Supplementary information for

Tuning morphology of manganese oxide nanostructures for obtaining both high gravimetric and volumetric capacitance

Jones de A. Pereira[1], Janiny N. Lacerda[1], Izabella F. Coelho[1], Cauê de S. C. Nogueira[2], Dante F. Franceschini[2], Eduardo A. Ponzio[3], Fernando B. Mainier[1], Yutao Xing[2]*

[1]Departamento de Engenharia Química e de Petróleo, Universidade Federal Fluminense, Niterói, 24210-346, Brasil

[2]Laboratório de Microscopia Eletrônica de Alta Resolução, Centro de Caracterização Avançada para Indústria de Petróleo (LaMAR/CAIPE), Universidade Federal Fluminense, 24210-346, Niterói, RJ, Brasil

[3]Grupo de Eletroquímica e Eletroanalítica (G_2E), Instituto de Química, Universidade Federal Fluminense, Campus Valonguinho, 24020-141, Niterói, RJ, Brasil

*****corresponding author: xy@id.uff.br

Table S1 Deposition conditions and other parameters for the MO nanostructures

Sample name	MO01	MO05	MO10	MO20
O_2 pressure (Torr)	0.1	0.5	1.0	2.0
Thickness (μm)[a]	0.607	0.995	4.98	20
Volume (cm^3)[b]	6.1×10^{-5}	1.0×10^{-4}	5.0×10^{-4}	2.0×10^{-3}

[a]Measured directly in the SEM at different places of the cross-sections with fresh broken perpendicularly mounted samples.

[b]Obtained with the area and thickness of each electrode

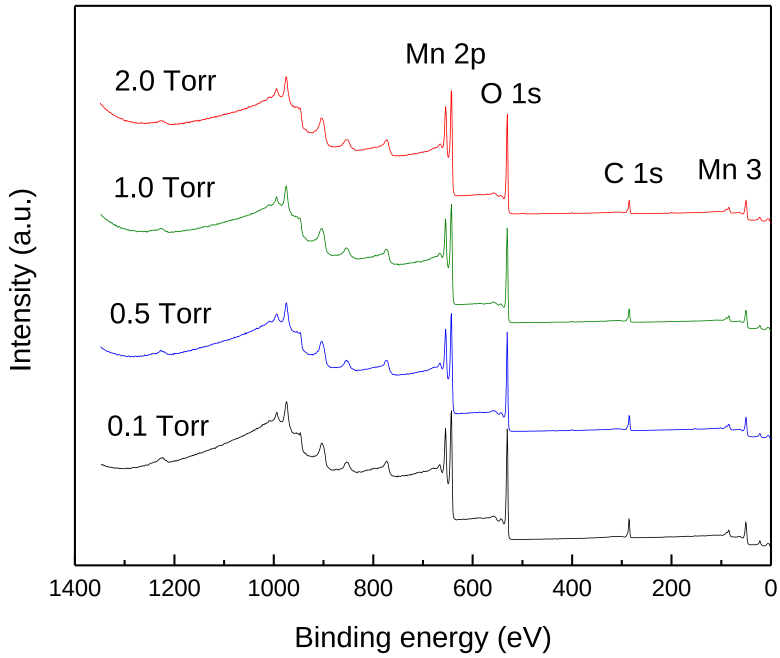

Fig. S1. XPS survey spectra of the MO nanostructures

Table S2. O 1s peak fitting results

Pressure (Torr)	O1s band	Peak Position (eV)	Peak width (eV)	Peak Area	Oxidation Number
0.1	O-Mn-O	529.8	0.95	52224	2.8
	Mn-O-H	530.5	2.15	34755	
	H-O-H	531.5	2.82	24881	
0.5	O-Mn-O	529.7	1.12	55620	2.9
	Mn-O-H	530.5	2.72	27524	
	H-O-H	531.5	1.71	15914	
1.0	O-Mn-O	529.7	1.11	48524	2.7
	Mn-O-H	530.5	2.18	32421	
	H-O-H	531.5	2.39	22842	
2.0	O-Mn-O	529.7	1.11	46804	3.2
	Mn-O-H	530.5	2.01	26200	
	H-O-H	531.5	2.54	21825	

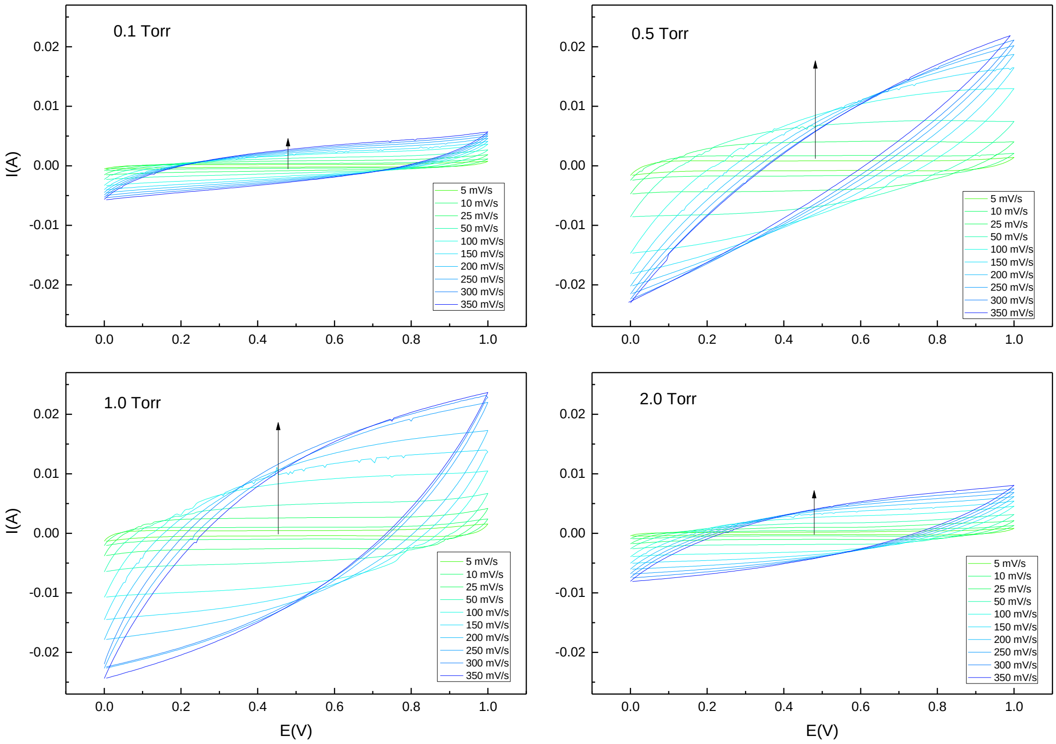

Fig. S2. Cyclic voltammetry with different voltage scan rates of MO nanostructures prepared with gas pressure of (a) 0.1 Torr, (b) 0.5 Torr, (c) 1.0 Torr and (d) 2.0 Torr.

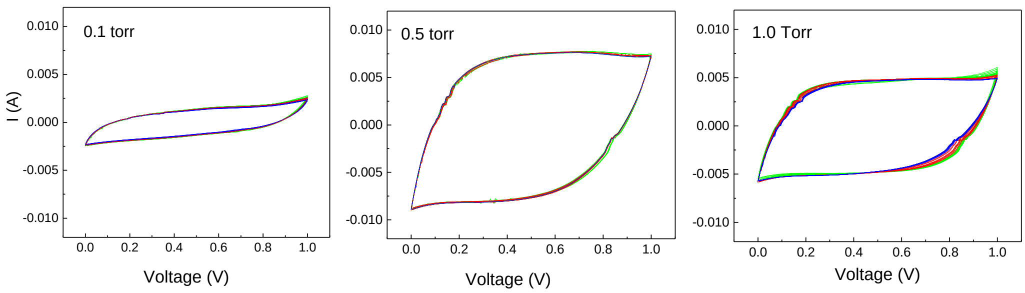

Fig. S3. Cycling stability profile for MO nanostructures at a voltage ramping rate of 50 mV/s.

Trasatti Method to calculate capacitive and diffusion controlled capacitance contributions

Trasatti method is used to evaluate electrical double layer capacitive (EDLC) and diffusion controlled pseudocapacitive contributions for the MO electrodes. The main steps are as follows.

In a supercapacitor with manganese oxide as active material, the total capacitance (C_T) can be divided into two parts: EDLC capacitance (C_c) and diffusion controlled pseudocapacitance (C_p) with

$C_T = C_c + C_p$

(Eq.S1)

C_T is assumed to be the value when the voltage scan rate $v \rightarrow 0$, in such a case both the process of charging and discharging for EDLC and diffusion have sufficient time to occur thoroughly. The C_c, on the other hand, is assumed as the capacitance when $v \rightarrow \infty$, where only the EDLC charging and discharging process can occur. Using the data collected during CV scanning, specific capacitance can be obtained as a function of voltage scan rate, as shown in Fig. 5 of the article.

By analyzing the charge and discharge process, we can have two different v dependence of $C(v)$:

$v \rightarrow 0$: $C(v)^{-1} = 1/C_T + K_1 v^{1/2}$,

$v \rightarrow \infty$: $C(v) = C_c + K_2 v^{-1/2}$

where K1 and K2 are constants.

By using the data obtained from the CV scans, two different curves can be plotted: first plot is $C(v)^{-1}$ as a function of $v^{1/2}$. In this plot we can do linear fitting of the data and the reciprocal of y- intercept is the C_T. The second plot is $C(v)$ as a function of $v^{-1/2}$ and after having the linear fitting for the curve, the y-intercept is the capacitive contribution C_c. With the values obtained, the pseudocapacitance can be calculated by Eq.S1. The percentage of the capacitive contribution is then can be calculated with C_c/C_t. In the following we give an example for sample MO01 and the C_c/C_T ratio is calculated as 8.1%.

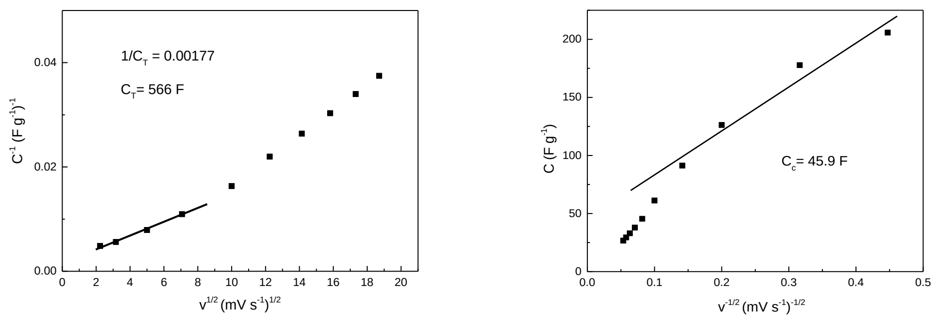

Fig. S4 two plots for C_T and C_c calculation.

Dunn method for the calculation of capacitive contribution at different voltage scan rates.

The Dunn method was used in this work to calculate the capacitive contribution at different voltage scan rates. The calculation is as follows.

At fixed potential, the current in CV scans can be divided into two parts: capacitive current $i_c(v)$ and diffusion-controlled current $ip(v)$ with different relations of v:

$i_c(v) = k_1 v$

and

$i_p(v) = k_2\, v^{1/2}$

So the total current cab be written as

$$i_T(v) = k_1 v + k_2 v^{1/2} \quad \text{(Eq. S2)}$$

k1 and k2 are constants.

With the CV curves at various scan rates, we can read the current at a fixed potential for different v, one example is at 0.7 V in this work. From Eq. S2 we can obtain:

$$i_T(v)/v^{1/2} = k_1 v^{1/2} + k_2 \quad \text{(Eq. S3)}$$

In this equation, the new variable $i_T(v)/v^{1/2}$ linearly depends on the square root of the v. We can plot the curve $i_T(v)/v^{1/2}$ as a function of $v^{1/2}$, the slope of the curve is k_1 and the y-intercept is then k_2.

With the two constants, we can divide the current into two parts:

$$i_T(v)= k_1 v + k_2 v^{1/2} = i_c + i_p \quad \text{(Eq. S4)}$$

Till now we separated the capacitive and diffusion-controlled contributions to the current. Repeating the process for other potentials, we can separate i_c and i_p for all the points in a CV curve. Using the similar method for capacitance calculation with a CV curve, the capacitance contribution at each scan rate can be obtained, as shown in Fig. 6 (b) in the article.