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Supplementary Information

The Joined Effect of Electric Conductivity of Carbon Supports and Surface Oxygen Functionalities on the Oxygen Reduction Reaction Studied over the Bare Supports and Spinel Mn-Co/Carbon Catalysts in Alkaline Media

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MATERIALS AND METHODS

Mesoporous carbons preparation: The carbon precursor was deposited in the pore system of silica by incipient wetness impregnation with sucrose. In a typical procedure, 1 g of silica template (dried initially at 120°C for 12 h) was impregnated with a solution containing 0.77 g of water, 0.19 g of sucrose (POCH) and 0.022 g of sulfuric acid (95–97%, Sigma-Aldrich). The obtained composites were dried overnight. Next, samples were placed in an oven at 100°C for 6 h. Subsequently, the temperature was raised to 160°C and the samples were kept at this temperature for the next 6 h. The procedure of impregnation and heating was repeated once, with a solution containing 0.64 g of water, 0.16 g of sucrose and 0.018 g of sulfuric acid. All obtained materials were carbonized in a tubular furnace at 650, 750, 850, 950 or 1050°C for 4 h (with a heating rate of 1°C min^{-1}) in an inert atmosphere (N_2, 5.2, Air Products). Finally, the silica templates were removed by a treatment with a 10% HF solution at room temperature for 1 h. The produced carbon replicas were filtered, washed with distilled water and ethanol (96%, Avantor) and dried at room temperature overnight. The procedure of silica dissolution was repeated once.

Catalyst preparation: To synthetize the spinel catalyst supported on the SPH carbon following procedure was applied. Briefly, 2.28 ml of 0.2 M $Co(CH_3COO)_2$ solution and 0.80 ml of 0.2 M $Mn(CH_3COO)_2$ solution were added to 20 ml mesoporous carbon ethanol suspension (0.01 g carbon per ml EtOH), followed by addition of 0.60 ml of 25 wt.% aqueous ammonia. Subsequently, the mixture was transferred into a microwave autoclave (Ertec/MAGNUM II) for the hydrothermal reaction at 140°C for 20 min. The resulting products were centrifuged and washed several times with pure ethanol and distilled water and then dried overnight at 80°C.

XRD: The diffraction patterns of obtained materials were collected using Cu Kα radiation with a wavelength λ = 1.540598 Å/1.54184 Å. Data were recorded in the 2θ range between 0.8° and 90° (depending on the sample) with a resolution of 0.02° and scans speed 1.5° min^{-1}. The average crystallite size of spinel nanoparticles was calculated based on the half-width of the peaks (determined by means of *Fityk* software[1]), using Scherrer's equation.

N_2 sorption: Prior to each low-temperature nitrogen adsorption-desorption measurements, a sample was degassed in vacuum (10^{-3} Pa) at 250°C for 6 h. Specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method. Values of total pore volume (V_{total}) were obtained from amounts of nitrogen adsorbed at relative pressure of 0.97. Micropores volume (V_{micro}) were determined using the *t*-plot equation.

TGA: Mass changes of carbon supports and catalysts were analyzed in in the flow of air (100 ml min^{-1} for C-SPH_*x* or 40 mL min^{-1} for Mn-Co/C-SPH_*x*) from room temperature up to 850°C, with a heating rate of 20 or 5°C min^{-1}.

TPD: Temperature-programmed desorption measurements were performed in a helium flow (50 cm^3/min) using 100 mg of a sample placed in a quartz microreactor, which was heated to 800 °C at a linear heating rate of 10 °C/min. Evolving CO and CO_2 were analyzed on-line with a quadrupole mass spectrometer (PREVAC) after calibration with calcium oxalate ($CaC_2O_4{\cdot}2H_2O$). The TPD profiles were deconvoluted with the Gaussian function using non-linear optimization procedure based on the Levenberg-Marquardt iteration algorithm.

RAMAN: The Raman spectra were collected in the spectral range 100–1000 cm^{-1}, with a resolution of 2 cm^{-1} and a 50x magnification lens. In the case of catalyst with Mn-Co spinel phase, an excitation wavelength of 785 nm was used and the laser power at the sample position was set as about 1.5 mW. While spectra of the C-SPH supports were registered by means of the green laser with an excitation wavelength of 514 nm and power at the sample position equal to 2.15 mW. Deconvolution of the carbon Raman spectra was carried out with the *Fityk*[1] software.

XPS: The spectra were collected using a monochromatized aluminum source Al K_α ($E = 1486.6$ eV). The base pressure in the analytical chamber was 5×10^{-9} mbar. The scale of the binding energy value was adjusted to the C 1s reference peak at 284.8 eV. The composition and chemical state of sample surface were analyzed in terms of areas and binding energies of O 1s, C 1s, N 1s and S 2p photoelectron peaks. The spectra were fitted using CasaXPS software. The XPS peak fitting was performed using the Shirley background and the GL(30) function. Maximum half-peak widths were limited to 2.0 eV in order to avoid excessive overlapping the peaks and to assign reliable binding energies.

DRS: Diffuse reflectance spectra were collected in the range of 200-2000 nm using a UV-vis-IR spectrophotometer (Shimadzu UV-3600) equipped with a 15 cm diameter integrating sphere. Samples were ground with the reference material (1:40 by mass). Obtained spectra were subsequently transformed to the Kubelka-Munk function (KM) and Tauc plots ($KM^{1/2}$ *vs*. E) for an indirect semiconductor. Optical energy gaps (E_g) were calculated from the intercept with x-axis of a straight line fitted to a linear fragment of the Tauc plot in the UV region. Mean number of aromatic rings in a cluster (M) was calculated based on the equation (S1)[2].

$$M = \left(\frac{5.8076}{E_g - 0.5413}\right)^2 \quad \text{(S1)}$$

TEM: The FEI Tecnai Osiris microscope was equipped with a 200 kV X-FEG Schottky field emitter and a High Angle Annular Dark Field (HAADF) detector (STEM mode). The information about the distribution of elements in the sample was obtained by EDX analysis, using a windowless 4-sector silicon drift detector (Super-X EDX) and the Bruker Esprit software. Prior to TEM observations, the sample was placed on the microscope copper grid covered with a holey carbon film.

Electrode preparation: For the RRDE, the mixture of 5.4 mg of catalyst or carbon powder, 62 µl of 5 wt.% Nafion solution, 200 µl of H_2O and 600 µl EtOH was sonicated for 60 min to achieve a good dispersion. In the case of the bare supports ink, isopropanol was used instead of water and ethanol. The Nafion-to-catalyst or carbon mass ratio was equal to 0.33. Then an appropriate amount of the selected ink was pipetted onto the surface of a glassy carbon disc electrode with the resultant loading on the electrode of 0.2 mg cm^{-2}. As a comparison, a commercial 20 wt.% Pt on Vulcan XC-72 catalyst was also tested. The ink was prepared according to the same procedure but in this case, consisted of 10 mg of Pt/C, 33 µl of 5 wt.% Nafion solution, 20 µl of deionized water, and 734 µl of isopropanol. The catalyst loading on the electrode (considering the total mass of the Pt and the C support) was the same as for spinel catalysts.

To elucidate the ORR pathway for the C-SPH support, Koutecky–Levich (K–L) theory was employed to estimate the overall ORR electron transfer numbers (*n*) according to the following equations[3,4]:

$$\frac{1}{j}=\frac{1}{j_k}+\frac{1}{j_l}=\frac{1}{j_k}+\frac{1}{0.201nFD^{2/3}\omega^{1/2}v^{-1/6}C_O}=A+\frac{1}{B\omega^{1/2}} \quad (S2)$$

$$B=0.201nFC_OD^{2/3}v^{-1/6}=3.5\times10^{-5}n \quad (S3)$$

where j is the measured current density, j_k is the kinetic current density, j_l is the diffusion-limited current density, n is the number of electrons, F is the Faraday constant (96.485 C mol^{-1}), D is the diffusion coefficient of oxygen in 0.1 M KOH (1.9×10^{-5} cm^2 s^{-1}), ω is the rotation rate of the electrode (rpm), v is the kinematic viscosity of the solution (0.01 cm^2 s^{-1}), C_O is the concentration of O_2 (saturated) (1.2×10^{-3} mol dm^{-3}), A is a constant which represents the nature of the catalyst site, and B is the Levich constant that can be obtained from the slopes of the K-L plots.

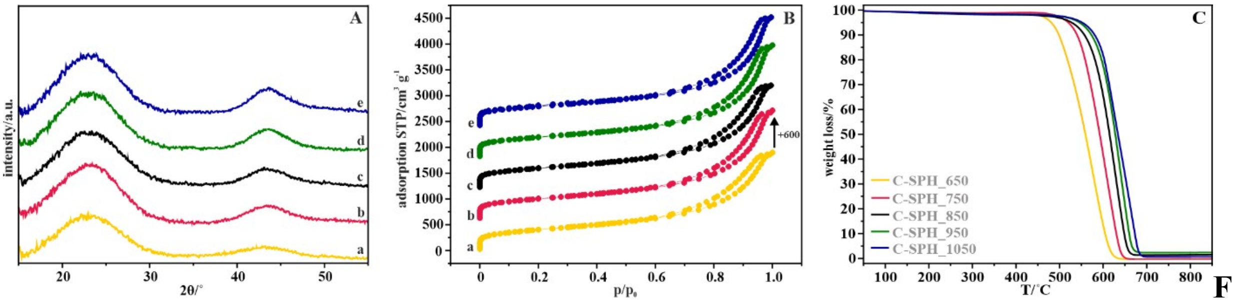

Figure S1. (A) XRD patterns, (B) N_2 adsorption-desorption isotherms, and (C) TG plots of the C-SPH carbon support, carbonized at different temperatures: (a) 650, (b) 750, (c) 850, (d) 950, and (e) 1050 ℃.

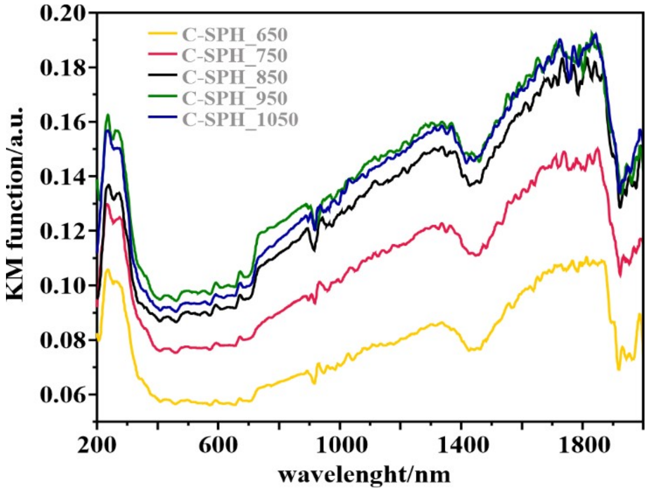

Figure S2. UV-Vis-NIR absorbance (in term of Kubelka–-Munk equivalent absorbance units) spectra of the C-SPH samples.

Table S1. Optical energy gap (E_g) and the mean number of aromatic rings in a cluster (M) of the C_SPH carbonized at different temperatures.

$T_{\mathrm{carbonization}}$/°C	E_g / eV	M
650	0.74	858
750	0.67	2166
850	0.65	3074
950	0.63	4186
1050	0.62	5579

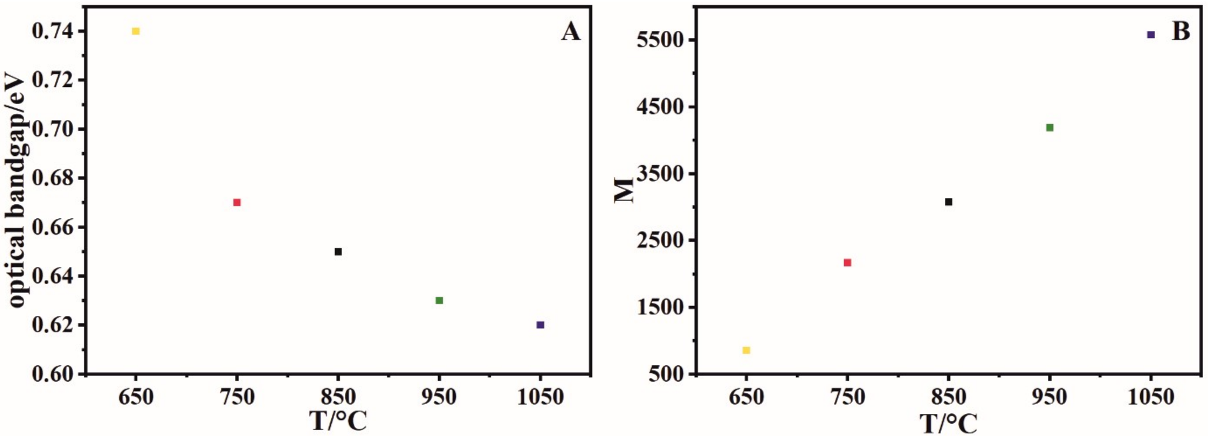

Figure S3. (A) Optical energy bandgaps and (B) calculated mean numbers of aromatic rings in clusters in investigated C-SPH materials.

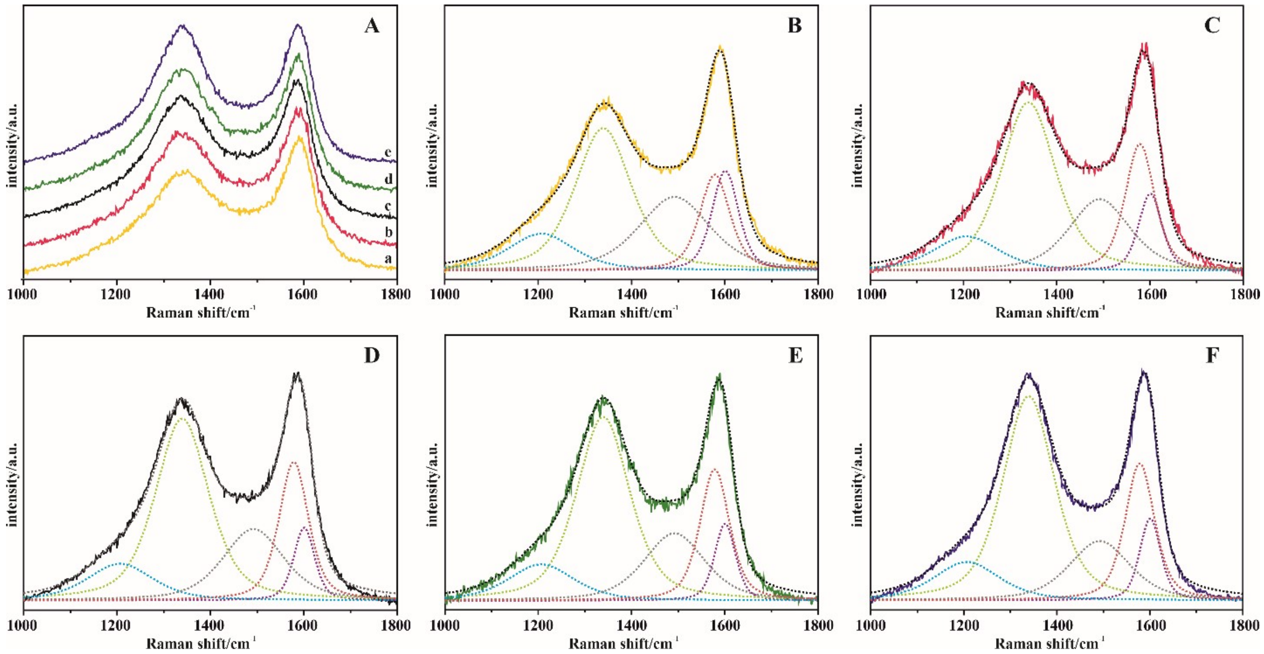

Figure S4. The Raman spectra (A) and their deconvolution into individual components signals (dash lines): G – red, D1 – light green, D2 – purple, D3 – grey, D4 – light blue, of the C-SPH carbon support, carbonized at different temperatures: (B) 650, (C) 750, (D) 850, (E) 950, and (F) 1050 ℃.

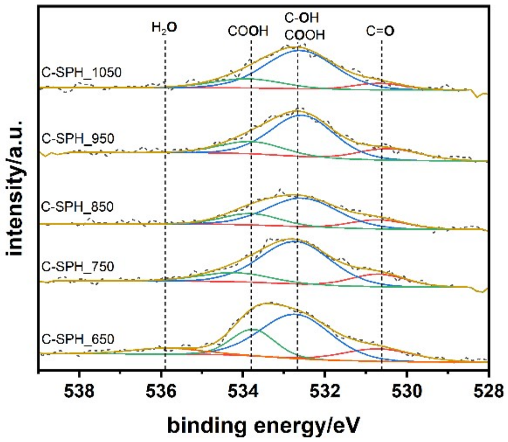

Figure S5. The XPS O 1s spectra collected for C-SPH samples and their deconvolution into individual components.

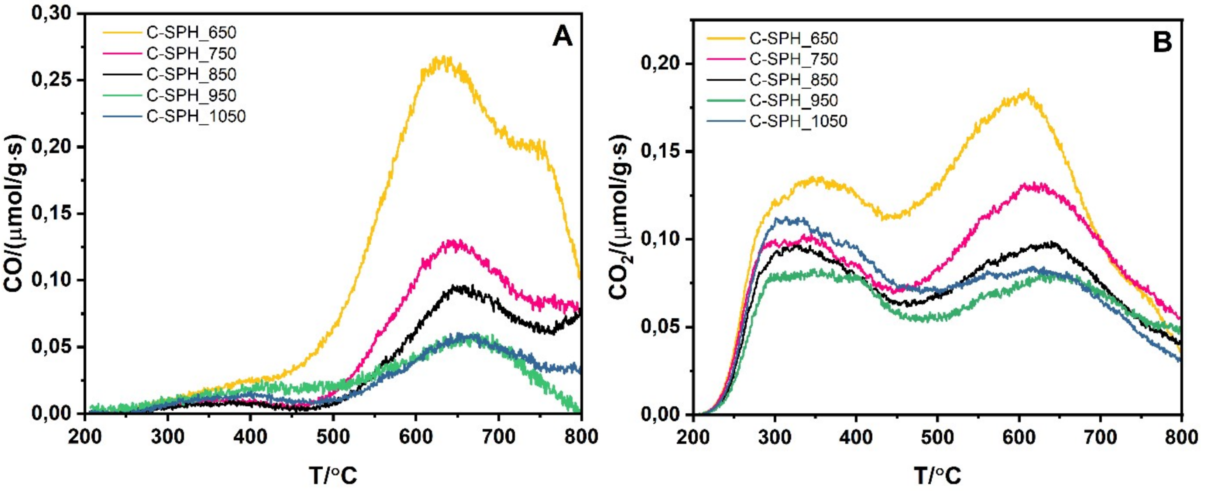

Figure S6. Temperature-programmed desorption profiles for C-SPH samples: CO (A) and CO_2 (B) evolution.

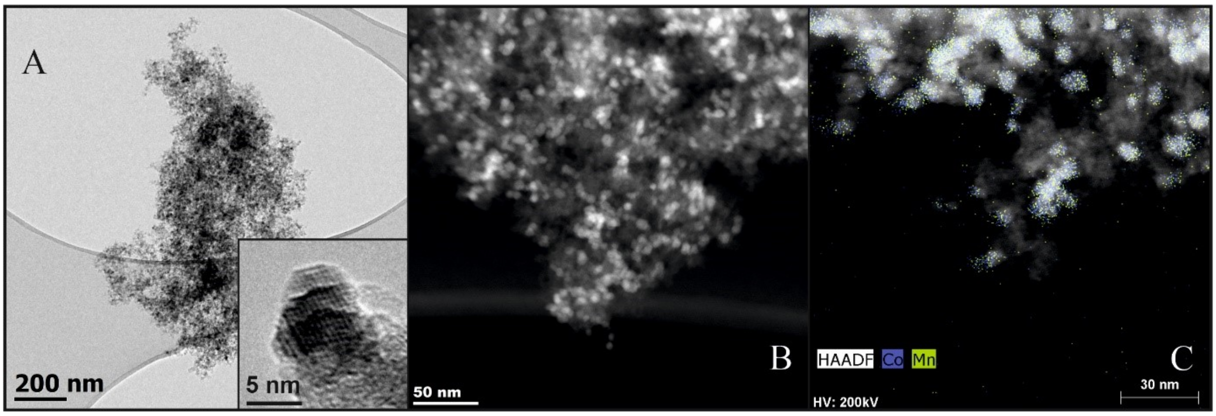

Figure S7. TEM image of Mn-Co/C-SPH_850 sample (A) HR TEM image of Mn-Co spinel nanocrystals (A, *insert*), STEM image of Mn-Co/C-SPH_850 sample (B) EDX analysis of Mn-Co/C-SPH_850 sample (C).

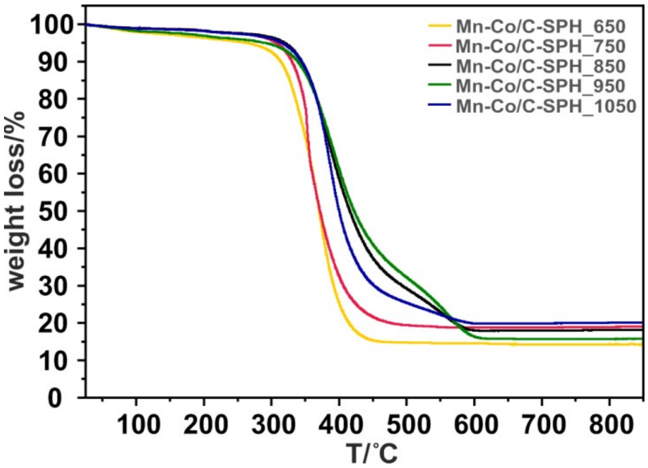

Figure S8. TGA plots of the Mn-Co spinel deposited on the C-SPH carbon support, carbonized at different temperatures.

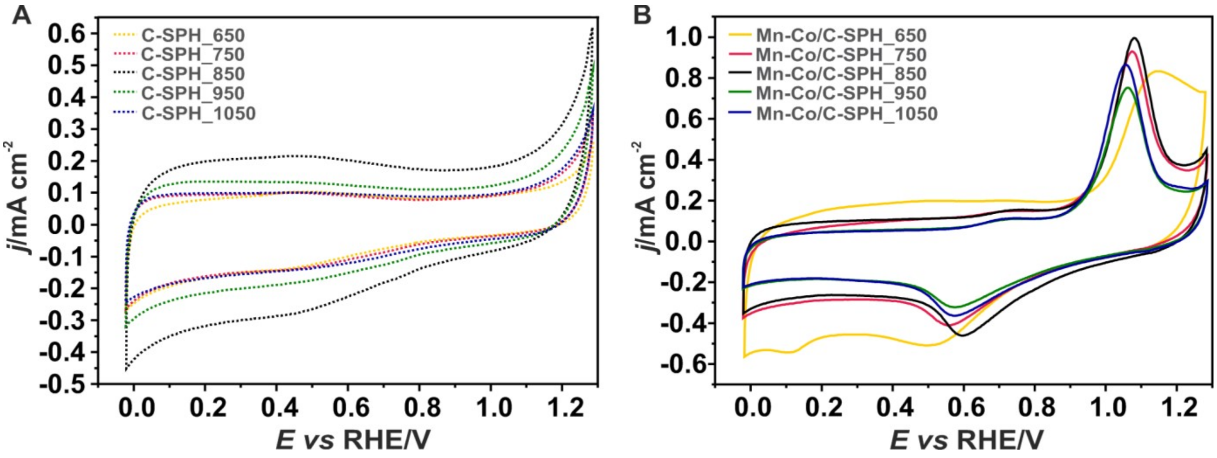

Figure S9. CV curves for the C-SPH samples carbonized at different temperatures (A), and the catalysts with the Mn-Co spinel active phase deposited on the C-SPH support (B), in Ar-saturated 0.1 M KOH solution at the scan rate 10 mV s^{-1}.

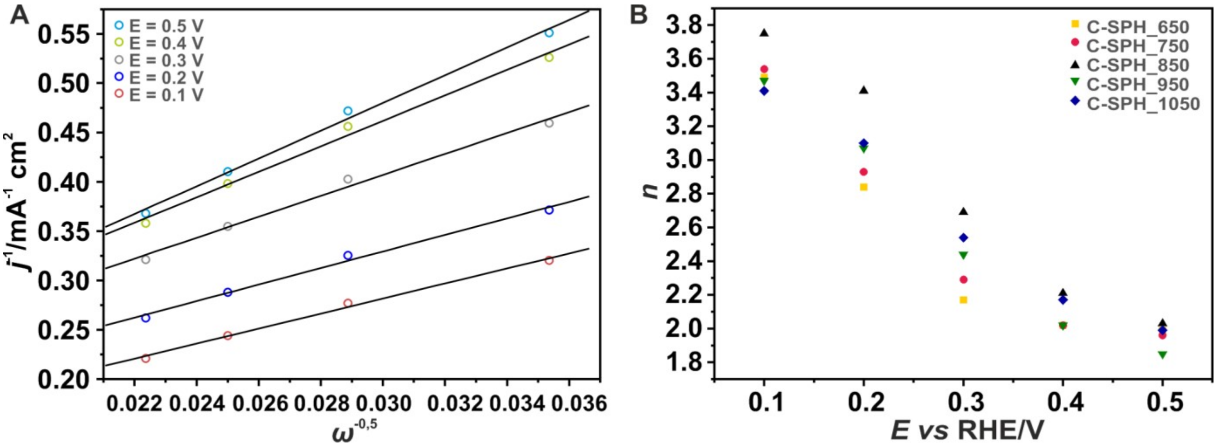

Figure S10. (A) Koutecky–Levich plots at different potentials for C-SPH_850, and (B) number of electrons transfer, calculated by means of K-L method for the C-SPH carbon supports.

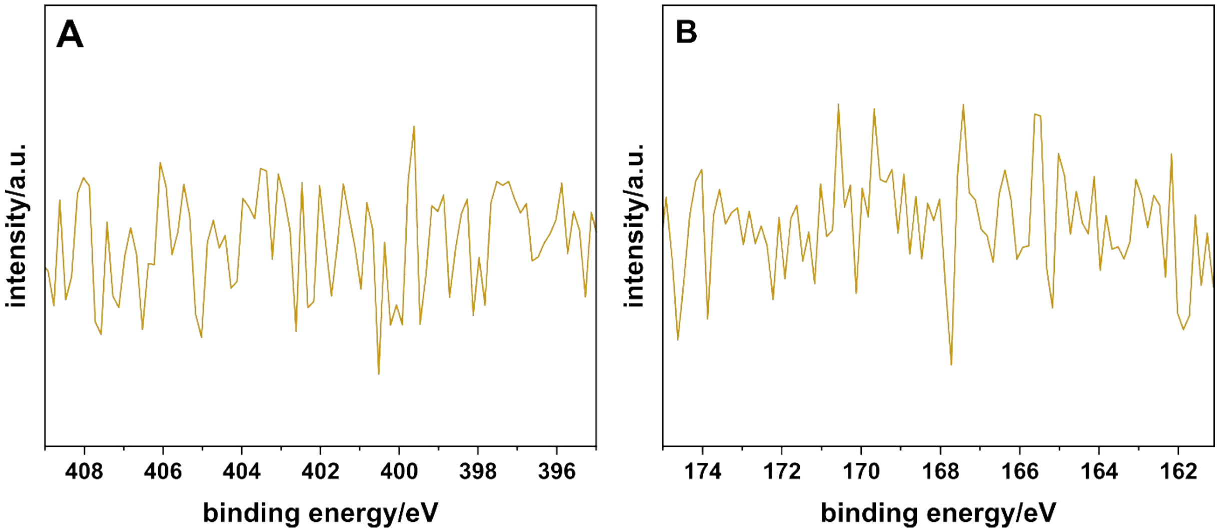

Figure S11. XPS spectra of the C-SPH_850 sample in the binding energy regions of N 1s (A) and S 2p (B).

Literature:

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