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Overlooking Issues and Prospective Resolutions Behind the Prosperity of Three-Dimensional Porous Carbon Supercapacitor Electrodes

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The past decade has witnessed the boom of porous carbon materials, especially three-dimensional (3D) ones, as supercapacitor electrode materials. Their large surface areas, tunable pore volumes, adjustable degrees of pore interconnectivity, and the potential to possess hierarchical porous networks have enabled them to achieve simultaneously high capacitance and excellent rate capability. This feature is challenging for non-3D counterparts but favorable for supercapacitors. However, behind the prosperity come the problems, and unfortunately, most of the issues are left unacknowledged and unaddressed in the literature available. This perspective aims to identify these problems, discuss the reasons for overlooking, and provide possible solutions to address these issues. The author wishes this article will draw the attention of researchers in electrochemical energy storage to tackle these roadblocks in the future development of 3D porous carbon electrodes in supercapacitors.

Keywords: three-dimensional, pore, carbon, supercapacitor, electrodes, overlooking issue

INTRODUCTION

Accompanying with the boom of electrochemical energy storage, three-dimensional (3D) porous carbon materials have emerged as rising stars of electrodes in supercapacitors. Supercapacitors, including electrical double-layer capacitors and pseudocapacitors, are electrochemical energy storage devices with power density typically about 100 times higher than those of rechargeable batteries. Their high power density bestows their applications in ultrafast charging and discharging scenarios (Miller and Simon, 2008; Salunkhe et al., 2014). As indispensable components in supercapacitors, electrodes having ultrasmall electrical resistance and ultrahigh surface areas are preferred. Therefore, a diverse array of highly conductive carbon materials with tunable morphologies have become supercapacitor electrode candidates for decades.

One of the representative conventional supercapacitor carbon electrodes is activated carbon. These carbon particles possess abundant micropores and surface areas surpassing $1,000\,\mathrm{m}^2$ g^{-1}. They store charges mainly *via* the formation of electrical double layers and are used in electrical double-layer capacitors (Ji et al., 2014) or capacitive electrodes in supercapacitor-battery hybrids (Liu H. et al., 2020). Activated carbon, however, is far from ideal. Its disadvantage is two-folded. On the one hand, its powdered form demands polymer binders when being processed into electrodes, which introduces unnecessary internal resistance born from the particle-particle contact resistance as well as the low electrical conductivity of the binders (Liu T. et al., 2020). On the other hand, the micropore-dominated porous structure of activated

carbon impedes ion diffusion throughout a particle, limiting the pore accessibility and, subsequently, the capacitance and energy density (Zhang et al., 2017). These two drawbacks make activated carbon unsuitable for storing large amounts of charges at elevated charge and discharge rates, the conditions under which supercapacitors are supposed to work.

The shortcomings of conventional powdered porous carbon materials have motivated the development of three-dimensional porous carbons as supercapacitor electrodes within the past decade. 3D porous carbons with high surface areas and easy ion-accessible pores allow capacitance and remarkable rate capability mutually achievable (Liu et al., 2017). Besides, the structural and morphological diversity and tunability derived from the versatility in sources and synthesis processes have generated a tremendous number of 3D carbon supercapacitor electrodes in the literature (Zhu et al., 2016; Zhang et al., 2017, 2019; Yang et al., 2019). The variety in structural parameters, including surface areas, pore interconnectivity, pore volumes, pore size distributions, and surface functionalities, is far more significant than those of non-3D carbon counterparts. These characteristics have also pushed the capacitance of carbon materials to beyond 300 F g^{-1} (Liu et al., 2017), a level unattainable by conventional porous carbon materials such as activated carbon.

The thrive of 3D porous carbon materials, however, brings about issues that compromise the scientific quality and integrity of relevant works. Unfortunately, most of the problems have been left unacknowledged and unaddressed (**Figure 1**). Without exhaustively examining the literature, this perspective aims to analyze these critical issues that the author hopes to initiate discussions and cultivate consensuses among the researchers in the field of electrochemical energy storage. Corresponding solutions are given in each section below.

COMPRESSING DAMAGES 3D STRUCTURE

Mechanical pressing or calendering, which improve the contact between carbon materials and their current collectors, are needed for manufacturing supercapacitor electrodes. These processes not only reduce the contact resistance of supercapacitor electrodes (Dsoke et al., 2013), but also increase the volumetric performance metrics such as volumetric capacitance, energy density, and power density, due to volumetric densification. As a result, most researchers mechanically compress their as-prepared 3D carbon materials onto conductive substrates, e.g., nickel foam (Zhang et al., 2017) and aluminum foil (Shah et al., 2020). In some cases, 3D porous carbon materials are ground into powders, blended with binders and carbon black (electrically conductive additive) when making electrodes (Deng et al., 2019; Nawwar et al., 2020). Inevitably, the delicate 3D architectures of the active materials are substantially altered, if not entirely demolished, after compression or grinding. Therefore, claiming that hierarchical porous structures facilitate ion diffusion or render outstanding rate capability based on morphologies before compression or grinding is inappropriate to reflect the actual working conditions of 3D porous carbon materials.
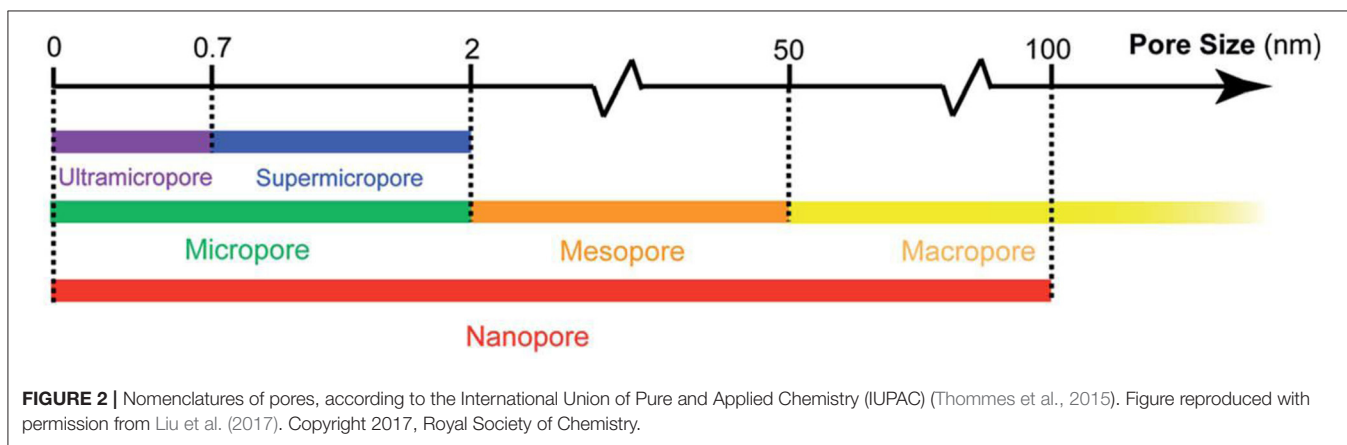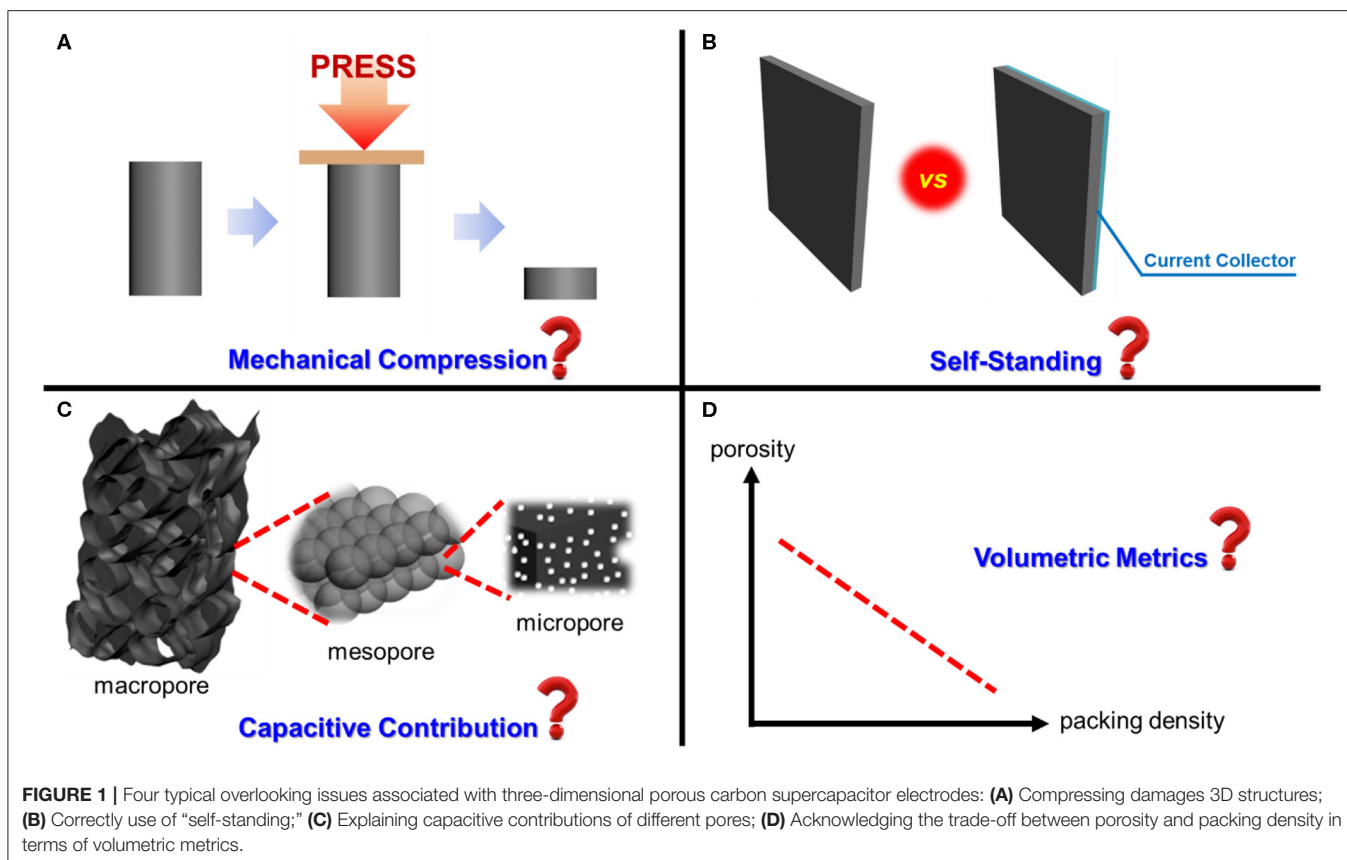
The most straightforward resolution is to avoid compressing or grinding 3D porous carbon materials. For example, Zhu et al. attached compressed Ni foam onto 3D-printed graphene aerogels using silver paste (Zhu et al., 2016), and Zhai et al. soldered copper foil onto Ni-foam-templated graphene foam (Zhai et al., 2015), both of which preserved the 3D morphologies of the active materials. However, silver or solder are prone to oxidation under positive biases, giving rise to unwanted oxidation current and redox peaks. These problems require proper sealing of the contact points (e.g., by epoxy) that complicates the fabrication, adds electrode dead mass, and leads to substantial performance deviations due to the variation in the sealant coverage. Additionally, the contact resistance might be large or small, depending on the adhesion strength between the electrodes and the current collectors. This factor makes the electrochemical performance irreproducible.

A relatively simple solution is to acknowledge the necessity of compression, but provide comprehensive characterizations to support discussions. Probing the morphologies of compressed 3D porous carbon materials is necessary. Based on the author's experience, compression only shrinks macropores. Still, it preserves mesopores and micropores, so the surface area of a 3D porous carbon material will unlikely decrease significantly compared to its uncompressed form. If macropores are partially maintained, the 3D porous network of the carbon material is still retained, though the morphology is different. Grinding, on the contrary, will most likely destroy 3D architectures entirely to broken particles and hence, is not recommended for processing 3D porous carbon materials. Top-view and cross-sectional-view scanning electron microscopy images are critical to illustrate the compressed morphologies of the active materials. Characterizing the compressed carbon materials with gas physisorption is imperative to gauge any subtle changes in the surface areas and pore size distributions. Both techniques provide foundations for discussing the structure-performance relationship of 3D porous carbon electrodes. For readers to gain comprehensive understandings of the reported materials, supplementing typical characterization results of as-prepared 3D porous carbon materials with those of compressed counterparts is encouraged.

TO BE OR NOT TO BE SELF-STANDING?

Self-standing has emerged as a fashion term to describe the feature of 3D porous carbon electrodes. However, arbitrarily using this word without considering the characteristic of the electrodes can lead to false and misleading information.

The difference between "self-standing material" and "self-standing electrode" must be strictly distinguished. Monolithic 3D porous carbon materials should be self-standing by nature, but whether they constitute self-standing electrodes depend on the fabrication method. If binders are used to bind 3D carbon materials or their grounded granules when making electrodes, such binder-containing electrodes can no longer be called self-standing. Rigorously speaking, electrodes are not self-standing if current collectors are used; however,

FIGURE 1 | Four typical overlooking issues associated with three-dimensional porous carbon supercapacitor electrodes: **(A)** Compressing damages 3D structures; **(B)** Correctly use of "self-standing;" **(C)** Explaining capacitive contributions of different pores; **(D)** Acknowledging the trade-off between porosity and packing density in terms of volumetric metrics.

FIGURE 2 | Nomenclatures of pores, according to the International Union of Pure and Applied Chemistry (IUPAC) (Thommes et al., 2015). Figure reproduced with permission from Liu et al. (2017). Copyright 2017, Royal Society of Chemistry.

the author believes that removing current collectors will create unnecessary technical challenges to the evaluation of supercapacitor electrodes, so calling binder-free electrodes self-standing is acceptable.

This issue calls for the transparency of experimental conditions. Authors reporting 3D carbon electrodes in supercapacitors or electrochemical energy storage, if broadly speaking, need to present explicitly how the electrodes are made. These conditions include the use of current collectors, compositions and manufacturers of current collectors, how carbon materials are adhered to current collectors (e.g.,

use of binders or direct compressing), as well as the mass loadings of active materials. The bottom line is that any researchers should be able to reproduce the experiments following the provided technical details with absolutely no confusion.

ELUCIDATING PORE CONTRIBUTIONS

One of the unique structural features of 3D porous carbon materials is their hierarchically porous structures, that is,

structures with interconnecting pores of different sizes (**Figure 2**) assembled into hierarchical networks. Porous materials that contain multiscale but spatially isolated pores are not hierarchical, because their pores cannot "communicate" with each other during charge and discharge processes. Due to the diversified pore sizes and shapes, differentiating the capacitive contributions of the pores becomes increasingly critical to rationalize the design of next-generation porous carbon supercapacitor electrodes.

Despite extensive investigations, the contributions of different pores have yet reached an agreement. The general belief is that macropores and mesopores contribute little to capacitance, but they help electrolyte infiltration and facilitate ion diffusion, both of which improve the ion accessibility to micropores (Yang et al., 2017). Zhang et al. have experimentally verified that sub-micron macropores and mesopores in a chitosan-derived carbon aerogel are indispensable for maintaining its excellent rate capability (Zhang et al., 2017). Micropores are mainly responsible for high surface areas and ion storage, resulting in capacitance. The general belief, however, is challenged by simulation works that show macropores and mesopores are unnecessary, as they facilitate electrolyte infiltration but not ion diffusion (Borchardt et al., 2018). Others have revealed that micropores of pore openings less than 1 nm can accelerate ion diffusion due to the ion packing patterns in ionophobic pores (Mo et al., 2020). Although the author is puzzled about the exact causes of the discrepancy between the simulation results and experimental observations, a possible reason is the different experimental setups. Most simulations choose ionic liquids as study objects because of their simplicity (no solvent molecules and ion solvation) to reduce calculation costs. In contrast, the majority of laboratory supercapacitors adopt aqueous electrolytes because of their safety, ease of fabrication, and intrinsically rapid ion diffusion.

Besides simulations, some experimental observations also contradict the general belief. For example, depending on the source, commercial activated carbon can contain mesopores slightly bigger than 2 nm, according to N_2-physisorption (Liu T. et al., 2020), but their capacitance still decreases dramatically at elevated discharging rates. Carbide-derived carbons, though possessing large numbers of mesopores and macropores, still exhibit satisfactory rate capability in aqueous electrolytes (Huang et al., 2016).

These outliers in the literature highlight the complex roles of various pores. Perhaps the pore geometry, surface functionality, and graphitization degrees of 3D porous carbon electrodes all profoundly alter the electrochemical responses. For example, Dyatkin et al. simulated that the oxygen functional groups inside pores attracted planar anions in ionic liquids. This attraction aligned the anions in parallel to the pore surface and provided relatively clear transport channels to enhance rate capability (Dyatkin et al., 2016). The alliance between experimentalists and theorists, as well as alignment between experimental conditions and computational inputs, are undoubtedly indispensable to drive future investigations on the charge-storage mechanisms of 3D porous carbon electrodes. Additionally, the progress of advanced characterization methods,

including quasi-elastic neutron scattering (Osti and Mamontov, 2020), quartz crystal microbalance (Levi et al., 2016), *in-situ* nuclear magnetic resonance spectroscopy (Forse et al., 2017), are vital tools for future investigations. Supporting experimental findings with simulation results in a research article is strongly encouraged if condition permits. This practice may become a new norm for publishing manuscripts in top-tier journals and can reward interdisciplinary researches with crystal-clear mutual communications among all the practitioners involved. The author believes that the role-determination of pores in versatile 3D porous carbon materials will remain as frontiers in electrochemical energy storage.

PACKING DENSITY *VS.* POROSITY

Perhaps the most common criticism of 3D porous carbon electrodes is their large porosity that declines the packing density of an electrode. Small packing density leads to low volumetric performance metrics, such as volumetric capacitance.

While the author fully agrees that volumetric metrics are crucial for rechargeable batteries whose working space is tight (Choi and Aurbach, 2016), the working environments of supercapacitors are far more diversified than those of batteries. 3D porous carbon materials with large porosity have the advantage of low volumetric density or lightweight. This characteristic makes them especially suitable for portable electronics needing high power density, such as drills and drones (Lin et al., 2018). In such cases, the volume of an energy-storage device is less considerable than its weight. Therefore, the author believes that it is unfair to criticize 3D porous carbon electrodes based on their low packing density. Comprehensive evaluations of a 3D porous carbon electrode and reporting a full set of gravimetric, areal, and volumetric performance metrics are highly recommended.

Another issue calling attention is the report of the gravimetric capacitance of 3D porous carbon materials. The relationship between the total capacitance (C_T) and gravimetric capacitance, or specific capacitance (C_m), of an electrode, is:

$$C_T = C_m \times m$$

where m is the mass of active materials. Based on this equation, achieving ultrahigh numbers of gravimetric capacitance becomes diminishingly meaningful if the mass loading of the active material is limited, as the total capacity is insignificant. Therefore, it is always a good practice to report gravimetric performance in the context of mass loading. For commercial viability, the mass loading of an electrode material must be 10 mg cm^{-2} or above (Chen et al., 2020). Still, this standard should not be rigid to restrict the development of laboratory-scale supercapacitors, which usually involve mass loadings of active materials between 1 and 10 mg cm^{-2}. Nevertheless, explicitly reporting mass loading and accurately characterizing the influence of mass loading on electrochemical performance are always welcome and practically meaningful (Lin et al., 2015). Additionally, as areal capacitance depends on mass loading, reporting both gravimetric capacitance

and areal capacitance for single electrodes is beneficial to avoid deceitfully excellent charge-storage performance.

CONCLUSIONS AND OUTLOOKS

This perspective highlights four main issues behind the prosperity of 3D porous carbon materials as supercapacitor electrodes. They are mostly overlooked in the existing literature, and if continually left unaddressed, are harmful to the healthy development of supercapacitors. Hence, the article presents the current understanding, points out the existing challenges, and discusses the possible resolutions of each issue. The author hopes this perspective will draw the attention of the practitioners in the electrochemical energy storage community to address the issues by intimate collaboration, protocol unification, and frequent idea exchange in the ensuing years.

AUTHOR CONTRIBUTIONS

The author confirms being the sole contributor of this work and has approved it for publication.

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