SUPPLEMENTARY MATERIALS

On the Effect of the Nature of Carbon Nanostructures on the Activity of Bifunctional Catalysts Based on Manganese Oxide Nanowires

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S1. Additional physical-chemical characterization of manganese oxide nanowires

S1.1. Morphology

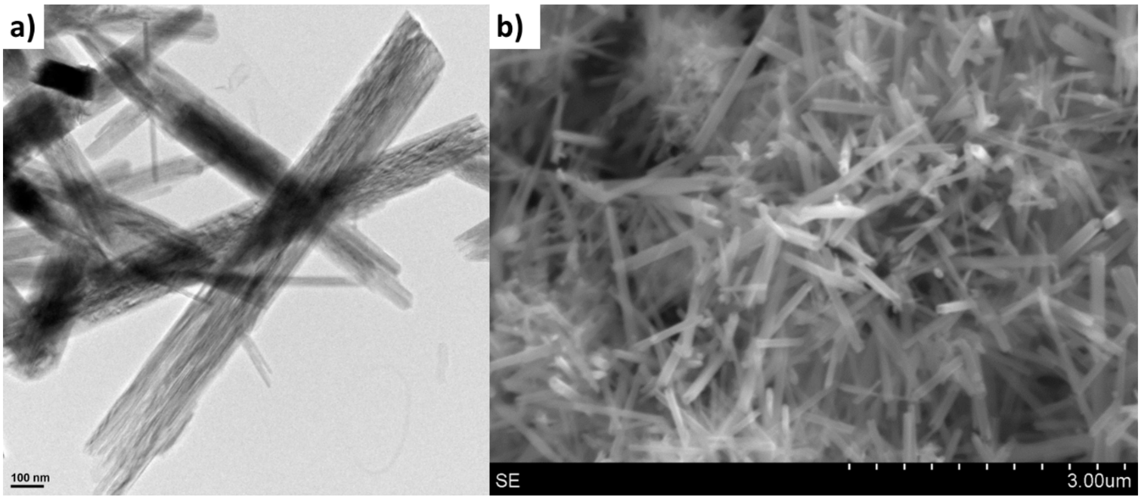

Figure S1. a) TEM and b) SEM micrographs for MONW.

S1.2. X-Ray diffraction

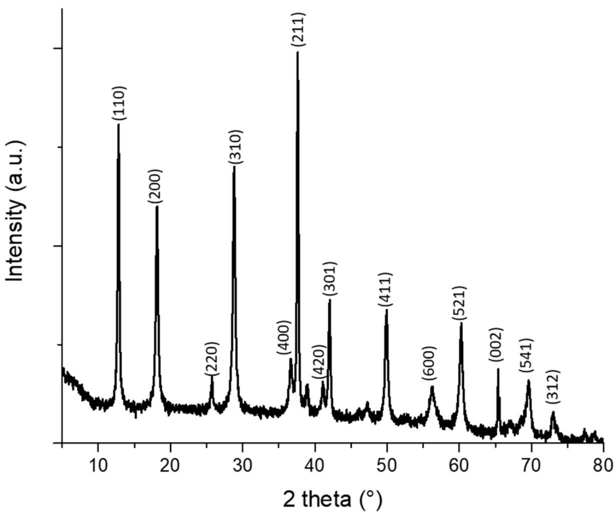

Figure S2. Diffractogram of MONW.

S1.3. X-ray photoelectron spectroscopy

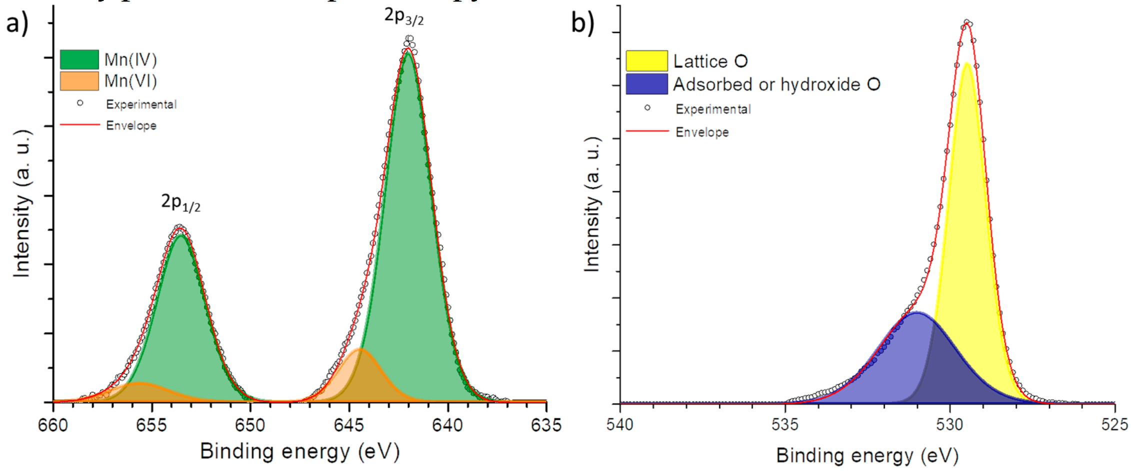

Figure S3. XPS spectra of orbitals: a) Mn2p and b) O1s of MONW.

S1.4. Nitrogen physisorption

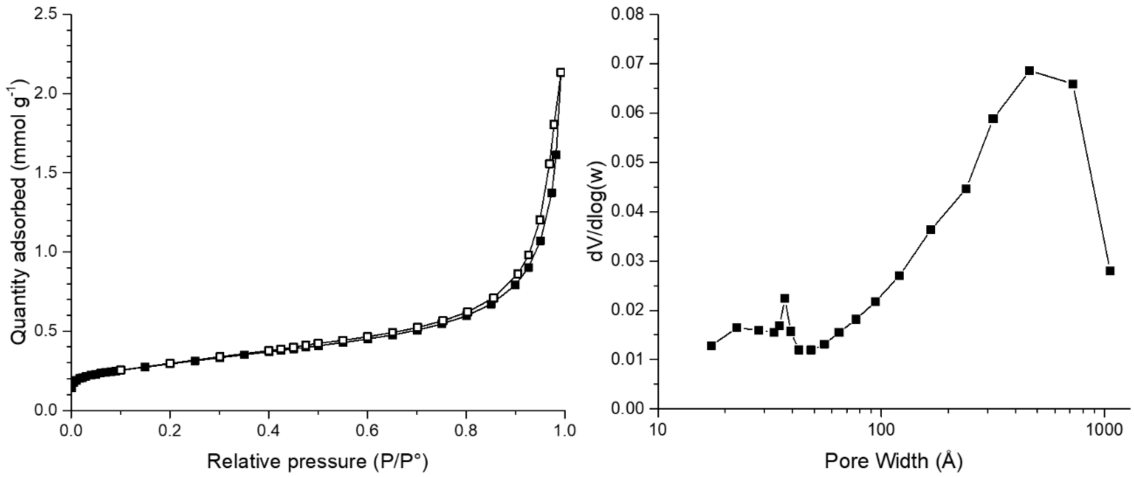

Figure S4. a) Nitrogen physisorption for MONW at 96 K and, b) Pore size distribution (BJH desorption).

S2. Additional electrochemical characterization of manganese oxide nanowire–carbon composites

S2.1 Effect of acid-leaching on carbon nanotubes

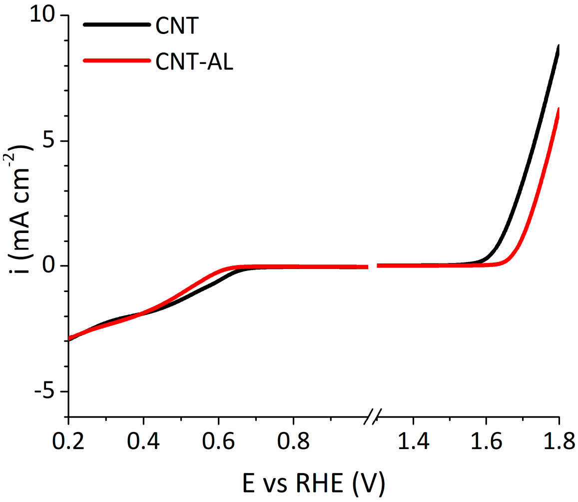

Figure S5. Comparison between the catalytic activities of pristine carbon nanotubes and acid-leached carbon nanotubes (CNT-AL)

S2.2. Comparison between the single materials and the composite catalysts

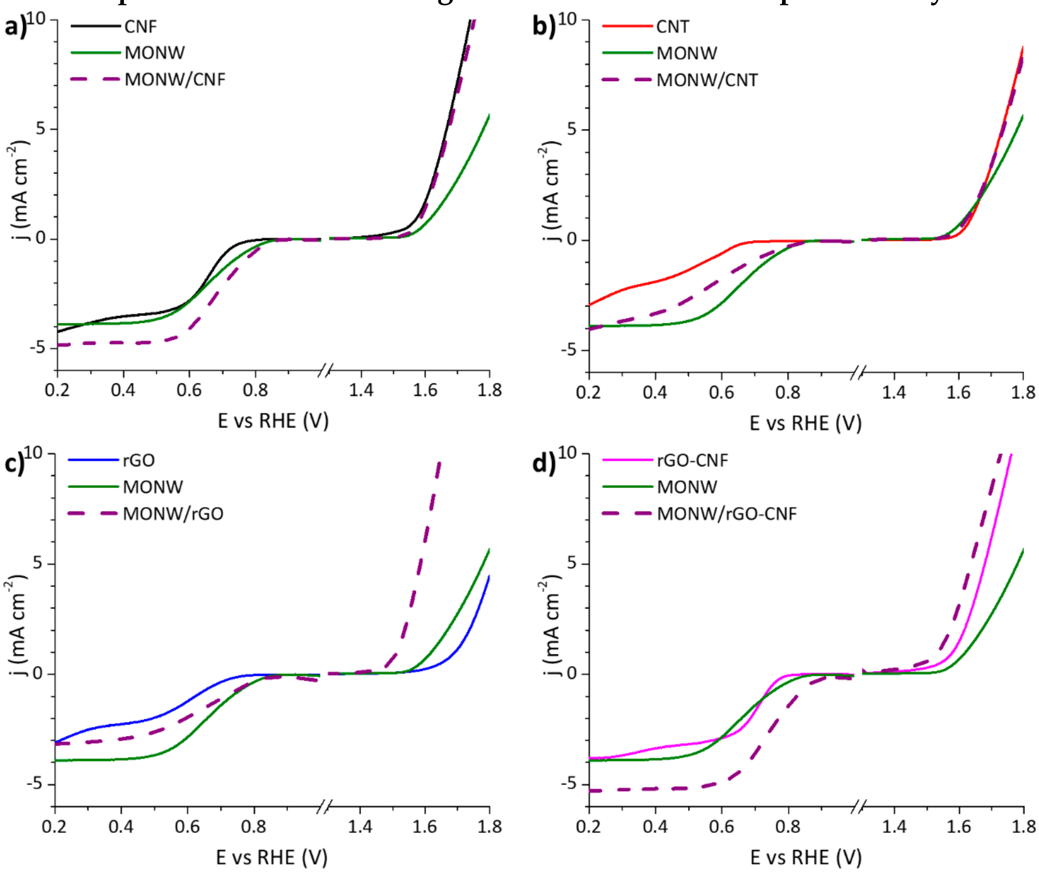

Figure S6. Comparison between the catalytic activities of carbon materials and their composites: a) CNF, b) CNT, c) rGO and, d) rGO-CNF.

S2.3. Koutecky–Levich plots

ORR LSVs were performed at 400, 625, 900, 1600 and 2500 rpm to obtain the number of electrons exchanged in the diffusional limit, using the Koutecky–Levich approach, applying Equation S1:

$$|j|^{-1} = |j_L|^{-1} + |j_k|^{-1} \qquad \text{(S1)}$$

Where j is the observed current density at E = 0.2 V *vs*. RHE, j_k is the intrinsic current density and j_L is the limiting current density, estimated using the Levich equation for rotating disk electrodes (Equation S2):

$$j_L = 1.95nFAC_{O2}^{*}D_{O2}^{1.5}\nu^{-(1/6)}f^{1/2} \qquad \text{(S2)}$$

In the Levich equation, n is the number of electrons transferred in the oxygen reduction reaction, C_{O2}^{*} is the saturation concentration of oxygen in the electrolyte, D_{O2} is the diffusivity of oxygen in the electrolyte, ν is the cinematic viscosity of the electrolyte and f is the rotation frequency of the electrode, F is the Faraday constant and A is the disc electrode area. Combining Equations S1 and S2, Equation S3 is obtained:

$$|j|^{-1} = |j_L|^{-1} + m_L f^{-0.5} \qquad \text{(S3)}$$

where $m_L = 1/(1.95nFAC_{O2}^{*}D_{O2}^{1.5}\nu^{-(1/6)})$.

Plotting the inverse of the observed current density vs. the inverse of the square root of the rotation frequency made it possible to obtain the number of electrons transferred from the slope of the fitted line. The parameters used are summarized in Table S1.

Table S1. Parameters and properties of the electrochemical system used in the Levich equation

Parameter	Value
F	96485 C mol^{-1}
A	1.96 x 10^{-5} m^2
C_{O2}^{*}	1.21 mol m^{-3}
D_{O2}	1.87 x 10^{-9} m^2 s^{-1}
ν	10^{-6} m^2 s^{-1}

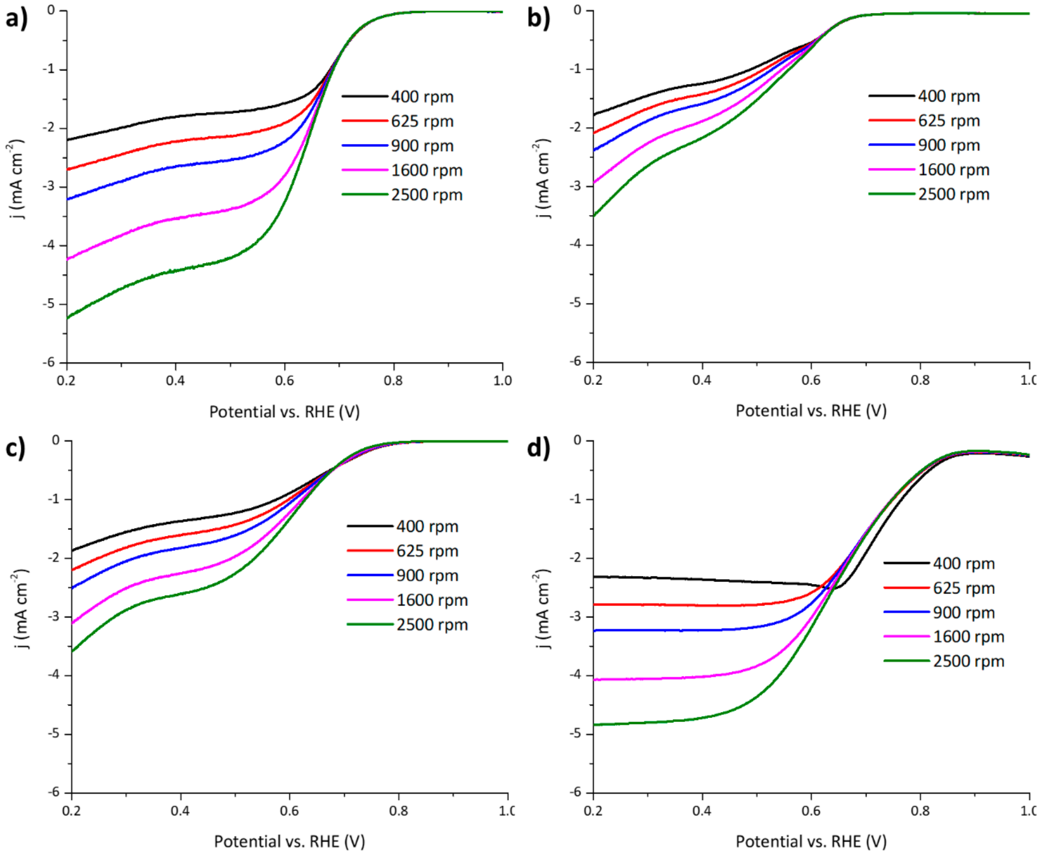

Figure S7. LSVs at 400, 625, 900, 1600 rpm rotation speed of materials: a) CNF, b) CNT, c) rGO and, d) MONW.

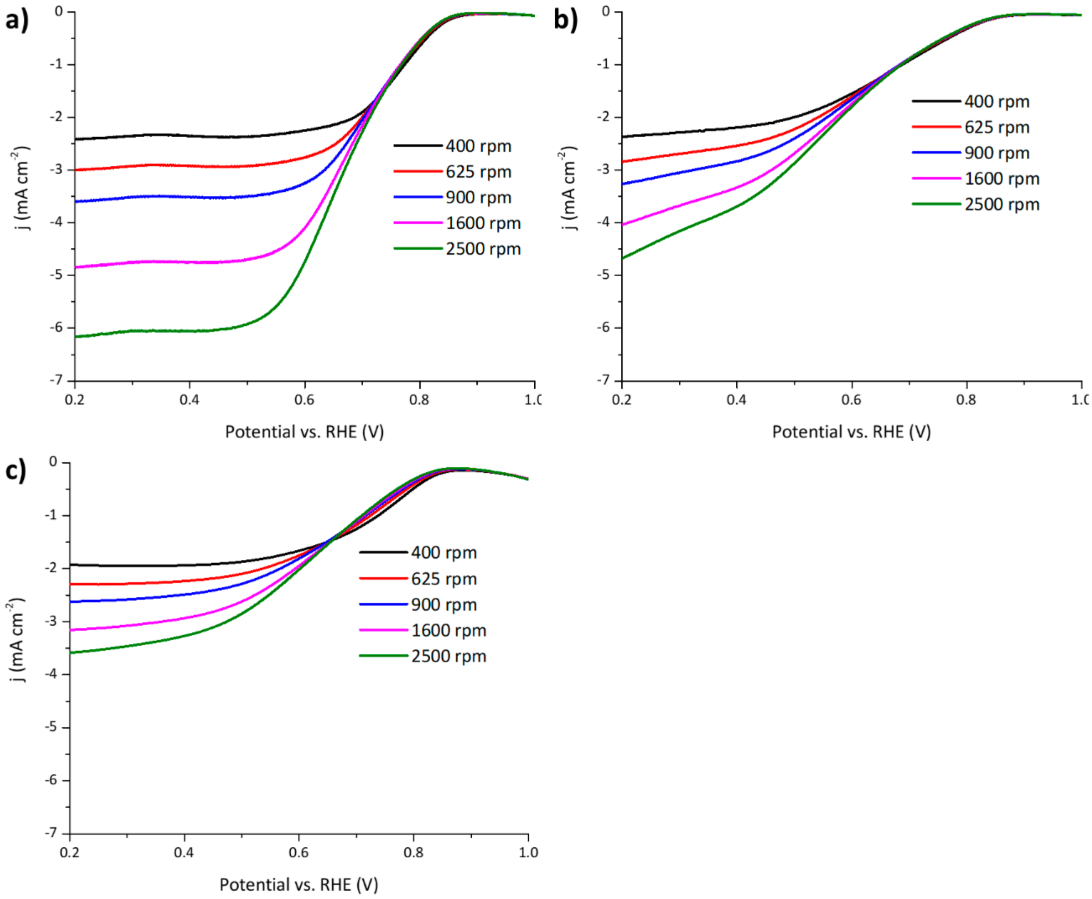

Figure S8. LSVs at 400, 625, 900, 1600 rpm rotation speed of materials: a) MONW/CNF, b) MONW/CNT and, c) MONW/rGO.

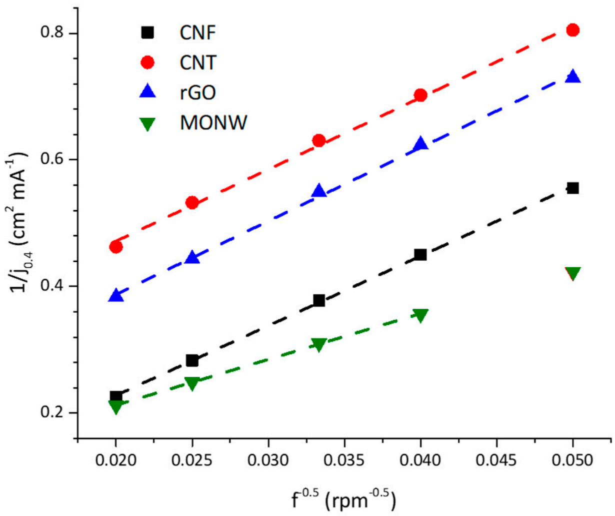

Figure S9. Koutecky–Levich plots at E = 0.4 V vs. RHE of carbon materials and manganese oxide.

S2.4. Tafel plots

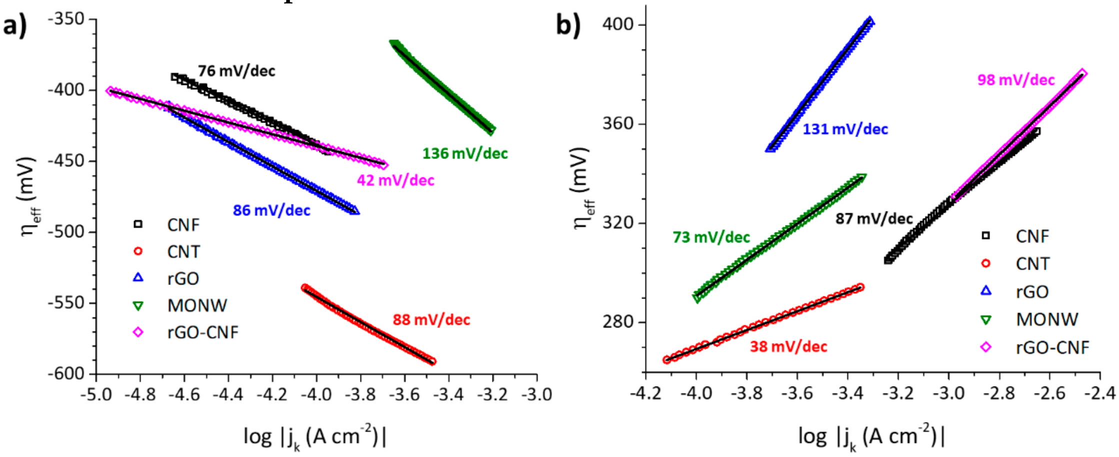

Figure S10. ORR (a) and OER (b) Tafel plots of non-composite catalysts. Experiments carried out over a RDE at 1600 rpm.

S2.5. Electrochemical characterization of composite MONW/mm[rGO-CNF]

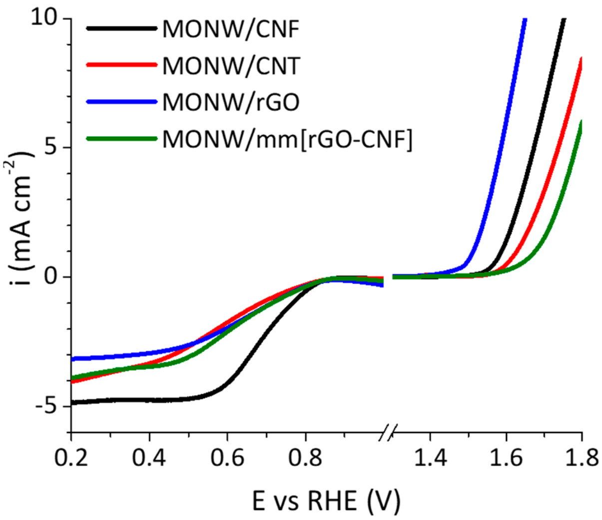

Figure S11. Comparative performance of composite MONW/mm[rGO-CNF] with respect to MONW/C catalysts.

S2.6. Durability tests

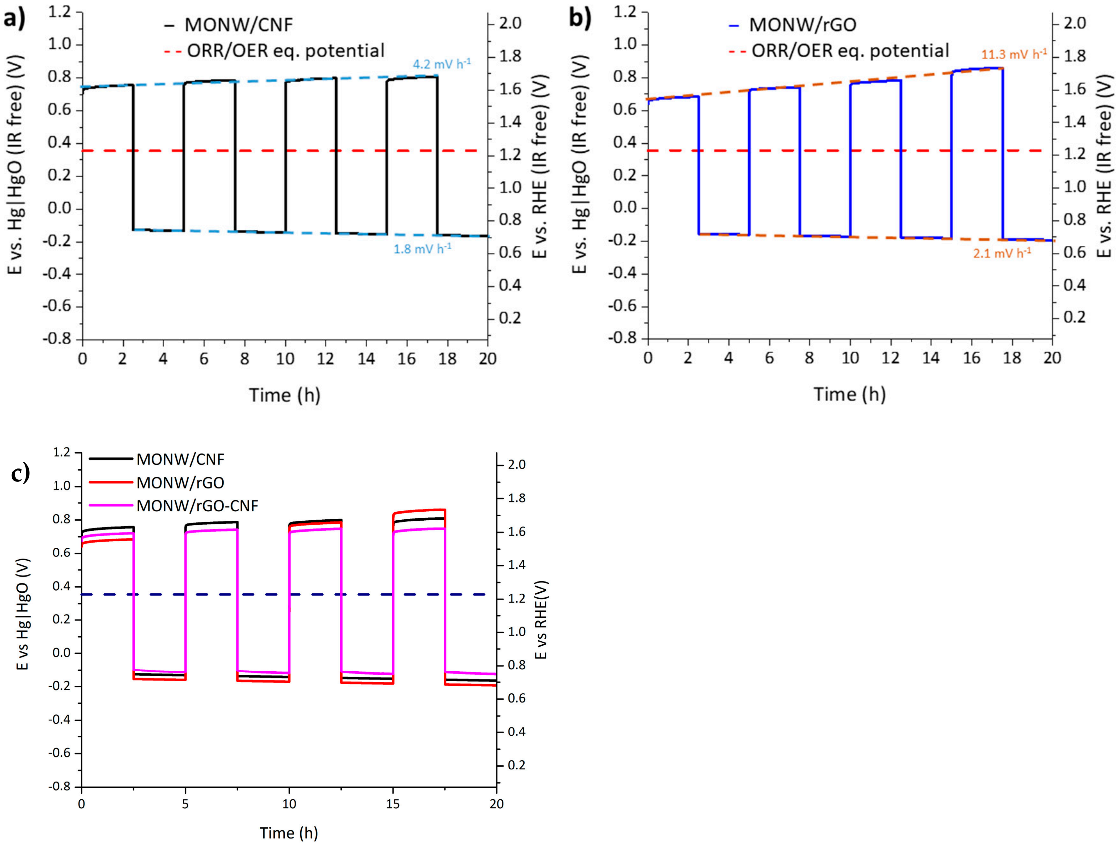

Figure S12. Endurance test carried out over a GDE with catalysts a) MONW/CNF and b) MONW/rGO in 6M KOH. Potentials corrected for IR.

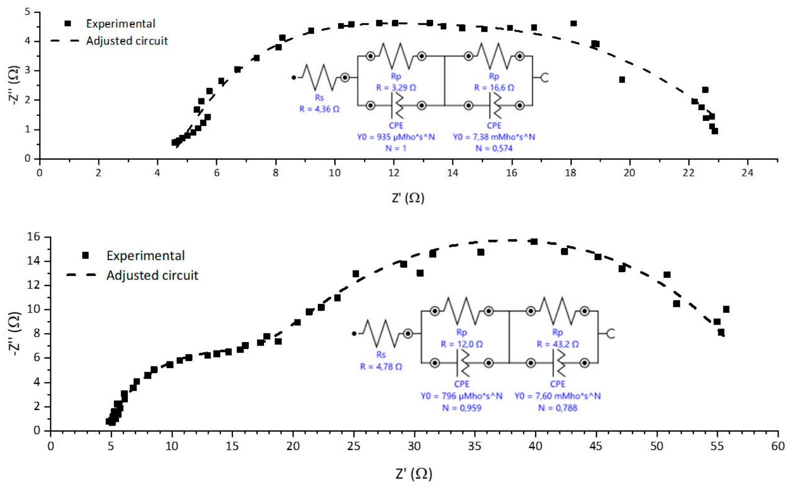

Figure S13. Nyquist diagrams (top: ORR, bottom: OER) for EIS tests for MONW/CNF-rGO.