Ultrathin Conformal oCVD PEDOT Coatings on Carbon Electrodes Enable Improved Performance of Redox Flow Batteries

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Surface engineering of porous carbon electrodes is an effective strategy to enhance the power output of redox flow batteries (RFBs) and may enable new cost reduction pathways for energy storage. Here, a surface modification strategy that enhances the electrochemical performance of RFBs in iron-based electrolytes is demonstrated. Nanometric films of poly-(3,4-ethylenedioxythiophene) (PEDOT) are grown conformally onto carbon cloth electrodes using oxidative chemical vapor deposition (oCVD) and the impact of film properties on electrode performance in model iron-based electrolytes is investigated. Depositing oCVD PEDOT films on the electrode surface is found to reduce ohmic, kinetic, and mass transport resistances, with the highest current densities and lowest resistances observed for electrodes coated with a ≈ 78 nm thick film. As compared to unmodified electrodes, coated electrodes enhance the maximum obtained current density at an applied overpotential of 350 mV by 6.7x and 3.7x in iron sulfate and iron chloride, respectively. The oCVD PEDOT film described here represents an initial step toward electrode surfaces of tailored activity, selectivity, and wettability for specific RFB chemistries and, more generally, electrochemical systems with liquid-phase reactants.
aqualous RFBs. We leverage poly(3,4-ethylenedioxythiophene) (PEDOT), which is the most extensively studied oCVD polymer to date.\[^{[27-27]}\] The oCVD approach provides remarkable capabilities for nanoscale control of thickness and crystallographic texture.\[^{[27-31]}\] The composition and properties of oCVD PEDOT are distinct from spin-applied PEDOT:PSS (polystyrene sulfonate). In this work, the dopant species for the oCVD PEDOT is the small anion, Cl\(^{-}\), whose greater mobility than PSS promotes ion exchange in the film, resulting in electrochemical activity.\[^{[10]}\] Additionally, the electrical conductivity of oCVD PEDOT can exceed 6000 S cm\(^{-1}\),\[^{[29]}\] several orders of magnitude higher than that of pristine PEDOT:PSS. Previous works demonstrated the ability to grow ultrathin, durable, and conformal PEDOT layers over the geometrically complex carbon surfaces.\[^{[20]}\]

In this work, we evaluate oCVD PEDOT modified carbon cloth electrodes in electrolytes utilized in RFBs. We employ a comprehensive set of spectroscopic techniques to assess the morphological, chemical, and structural characteristics of the oCVD PEDOT films. Using cyclic voltammetry, we show that the PEDOT-coated electrode is electrochemically active in quiescent iron electrolytes containing chloride or sulfate supporting salts. In a single-electrolyte diagnostic flow cell, we then examine the performance of oCVD PEDOT modified electrodes using polarization and assess sources of overpotential losses via impedance spectroscopy, revealing that PEDOT films mitigate ohmic, kinetic, and mass transport losses. By varying the thickness, we identify that mass transport through the film is dependent on both flow rate and thickness; we further study the role of mass transfer by varying electrolyte concentration in iron chloride electrolyte. Ultimately, we seek to demonstrate the potential of oCVD processes in tuning the performance of porous carbon electrodes and inspire the contemplation of new chemistries to address acute needs in specific electrochemical systems.

A conceptual image of PEDOT thin film deposition by the oCVD method is shown in Figure 1a. The monomer (here, 3,4-ethylenedioxythiophene (EDOT)) and oxidant (here, vanadium oxytrichloride VOCl\(_3\)) species are introduced into a hot-wall vacuum reactor and strike on the surface of the temperature-controlled substrate through the vapor phase. The polymerization of a conducting polymer in the oCVD method proceeds through the step-growth mechanism and the increase in molecular weight occurs geometrically through the formation of dimers, tetramers, and high 2N-mers.\[^{[17,32]}\] Here, the growth temperature and film thickness of PEDOT, at the fixed monomer and oxidant flow rates into the reactor, are the primary variables for synthesizing and tuning oCVD PEDOT film properties. The experimental details related to process conditions are provided in the Supporting Information. Experimental details and information related to the equilibrium surface concentration of the reactants, determined from the saturation ratio \(P/P_{sat}\), where \(P\) and \(P_{sat}\) are partial pressure and saturation pressure, respectively, are provided in Table S1, Supporting Information.

The morphology of pristine, oCVD-coated PEDOT, and spin-coated PEDOT:PSS carbon cloth electrodes are shown in Figure 1b–d. Carbon cloth electrodes (specifically, untreated AvCarb 1071) were chosen as model porous carbon electrodes for this study due to their well-defined bimodal and binder-less woven structure, thus avoiding extraneous factors in the subsequent analysis of oCVD PEDOT coatings. The uncoated carbon fibers are \(\approx 8\ \mu m\) in diameter (Figure 1b). As predicted, the vapor deposition of PEDOT via oCVD yields a uniform and highly conformal coating that retains the fibrillar nature of the carbon fibers (Figure 1c). However, the spin-cast PEDOT:PSS-coated carbon fibers (Figure 1d) exhibit disadvantages, including liquid bridging, non-conformality, and delamination. In contrast to the spin-coated method, the formation of conformal coating by the oCVD method on any porous and non-planar surfaces is due to the absence of surface tension effects such as liquid thinning, air gap formation, bridging, and meniscus formation.\[^{[17,18]}\]

Figure 2a further demonstrates the high conformality of oCVD PEDOT on carbon fibers via cross-sectional scanning electron microscopy (SEM) images; additional micrographs displaying the conformality of the coatings on porous carbon fibers can be found in Figure S1, Supporting Information. The oCVD method also provides remarkable capabilities for control of conformal PEDOT thickness in various porous structures.\[^{[17,18,30]}\] The thickness of conformally coated oCVD PEDOT thin films and penetration depth of reactants throughout the mesh electrode thickness can be adjusted by tuning the saturation ratio of oxidant and monomer. The aspect ratio (height/width ratio) in the case of carbon cloth electrode can be estimated by dividing the half-thickness of carbon cloth to the average characteristic length of the spacing between fibers \((\approx \frac{1}{20(0.8\ \mu m)} = 10)\). The half-thickness of carbon cloth is considered as a consequence of the availability of the reactants vapor species on both sides of the carbon cloth due to: i) the presence of a gap between the heated substrate and sample, ii) the existence of a large void space between each carbon bundle with an average size of \(\approx 85\ \mu m\), and iii) the constitution of a cloth thickness with upper and lower wounded bundles. While measuring the penetration depth directly on the carbon cloth is experimentally challenging, the penetration depth can be estimated from measurements taken on more controlled geometries such as trench wafers. Recently, the conformality of an oCVD PEDOT thin film grown with a volatile oxidant such as VOCl\(_3\) was demonstrated on a trench wafer with an aspect ratio of \(\approx 11\) (height and width of 75 and 0.7 \(\mu m\), respectively).\[^{[27]}\] It is noteworthy to mention that a high degree of penetration would be expected in the case of a porous structure. A high degree of penetration and deposition of ultrathin conformal oCVD PEDOT film was reported in aligned carbon nanotubes (A-CNTs) with an extremely high aspect ratio of 10 000.\[^{[13]}\]

Achieving conformal PEDOT coatings by the oCVD method has two significant advantages for electrochemical applications compared to the PEDOT:PSS solution-applied process: i) maintaining a high surface area for effective contact with the electrolyte, and ii) enabling changes in polymer thickness upon ion exchange without the development of significant mechanical strain by leaving the void space open throughout the mesh electrode thickness.\[^{[14]}\] In addition, due to its unique doping process, the oCVD PEDOT has a significant advantage in electrochemical applications over its PEDOT:PSS counterpart. The small anion dopant, here chloride (Cl\(^{-}\)), makes oCVD PEDOT films compositionally distinct from spin-cast PEDOT:PSS. The small anion Cl\(^{-}\) dopants in oCVD PEDOT undergo
redox exchange more readily than the large macromolecular PSS dopants in PEDOT:PSS.[17,30,35] The Raman analyses (Figure S2, Supporting Information) and attenuated total reflection–Fourier transform infrared (ATR–FTIR) spectroscopy (Figure S3, Supporting Information) confirm the polymerization and no significant structural bond changes in oCVD PEDOT films grown at different process conditions. Therefore, the texture and nanostructure of PEDOT films govern the electrical conductivity, which is in consonance with previous studies.[27–29]

The grazing incidence X-ray diffraction (GIXRD) patterns reveal that the resulting oCVD PEDOT films, grown on silicon wafers as reference samples, have an excellent ordered structure with different preferential semi-crystalline orientation
The diffraction of (100) and (020) planes at 2θ values of ≈6.4° and 25.5° correspond to the edge-on and face-on orientations, respectively. The conjugated backbone is parallel to the surface substrate in both orientations and the only difference is related to the orientation of the π–π interchain stacking, which is perpendicular and parallel to the surface substrate in face-on and edge-on orientation, respectively.

The extracted a-axis and b-axis lattice parameters were in the range of 13.80–13.84 Å and 6.97–6.99 Å, respectively. The Lorentz polarization (LP) factor, defined as: $\text{LP}(\theta) = \frac{1 + \cos^2(2\theta)}{\sin(\theta) \cos(\theta)}$ \cite{27,36}, was used to quantify the percentage of preferential orientation (Table S2, Supporting Information). The change in crystallization orientation, as a function of growth temperature and film thickness, is attributed to the intermolecular interaction and energy minimization of growing film and interfaces. The obtained in-plane electrical conductivity of these samples with different preferential orientations are shown in Table S2, Supporting Information, with higher conductivities observed for films with greater fractions of face-on orientation.

Normally, face-on orientation correlates with a low energy barrier for intercrystallite charge transport and induces high in-plane carrier mobility and electrical conductivity \cite{27,35,37}. Typically, there is a trade-off between in-plane and out-of-plane electrical conductivity in conducting polymers and the sample with high in-plane conductivity exhibits low out-of-plane conductivity and vice versa \cite{29,35}.

To better understand the role of the PEDOT film chemical composition on electrochemistry, X-ray photoelectron spectroscopy (XPS) analysis was performed on an oCVD PEDOT-coated planar substrate of graphene that was exposed overnight to iron chloride electrolyte (Figure 2d). We deposited oCVD PEDOT onto ten monolayers of graphene (Figure S4, Supporting Information) to avoid the shadowing effects that carbon fibers have on XPS measurements. The iron chloride electrolyte was composed of 0.5 M actives at 50% state of charge (SoC) in 2 M HCl.
The iron penetration into the oCVD PEDOT thin film can be observed based on the appeared peaks with low intensities at ≈712 and 724 eV, which are related to the Fe 2p_{3/2} and Fe 2p_{1/2}, respectively. The elemental composition was estimated from the XPS spectra of pristine PEDOT (Figure S5, Supporting Information) and exposed PEDOT film to the electrolyte (Figure 2d) and summarized in Table S3, Supporting Information. In addition to the presence of iron, elemental analysis reveals that the ratio of chlorine/sulfur (Cl/S), an indication of doping level, slightly decreases from its initial as-grown value of 0.37–0.30 after being exposed to the electrolyte.

The surface topography of the oCVD PEDOT film grown at a deposition temperature of 80 °C with a thickness of ≈78 nm was evaluated by atomic force microscopy (AFM) and is depicted in Figure 2e. The extracted surface roughness of oCVD PEDOT thin film was ≈2.1 nm. The wetting properties of planar oCVD PEDOT thin films were previously investigated and exhibited an advancing water contact angle (WCA) of 62° and receding WCA of 22°.[38] Generally, in PEDOT thin films, the WCA depends on the root mean square (rms) roughness and the morphology of the surface based on the Cassie–Baxter equation.[39] The series of PEDOT thin films with different thicknesses grown with the same oxidant by the oCVD method exhibited approximately the same rms values, suggesting that the wetting properties were similar for all of the coated electrodes in this study. The film smoothness is of importance for some applications, such as the avoidance of unwanted current leakage from inter-electrode shorting within photovoltaics,[37] but is anticipated to be of less relevance to RFB applications.

A photograph and schematic of oCVD PEDOT-coated carbon fibers that were directly integrated into the RFB is shown in Figure 3a. Cyclic voltammograms (CVs) were conducted in aqueous acidic electrolytes containing iron salts to qualitatively assess oCVD PEDOT-coated electrode activity (Figure 3b,c). In all experiments, the working electrode consisted of either untreated AvCarb 1071 (pristine) or oCVD PEDOT-coated AvCarb 1071. The solution compositions in cyclic voltammetry and flow cell testing consisted of a total active species concentration of 0.5 M with 50% SoC for electroactive compounds, while the concentration of the supporting electrolyte was 2 M.

To examine the impact of supporting salt counter-anion on oCVD PEDOT-coated electrodes, electrolytes with either hydrochloric acid (HCl) or sulfuric acid (H_2SO_4) were employed. Redox peaks were evident in all CVs for coated electrodes in iron-based solutions, indicating that coated electrodes are electrochemically active in the iron solution regardless of the counter-anion. We are cautious about drawing definite conclusions from CVs due to the complexity of interpreting results for non-planar, porous materials during potentiodynamic measurements.[40–42] The redox potential for the CVs (Figure 3b,c) were consistently ≈0.435 V versus Ag/AgCl, in agreement with prior art.[43]

Based on the results from the CVs, we evaluate the performance of PEDOT-coated electrodes in iron-based solutions using a single-electrolyte flow cell configuration, quantifying resistive losses via electrochemical impedance spectroscopy (EIS) and cell polarization at steady-state conditions and 50% SoC (schematic shown in Figure 4a).[43,44] In this setup, the electrolyte is first oxidized at the positive electrode and then reduced at the negative electrode before re-circulation into the reservoir. The single-electrolyte flow cell configuration enables identification of individual contributions from ohmic, kinetic, and mass transport resistances in operation, without introducing additional extraneous variables that obfuscate the direct effect of the coating on electrode performance. The relative contribution of ohmic, kinetic, and mass transport resistances can be isolated by fitting an equivalent Randles-like circuit with bounded Warburg diffusion to Nyquist plots obtained using EIS. In this circuit, \( R_\delta \) corresponds to ohmics, \( R_{CT} \) to charge-transfer resistance, and \( R_{MT} \) extracted from bounded Warburg diffusion (\( \delta \)) relates to mass-transfer resistance.[37,45]

Figure 4b shows a comparison of cell polarization for pristine and PEDOT-coated electrodes with the best performance \( (T_e = 80 °C, 78 \text{ nm thickness}) \) in iron chloride and iron sulfate electrolytes with an active species concentration of 0.5 M Fe^{2+}/Fe^{3+}. In both electrolytes, coated electrodes demonstrate higher currents at similar applied overpotentials than uncoated electrodes, indicating lower resistance and higher power capabilities. The best-performing combination is the PEDOT-coated electrode in iron chloride, in part due to the larger...
Figure 4. PEDOT-coated electrodes improve performance in iron-based electrolytes. a) Schematic of single-electrolyte flow cell configuration, using $\text{Fe}^{2+}/\text{Fe}^{3+}$ as a model redox couple, for evaluating electrode performance. b) Cell polarization data for 50% state-of-charge (0.25 m $\text{Fe}^{2+}$/0.25 m $\text{Fe}^{3+}$) at a flow rate of 15 mL min$^{-1}$. Nyquist plots obtained using EIS for oCVD PEDOT and pristine carbon fiber in c) HCl supporting salt and d) $\text{H}_2\text{SO}_4$ supporting salt, with the same conditions as (b). The equivalent circuit used to fit the impedance data is shown in (c). Insets are closer views of the PEDOT Nyquist plots. e) Mass transport overpotential determined from the equivalent circuit as a function of PEDOT layer thickness at two different flow rates (5 and 15 mL min$^{-1}$).
kinetic and mass transport resistances for iron sulfate compared to iron chloride.\cite{46} However, at an applied overpotential of 350 mV, the relative increase in current for PEDOT-coated electrodes as compared to uncoated electrodes is greater in iron sulfate ($\approx$6.7%) than in iron chloride ($\approx$3.7%). The greater multiplicative enhancement of obtained current may be attributed to the improvement in crystallinity characteristics of PEDOT in H$_2$SO$_4$ primarily an increase in the crystallite size. The obtained crystallite size in the a-axis direction (edge-on orientation) of pristine PEDOT and PEDOT treated with HCl and H$_2$SO$_4$ are 5.7, 6.0, and 76 nm, respectively (Figure S6, Supporting Information). The crystallinity enhancement of PEDOT is hypothesized to improve the kinetics of electron-transfer rate by enabling better energetic overlapping of the density of state (DOS) between PEDOT and redox-active species as predicted by the Marcus–Gerischer model.\cite{31,35,47} The enhancement of electrochemical performance by improved crystallinity is also reported in poly(3-hexylthiophene) (P3HT) due to better DOS overlapping of the electrode and redox-active species.\cite{48}

Encouragingly, we observe from fitted EIS data that the PEDOT coating reduces all forms of overpotential (Figure 4c,d), indicating that the conducting polymer film imparts multiple benefits. We attribute reduction in ohmics to result from better contact between current collector/electrode/membrane components due to polymeric interlayers. Improved surface area from better wetting\cite{39} may partially explain kinetic enhancement, but the convolution of relevant factors pertaining to kinetics (i.e., available surface area, accessibility through PEDOT film, reactivity of carbon/PEDOT interface) are outside the scope of this initial report.

Of special pertinence, however, is the role of mass transport through the PEDOT film. While ohmics and kinetics are more difficult to tune, an understanding of ion transport through the nanolayer affords the possibility of using factors such as flow rate and electrolyte concentration to reduce mass-transfer resistance in convection-enhanced electrochemical cells. To this end, the performance of six electrodes with coating thicknesses of 14, 29, 78, 202, 370, and 470 nm was evaluated in the single-electrolyte flow cell in iron chloride (Figure S7, Supporting Information). In our experimental setup, the highest currents were observed with a thickness of 78 nm, although shifts in performance across the film thicknesses were marginal relative to improvements over the pristine electrode. We note that the optimal coating thickness for highest power output will depend on system level factors such as operating flow rate, reactor configuration, and flow channel; furthermore, the optimal thickness is dependent on the desired electrochemical application and film material properties. The best-performing 78 nm thick semi-crystalline PEDOT film, grown at the deposition temperature of 80 °C, contains both edge-on ($\approx$8.1%) and face-on ($\approx$91.9%) orientations (Table S2, Supporting Information). It is postulated that the presence of edge-on orientation, with sufficient electrical conductivity, is favorable for electrochemical applications and for facilitating ion transport.\cite{30,33} Thus, the better electrochemical performance of 78 nm thick semi-crystalline PEDOT film grown at 80 °C can be attributed to the higher preferential edge-on orientation in that sample compared to its counterparts grown at 140 °C as well as those samples grown at 80 °C with the lower thickness. In addition to the preferential orientation, the thickness limit is another important parameter that needs to be considered. As mentioned earlier, conductive polymers are ionically permeable, and the upper thickness limit needs to be considered for enhanced ionic permeability characteristics of conducting polymers such as PEDOT. Xu et al.\cite{36} also reported the presence of a thickness limit in PEDOT thin films for electrochemical applications. Specifically, they reported an optimal oCVD PEDOT film thickness of 20 nm to obtain the best performance in layered lithium transition metal oxide cathodes such as LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ (NCM111).

Magnitudes of mass transport overpotential at flow rates of 5 and 15 mL min$^{-1}$ are detailed in Figure 4e. Mass transport overpotential as a function of thickness is discontinuous at $\approx$50 nm, which we tentatively ascribe to a transition from lower- to higher-dimensional transport regimes.\cite{28} Above 50 nm thickness, mass transport increases linearly, suggesting thicker PEDOT layers increase resistance to active species diffusion to a buried reactive carbon/PEDOT interface. Mass transport is also convection dependent, as the higher flow rate exhibits the same trend as the lower flow rate, but with lower overpotential. Therefore, both convection and thickness affect mass transport, operating simultaneously during flow cell operation. Figure 4e suggests that partitioning of reactive iron species between the electrolyte and PEDOT film occurs, in which Fe$_2^{2+/3+}$ becomes entrapped in the PEDOT film, reducing the effective boundary layer required for the redox actives to diffuse to the reactive carbon interface. In this scenario, we hypothesize that convection influences total mass transport by homogenizing the concentration of the bulk electrolyte, forming a boundary layer as actives diffuse from the bulk electrolyte to the PEDOT film, thus influencing the partitioning and concentration of iron actives at the electrolyte/PEDOT surface.

Insights into the structure of coated carbon fiber exposed to iron-based electrolyte reveal that the durable and stable nature of the conformal oCVD PEDOT film was maintained after electrochemical tests within the flow cell (Figure 5a). There was no observed delamination, and the integrity of the oCVD PEDOT film was maintained after electrochemical reactions, as determined from electrode cross-section energy dispersive spectroscopy (EDS) mapping of the oxygen element (Figure 5b) and other elemental components of PEDOT (Figure S8, Supporting Information). Traces of iron can be observed in the elemental EDS mapping (Figure S5c), which is consistent with the obtained XPS results (Figure 2d), adding support to our earlier hypotheses on the penetration of iron cations into the nanometric film. To further examine mass transport behavior through the film, polarization and EIS for the relatively thicker 202 nm PEDOT-coated electrode was evaluated across a range of iron chloride electrolyte concentrations (0.02, 0.5, and 1.0 M Fe$_2^{2+/3+}$) and compared to the uncoated electrode, shown in Figure 5. For uncoated electrodes, the resistance distribution (Figure 5e) based on equivalent circuit fits to Nyquist plots (Figure 5d) shows a consistent reduction in kinetic and mass transport resistance with increasing concentration, in agreement with prior art.\cite{49,50} Interestingly, in PEDOT-coated electrodes, mass transport resistance reduces significantly as concentration increases from 0.02 to 0.5 M, but experiences diminishing returns from 0.5 to 1.0 M, despite similar ohmic and kinetic resistances at all concentrations (Figure 5g,h). Cell polarization of coated electrodes
(Figure 5i) shows marked performance improvement between 0.02 and 0.5 m concentrations, while 0.5 and 1.0 m are nearly identical. This observation appears to indicate that, in this concentration range, the overall mass-transfer coefficient is independent of iron concentration in the flowing electrolyte as the iron concentration partitioned into the PEDOT film is at saturation. Surprisingly, despite the PEDOT film acting as a second resistance to mass transport, overall redox rate increases. We hypothesize that preferential segregation of iron into the PEDOT as observed by XPS after film exposure to the electrolyte still reduces effective iron concentration gradients at the electrode surface, thus lowering overall mass transport resistance.

To conclude the discussion on transport, the results suggest that two modes of mass transport resistance act for the coated electrodes: 1) diffusion from the bulk electrolyte to the PEDOT surface, which is not significantly affected by the presence of the coating, and 2) assisted diffusion unique to the oCVD PEDOT coatings whereby iron active species partitioning into the nanometric film improve overall mass transfer. This phenomenon will be explored in detail in a subsequent publication.

To investigate the longevity of the PEDOT coating, a symmetric cell galvanostatic cycling experiment was performed in iron chloride electrolyte over the course of ≈2.9 days (Figure 6). Specifically, a rate study was performed with cells cycled for five times at current densities of 50, 75, 100, 125, 150, and again at 50 mA cm⁻² (corresponding to applied currents of 127.5, 191.25, 255, 318.75, 382.5, and 127.5 mA, respectively) to assess changes in performance and stability. Current density was determined by normalizing applied current by the 2.55 cm² geometric electrode area. We report the cycling results in terms of current density to facilitate comparison with other reports. Figure 6a,b reveal that PEDOT-coated electrodes cycle longer than pristine
electrodes due to fewer overpotential losses. Nyquist plots before and after cycling are similar in appearance and overall resistance, demonstrating that the PEDOT-coated electrode is stable (Figure 6c) without any delamination issue as shown in Figure 5a–c and Figure S8, Supporting Information. Furthermore, the discharge capacity exceeds 80% even after several days of cycling, exceeding that of the pristine (Figure 6d). Therefore, we show that the benefits from using PEDOT coatings on electrodes are electrochemically and mechanically resilient over longer durations.

In summary, we demonstrate that ultraconformal semi-crystalline oCVD PEDOT-coated carbon fiber electrodes are promising for RFBs. PEDOT-coated electrodes enhanced maximum current density by \( \approx 6.7 \times \) in iron sulfate, and \( \approx 3.7 \times \) in iron chloride, due to a reduction in ohmic, kinetic, and mass transport overpotentials. To examine the transport of iron through the PEDOT film, we tested PEDOT films of varying thicknesses, under conditions with different electrolyte flow rates and concentrations, finding that mass transport overpotential varies as a function of thickness and convection. The dependence on both factors suggests the mass transport limitation has two components in series, the first consisting of transport through the boundary layer of the electrolyte and the second consisting of transport through the oCVD PEDOT layer. An optimal oCVD PEDOT thickness of 78 nm at a 15 mL min\(^{-1}\) flow rate was identified. The demonstration of oCVD PEDOT-coated electrodes

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**Figure 6.** PEDOT films remain stable and are durable after cycling for several days. Symmetric cell galvanostatic cycling at several current densities in iron chloride of a) oCVD PEDOT-coated electrodes and b) pristine electrodes. c) Impedance spectroscopy before and after cycling for both oCVD PEDOT and pristine electrodes. d) Discharge efficiency versus cycle number using theoretical discharge capacity as a basis.
enhancing performance presents future opportunities for the advanced surface engineering of porous materials in RFBs to mediate desired electrochemistry.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Author Contributions
M.H.G. and C.T.-C.W. contributed equally to this work. M.H.G.: conceptualization, methodology, validation, formal analysis, investigation, data curation, writing—original draft, writing—review and editing, visualization; C.T.-C.W.: conceptualization, methodology, validation, formal analysis, investigation, data curation, writing—original draft, writing—review and editing, visualization; Y.A.G.: validation, formal analysis, investigation, data curation, writing—review and editing; K.V.G.: validation, investigation, writing—review and editing; A.F.-C.: conceptualization, methodology, writing—review and editing; Y.-M.C.: resources; F.R.B.: conceptualization, resources, writing—original draft, writing—review and editing, supervision; K.K.G.: conceptualization, resources, writing—original draft, writing—review and editing, supervision.

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