

Supplementary Information for

**Effects of N-functional groups on the electron transfer kinetics of
VO²⁺/VO₂⁺ at carbon: Decoupling morphology from chemical
effects using model systems**

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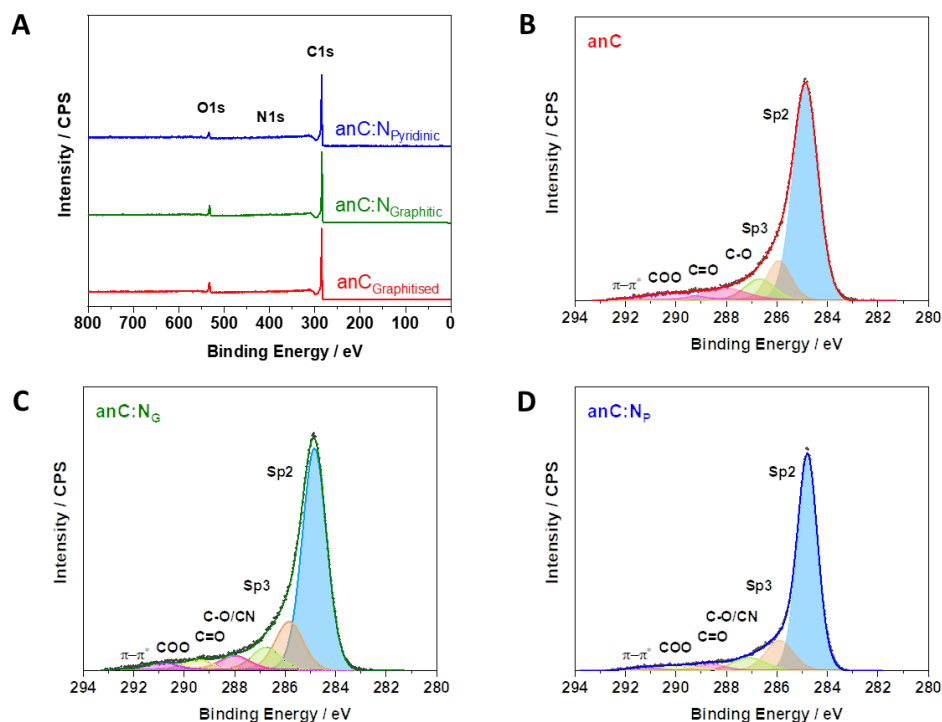


Figure S1. XPS characterization of anC (red line), anC:N_G (green line) and anC:N_P (blue line) catalysts. The figure shows survey spectra (A) and C1s fits (B, C and D). (C) and (D) and details of their analysis can be found in our previous work [1].

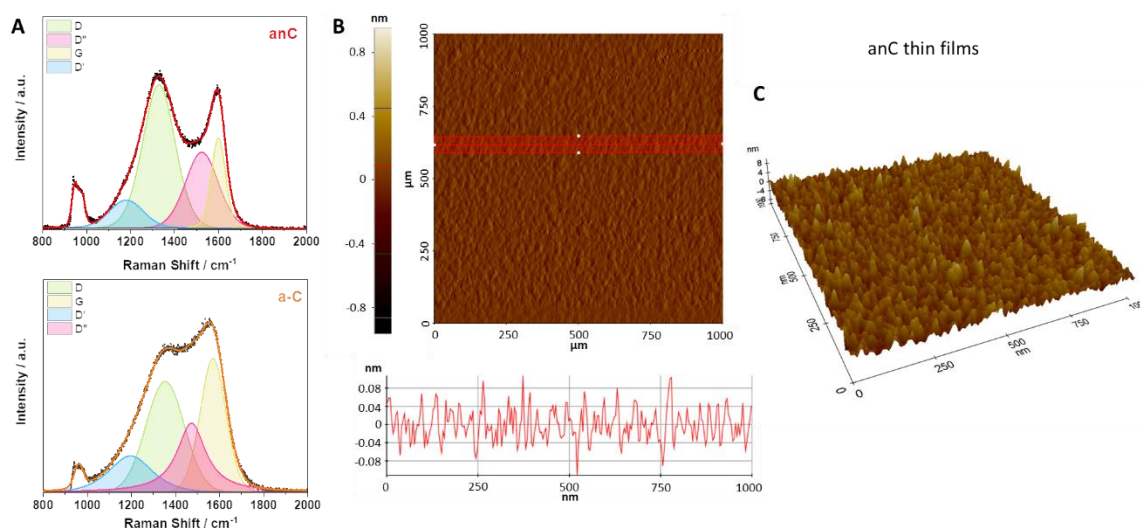


Figure S2. Raman spectra of carbon thin films prepared by sputtering (a-C) and after annealing (anC) (A). AFM characterization of roughness (B) and topography (C) of anC.

Table S1. Summary of sample fabrication processes.

Sample	Sputtering gas	High temperature treatments
anC	Ar, 50 sccm	N ₂ , 200 sccm 1 h @900 °C
anC:N _G	N ₂ /Ar, 1/49 sccm	N ₂ , 200 sccm 1 h @900 °C
anC:N _P	Ar, 50 sccm	a. N ₂ , 200 sccm 1 h @900 °C b. NH ₃ /N ₂ 100/100 sccm 0.5 h @900 °C

Table S2. Raman parameters, %-content of trigonally bonded carbons (C_{sp^2}/C_{tot}) and water contact angle (WCA) for carbon thin films tested. C_{sp^2}/C_{tot} was estimated as the %-area of the component at 284.6 eV in the C1s high-resolution XPS spectrum. Data for anC:N_P and anC:N_G are discussed and reported in previous work [1] and are shown here for comparison purposes.

Carbon electrodes	Bands (cm ⁻¹)		Interbands (cm ⁻¹)		I _D /I _G ratio	C _{sp²} /C _{tot}	WCA
	D	G	D*	D''			
anC	1327.6	1521.9	1161.8	1599.9	1.11	68%	85° ± 2°
anC:N _G	1343.1	1595.9	1206.1	1510.0	1.33	68%	84° ± 2°
anC:N _P	1319.2	1599.1	1177.3	1510.0	1.39	71%	69° ± 4°

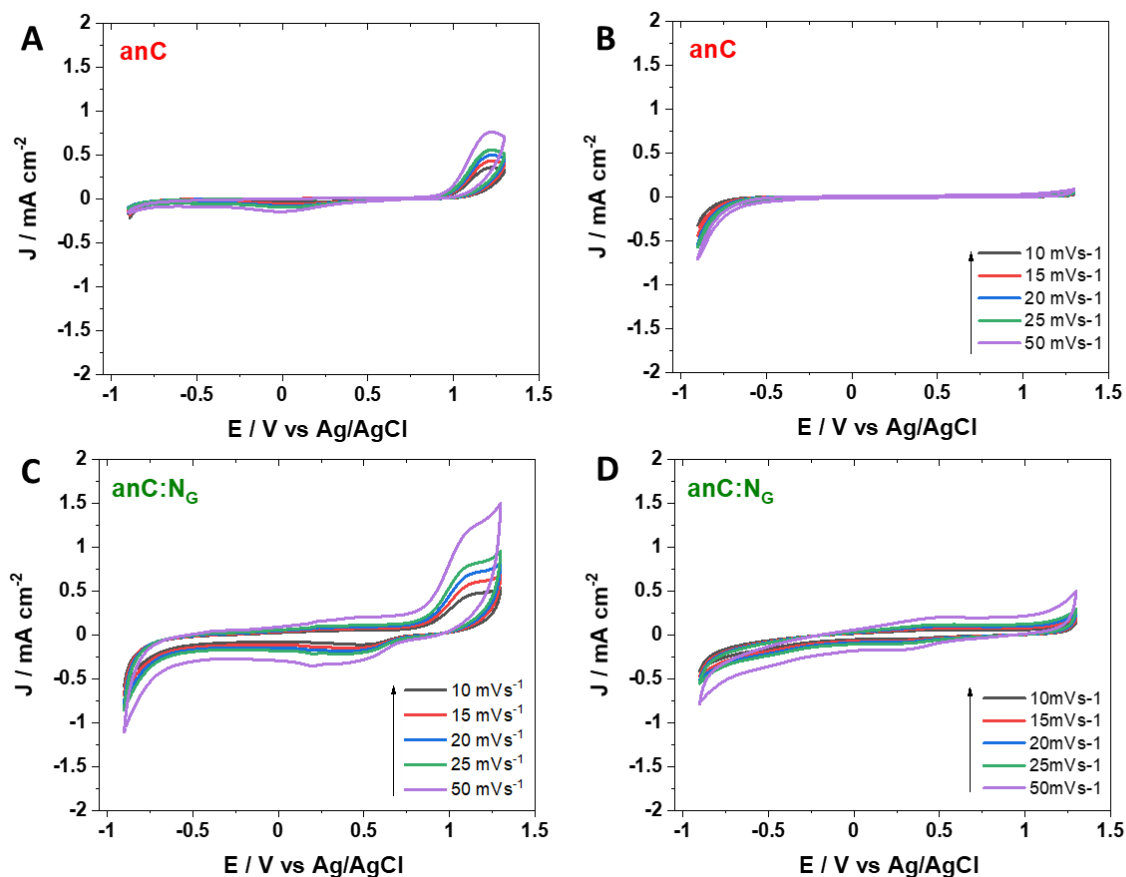


Figure S3. Cyclic voltammograms at scan rates from 10 to 50 mVs⁻¹ in 1.5 M H₂SO₄ with 15 mM VOSO₄ of anC and anC:N_G (A and C); the respective capacitive CVs are shown in panels (B and D).

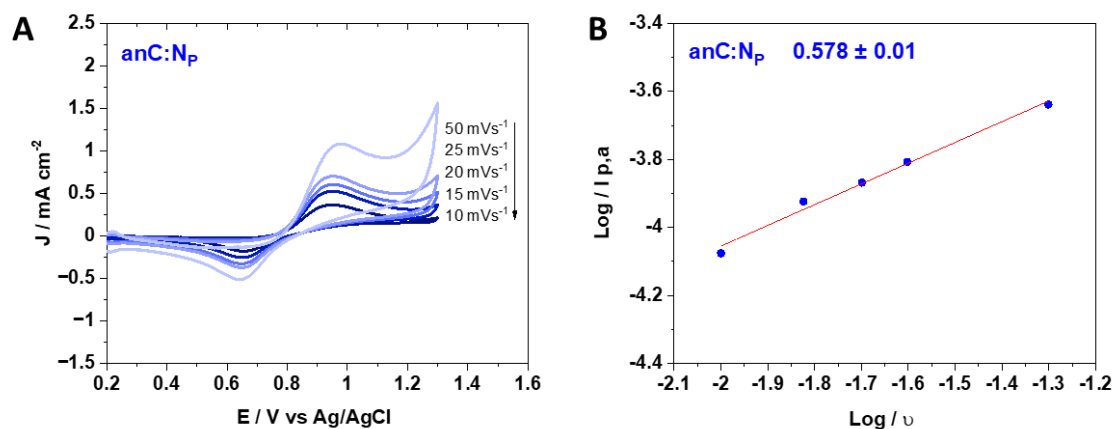


Fig S4. (A) CVs of anC:N_P electrodes obtained as a function of scan rate (10 to 50 mV s⁻¹) in 0.015 M VO²⁺/1.5 M H₂SO₄. (B) Representative log-log plot of anodic peak current (*I*_{pa}) vs. scan rate (*ν*) for anC:N_P obtained from CVs in 1.5 M H₂SO₄ with 15 mM VOSO₄. Slope values calculated from three separate disks are also shown in the graph.

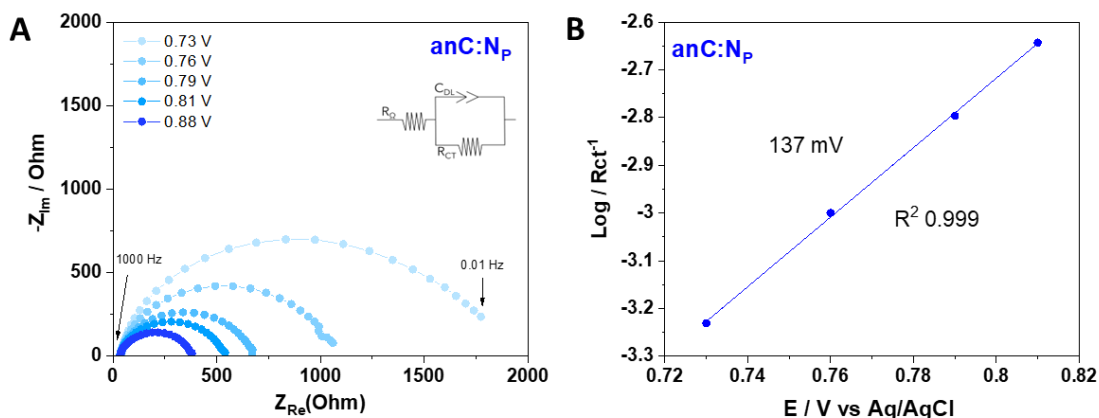


Figure S5. (A) Nyquist plots at 1600 rpm in 1.5 M H_2SO_4 with 15 mM VOSO_4 and the circuit used to extrapolate the impedance parameters of anC: N_P shown in table S2. (B) Tafel plot and slope obtained over potential range of 0.7 to 0.8 V.

Table S3. Electrochemical parameters of a anC: N_P disk electrode obtained by Nyquist plot fits over a potential range between 0.71 and 0.88 V vs Ag/AgCl at 1600 rpm in 1.5 M H_2SO_4 + 15 mM VOSO_4 (all fit errors were <0.5%).

Potential (V vs Ag/AgCl)	R_Ω (Ω)	R_{ct} (Ω)	T ($\text{F s}^{\text{p-1}}$)	p
0.73	37.7	1702	7.8×10^{-4}	0.91
0.76	36.0	999.5	7.2×10^{-4}	0.91
0.79	34.8	625.4	7.2×10^{-4}	0.91
0.81	34.2	439.3	7.1×10^{-4}	0.91
0.88	34.4	341.3	7.6×10^{-4}	0.9

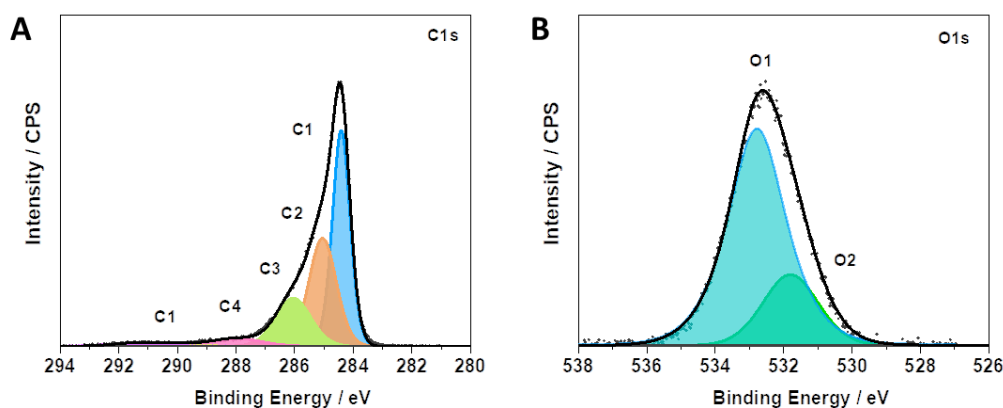


Figure S6. High resolution XPS spectra in the (A) C 1s and (B) O 1s regions of anC-EPy samples.

Table S4. Summary of peak positions and atomic %-compositions obtained from best fits of XPS spectra of anC-EPy together with suggested assignments based on prior literature.

	At. %	Suggested assignment	BE (eV)	%-area	Ref.
N 1s	5.9	Weakly H-accepting pyridyl	399.3	65	[2]
		N=N azo-groups	400.5	26	[3]
		Protonated pyridyl	401.9	9.0	[2, 4]
O 1s	9.4	Hydroxide	531.8	22.5	[2]
		H-donating water	532.8	77.5	[2]
C 1s	85	sp^2 -C in substrate, C in <i>meta</i> & <i>para</i> in pyridine	284.4	42	[2]
		C-N in azo-linkers and pyridine	285.0	33	[2, 5]
		C-N in protonated pyridine	286.0	18	[6, 7]
		substrate C=O and/or shake up in polyphenyls	288.0	4.6	[2, 7-9]
		Shake-up	291.0	2.4	[8]

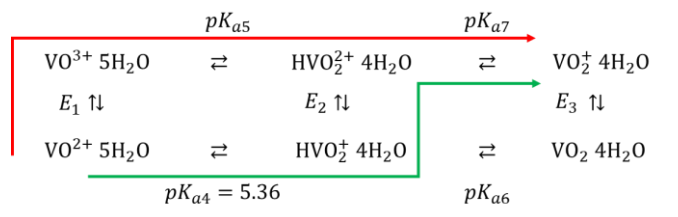


Figure S7. Reaction mechanisms as proposed by Gattrell et al. [10] with evidenced ECC (red), CEC (green) and CCE (blue) pathways. The value of pK_{a4} is known from [11].

Details of voltammogram simulations

Finite element simulations (FES) were carried out using an axisymmetric model using COMSOL Multiphysics 5.4 software. A scheme of the simulated heterogeneous E step and homogenous C step for the involved i species (i being VO^{2+} , intermediate VO^{3+} or final product VO_2^+) is shown in **Fig. S8A**. **Fig. S8B** shows the implemented geometry with the corresponding boundaries and domains highlighted. Coordinates and boundary conditions are listed in **Table S5**; parameters used in the simulation are summarized in **Table S6**. Initial conditions set concentrations in the electrolyte domain as $c_{VO^{2+}} = 15 \text{ mM}$, $c_{VO^{3+}} = 0 \text{ mM}$ and $c_{VO_2^+} = 0 \text{ mM}$. A time-dependent simulation was solved with an intermediate time step of 0.1 s. The scan rate used for the simulation is equal of the experimental value of 0.020 V s^{-1} . Simulations were carried out with triangular mesh elements with highest resolution near the solution/electrode interface with a maximum element size of 1/200 of the $r_{electrode}$. **Figure S8C** shows an image of the mesh used for all simulations.

The time-dependent diffusion transport of i species within the domain was simulated using Fick's second law:

$$\frac{\partial c_i}{\partial t} - D_i \nabla^2 c_i = 0 \quad (\text{Eq. S1})$$

where c_i is the concentration of i species, D_i is their diffusion coefficient and t is time.

For the E step, the flux of electrochemically active species (VO^{2+} and VO^{3+}) at the electrode surface is defined by Butler-Volmer kinetics:

$$k_{an} = k^0 e^{\left(\frac{(1-\alpha)F\eta}{RT}\right)} \quad (\text{Eq. S2})$$

$$k_{cat} = k^0 e^{\left(\frac{-\alpha F\eta}{RT}\right)} \quad (\text{Eq. S3})$$

where F is Faraday's constant, k^0 is the standard heterogeneous electron transfer rate constant in cm s^{-1} , $\alpha = 0.5$, R is the ideal gas constant, $T = 298 \text{ K}$, $\eta = E - E^0$ is the overpotential, where $E^0 = -0.802 \text{ V vs sat. Ag/AgCl}$ and E is the electrode potential, ramped at 0.020 V s^{-1} .

For the C step, the variation of the participating species (VO^{3+} and VO_2^+) is defined by rate constants k_{cf} and k_{cr} with units of s^{-1} and $K = k_{cf}/k_{cr}$ (see **Table S5**). The range of k^0 , k_{cf} and k_{cf}/k_{cr} values were generated by a geometric progression as:

$$\text{parameter} = a_1 \cdot r^{(n-1)} \quad (\text{Eq. S4})$$

where a_1 is the initial value of the progression, r is the common ratio and n is the index within the sequence. For instance, the range of k^0 values simulated are obtained by utilizing $a_1 = 1 \cdot 10^{-8} \text{ cm/s}$, $r = 1.05$ and $n = 1:250$. The geometric progression values used to obtain k^0 , k_{cf} and k_{cf}/k_{cr} geometric sequences are reported in **Table S6**.

Best-fits (**Fig. S9 and S10**) were identified by locating the minimum of the sum of square errors (SSE). Uncertainties on best-fit parameters were obtained by identifying the uniqueness range, defined by a 10% increase in SSE relative to the best-fit minimum [12, 13]. The low and high boundaries thus defined for k^0 , k_{cf} and k_{cf}/k_{cr} are reported in **Table S7**. For k^0 the SSE function is one dimensional (**Fig. 5D**) and the uncertainty range can be obtained by interpolation. For k_{cf} and k_{cf}/k_{cr} a bidimensional SSE is generated (**Fig. 6D**) and the 10% criterion yields contours, shown in **Figure S11**. Uncertainties on k_{cf} and k_{cf}/k_{cr} are defined by the maximum and minimum values of the contour (dotted lines in **Fig. S11**).

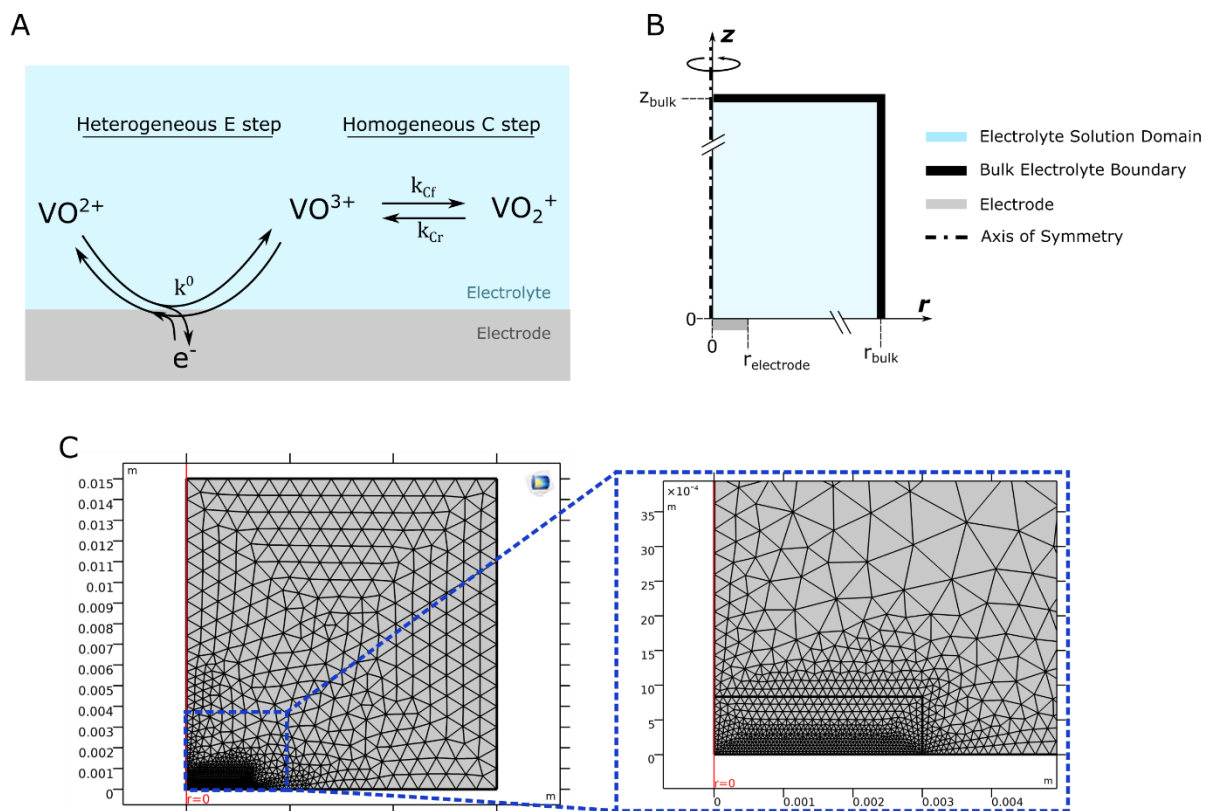


Figure S8. (A) EC reaction scheme used for the simulation of cyclic voltammograms. (B) Electrode geometry used for finite element simulations. (C) Mesh used for finite element simulations (left) and expanded view (right) of the region near the electrode surface.

Table S5: Cylindrical coordinates (r and z) used to describe each boundary and domain in the finite element simulation as detailed in Fig. S8, and corresponding mass transport and chemical reaction conditions. c_i refers to the concentration of i species.

Description	Coordinates		Boundary condition
	z	r	
Axis of Symmetry	$0 \leq z \leq z_{bulk}$	0	—
Bulk Electrolyte (boundaries)	z_{bulk}	$0 \leq r \leq r_{bulk}$	$c_{VO^{2+}} = 15 \text{ mM}$ $c_{VO^{3+}} = 0 \text{ mM}$ $c_{VO_2^+} = 0 \text{ mM}$
	$0 \leq z \leq z_{bulk}$	r_{bulk}	
Inert Surface (boundary)	0	$r_{electrode} \leq r \leq r_{bulk}$	$J = 0$ (No flux)
Electrode Surface (boundary)	0	$0 \leq r \leq r_{electrode}$	$\nabla c_{VO^{2+}} = -k_{an} \cdot c_{VO^{2+}} + k_{cat} \cdot c_{VO^{3+}}$ $\nabla c_{VO^{3+}} = -k_{cat} \cdot c_{VO^{3+}} + k_{an} \cdot c_{VO^{2+}}$
Electrolyte Solution (domain used for E)	$0 \leq z \leq z_{bulk}$	$0 \leq r \leq r_{electrode}$	$\Delta c_{VO^{2+}} = \Delta c_{VO^{3+}} = 0$ (no homogeneous reaction)
Electrolyte Solution (domain used in EC)	$0 \leq z \leq z_{bulk}$	$0 \leq r \leq r_{electrode}$	$\Delta c_{VO^{3+}} = -k_{cf} \cdot c_{VO^{3+}} + k_{cr} \cdot c_{VO_2^+}$ $\Delta c_{VO_2^+} = +k_{cf} \cdot c_{VO^{3+}} - k_{cr} \cdot c_{VO_2^+}$

Table S6: Summary of parameters used for simulations.

Variable symbol	Value	Units	Description
r_{bulk}	15	mm	Radius of the simulated boundary domain.
h_{bulk}	15	mm	Height of the simulated boundary domain.
$r_{electrode}$	2.5	mm	Electrode radius.
k^0	$k^0 = a_1 \cdot r^{(n-1)}$ $a_1 = 1 \cdot 10^{-8}$ $r = 1.05$ $n = 1:250$	cm s^{-1}	Heterogeneous rate constant
k_{cf}^*	$k_{cf} = a_1 \cdot r^{(n-1)}$ coarse: $a_1 = 0.002$ $r = 1.4$ $n = 1:21$ fine <i>anCNp</i> : $a_1 = 0.03$ $r = 1.1$ $n = 1:26$ fine <i>anCNg</i> : $a_1 = 0.012$ $r = 1.1$ $n = 1:26$ fine <i>anC</i> : $a_1 = 0.0025$ $r = 1.1$ $n = 1:26$	s^{-1}	Forward rate constant.
K^*	$K = a_1 \cdot r^{(n-1)}$ coarse: $a_1 = 0.05$ $r = 1.5$ $n = 1:19$ fine <i>anCNp</i> : $a_1 = 0.3$ $r = 1.1$ $n = 1:26$ fine <i>anCNg</i> : $a_1 = 1$ $r = 1.1$ $n = 1:26$ fine <i>anC</i> : $a_1 = 3$ $r = 1.1$ $n = 1:38$	-	k_{cf}/k_{cr} ratio
E^0	0.802	V	Standard potential of $\text{VO}^{2+}/\text{VO}_2^+$ redox couple
α	0.5	-	Butler-Volmer Transfer coefficient
$D_{\text{VO}^{2+}}$	$2.1 \cdot 10^{-6}$	$\text{cm}^2 \text{s}^{-1}$	Diffusion coefficient of VO^{2+}
$D_{\text{VO}_2^+}$	$2.8 \cdot 10^{-6}$	$\text{cm}^2 \text{s}^{-1}$	Diffusion coefficient of VO_2^+
D_{int}	$2.8 \cdot 10^{-6}$	$\text{cm}^2 \text{s}^{-1}$	Diffusion coefficient of VO^{3+} species
$c_{\text{VO}^{2+}}$	15	mM	Initial concentration of VO^{2+} in the electrolyte solution domain
$c_{\text{VO}_2^+}$	0	mM	Initial concentration of VO_2^+ in the electrolyte solution domain
$c_{\text{VO}^{3+}}$	0	mM	Initial concentration of VO^{3+} in the electrolyte solution domain

* *coarse* parameters were used for a first best-fit approach; *fine* parameters were used for refining the best fit values.

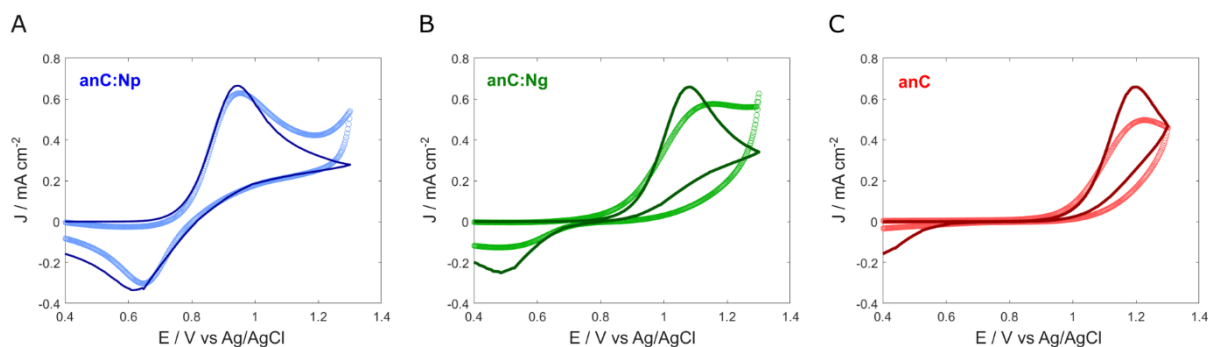


Figure S9. Comparison of experimental CVs for (A) anC:N_P, (B) anC:N_G and (C) anC vs the best fit simulated voltammograms according to an E-mechanism.

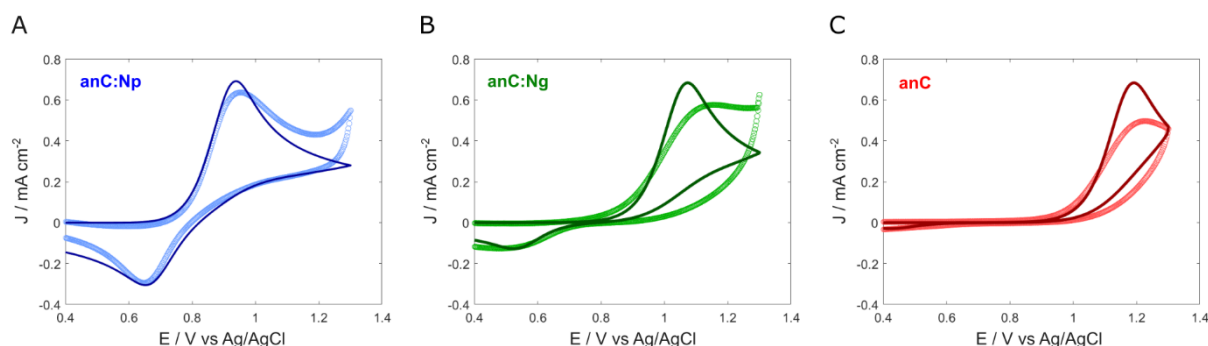


Figure S10. Comparison of experimental CVs for (A) anC:N_P, (B) anC:N_G and (C) anC vs the best fit simulated voltammograms according to an EC mechanism.

Table S7. Summary of best fit parameters and uncertainties; %-values indicate the deviation from the best fit value.

	k^0 (cm/s)			k_{cf} (1/s)			k_{cf}/k_{cr}		
	Low of +10% SSE	min SSE	High of +10% SSE	Low of +10% SSE	min SSE	High of +10% SSE	Low of +10% SSE	min SSE	High of +10% SSE
anC	9.09×10^{-7} [97%]	9.34×10^{-7}	9.97×10^{-7} [107%]	0.0472 [96%]	0.0487	0.0499 [102%]	26.12 [60%]	43.26	104.7 [235%]
anC:N _G	8.71×10^{-6} [94%]	9.25×10^{-6}	10.3×10^{-6} [111%]	0.0451 [90%]	0.050	0.0728 [145%]	1.93 [90%]	2.14	2.20 [103%]
anC:N _P	1.25×10^{-4} [97%]	1.29×10^{-4}	1.30×10^{-4} [101%]	0.0830 [80%]	0.103	0.154 [150%]	0.640 [90%]	0.707	0.812 [115%]

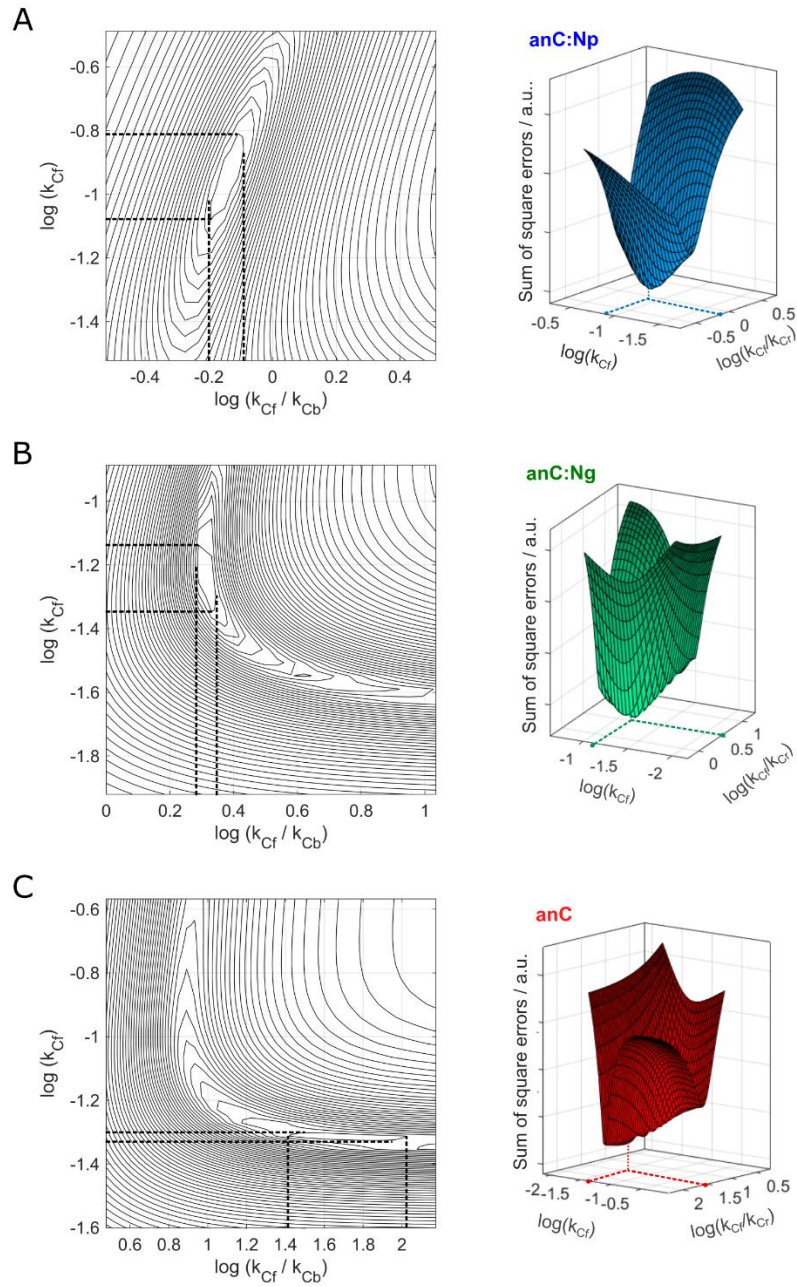


Figure S11: Contour plots (left) and 3D plots (right) of the SSE; the contour plots show the range of values (dotted lines) corresponding to increases of +10% relative to the SSE minimum for (A) anC:N_p, (B) anC:N_G and (C) anC.

Table S8. Selected determinations of charge transfer kinetics parameters for $\text{VO}^{2+}/\text{VO}_2^+$ at different types of carbon electrodes.

Carbon electrodes	j_0 (mA cm ⁻²)	k_0 (cm s ⁻¹)	Methods	Electrolyte concentrations	Ref.
anC		9.34×10^{-7}	CV	0.015 M VOSO ₄ in 1.5 M H ₂ SO ₄	This work
anC:N _G		9.25×10^{-6}	CV	0.015 M VOSO ₄ in 1.5 M H ₂ SO ₄	This work
anC:N _P		1.29×10^{-4}	CV	0.015 M VOSO ₄ in 1.5 M H ₂ SO ₄	This work
anC:N _P		1.02×10^{-4}	EIS	0.015 M VOSO ₄ in 1.5 M H ₂ SO ₄	This work
Graphite electrode	0.109	5.65×10^{-7}	Polarization curve	2.0 M VOSO ₄ in 1-4 M H ₂ SO ₄	[14]
Graphite electrode	-	3.0×10^{-7}	Tafel plot	0.031 M VO ²⁺ , 0.019 M VO ₂ ⁺ , 1 M H ₂ SO ₄	[10]
Smooth carbon- plastic composite	1.26×10^{-4}	1.31×10^{-7} ^a	Tafel plot	0.010 M VO ²⁺ , 0.010 M VO ₂ ⁺ , 2 M H ₂ SO ₄	[15]
Glassy carbon	n/a	1.35×10^{-5}	Tafel plot	0.02 M VOSO ₄ in 2 M H ₂ SO ₄	[16]
Glassy carbon	n/a	4.0×10^{-7}	CV	0.005 M VOSO ₄ in 1 M H ₂ SO ₄	[17]
Oxidized graphite electrodes	n/a	$1.93 - 2.63$ $\times 10^{-3}$	Tafel plot	0.1 M VOSO ₄ in 3.0 M H ₂ SO ₄	[18]
Carbon Fibers (PAN)	n/a	2.5×10^{-5}	Tafel plot	4M VOSO ₄ in 4M H ₂ SO ₄	[19]
N-doped ordered mesoporous carbon	n/a	7.0×10^{-7}	CV	0.050 M VO ²⁺ , 0.050 M VO ₂ ⁺ , 1 M H ₂ SO ₄	[20]
Vulcan XC-72 on GC	1.9–2.62	n/a	Tafel plot	1 M VOSO ₄ in 3M H ₂ SO ₄	[21]
Carbon felt	ca. 3	ca. 10^{-5}	Tafel plot	1.7 M VO ²⁺ /VO ₂ ⁺ 4 M H ₂ SO ₄	[22]
Carbon felt	432 A m ⁻² (j_{00})	2.3×10^{-5}	Polarization curves	5 mM V ^{4/5} in 4 M H ₂ SO ₄	[23]

a – value estimated from reported data.

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