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Exploration of Biomass-Derived Activated Carbons for Use in Vanadium Redox Flow Batteries

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ABSTRACT: Increasing redox reaction rates on carbon electrodes is an important step to reducing the cost of all-vanadium redox flow batteries (VRFBs). Biomass-derived activated carbons (ACs) hold promise as they may obviate the need for post-synthetic modifications common to conventional materials. While initial efforts have shown that these materials can enhance VRFB performance, the wide selection of potentially inexpensive feedstocks and synthesis routes lead to a collection of electrocatalytic materials with disparate physical, chemical, and electrochemical properties, challenging the development of generalizable design principles. Here, we employ a hydrothermal processing (HTP) technique to produce elementally diverse ACs, varying biomass feedstock composition, and HTP temperature. Specifically, we study ACs derived from chitin, which contain nitrogen and oxygen functionalities, and ACs derived from pine wood, which contain oxygen functionalities. Using Vulcan XC72 as a comparator, we apply spectroscopic, electrochemical, and computational techniques, finding electrochemically accessible surface area, rather than the heteroatom composition, to be the more representative performance indicator. Evaluation of the best-performing AC in a VRFB reveals $\sim 100 \text{ mW cm}^{-2}$ improvement in peak power density when deposited into felt electrodes. The feedstock-processing-property relationships studied in this work represent a systematic approach to advancing biomass-based functional materials for use in energy applications.

KEYWORDS: biomass, vanadium redox flow battery, electrocatalyst, chitin, wood

INTRODUCTION

Stationary electric energy storage is anticipated to play an increasingly important role in the efficient, reliable, and sustainable delivery of electricity, especially with increasing deployment of low-cost variable energy sources. Redox flow batteries (RFBs) are an emerging electrochemical technology whose decoupling of power and energy scaling, long operational lifetimes, and safety are particularly appealing for long-duration energy storage.^{1–4} Considered the state of the art system, the all-vanadium redox flow battery (VRFB) leverages four different stable oxidation states of vanadium dissolved in an acidic aqueous electrolyte with the negative (V(II)/V(III)) and positive (V(IV)/V(V)) redox couples separated by a permselective membrane.⁵ As both redox couples are based on the same element, crossover tolerance is an enabling feature as any capacity lost due to undesirable species transport across the membrane can be recovered through periodic rebalancing. Unfortunately, contemporary VRFB technologies are considered too expensive for many emerging grid services, motivating research into alternate redox electrolyte formulations,^{6,7} separation strategies,^{8–11} and reactor formats.^{12–15}

An effective cost-reduction strategy is to improve the power performance of the electrochemical stack, thus reducing the reactor size and material requirements. Historically, carbon or

graphite felts and papers derived from polyacrylonitrile or Rayon have been used as RFB electrodes due to their relatively high volumetric surface area, three-dimensional network structure, high electrical conductivity, and suitable mechanical, chemical, and electrochemical stability, satisfying the criteria for a functional electrode.^{16–21} For VRFBs, the sluggish reaction kinetics of both the positive and negative redox couples ($k_0 \sim \text{O}(10^{-5}) \text{ cm s}^{-1}$) on carbon surfaces^{22–25} limit battery performance. A pretreatment strategy to overcome this issue is to thermally oxidize the electrodes in air or other gaseous mixtures (e.g., ozone, ammonia) in order to modify functional groups on the surface and increase electrochemically accessible surface area (ECSA).^{26–29} Electrochemical^{30–32} and chemical oxidation³³ strategies have also been pursued. However, these methods involve post-process surface modification of existing carbon diffusion media suggesting that, ultimately, imparted performance improvements may be

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incremental, limited by the properties inherent to the substrate material.

Re-envisioning RFB electrodes derived from low-cost, sustainable precursors with inherently favorable properties may offer a pathway to simultaneous performance enhancement and cost reduction. Strategically targeting source materials that already contain desired properties would lead to fewer process steps than the current approach of high-temperature conversion of polyacrylonitrile to graphitized carbon followed by energy-intensive or laborious post-synthetic modification methods.³⁴ To this end, prior literature has shown that electrochemically active materials can be synthesized from diverse biomass sources through carbonization and thermal activation for a broad set of electrochemical systems.^{35–47} Recent exploratory studies of biomass-based electrodes in VRFBs have demonstrated performance improvements compared to analogous pristine carbon substrates with a wide range of altered properties cited as the underlying cause including improvements in wetting, incorporation of catalytic functional groups, increases in ECSA, and reductions in mass transport resistance.^{48–55} The range is, in part, reflective of the dependence on the precursor origin, processing conditions, and electrode form factor. Hence, there is a need to identify enabling chemical functionalities and structural features within precursor materials, establishing synthetic routes to generate appropriate catalyst phases, compositions, and form factors, and finally effectively incorporating these materials into electrochemical platforms to evaluate their efficacy—the feedstock-processing-property relationships for biomass-derived activated carbons (ACs). Advancing our understanding of such relationships is key for optimizing biomass-derived ACs.

Pursuant to these goals, we present a study of biomass-derived activated carbons for use in VRFBs, produced via hydrothermal processing (HTP)³⁵ of two sustainable, low-value feedstocks, pine wood and chitin from shrimp shells. These feedstocks are selected for their high carbohydrate content, which is prone to the formation of hydrochar under HTP conditions.⁵⁶ Moreover, they display different heteroatom functional groups, oxygen in pine wood and nitrogen and oxygen in chitin. We vary feedstock type and HTP temperature and relate resulting differences in elemental composition, bonding structure, and material properties to electrochemical performance (Figure 1). A comprehensive set of spectroscopic, microscopic, electrochemical, and analytical techniques are used to determine which properties most impact vanadium electrochemistry. We compare these results to Vulcan XC72, a commercially available carbon-black material with similar physical properties to the ACs tested here but without heteroatoms. Finally, the best-performing AC was deposited into a graphite-felt electrode and evaluated in a VRFB cell to determine whether the enhancements observed in isolation could be realized in a more practical embodiment. We anticipate that, beyond the specific materials assessed in this study, the methods and analyses described in this work will prove valuable for future efforts seeking to advance biomass-derived materials for energy storage applications.

RESULTS AND DISCUSSION

Hydrothermal Synthesis of ACs. The features of ACs (e.g., porosity, heteroatom content, and chemical functionalities) can be engineered by adjusting HTP parameters like feedstock, temperature, reaction time, or reactor type. HTP

Figure 1. Scheme of the work presented in this study: biomass from either shrimp shell-derived chitin or from pine wood is subjected to HTP to produce ACs that are incorporated into felt electrodes. These electrodes are implemented into a VRFB to evaluate their performance.

converts wet bioresources into a precursor of AC termed hydrochar in higher yields, with better thermal stability and larger surface areas,⁵⁷ while avoiding the energy-intensive drying of biomass. During HTP, biomass is heated to temperatures of 200–300 °C in an aqueous environment, undergoing reactions including dehydration, hydrolysis, decarboxylation, aldol condensation, solid–solid, Maillard, and repolymerization,^{58–60} which decompose the biomass into incondensable gas, biocrude oil, hydrochar, and water-soluble organics. After separations (described in the [Supporting Information](#)), the hydrochar is converted into AC via a thermal activation step that increases the aromatization of its carbon structure. This promotes the formation of randomly distributed stacks of graphite sheets⁵⁷ and a hierarchical porous structure.

ACs from shrimp shell-extracted chitin and pine wood were obtained via HTP at 200 and 300 °C, followed by thermal activation at 850 °C under a nitrogen flow. From here on, these samples will be referred to as C200, C300, W200, and W300, where W and C stand for wood and chitin, respectively, and the number indicates the HTP temperature applied. The AC yield was similar for both feedstocks, oscillating between 22.0 ± 3.2 and 26.5 ± 1.2 wt % of the starting dry biomass ([Table S1](#)). These yields are on the high end of those typical of other biomass types, including macroalgae,⁴⁴ spent coffee beans,⁵² chitosan,⁶¹ or sugar cane bagasse,⁶² which we attribute to the high thermal stability of the two feedstocks used in this study, due to the *N*-acetyl amine group in the C2 position for chitin^{63,64} and the lignin in pine wood.⁶⁵

Physical and Chemical Characterization of Synthesized ACs. Fourier-transform infrared (FTIR) spectra of hydrochars and ACs were used to assess the chemical changes that occurred during HTP and thermal activation. FTIR spectra ([Figure 2a,b](#)) of hydrochars produced at 200 °C were similar to the spectra of their corresponding feedstock, whereas the number of peaks decreased in hydrochars produced at 300 °C, due to dehydration. Regardless of the HTP temperature, a reduction in the number of peaks was found in all of the ACs, due to cleavage of most of the IR-active functional groups from hydrochar and aromatization of the carbon structure. FTIR spectra for both wood- and chitin-derived ACs were similar,

Figure 2. Characterization of biomass-derived material surface chemistry, morphology, and surface area at two HTP temperatures. Attenuated total reflectance Fourier-transform infrared (FTIR) spectroscopy of feedstock, hydrochar, and AC for (a) wood and (b) chitin. (c) Representative X-ray photoelectron spectroscopy (XPS) on ACs to determine specific functionalities. Please refer to Figure S1 in the Supporting Information for XPS fittings with deconvoluted spectra. (d) Representative Raman spectroscopy with deconvoluted I_D vs I_G band structures. (e) Nitrogen physisorption of ACs, along with (f) pore-size distribution estimated using the nonlocal density functional theory. Refer to Table S2 for a summary of the nitrogen physisorption results. (g) ECSA of AC films on glassy carbon electrodes (GCE) estimated from double-layer capacitance. Representative cyclic voltammograms (CV) used to determine double-layer capacitance can be found in Figure S2 in the Supporting Information. (h) Static water droplet measurements on AC films dropcast onto a glass substrate. Enlarged images of the droplets can be found in Figure S3 in the Supporting Information.

revealing only a few peaks attributable to C–C bonds or out-of-plane bending vibrations of C–H bonds in aromatic systems.⁶⁶ Nonetheless, a peak at 1500–1750 cm^{-1} associated with nitrogen-containing heterocyclic aromatic structures⁶⁷ was only present in chitin-derived ACs. This confirms the presence of nitrogen functionalities on chitin-derived ACs at both HTP temperatures applied.

High-resolution X-ray photoelectron spectroscopy (XPS) was performed to study the binding environment of carbon, oxygen, and nitrogen atoms in ACs (Figure 2c). The results revealed that the ACs were mainly composed of carbon (>85 wt % for chitin, >90 wt % for wood), and that nitrogen and oxygen functionalities were incorporated in the AC structure as dopants. The concentration of those functionalities was more dependent on the feedstock than on the HTP temperature. 59.5–65.7% of the carbon was aromatic, followed by C1 carbon (ascribed to aliphatic chains or pyridinic groups). The content of C1 carbon was higher in chitin-derived ACs (22.7–22.8%), suggesting a higher content of pyridinic nitrogen. The main binding environment for oxygen was O2 (45.7–55.2%), related to ethers, epoxys, alcohols, or esters. Nitrogen (only present in chitin-derived ACs) appeared to be incorporated on the edges of graphitic planes (>90%) in five- or six-membered rings (pyridines and pyrroles, mainly), whereas the content of nitrogen in the graphitic plane (N3) was 5.0–7.1%.

The impact of the heteroatoms on the aromatic structure of the material was assessed by Raman spectroscopy (Figure 2d). In such analyses, the D band (ca. 1350–1360 cm^{-1}) represents graphitic edges, symmetry-breaking topological defects, or vacancies, whereas the G band (ca. 1570–1580 cm^{-1}) arises from in-plane vibration of sp^2 atoms. The intensity ratio of the D and G bands (I_D/I_G) was used to assess the existence of defects in synthesized ACs. This ratio was higher for the ACs than for Vulcan XC72 (0.90), revealing their abundance in lattice edges and defects. The I_D/I_G ratio was also more sensitive to the biomass feedstock (1.02–1.05 for wood-derived ACs, 1.26–1.28 for chitin-derived ACs) than to the HTP temperature.

The nitrogen adsorption–desorption isotherms (Figure 2e) for all ACs exhibited prominent uptake at low relative pressures, indicating the presence of micropores. The isotherms for W200, W300, and C300 resemble characteristic type I isotherms typical for microporous solids.^{68,69} W200 and W300 display nearly identical isotherm shapes, while those of C200 and C300 differ. Only the C200 features type I and type IV isotherm characteristics, suggesting capillary condensation effects taking place in mesoporous regions formed at lower HTP temperature. Additionally, for C200, H3 type hysteresis is observed between adsorption and desorption isotherms in the 0.40–0.99 P/P_0 range, suggesting the presence of aggregates of

plate-like particles that give rise to slit-like pores.^{68,69} The coexistence of both type I and type IV characteristics along with hysteresis in the C200 isotherms indicates that the C200 porous structure consists of a hierarchical, interconnected network of mesoporous channels with micropores (Figure 2f).⁶⁸ Assuming full wettability, this structure appears advantageous for electrolyte penetration through mesopores and access to reaction sites within the micropores. Pore-size distributions calculated using nonlocal density functional theory showed evidence of micropores (<2 nm) in all samples as well as mesopores. The Brunauer–Emmett–Teller (BET) surface area was of relatively similar magnitude for W200 (494 m² g⁻¹) and W300 (436 m² g⁻¹). C200 had the largest BET surface area (616 m² g⁻¹) and C300 the smallest (102 m² g⁻¹), highlighting the opportunity for controlling the surface area of the ACs for electrochemical applications by adjusting HTP parameters. The measured BET surface area values are in general agreement with other thermally activated ACs produced from spent coffee beans (541–1113 m² g⁻¹)⁵² or chitosan (523 m² g⁻¹)⁶¹ but are significantly lower than ACs chemically activated with KOH (maximum ca. 1579 m² g⁻¹).^{70,71} To visualize the pore morphology and distributions of the biomass, the particles were imaged via scanning electron microscopy (SEM), demonstrating a distribution of sizes averaging ca. 10–20 μ m (Figure S4). C200 appears to exhibit textured surfaces, which are less pronounced in C300, possibly explaining the observed difference in surface area. W200 and W300 are of similar microstructure, which is in agreement with the BET measurements, and also coincident with the globular shape commonly reported in the literature for activated carbons derived from cellulose-rich biomass.^{41,59}

While gas physisorption provides information about the total electrode surface area and morphology, it may not reflect the actual utilized surface area in electrochemical systems.⁷² Therefore, a potentially more representative metric is the electrochemically accessible surface areas (ECSAs) of the ACs. To this end, we performed double-layer capacitance measurements in a three-electrode electrochemical cell where the working electrode was a glassy carbon electrode coated by a thin film of the respective ACs (see procedure and calculations in the Experimental Section). The estimated ECSAs for C200 and C300 were $\sim 8\times$ and $\sim 3\times$ greater than that of Vulcan XC72 (Figure 2g), respectively, whereas W300 exhibited a similar capacitance to the Vulcan XC72. The relatively high surface area predicted using ECSA for C200 compared to Vulcan XC72 is in agreement with the BET surface area. However, the ECSA measured for C300 is unexpectedly higher than that of Vulcan XC72, contradicting BET surface area results. Similarly, the predicted ECSAs for both W200 and W300 relative to Vulcan XC72 are lower than predicted by BET. A possible explanation is that capacitance measurements are more sensitive to microstructural defects and edge sites in the carbon structure, since the capacitance of edge plane carbon is an order of magnitude greater than that of basal plane carbon.⁷² As shown in Raman spectroscopy and discussed in an earlier section, chitin-derived ACs prepared at both HTP temperatures have abundant lattice edges and defects, enhancing capacitance and ECSA, but having less of an impact on gas sorption measurements. It should be noted that the differences in BET and ECSA measurement methodologies and test conditions have been reported to lead to discrepancies in estimated surface area values.^{73–75} While a detailed discussion on the nuances of surface area measurements are

outside the scope of this study, we postulate that the ECSA measured via double-layer capacitance is more representative of the actual utilizable electrode area in solution-based electrochemistry since it more closely captures the electrode environment during operation. Capacitance also increases as a function of wettability, gauged by apparent water contact angle measurements on dropcast and dried AC films on a flat glass surface.^{76,77} The apparent contact angles for synthesized ACs (54–60°) at droplet volumes of 10 μ L were much lower than that of Vulcan XC72 (130°) despite sharing pore sizes of the same order and having similar micro-/mesoporous morphology,⁷⁸ suggesting that the ACs are more hydrophilic (Figure 2h), which we attribute to the presence of oxygen and nitrogen functionalities, conducive to wetting, on the AC surfaces.^{26,67,79–81}

Ex Situ Electrochemical Evaluation of Synthesized ACs. Cyclic voltammetry (CV) measurements were performed to assess the suitability of ACs as electrocatalysts for vanadium redox reactions and to identify the best-performing AC for full-cell testing. In all experiments, the working electrode was a glassy carbon electrode (GCE) with a thin film of ACs dropcasted onto the surface. In brief, the catalyst ink consisted of a suspension of AC particles (~ 10 to $20\ \mu$ m size as measured via SEM) and Nafion binder in a mixture of water and *N*-methyl-2-pyrrolidone; further details can be found in the Experimental Section. CVs were performed in both the 0.1 M V(IV) in 0.1 M H₂SO₄ supporting electrolyte and in the electrochemically generated 1 M V(II) in 2 M H₂SO₄ supporting electrolyte. A lower active species concentration was used for V(IV)/V(V) redox couple as higher concentrations were found to promote oxidation of Vulcan XC72, which leads to performance changes during the experiment. Figure 3a shows CVs at scan rates of 10, 20, 30, 40, and 50 mV s⁻¹ in both electrolytes for C200 (black lines) and W300 (blue lines), the top-performing ACs for each feedstock, along with Vulcan XC72 (red lines) for comparison. Figure 3b–e shows peak current and peak separation as a function of the scan rate. Note that, for clarity, C300 and W200 were omitted from Figure 3 as their respective CVs displayed characteristics of slower redox kinetics (i.e., less well-defined, broader peak shapes) as compared to those shown here. A full range of CVs and tabulated figures of merit across multiple scan rates and for all materials can be found in Tables S3 and S4 and Figures S5 and S6 in the Supporting Information.

Analysis of the variations in the separation between oxidative and reductive peaks as well as the relative peak currents as a function of the scan rate provide insight into the comparative reversibility and electrochemical activity of the respective vanadium redox reactions on the different carbons (Figure 3c,e). In all cases, the peak-to-peak separation (ΔE), after 100% *i*R compensation, increases significantly with the increasing scan rate, indicating that, under these experimental conditions, the kinetics are quasi-reversible to electrochemically irreversible for both redox couples. This observation is in agreement with numerous prior studies of vanadium redox reactions on a range of carbon electrocatalysts and electrodes.^{23,32,82–85} In both electrolytes, C200 exhibited the smallest peak-to-peak separations and highest peak currents of all materials examined. While intrinsic kinetic rate constants could not be unambiguously resolved in this work due to the challenges associated with rigorous analysis of electrocatalysts embedded in rough films with heterogeneous porosity, morphology, and wettability,^{86–88} from a semiquantitative

Figure 3. (a) Cyclic voltammograms of Vulcan XC72 (red lines), W300 AC (blue lines), and C200 AC (black lines) at scan rates of 10, 20, 30, 40, and 50 mV s⁻¹. Electrolyte compositions were 1 M V(II) in 2 M H₂SO₄ and 0.1 M V(IV) in 0.1 M H₂SO₄. Peak currents for (b) V(II) and (d) V(IV) electrolytes as a function of the scan rate. Peak-to-peak separation for (c) V(II) and (e) V(IV) electrolytes as a function of the scan rate. The scan rates used were 10, 20, 30, 40, 50, 75, 100, 150, and 200 mV s⁻¹ for the V(II) electrolyte and 5, 10, 20, 30, 40, and 50 mV s⁻¹ for the V(IV) electrolyte. Scan rates were chosen to capture a range over which peaks were clearly visible for a given electrolyte. The working, counter, and reference electrodes used were a 3 mm glassy carbon disk coated with a thin film of ACs, a Pt wire, and Ag/AgCl in 3 M NaCl.

perspective, reduced ΔE is indicative of greater reversibility. For the V(II) electrolyte, at a scan rate of 50 mV s⁻¹, the $\Delta E_{V(II)}$ for C200 (0.242 ± 0.053 V) was smaller than that of Vulcan XC72 (0.423 ± 0.020 V) as well as that of W300 (0.526 ± 0.084 V). Similarly, although closer, in the V(IV) electrolyte, the $\Delta E_{V(IV)}$ for C200 (0.147 ± 0.014 V) was smaller than that of W300 (0.198 ± 0.056 V) and Vulcan XC72 (0.207 ± 0.008 V). Analysis of peak currents also suggests that C200 is the most kinetically active catalyst of the ACs, with the greatest magnitudes for both anodic and cathodic peak currents across all scan rates for both redox couples (Figure 3b,d). This is especially apparent in the V(IV) electrolyte, in which the peak anodic current for C200 relating to V(IV) oxidation is $\sim 1.9\times$ that of Vulcan XC72 and $\sim 1.7\times$ that of W300 at 50 mV s⁻¹. In the V(II) electrolyte, the peak reductive current for C200 relating to V(II) reduction is $\sim 1.2\times$ that of Vulcan XC72 and $\sim 1.9\times$ that of W300 at 50 mV s⁻¹. Additionally, we observe that peak currents scale linearly with the square root of the scan rate with similar slopes for the V(II) electrolyte but a steeper slope for the C200 in the V(IV)

electrolyte. As the magnitude of the slope is proportional to vanadium ion diffusivity, we tentatively attribute differences observed in Figure 3d to differences in effective vanadium diffusivity in the porous thin films, which is dependent on electrolyte uptake.

Comparing CVs of the same feedstock at different HTP temperature offers insight into the interplay between and relative importance of surface area and surface chemistry. For example, while the elemental compositions of C200 and C300 are near identical, C200 significantly outperforms C300 in voltammetry studies. Surface area is the major difference between C200 and C300 as evinced by both nitrogen adsorption–desorption and double-layer capacitance (see Figure 2e,g). Specifically, the BET surface area of C200 ($616 \text{ m}^2 \text{ g}^{-1}$) greatly exceeds that of C300 ($102 \text{ m}^2 \text{ g}^{-1}$) and the ECSA for C200 ($3.76 \times 10^4 \mu\text{F cm}^{-2}$) is more than double that of C300 ($1.45 \times 10^4 \mu\text{F cm}^{-2}$). This suggests that the source of the performance enhancement of C200 is the abundance of active sites, due to the higher surface area, rather than the specific elemental composition of those sites. The responses for ACs derived from pine wood are more nuanced, but the importance of ECSA remains clear. For wood-based ACs, although CV analysis indicates W300 to be the better electrocatalyst, both W200 and W300 have very similar chemical functionalities and nitrogen isotherm shapes. However, while W200 exhibits a slightly higher calculated BET surface area than W300 (494 vs $436 \text{ m}^2 \text{ g}^{-1}$, respectively), the ECSA for W300 ($5.61 \times 10^3 \mu\text{F cm}^{-2}$) is $\sim 1.45\times$ that of W200 ($3.88 \times 10^3 \mu\text{F cm}^{-2}$). The results suggest that ECSA is a critical indicator of electrochemical rates, with higher ECSA correlated to enhanced electrochemical performance for a given feedstock. Intuitively, a higher ECSA means that the electrolyte is able to infiltrate and interact with more active sites on the electrode surface, a result of better wettability and/or a pore morphology that enables access into more recessed regions. Full utilization of the electrode area is critical to maximizing contributions from active sites. Thus, for these AC materials, ECSA acts as a qualitative metric for electrochemical properties within a given feedstock.

While the microstructure and surface area play an important role in electrochemical performance, the impact of functional groups is critical to fully understand the electrochemical reactivity of element-rich ACs and warrants further contemplation. Indeed, several studies have shown that oxygen functional groups have little influence or impede the V(IV)/V(V) reaction but reduce V(II)/V(III) charge-transfer resistance.^{24,32,89} However, all ACs in this study contain approximately the same absolute amount of the oxygen content without significant variation in binding environment, barring the direct correlation of the oxygen content to performance. Pertinent to chitin, nitrogen heteroatoms have been reported as effective electrocatalysts due to their ability to preferentially attract charged ions in solution, introduce defect sites, and facilitate the formation of a transitional state.^{79,90–94} While a direct correlation between the nitrogen content and electrochemical behavior could not be observed in this study, since chitin elemental composition proved insensitive to HTP temperature, it is worth noting the nitrogen content in the chitin-based ACs is relatively low, as compared to the number of carbon sites, potentially diluting their impact (Table S1). Since quantitative information and contributions from nitrogen heteroatoms were not measurable via experiments, we performed density functional theory (DFT) calculations to

predict nitrogen and carbon interactions with vanadium (Section S3 in the Supporting Information), confirming that bond distances indicate a preference of vanadium toward the nitrogen atoms for both V(II)/V(III) (Figure S7) and V(IV)/V(V) (Figure S8 and Table S5). While the DFT results describe carbon systems in a neutral state, future work will address interactions in acidic environment with applied electrode potential, relevant to the VRFB system. An in-depth discussion is provided in the Supporting Information.

Evaluation of Deposited C200 in a VRFB Single Cell.

Based on its observed promising physical and electrochemical properties, C200 was deposited on carbon felt electrodes via a passive flow method, reported by Aaron et al.,⁹⁵ which is facile, robust, and binder free. Passive deposition relies on the physical adhesion of the AC particles to the electrode scaffold (see Figures S9 and S10). Since implementing this technique does not require substantial changes to RFB architectures, flow deposition may offer a simple and effective way of incorporating catalytic or surface-modifying materials into existing vanadium flow cells. We note that the purpose of the full-cell performance is to explore an effective and rapid method of biomass implementation for immediately realizable benefits and not to offer additional or definitive conclusions on the fundamental properties of the biomass due to obfuscation from complex and dynamic device-level variables.

To evaluate the hypothesis that high surface area ACs doped with N and O can provide benefits in VRFB cells, we compared discharge polarization and power density curves, as well as electrochemical impedance spectroscopy (EIS) of full cells at 50% state-of-charge (Figure 4). Heat-treated and pristine carbon felt electrodes with and without deposited C200 were examined. The results showed an enhancement in kinetics and maximum attainable power density due to C200 deposition for both the pristine and heat-treated electrodes (Figure 4a). The area-specific Ohmic resistance (R_Ω) was determined using the high-frequency intercepts from Nyquist plots (Figure 4b) and subtracted in subsequent analyses to isolate kinetic and mass transport effects. R_Ω is largely determined by membrane resistance, compression ratio, and cell architecture; it was similar in magnitude among all cells at $0.79 \pm 0.09 \Omega \text{ cm}^2$, although cells with the pristine electrodes had slightly higher Ohmic resistances than those with heat-treated electrodes possibly due to incomplete wetting (see Table S6). The use of thicker carbon felt electrodes (6 mm) contributes to the higher area-specific Ohmic resistance and consequently the greater Ohmic losses and reduced energy efficiency as compared to VRFB cells that utilize thinner electrodes.⁹⁶ However, the use of thick felts is effective for the purpose of comparative analysis between pristine and biomass-coated electrodes and minimizes the likelihood of clogging. The addition of biomass onto the felt is expected to have minimal effect on overall electrode porosity (ca. 90%) given the relative loading amount and estimated bulk densities of both carbon felt and biomass microparticles. Although assessing spatial heterogeneities in porosity is difficult, the average felt pore size ($\sim 60 \mu\text{m}$)²¹ and biomass particle diameters (~ 10 to $20 \mu\text{m}$) differ sufficiently such that widespread clogging is unlikely at these loadings. To investigate differences in kinetic and mass transport contributions, we assess iR_Ω -corrected Nyquist plots at open circuit voltage (OCV). The higher-frequency semicircle related to charge-transfer resistance was smaller with the addition of C200, comparable in size between C200 + pristine and heat-

Figure 4. Evaluation of C200 AC in a full-cell configuration, with a starting solution of 1.5 M V in 2.6 M H_2SO_4 charged to 50% SOC. C200 AC was deposited onto carbon felts via circulation at 50 mL min^{-1} for 2 days. (a) Discharge polarization and power density curves and (b) iR_Ω -corrected Nyquist plots from EIS at OCV for pristine felt (red squares), C200 AC + pristine (black circles), heat-treated felt at 450°C (blue triangles), and C200 AC + heat-treated felt (green diamonds) at 80 mL min^{-1} flow rate, corresponding to a 2.24 cm s^{-1} superficial linear velocity.

treated, and smallest for C200 + heat-treated, indicating an improvement in kinetics upon C200 deposition. The lower-frequency semicircle corresponding to mass transport resistance was clearly pronounced for pristine electrodes, likely due to incomplete wetting, and reduced in size but still observable for heat-treated electrodes. However, the low-frequency arc was barely discernible and smaller for both C200 + pristine and C200 + heat-treated. This decrease in mass transport resistance regardless of thermal activation indicates that C200 has a clear beneficial impact on mass transport, although the precise mechanism is unclear.

In order to extract a more quantitative parameter to capture the kinetic enhancement observed in the Nyquist plots, the Butler–Volmer model for charge-transfer kinetics was used on the linear portion of iR_Ω -corrected polarization curves at low current density ($<50 \text{ mA cm}^{-2}$) to determine global exchange current densities (Table S6). Direct comparison of pristine and heat-treated electrodes with and without C200 revealed a lower activation overpotential after depositing C200. In accordance with BET and ex situ ECSA measurements, the deposition of C200 onto the felt electrodes increased the accessible surface area as estimated from the capacitance measurements in the flow cells using 2.6 M H_2SO_4 as the electrolyte (Figure S11), which we posit is the primary driver for improved kinetics. Coincidentally, the heat-treated electro-

des and the pristine electrodes with C200 deposited had similar geometric exchange current densities, suggesting that the effects of surface chemistry and higher surface area owed to C200 deposited onto the pristine felt had a similar net effect as the oxygen functionalization of the felt from heat treatment.

Encouragingly, improvements in maximum attainable power density of $\sim 100 \text{ mW cm}^{-2}$ were observed upon depositing C200 onto pristine and heat-treated felts. This suggested that the coupling of a macroporous but lower surface area scaffold, here the felt, with a microporous but higher surface area catalytic material, here the C200 AC, can work in tandem to form an effective hierarchical electrode structure. We note that while the observed improvement due to the adhered biomass microparticles is apparent here, quantitative comparison with other reported systems is complicated by laboratory-to-laboratory differences in electrolyte composition, cell geometry, and cell operating conditions. Galvanostatic cycling of C200 deposited onto pristine felt was performed to assess the durability of the deposited particles on the performance of the felt over the course of 10 cycles lasting 4 days, demonstrating no significant performance loss (Figure S12 and Table S7) and that biomass adhered to the carbon felt post-cycling in vanadium (Figure S13). Aaron et al. observed similar performance improvements and cycle stability for RFBs containing carbon felt electrodes decorated with passively deposited high surface area materials.⁹⁵ Ultimately, the combination of heat treatment and C200 deposition proves additive resulting in a power density of 438 mW cm^{-2} , the highest attained in this experimental set. We hypothesize that, as the heat-treated electrode has improved wettability, increased surface oxygen content, and higher surface area, not only is the base scaffold more active but also C200 adheres more easily throughout the structure.

CONCLUSIONS

Electrode materials synthesized from biomass precursors containing inherently favorable properties hold promise for reducing system costs while elevating reactor performance. To date, the establishment of design principles for biomass-derived electrodes has been complicated by the range of viable biomass sources, synthesis routes, and resulting electrode form factors. In this study, we convert two biomass feedstocks, chitin from shrimp shells and pine wood, into electrochemically active, high-surface-area, N- and/or O-doped ACs using a practical and effective HTP process followed by thermal activation. Physicochemical characterization reveals feedstock-processing-property relationships for biomass-derived ACs with regard to biomass source and HTP temperature. Although our synthesis process preserves elementally diverse heteroatoms and creates high surface area ACs, the HTP temperature does not strongly vary AC yield, elemental composition, functional groups, and structural order for a given feedstock, but instead can be a feedstock-dependent lever for controlling AC surface area. Subsequent ex situ analysis based on double-layer capacitance to determine ECSA and CVs as a proxy for electrochemical reactivity suggests that ECSA serves as a qualitative indicator for electrochemical performance. While all ACs produced were electrochemically active, chitin subjected to an HTP temperature of 200°C (C200) demonstrated the best performance, even compared to Vulcan XC72, a commercial porous carbon-based material lacking heteroatoms. Despite having nearly identical chemical composition to C200, chitin treated at an HTP temperature of

300°C (C300) had a much lower ECSA and BET surface area and poorer electrochemical performance. Based on the physicochemical and ex situ analyses, C200 was chosen as a model compound to be flow-deposited onto carbon felt electrodes in a full VRFB to assess if the prior observed benefits manifest in a practical setting. Depositing C200 resulted in both kinetic enhancement as well as an increase in maximum power density of $\sim 100 \text{ mW cm}^{-2}$ for both pristine and heat-treated electrodes. Furthermore, the highest peak power density of 438 mW cm^{-2} was achieved with C200 deposited onto heat-treated electrodes, a $\sim 30\%$ increase in maximum power density as compared to solely heat-treated, suggesting that heat treatment and C200 act in tandem to boost VRFB performance. We hypothesize that the combination of a lower surface area macroporous scaffold with a higher surface area microporous catalytic material is an effective method for boosting the performance of flow batteries based on kinetically sluggish, redox reactions. These findings suggest a pathway to designing advanced electrode materials with tailored properties via the use of low-cost and sustainable feedstocks, while simultaneously enabling less energy-intensive synthesis routes (i.e., low temperature) as compared to traditional graphitization processes. These results are relevant for the development of feedstock-processing-property relationships for HTP, in order to fine-tune key properties of resultant ACs with an ultimate goal of developing freestanding porous materials that can serve as both the catalytic material and the macroporous scaffold.

EXPERIMENTAL SECTION

Hydrothermal Processing (HTP). Coarse flakes (sieved $<5 \text{ mm}$) of pine wood sawdust and chitin from shrimp shells were used as received and subjected to HTP in a 75 mL autoclave at two temperatures (200 and 300°C), with a reaction time of 6 h , using a biomass:water slurry with $15 \text{ wt } \%$ biomass. Prior to each experiment, the autoclave was tightly sealed and flushed 3 times with nitrogen (20 bar) to remove the air from the reaction vessel. All of the experiments were carried out at least in triplicate to assess the reproducibility. Once the reaction time was completed, the gas was vented, and the remaining HTP products (biocrude oil, aqueous phase, and hydrochar) were then recovered from inside the vessel. First, the aqueous product was separated by vacuum filtration (glass microfiber filter, Whatman GF/B, $1 \mu\text{m}$ pore size). Subsequently, to separate the biocrude oil from the hydrochar, the remaining reactor contents and filter cake were washed with dichloromethane. The hydrochar remained on top of the filter and was dried at 105°C . Thereafter, the hydrochar was subjected to thermal activation in a tube furnace under a continuous flow of nitrogen. The temperature was ramped from room temperature to 850°C at 5°C/min and subsequently held for 2 h . The furnace was then allowed to cool down to room temperature before opening. The resulting AC was then ball-milled for 5 min to obtain a fine powder, which was subsequently used for analysis and electrochemical characterization. Technical details of the equipment and reagents used can be found in the [Supporting Information](#).

Material Characterization of AC. ACs were characterized by Fourier-transform infrared (FTIR) spectroscopy, Raman spectroscopy, scanning electron microscopy, X-ray photoelectron spectroscopy, and nitrogen physisorption to evaluate their material properties. The reader is referred to the [Supporting Information](#) for detailed descriptions of characterization procedures.

Ex Situ AC Electrochemical Evaluation. Catalyst inks of ACs were dropcast onto mirror-polished 3 mm diameter glassy carbon electrodes (CH Instruments). Prior to dropcasting, glassy carbon electrodes were polished in a $0.05 \mu\text{m}$ MicroPolish alumina powder (Buehler) slurry on a microcloth disk, rinsed in acetone and

isopropanol, sonicated in DI water, rinsed again with DI water, and finally air-dried. The inks were composed of 20 mg of AC powder, 400 μL of water, 400 μL of *N*-methyl pyrrolidone, and 70 μL of Liquion (5 wt % Nafion dispersion). This particular composition was selected after varying relative amounts of components to optimize the conformity of the ink coverage on the GCE. The mixture was then ultrasonicated for 1 h. Two μL of the resulting suspension was then dropcast onto the GCE with a pipette and left to air dry overnight to ensure slow evaporation and thus a more uniform coating.

Cyclic voltammetry and electrochemical surface area (ECSA) measurements were performed in a three-electrode cell with a Pt wire counter electrode, Ag/AgCl in a 3 M NaCl reference electrode (BASi), and carbon-coated GCE working electrode. Vulcan XC72 (Cabot Corporation) was used as the conductive carbon black for comparing against the biomass-derived ACs. All electrolytes were based on solutions containing different concentrations of sulfuric acid (H_2SO_4 , 95.0–98.0 w/w %, Sigma-Aldrich) and vanadium(IV) sulfate oxide hydrate ($\text{VOSO}_4 \cdot \text{H}_2\text{O}$, 99.9% metals basis, Alfa Aesar). The electrolyte for testing the V(II)/V(III) redox couple was 1 M V(II) in 2 M H_2SO_4 and was electrochemically generated from 1 M VOSO_4 in 2 M H_2SO_4 as described in the prior literature.^{26,97} The V(II) solution was stored under humidified nitrogen to prevent oxidation. The electrolyte for testing the V(IV)/V(V) redox couple was 0.1 M VOSO_4 in 0.1 M H_2SO_4 . Five mL of the electrolyte was used for each experiment. Three cycles were performed at each scan rate, with the data from the last cycle reported and used for analysis.

Porous electrode capacitance was used as an approximation of the electrochemically active surface area by performing cyclic voltammetry in 0.1 M H_2SO_4 in a three-electrode setup. The capacitance was calculated using eq 1

$$i = C \frac{dV}{dt} \quad (1)$$

where i represents the current (A), C represents the capacitance (F), and dV/dt represents the scan rate (V s^{-1}). Scan rates used were 20, 50, 100, and 200 mV s^{-1} , with a cell voltage window of 0.1–0.4 V chosen to avoid water dissociation and current values taken at 0.25 V (center of the measured interval) to calculate capacitance and avoid the influence of any pseudocapacitance. All cyclic voltammetry and ECSA are iR -corrected to prevent distortion from Ohmic losses. Cyclic voltammetry was performed using a VMP3 Bio-Logic potentiostat (Bio-Logic USA, Knoxville, TN).

Evaluation of AC Performance as an Electrocatalyst in Flow Cell Testing. The flow cell experimental setup used in this study has already been described in prior art.⁹⁸ In-depth description of the flow cell setup and electrochemical settings can be found in the [Supporting Information](#). Briefly, electrochemical testing was performed in a 2.55 cm^2 zero-gap flow cell architecture with flow through flow fields, presoaked Nafion 212 membrane, and carbon felt electrodes (6 mm thick), with an electrode compression of 34%. VRFB electrolytes were electrochemically generated and stored under humidified nitrogen. Double-layer capacitance was conducted on the full-cell configuration with 2.6 M H_2SO_4 electrolyte in two 50 mL reservoirs.

The capability of ACs as electrocatalysts for full-cell performance was tested by depositing C200, as a model material, onto graphite-felt electrodes (AvCarb G250-12) using a technique described by Aaron et al.⁹⁵ Fifteen mg of ball-milled carbon was suspended and dispersed in 3 mL of Millipore water and sonicated for at least 20 min. One and half mL of the resulting suspension was then pipetted into both electrolyte reservoirs and circulated for 2 days at a flow rate of 50 mL min^{-1} prior to any electrochemical testing to ensure that the chitin-derived AC was deposited into the felt electrodes. Note that thicker felt electrodes were chosen as thinner carbon electrodes (e.g., paper, cloth) are reported to clog when passively deposited with fine particulates.⁹⁵

The performance of thermally pretreated electrodes with AC passive deposition was evaluated by thermally oxidizing the carbon felt electrodes in air in a Barnstead Thermolyne Type 47900 box furnace at 450 $^\circ\text{C}$ for 6 h. These electrodes were placed on aluminum foil to prevent contamination, while making sure that the electrodes

did not overlap. Post-treatment, the electrodes were cooled at room temperature and stored in plastic containers in ambient conditions.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.0c02427>.

Full experimental details; additional characterization, ex situ, and flow cell data; density functional theory simulations and analysis ([PDF](#))

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Notes

The authors declare no competing financial interest.

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