

Supplementary Information

Morphology and Dispersion of Nanostructured Manganese-Cobalt Spinel on Various Carbon Supports: the Effect on the Oxygen Reduction Reaction in Alkaline Media

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The results of X-ray diffraction measurements of the investigated materials are shown in *Fig. S1A*. The diffraction peaks located at 2θ angles: 19° , 31° , 36° , 45° , 59° , 65° were attributed to (111), (220), (311), (400), (511), and (440) reflections, respectively, and indicate the presence of the manganese-cobalt spinel structure.

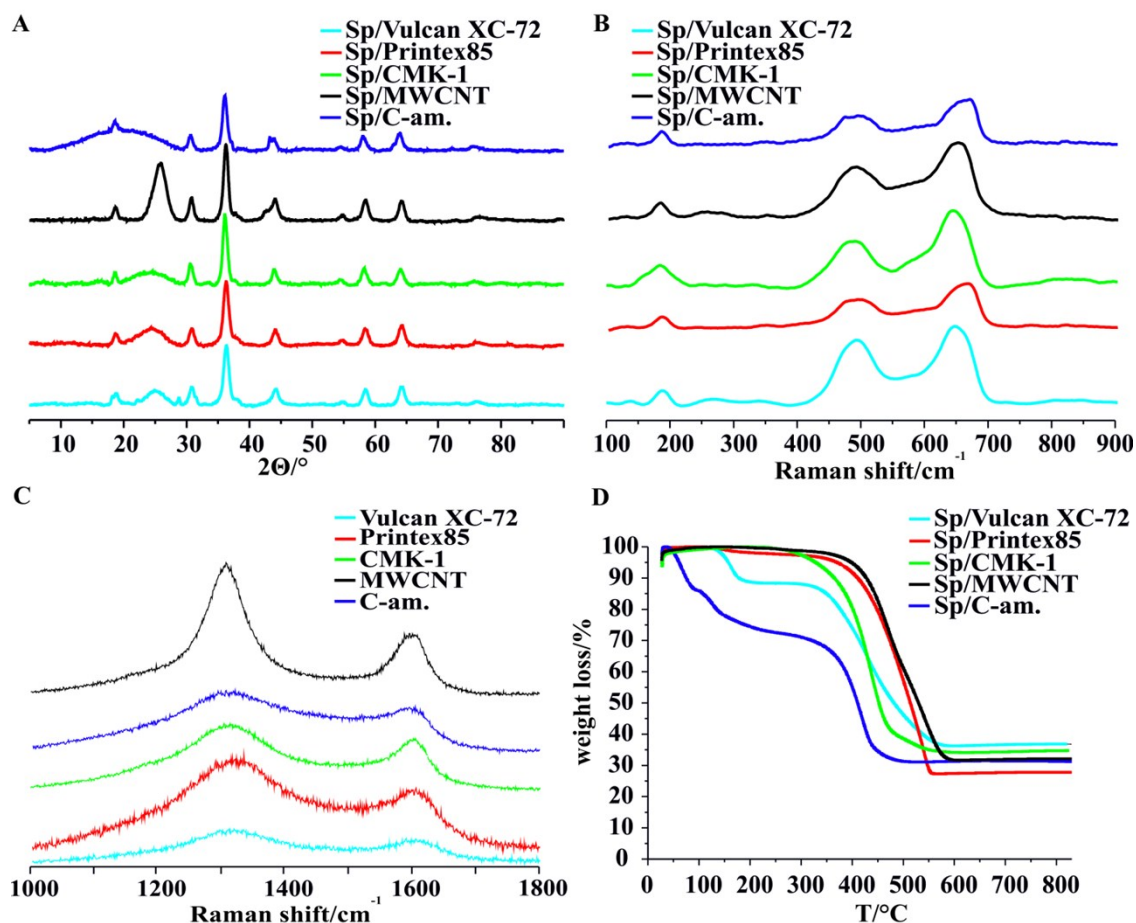


Figure S1. (A) XRD patterns of the spinel on different carbon supports; (B) Raman spectra of the spinel on different carbon supports; (C) Raman spectra of the different carbon supports; (D) TG plots of the spinel on different carbon supports.

The XRD patterns for all samples show also a broad peak at the angle $\sim 25^\circ$ which corresponds to the graphite (002) plane.¹ However, there is a minor discrepancy in the distribution of this peak on the different carbon supports. Especially, in the case of C-am., the (002) peak of

carbon is much broader and less evident, in agreement with the lower crystallinity of this carbon support. The Raman spectra (*Fig. S1B*) confirmed the presence of manganese-cobalt spinel in the investigated samples. The observed band at 189 cm^{-1} was assigned to the F_{2g} mode which is the characteristic vibration of spinel phase. The other two bands at 494 cm^{-1} , and 663 cm^{-1} were corresponded to E_g , and A_{1g} vibration modes of M-O (M = Mn, Co)².

Measurements in a broader range (*Fig. S1C*), between 1000 and 3000 cm^{-1} , revealed additional bands at $\sim 1350\text{ cm}^{-1}$ and $\sim 1590\text{ cm}^{-1}$ which were assigned to the carbon support.

The mass ratio of the spinel-to-carbon support was determined by TGA (*Fig S1D*). Each of the investigated catalyst was heated up to $825\text{ }^\circ\text{C}$ under 5% O₂/Ar atmosphere. A weight loss of $\sim 70\%$ was measured for all the samples (*Fig. S1D*).

Table S1. The Mn:Co ratio in the obtained materials measured by XRF and calculated values of the characteristic ratios of the peak intensities obtained from fitting of the Raman spectra of the carbon supports.

Catalyst	spinel loading on carbon supports (from TGA/wt.%)	XRF chemical composition of the investigated samples/wt.%		Raman intensity	
		Mn	Co	I_{D3}/I_G	$I_{D1}/I_{(G+D1+D2)}$
Sp/Vulcan XC-72	36	23	77	4.55	0.71
Sp/Printex85	27	22	78	12.82	0.80
Sp/MWCNT	32	21	79	1.95	0.79
Sp/CMK-1	34	19	81	3.62	0.78
Sp/C-am.	32	18	82	9.33	0.82

The spinels on Printex85, CMK-1 and MWCNT exhibit similar TG-profiles with no significant amount of water released. For these samples, the weight loss observed from 380 to 580 °C results from oxidation of the carbon support. In the case of the spinels dispersed on the Vulcan XC-72 and C-am., the initial weight loss observed until 170 °C was due to elimination of water. The final combustion of these carbon supports started at ~320 °C.

Table S2. BET-specific surface area for different carbon supports.

Carbon support	BET-specific surface area /m ² ·g ⁻¹
Printex85	200
MWCNT	247
Vulcan XC-72	254
CMK-1	1144
C-am.	n.d.

n.d. not determined

The BET-specific surface area for commercial carbon supports (Printex85, Vulcan XC-72, MWCNT) were provided by the producer in the safety data sheets. Mesoporous carbon (CMK-1) was synthesized and characterized by Leżańska et al.³

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- 2 N. Padmanathan and S. Selladurai, *Ionics (Kiel)*, 2014, **20**, 479–487.
- 3 M. Leżańska, P. Pietrzyk, A. Dudek and J. Włoch, *Mater. Chem. Phys.*, 2015, **149**, 539–552.