

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

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Abstract

Vanadium redox flow batteries (VRFB) are promising devices for energy storage. However, sluggish kinetics at conventional porous carbon electrodes can limit efficiency, thus prompting interest in N-functionalization for improving performance. Herein synergistic impacts of changes in wettability and chemical reactivity arising from surface pyridinic-N functionalities are investigated. First, fabrication of model carbon electrodes with smooth topography and disk geometry, grafted with pyridyl groups at varying coverage is reported. These are used to unambiguously determine the impact of pyridinic-N sites on the intrinsic activity of carbon surfaces towards $\text{VO}_2^+/\text{VO}^{2+}$ reactions. Combined voltammetry and finite element simulations provided estimates of heterogeneous charge-transfer constants, k^0 , which increase by up to 50-fold upon pyridyl grafting. Pyridyl groups also increase wettability however this is not sufficient to improve charge-transfer kinetics at carbon: indeed, treatments that increase hydrophilicity without grafting pyridyl groups yield no change in k^0 . The impact of pyridyl grafting at porous carbon collectors is then investigated using voltammetry and VRFB tests. Results indicate that wettability changes overwhelmingly determine the response and obscure the effects of pyridinic-N on intrinsic activity. All surface treatments that increase wettability lead to comparable responses, thus evidencing key challenges in applying chemical design principles to complex carbon electrode architectures.

1. Introduction

The design of high-performance carbon electrodes for vanadium redox flow batteries (VRFBs) remains a critical challenge in advancing sustainable energy storage technologies [1, 2]. VRFB systems rely on the efficient and reversible electrochemical reactions of vanadium species, which are highly dependent on electrode surface properties [3-5]. Numerous studies have focused on porous carbon-based electrodes, which offer enhanced surface areas and mass transport properties, but the inherent complexities introduced by porosity restrict the fundamental understanding of how specific surface functionalities impact redox kinetics [6-9]. To address these limitations, the use of model carbon electrodes with smooth surfaces and well-defined active sites has emerged as a promising approach to decouple the effects of porosity/nanostructure and functional group chemistry [10, 11].

Surface functionalisation plays a pivotal role in modulating the electrochemical performance of carbon electrodes [3, 5, 12]. Heteroatom functionalities, such as nitrogen-containing groups (e.g. pyridyl-, pyrrolic-, and graphitic-N) [4, 10], as well as oxygen-containing groups (e.g. hydroxyl, carbonyl) [8, 13] have been widely explored in the literature due to their potential to enhance electron transfer kinetics and/or modify surface wettability [14]. However, contradictory findings persist regarding their specific contributions. For instance, several studies suggest that oxygen groups primarily influence carbon wettability [14, 15] and carbon-electrolyte interactions [5, 8], while others propose their direct involvement as active sites for redox reactions [13, 16, 17]. Similarly, the influence of nitrogen functionalities appears to be highly dependent on their chemical nature and reactivity, with pyridinic and pyrrolic nitrogen often reported as more active compared to graphitic nitrogen [4, 18], while selected studies reported that quaternary nitrogen enhance the electrode stability and rate of vanadium redox processes [19, 20]. These discrepancies underscore the need for studies that isolate the effects of individual and combined functionalities.

In this work we fabricate surface functionalized carbon model electrodes and porous current collectors and demonstrate that these materials can be used to isolate the effects of carbon chemical functionalities from those of wettability in the vanadyl/pervanadyl oxidation reaction. Model electrodes provide a unique platform for resolving these ambiguities by eliminating the confounding factors introduced by the complexity of high surface area electrodes and porosity [10, 21]. Mass transport effects arising from morphology changes can often obscure those effects arising from reaction kinetics at specific active sites [22, 23], making it challenging to isolate performance improvements originating from specific active sites [3, 9, 24]. Model electrodes, fabricated via sputtering with low thickness, high graphitisation and smooth topography, were modified by chemical grafting of pyridyl adlayers and by reductive treatments that increase wettability. The use of the reductive functionalization routes minimises interference from adventitious oxidation processes at the carbon surface, which are known to confound the interpretation of changes in the electrochemical response [8, 25]. Our results unambiguously show that pyridyl groups significantly enhance charge transfer rates while wettability changes alone have no impact on the intrinsic surface kinetics. However, for the first time we show that, when porous electrodes are subject to identical surface modifications, the beneficial effects of functionalities on carbon intrinsic activity can be entirely obscured by wettability changes. Importantly, we demonstrate how this translates into cell performances in VRFB device tests. Our results highlight the distinct contributions of active sites and porosity to overall redox kinetics. These findings provide valuable insights for the design of advanced electrode materials for VRFBs, bridging the gap between fundamental carbon surface chemistry and practical porous electrode architectures.

2. Experimental

Materials. Vanadyl sulfate hydrate (99.999%), sulfuric acid (99.99%), 3-aminopyridine (99.99%), hydrochloric acid (37%), sodium nitrite (99%), hypophosphorous acid (50 wt. % in H₂O) and methanol (HPLC grade 99.9%) were purchased from Sigma Aldrich. Alumina slurries (1, 0.3 and 0.05 μ m particle size) and polishing cloths (MicroCloth and Nylon Polishing cloths) were purchased from Ted Pella and Buehler, respectively. A carbon graphite target (99.999%, $\varnothing$ 2 in., 0.125 in. thick; Kurt J. Lesker), was used as sputtering source. Si wafers (300 nm thermal oxide) and glassy carbon disks (GC, $\varnothing$ 5 mm, HTW GmbH) were used as substrate materials. Carbon cloth (CC, MPL 410 μ m, Fuel Cell Store) was used as electrode material in VRFB device studies.

Fabrication of carbon thin film electrodes. GC disks and Si were used as substrates for the fabrication of highly graphitized and smooth carbon thin-film electrodes. GC disks were polished to obtain a smooth surface, as previously reported [26], prior to any deposition. First, amorphous carbon thin films (a-C) were deposited onto the substrates using a graphite target, under a total flow of 50 sccm Ar in a DC magnetron sputtering chamber (Torr International, Inc.) at $< 2 \times 10^{-6}$ mbar base pressure and $2 \pm 1 \times 10^{-2}$ mbar deposition pressure. a-C films were subsequently annealed at 900 °C for 1 h under a 200 sccm N₂ flow, yielding graphitized thin films used for electrochemical studies referred to as anC, in **Figure 1A**. Additional details on the synthesis and properties of these graphitized thin films is reported in prior work, including details on the reproducibility and homogeneity of their electrochemical response [10, 27-29]. Surface functionalisations were carried out using 3-aminopyridine as a precursor for in situ diazotization, to form pyridyl adlayers via dediazonation reactions [10, 30, 31]. A 5.0 mM solution of 3-aminopyridine in 0.625 M hydrochloric acid (HCl) containing 2% methanol was first prepared; to this, a 50 mM stock solution of NaNO₂ was added to yield final 4 mM 3-aminopyridine and 10 mM NaNO₂ concentrations. Both solutions were cooled in a fridge for

1 h and in an ice bath for 30 min prior to mixing to ensure a controlled rate of diazotization. Functionalisation with pyridyl groups, **Figure 1B**, was carried out via spontaneous reaction following immersion of the carbon substrate in this freshly prepared solution; in the case of carbon cloth electrodes, the functionalization step was preceded by a brief immersion of the substrate in methanol for 1 min to improve wetting. Also, reductant-assisted chemical functionalisation was carried in a similar manner but by further adding hypophosphorous acid (H_3PO_2) at 80 mM concentration to the functionalization solution. Control samples that underwent immersion in the H_3PO_2 -containing solution but in the absence of 3-aminopyridine, were also prepared. Samples were left immersed for 1 h in the dark; then, they were rinsed with deionized water and methanol and dried under N_2 flow prior to further studies.

Characterisation. X-ray photoelectron spectroscopy (XPS) was carried out in a UHV system equipped with a monochromatic Al $\text{K}\alpha$ source (1486.7 eV). Survey and high-resolution spectra were obtained using pass energies of 50 eV and 15 eV, respectively, and at 90° take-off angle. Commercial software (CasaXPS) was used to fit spectra using Shirley backgrounds and Voigt peak functions; all binding energies are referenced against the sp^2 -C component maximum, set at 284.6 eV. Atomic compositions were determined from peak area ratios, after correction for relative sensitivity factors ($\text{C} = 1.0$, $\text{N} = 1.8$, and $\text{O} = 2.93$). Water contact angles were determined using a static contact angle goniometer (FTA1000); triplicate 2 μL droplets were dispensed on each surface, and angle measurements were carried out using video capture software. Scanning electron microscopy (SEM) images were obtained on a Zeiss Ultra microscope with an accelerating voltage of 5.00 kV and an In-Lens detector. UV-Vis spectra were obtained on a Lambda 35 spectrophotometer (PerkinElmer) using quartz cuvettes at 2 nm resolution.

Voltammetry studies were carried out using a potentiostat (Autolab AUT50324) and a three-electrode cell consisting of a graphite rod as the counter electrode (CE), Ag/AgCl (sat.1 M

KCl) as reference electrode (RE), and either GC disks (0.196 cm²) or carbon cloth (CC, 0.36 cm²) as working electrodes (WE). The electrolyte was 1.5 M H₂SO₄ with and without 15.0 mM VOSO₄, a concentration similar to those previously used for kinetic studies [10, 32, 33]. Prior to all measurements the cell was thermostated at 20 °C, the electrolyte was purged with pure Ar for 10 min, and ohmic iR drops were measured to confirm that overvoltage contributions were negligible (10 ± 0.6 Ω). Digital simulations of voltammograms for carbon thin-film model electrodes were carried out using finite element methods (COMSOL Multiphysics v5.3a); details of simulation and parameters used are provided in Supporting Information.

The performance of high-surface-area CC electrodes was investigated in a VRFB single-stack setup consisting of anode and cathode (10 cm²) separated by an ion-conducting membrane (Nafion 115) and two graphite bipolar plates with parallel flow field. CC is a frequently used porous carbon for VRFB applications [34]. The catholyte consisted of 1.0 M VOSO₄ in 2.0 M H₂SO₄ solution. The catholyte was prepared by galvanostatic reduction of the anolyte to form V³⁺ in 2.0 M H₂SO₄: briefly, 50 mL electrolyte tanks were filled with solution and degassed with pure N₂ gas, then 1.8 V were applied leading to reduction of VO₂⁺ to V³⁺. The catholyte tank was then replaced with fresh 50 mL of 1.0 M VO²⁺ in 2.0 M H₂SO₄ electrolyte, and both electrodes were deaerated with N₂ gas. Charging and discharging tests were conducted at cutoff voltages of 1.65 V (charging) to 0.8 V (discharging) at different current densities (10, 20, and 40 mA cm⁻²). Measurements were performed at 30 mL min⁻¹ flow rate, using a peristaltic pump (BT100-3J) and at 30 °C. Ohmic drops were measured to confirm overvoltage contributions.

Voltage efficiency ($VE\% = \frac{\int V_{discharge} dt}{\int V_{charge} dt} \times 100$), coulombic efficiency ($CE\% = \frac{\int I_{discharge} dt}{\int I_{charge} dt} \times 100$) and energy efficiency ($EE\% = CE \times VE$) were calculated following previously reported methods [35-37].

3. Results and discussion

3.1 Studies of N-modified carbon thin film electrodes

To investigate the individual and synergistic effects of N- and O-containing functionalities on the electrochemical response of carbon electrodes in the vanadyl oxidation, we first studied this reaction via voltammetry at thin film electrodes with well-defined geometry, surface chemistry, and smooth topography. Electrodes were fabricated using well established protocols previously reported by our group [10, 11, 27, 28] to create pure graphitized carbon surfaces, and were then modified via reactions in solution to introduce bespoke heteroatom surface functionalities, as schematically shown in **Figure 1**. Briefly, amorphous carbon thin films were first sputtered onto polished GC and then annealed under inert gas flow to obtain graphitized carbon thin films anC, as in **Figure 1A**, yielding electrodes with low intrinsic roughness (RMS = 0.7 nm) [28] that are conformal to the conductive polished GC substrate. Prior work on the characterization of anC [11, 27] showed that these materials are nitrogen-free and possess a low O-content (see also below). Importantly, electrochemical microscopy studies also demonstrated that they display a highly homogeneous/uniform response across their surface area [11, 28]. anC thin films were then modified with chemical functionalities via reactions from solution, yielding three different types of electrode surfaces as in **Figure 1B** (see also **Table S1**). First, pyridyl groups were introduced via spontaneous aryldiazonium grafting from solutions of 3-aminopyridine diazotized in situ [10, 38], yielding samples referred to as anC-Spy. Pyridyl groups were also introduced via reductant-assisted dediazonation by adding hypophosphorous acid to the 3-aminopyridine functionalization solution [39-41], yielding samples referred to as anC-Rpy. Finally, anC films were treated with 80 mM solutions of hypophosphorous acid alone, yielding samples referred to as anC-R.

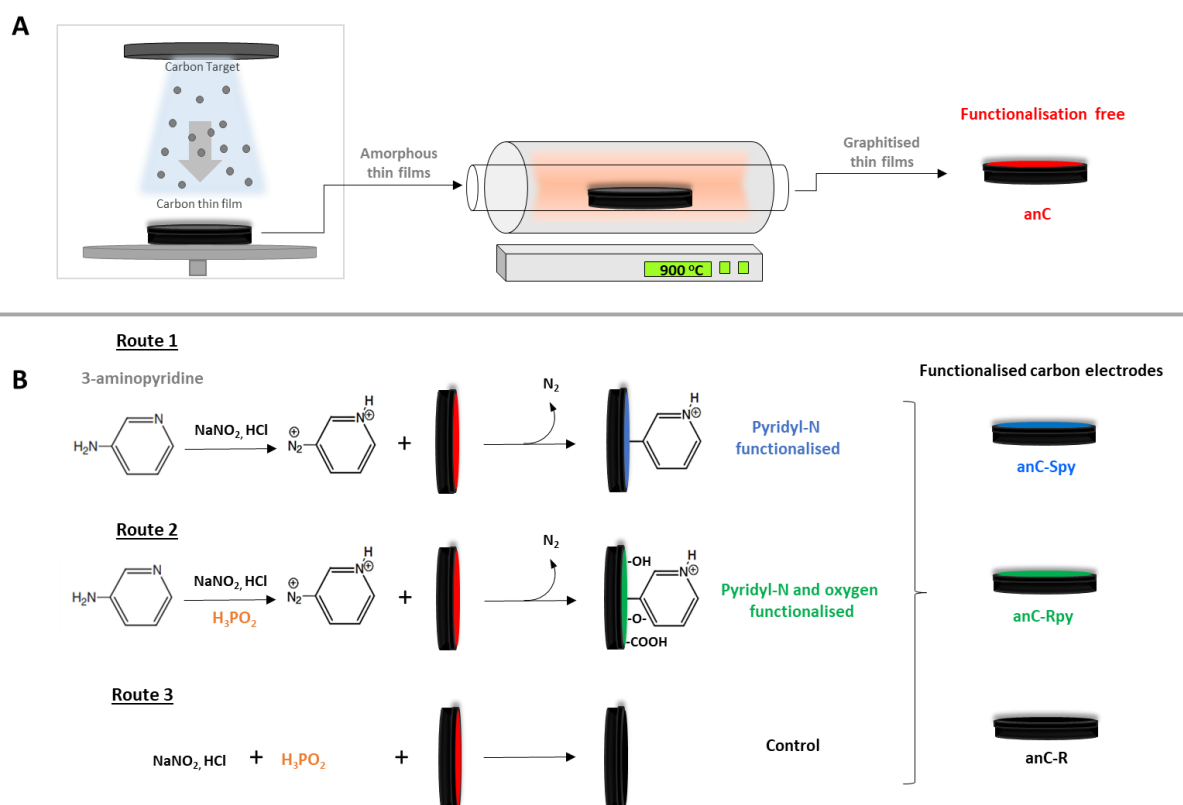


Figure 1: Scheme showing fabrication protocols used for carbon thin film electrodes: (A) preparation of thin films on GC substrates and (B) surface chemistry reactions used to prepare functionalized thin film electrodes (anC, anC-Spy, anC-Rpy and anC-R). Analogous functionalization processes were used for the modification of carbon cloth substrates (CC).

XPS spectra show evidence of the change in composition resulting from functionalization; a summary of main results from best-fits is reported in **Table 1** while details of all peak positions, %-areas and assignments are reported in **Table S2**. Survey spectra, **Figure S1**, show that all samples display peaks characteristic of C 1s (ca. 284 eV) and O 1s (ca. 532 eV) ionizations, while anC-Spy and anC-Rpy also show peaks associated with N 1s (ca. 400 eV), thus supporting successful functionalization. No peaks arising from P 2p or P 2s ionizations were detected at either of anC-Rpy or anC-R, thus indicating that addition of hypophosphorous acid does not result in P-functionalities. **Figure 2A and 2B** show high resolution spectra in the N 1s region for anC-Spy and anC-Rpy, respectively. Best fits were obtained by using two main contributions at ca. 399.1, and 401.8 eV attributed to pyridinic-N and its protonated pyridinium-N form, respectively [42, 43]. A third component at ca. 400.6 eV is attributed to

azo-groups, which result from incomplete dediazonation during aryldiazonium functionalization [30, 44, 45]. A comparison of anC-Rpy vs anC-Spy samples shows an increase in total N/C content and a decrease in the proportion of residual azo-groups; this is consistent with enhancement of dediazonation rates due to hypophosphite addition as a solution-based reductant. Results from the N 1s analysis at anC-Spy and anC-Rpy surfaces are in good agreement with those obtained after electrochemical grafting of 3-aminopyridyl groups onto anC reported in our prior work [10]. Nonetheless, the final coverage obtained herein via chemical functionalization is, as expected, lower than the one previously achieved via potentiostatic reduction.

High resolution spectra in the C 1s and O 1s regions also show changes arising from functionalization. **Figure S1B and S1C** show the C 1s and O 1s spectra and best-fits, respectively, of bare anC. The C 1s spectrum displays the typical asymmetric line of graphitized carbon with a main sp^2 -C peak (284.6 eV) and contributions from residual oxidized carbon at high binding energies (CO_{ox} in **Table 1**), whereas the O 1s region shows a main peak (78%) arising from adsorbed molecular water (535.6 eV) [42, 46, 47] with only small contributions from C-O/C=O at lower binding energies [46, 47]. The C 1s spectra of anC-Spy and anC-Rpy in **Figure 2C and 2D**, respectively, show increased sp^2 -C and lower oxidized carbon contributions to the C 1s, consistent with functionalization with pyridyl adlayers. The O 1s spectra and best-fits for anC-Spy and anC-Rpy, in **Figure 2E and 2F**, are consistent with increased water adsorption after anC functionalization: the intensity increases due to prominent low binding energy peaks at 532.8 and 531.5 eV, assigned to H-donating adsorbed water and hydroxide anions, respectively, that are in excellent agreement with XPS studies by Grunze and co-workers on pyridyl monolayers on gold [42]. Finally, control anC-R surfaces, treated with hypophosphorous acid but without 3-aminopyridine in **Figure S1D and S1E**, show contributions from oxidized carbon groups to the C 1s spectrum that are comparable to those

of anC, as expected from the absence of pyridyl adlayers. The O 1s peak shows evidence of water adsorption with low binding energy contributions from hydroxide species, due to partial reduction of oxidized functionalities at anC surfaces by hypophosphite [48-50].

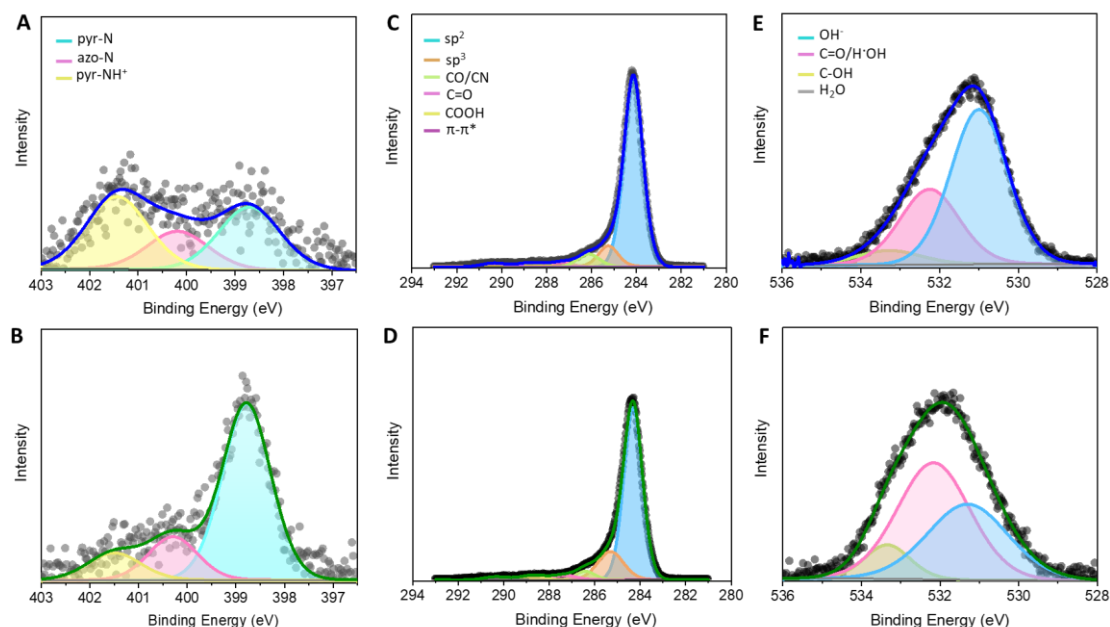


Figure 2: XPS spectra and best fits of the N 1s (left column), C 1s (center column) and O 1s (right column) high-resolution regions for anC-Spy (A, C, E) and anC-Rpy (B, D, F) electrodes.

Table 1. Atomic %-composition obtained from best-fits of high-resolution spectra in the N 1s, C 1s and O 1s regions. Details of peak positions, assignments and peak areas for all components from best-fits are reported in **Table S2**.

Electrode	N 1s				C 1s	O 1s
	N/C _{tot}	Pyridinic-N/N _{tot}	Azo-N/N _{tot}	Pyridinium-NH ⁺ /N _{tot}	CO _{ox} /C _{tot} ^a	O/C _{tot}
anC	-	-	-	-	15%	4.5%
anC-Spy	1.1%	36%	22%	42%	11%	10%
anC-Rpy	1.5%	70%	18%	12%	9.2%	6.1%
anC-R	-	-	-	-	15%	9.4%

^a -%-area of components in the range 286.5 – 289.0 eV (see **Table S2**) relative to the total intensity of the C 1s peak.

The effect of surface treatments on wettability was investigated via water contact angle determinations, which yielded values of $83^\circ \pm 7^\circ$, $54^\circ \pm 3^\circ$ and $21^\circ \pm 1^\circ$ for anC, anC-Spy and anC-Rpy, respectively (uncertainties indicate 95% C.I.). The value of anC is in good agreement

with our previous work [10], whereas those of the pyridyl-modified surfaces are significantly lower. Interestingly, the contact angle of anC-R was $16^\circ \pm 2^\circ$ thus indicating that surface treatment with hypophosphorous acid leads to increased wettability. These results are consistent with conclusions from the O 1s analysis that indicate greater tendency towards water/hydroxide adsorption at all three treated surfaces relative to the bare graphitized anC.

The electrochemical performance of functionalised and unfunctionalized anC thin-film electrodes was investigated via voltammetry in 1.5 M H_2SO_4 in the absence and presence of 15 mM $\text{VO}(\text{SO}_4)_2$. **Figure 3A** shows cyclic voltammograms of anC-Rpy at 20 mV s^{-1} , in the presence of 15 mM VO^{2+} (green traces) and in supporting electrolyte alone (black trace). The faradaic response associated with vanadyl species can then be obtained by subtracting the capacitive cycle (solid green trace): the capacitance-corrected CV displays well defined peaks associated with the $\text{VO}^{2+}/\text{VO}_2^+$ couple at the anC-Rpy electrode. Capacitive background corrections were also applied to anC-Spy, anC-R and anC as shown **Figure S2**. **Figure 3B** shows a comparison of the capacitance-corrected voltammograms of anC-Spy, anC-Rpy, anC-R, and anC, while **Table 2** provides a summary of overpotentials and peak-to-peak (ΔE_{peak}) separations obtained from CV data. The vanadyl/pervanadyl response is irreversible for anC and anC-R, whereas greater faradaic reversibility is observed for both anC-Spy and anC-Rpy electrodes. ΔE_{peak} values decrease in the order $\text{anC} > \text{anC-R} > \text{anC-Spy} > \text{anC-Rpy}$, thus suggesting that performance improves vs pyridyl surface coverage. The presence of pyridyl adlayers also leads to a reduced overpotential for the vanadyl oxidation, in agreement with our previous work [10], while hypophosphite treatment alone leads to an anodic shift in the response, as seen for anC-R surfaces. CV were also collected at a varying scan rate (ν) over the range $10\text{-}50 \text{ mV s}^{-1}$, **Figure S3**; the slope of log-log plots of peak current density (j_p) vs ν yielded values close to 0.5, **Table S3**, as expected from diffusion-controlled processes. Tafel slope values were obtained from the anodic waves at 10 mV s^{-1} . The slope for anC is close to that previously reported from similar

measurements [10], while slope values for anC-Spy, anC-Rpy and anC-R were comparable and close to 120 mV, **Table 2**, thus suggesting that currents are limited by a 1-electron electrochemical step (E-step) [10].

The effect of surface modifications is also evident from a comparison of capacitances, in **Figure 3C**. These were estimated from the integrated charge of the CV in supporting electrolyte, and were found to increase in the order $\text{anC} < \text{anC-R} < \text{anC-Spy} < \text{anC-Rpy}$. The capacitance of anC is comparable to that estimated for glassy carbons using linear sweeps in H_2SO_4 [51, 52] and suggests low microroughness ($\sigma \sim 2$). The larger values observed for anC-Spy and anC-Rpy are consistent with the presence of molecular adlayers with protonated surface functionalities, as these are known to increase capacitance at low pH [53, 54]. Further, broad peaks at ca. 0.35 V (see arrow in **Figure 3A**) associated with pseudocapacitive contributions can also be observed after pyridyl modification but are absent for anC or anC-R (**Figure S2**). Their intensity increases with increasing N/C coverage, indicating that they are associated with functional groups in the pyridyl adlayers. Prior studies of 4-mercaptopyridyl and oligopyridyl monolayers on gold by Kolb and co-workers demonstrated that these peaks arise from potential-dependent coordination of sulfate anions to pyridinium groups [55, 56]. Finally, it is important to note that anC-R electrodes display capacitances that are intermediate between those of anC and pyridyl-modified carbons. This indicates that treatment with hypophosphorous acid leads to changes in surface chemistry that affect the double layer region. Given that XPS analysis of the C 1s did not reveal a significant increase in %-contributions from oxidized groups, the observed increase in capacitance relative to anC is possibly the result of greater basicity of oxidized functionalities, which is reported to positively correlate with carbon capacitance in acid electrolytes [49, 57]. Importantly, the change in surface chemistry detected at anC-R from capacitive cycles is not sufficient to achieve a fast response in the

faradaic vanadyl/pervanadyl reaction, as evidenced by the trends in faradaic CVs in **Figure 3B**. This is discussed in greater detail below with the support of numerical simulations.

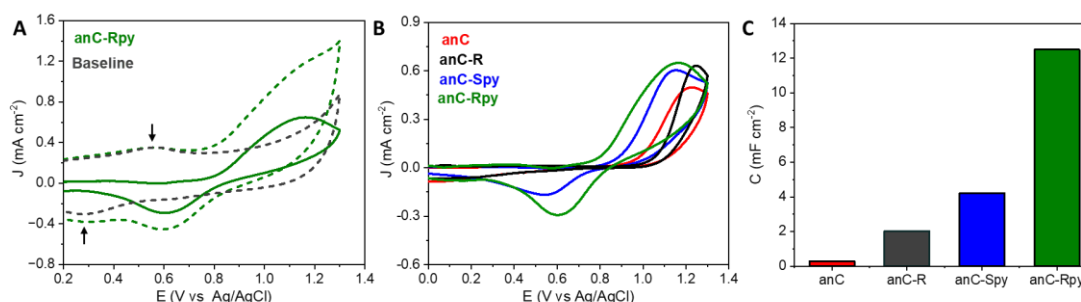


Figure 3: (A) CV of anC-Rpy at 20 mV s⁻¹ in 1.5 M H₂SO₂ in the absence (dashed black trace) and presence (dashed green trace) of 15 mM VOSO₄; the CV is also shown after correction by the capacitive background (continuous green trace). (B) Comparison of capacitance-corrected CV obtained at 20 mV s⁻¹ in 15 mM VOSO₄ in 1.5 M H₂SO₄ for all four electrodes investigated. (C) Comparison of capacitances obtained by integration of CV at 20 mV s⁻¹ in 1.5 M H₂SO₄ for all four electrodes investigated.

Table 2. Potentials and ΔE_{peak} values obtained from CVs at 20 mV s⁻¹ in 15 mM VOSO₄ in 1.5 M H₂SO₄. and Tafel slope at 10 mV s⁻¹. Values reported are the mean and standard deviation of three electrodes (N = 2).

Electrodes	E (V vs Ag/AgCl) @ 0.3 mA cm ⁻²	ΔE_{peak} (V)	Tafel slope (mV)
anC	1.12 ± 0.02	1.17	182 ± 4
anC-R	1.14 ± 0.03	1.15 ± 0.03	133 ± 4
anC-Spy	1.02 ± 0.02	0.60 ± 0.01	135 ± 5
anC-Rpy	0.90 ± 0.02	0.52 ± 0.01	122.5 ± 0.5

To better understand the impact of surface modifications, we carried out numerical simulations of the anodic wave to estimate the heterogeneous rate constant for the E-step at all four surfaces investigated. The rising edge of the anodic current was modelled using finite element methods, adopting the same approach demonstrated in our prior work and based on the reaction scheme proposed by Gattrell et al. [10, 32]. Briefly, an axisymmetric disk electrode geometry was assumed and the concentrations of VO²⁺ and its oxidized intermediate VO³⁺ were set at 15 and 0 mM, respectively, at time zero. Charge transfer was assumed to follow Butler-Volmer kinetics with transfer coefficient of 0.5. Diffusion equations were used to describe mass

transport using coefficients based on literature values [58, 59]. The geometry of the solution domain, the electrolyte and electrode surface boundaries, and the details of the mesh used for calculations are shown in **Figure S4**. Equations and a summary of parameters and constants used for all simulations are reported in **Supporting Information**.

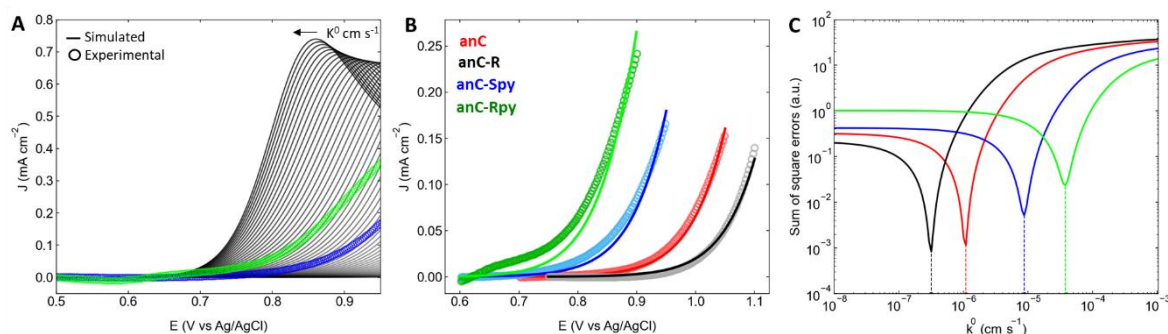


Figure 4: (A) Simulated voltammograms for an E-step with k^0 ranging from 10^{-8} to 10^{-3} cm s⁻¹ compared to the experimental anodic waves of anC-Spy and anC-Rpy at 0.020 V s⁻¹. (B) Best fits of simulated (dotted lines) and experimental (continuous lines) anodic waves for VO²⁺ oxidation. (C) SSE figure of merit vs k^0 values used in simulations, for all four surfaces investigated; the minimum in each of the four curves indicates the best fit value of k^0 .

Figure 4A shows a series of anodic waves simulated with varying values of k^0 in the 10^{-8} to 10^{-3} cm s⁻¹ range, compared to the experimental anodic waves of anC-Rpy and anC-Spy; **Figure S5** shows a similar comparison for the anodic waves of anC and anC-R electrodes. The best fits of the 1-electron E-step for all four surfaces are shown in **Figure 4B**; these were obtained by identifying the minimum of the sum of squared errors (SSE) over the potential window preceding the peak potential. **Figure 4C** shows the SSE minima that defined best-fit values of k^0 , listed in **Table 3**. The minimum in the SSE for $k^0 = 1.082 \times 10^{-6}$ cm s⁻¹ at bare anC is in excellent agreement with previous determinations for the same material and for other graphitic carbons (e.g. GC) [10, 11, 32, 33, 60] and indicates sluggish vanadyl kinetics in the absence of functionalities. The control surface anC-R displays very similar k^0 values, thus confirming that immersion in hypophosphite alone does not significantly affect vanadyl kinetics. On the other hand, pyridyl-N adlayers at anC-Spy and anC-Rpy result in faster kinetics than bare carbon, by

approximately an order of magnitude. Further, a larger k^0 value was obtained for anC-Rpy compared to anC-Spy thus suggesting that surface coverage positively correlates with charge transfer rates. The stabilizing role of pyridyl functionalities as coordinating ligands in the inorganic chemistry of V(IV) and V(V) complexes is known and these results are consistent with the impact of such interactions on oxidation overpotentials [10, 61, 62].

Table 3. Best-fit values and uncertainties for heterogeneous rate constants obtained from simulations of the anodic wave over the potential window indicated in the table; uncertainties were calculated by identifying the 10% uniqueness range of the SSE surface [10, 63].

Electrodes	k^0 (cm s ⁻¹)	Uncertainty intervals for k^0 (cm s ⁻¹)	Potential windows
anC	1.082×10^{-6}	$[1.060, 1.086] \times 10^{-6}$	0.7 to 1.05
anC-R	3.195×10^{-7}	$[3.043, 3.210] \times 10^{-7}$	0.75 to 1.1
anC-Spy	8.817×10^{-6}	$[8.326, 8.976] \times 10^{-6}$	0.6 to 0.95
anC-Rpy	4.863×10^{-5}	$[4.461, 5.113] \times 10^{-5}$	0.5 to 0.85

3.2 Studies of N-modified carbon cloth electrodes

To investigate whether the trends observed at thin film electrodes translate into differences in performance at porous current collectors typically used in VRFB devices, studies were carried out using commercial carbon cloth (CC). CC electrodes were prepared following the methods described in the experimental section and schematically illustrated in **Figure S6**; a summary of preparation conditions is reported in **Table S6**. Initial tests used CC samples modified via the exact same approach as that used for thin film electrodes. However, the response was found to be sluggish at both unmodified and pyridyl-modified CC, although functionalisation did slightly improve the reversibility of the CV. This is exemplified in CV shown in **Figure S7** for as received CC and for CC modified via aryldiazonium cations with hypophosphorous acid (CC-Rpy). The poor faradaic responses observed are due to the hydrophobic nature and polymeric content of pristine carbon cloth, which is fluorine-rich to prevent swelling and ensure long-term electrode stability [64-66]. Further details on elemental composition from

XPS analysis support this statement as shown in **Table S7** and **Figure S8** while SEM images of the CC structure are shown in **Figure S9**.

To improve wetting of the CC surface, the electrodes were therefore immersed in methanol [67-69], yielding samples referred to as CC-T, and only then subjected to functionalization reactions involving spontaneous (CC-T-Spy) and reductant-assisted (CC-T-Rpy) 3-aminopyridyl diazonium grafting. A control sample, CC-T-R, was also prepared by exposing CC to hypophosphorous acid in the absence of 3-aminopyridine (**Table S6**). **Figure S10** shows CV at varying scan rates obtained in 1.5 M H₂SO₄ in the presence and absence of 15 mM VOSO₄ for the bare CC-T electrode, surface-modified CC-Spy and CC-T-Rpy and the control sample CC-T-R. **Figure 5A** shows a comparison of the capacitance-corrected CV obtained at 20 mV s⁻¹ for the four electrodes. The CV at CC-T-Spy, CC-T-Rpy and CC-T-R show clear faradaic peaks, with high peak current densities and excellent reversibility, associated with vanadyl/pervanadyl processes. However, at CC-T electrodes only negligible peaks were observed over the same potential window, with the main anodic wave of vanadyl oxidation observed at a higher overpotential (**Figure S11**), and comparable to that at untreated CC electrodes. This indicates that immersion in methanol alone, as expected, does not alter the response to VO₂⁺/VO²⁺ couples, but pre-immersion in methanol does affect the impact of subsequent surface modification treatments on VO₂⁺/VO²⁺ faradaic currents. This is further exemplified in **Figure 5B** comparing the CV of pyridyl modified CC electrodes prepared with and without pre-immersion in methanol: it is clear that the pre-immersion step enhances the effects of the pyridyl grafting reactions on the reversibility and overpotential of the vanadyl oxidation reaction. It is important to note that the peak current densities of CC-Rpy and CC-Spy in **Figure 5A** are higher than those observed at disk film electrodes under identical conditions (cf. **Figure 3B**); furthermore, peak positions at lower overpotentials and small ΔE_{peak} values are also observed, **Table S8**. This suggests that the fast faradaic responses

observed at CC-Spy, CC-Rpy and CC-R are influenced by redox processes in the electrochemically available pore volume (ECPV) of the carbon cloth. As discussed by Punckt et al. [70, 71] and more recently by Kinkelin et al. [72], small ΔE_{peak} and apparent low overpotentials in the CV of porous electrodes may result from reactant depletion in the solution reservoir within pores, such as those within the woven cloth and diffusion layer of CC.

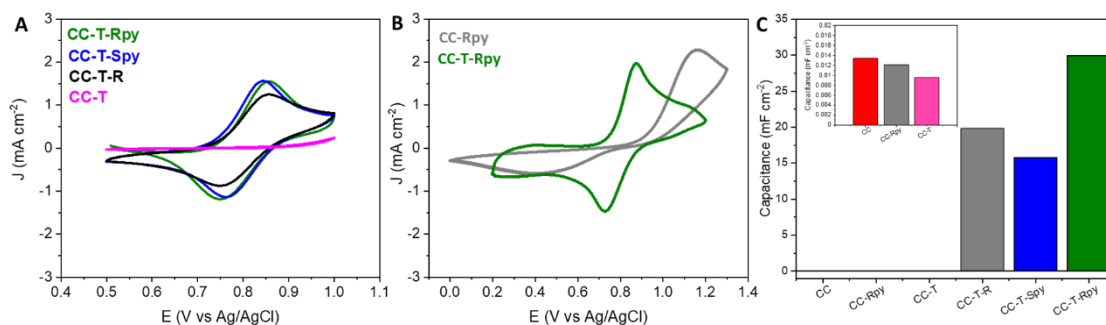


Figure 5. (A) CV of CC-T-Spy, CC-T-Rpy, CC-R and CC-T at 20 mV s⁻¹ in 15 mM VOSO₄ in 1.5 M H₂SO₄. (B) Comparison of CV at 20 mV s⁻¹ in 15 mM VOSO₄ in 1.5 M H₂SO₄ at a CC electrode modified via reductant-assisted modifications with (green trace) and without methanol pre-treatment (gray trace). (C) Capacitances of all CC electrodes tested, normalized by geometric area; the inset shows an expanded view of capacitances for CC, CC-Rpy and CC-T electrodes.

The effect of methanol pre-immersion on pore access at surface-modified CC electrodes is also supported by changes in capacitive background arising from CC treatments. Estimates of capacitance for all CC electrodes tested are shown in **Figure 5C** (also **Table S8**). Access to the internal electrochemically active surface area (ECSA) is improved by combining the methanol pre-wetting step with chemical modifications of the CC surface. This is evidenced e.g. by a comparison between the capacitances of CC-Rpy vs CC-T-Rpy: despite both electrodes undergoing the same functionalization protocol, pre-wetting leads to much higher capacitive currents, diagnostic of improved access to the internal ECSA after functionalization. The capacitance of CC-T-Spy is also high and closer to that of CC-T-Rpy than that of the bare CC electrodes. Therefore, the reversible CV responses observed at CC-T-Spy and CC-T-Rpy can be concluded to result from synergistic effects of enhanced wettability and covalently

immobilized pyridyl functionalities. It is interesting to also note that the areal capacitances of the CC and CC-T electrodes are much smaller than that of the thin film anC. This indicates that when CC is not subject to surface modification reactions there is incomplete wetting even of their geometric cross-section. Finally, immersion of CC-T in hypophosphorous acid alone results in a response from CC-T-R electrodes that is only marginally inferior to that resulting from pyridyl adlayers, **Figure 5A**; this is also reflected in the effect of this treatment on its capacitance, which is intermediate between that of CC-T-Spy and CC-T-Rpy. This indicates that wettability changes resulting from reductant-treatment alone have a similar impact on the response of CC as those obtained from pyridyl immobilization. Therefore, they cannot be meaningfully distinguished from the effects of pyridyl functionalities on the intrinsic surface activity based on the CV response of porous electrodes alone.

Given the contrast between trends in CV responses obtained at thin film and at CC electrodes when subject to identical surface modifications, it is useful to examine the differences in porosity and ECPV at these two different morphologies. **Figure 6A and 6B** shows SEM images of bare anC and CC that reveal a dramatic contrast between the smooth anC film and the rough, porous topography of CC. The porosity and impact of ECPV at all electrodes studied was assessed from voltammograms by calculating the porosity factor p ($p = j_{p,1}\sqrt{v_2}/j_{p,2}\sqrt{v_1}$) based on the normalized peak anodic currents at 50 and 10 mV s⁻¹, as described by Punckt et al. [71] For an ideal planar electrode $p = 1$, while $p > 1$ indicates a dispersion in the current vs v relationship that is diagnostic of high porosity. **Figure 6C** shows values of peak-to-peak separation at 20 mV s⁻¹ vs p values thus calculated. All of the thin film electrodes display $p \approx 1$ and high dispersion in the ΔE_{peak} value depending on their surface termination. On the other hand, CC electrodes show high dispersion in their p values and ΔE_{peak} that is nearly independent of the type of surface treatment. This confirms that it is the CC electrode porosity that leads to an apparent improvement of vanadyl oxidation rates and reversibility in the CV. Electrode

morphology and internal pore volume have an overwhelming impact on the CV response of CC collectors: wettability of the internal ECSA is the dominant effect and obscures any differences in the intrinsic electrochemical kinetics at specific active sites. These results are in agreement with the effect of porosity highlighted by fundamental studies using reversible and quasi reversible redox couples [24, 70-72], and is consistent with the complexities previously identified in the interpretation of performance at modified porous electrodes in vanadium redox flow battery applications [9, 22, 23, 25, 33, 73]. The use of thin film electrodes with well-defined surface termination and geometry, coupled to a smooth topography, can clearly assist in disambiguating and quantitatively assessing the impact of specific chemical functionalities in the absence of complex mass transport effects arising from reactions in the ECPV.

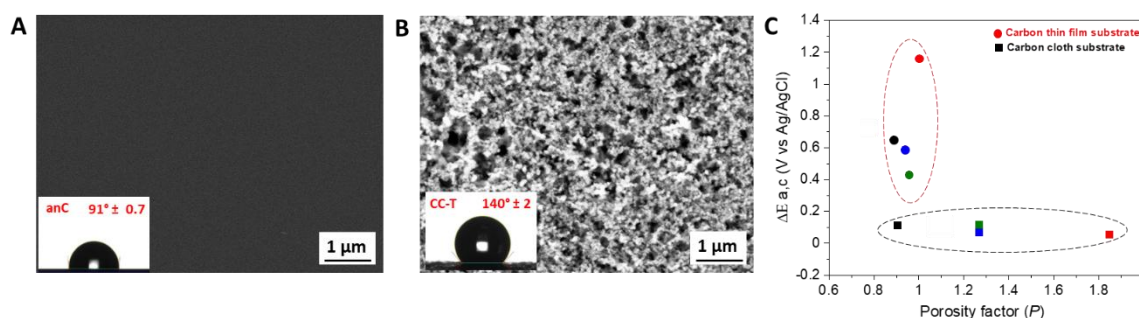


Figure 6. Comparison of model disk electrodes vs high surface area electrodes: SEM images, of unmodified carbon thin film (A) and carbon cloth (B) electrodes with respective water contact angle measurements. Porous factor (C) of functionalised carbon thin film and carbon cloth electrodes.

Beyond CV studies, the response of the different CC electrodes was investigated in a single stack VRFB device. The full cell cycling tests were performed using conditions described in the experimental section. A potential of 1.23 V was applied to investigate resistances related to charge transfer and mass transport limitations; this potential is near the midpoint difference of the vanadium redox couples involved ($V^{3+/2+}$ and $V^{5+/4+}$). **Figure 7A** shows Nyquist plots obtained from electrochemical impedance spectroscopy (EIS) at frequencies in the range 10^6 to 10^{-2} Hz. The charge transfer resistances were similar for CC, CC-T-R, CC-T-Spy, and CC-

T-Rpy electrodes, with a value of approximately 2.4Ω (inset). **Figure 7B** shows charge-discharge profiles at a constant current of 20 mA cm^{-2} . The discharge cycles exhibit irregular curve responses, indicating that the discharge reactions were not fully completed under the applied conditions [74-76]; this is also supported by spectroscopic characterisation of the electrolyte as shown in **Figure S13**. The functionalised electrodes have longer charge and discharge durations than the pristine electrode. This implies that treated functionalised electrodes, particularly CC-T-Spy, have higher electrochemical capacities since more charge is stored and released over time at the same current. Additionally, pristine CC shows a voltage gap between charging and discharging, indicating poor redox kinetics and worse overpotential. The coulombic, voltage and energy efficiencies of CC, CC-T-R, CC-T-Rpy and CC-T-Spy at 20 mA cm^{-2} are shown in **Figure 7C**: values are similar for all functionalised electrodes and higher than those measured at bare CC. In the case of functionalised electrodes, the capacity during charge and discharge cycles was also investigated at varying current densities of 10, 20, and 40 mA cm^{-2} to assess stability and reversibility (see also **Table S9**). Coulombic efficiencies (CE%), **Figure 7D**, were similar across all three electrodes at all current conditions tested, suggesting high selectivity, minimal parasitic responses and limited vanadium crossover [77]. CE values of ca. 98% align well with those previously reported for carbon cloth electrodes in the VRFB literature [73, 78, 79]. Voltage efficiencies (VE%) correlate with catalytic activity, kinetics, and conductivity within the system. VE results, **Figure 7E**, indicate that CC-T-R, maintained stability across the current densities with a VE% of $80 \pm 4\%$. In contrast, electrodes functionalised with pyridyl groups exhibited more significant VE% variation, which suggests increased polarisation and internal resistance, leading to higher losses [73, 80, 81], which are more evident at the highest current density tested. Energy efficiency (EE%), **Figure 7F**, followed the same trend as the VE% values for all electrodes, indicating that the overall performance is influenced by chemical and electrochemical losses. Among the functionalised

electrodes, CC-T-R displays higher stability across current densities compared to CC-T-Rpy and CC-T-Spy functionalised with pyridyl-N. We speculate that could be from pyridyl adlayer deactivation or surface chemistry changes under operational conditions. Preliminary stability tests of CC-T-Rpy [82], i.e. the electrode with the highest pyridyl surface coverage, show a decline after ca. 12 cycles at the lowest current density tested (**Figure S14, Table S10**) supporting that the surface chemistry might undergo changes over prolonged galvanostatic cycling. Despite these differences, the efficiency values were similar across the three surface functionalised electrodes, a result that reflects findings from CV studies on CC samples that support porosity and wettability effects dominate the overall performance, contributing to pore volume accessibility, and in turn preventing any discrimination of electrochemical behaviour specific of surface chemical sites [3, 5, 83].

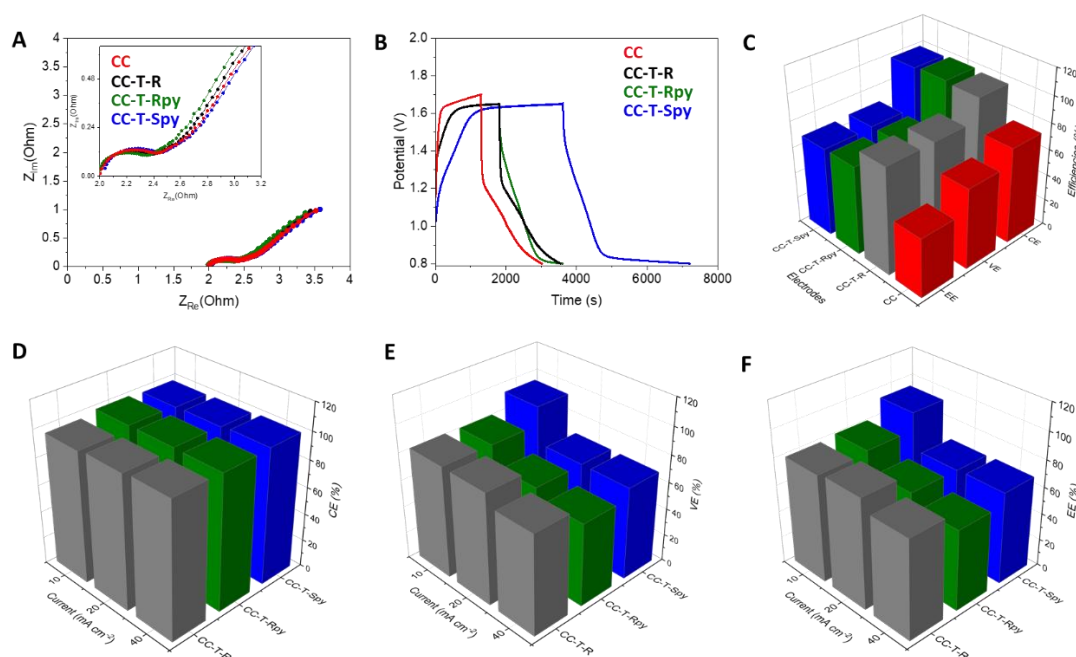


Figure 7. Results of VRFB cycling tests. (A) Nyquist plot at 1.23 V for frequencies in the range 10^{-2} - 10^6 Hz; the inset shows details of the high frequency region. (B) Charge-discharge cycles at 20 mA cm⁻². (C) Comparison of coulombic (CE), voltage (VE) and energy efficiencies (EE) at 20 mA cm⁻² for CC, CC-T-R, CC-Rpy and CC-T-Spy. Comparisons of (D) CE, (E) VE and (F) EE of functionalized CC-T-R, CC-T-Spy and CC-T-Rpy at 10, 20 and 40 mA cm⁻².

4. Conclusions

Model thin film electrodes with smooth topography and disk geometry were fabricated to investigate the effect of pyridinic-N functionalities anchored at carbon substrates on the vanadyl/pervanadyl redox process. Electrodes modified with pyridyl groups via aryldiazonium chemistry displayed faster charge transfer and improved reversibility compared to N-free electrodes. No improvements were observed in the absence of surface pyridyl groups and simulations showed that the heterogeneous rate constant increases with pyridyl surface coverage. Indeed, rate constants approximately 50-fold larger than those of unmodified electrodes were determined using finite element methods. These results indicate that this surface functionality catalyses vanadyl oxidation. Pyridyl functionalization was also found to increase wettability at the carbon surface, however, surface treatments that increased wettability alone, i.e. without achieving grafting of pyridyl groups, did not lead to significant improvement in vanadyl charge transfer rates at thin film electrodes.

Surface modifications were then applied to typical porous carbon electrodes used in VRFB devices. All surface treatments that increased wettability and consequently access to the internal pore volume and ECSA of the electrodes led to an apparently fast electrochemical response. The effect of wettability completely dominated the anodic response at low overpotentials and prevented discrimination of any effects arising from specific chemical functionalities. This was also the case when carbon cloth electrodes were tested in VRFB devices: all surface functionalization reactions that led to increased wettability improved performance indicators with no evidence of advantages arising from increased intrinsic activity at pyridyl modified surfaces. Therefore, our findings indicate that while surface chemistry is essential in determining intrinsic catalytic activity, porosity-related effects often dominate in determining the electrocatalytic and charge-discharge performances at porous electrodes. This

highlights the importance of using model electrodes with controlled surface properties to unambiguously identify surface functionalities that impart catalytic activity.

Acknowledgements

This publication has emanated from research conducted with the financial support of Taighde Éireann – Research Ireland under Grant numbers GOIPD/2021/530, 19/FFP/6761 and 21/FFP-A/9161. SEM imaging was carried out at the Advanced Microscopy Laboratory (AML) at the AMBER Research Centre, Trinity College Dublin, Ireland. Use of the XPS of I. V. Shvets and C. McGuinness provided under SFI Equipment Infrastructure funds.

Conflict of Interests

The authors declare no conflict of interest.

Supporting Information

Supporting Information containing additional information on sample preparation, XPS analysis, cyclic voltammetry results, parameters and conditions used for numerical simulations, and VRFB cell performance is available online.

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