_3O_4[2]	-	180(122)	720(49)	1.76(4)

* 5th cycle

We note that 1.58 V is very close to the onset of the OER on $LiMn_2O_4$ and thus produces large errors.

References

1 K. Momma, F. Izumi and IUCr, *J. Appl. Crystallogr.*, 2011, **44**, 1272–1276.

2 S. Jung, C. C. L. McCrory, I. M. Ferrer, J. C. Peters and T. F. Jaramillo, *J. Mater. Chem. A*, 2016, **4**, 3068–3076.