Investigation on the applicable pore size of nanoporous carbon for electrochemical double-layer formation at different current densities

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A B S T R A C T

Considering the wide application of nanoporous carbon material in electrochemical double-layer capacitors (EDLCs), the investigation of the structure-performance relationship is critical to constructing suitable nanostructure for high performance EDLCs. Herein, we focus on an important but neglected issue of different applicable pore sizes for electrochemical double-layer (EDL) formation at different current loadings. Small-sized pores with different sizes/distributions are introduced for energy storage while a developed 3D large meso/macroporous structure is constructed for guaranteeing rapid mass transfer. An interesting result is obtained that the applicable pore size greatly depends on the current loadings. For instance, pores larger than 0.59 nm are responsible for EDL formation at a low current density of 0.1 A g^{-1} in aqueous electrolyte. As increasing the current density to 1 and 10 A g^{-1}, the most effective pore size increases to larger than 0.73 and 0.93 nm, respectively, which is attributed to the insufficient time of solvent shell removing, squeezing behavior of solvated ions and charge arrangement at higher current densities. These encouraging results may raise concerns about constructing suitable pore size more precisely to realize a target oriented use, particularly those targeting higher power EDLCs applications.

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1. Introduction

Nanoporous carbon material (NCM) has attracted numerous scientific and technological interests in electrochemical double-layer capacitors (EDLCs) by serving as electrode materials due to its chemical and thermal stability, high conductivity and relatively low cost [1–18]. The past decades have witnessed the significant progress of the design and fabrication of many novel NCMs with well-defined nanostructure for EDLCs application, including activated carbon [1,2], carbon nanospheres [3,4], carbon aerogel [5–8], ordered mesoporous carbon [9,10], carbon nanosheets [11] and nitrogen-doped carbons [12,13], etc [14–20]. It has been experimentally demonstrated that the capacitance is not only related to the specific surface area (SSA) of NCMs, but also affected by the size of the electrolyte ions as well as the pore structure of NCMs, such as porosity, pore shape, pore size and its distribution [15–20].

Previous efforts have been devoted to providing insight into the relationship between pore size and specific gravimetric capacitance (C_g) in different electrolyte with the aim of better designing the nanostructure of NCM-based electrode materials [17–31]. This issue, to some extent, is more important than the investigation of the relevance between SSA and C_g because as we know, capacitance is not directly proportional to surface area in many studies, even though a large surface area is considered necessary for a high energy density electrode material [16–18,30,32,33]. This non-proportional relation is attributed to the different mass transfer capability and electrochemical double-layer (EDL) formation efficiency of various pore structures [16,21,23,28,34]. The IUPAC definition has classified the pores into ultramicropores (<0.7 nm), micropores (<2 nm), mesopores (2–50 nm) and macropores (>50 nm). According to different roles during the repeated charge adsorption-release processes, nano-scale pores can also be divided into two classes, energy-storage-type pore (ES pore) primarily contributed by small-sized pores [23,24,27,35] and mass-transfer-type pore (MT pore) derived from macro- and large mesopores [10,35–37]. Thus, the influence of the pore structure on EDL formation involves the following two aspects.

First, the existence of certain MT pores combining with high-efficient pore morphology is believed to minimize the transfer resistance of the electrolyte [9,16,34–32]. It has been proven that in

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enough large pores (>10 nm) [37], the collision probability in electrolyte ion–carbon wall interactions is close to zero, resulting in fast ion transport behavior. In addition, several pore morphology models with high mass transfer efficiency have been proposed, such as 3–D continuous macro-/large meso- porous structure [37,38] and interconnected ordered channel-like macro/mesopore morphology [10].

Secondly, although it still remains a primary dispute that whether micropores only, combination of micropores and mesopores, or mesopores only are optimal for charge accumulation, the mechanism arisen in recent years has been generally accepted that small-sized pores (including micropores and small mesopores) providing intensive adsorbability and donating the majority of the surface area are most responsible for charge accumulation [17,23,25,29]. Tailoring ES pores with suitable pore size will increase the utilization of surface area in different electrolyte, promoting rapid EDL formation [17,22,28,29]. In other words, these pores must be electrochemically accessible for ions, namely, the ion-accessible surface area. Hitherto, great achievements have been made in the investigation of the applicable ES pore size for EDL formation [17,18,21–30]. For example, several studies suggested that an average ES pore size of c.a. 0.7 nm could maximize the C_g at low current loadings [18,22,25,27]. A slight difference of the optimal average ES pore size in 2 M H_2SO_4 electrolyte around 0.9–1.0 nm was proposed by Fernández [24]. Desolvation of ions [17,21] and squeezing behavior of the solvated ions along with distortion [21,23] were demonstrated to explain the energy storage mechanism within the pores slightly smaller than the ion dimensions. Xing et al. also suggested that a relatively large ES pore size was beneficial to improving the rate performance by facilitating ion diffusion and thereby increasing the ion-accessible surface area for charge arrangement [30].

However, as far as we know, these studies usually focused on the optimal ES pore size under low current loadings in order to provide sufficient time for enhancing the ion accessibility as well as the formation of EDL. In addition, statistically average values of the pore size were used to represent the actual pore size distribution. One neglected aspect is the different capability of EDL formation in ES pores with different size distribution under higher current loadings. This becomes a major barrier for further targeting applications. The main reason could be ascribed to the incompletely clear energy storage mechanism and the difficulty to employ a targeted porous structure as the investigation model. It is well known that high power density is one of the most attractive properties of EDLCs, leading to their diversified applications under wide current loadings ranging from portable electronic devices to large equipment represented by electric vehicles, especially where peak power is highly needed. While constructing mass transfer pathways for electrolyte, the capacitance under different current loadings will be undoubtedly influenced by different ES pore sizes, i.e., the effective ES pores reduce at high current loadings. ES pores with relatively small sizes may not be well utilized owing to the insufficient time of solvent shell removing [17–21], squeezing behavior of solvated ions into the pores [16,18], ion diffusion and charge arrangement [28,30]. On the other hand, increasing the pore size unlimitedly may result in a sharp decrease of the surface area. Therefore, the investigation of the capacitive dependence on different ES pore size at different current loadings becomes very critical to precisely constructing desired ES pore size for different applications, particularly those targeting higher power purposes.

Herein, we propose an interesting insight into the aforementioned important but neglected issue by focusing on the applicable ES pore size at different current loadings in both aqueous and organic electrolyte. As shown in Fig. 1 and S1, this is realized by constructing a carbonaceous porous network which processes hierarchically 3D macro-meso-porous nanostructure for ensuring sufficient mass transfer pathways. Then different amount of KOH activated agent was served to introduce small-sized pores with different sizes and distributions while maintaining similar MT pore structure. Density functional theory (DFT) was used to calculate the corresponding SSA of the NCMs in different pore size range. Combining with their electrochemical performances, we find that the most effective ES pore size varies based on the different I_D. Relatively larger ES pore size increases the ion-accessible surface and facilitates rapid EDL formation at higher current loadings.

In brief, the preparation method of NCMs can be described as follows (Fig. S1 in the Supplementary Information): a polymeric network (PN) was first synthesized based upon the Friedel-Crafts
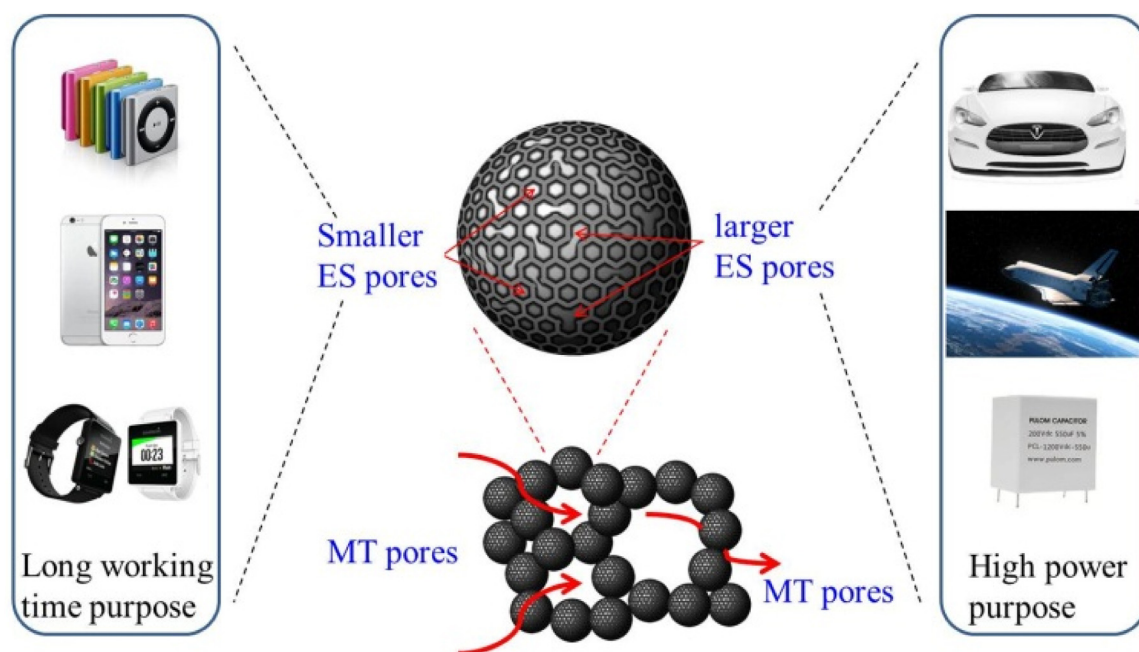

Fig. 1. Scheme model of ANCM.