

Supporting Information for

Synergistic effects of surface chemistry and porosity in vanadium redox reactions: from smooth thin films to high surface area carbon electrodes

Maida A. Costa de Oliveira,¹ Runbo Zhang,¹ Christian Schröder,¹ Filippo Pota,¹ Marc Brunet Cabré,¹ Kim McKelvey² and Paula E. Colavita^{1}*

1 - School of Chemistry, Trinity College Dublin, College Green, Dublin 2, Ireland

2 - MacDiarmid Institute for Advanced Materials and Nanotechnology and School of Chemical and Physical Sciences, Victoria University of Wellington, Wellington 6012, New Zealand

* Corresponding author Email: colavitp@tcd.ie

Table S1. Summary of thin film carbon electrodes used in this work and their preparation routes.

Name	Electrode fabrication	Surface modification solution
anC	N-free sputtered carbon thin-film annealed at 900 °C in N ₂	None
anC-Spy	N-free sputtered carbon thin-film annealed at 900 °C in N ₂	4.0 mM 3-aminopyridine in 10 mM NaNO ₂ , 0.5 M HCl
anC-Rpy	N-free sputtered carbon thin-film annealed at 900 °C in N ₂	4.0 mM 3-aminopyridine in 10 mM NaNO ₂ , 0.5 M HCl and 80 mM H ₃ PO ₂
anC-R	N-free sputtered carbon thin-film annealed at 900 °C in N ₂	10 mM NaNO ₂ , 0.5 M HCl and 80 mM H ₃ PO ₂

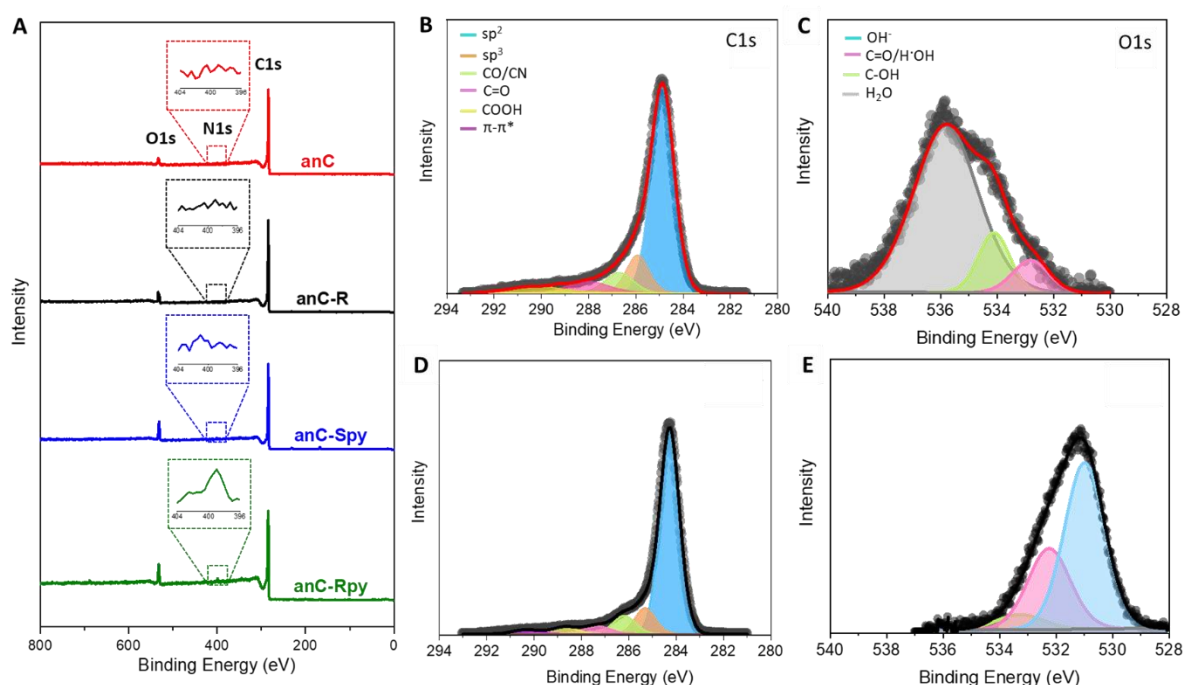


Figure S1. (A) Survey XPS spectra of anC, anC-Spy, anC-Rpy and anC-R samples. High resolution spectra and best-fits in the C 1s regions for (B) anC and (D) anC-R. High resolution spectra and best-fits in the O 1s regions for (C) anC and (E) anC-R. Assignments and positions are summarised in Table S2.

Table S2. Summary of peak positions, assignments and %-atomic compositions obtained from best-fits of C 1s, N 1s and O 1s spectra.

		anC ^a		anC-Spy		anC-Rpy		anC-R	
C 1s	Atomic-%	95.7%		90.0%		92.9%		91.4%	
		BE (eV)	%A	BE (eV)	%A	BE (eV)	%A	BE (eV)	%A
	sp ² -C [1, 2]	284.6	67.6	284.6	78.3	284.6	72.3	284.6	73.6
	sp ³ -C/CN [3, 4]	285.5	11.9	285.7	8.5	285.7	16.6	285.6	9.5
	CO/CNH ⁺ [5, 6]	286.4	7.4	286.6	6.1	286.6	2.7	286.5	7.6
	C=O [4, 6, 7]	287.5	5.7	287.8	2.7	287.8	3.8	287.6	3.9
	COOH [1, 2]	288.7	2.1	289.2	2.3	289.2	2.7	289.0	3.3
	π - π^* [7]	290.1	5.3	290.8	2.1	290.8	1.9	290.6	2.1
O 1s	Atomic-%	4.3%		9.0%		5.7%		8.6%	
		BE (eV)	%A	BE (eV)	%A	BE (eV)	%A	BE (eV)	%A
	OH ⁻ [4]	-	-	531.5	61.8	531.6	37.9	531.8	57.5
	C=O/H-bonded	532.6	8	532.7	31.6	532.5	52.6	532.9	33.9
	H ₂ O[1, 2, 4]	533.9	14	533.8	6.6	533.6	9.5	533.9	8.6
	C-OH[1, 2]	535.6	78	-	-	-	-	-	-
	Mol. H ₂ O[1, 2, 4]								
N 1s	Atomic-%	1.0		1.4					
		BE (eV)	%A	BE (eV)	%A	BE (eV)	%A	BE (eV)	%A
	Pyridinic-N [4]	399.2	36.3	399.1	70.4				
	-N=N- [8-10]	400.7	22.0	400.6	17.5				
	Pyridinium-N [4, 11]	401.9	41.7	401.8	12.1				

a – Details of the analysis of anC surfaces can also be found in our previous work [12].

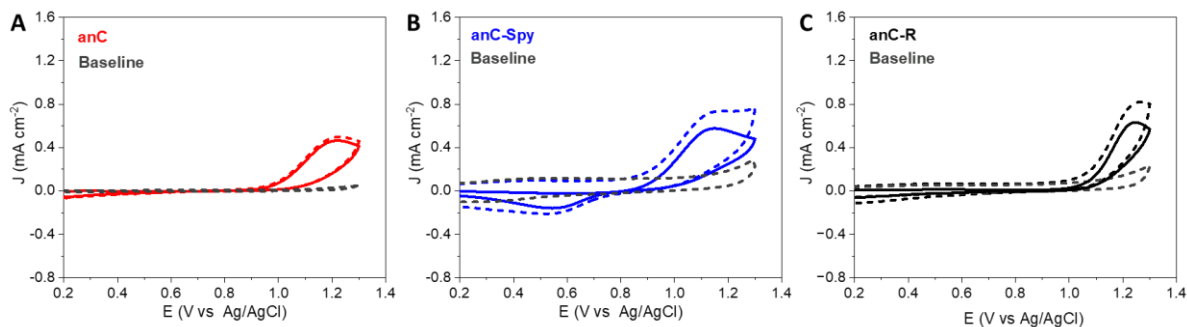


Figure S2. Cyclic voltammograms at scan rate 0.020 V s^{-1} in $1.5 \text{ M H}_2\text{SO}_4$ (dark grey dashed line), and in 15 mM VOSO_4 in $1.5 \text{ M H}_2\text{SO}_4$ (colored dashed lines) of anC (red), anC-Spy (blue) and anC-R (black). Solid traces show the capacitance-corrected CV obtained after subtraction.

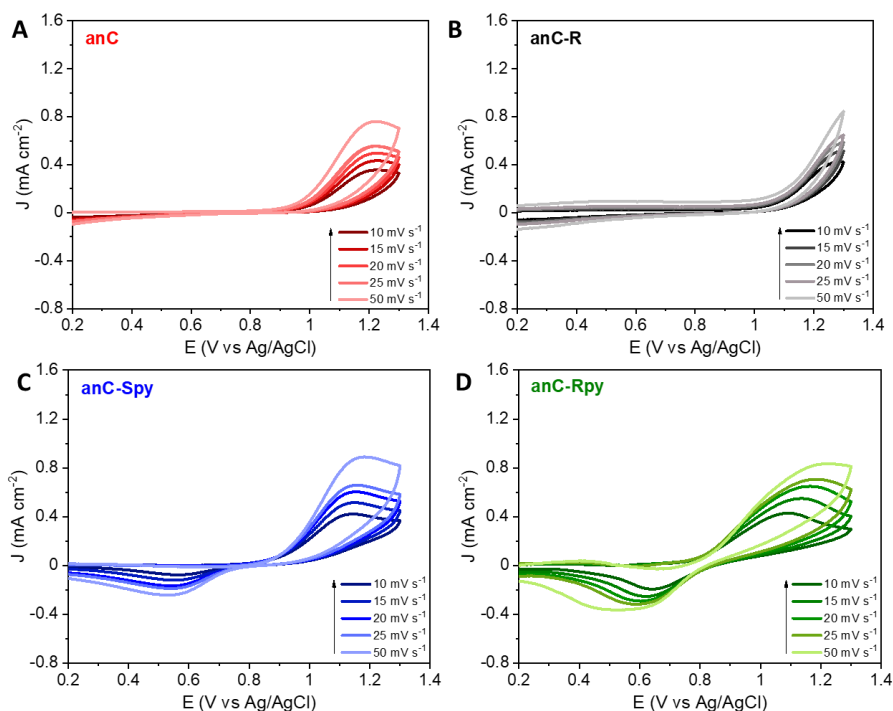


Figure S3. Cyclic voltammograms with capacitance contributions were corrected and recorded at scan rates from 0.05 to 0.01 V s^{-1} under 15 mM VOSO_4 in $15 \text{ M H}_2\text{SO}_4$ electrolyte.

Table S3. Peak current densities ($J_{a,p}$ and $J_{c,p}$) obtained at 20 mV s^{-1} from capacitance-corrected CV curves in 15 mM VO_2 in $1.5 \text{ M H}_2\text{SO}_4$; slope values for log-log plots of current density vs scan rate; and capacitance values calculated from CV at 20 mV s^{-1} in $1.5 \text{ M H}_2\text{SO}_4$ (0.2 – 0.8 V range).

Electrodes	$J_{a,p}$ (mA/cm ²)	$J_{c,p}$ (mA/cm ²)	Slope of Log j -Log ν	C @20 mV s ⁻¹ (mF/cm ²)
anC	0.49 @ 1.2 V	-0.09 @ 0.05 V	0.42	0.28
anC-R	0.63 @ 1.2 V	-0.06 @ 0.1 V	0.39	2.01
anC-Spy	0.60 @ 1.1 V	-0.16 @ 0.5 V	0.42	4.22
anC-Rpy	0.62 @ 1.1 V	-0.29 @ 0.6 V	0.39	12.5

Text S1. Details of simulations

COMSOL Multiphysics 5.4 was used to carry out finite element simulations (FES) of the anodic waves of the voltammograms, following the same approach reported in our previous work [12]. The heterogeneous E-step and the electrode geometry used are shown in **Figure S4**, with the simulation boundaries highlighted in the scheme. The reaction cell was axisymmetric and defined as a cylinder with radius r_{bulk} and height z_{bulk} defined both at 15 mm; at the centre of this cylinder, an electroactive circular area of radius $r_{el} = 2.5$ mm was positioned, matching the radius of disk electrodes used in our experiments. Coordinates and boundary conditions are listed in **Table S4**, and parameters used are listed in **Table S5**.

A triangular mesh was used, with the highest resolution near the electrode surface set to have a maximum element size equivalent to $r_{el}/200$. To control the precision near the electrode surface, an auxiliary rectangular region with a maximum element size of $r_{el}/50$ and a maximum growth rate of 1.05 was also defined (**Figure S4**). The concentrations of the i species ($i = \text{VO}^{2+}$ or VO^{3+}) were matched to those in the electrolyte at time zero, and the scan rate v was set at 20 mV s^{-1} to replicate the experimental conditions. The time-dependent simulation was solved with an intermediate time step of 0.1 s. The diffusion of the i species in solution followed Fick's law:

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

Where C_i is the concentration, t is time and D_i is the diffusion coefficient of the i species. We assumed no convection or other migration mechanisms within the cell. The diffusion coefficient for VO^{2+} was set at its literature value of $2.1 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, whereas that of VO^{3+} was set to that of the pervanadyl final product VO_2^+ , as in our previous report [12]. Butler-Volmer kinetics was used to describe the flux at the electrode surface, according to:

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

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

Where k^0 is the electrochemical rate constant (cm s^{-1}), α is the electron transfer coefficient, assumed to be 0.5, F is Faraday's constant, $\eta = E - E^0$ is the overpotential, R is the ideal gas constant, $T = 298$ K. The equilibrium potential was set at $E^0 = + 0.802$ V vs. Ag/AgCl. The flux of species at the electrode surface resulting from the overpotential was thus calculated as:

$$\nabla c_{\text{VO}^{2+}} = -k_{\text{anodic}} \cdot c_{\text{VO}^{2+}} + k_{\text{cathodic}} \cdot c_{\text{VO}^{3+}} \quad (\text{Eq. S4})$$

The current density was calculated from the surface integral of the net flux of species VO^{2+} . Voltammograms with a geometric progression series of k^0 values were simulated using a parametric sweep. The sum of square errors (SSE) of each voltammogram was calculated using the simulated and experimental curves over potential windows between the onset and the peak. The minima of the SSE vs k^0 yielded the best estimate of k^0 for each sample and uncertainties were determined as the range of k^0 values corresponding to a 10% increase in SSE in the interpolated SSE versus k^0 plot [12, 13].

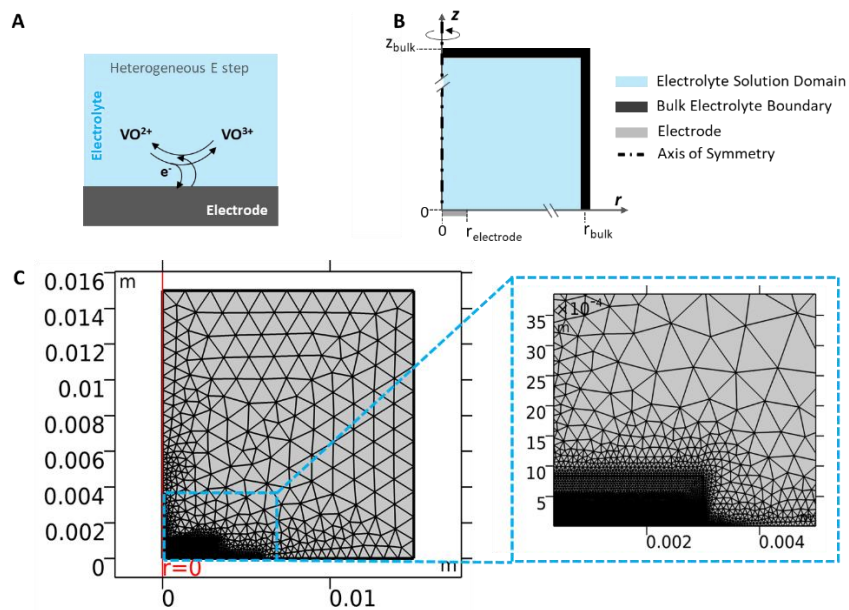


Figure S4. (A) Scheme of the simulated E-step. (B) Electrode and cell geometry used for the simulation of cyclic voltammograms. (C) Details of the mesh used for finite element simulations showing an expanded view of the region near the electrode surface.

Table S4: 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	$0 \leq z \leq z_{\text{bulk}}$	0	—
Bulk Electrolyte (boundaries)	z_{bulk}	$0 \leq r \leq r_{\text{bulk}}$	$c_{\text{VO}^{2+}} = 15 \text{ mM}$ $c_{\text{VO}_2^+} = 0 \text{ mM}$
	$0 \leq z \leq z_{\text{bulk}}$	r_{bulk}	
Inert Surface (boundary)	0	$r_{\text{electrode}} \leq r \leq r_{\text{bulk}}$	$J = 0$ (No flux)
Electrode Surface (boundary)	0	$0 \leq r \leq r_{\text{electrode}}$	$\nabla c_{\text{VO}^{2+}} = -k_{\text{an}} \cdot c_{\text{VO}^{2+}} + k_{\text{cat}} \cdot c_{\text{VO}_2^+}$ $\nabla c_{\text{VO}_2^+} = -k_{\text{cat}} \cdot c_{\text{VO}_2^+} + k_{\text{an}} \cdot c_{\text{VO}^{2+}}$
Electrolyte Solution (domain used for E)	$0 \leq z \leq z_{\text{bulk}}$	$0 \leq r \leq r_{\text{electrode}}$	$\frac{dc_{\text{VO}^{3+}}}{dt} \approx 0$ (assumed rapid chemical reaction)

Table S5: Summary of parameters used for simulations.

Variable symbol	Value	Units	Description
r_{bulk}	15	mm	Radius of the simulated boundary domain.
z_{bulk}	15	mm	Height of the simulated boundary domain.
$r_{\text{electrode}}$	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
E^0	0.802	V	Standard potential of $\text{VO}_2^{2+}/\text{VO}_2^+$ redox couple
α	0.5	-	Butler-Volmer Transfer coefficient
$D_{\text{VO}_2^{2+}}$	$2.1 \cdot 10^{-6}$	$\text{cm}^2 \text{s}^{-1}$	Diffusion coefficient of VO_2^{2+}
$D_{\text{VO}_3^+}$	$2.8 \cdot 10^{-6}$	$\text{cm}^2 \text{s}^{-1}$	Diffusion coefficient of VO_3^+
$c_{\text{VO}_2^{2+}}^0$	15	mM	Initial concentration of VO_2^{2+} in the electrolyte solution domain
$c_{\text{VO}_3^+}^0$	0	mM	Initial concentration of VO_2^+ 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.

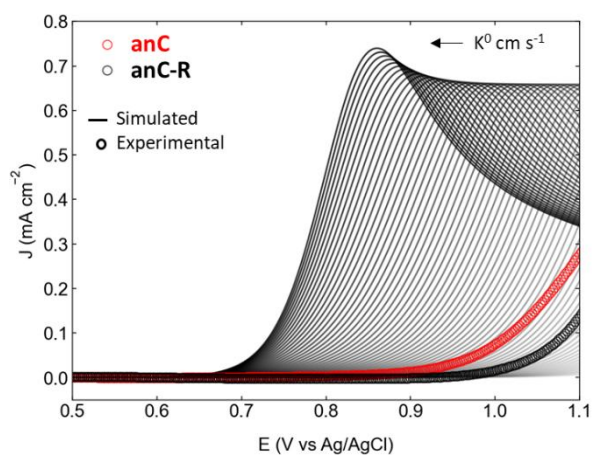


Figure S5. Simulated voltammograms for an E-step with k^0 ranging from 10^{-8} to $10^{-3} \text{ cm s}^{-1}$ compared to the experimental CVs recorded at 0.020 V s^{-1} vs Ag/AgCl of anC and anC-R electrodes.

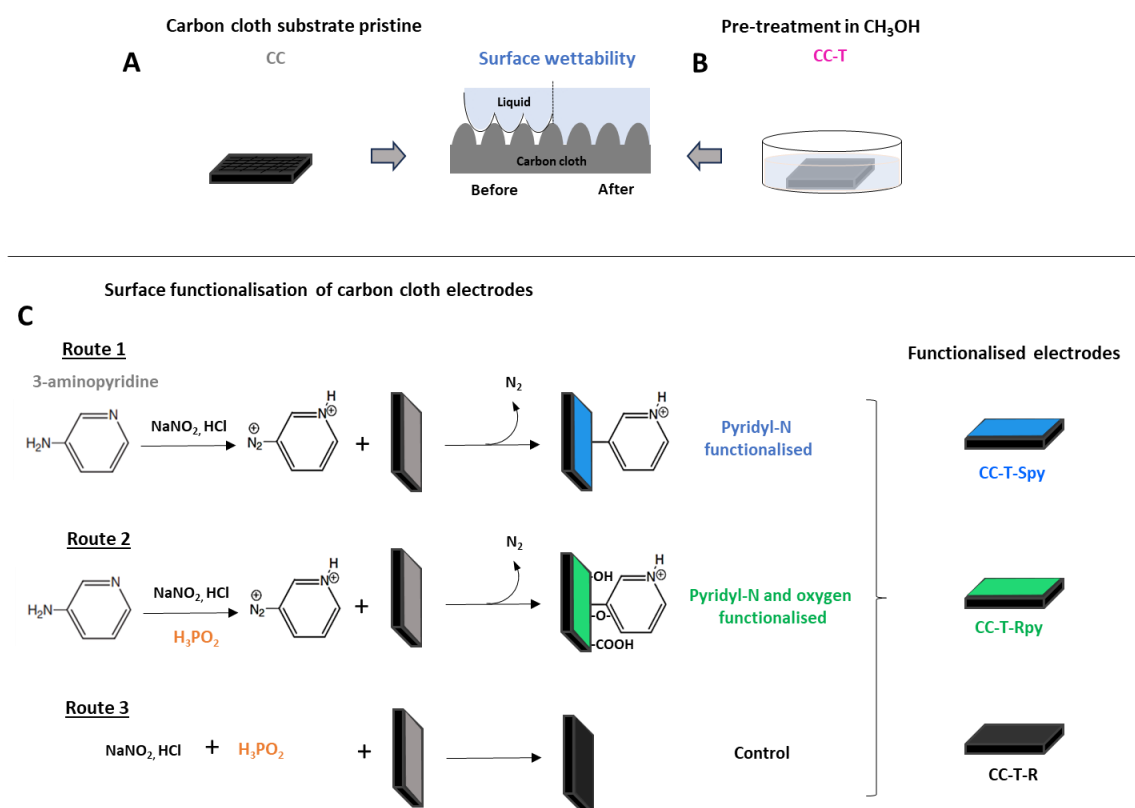


Figure S6. Carbon cloth electrode preparation processes. Pristine carbon cloth (A), its treatment in methanol for 1 min (B), and surface functionalisation routes (C).

Table S6. Summary of carbon cloth electrode preparation protocols.

Electrodes	Pre-treatment	Functionalisation route
CC	n.a	n.a.
CC-Rpy	n.a.	Route 2
CC-T	1 min in CH_3OH	n.a.
CC-T-Spy	1 min in CH_3OH	Route 1
CC-T-Rpy	1 min in CH_3OH	Route 2
CC-T-R	1 min in CH_3OH	Route 3

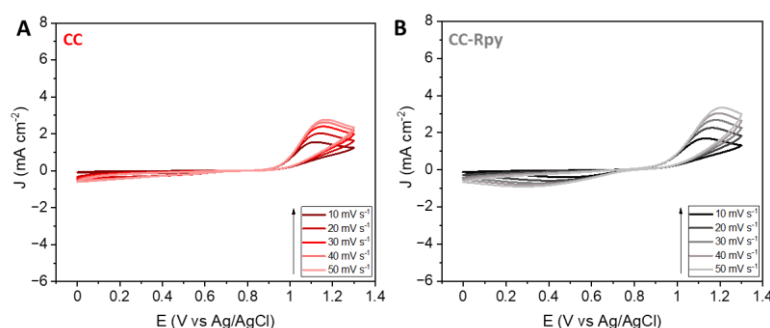


Figure S7. Cyclic voltammograms in 15 mM $\text{VO}^{2+}/\text{VO}_2^+$ in 1.5 M H_2SO_4 at (A) unmodified CC and (B) functionalised CC-Rpy electrodes.

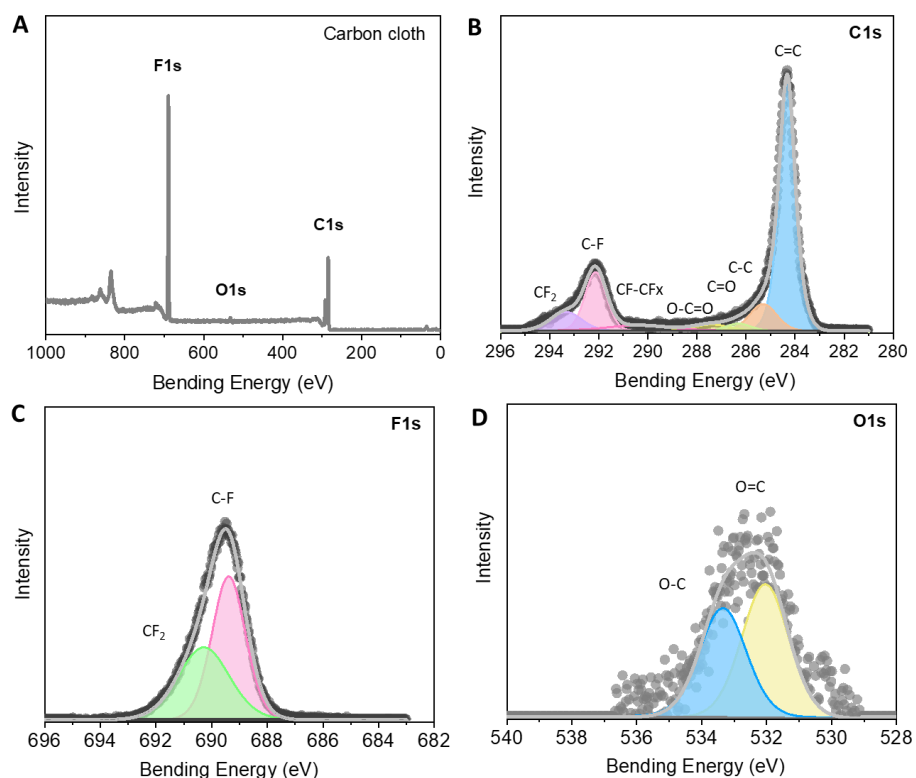


Figure S8. XPS characterization of the carbon cloth pristine: survey spectra (A) and high-resolution C1s (B), F1s (C) and O1s (D).

Table S7. Elemental atomic %-compositions and components obtained from high-resolution spectra and best-fits of C 1s, F 1s and O 1s of pristine carbon cloth electrode.

Components assignments	Components (at. %)	Binding Energy (eV)	Components ratio	
C1s	63.1	284.3	F/C	O/C
F1s	36.6	689.5		
O1s	1.6	532.3	0.6	0.03

Peak	Component assignment	BE (eV)
C 1s	sp ² -C [1, 2]	284.6
	sp ³ -C [3, 4]	285.6
	CO [5, 6]	286.6
	C=O [4, 6, 7]	287.7
	CF-CFx [14-16]	290.7
	C—F [14-16]	292.4
	CF ₂ [14-16]	293.6
O 1s	C=O[1, 2]	532.3
	C-OH[1, 2]	533.6
F 1s	C—F [15, 17]	689.7
	CF ₂ [15, 17]	690.7

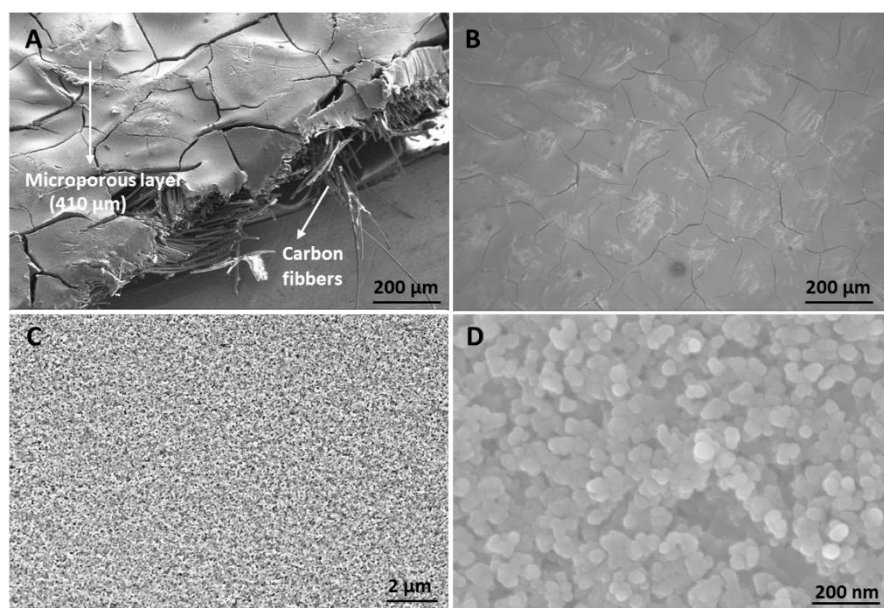


Figure S9. SEM images of carbon cloth pristine, obtained under 5.00 kV and Signal A = SE2 (A and C) and InLens (B and D).

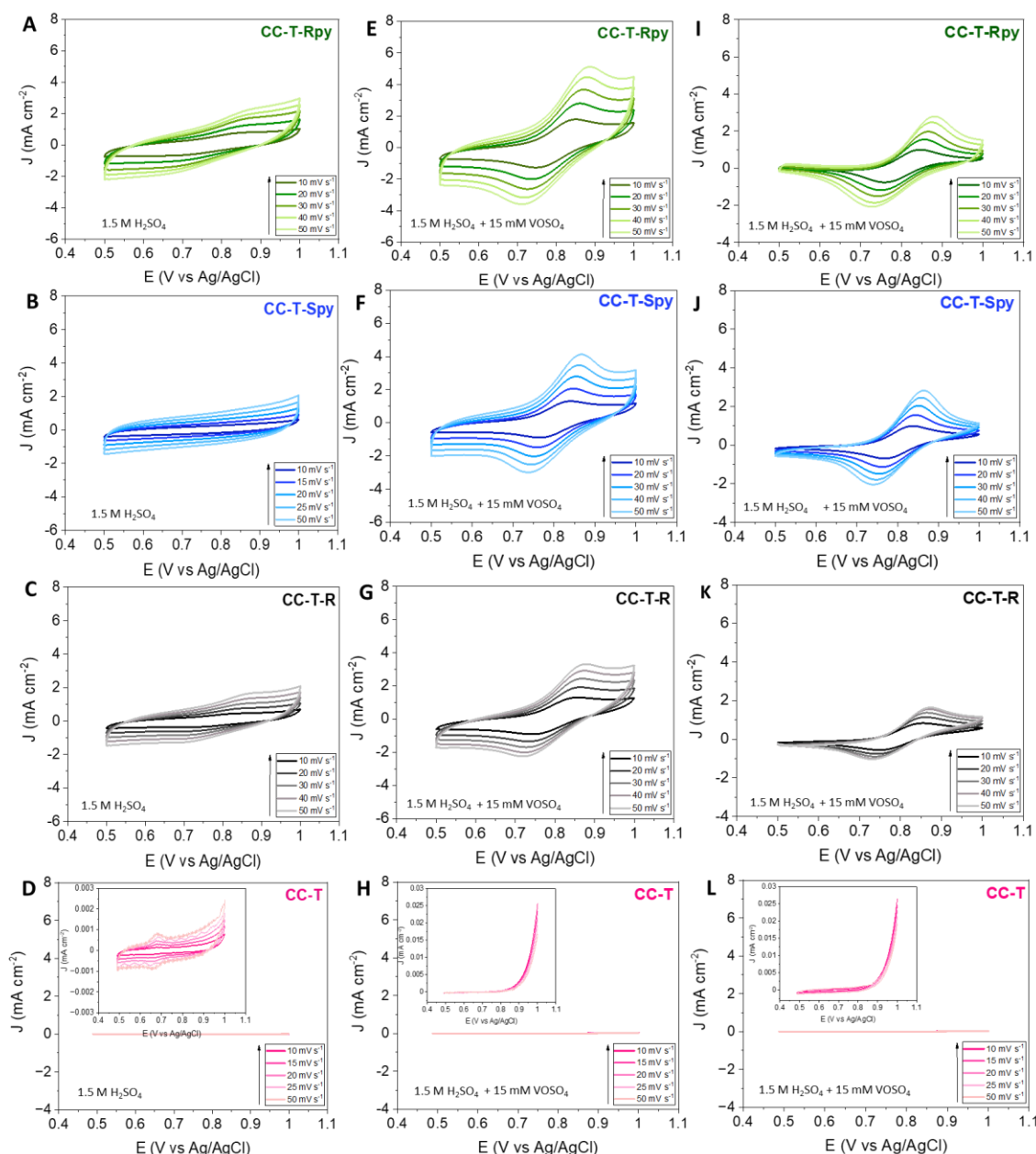


Figure S10. CV of CC-T-Rpy, CC-T-Spy, CC-T-R and CC-T electrodes recorded at scan rates from 0.05 to 0.01 V s⁻¹. (A-D) CV in supporting electrolyte 1.5 M H₂SO₄ for each sample are shown in the left-most column. (E-H) CV in 15 mM VO²⁺ in 1.5 M H₂SO₄ are shown in the center column. (I-L) Capacitance-corrected CV are shown in the right-most column.

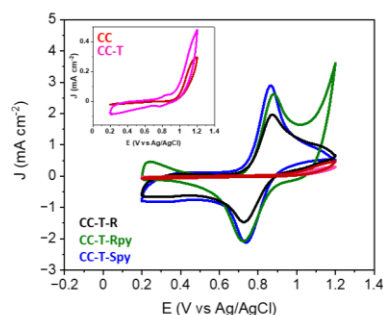


Figure S11. CV in 15 mM VOSO₄ and 1.5 M H₂SO₄ at 50 mV s⁻¹ of all CC electrodes described in **Table S7**, collected over a wider potential window than in **Figure S7**.

Table S8. Electrochemical performance indicators at carbon cloth electrodes. The tests were performed in 15 mM VOSO₄ in 1.5 M H₂SO₄ electrolyte and using 1 M KCl sat. Ag/AgCl as the reference electrode. Capacitance values were estimated from CV in 0.1 M Na₂SO₄ at 0.1 V s⁻¹ via charge integration.

Electrodes	Capacitance (mF/cm ²)	Porosity (P)	ΔE_{peak} (V)	$J_{\text{a,p}}$ (mA/cm) @ 20 mVs ⁻¹	$J_{\text{c,p}}$ (mA/cm) @ 20 mVs ⁻¹
CC	0.01	0.80	n.a	2.3	n.a
CC-T	0.01	1.85	0.03	0.02	-0.01
CC-Spy	15.8	1.27	0.07	1.5	-1.1
CC-R	19.8	0.90	0.11	1.2	-0.8
CC-Rpy	30.0	1.27	0.1	1.5	-1.2

Table S9. Coulombic Efficiency (CE), Voltage Efficiency (VE) and Energy Efficiency (EE) of CC-T-R, CC-T-Spy and CC-T-Rpy extrapolated from the charge and discharge curves at 10, 20 and 40 mA cm⁻².

Electrode	Current (mA cm ⁻²)	CE %	VE %	EE%
CC	10	98.0	68.3	66.9
	20	73.7	62.0	45.6
CC-T-R	10	98.5	82.7	81.5
	20	95.7	82.3	78.8
	40	93.5	73.9	69.1
CC-T-Spy	10	99.3	95.0	94.4
	20	99.9	68.6	68.5
	40	98.7	68.5	67.6
CC-T-Rpy	10	99.4	82.2	77.5
	20	99.6	68.5	68.2
	40	98.2	61.3	60.1

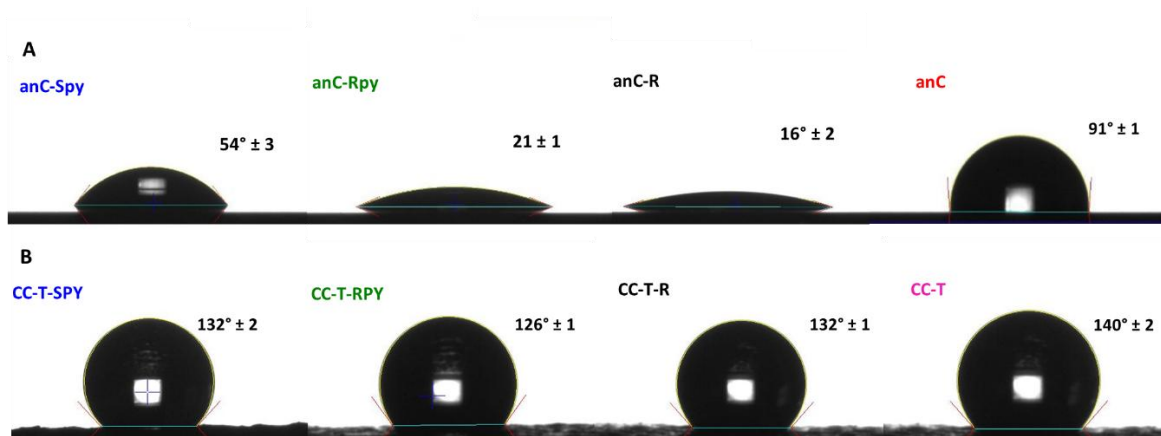


Figure S12. Water contact angle data used for comparing wettability at (A) thin film electrodes and (B) carbon cloth electrodes.

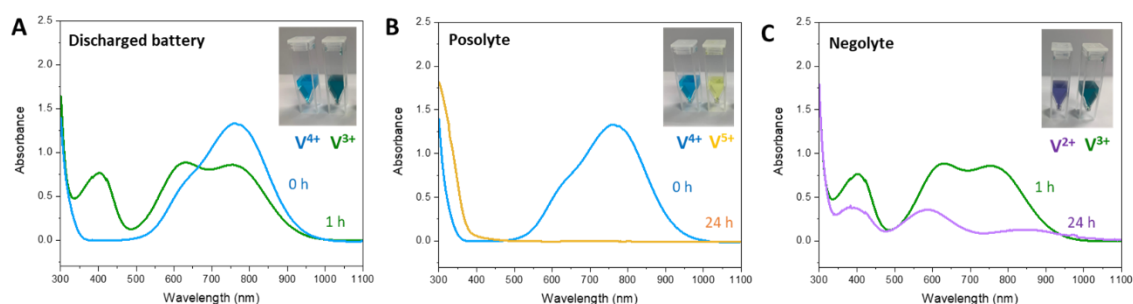


Figure S13. Vanadium solutions and respective UV-Vis absorption spectra. (A) The initial electrolyte (0 h) was obtained starting from 1 M VOSO₄ in 2 M H₂SO₄ and shows the characteristic peak of V⁴⁺ at ca. 760 nm (spectrum shown after dilution to achieve A < 1.5) [18-20]. After 1 h the negolyte shows peaks at ca. 630 and 402 nm corresponding to V³⁺ species [18-20]. (B) Spectral changes in the (B) positive and (C) negative compartment after 24 h of charge/discharge cycling at 20 mA cm⁻². The loss of the peak at 760 nm in (B) supports the complete conversion to V⁵⁺ in the posolyte. The presence of peaks at 402, 580 and 870 nm indicate the presence of both V³⁺ and V²⁺ in the solution [18-20] and suggest that faradaic imbalances likely contribute to irregular discharge curves [21].

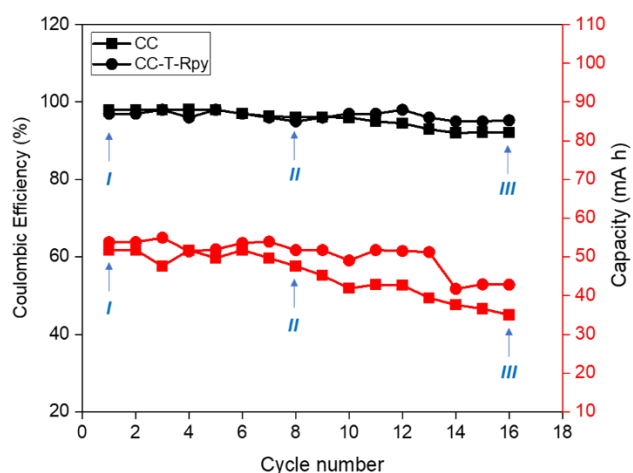


Figure S14. Cycling stability tests at 10 mA/cm² for CC and CC-T-Rpy electrodes. Red and black traces display battery capacity (mA h) and Coulombic efficiency (%), respectively. Three regions are highlighted as region I, region II, and region III, corresponding to the start, middle, and end of the cycling tests. The tests and data analysis were conducted under the conditions described in the experimental section. Battery capacity was determined according to the equation reported in previous work [22].

Table S10. Performance parameters for CC and CC-T-Rpy electrodes in regions I, II, and III, corresponding to the start, middle, and end of the cycling tests in **Figure S14**.

Electrodes	Coulombic Efficiency (%)			Capacity (mA h)		
	I	II	III	I	II	III
CC	98	96	92	52	47	35
CC-T-Rpy	97	92	95	54	51	43

References:

- [1] N. Hellgren, R.T. Haasch, S. Schmidt, L. Hultman, I. Petrov, Interpretation of X-ray photoelectron spectra of carbon-nitride thin films: New insights from in situ XPS, *Carbon*, 108 (2016) 242-252.
- [2] S. Reiche, R. Blume, X.C. Zhao, D. Su, E. Kunkes, M. Behrens, et al., Reactivity of mesoporous carbon against water – An in-situ XPS study, *Carbon*, 77 (2014) 175-183.
- [3] R. Schmidt, E. McNellis, W. Freyer, D. Brete, T. Gießel, C. Gahl, et al., Azobenzene-functionalized alkanethiols in self-assembled monolayers on gold, *Appl. Phys. A*, 93 (2008) 267-275.
- [4] Y. Zubavichus, M. Zharnikov, Y. Yang, O. Fuchs, E. Umbach, C. Heske, et al., X-ray Photoelectron Spectroscopy and Near-Edge X-ray Absorption Fine Structure Study of Water Adsorption on Pyridine-Terminated Thiolate Self-Assembled Monolayers, *Langmuir*, 20 (2004) 11022-11029.
- [5] D. Ullien, P.C. Thüne, W.F. Jager, E.J.R. Sudhölter, L.C.P.M. de Smet, Controlled amino-functionalization by electrochemical reduction of bromo and nitro azobenzene layers bound to Si(111) surfaces, *Phys. Chem. Chem. Phys.*, 16 (2014) 19258-19265.
- [6] C. Silien, M. Buck, G. Goretzki, D. Lahaye, N.R. Champness, T. Weidner, et al., Self-Assembly of a Pyridine-Terminated Thiol Monolayer on Au(111), *Langmuir*, 25 (2009) 959-967.
- [7] C. Enkvist, S. Lunell, S. Svensson, Experimental and theoretical study of the Cls shakeup spectra from biphenyl and p-terphenyl, *Chem. Phys.*, 214 (1997) 123-130.
- [8] J. Agullo, M. Morin, D. Bélanger, Modification of Glassy Carbon Electrode by Electrografting of In Situ Generated 3-diazopyridinium Cations, *J. Electrochem. Soc.*, 159 (2012) H758-H764.
- [9] A. Laforgue, T. Addou, D. Bélanger, Characterization of the Deposition of Organic Molecules at the Surface of Gold by the Electrochemical Reduction of Aryldiazonium Cations, *Langmuir*, 21 (2005) 6855-6865.
- [10] D.R. Jayasundara, R.J. Cullen, P.E. Colavita, In Situ and Real Time Characterization of Spontaneous Grafting of Aryldiazonium Salts at Carbon Surfaces, *Chem. Mater.*, 25 (2013) 1144-1152.
- [11] A. Boucly, F. Rochet, Q. Arnoux, J.-J. Gallet, F. Bournel, H. Tissot, et al., Soft X-ray Heterogeneous Radiolysis of Pyridine in the Presence of Hydrated Strontium-Hydroxyhectorite and its Monitoring by Near-Ambient Pressure Photoelectron Spectroscopy, *Sci. Rep.*, 8 (2018) 6164.
- [12] M.A. Costa de Oliveira, C. Schröder, M. Brunet Cabré, H. Nolan, A. Forner-Cuenca, T.S. Perova, et al., Effects of N-functional groups on the electron transfer kinetics of $\text{VO}^{2+}/\text{VO}_2^+$ at carbon: Decoupling morphology from chemical effects using model systems, *Electrochim. Acta*, 475 (2024) 143640.

- [13] J.N. Hilfiker, N. Singh, T. Tiwald, D. Convey, S.M. Smith, J.H. Baker, et al., Survey of methods to characterize thin absorbing films with Spectroscopic Ellipsometry, *Thin Solid Films*, 516 (2008) 7979-7989.
- [14] T. Gu, Q. Zhang, R. Shi, J. Yan, J. Guo, W. Qian, et al., Superhydrophobic Carbon Functionalized by Chemical Grafting of Fluoroalkylsilane Enables an Efficient Microporous Layer for Proton-Exchange Membrane Fuel Cells, *ACS Sustain. Chem. Eng.*, 10 (2022) 15243-15249.
- [15] G. Nansé, E. Papirer, P. Fioux, F. Moguet, A. Tressaud, Fluorination of carbon blacks: An X-ray photoelectron spectroscopy study: I. A literature review of XPS studies of fluorinated carbons. XPS investigation of some reference compounds, *Carbon*, 35 (1997) 175-194.
- [16] B. Zahiri, R.M. Felix, A. Hill, C.H. Kung, T. Sharma, J.D. Real, et al., Through-plane wettability tuning of fibrous carbon layers via O₂ plasma treatment for enhanced water management, *Appl. Surf. Sci.*, 458 (2018) 32-42.
- [17] Y.M. Shulga, T.-C. Tien, C.-C. Huang, S.-C. Lo, V.E. Muradyan, N.V. Polyakova, et al., XPS study of fluorinated carbon multi-walled nanotubes, *J. Electron Spectrosc. Relat. Phenom.*, 160 (2007) 22-28.
- [18] J. Heiß, M. Kohns, Open circuit voltage of an all-vanadium redox flow battery as a function of the state of charge obtained from UV-Vis spectroscopy, *Energy Advances*, 3 (2024) 2597-2603.
- [19] P. Loktionov, R. Pichugov, D. Konev, M. Petrov, A. Pustovalova, A. Antipov, Operando UV/Vis spectra deconvolution for comprehensive electrolytes analysis of vanadium redox flow battery, *J. Electroanal. Chem.*, 925 (2022) 116912.
- [20] A.A. Maurice, A.E. Quintero, M. Vera, A comprehensive guide for measuring total vanadium concentration and state of charge of vanadium electrolytes using UV-Visible spectroscopy, *Electrochim. Acta*, 482 (2024) 144003.
- [21] M. Nourani, C.R. Dennison, X. Jin, F. Liu, E. Agar, Elucidating Effects of Faradaic Imbalance on Vanadium Redox Flow Battery Performance: Experimental Characterization, *J. Electrochem. Soc.*, 166 (2019) A3844.
- [22] M. Bureš, D. Götz, J. Charvát, M. Svoboda, J. Pocič, J. Kosek, et al., Evaluation of mitigation of capacity decay in vanadium redox flow batteries for cation- and anion-exchange membrane by validated mathematical modelling, *J. Power Sources*, 591 (2024) 233769.