SUPPLEMENTARY MATERIALS

MnOx- graphitic carbon composite from CO₂ for sustainable Li-ion battery anodes.

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1. Scanning Electron Microscopy

The SEM images in Figure S1a and S1b show the great heterogeneity of C despite grinding. Big particles and aggregates are present together with smaller particles, which affects the contact with the current collector. Bright spots in the images indicates the presence of metals. EDS analysis (Table S1) confirmed the presence of W (from the jar of the first sample grinding) and of other metals, specifically of Mn (up to 12% atomic, 33% weight), and a great amount of oxygen (44% atomic, 34% weight). To avoid the presence of W in the electrode preparation, the second sample of the pristine carbonaceous material was milled in an agata jar.



Figure S1. SEM images of (a) C, (b) C used for EDS analysis,

Element	App	Intensity	Weight%	Weight%	Atomic%
	Conc.	Corrn.		Sigma	
СК	60.97	0.5238	21.98	1.01	38.19
O K	149.85	0.8409	33.64	0.70	43.89
S K	25.14	0.9194	5.16	0.16	3.36
K K	16.87	1.0810	2.95	0.12	1.57
Mn K	147.37	0.8522	32.65	0.59	12.40
Co K	2.89	0.8048	0.68	0.15	0.24
W M	10.95	0.7031	2.94	0.29	0.33

Table S1. Elemental analysis of C grund in WC jar

Element	App	Intensity	Weight%	Weight%	Atomic%
	Conc.	Corrn.		Sigma	
СК	196.56	0.5795	33.78	0.59	47.86
O K	282.36	0.7028	40.01	0.48	42.56
Si K	0.73	0.8522	0.09	0.03	0.05
S K	53.01	0.9518	5.55	0.10	2.94
K K	17.78	1.0621	1.67	0.05	0.73
Mn K	154.40	0.8126	18.92	0.25	5.86

Table S2. Elemental analysis of C grund in agate mortar

2. X-ray Photoelectron Spectroscopy



Figure S2. High-resolution XPS spectra and fitting of S2p region of the carbon material ground in agata jar.

C1s	Binding energy (eV)	Abundancy (%)
C=C	284.4	45.6
C-H	285.3	34.6
C-O-R	286.4	10.6
COOH	288.0	4.3
π-π	288.9	5

Table S3. Integrals of deconvoluted high-resolution XPS spectra of C1s region.

Table S4. Integrals of deconvoluted high-resolution XPS spectra of O1s region.

O1s	Binding energy (eV)	Abundancy (%)
MnOMn	529.6	8.9
MnOH	531.6	75.2
OH	533.1	15.8

Mn2p _{3/2}	Binding energy	Abundancy	Abundancy vs. total	O bonded to Mn
	(eV)	(%)	(%)	(%)
Mn ₂ O ₃	641.2	57.5	9.8	14.7
MnO ₂	642.6	42.5	7.4	14.8

Table S5. Integrals of deconvoluted high-resolution XPS spectra of Mn2p_{3/2} region.

The carbon and manganese oxides weight content were estimated from XPS deconvolution (Table S5). Material composition is expected to be homogenous in consequence of the milling protocol. The atomic percentage of Mn and their composition obtained from the Mn2p high-resolution XPS spectrum deconvolution were used to split the atomic oxygen percentage in the fraction bonded to the Mn and the part involved in the oxygen-functional groups the carbonaceous phase. The atomic fraction of oxygen involved in the Mn-oxide phase (At_{O-Mn}) corresponds to the sum of the oxygen involved in the Mn2O₃ phase (At_{Mn2O3}) and the oxygen in the MnO₂ phase (At_{MnO2}). The weight percentages were obtained by diving the atomic percentage for the atomic weight.

 At_{O-Mn} (%) = At_{Mn2O3} + At_{MnO2} = 29.5 (20.4 % wt.)

The percentual weight of the manganese phase $(m_{Mn-oxides})$ was obtained summing the corresponding weight percentage from XPS deconvolution of Mn $(m\%_{Mn})$ and oxygen $(m\%_{O})$

 $m_{Mn\text{-}oxides}$ (%) = m% $_{Mn}$ +m% $_{O}$ = 61.4%

From the C1s high-resolution XPS deconvolution, the atomic percentage of oxygen contained in oxygen functional groups of the carbonaceous phase was 22.2 % (15.3% wt.). The sum of the oxygen-carbon bounded (m $\%_{O-C}$), and carbon abundancy (m $\%_C$) was taken as amount of the graphitic carbon phase (m_{carbon}).

 m_{carbon} (%): $m\%_{O-C} + m\%_{C} = 31.1\%$

The remaining 7.5% is attributed to sulphur and potassium traces in the synthetized active material.

3. Electrochemical characterization

In Figure S3a and S3b are reported the rate capability performance of #3 with and without the vinylene carbonate (VC) additive to 1M LiPF₆ EC:DMC 1:1 electrolyte. The C-rates reported have been calculate on the theoretical capacity of graphite (372 mAh g⁻¹). A significant difference in the initial capacity in the two conditions was observed. The #3 in LP30 shows the first cycle with a specific capacity during the insertion and the SEI formation of 662 mAh g⁻¹ and 582 mAh g⁻¹ during the deinsertion with a quite high coulombic efficiency (88%). On the other hand, rate capability tests in LP30 + 2% VC (Figure S3b) showed a first cycle with a specific capacity of 1062 mAh g⁻¹ during the insertion and the SEI formation, and of 384 mAhg⁻¹ during the deinsertion with a low coulombic efficiency (36%). Until the 5th-6th cycle, the electrode capacity critically drops around 400 mAhg⁻¹. Then the specific capacity slowly decreases; evidence of this, the second series of C/5 cycles results more stable than the first C/5 cycles with a specific capacity comparable to the last cycle of the previous C/5 series.



Figure S3. Rate capability of #3 in (a) LP30 and (b) LP30 + 2% VC. Specific capacity and coulombic efficiency stability of C-W in LP30 and LP30 + 2% VC (c).

The active material's percentual composition ($m_{Mn-oxides}$ and m_{carbon}) of the active material was used to calculate the respective contribution to the electrode capacity. As an example, for 1g of active material, 0.31 g are graphitic carbon (theoretical capacity: 372 mAhg⁻¹), and 0.61 g are present as manganese oxides. (756 mAhg⁻¹). Hence, the two separate contributions (c_{carbon} and $c_{Mn-oxides}$) to the theoretical capacity of 1g of active material corresponds to:

$$c_{carbon} = m_{carbon} (g) \times 372 \ mAhg^{-1} = 115.3 \ mAh$$

 $c_{Mn-oxides} = m_{Mn-oxides} (g) \times 756 \ mAhg^{-1} = 461.2 \ mAh$

Hence, the active material theoretical capacity cactive is:

 $c_{active} = c_{carbon} + c_{Mn-oxides} = 576.5 \text{ mAh}$

The percentual contribution of the two phases can be found as:

$$c\%_{carbon} = \frac{c_{carbon}}{c_{active}} \times 100 = 20\%$$
$$c\%_{Mn-oxides} = \frac{c_{Mn-oxides}}{c_{active}} \times 100 = 80\%$$