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Engineering porous electrodes for next-generation redox flow batteries: recent progress and opportunities
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Abstract
Redox flow batteries are a promising electrochemical technology for energy-intensive grid storage applications, but further cost reductions are needed for universal adoption. As porous electrodes are responsible for functions within the flow cell that impact charge transfer, ohmics, and mass transport, improvements in electrode materials and design may yield significant performance and economic benefits. This mini-review summarizes recent developments in the design and characterization of porous electrodes with a focus on understanding and controlling both the microstructure and surface chemistry, which broadly align with mass transport and reaction kinetics. Key opportunities and challenges in the science and engineering of these materials are also presented with the goal of engaging the broader community and accelerating progress towards chemistry-specific flow battery electrodes.

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Introduction
The threat of global climate change creates a profound need to decouple carbon emissions from economic activity without stifling societal development. As the deployment of low-cost, but intermittent, renewable resources continues to expand, electric energy storage will play an increasingly crucial role in the efficient, reliable, and sustainable delivery of carbon-free electricity. Redox flow batteries (RFBs) are an emerging electrochemical energy storage option. In an RFB, energy is stored in flowable solutions or suspensions of redox-active materials that are housed in external tanks and pumped through an electrochemical stack to charge and discharge the battery (Figure 1(a)). As compared to enclosed batteries (e.g., lithium(Li)-ion, lead-acid), this configuration offers a number of appealing advantages including the ability to decouple power rating (stack size) from energy capacity (tank size), long service lifetimes with full charge/discharge cycles, simplified thermal management and maintenance, and improved safety [2]. Because of their low energy density and integrated design requirements, RFBs are best suited for large-scale, long-duration stationary energy storage. Despite this promise, current RFB systems are considered too expensive for ubiquitous adoption, thus spurring research and development targeting new redox chemistries and reactor designs that may improve performance and lower costs [3].

An effective means of lowering RFB system costs is to design next-generation electrochemical stacks with increased power output, reduced size, and higher roundtrip efficiency. This mini-review focuses on the role that porous electrodes may have in technology advancement. These components are integral to RFB operation as they support multiple performance-relevant functions including the provision of active and selective surfaces for electrochemical reactions, the distribution of liquid electrolytes throughout a volumetric reaction zone, the cushioning of mechanical compression necessary to seal the system and minimize contact resistance between adjacent components, and the conduction of electrons to and from the electrified interfaces [4]. As such, electrodes contribute to charge transfer, ohmic, and mass transport overpotentials within the electrochemical cell and, to be successful, any selected material must possess property sets that align with requirements specific to an RFB system [5]. Favorable attributes include large surface areas rich in accessible active sites, high electronic conductivity and low contact resistances, and high permeability, to reduce...
charge transfer, ohmic, and mass transfer losses, respectively. While all of these attributes are desirable, the relative importance of each is dependent on the redox couple, electrolyte composition, and operating conditions.

Most current RFB systems utilize fiber bed electrodes consisting of micrometric fibers (ca. 7–10 μm dia.), typically synthesized by carbonization of polymer precursors (e.g., polyacrylonitrile (PAN)), which are consolidated into a coherent freestanding structure using a binder or other methods. Carbon is a desirable material because of its high electronic conductivity, proven robustness in complex (electro)chemical environments, and many allotropes that enable the formation of materials with diverse electrochemical and physical properties that can often be synthesized at reasonable costs. Though not discussed in detail here, electrodes may also be constructed from other materials, most notably metals (e.g., Pt, Ni, Cu) provided they are stable and selective in the RFB electrolytes over the range of operating conditions [6]. Historically, graphite felts, typically several millimeters thick, have been the preferred electrode material [7], but recent advances in the RFB literature have shown dramatic power density increases by using carbon papers (ca. 200 μm thick), like those used as gas diffusion layers in polymer electrolyte fuel cells (PEFCs), as well as structured flow fields [8,9]. The electrodes used in these systems are typically derived from the composite gas diffusion layers used in PEFCs, specifically the carbon fiber substrate which serves to distribute gaseous reactants across the catalyst layer–membrane interface and remove liquid products (e.g., water produced from the acidic oxygen reduction reaction). While there is overlap in the desired property profiles of these functional materials, the carbon fiber substrates used in PEFCs are not designed to meet the specific needs of RFB systems as, in general, they have low surface area (\(\sim 0.1–10 \text{ m}^2/\text{g}\)), variable and heterogeneous surface composition, and broad pore size distribution. Thus, while they are effective, as compared to prior materials, there is considerable room for improvement. To this end, we describe some of the recent advances in the design, synthesis, and characterization of porous electrodes for RFBs as well as highlight future directions for the research community.
In-situ electrochemical methods for assessing electrode performance

The past decade has seen a dramatic increase in publications focused on RFB electrodes concomitant with growing interest in the technology for grid energy storage and likely inspired by the relatively rapid rate of technology advancement as compared to similar electrochemical systems (e.g., PEFCs, Li-ion batteries). However, the RFB community is still developing and, at this stage, the archetypal material sets, well-defined testing protocols, and rigorous benchmarking of performance metrics, which underpin mature fields, have yet to be established. Presently, quantitative comparisons between different studies are challenged by the diversity of redox chemistries, cell geometries, and operating conditions used. Many reports of new materials provide detailed spectroscopic and microscopic characterization but limited electrochemical analysis; namely, polarization and galvanostatic cycling in a full redox flow cell under a unique set of conditions and compared against an arbitrary baseline material. Thus, while the outcomes of these studies have value, difficulties arise in accurately reproducing findings to validate results, even in the context of relatively well-studied redox chemistries (e.g., vanadium redox couples), let alone generalizing findings between different systems. As such, there is a need for new tools that enable unambiguous performance analysis through the use of platform chemistries with well-defined properties as redox probes.

The recent introduction of two diagnostic configurations for RFB analysis has started to address some of these aforementioned challenges. The single electrolyte, or double half-cell, configuration enables steady-state operation of a redox flow cell by circulating an electrolyte stream, at 50% state of charge, through the flow cell oxidizing on the anode and reducing on the cathode (Figure 2(b)) [11]. Furthermore, crossover effects do not degrade performance because the same electrolyte composition is present on both sides of the cell. Thus, this technique offers simple cell-level analysis of a wide variety of cell components (e.g., electrodes, flow fields) and over a range of operation conditions (e.g., current density, electrolyte flow rate), without reference electrodes, since nearly identical processes occur on both sides of the cell [12–14].

Evaluation of electrode performance in a full cell (Figure 2(a)) requires two stable redox couples of disparate potentials, separated by a selective membrane. If suitable candidates cannot be identified, electrochemical analyses are complicated by poor performance related to either materials degradation (e.g., instability, insolubility, incompatibility) or shortcomings in cell design (e.g., crossover, high resistance). This, in turn, may limit the scope of experiments that can be performed to compare different electrode materials or, worst yet, may mask the true electrode characteristics by surface fouling, side reactions, or other complicating factors. As such, there is a need for new tools that enable unambiguous performance analysis through the use of platform chemistries with well-defined properties as redox probes.

Figure 2

(a) A schematic of a full cell with two reservoirs each with a different redox couple and a selective membrane. This assembly is suitable for assessing cell polarization, cycling, and capacity decay over a range of operating conditions. (b) The single electrolyte flow cell is typically used with a stable, well-defined redox couple. The SOC is well-controlled through the concentration of the active species in the reservoir and can be used to deconvolute resistive losses through impedance analysis. (c) The symmetric flow cell uses the same redox couple in each of the two reservoirs. This configuration affords performance and decay analysis of a single stable, well-defined redox couple.
controlled electrolyte environment by removing the need for a counter electrode of dissimilar material, eliminating the possibility of side-product species crossover from the counter electrode chamber, which would contaminate the working electrode. The flowing electrolyte also improves mass transfer, enabling higher concentration cycling studies, and investigates active material stability on porous carbon electrodes relevant to flow battery applications instead of reticulated vitreous or glassy carbon. Independently sizing the reservoirs such that the working electrode half-cell is of limiting capacity enables refined analysis of molecular decay processes [17]. These two configurations enable simpler, quicker, and clearer assessment of different RFB materials and are amenable to the potential incorporation of more advanced characterization approaches leveraging electrochemical methods (e.g., electrochemical impedance spectroscopy), imaging techniques (e.g., x-ray tomographic microscopy, neutron radiography), and computational analyses.

On the role of electrode microstructure
Microstructure refers to the three-dimensional (3D) geometrical configuration of the porous electrode at the micron-scale or smaller that primarily impacts mass and momentum transfer. As such, engineered design of electrode microstructure necessitates optimization at a multitude of length scales (Figure 1(b)), which, in turn, can enable improvements in performance and durability. Any aspect of the microstructure that is poorly designed will have significant implications on cell performance as evinced by increasing mass transfer or ohmic overpotentials. To mitigate these inefficiencies, it is important that thoughtful design and selection of electrode microstructure is undertaken during the construction of an RFB system.

As might be expected, different manufacturing processes for these electrodes result in drastically different microstructures—even for the same polyacrylonitrile-based fibers (Figure 3(a)). In turn, electrodes that have been manufactured in different ways may behave significantly differently during RFB operation. At large scale, the carbon fibers are first synthesized by PAN extrusion followed by carbonization. Fibers are arranged together via distinct processes (e.g., compacting, hydroentangling, weaving) to impart the final microstructure and thickness. Alternatively, electrospinning has been employed to synthesize carbonaceous electrodes with thinner fiber diameters and larger surface areas (Figure 3(a)) [18]. Electrospinning has recently been leveraged to preferentially align fibers [19] or self-assemble the fibers into tows [20]. While these synthetic approaches have been shown to have a significant impact on overall RFB performance, there remain many open questions surrounding the fundamental behavior of these electrodes depending on the synthesis conditions and the scalability potential.

To most effectively design the microstructure of these electrodes, engineers must reach a delicate balance between generating high surface areas to maximize reaction kinetics, providing small pores such that diffusion distances are minimized, and simultaneously incorporating large pores to minimize the pressure drop that occurs through the electrode. We have recently shown that woven electrodes, featuring a bimodal pore size distribution, provide reduced mass transfer overpotentials and low pressure drop [14] which promotes a new direction for research into woven electrodes. Indeed, woven electrodes outperform a multilayered carbon paper electrode, suggesting that the presence of these multi-modal pore size distributions are critical to the observed performance benefits [21].

The use of models is critical to further explore electrode design space. Often, the prevalence of the multiple length scales in RFB electrodes make traditional fluid dynamic simulations vastly computationally expensive, and thus require domain or physics simplifications. Approximating the electrode pores and throats as spheres and cylinders, respectively, pore network models (PNMs) are a computationally-light technique for simulating flow and electrochemistry in porous media. In their recent use, PNsMs have been used to investigate the trade-off between active surface area (Figure 3(b)) and porosity. The results suggest that benefits obtained from increasing pore size outweigh the detrimental loss of reactive area [22]. To enable further predictive simulations with improved accuracy, Zhang et al. deployed lattice Boltzmann simulations using tomographic microscopy images as the input geometry and solved the coupled transport and electrochemical kinetics for three different electrode microstructures [23]. This type of framework can be leveraged to optimize electrode microstructure in silico (Figure 3(c)). The ability to design the geometry of these porous electrodes offers a powerful toolkit to directly tune the electrode performance within the final RFB system. Based on these observations, we hypothesize that hierarchically-organized porous electrodes with a multimodal pore size distribution will afford benefits in decreasing mass transfer overpotential [24].

Several groups have focused on attempting to generate multi-scale pore size distributions through post-synthetic modifications of commercial carbon fiber substrates. First, high surface-area, catalytically-active layers [21]—similar to those found in PEFCs—and decreased porosity near electrode inlets [25] have both been used to increase the overall performance of RFB systems through improved reaction rate and increased
Electrolyte concentration at the electrode interface. Next, electrodes that have been systematically perforated may improve performance via direct flow channels that decrease pressure drop [26] and slotted electrodes (Figure 3(d)) with interdigitated flow field designs have been reported to reduce pressure drop by 40% and increase electrode utilization [27]. Additional post-synthetic modifications of these electrodes can be used to incorporate nanometer-sized pores within the carbon fibers (Figure 3(e)). This is typically accomplished by contact with a weak oxidant such as K2FeO4 [28], CO2 [29], or FeOOH [30] followed by thermal treatment. While the authors claim that a combination of micro-, meso-, and nanoscale pores provide a favorable balance to enhance both mass transport and kinetics, there remain opportunities for the field to more effectively decouple the effects of mass transfer from kinetics.

In sum, there is a need for targeted synthesis and engineering of porous materials with tailored properties which is difficult to execute as it requires solving a multivariable optimization problem at different length-scales with coupled transport and kinetics. This fundamental challenge requires controlling the pore shape and alignment to develop electrodes with high surface area and mass transfer while retaining high permeability. We anticipate the emergence of structures with spatial gradients in porosity achieved in either a continuous media or multi-layer stacks of constituent electrodes will play a major role in the future. From the standpoint of scalability, it is also important to holistically consider...
fabrication limits, mechanical properties, and costs \cite{31} for high-throughput manufacturing.

**On the role of electrode surface chemistry and active sites**

The interaction between active species in solution and the solid electrode surface (i.e., electrode–electrolyte interface) defines the activity, selectivity, and stability of a materials pair which are central to the performance and durability of the larger system. Electrode surface reactivity can be viewed as a function of (1) the number of active sites governed by electrochemically accessible surface area (ECSA), and (2) the intrinsic rate constant towards the redox couple dictated by functional groups and material properties. Rationally functionalizing pristine electrode surfaces is crucial for minimizing charge transfer overpotential for kinetically-sluggish redox couples, including vanadium \cite{33}, cerium \cite{34}, and iron \cite{35}. Optimizing the electrode surface chemistry and available active sites can enable increases in power density and voltage efficiency, but currently there are a lack of guiding fundamental structure-function relationships to design tailored electrocatalytic surfaces. Although a very active area of research, robust and ubiquitous learnings have been hindered by the complex coupling between wetting, surface area, and surface composition \cite{36} (Figure 4(a)). As previously described, few efforts have been dedicated to deconvoluting the intrinsic kinetic activity of surfaces, thus frustrating the development of rational design strategies. However, from an application standpoint, effective approaches can be broadly divided in three main areas, namely (1) direct functionalization of carbon, (2) deposition of electrocatalytic nanomaterials, and (3) replacement of the carbon fiber precursor material. Most of these efforts have targeted the vanadium RFB systems due to a combination of kinetically-limiting electrode reactions and technology prominence. Here, we briefly summarize important research advances and efforts to improve electrode surface properties.

**Towards understanding reaction mechanism and kinetics**

(a) Oxygen functionalization with thermal treatments, adapted from Ref. \cite{36} with permission. (b) Copper nanoparticles deposited onto felt electrodes, adapted from Ref. \cite{48} with permission. (c) PAN versus rayon precursor adapted from Ref. \cite{54}. (d) First-principle calculation on model carbonaceous surfaces to predict vanadium kinetics, adapted from Ref. \cite{42} with permission. (e) Novel concept for preparing model electrodes with controlled surface coatings, adapted from Ref. \cite{60} with permission. (f) An illustration of a liquid electrolyte in contact with a solid electrode for performance in-situ spectroscopic measurement during electrochemical operation. Adapted from Ref. \cite{61} with permission.
Directly functionalizing carbon materials via oxidation of the electrode surface has been the most widespread approach to improving properties. Thermally pretreating carbon electrodes is the most common electrode treatment for vanadium RFBs stemming from its initial investigation by Sun et al. [20]. This approach has been shown to improve electrode wettability, increase surface area, and impart electrocatalytic oxygen functional groups, which all contribute to enhanced performance [36–39]. Besides thermal treatment, other methods of functionalizing carbon electrodes with oxygen groups include oxygen plasma treatment [40] and acid treatment [41]. Elementally diverse functional groups including nitrogen [28], boron [42], phosphorus [42], and sulfur [43] have been shown to be beneficial to electrode performance.

A wide variety of nanomaterials have also been proposed for use as electrocatalysts for the vanadium RFB. Though too numerous to review in this format, interested readers are referred to the exhaustive review on this topic by Wu and Holze [44]. In brief, carbon nanomaterials in different forms have been deposited onto or grown on porous carbon fiber substrates, including carbon nanorods [45], graphene nanoplatelets [46], and carbon nanospheres [47]. The performance improvements were attributed to increases in surface area [46] and durability [47]. In addition, several studies have investigated the use of inorganic electrocatalytic materials for the vanadium RFB. Some of these catalysts were deposited onto carbon substrates, including copper nanoparticles [48] (Figure 4(b)), SnO2 nanoparticles [49], MnO2 [50], and bismuth sulfate [51]. Others have synthesized freestanding metal oxide substrates, including mesoporous tungsten oxide and oxynitride [52] and cerium zirconium oxide [53]. The aforementioned studies reported improvements on the overall RFB performance and some attributed the enhancement to increases in electron transfer rate and/or diffusion coefficient; however, the effect of intrinsic electrocatalysis (i.e., improvements in kinetics due to catalysis) was not unambiguously deconvoluted from the increase in ECSA.

Typical carbon fiber-based electrodes are purchased directly from commercial vendors; however, fabricating electrodes from different precursor materials has shown to be a promising approach to introducing properties desirable for RFB performance. Different carbon fiber precursors may be used; for example, rayon instead of polyacrylonitrile [54] (Figure 4(e)). Additionally, electrodes may be synthesized from a wide range of biomass-derived precursors, which contain molecular functionalities or heteroatoms though useful for promoting redox reactions, including, but not limited to, cotton [55], tomatoes [56], and fungi [57]. These biomass-based electrodes also provide a pathway towards sustainable, inexpensive electrode materials for future RFB applications.

In each of the studies described above, electrode synthesis and modification are powerful tools to improve RFB performance. However, composition-structure-performance relationships for the electrocatalytic surfaces remain unclear and, as such, the underlying reasons for performance improvements are not well understood. The electrode performance and the underlying descriptors are expected to be active species and solvent dependent, so there is a need to develop chemistry-specific guidelines to tailor electrode properties. In situ spectroscopy will be employed to elucidate reaction mechanisms and to unravel fundamental processes that can be leveraged to design optimal electrocatalytic interfaces with superior durability. We anticipate that future work will leverage first-principle calculations (e.g., density functional theory, molecular dynamics simulations) to elucidate surface chemistry-redox kinetics relationships. Results generated from these models (Figure 4(d)) will need to be validated against model electrode surfaces prepared with methods (Figure 4(e)) that enable precise and spatially-resolved control over the surface properties (i.e., morphology, composition). However, what constitutes a physically representative model electrode surface is still a topic of debate, with glassy carbon, highly oriented pyrolytic graphite, and single carbon fibers all currently under investigation.

To enable this understanding, in situ techniques that can be performed on 3D porous electrodes must also be developed (Figure 4(f)). Currently, fundamental redox kinetics are typically studied on 2D model surfaces. As such, there is a challenge to translate learnings from flat substrates used in these experiments to the structures employed in flow cells. In situ 3-electrode setups under flow and controlled compression [58] may aid in addressing this challenge. Electrode surface area is a quantity that can be measured in situ via capacitance to understand kinetics of porous electrodes; however, this calculation requires prior knowledge of specific capacitance of a model material with a known, well-defined area, such as glassy carbon. These model materials may not be representative of carbon fiber electrodes, as the presence of graphitic edge sites and surface functionalization differ [59]. Additionally, ECSA calculated with this method may significantly underestimate physical surface area as compared to nitrogen adsorption isotherms or mercury intrusion porosimetry [37]. It is unknown whether this discrepancy is a shortcoming of the capacitance measurement technique or rather an indication that much of the electrode surface area is inaccessible for redox reactions. Thus, there is a need to further understand the role of ECSA to develop reliable and quantitative characterization techniques.
Conclusions and outlook
In this short review, we have highlighted the efforts of the RFB community to develop porous electrode materials with properties tailored for the unique conditions present in RFB operation. While initial approaches have largely focused on selection and post-synthetic modification of carbon fiber substrates derived from PEFC gas diffusion layers, continued technology advancement necessitates new and more fundamental approaches to electrode development. First, the ability to design hierarchical materials with gradients in porosity and a tunable microstructure would enable operation with minimized mass transfer losses. Second, precise control of electrode surface functionality would allow for chemistry specific design of electrode—electrolyte interfaces. However, such efforts are contingent upon the ability to accurately measure and compare different electrode materials in a quantitative fashion, perhaps drawing lessons and guidance from more mature electrochemical systems such as PEFCs or Li-ion batteries which have undergone similar transitions in the past. As the field of designer porous electrode materials with gradients in porosity and a tunable microstructure would enable operation with minimized mass transfer losses. Second, precise control of electrode surface functionality would allow for chemistry specific design of electrode—electrolyte interfaces. However, such efforts are contingent upon the ability to accurately measure and compare different electrode materials in a quantitative fashion, perhaps drawing lessons and guidance from more mature electrochemical systems such as PEFCs or Li-ion batteries which have undergone similar transitions in the past. As the field of designer porous electrode materials continues to expand, we anticipate contributions from machine learning to enable the computational design of microstructure for reactive media, first-principle electronic structure calculations to guide surface functionalization, and novel bottom-up and top-down manufacturing techniques that allow for greater control over the final electrode structures beyond what is presently achievable.

Conflict of interest statement
Nothing declared.

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References
Papers of particular interest, published within the period of review, have been highlighted as:
  * of special interest
  ** of outstanding interest


Demonstration of an unbalanced compositionally-symmetric flow cell and a potentiostatic cycling protocol to assess slow decay processes for aqueous redox couples. This approach has the potential for analyzing deleterious time- and potential-dependent electrode–electrolyte interactions.


The authors synthesized electrospun RFB electrodes with distinct primary fiber orientations and studied mass transport characteristics using x-ray tomographic microscopy in tandem with direct numerical simulations.


A systematic investigation of the effect of pretreatment temperature on carbon paper electrode performance in a vanadium RFB highlighting the convoluting effects of wetting, active surface area, surface composition, and microstructure on performance.


Pursuant to understanding changes in electrode surface area as a function of thermal pretreatments, the authors correlate electrochemical double layer capacitance with the active surface area (as obtained with oxygen chemisorption and desorption) and the total surface area (as obtained by Kr BET).


Current densities (150 mA cm\(^{-2}\)) at cycling rate and stable performance over 5000 cycles at moderate current densities (150 mA cm\(^{-2}\)).


A carbon layer-coated sphere is synthesized that results in improved cycling rate and stable performance over 5000 cycles at moderate current densities (150 mA cm\(^{-2}\)).


A simple three-electrode cell design that enables porous electrode compression and the use of a reference electrode to obtain reproducible cyclic voltammetry.

