Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

# Electronic Supplementary Information

## Carbon nanotube containing polyacrylonitrile materials for the efficient oxygen evolution reaction – correlation of electron transfer and substrate adsorption

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# 1 Content

# 2 Experimental

Chemicals were purchased from ACS (ammonium persulfate), Chemsolute (EtOH, KOH), Metrohm (KCl electrolyte solution), Sigma-Aldrich (acrylonitrile, Nafion solution (5%), multiwalled carbon nanotubes), and Westfalen ($N_2$, $CO_2$).

## 2.1 Catalyst preparation

Typically, CNT were dispersed in 6 mL deionised water (varying amounts see Table S1) under sonication for 30 min. Then, acrylonitrile (2.4 g) and 6 mL EtOH were added to the solution and stirred for 5 min. Afterwards, 0.4 mL of a ammonium persulfate solution (180 mg/mL APS in water) was added and stirred for 3 min at RT. The obtained black homogeneous aqueous solution was stirred at 70 °C for 7 h under inert gas atmosphere. The solution quickly solidified. The as-made polymer monolith was dried at RT and at 50 °C for 24 h each followed by stabilization at 270 °C for 4h in air and carbonisation at 800 °C for 2h under $N_2$ atmosphere. The sample was heated with 3 K/min and a gas flow of 100 mL/min was used. After pyrolysis, the sample was also activated in $CO_2$ at 900 °C. Therefore, the sample was heated to 900 °C in $N_2$-atmosphere with 5 K/min. When the desired temperature was reached, the gas was changed to $CO_2$ for 1 h. Cooling took place under $N_2$-atmosphere.

**Table S1:** Amount CNT for synthesis of the different PAN-CNT composite materials.

| **Name** | **m(CNT) [mg]** |
|---|---|
| PAN-0%CNT | 0 |
| PAN-1.5%CNT | 36 |
| PAN-2.9%CNT | 72 |
| PAN-5.6%CNT | 144 |
| PAN-12.8%CNT | 360 |
| PAN-23.1%CNT | 720 |
| PAN-42.9%CNT | 1800 |

## *2.2 Electrochemical measurments*

Electrochemical measurements were performed using an Autolab PGSTAT 302 N electrochemical workstation with a three-electrode cell. A glassy carbon rod and Ag/AgCl (in 3 M KCl solution) were used as the counter electrode and reference electrode, respectively. A rotating disk electrode (glassy carbon electrode, 4 mm diameter, 0.126 cm$^2$ surface) impregnated with a catalyst was used as the working electrode. Typically, 2.2 mg catalyst was mixed with 400 µL Nafion solution (49 v% $H_2O$, 49v% EtOH and 2v% Nafion solution) followed by a treatment in an ultrasonic bath to obtain a well-dispersed suspension. 5 µL catalyst ink was dropped onto the glassy carbon electrode to obtain a catalyst loading of 0.24 mg cm$^{-2}$ and was dried under atmospheric conditions. The measurements were carried out at room temperature in a 1 M KOH solution (pH = 13.55). Before recording any data, the catalysts were first subjected to continuous potential cycling (CV) until steady voltammograms were obtained (100 CVs @ 0.1 V/s). Afterwards linear sweep voltammetry (LSV) was carried out in a potential range of 1.00 to 1.86V at a rotation speed of the working electrode of 2500 rpm and a scan rate of 0.1 V/s. Double layer capacitances were measured by cyclic voltammetry scans at various scan rates in the range 1.0 to 1.1 V vs. RHE. Electro-chemical impedance spectroscopy (EIS) was performed at an over potential of 179 mV with an amplitude of the sinusoidal voltage perturbation of 10 mV over a frequency range of 100 kHz to 50 mHz.

The chronoamperometric measurement was carried out by keeping the material at a current density of 10 mA/cm$^2$. The measurement was stopped when the potential increased to values above 1.9 V.

### 2.3 Characterisation

The materials were characterized using $N_2$-Physisorption, water vapour physisorption, XRD, XPS, Raman Spectroscopy, SEM and CHN-analysis. X-ray photoelectron spectroscopy (XPS) data were obtained on a Phi5000 VersaProbe II spectrometer (ULVAC-Phi Inc., USA) using $Al_{K\alpha}$ as the excitation source (1.486 keV) and operated at 15 kV. Elemental analysis was conducted on a 2400 CHNS/O Series II System by PerkinElmer, $N_2$-physisorption on a Quadrasorb SI by Quantachrome Instruments (materials were degassed in a FloVac Degasser by Quantachrome Instruments in vacuum at 393 K for at least 4 h) and SEM on a SU-9000 by Hitachi. The Raman spectra were taken with a confocal WITec Alpha 300R microscope, equipped with a 532nm solid state laser. X-ray diffraction measurements were performed with a Siemens D5000 diffractometer with Cu Kα (λ = 0.15409 nm, 40 kV, 40 mA) radiation and a scanning step width of 0.02°. Water vapor physisorption isotherms were measured at 20 °C on an Autosorb iQ by Quantachrome Instruments (materials were degassed in a FloVac Degasser by Quantachrome Instruments in vacuum at 393 K for at least 4 h). In order to relate the pore volume occupied by adsorbed water at high relative pressure to the total pore volume in the sample, the pore filling degree was calculated as quotient of the pore volume from water adsorption at p/p0=0.95 and the total pore volume determined from $N_{2-}$physisorption.

## 3 physisorption.Activation of PAN-CNT materials

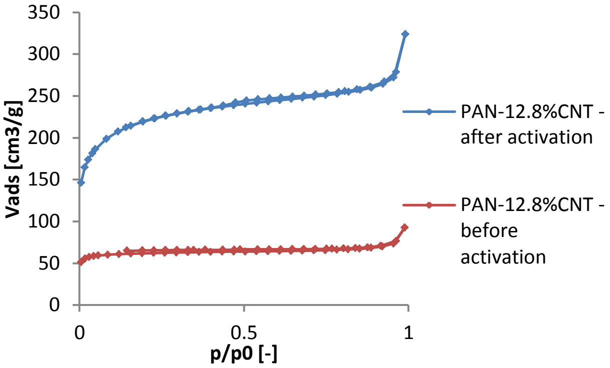


**Figure S1:** $N_2$-physisorption isotherms for PAN-12.8%CNT before and after activation with $CO_2$.

## 4 N₂-physisorption measurement of PAN-CNT materials

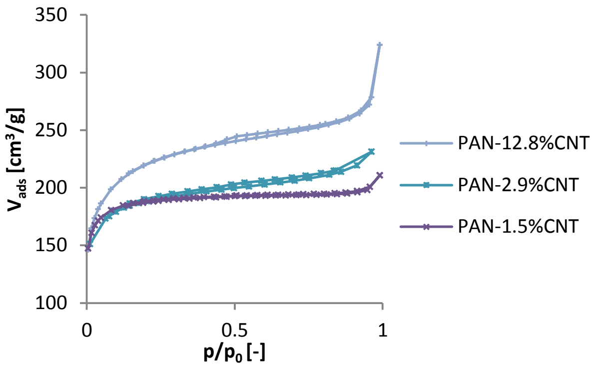


**Figure S2:** $N_2$-physisorption isotherms for prepared catalysts.

## 5 XRD analysis of PAN-CNT materials

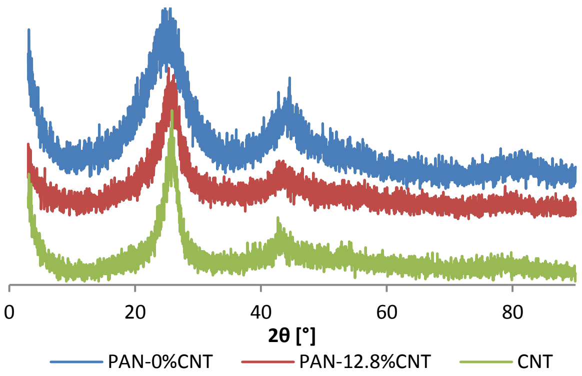


**Figure S3:** XRD analysis of PAN-CNT materials.

# 6 Water vapor physisorption measurement of PAN-CNT-materials - overview

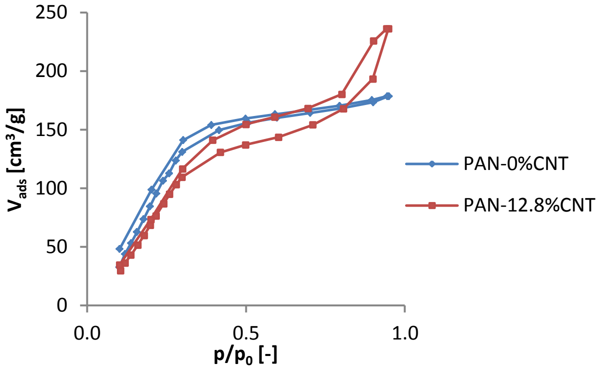


**Figure S4:** Water vapor physisorption isotherms for prepared catalysts.

# 7 Water vapor physisorption measurement of PAN-CNT-materials – low partial pressure

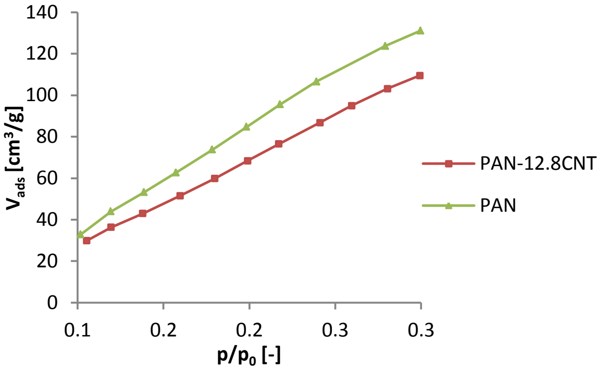


**Figure S5:** Water vapor physisorption adsorption isotherms for prepared catalysts in low partial pressure region.

# 8 Raman spectroscopy

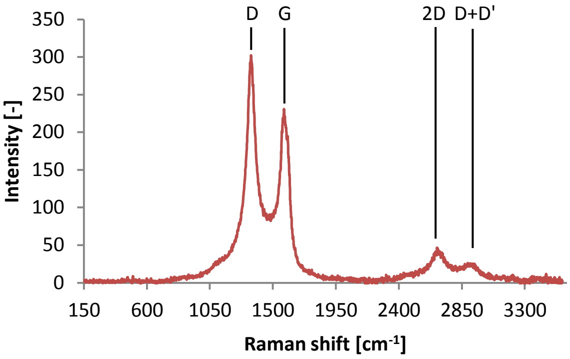


**Figure S6:** Full Raman spectrum for PAN-12.8%CNT.

# 9 Calculation of the Electrochemical surface area (ECSA)

$$ECSA = \frac{c_{DL}}{c_S} \cdot S_g \tag{S1}$$

| | |
|---|---|
| $ECSA$ | electrochemical surface area [-] |
| $c_{DL}$ | double layer capacitance [F/cm$^2$] |
| $c_s$ | substrate capacitance (0.026 mF cm$^{-2}$ for solid materials)[22] |
| $S_g$ | geometric surface area [m$^2$] |

# 10 Determination of the double layer capacitance $c_{DL}$

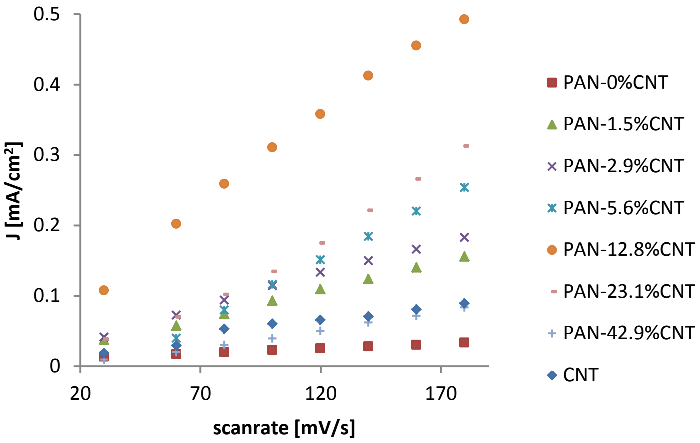


**Figure S7:** Double layer capacitance ($c_{DL}$) measurements for prepared catalysts.

**Table S2:** Values of the double layer capacitance ($c_{DL}$) for prepared catalysts.

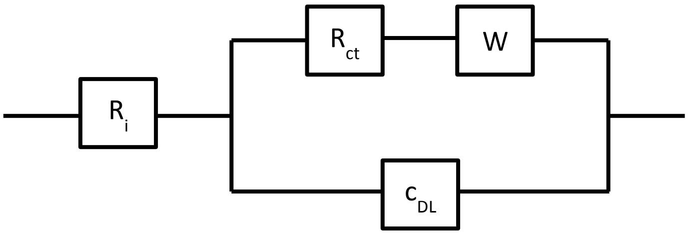
| **Catalyst** | $c_{DL} = \frac{m}{2}$ **[mF/cm²]** |
|---|---|
| PAN | 0.07 |
| PAN-1.5%CNT | 0.40 |
| PAN-2.9%CNT | 0.47 |
| PAN-5.6%CNT | 0.89 |
| PAN-12.8%CNT | 1.25 |
| PAN-23.1%CNT | 0.83 |
| PAN-42.9%CNT | 0.25 |
| CNT | 0.23 |

# 11 Calculation of the normalised activity ($J_{ECSA}$)

$$J_{ECSA} = \frac{J_{1.6\,V}}{ECSA} \tag{S2}$$

| | |
|---|---|
| $J_{ECSA}$ | normalised activitiy [mA/cm$^2$] |
| $J_{1.6V}$ | current density at 1.6 V [mA/cm$^2$] |

# 12 Randles circuit



**Scheme S1:** Randles circuit.

# 13 Calculation of the exchange current density

$$j_0 = \frac{R \cdot T}{n \cdot F \cdot \frac{R_{ct}}{s_g}} \tag{S3}$$

| | |
|---|---|
| $j_0$ | exchange current density [A/m$^2$] |
| $R$ | ideal gas constant [J/(K·mol)] |
| $T$ | Temperature [K] |
| $n$ | number of transferred electrons [-] |
| $F$ | Faraday constant [C/mol] |
| $R_{ct}$ | charge transfer resistance [Ω] |

# 14 Overpotential, normalised activity and exchange current density of the prepared electrocatalysts

**Table S3:** Overpotential (OP), normalised activity and exchange current density ($j_0$) of the prepared electrocatalysts.

| CNT amount [%] | OP [mV] at 10 mA/s | normalised activity [mA/cm$^2$] | $j_0$/10$^{-10}$ [mA/cm$^2$] |
|---|---|---|---|
| 0 | - | 0.266 | 0.046 |
| 1.5 | 600 | 0.186 | 0.129 |
| 2.9 | 487 | 0.269 | 0.088 |
| 5.6 | 475 | 0.561 | 0.171 |
| 12.8 | 368 | 1.490 | 1.149 |
| 23.1 | 440 | 0.240 | 0.448 |
| 42.9 | 490 | 0.864 | 0.142 |
| 100 | 540 | 0.599 | 0.054 |

# 15 Stability of PAN-12.8%CNT

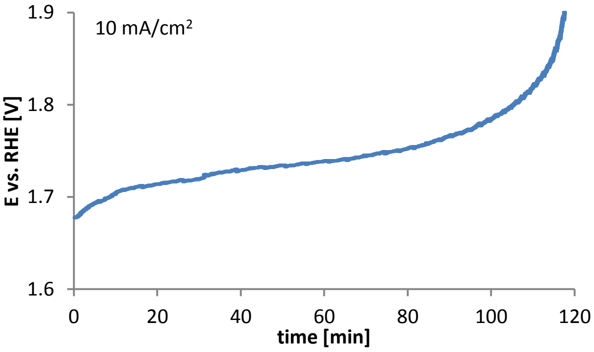


**Figure S8:** Chronoamperometric response at a constant current density of 10 mA/cm$^2$ for PAN-12.8%CNT.