Effect of Oxidation of Carbon Material on Suspension Electrodes for Flow Electrode Capacitive Deionization

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Supporting Information

ABSTRACT: Flow electrode deionization (FCDI) is an emerging area for continuous and scalable deionization, but the electrochemical and flow properties of the flow electrode need to be improved to minimize energy consumption. Chemical oxidation of granular activated carbon (AC) was examined here to study the role of surface heteroatoms on rheology and electrochemical performance of a flow electrode (carbon slurry) for deionization processes. Moreover, it was demonstrated that higher mass densities could be used without increasing energy for pumping when using oxidized active material. High mass-loaded flow electrodes (28% carbon content) based on oxidized AC displayed similar viscosities (∼21 Pa s) to lower mass-loaded flow electrodes (20% carbon content) based on nonoxidized AC. The 40% increased mass loading (from 20% to 28%) resulted in a 25% increase in flow electrode gravimetric capacitance (from 65 to 83 F g⁻¹) without sacrificing flowability (viscosity). The electrical energy required to remove ~18% of the ions (desalt) from of the feed solution (Figure S1a, Supporting Information).16 Gravimetrically, the flow electrodes are being explored.9

INTRODUCTION

There is a global need for additional potable water production to address scarcity. Reverse osmosis (RO), electrodialysis (ED), multiple effect distillation (MED), and multistage flash desalination (MSF)¹ are the main technologies currently being used for large-scale seawater and brackish water desalination. For high salt concentration sources (seawater), RO is a preferred technology. RO operates by removing the majority component (water) with membranes rather than the minority component (ions) and becomes less efficient at low salt concentrations. For ion removal from brackish waters, capacitive deionization (CDI) has gained increasing attention in the past decade primarily because CDI is effective at deionizing solutions and has the potential to be less costly and more energy efficient than RO.²

The three main CDI electrode architectures are flow-by,³ flow-through,⁴,⁵ and flowable electrodes.⁶–¹⁰ Traditional CDI⁵ and MCDI¹¹ systems utilize a flow-by architecture where a feed channel is created between two porous carbon electrodes placed in parallel. At the inlet, an ionized solution is fed into the channel and a potential (typically ~1 V) is applied across the electrodes. The applied potential results in specific adsorption of Na⁺ and Cl⁻ ions in an electric double layer at the surface of the active material. One challenge facing CDI is its complicated system operation because the deionization process is limited by the overall pore volume and pore size distribution of the active material (usually activated carbon).¹² As the pores become saturated with ions, the electrodes cannot remove ions until they are regenerated.¹³ Typical CDI systems function in an intermittent manner, with an applied voltage period (deionization) followed by a short circuit period (regeneration).¹⁴ To address the challenge of intermittent operation, CDI based on flow electrodes are being explored.⁹

Flow electrodes, first reported by Kastening,¹⁵ are composed of a capacitive granular material suspended in an electrolyte (Figure S1a, Supporting Information).¹⁶ Gravimetrically, the electrolyte is the majority component and physically transports...
the active material. By continuously replenishing the electroactive region (Figure 1a) with uncharged material, flow electrodes allow for continuous ion removal. This principle enables scalable and continuous deionization. The active material’s morphology, composition, and flow behavior all dictate the electrodes electronic and ionic transport properties. It is ideal to have a high active material mass loading for greater ion removal and enhanced charge transport through the creation of connecting percolation networks (Figure 1a). The limiting aspect with high mass loading is the flowability (rheological properties) of the electrode. Previously, it has been shown that the use of spherical particles on the order of 125 μm decreases flow electrode viscosity. However, for cost and scalability, it would be attractive to replace them with mass produced, fine-grained activated carbon powders, used in conventional CDI devices and already optimized for achieving good capacitance. This would decrease the cost and, possibly, improve the performance. However, those powders form very viscous slurries, making it challenging to flow (without clogging) above 20 wt %. There is a need to further understand the trade-offs between active material surface chemistry, active material loading, suspension stability, viscosity, and the deionization/regeneration performance characteristics of (suspension-type) flow electrodes.

Previously, oxidation methods have been shown to improve energy storage properties in supercapacitors (due to increased wettability and greater surface accessibility for ions) and to increase carbon nanotube suspension stability (via increased repulsion between particles). Suspension stability is indicative of less aggregation and a more monodisperse distribution of the active material. Here, we induce different structural orderings of the flow electrodes by oxidizing the active material and comparing its rheological and electrochemical properties to a flow electrode composed of nonoxidized activated carbon. The functionalized carbon surface holding an electric charge acts to align the water molecule dipoles. The Debye length extends up to 10 nm into the solution and may lead to separation of particles and keep the slurry flowing. Moreover, greater active material dispersibility (suspension stability) and less aggregation is expected to alter the flowability of suspension-type flow electrodes. Our rheological experiments demonstrated different flow behaviors (viscosities) for the flow electrodes composed of oxidized and nonoxidized activated carbon, indicating different active material interactions (Figure 2a).

These rheological properties were translated into parasitic pumping losses using a 1-D continuum physics based model, and electrical and pumping energy requirements were reported for oxidized and nonoxidized flow electrodes (Figure 5b). To study the surface chemistry, the active material (activated carbon) was characterized using X-ray photoelectron spectroscopy (XPS) before and after an acid treatment (oxidation). The flow electrodes were electrochemically evaluated in terms of dynamic gravimetric capacitance through cyclic voltammetry (CV) and resistance using electrochemical impedance spectroscopy (EIS). To investigate the deionization performance, flow based deionization testing was completed on a small scale.
flow electrode capacitive deionization (FCDI) system using a constant current operating condition (Figure 1b). The salt flux, current efficiency, and energy efficiency during the salt adsorption process was measured for the range of mass densities previously employed within FCDI literature for both oxidized and nonoxidized materials (5, 13, and 23 wt %).

### MATERIALS AND METHODS

Materials and Characterization. YP-50F activated carbon (Kuraray Chemical Company, USA) was chosen as the test material as it is commonly used in flow electrodes. A wet oxidation method with nitric acid was used to enrich the surface of the activated carbon (AC) with oxygen heteroatoms. A light oxidation procedure was followed in order to avoid changing the morphology and specific surface area of the material. AC samples were submerged in 0.5 M HNO₃ solution (Fisher Reagent ACS grade) and stirred for 1 h at room temperature. After oxidation, the sample was thoroughly washed with deionized water by centrifugation and dried in an oven at 90 °C for 12 h.

X-ray photoelectron spectroscopy (XPS) analysis was performed on each sample with a Physical Electronics VersaProbe 5000 instrument employing 100 μm monochromatic Al Kα X-rays to irradiate the surface of the samples (Figure 3a and Figure S4, Supporting Information). Emitted photoelectrons were collected by a 180° hemispherical electron energy analyzer. Samples were analyzed at a 45° takeoff angle between the sample surface and the path to the analyzer. Survey spectra were taken at a pass energy of 117.4 eV and with a step size of 0.5 eV to confirm the fidelity of the samples. High-resolution spectra were taken at a pass energy of 23.50 eV and with a step size of 0.05 eV. To avoid broadening of the XPS spectra caused by sample charging, an electron flood gun and ion neutralization were used while recording the data. The spectra were taken after the sample was sputtered with an Ar⁺ beam operating at 4 kV and 7 μA for 15 min, and all binding energies were referenced to that of adventitious carbon at 284.8 eV. The quantification and peak fitting were carried out using CasaXPS Version 2.3.16 RP 1.6. When fitting C 1s regions, all fwhm of components were restricted to be equal and peak positions were restricted to fit in line with literature values within a 0.3 eV window. When fitting O 1s regions, fwhm of components were restricted to be less than 3 eV and peak positions were allowed to float.

The oxidized and nonoxidized AC was characterized with gas sorption. Gas sorption at a relative pressure range from 0.05 to 1.0 P/P₀ was performed (Quadrasorb, Quantachrome, USA) with N₂ at −196 °C to determine the specific surface area (SSA) and pore size distribution. The average, volume-weighted pore size was derived from the cumulative pore volume by assuming slit-shaped pores and employing quenched-solid density functional theory (QSDFT) deconvolution of N₂-sorption isotherms (Figure 3b and Figure S3, Supporting Information).

Rheology. The viscosity of the flow electrodes (20/28 wt % AC and AC OX) was characterized through rheological studies (Figure 2a). For these studies, an AR 2000 rheometer (TA Instruments, USA) was used at room temperature at shear rates ranging from 1 to 200 s⁻¹. Each suspension (∼25 mL) was tested with a concentric cylinders geometry setup. The flow electrodes demonstrate shear-thinning (pseudoplastic) behavior. The experimental data was modeled with the Ostwald-de Waele power law model

\[ \eta = k\gamma^{n-1} \]

where \( \eta \) is the viscosity, \( k \) is the consistency index, \( \gamma \) is the shear rate, and \( n \) is the shear thinning index (Table 1). As \( k \) increases, the flow electrode becomes more viscous.

<table>
<thead>
<tr>
<th>active material</th>
<th>solid, wt %</th>
<th>consistency index, ( k )</th>
<th>shear thinning index, ( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC OX</td>
<td>20</td>
<td>3.46</td>
<td>0.087</td>
</tr>
<tr>
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<td>20</td>
<td>12.07</td>
<td>0.041</td>
</tr>
<tr>
<td>AC OX</td>
<td>28</td>
<td>20.85</td>
<td>0.103</td>
</tr>
<tr>
<td>AC</td>
<td>28</td>
<td>106.79</td>
<td>0.118</td>
</tr>
</tbody>
</table>

Flow Electrode Preparation and Electrochemical Characterization. Activated carbon (AC) flow electrodes were prepared by mixing the active material (AC or AC oxidized) with 10 g/L (172 mM) NaCl (ACS certified, Fisher Scientific). The solid/(liquid + solid) mass ratio was kept constant at 20%/28% by mass for the rheology studies. For flow capacitive deionization tests, a wider range of wt % slurries were studied (5/13/23 wt %). Table S1, Supporting Information, provides a summary of the feedwater and flow electrode electrolyte concentrations reported throughout the literature.

Electrochemical measurements were performed at room temperature using a potentiostat (VMP3, BioLogic, France). Cyclic voltammetry (CV) was used to determine the specific gravimetric capacitance (\( C_{sp} \)), which can be derived using

\[ C_{sp} = \frac{2}{\Delta E} \frac{\int i dV}{\nu m} \]

where \( \Delta E \) is the width of the voltage window, \( i \) is the discharge current, \( V \) is the voltage, \( \nu \) is the sweep rate, and \( m \) is the mass.
of carbon in one electrode. The factor of 2 accounts for the two electrode setup, assuming that the charge is evenly distributed between two capacitors in series. Each flow electrode was also tested with potentiodynamic electrochemical impedance spectroscopy (PEIS) to understand how composition affected electrode kinetics and conductivity.

Flow Capacitive Deionization Testing. The small scale FCDI setup consisted of two end plates (0.95 cm thickness) made from rigid HDPE polyethylene (McMasterCarr, Elmhurst IL). Plastic tube fittings with a pipe size of 3.2 mm and tube ID of 0.32 cm were tapped into the end plates (McMasterCarr, Elmhurst, IL). The current collector and flow electrode chamber was carved from a graphite plate (thickness of 3.2 mm; graphitestore.com). The flow path consisted of one straight channel with dimensions (L × W × H) of 3.18 × 0.53 × 0.20 cm. Two silicon gaskets (thickness of 1.5 mm) were used to carve the flow path for the flow electrodes and for electrical insulation between the graphite current collector and ion exchange membrane. Two ion exchange membranes (1 cation- and 1 anion-exchange membranes, Selemion CMV and AMV (0.12 mm thick), Asahi glass, Japan) were used to separate the feed channel from the flow electrode chamber. Each membrane had an active area of ~2.32 cm². The feed electrode channel was cut out from the silicon gasket (thickness of 0.15 cm) (Figure 1b).

Flow electrodes (20 mL in volume) were composed of varying mass densities of activated carbon (5, 13, and 23 wt %) and different active materials (nonoxidized and oxidized) YP-50F AC. In all experiments, the flow electrodes were made by mixing YP-50 with 10 g L⁻¹ NaCl. The flow electrode and feed solutions were recycled during testing at a constant flow rate of 5 mL min⁻¹ using a peristaltic pump (Cole Parmer, IL). The feedwater solution consisted of 20 mL of 5 g L⁻¹ NaCl (Table S1, Supporting Information). The concentration of salt in the feedwater was measured continuously using a Thermo Scientific Orion VERSA STAR benchtop conductivity meter and probe (Fisher Scientific, Waltham, Ma). During testing, the current was held constant at 30 A m⁻², and the salt removal (C/C₀) and whole cell voltage (U) were measured. The salt flux was calculated:

\[ J_{\text{salt}} = \Phi \frac{dc_{\text{salt}}}{dz} A \]  

(3)

where \( J_{\text{salt}} \) is the flux, \( \Phi \) is the flow rate, \( dc_{\text{salt}}/dz \) is the change in the feedwater concentration over the length of the channel, \( A \) is the membrane area, and \( L \) is the channel length. Since all tests were done in a constant current fashion, it was expected that the salt transport would be nearly identical across all tests, with differences observed in their respective deionization voltages. Through using constant current operation, the same amount of coulombs of charge would pass through each system regardless of the electrode material or its loading. The current efficiency for each test was calculated by

\[ \lambda = \frac{I_{\text{salt}}}{I} \]  

(4)

where \( I \) is the current and \( F \) is Faraday’s constant (96 485 C mol⁻¹) and the energy consumed per ion removed was calculated by

\[ E_{\text{ion}}(\text{kJ per ion}) = \frac{I \int V \, dt}{(RT)2(\Phi(\zeta_{\text{in}} - \zeta_{\text{out}}))} \]  

(5)

where \( R \) is the universal gas constant (8.314 J/K mol⁻¹) and \( T \) is the absolute temperature.

RESULTS AND DISCUSSION

Flow Electrode Viscosity and Pumping Energy. The flow electrode based on 28 wt % oxidized AC demonstrated similar flow behavior to a flow electrode composed of 20 wt % AC (Figure 2a). The oxidized sample at 20 wt % was less viscous than the nonoxidized 20 wt %, which was reflected by lower consistency indices (Table 1). The 28 wt % AC was very viscous and was considered unflowable. The presence of oxygen functional groups acquired through the acid treatment (discussed in the Activated Carbon Structural Properties and Surface Chemistry section) positively enhanced the flowability of suspension electrodes. The increased flowability was in part due to a decrease in hydrophobic interactions between carbon particles as the surface becomes more acidic and hydrophilic in nature, improving the solvation of particles and decreasing hydrophobic interactions between carbon particles. In high concentration electrolyte solutions (>0.1 M), diffusion limited aggregation kinetics dominate in flow electrodes and carbon particles tend to aggregate due to high van der Waals interaction forces. Recently, Porada et al. experimentally observed these dynamics and reported suspension viscosities that increased with ion concentration. In this study, oxidation of the carbon results in greater active material hydrophilicity and dispersibility (less aggregated) properties (for lower viscosities).

The experimentally obtained rheological data was used in the development of a 1-D, steady state, fluid mechanics based model for the various non-Newtonian flow electrodes (see Supporting Information). The model was used calculate the pressure drop (and thus pumping power) required to maintain a constant flow rate for the different flow electrodes studied. Across the FCDI literature, there has been a range of flow rates studied (2–30 mL min⁻¹) as well as compositional loadings (5–25 wt %). As demonstrated here, the flow rate and material loading greatly influence the required pumping power and the energy required for deionization (Figures 2b and 5b). At a flow rate of 5 mL min⁻¹, a flow electrode composed of 28 wt % as received AC required 4.80 mW to pump through a 20 cm long by 1 mm wide channel, whereas a 28 wt % flow electrode based on oxidized AC only required 2.55 mW. At high mass loadings (28 wt %) across all flow rates studied, flow electrodes composed of oxidized AC require half as much pumping power, which is in line with the decreased viscosity of oxidized AC observed in experiments. The flow behavior (velocity profile) demonstrates large velocity gradients with increasing flow rate (Figure S2, Supporting Information). Velocity gradients can induce mixing dynamics and lead to decreases in electrochemical and energy efficiencies. Recently, Smith et al. showed that nonuniform (parabola-shaped) velocity profiles in non-Newtonian suspension systems contribute to reduced Coulombic and energetic inefficiencies. Inefficiencies were attributed to the extension of charge transfer processes outside the electroactive region. The presence of a distributed velocity profile motivates plug flow (not yet studied in FCDI) or low flow rate operational modes. While the pumping power is often thought to be trivial in CDI and MCDI.
systems, it has been shown here that pumping power is significant (and will be discussed in more detail in the Deionization Performance and Electrical Energy section). The ability to simultaneously increase the carbon loading while not increasing the pumping power and electrical energy will be an important challenge to attain low-energy consuming deionization processes.

**Activated Carbon Structural Properties and Surface Chemistry.** XPS was performed to probe the chemical state in the C 1s and O 1s regions and determine the degree of oxidation for the two samples. Prior to treatment in nitric acid, a high-resolution spectrum in the C 1s region (Figure S4a, Supporting Information) revealed a peak that was best fit by components at 284.4 eV (C−C), 285.3 eV (C−H), 286.1 eV (C−OH), and 288.0 eV (C=O).33 The peaks corresponding to C−OH and C==O comprise 5.4% and 1.9% of C 1s photoemission, respectively, indicating that the surface has a small degree of these terminations. A high-resolution scan in the O 1s region (Figure 3a−bottom) and Figure S4c, Supporting Information), confirms this result, as the photoemission was best fit by two components corresponding to the same species (531.4 eV, C−OH; 533.1 eV, C=O).38 This spectrum is consistent with functional groups commonly present on carbon exposed to air.

After treatment in nitric acid, a high-resolution spectrum in the C 1s region (Figure S4b, Supporting Information) revealed a peak that was best fit by components at 284.4 eV (C−C), 285.3 eV (C−H), 286.2 eV (C−OH), 287.1 eV (C=O), and 288.5 eV (COOH).33 The appearance of the component corresponding to COOH (1.6% of C 1s photoemission) and the increase in the components corresponding to C−OH (7.1% of C 1s photoemission) and C==O (2.9% of C 1s photoemission) indicate that the surface of the carbon has been oxidized. Again, this was confirmed by a high-resolution scan in the O 1s region (Figure 3a−top). Photoemission was best fit by a single, broad component (532.6 eV) corresponding to COOH, C==O, and C−OH.38 The increase in O 1s photoemission is consistent with the increase in oxygen-containing surface groups.

The gas sorption data (Figure 3b and Figure S3, Supporting Information) demonstrates only minor morphological changes in the oxidized material, with the material remaining microporous in nature. The untreated AC exhibited a type I isotherm which is typical of a microporous material, while the oxidized activated carbon sample demonstrated some type IV isotherm, with some apparent hysteresis (Figure 3b). The hysteresis suggests that there are some large pores (mesopores) in the structure (Figure S3, Supporting Information). Both samples seem to have a great portion of the pores located around 1 nm. Nevertheless, the peak in the oxidized sample is less severe, indicating that the sample is not entirely microporous but has a slightly more distributed pore distribution. The specific surface for the oxidized samples was calculated to be ∼1270 m²g⁻¹, while the nonoxidized AC sample was ∼1322 m²g⁻¹ using a DFT procedure. The slight decrease in surface area could be attributed to pore wall destruction or surface functional groups blocking accessibility to the micropores.39 Nevertheless, the samples were not substantially altered through the light oxidation procedure.

**Electrochemical Characterization.** Flow electrodes composed of 28% oxidized activated carbon and 20% activated carbon displayed similar flow characteristics, and therefore, these two flow electrodes were electrochemically characterized in a static symmetric two-electrode configuration to compare their dynamic gravimetric capacitance. The flow electrode composed of oxidized active material demonstrated a stable voltage window of 0.9 V while the nonoxidized AC flow electrode demonstrated voltage window of 1.0 V in 10 g L⁻¹ NaCl (Figure S5, Supporting Information). At 2 mV s⁻¹ the curves display a polarizable behavior as the shape is pseudorectangular. The high mass loaded flow electrode (28 wt %) had a wider CV indicating a greater capacitance (83 F g⁻¹) than when compared to 20 wt % nonoxidized AC flowable electrode (65 F g⁻¹). Flow electrode performance depends on active material aggregation for developing efficient percolation pathways. These pathways are induced by diffusion limited cluster aggregation kinetics and naturally through the increase of active material connectivity (contact points) which occurs as a result of increasing the carbon content (composition).40,41 The effect of flow electrode connectivity and system interfacial resistances can be seen in the Nyquist plots for the oxidized and nonoxidized samples at low and high carbon loadings (Figure S6b,c, Supporting Information). In the high frequency region of the impedance spectra, both flow electrodes (23 wt %) have x-intercepts at ∼2.5 Ω which represents the whole cell impedance: membraneflow electrode, membranefeedwater, and flow electrodecurrent collector. The small semicircle is traditionally representative of charge transfer resistances between active material particles in suspension electrodes. Charge transfer resistance emerges as a result of a loss of contact points between active material particles and/or with the current collector. A wider semicircle results in more tortuous pathways which may inhibit ion removal.42 In the low frequency region, lower wt % flow electrodes show a wider response which is indicative of diffusion challenges and perhaps lower connectivity (Figure S6c, Supporting Information).33

**Deionization Performance and Electrical Energy.** Over the 95 min of testing with a fixed current density (30 A m⁻²), the ion salt removal for each flow electrode (nonoxidized AC and oxidized AC) with varying wt % (5, 13, 23 wt %) was 18 ± 2% (Figure 4A). Figure 4 reports experimental data from one test, while Figure 5 presents an average of three tests. The decrease in concentration was similar (and linear) for all samples, because deionization was done in a constant current operation. However, the whole cell voltage needed to sustain the constant current increased with decreasing electrode wt %. The steady state voltage for the 5 wt % nonoxidized and oxidized electrodes was measured to be ∼2.26 and ∼2.65 V. As the mass loading increased, the voltage decreased to ∼1.48 ± 0.04 V (13 wt %) and 0.74 ± 0.11 V (23 wt %) (Figure 4b). The deionization voltages observed for each flow electrode are inversely related to the flow electrodes impedances as defined by Ohms law. Flow electrodes with a low carbon content exhibit greater impedances (sluggish kinetics) because of less defined percolation pathways (Figure 4c). For each loading, the oxidized electrode required slightly higher potential, which was consistent with the smaller voltage window obtained during the cyclic voltammetry with the oxidized carbon (Figure S6, Supporting Information).

Increasing whole cell voltage with decreasing carbon loading influenced the electrical energy consumed during the deionization process. Over the testing period, 92 ± 7, 53 ± 11, and 28 ± 2.7 J of energy was consumed to remove ∼18% of the salt from the feed solution with the 5, 13, and 23 wt % electrodes based on oxidized AC. The ratio of energy consumed to the ions desalted is calculated using the kT per ion term.44 The
energy required to remove an ion was significantly affected ($P = 6 \times 10^{-4}$) by the flow electrode compositional loading, while oxidized and nonoxidized samples at similar wt % were not significantly different (Figure 5a). Previous studies on solid electrodes have reported $kT$ per ion removed values during adsorption to be $\sim$50 for CDI and $\sim$25 for mCDI under constant current operation conditions.$^{44,45}$ Here, we see that at low loadings the energy required to remove an ion is nearly 5X that of solid electrodes. However, at high carbon content (23%), the energy approaches that of film electrodes (when neglecting pumping energies and energy recovery) (Figure 5a). These values are in agreement with the recent study by Porada et al., who demonstrated increases in the salt-removal rate with carbon content.$^6$ Figure 5b gives a breakdown for the electrical and pumping energies for a FCDI system (for a description of the calculation, see the Supporting Information). The surface chemistry of the active material affects the pumping energy and electrical energy. Oxidized carbon demonstrates lower pumping energies but at the cost of a higher electrical energy. The results demonstrate that pumping energy consumption is significant in FCDI systems and motivates either low flow rates, high carbon content, and or intermittent operational modes. Moreover, these results demonstrate that active material surface chemistry plays a nontrivial role in the overall suspension electrode performance. The current efficiencies ranged between 60% and 80% (Figure S7, Supporting Information), which was consistent with previous results.$^6$ The current efficiency can be further improved through decreasing the operating current density or feed solution concentration.

FCDI systems based on low-cost and abundant materials (e.g., carbon) can make a lasting impact on the field of brackish water desalination, as the process is both scalable and continuous. However, the development of flow electrodes with a high mass loading for FCDI is necessary for optimal deionization and energy recovery.$^7$ Reducing the energy consumed during deionization and through pumping are important emerging concerns. Through increasing the oxygen containing functional groups at the surface of a flow electrode active material, the rheological performance of a FCDI was improved at the sacrifice of electrical energy consumption. These results motivate future studies on more synergistic heteroatom modification (nitrogen/oxygen) as avenues toward the design of flowable and electrically low consuming suspension electrodes. The electrode mass loading was increased by nearly 40% without sacrificing the flowability (viscosity) and decreased pumping power through using a facile wet oxidation method. Increasing the mass loading from 5 to 23 wt % decreased the deionization energy requirements by $\sim$3X (from $123 \pm 7$ to $29 \pm 6$ kT), which indicates that the energy required for deionization can approach that of flow-traditional solid film electrodes (without considering pumping energy and/or energy recovery). For energy efficient flow capacitive deionization to be fully realized, scale-up and comprehensive studies regarding continuous flow and plug flow operational modes should also be considered.

ASSOCIATED CONTENT

* Supporting Information
Experimental details and additional material characterization (XPS, gas sorption, and electrochemical). This material is available free of charge via the Internet at http://pubs.acs.org.

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