



Review Article

The critical role of nanostructured carbon pores in supercapacitors

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Abstract

Carbon materials exist in several morphologies; however, the most famous one for supercapacitors electrode is the nanoporous carbon with large surface area (from 1500–2500 m² g⁻¹). For rapid charge/discharge in supercapacitors, alignment between the shape of the pores and the size of the solvated ions is necessary. Due to recent improvements focused on enhancing specific energy, power performance of supercapacitors is mostly ignored/compromised. In addition, the size and shape of the carbon pores are critical for the low-temperature performance of supercapacitors. This is because the interactions between carbon pore walls and the electrolyte affect its freezing/melting behavior and consequently the operation at sub-ambient conditions. In this review, we explain why nanostructuring of carbon pores is necessary for supercapacitors. Further, the latest progress in this research field, the trade-off between energy and power, and the processes at the interplay of pore/ion in non-aqueous and aqueous electrolytes have been discussed.

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Keywords

Pore architecture, Carbon, Supercapacitor, Power density, Energy density, Low-temperature performance, Confinement effect, Machine learning, Nanostructured pore.

Introduction

Activated carbons (ACs) are also sometimes called nanoporous carbons, which exist in the form of fiber, felt, cloth or powder. ACs are characterized by a large surface area and pore sizes distributed in a wide range from micropores to meso- and macropores. These characteristics combined with low cost enable the large-scale application of nanoporous carbons in the fields of adsorbents and energy storage. Another important aspect of these materials is the possibility of tuning the porous texture by controlling the production parameters such as activation at high temperatures, which leads to the formation of small pores in the range of 1–2 nm. In electrochemical energy storage devices such as supercapacitors (SCs), large pores i.e., mesopores (from 2 nm to 50 nm, according to the IUPAC classification) facilitate the movement of ions to micropores (less than 2 nm). These two types of pores open into the macropores (larger than 50 nm) and are interconnected, thus leading to easy transportation of ionic species to form electric double-layer (EDL) during charging [1,2]. The bi-model pore size distribution indicates well-connected micropores and mesopores that facilitate the transport of electrolytes or solutions.

In the case of electrochemical capacitors or supercapacitors, carbon pores play an important role in determining energy and power performance. Depending on the activation conditions, these pores exist in several configurations and architectures (e.g., narrow, wide, bottle-necked, elongated or conical). The shape of these pores directly affects the ion transport near the EDL. In the past decade, studies have been conducted to elucidate effects of carbon pore size on the charge storage mechanisms in non-aqueous electrolytes [3–6]. These works have been carried out on electrolyte-impregnated porous carbon materials by electrochemical quartz crystal microbalance (EQCM), nuclear magnetic resonance (NMR) and electrochemical dilatometry [7–9]. While much effort has been devoted to understand the proper screening of charges within the pores, it has been also shown that the ions are partially or completely desolvated into the carbon pores according to the structure of the pore and the size of the solvated anion/cation. The extensive works on ion desolvation and pore/ion size matching elaborated the charging behavior of porous carbon electrodes and its correlation with the capacitance of device [10–13].

Since the surface area and the porosity of carbon electrodes can be improved to a certain limit, other efforts have been made to increase the capacitance and energy of supercapacitors. This includes the modification of electrode via in situ growth of different electroactive species (e.g., iodine) in the pores or onto the surface of electrode materials [14]. Another approach is regarding electrolyte where water-in-salt solutions have been used to achieve high voltage window [15]. However, with increased concentration, parameters such as ionic association, hydration degree of ions and meso-/micropore sizes greatly affect the rate performance of the device. The in-pore freezing/melting of electrolyte is another important aspect that affects the low-temperature operation of supercapacitors.

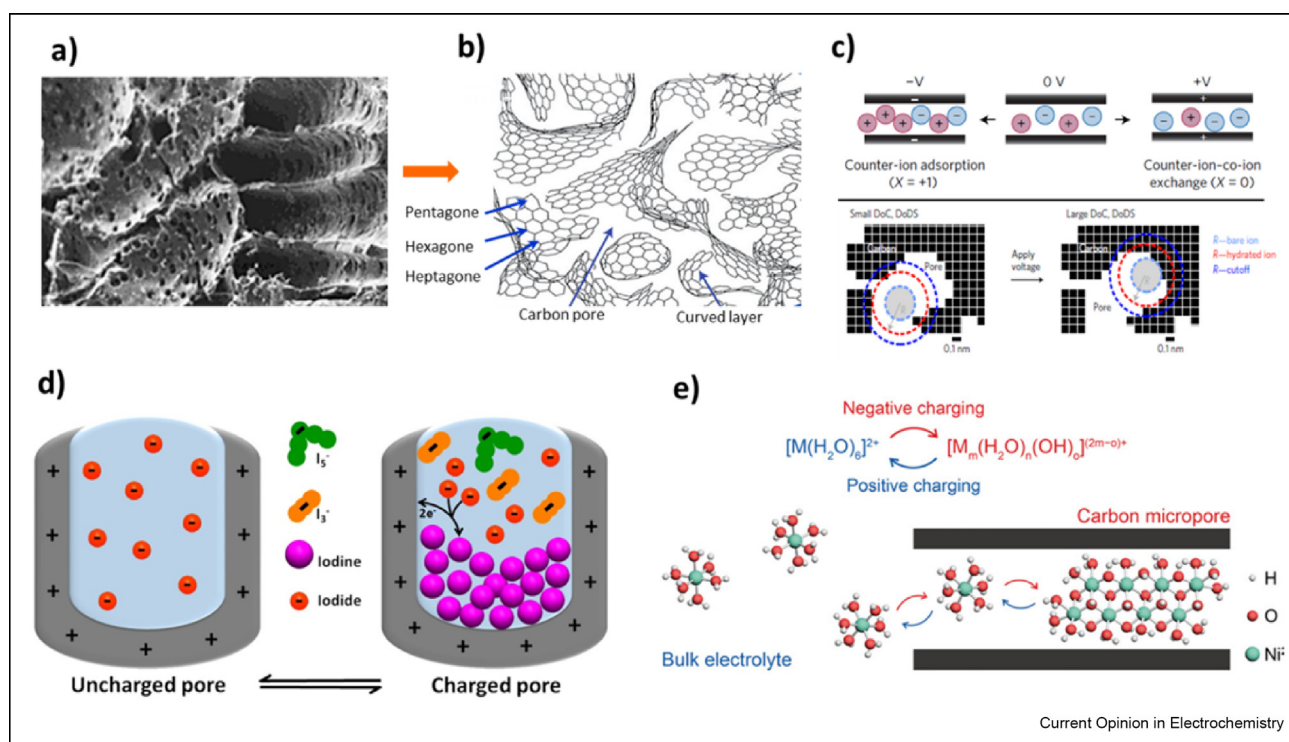
Confinement effects and nanostructuring of carbons by in situ growth of electroactive species

The majority of micropores in ACs are interconnected with larger pores (i.e., mesopores and macropores), providing facile pathways for electrolyte movement (Figure 1a). Due to the existence of pentagonal and heptagonal rings, the curved carbon/graphene layers are generated, which form various pore shapes i.e. cylindrical pores or slit-shape pore (Figure 1b) [16]. To understand the ionic electrosorption in the carbon pores, C.

Prehal et al., introduced the so-called degree of confinement (DoC) that allows quantifying the local ion concentration changes in confinement. By combining in situ SAXS experimental data and simulation studies, it was found that the changes in ion concentration inside carbon pores were related to local ion rearrangements (Figure 1c, lower panel) [17]. Pulsed-field gradient NMR was used for understanding the in-pore ion dynamics that are strongly dependent on charging and discharging rate [18]. These findings confirmed that the diffusion coefficient of ions in the pores is reduced by two to three orders of magnitude under confinement (Figure 1c, upper panel), and to improve these parameters and achieve extremely fast charge/discharge, carbons with hierarchical and defined porosity should be used as electrodes [1,18]. A combination of EQCM and simulation studies also revealed that EDL formation is dominated by the ions with higher diffusion coefficients, and pointed out that capacitance could be improved by employing electrode materials with tailored layer structures [8].

Hierarchical pore size distribution with majority of pores in the range of 0.55 nm–2.53 nm were achieved in bio-based carbon which showed high energy of 12.4 Wh kg⁻¹ at 5.7 kW kg⁻¹ in a symmetric device [19]. Pore

Figure 1



a) Micrograph of AC obtained from coconut shell activation, b) curved carbon/graphene layers and carbon pores development [16], c) ionic adsorption in positively and negatively charged pores (upper panel), confinement effects in nanoporous carbon for alkali cations (lower panel) [18], d) confinement of iodine electrodeposited via electrooxidation of iodide ions in carbon pore filled with iodide-aqueous electrolyte [27], e) oligomerization or association of metal ions inside the carbon micropore during charging [28].

tuning in hollow carbon spheres improved supercapacitor performance exhibiting 3.6 Wh kg^{-1} at 2.2 kW kg^{-1} [20]. Heteroatom-doped hierarchical carbon at a high yield was synthesized from poly(ionic liquid) to achieve good matching of pore and ion size, and the device maintained 41.7 Wh kg^{-1} at a high power-output of 19.7 kW kg^{-1} [21]. High power density values have been also demonstrated in supercapacitors via tuning the pore walls in carbon nanotubes and activated carbons based electrodes [22–24]. Carbon with exceptionally high surface area obtained from natural anthracite showed high rate performance in supercapacitors with energy density of 83 Wh kg^{-1} at 3.5 kW kg^{-1} [25]. Defective graphene nanosheets obtained from template of polystyrene sphere with glucose precursor showed high volumetric capacitance of 392 F cm^{-3} (energy density = 13.8 Wh L^{-1}) with high rate performance [26].

Quantitatively, the capacitance enhancement due to the effective screening of highly confined ions is still not very large. Therefore, to overcome low EDL capacitance, carbon electrodes have been modified by in situ electrodeposition of active species [29]. A combination of in situ Raman spectroscopy and SAXS measurements has revealed the iodine electrodeposition and chemical bonding exhibited via charge transfer in the nanoconfinement of electrified carbon pores in an aqueous iodide-based electrolyte (Fig. 1d) [30]. The shuttling of polyiodides has been reduced by various studies such as using water-in-choline salt electrolyte [31], anchoring with starch as biopolymer material [32], or by confining in the metal–organic frameworks [33]. Nickel–based transition metal nanosheet arrays in SCs showed energy density of 87.9 Wh kg^{-1} at a low power density of 433.6 W kg^{-1} [34], and Fe_3O_4 nanoparticles stable capacitance for only 5000 cycles [35], both were in situ grown in the carbon cloth and used as electrode. Similarly, low cycle life (5000 cycles) was noted for sodium ions pre-intercalated MnO_2 nanoflakes grown on three-dimensional graphene support materials and used as a positive electrode in hybrid supercapacitors [36]. Likewise, nickel was directly grown on the nickel foam structure in metal–organic frameworks to be used as a battery-like electrode in a hybrid supercapacitor to achieve a high specific energy of $586.7 \text{ mWh cm}^{-2}$ at a specific power of 3679 mW cm^{-2} [37]. Polyaniline nanofiber arrays supported by graphene sheets were grown onto carbon cloth that exhibited energy density of $46.6 \text{ } \mu\text{Wh cm}^{-2}$ at $498.9 \text{ } \mu\text{W cm}^{-2}$ and capacitance retention of 94.1% for only 2000 cycles in hybrid supercapacitors [38].

In other works, using in situ X-ray absorption spectroscopy, it has been found that metal ions strongly associate in a negatively charged carbon pore to form oligomers [28]. Under the spatial confinement and screening effects, the metal cations form an ionic association which might be the reason for their poor dissociation kinetics

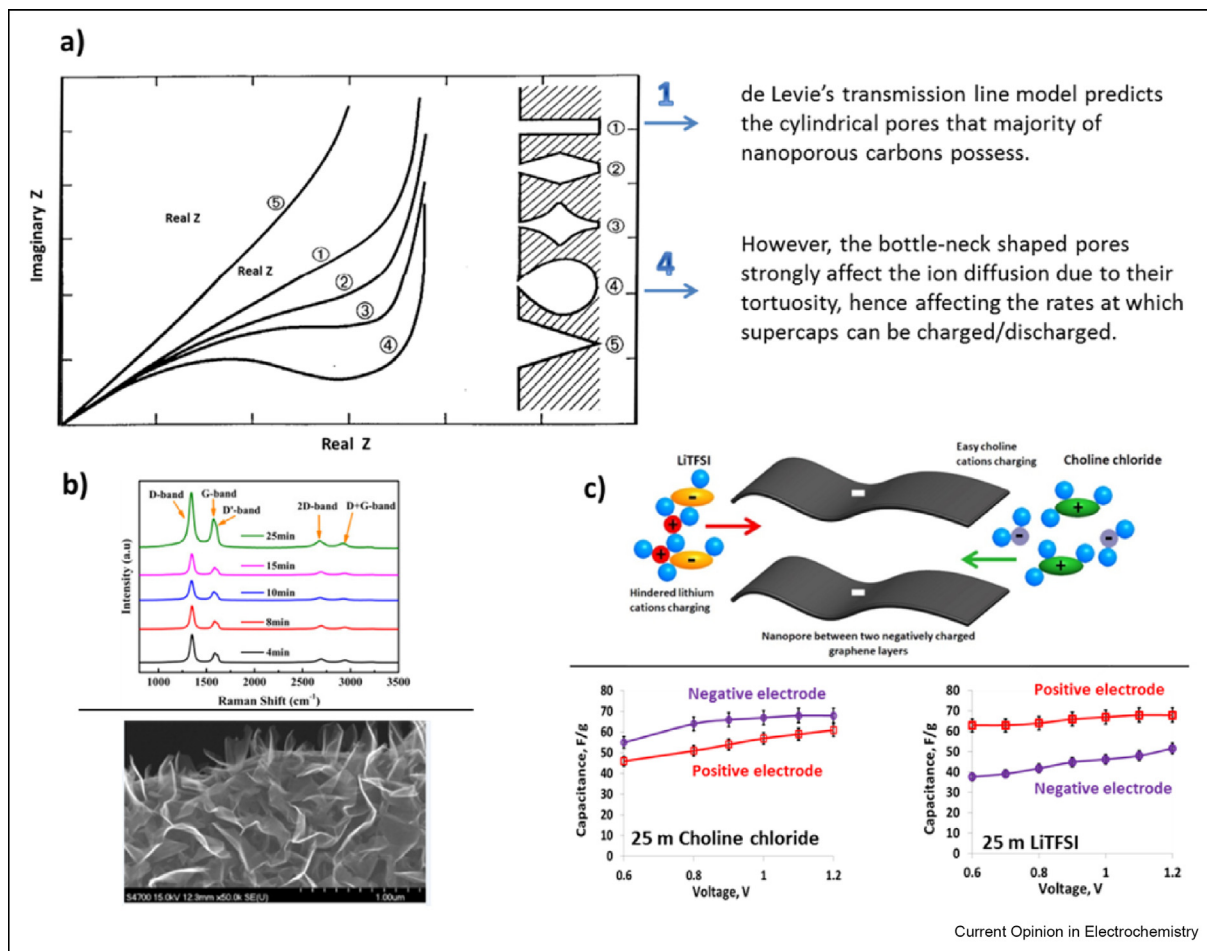
leading to capacitance fading during cycling (Fig. 1e). Contrary to metal ions association, confinement of polyoxometallate cluster in the molecular scale cages of CNT framework enhanced the supercapacitor energy density to $67.5 \text{ } \mu\text{Wh cm}^{-2}$ at a power density of $700 \text{ } \mu\text{W cm}^{-2}$ but with low capacitance retention of 85.7% after only 3000 cycles [39]. Redox-active $\text{K}_3\text{Fe}(\text{CN})_6$ was successfully confined in the functionalized porous carbon to increase the specific energy and cyclability of hybrid supercapacitors, yet the power performance was low (36.9 W h kg^{-1} at the power density of only 225 W kg^{-1}) [40]. Three-dimensional metal carbides, nitrides, and carbonitrides/metal–organic frameworks (MOFs) composites were produced and implemented in SCs that exhibited capacitance retention of 94.4% retention after 4000 cycles [41]. Overall, the onset of redox reactions at either of the electrodes greatly impacts the power performance and cycling stability, the main reason being the charge transfer between the carbon matrix and the ionic species and consequent phase changes.

Carbon pore architecture and power performance of supercapacitors

From the foregoing, significant research efforts in recent past dedicated to overcome the low specific energy of SCs ignored the power metrics. To overcome this, an understanding of charging mechanisms at both positive and negative polarities is important. Care must be taken in the design process of electrodes and electrolytes, the matching of ions and pores as well as the chemical interactions with ionic species. Figure 2a shows the pore models and corresponding Nyquist plots. Here, the pore behavior in nr. 1 is explained by de Levie model [42,43], which expresses impedances and resistances distributed in a cylindrical pore and depend on pore length, pore radius and number of pores. However, ACs possess majority of pores with random geometry which strongly impact the charge/discharge rate owing to their unique structure imposing diffusion limitations [44]. One electrode material that stands out in terms of fast charging (RC time constant less than $200 \text{ } \mu\text{s}$) and shape-wise probably matches closely to the cylindrical pores, is vertically aligned graphene oxide (VAGO) as shown in Figure 2b (lower panel) [45,46]. The graphene layers in this material are vertically arranged with exposed edge planes, providing easy wetting and ion accessibility during EDL charge/discharge, thus retaining high capacitance up to high frequencies. Supercapacitors produced with VAG electrodes in TEABF₄/PC (propylene carbonate) electrolyte exhibited a cell voltage of 4.0 V with energy density of 52 W h kg^{-1} at 8 kW kg^{-1} , and nearly 100% capacitance retention after 10,000 cycles [45–48].

To better understand the pore/ion alignment effect on capacitance, two water-in-salt electrolytes (25 mol kg^{-1} choline chloride and 20 mol kg^{-1} LiTFSI) were used to determine the charge/discharge rates and capacitance

Figure 2



a) Various geometries of carbon pores, here, nr. 1 is explained by the simple de Levie model applicable to the cylindrical pores and nr. 4 concerns the bottle-neck pores which are present in the large fraction in a highly microporous carbon [49], **b)** Raman spectra of vertically aligned graphene nanosheets at a different duration of treatment period [45] and the corresponding development of 2D-band (upper panel) and micrograph of the VAGs (lower panel), **c)** Charging of nanopore in water-in-salt electrolyte [31], cation–anion pairing for water-in-LiTFSI electrolyte and higher ion-dissociation in water-in-choline chloride electrolyte (upper panel), capacitance values of positive and negative electrodes extracted from galvanostatic discharge curves for water-in-choline chloride and water-in-LiTFSI (lower panel).

values (Figure 2c) [31]. In a highly microporous carbon, positive and negative electrodes show similar capacitance in a water-in-choline electrolyte. On the other hand, the negative electrode (37 F g^{-1} at 1.2 V) in water-in-LiTFSI electrolyte displays low capacitance than the positive one (63 F g^{-1} at 1.2 V). This difference can be explained by the strong ionic association in LiTFSI due to the high charge density of lithium and the obstruction of its penetration in pores. In the case of bulky choline cation, the dissociation of the ions is independent of concentration increase and thereby shows $\sim 100\%$ capacitance retention for 20,000 cycles. Potassium acetate based water-in-salt electrolyte was used in a symmetric supercapacitor that showed stable capacitance at 2.0 V , and energy density of 10 Wh kg^{-1} could be extracted at $\sim 2.0 \text{ kW kg}^{-1}$ [50]. Hybrid supercapacitors produced from highly concentrated aqueous electrolytes could operate up to high voltage over 2.2 V

and maintained stable capacitance for 20,000 cycles [51,52].

The EDL charging behavior of carbon electrodes in water-in-salt electrolytes is different than in diluted electrolytes [53,54], similar to ionic liquids, which possess comparable conductivity values. However, the limiting factor for power performance in EDL electrodes is the in-pore ionic diffusion which is around two orders of magnitude lower (due to confinement effects) than in bulk electrolyte. The ionic diffusion is not only influenced by the electrolyte properties but also the shape of pores and the tortuosity of electrode which impacts the power of supercapacitor. According to equation $D_{\text{eff}} = \frac{\epsilon}{\tau} D_0$, where D_{eff} and D_0 are in-pore and bulk diffusion coefficients respectively, ϵ the porosity and τ the tortuosity [55,56], the latter can be indirectly determined by NMR [57], electrochemical impedance spectroscopy [58] or by

applying Warburg model [59]. By using template materials, less tortuous carbon electrodes were produced and used in SCs which exhibited energy density of $101.7 \mu\text{Wh cm}^{-2}$ at a power density of 5 mW cm^{-2} [60], and high rate performance [61].

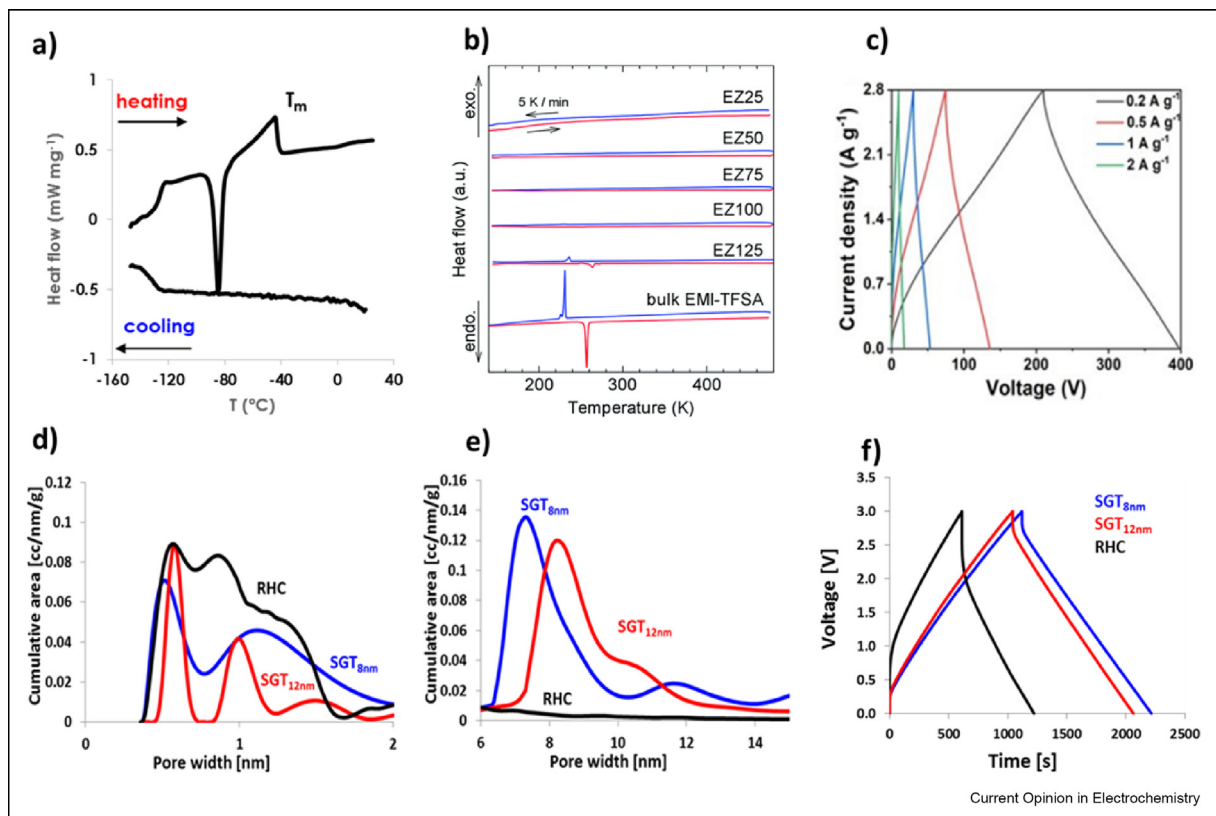
Correlation between electrode porosity and supercapacitors' performance at sub-ambient conditions

The confinement of liquid materials inside the carbon nanopores affects their freezing/melting behavior [62,63]. More recently, this topic has attracted interest due to the need to operate energy storage devices at low temperatures. Microporous carbon was found to be more suitable for salt aqueous electrolyte in water/methanol mixture as a solvent due to the preferential water adsorption and therefore increased local methanol concentration near the EDL than in bulk electrolyte [64]. Recently, aqueous choline nitrate (5 mol kg^{-1}) showed no freezing down to $-100 \text{ }^\circ\text{C}$ and only glass transition was observed (Figure 3a). Hybrid SC using mixture of choline nitrate and choline iodide ($5 \text{ mol kg}^{-1} \text{ ChNO}_3 + 0.5 \text{ mol kg}^{-1}$

ChI) exhibited 11.6 Wh kg^{-1} at 3 kW kg^{-1} ($24 \text{ }^\circ\text{C}$) and 0.8 Wh kg^{-1} at 1.5 kW kg^{-1} ($-40 \text{ }^\circ\text{C}$) [65].

In case of non-aqueous media, the freezing and melting behavior of EMI-TFSA has been studied in microporous metal–organic frameworks [67]. It has been shown that the ionic conductivity of bulk ionic liquid decreases with temperature decrease, however, the conductivity under confinement in MOFs was always higher than that of the bulk EMI-TFSA. Ionic liquids were also mixed with low-melting organic solvents to prepare electrolytes for low-temperature applications, displaying symmetric galvanostatic charge/discharge curves down to $-70 \text{ }^\circ\text{C}$ [68]. Indeed, the freezing ionic liquid in confinement can be very different from the bulk electrolyte, and some strategy for using mixed ionic liquids has been adopted for low-temperature supercapacitors [69]. This comparative study includes two templated carbons with a large fraction of mesopores and a highly microporous carbon. It was shown that the pore structure of carbons plays a key role in determining supercapacitors' low-temperature performance and mesopores are crucial because they keep away

Figure 3



Differential scanning calorimetry (DSC) of 5 mol kg^{-1} choline nitrate in water at $10 \text{ }^\circ\text{C min}^{-1}$ from $25 \text{ }^\circ\text{C}$ to $-150 \text{ }^\circ\text{C}$ [66], **b**) DSC curves of EMI-TFSA in bulk and in confinement within the MOF at a scan rate of 5 K min^{-1} [67], **c**) galvanostatic charge/discharge curves of supercapacitor with PMImNTf₂ in acetonitrile down to $-60 \text{ }^\circ\text{C}$ [68], **d**) comparison of pore size distribution for two templated carbons (SGT_{8nm} and SGT_{12nm}) and a rice husk-based carbon evaluated from the N₂ gas adsorption/desorption data **a**) in a limited range up to 2 nm, **e**) in large pore diameter range 6–12 nm, **f**) comparison of galvanostatic charge/discharge curves of supercapacitors using these carbons with ionic liquid based electrolyte at $-40 \text{ }^\circ\text{C}$ [69].

from significant pore-wall interactions and preventing freezing, thus maintaining the bulk-like properties by serving as a reservoir for the electrolyte. At 24 °C, SCs with all three carbons showed similar energy at a power of 2 kW kg⁻¹. However, the power of microporous-based SC decreased dramatically, i.e. no energy could be extracted at -40 °C beyond 0.6 kW kg⁻¹, while the templated carbons-based SCs showed 2–3 Wh kg⁻¹ at 1.5 kW kg⁻¹ at such low temperatures [69].

Simulation studies and machine learning to predict processes in the carbon pores

Several theoretical advances have been made to understand the dynamics of ionic species in the carbon nanopores and to elaborate the charge storage mechanisms in supercapacitors [70]. In terms of capacitance, the influence of ion desolvation in the nanopores has been evaluated, where molecular density functional theory (DFT) was applied to determine ion solvation diameters in confined acetonitrile [71]. Effects of small water contents in protic ionic liquid confined in the carbon nanopores were investigated by molecular dynamic simulation, revealing that the water molecules were dispersed in the ionic liquid instead of forming aggregates [72]. This enhances the ionic dissociation effects and the diffusion of ionic species to deliver high-performance supercapacitors. Combined with experimental and molecular dynamic research, the ionic conductivity and hydrodynamic radius derived from PFG-NMR were used to find out the degree of ionic dissociation and coordination [73]. Under the condition that long-chain solvent molecules affected the ionic diffusivity, the predicted values based on experiments and simulations showed excellent consistency. MD simulation of a series of ionic liquids with different anions studies and MXene electrodes with different surface functional groups was carried out [74]. It was found that no matter what type of anion, the electrodes expand when negatively charged, and anion size has a strong influence on the charging mechanism of porous materials, which is also correlated with surface functional groups. MD simulations also confirm the previous experimental finding that more ordered pore structures and defined pore sizes contribute to achieving high capacitance values [75]. Artificial neural network has been used to produce zeolites, and has potential for designing porous carbons [76]. Machine learning based prediction enabled designing carbon with micropores area of 997 m² g⁻¹ and mesoporous area of 628 m² g⁻¹ [77], and showed great potential for advanced analytical methods to improve performance of SCs.

Conclusions

In the last two decades, structure of EDL in nanoporous carbons has been investigated with a range of methods from experimental (NMR, SAXS and PFG-NMR) to molecular dynamic simulations. Especially the PFG-NMR has revealed a valuable set of information

regarding desolvation, ion dynamics and in-pore ion transport [78]. However, with the arrival of water-in-salt electrolytes and in situ generated battery-like electrodes, the in-pore understanding of charge storage mechanisms becomes even more important. The ion-diffusion data in the carbon pores obtained from these techniques can be verified by using electrochemical impedance spectroscopy. In case of hybrid supercapacitors, during surface modification or in situ phase changes in a battery electrode, the porosity of counter electrode (EDL one) must be properly optimized to deliver high power and compensate for the losses at the other electrode. For example, VAGs-like materials could replace the traditional microporous carbons as counter electrode in hybrid cells to overcome the reduced specific power. The recent studies reveal that for EDL charging, in situ growth of electroactive species or for low temperature applications, the porosity of carbons must be properly adjusted, and carbons with hierarchical pore size appear to be promising. When it comes to selection of electrode materials, machine learning and advanced analytical tools can be used for nanostructuring carbon pores that match the ions dimensions, and result in optimum trade-off between energy and power metrics.

CRedit authorship contribution statement

Zhazira Supiyeva: Visualization, Conceptualization, Writing – original draft. Xuexue Pan: Validation, Funding acquisition, Writing – review & editing. Qamar Abbas: Visualization, Supervision, Resources, Project administration, Conceptualization, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data were used for the research described in the article.

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- ** of outstanding interest

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